

Silica Coated Metal-CdS Hybrid Nanocomposites for Photocatalytic Reactions

*Thesis submitted in fulfilment of the
requirement of the degree of*
Doctor of Philosophy

By

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July 2013

Dedicated to my parents



Certificate

Certified that the thesis entitled "*Silica Coated Metal-CdS Hybrid Nanocomposites for Photocatalytic Reactions*" which is submitted by Miss. Nidhi Gupta in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a record of candidate's own independent and original research work carried out by her under our supervision and guidance. The material embodied in this thesis has not been submitted in part or full to any other University or Institute for the award of any degree.


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Candidate's Declaration

I, hereby declare that the work presented in the thesis entitled "*Silica Coated Metal-CdS Hybrid Nanocomposites for Photocatalytic Reactions*" in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy, School of Chemistry and Biochemistry, Thapar University, Patiala, is an authentic record of my own work carried out under the supervision of Dr. Bonamali Pal, Associate Professor, School of Chemistry and Biochemistry, Thapar University, Patiala, India. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree in India or Abroad.

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List of Symbols/Abbreviations

UV	Ultraviolet
Vis	Visible
VB	Valence Band
CB	Conduction Band
e ⁻	Electron
h ⁺	Hole
E _g	Band gap
OH [·]	Hydroxyl radical
CdS	Cadmium sulphide
TiO ₂	Titanium dioxide
NP	Nanoparticle
NC	Nanocrystal
SPR	Surface Plasmon Resonance
M	Metal
SC	Semiconductor
CE	Chemical etching
HSNS	Hollow silica nanosphere
HSNT	Hollow silica nanotube
CdS-NS	CdS nanosphere
CdS-NR	CdS nanorod
CdS-NSH	CdS nanosphere hexagonal
SF-CdS-2 h	Spongy flower like CdS
SiO ₂ @CdS-NS	Silica coated CdS nanosphere
SiO ₂ @CdS-NR	Silica coated CdS nanorod
SiO ₂ @CdS-NS(PE)	Photoetched SiO ₂ @CdS-NS
SiO ₂ @CdS-NR(PE)	Photoetched SiO ₂ @CdS-NR
HPLC	High pressure liquid chromatography
GC	Gas chromatography
TCD	Thermal conductivity detector
MS	Mass spectrophotometry
TEM	Transmission electron microscopy
HR-TEM	High resolution transmission electron microscopy
SEM	Scanning electron microscopy

List of Symbols/Abbreviations

EDX	Energy dispersive X-ray spectrophotometry
LB films	Langmuir Blodgett films
BET	Brauner Emmett Teller
SA	Surface area
XRD	X-ray diffraction
SAED	Selected area diffraction pattern
PL	Photoluminescence
m	Metre
M	Molar
min	Minutes
mL	Millilitre
mM	Milli molar
µg	Micro gram
µL	Micro litre
µm	Micro meter
µmol	Micro mol
nm	Nano meter
Å	Angstrom
%	Percentage
at%	Atomic percentage
wt%	Weight percentage
vol%	Volume percentage
ca.	Calculated
ppm	Part per million
λ	Wavelength
L	Length
D	Diameter
Cd(NO ₃) ₂ .4H ₂ O	Cadmium nitrate tetrahydrate
Na ₂ S.9H ₂ O	Sodium sulphide
BaSO ₄	Barium Sulphate
CdCl ₂	Cadmium chloride
en	Ethylenediamine
L-cys	L-cysteine
IPA	Iso-propyl alcohol

List of Symbols/Abbreviations

$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$	Chloroplatinic acid
RhCl_3	Rhodium chloride
PdCl_4	Palladium chloride
<i>m</i> -AN	<i>m</i> -nitroaniline
<i>m</i> -PDA	<i>m</i> -phenylenediamine
PNP	<i>p</i> -nitrophenol
PAP	<i>p</i> -aminophenol
NaBH_4	Sodium borohydride
$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Cupric nitrate
HNO_3	Nitric acid
NH_2CSNH_2	Thiourea
MO	Methyl orange
<i>m</i> -DNB	<i>m</i> -dinitrobenzene
AOT	Sodium di (2-ethylhexyl) sulfo-succinate
MV^{2+}	Methyl viologen
MPTMS	3-mercaptopropyltrimethoxysilane
TEOS	Tetraethoxysilane
$\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$	Chloroauric acid
AgNO_3	Silver nitrate

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1. Introduction and Literature

1.1 Photocatalysis and metal loading

The acceleration of a photoreaction in the presence of a catalyst is presently used in a large variety of applications. A general picture of a photocatalytic process is well known: a photocatalyst absorbs ultraviolet (UV) and/or visible (Vis) light irradiation from sunlight or an illuminated light source of energy equal to or more than the band gap energy (E_g) of a photocatalyst i.e. semiconductor (SC). The negative – electrons (e^-) in the valence band (VB) of the photocatalyst is excited to the conduction band (CB), while the positive- holes (h^+) is left in the VB. This stage is referred to the semiconductor's “photo-excited” state. The energy difference between the VB and the CB is known as the “band gap” which must correspond to the wavelength of the light for it to be effectively absorbed by the photocatalyst. After photoexcitation, the excited e^-h^+ pairs can recombine, releasing the input energy as heat or get trapped into meta-stable surface states, with no chemical effect. However, if they (e^-h^+ pair) separate and transport to different reactive sites, they can be utilized in a various

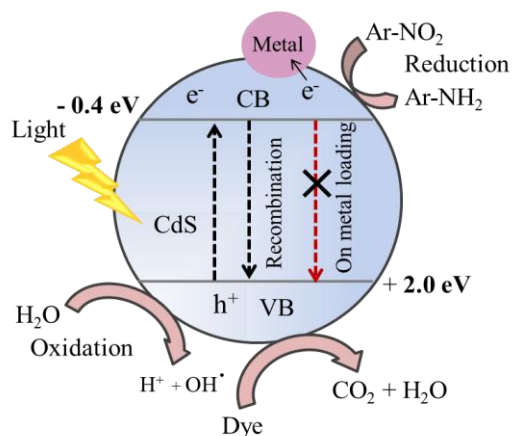
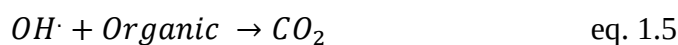
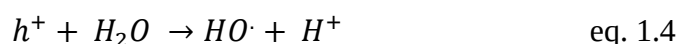
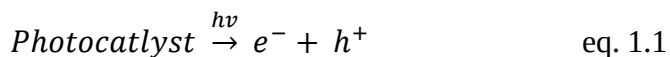


Figure 1.1. Mechanism of photocatalysis.

chemical reaction with adsorbed species. As a consequence, inorganic species form various groups of hydroxyl ($HO\cdot$) radicals and H^+ ions as shown in the following equations.



The positively charged h^+ in VB produce $HO\cdot$ radicals. They are the powerful oxidants (+ 2.8 V against NHE) that induce the oxidative decomposition of environmental pollutants. The e^- in CB are good reductants (+ 0.5 to - 1.5 V against

NHE) and are more importantly used for H₂ production from water splitting and for the reduction of various organic compounds (Kamat, 1993; Mills and Hunte, 1993; Hoffmann et al. 1995; Carp et al. 2004; Sagatelian et al. 2005; Paz, 2013) as shown in Fig. 1.1. The excited e^-h^+ pairs of particular importance are gaining insight into the nature of photogenerated carriers as they play a central role in all the basic steps of a photocatalytic process.

Metal loading is commonly used to improve the photochemical properties of SC particle is metal loading. Metal (M)-SC hybrid nanoparticles (NPs) with controllable topologies, sometimes called as *Janus particles* are promising candidates for applications in solar energy conversion, photocatalysis, and electronic devices (Litter, 1999; Choi et al. 2010; Rani et al. 2012; Gupta and Pal, 2013). M-SC hybrids often exhibit markedly different properties than the individual components due to the confinement in the semiconducting part and the dielectric confinement in the M part (Subramanian et al. 2004; Buso et al. 2007). The charges generated by the optical excitation of the SC domain can be transferred efficiently to the M part. Which shifts the plasmon frequency and/or promotes redox reactions by suppressing the recombination of photogenerated charge species shown in Fig. 1.1. Another recently found advantageous function of noble metals is the comprehensible and incoherent interactions between the M and the SC lead to broadening and extended the absorbance spectra of a SC to the visible region (Ohtani et al. 1997; Di Paola et al. 2002).

Generally noble metals (e.g. Au, Ag, Ni, Cu, Pt, Rh, and Pd) with Fermi level lower than SC catalyst should have been deposited on the SC surface for enhanced charge separation (Ni et al., 2007; Yuzawa et al 2012). Studies have shown that Ag and Au NPs, under visible light can enhance the local electric field of the neighboring SCs, such as TiO₂ and CdS, to increase the original photocatalytic activities of the SC. Noble M-loaded TiO₂ photoreaction systems seem advantageous compared with other photosensitization systems using, for example dye molecules, since noble metal deposits are relatively stable even under photoirradiation in an aerated atmosphere (Kowalska et al. 2009). These metals were reported to enhance electron transfer, but require good knowledge on the optimal deposited amount needed during the fabrication process (Haick and Paz, 2003; Lee and Choi, 2005).

SC photocatalysis has received much attention during last three decades because of a favorable combination of electronic structure, light absorption

properties, charge transport characteristics and excited state lifetimes (Thiruvengatachari et al. 2008). The very first photoinduced redox reaction was discovered by Fujishima and Honda in 1972. They used an n-type TiO_2 SC electrode for the photo-electrochemical decomposition of water into hydrogen and oxygen under UV light irradiation (Fujishima and Honda, 1972). Same concept was later applied by Bard to the invention of a photocatalytic system using SC particles or powders as photocatalysts (Bard, 1979). This discovery suggested a large number of potential applications, including photovoltaic cells, photoinduced superhydrophilicity, organic synthesis, degradation of pollutants and photolysis of water etc. (Mohajerani et al. 2009; Abdel-Jabbar et al. 2010). Although TiO_2 was the SC initially used by Fujishima and Honda, many other SCs such as CdO , CdS , CdSe , ZnS , ZnO , WO_3 etc. have been identified and used in different experiments.

The extent of desired photoreduction and photooxidation of a chemical reaction induced by a SC photocatalyst largely depends on its band edge position of the CB and VB. Although little experimental evidence has obtained for bulk photocatalysts, it is believed that the position of CB and VB edges determine their reduction and oxidation abilities, respectively. In an ideal system, the CB level should be more negative than the reduction potential level of the substrate to be reduced. Whereas the VB edge should be more positive than the

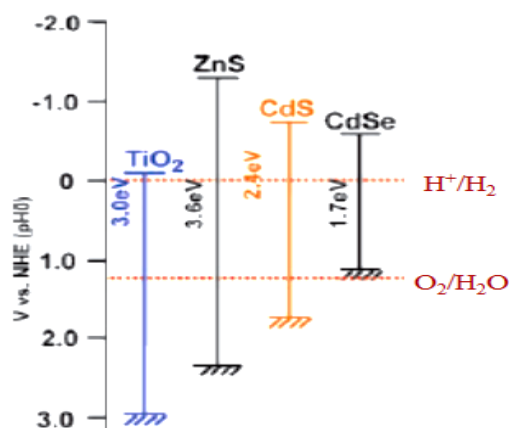


Figure 1.2. Relationship between the band structure and redox potential of water splitting.

oxidation potential level of the substrate for an efficient photocatalysis (Piccinini et al. 1997; Ferry and Glaze, 1998; Ohtani et al. 2003; Tada et al. 2004). Generally, metal oxides are used for oxidation processes due to their high positive VB position ($\text{TiO}_2 + 3.1 \text{ eV}$ and $\text{ZnO} + 3.0 \text{ eV}$), whereas chalcogenides are used in reduction processes for their high negative CB potential ($\text{CdS} - 0.4 \text{ eV}$, $\text{ZnS} - 2.3 \text{ eV}$ and $\text{CdSe} - 0.1 \text{ eV}$). Fig. 1.2. shows the relationship between the band structures of the various types of photocatalysts and redox potential of water splitting.

In past decades, extensive work had been performed by using the bulk SC particles. Microscopic quantum mechanical theory has enabled the study of a single

molecule. Modern technologies provide great opportunities to produce materials with an average crystallite size below 100 nm that are of considerable interest due to their different morphological and optical properties. From the available SCs, most studies have been focused on TiO₂ nanostructures. There are indeed good reasons for favoring TiO₂ which includes- strong oxidizing power, photogenerated e⁻ that are reducing enough to produce superoxide from dioxygen, anti-bacterial activity, self-cleaning, cheap, nontoxic, chemically inert, and stable and possess suitable electronic structure etc. The only exception of TiO₂ is UV light sensitivity (Mills et al. 2002; Carp et al. 2004). On the other side, CdS is a visible light SC and is promising in terms of enhanced photoresponse and better light absorption.

1.2 Significance of CdS nanoparticles

CdS is a n-type semiconductor with a direct wide band gap, $E_g \approx 2.42$ eV at room temperature (RT). It exists in mainly hexagonal wurtzite (thermodynamically stable) and cubic zinc blend phase (Zou et al. 1999). CdS exhibits the phenomena of cathodoluminescence and phosphorescence (Sekhar and Rao, 2013). It is an attractive candidate due to its stability, photochemical property, and ease of preparation as well as handling. It has been used in gas sensing, dye sensitized solar cells, photovoltaic, sensors, magnetism, biology, light emitting diodes and other optoelectronic devices due to its non-linear properties (Gao et al. 2002; Park et al. 2004; Patil et al. 2004a and b; Bhosale et al. 2005;

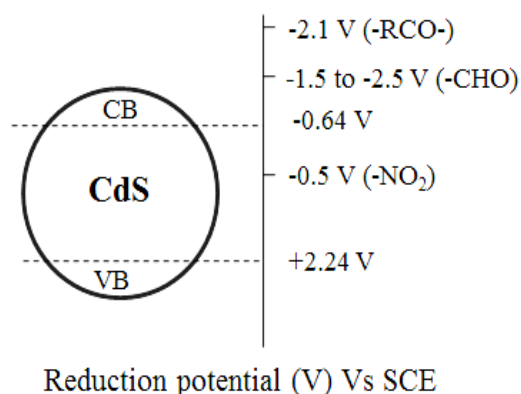


Figure 1.3. Reduction potential of various functional groups v/s CdS band position.

Lei et al. 2007; Shinde and Bhosale, 2008). Owing to its suitable oxidation potential (+ 2.0 eV vs NHE), it is employed for the waste water treatment and dye decolourization (Wang et al. 2009; Shen et al. 2010; Dawei et al. 2011; Pathania et al. 2011; Li et al. 2012). But it is predominantly used for hydrogen production (Girginer et al. 2009; Liu et al. 2012; Deshpande and Gupta, 2010) and reduction of pharmaceutically important nitrocompounds (Maldotti et al. 2000; Ferry and Glaze, 1998) because of their high reduction potential over nitro group as shown in Fig. 1.3.

Recently, it has been discovered that the fate of photoelectrochemical reactions, optoelectronic and other physical properties of SC particle has been drastically changed with their size, shape and crystalline structure (Marandi et al. 2005; Datta et al. 2008). Thus, the synthesis of nano- to microscopic-scale CdS materials with controlled shape is of great interest owing to their novel

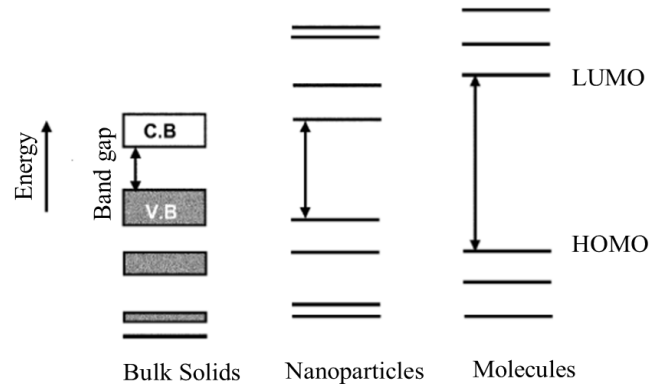


Figure 1.4. Comparative energetics of bulk and nanostructured particles.

properties and potential applications in various fields. Nanostructure of SC materials with diameters ranging between 1 and 10 nm exhibit quantization effect and possess properties different from their bulk particle. Size quantization of SC particles will lead to the change in the position of CB and VB to higher and lower values, respectively as shown in Fig. 1.4. This results in the widening of forbidden gap, quantization and decrease in the densities of electronic states at the edges of the CB and VB (Stroyuk et al. 2005; Antolini et al. 2012). Such variations lead to considerable change in the recombination of e^- and h^+ trapped at spatially separated donors and acceptors (Yang, 2003; Whang et al. 2003; Hupp and Poeppelmeier, 2005). E_g is an important parameter that determines their electronic and optical properties (Sekhar and Rao, 2012). The widening of the band gap can be witnessed by optical absorption spectroscopy, in which a blue shift is observed with reduction in particle size (Fang et al. 2007). Brus has developed a theory to explain the observed spectral shifts known as an effective mass approximation (Brus, 1983), according to which size-dependent E_g of nanoparticles (NPs) is given as

$$E' = E_g + \Delta E \quad \text{eq. 1.6}$$

$$E' = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon_2 R} + \text{polarization term} \quad \text{eq. 1.7}$$

Where E' is the energies of excited state, $E' = hc / \lambda$, m_e is the electron effective mass, m_h is the hole mass, ϵ is dielectric constant, R is radius of particle and finally, the parameter (E_g) is identified as bulk band gap, 2.58 eV.

The other positive advantages of small size are the specific surface area, increased exposed surface atoms ($\sim 50\%$ atoms) and high surface- to- volume ratio (Chen et al. 2005; Zhao and Xu, 2006; Ferrando et al. 2008). The high surface area brought about by the small particle size is beneficial to many SC based devices. It facilitates an interaction between the devices and the interacting media, which mainly occurs on the surface or at the interface and strongly depends on the surface area of the material. Decrease in the size of NPs led to quick diffusion of photoexcited charge carriers to reach the surface and react instantaneously with the species adsorbed on the photocatalysts surface. Therefore, it would be possible to control the redox ability of photocatalyst NPs by changing their size.

In past decades, synthesis of CdS materials of many simple shapes such as dot, wire, tube, rod as well as hierarchical structure based morphologies, such as comb-like (Sun et al. 2008), dendron-like (Yan and Xue 2008; Wang et al. 2009), urchin-like (Du and Cao, 2008; Zhou et al. 2008), and flower-like (Sanjanlal et al. 2008) patterns and structures, of various sizes were ranged down to a few nanometers. Recent approaches to tune the shape of colloidal nanocrystals lead to the formation of a variety of highly faceted geometries, including nanoprisms (Chu et al. 2005), hexagon, cubes, and pyramids, nanowires of $D - 25 \text{ nm}$ and $L - 20\text{-}40 \text{ }\mu\text{m}$ (Xu et al. 2005), nanoflowers, nanotrees (Dick et al. 2004; Yao et al. 2006) and branched structures such as tetrapods and multipods have been obtained within the cadmium chalcogenide system (Fang et al. 2007; Yan et al. 2008). Joo et al. converted rods, bipods and tripods to spheres by changing the molar ratio of Cd and S from 1:6 to 2:1, respectively (Joo et al. 2003). Shieh group (Shieh et al. 2005) addressed a general synthetic method for the formation of shape-controlled; sphere or rod like CdS, CdSe and CdTe nanocrystals and mixed-SC heterostructures by changing the injection rate of the chalcogen precursor without changing the other parameters.

The above mentioned structures exhibit different optoelectronic properties due to the difference in the arrangement of energy levels. Measurements of Cao group (Cao et al. 2009) indicated tunable optical properties just through a change in the shape of the CdS nanocrystals from dot to CdS wire. They report a band-edge emission at $\lambda = 426 \text{ nm}$ as well as a weaker trap-state green emission at 530 nm for CdS nanowires and only band edge emission at $\lambda = 426$ for CdS dots. It is noticed that recently synthesized CdS quantum disks of uniform thickness displayed weak quantum confinement. Their photoluminescence lifetime (tens of picoseconds) was

about two orders of magnitude shorter compared to CdS quantum dots (QD's) and rods (Li et al. 2012). It has been reported that elongated nanocrystals facilitate the electric field effect on the electronic wave function due to increased delocalization volume in contrast to spherical QD's (Muller et al. 2005; Smith et al. 2011). These groups reported the strong decrease in emission rate with increase in the aspect ratio of CdSe particle from 1.6 (nearly spherical) to 4 nm (lengthy nanorod). The fact was explained due to the difference in the level of confinement of e^- and h^+ . On the other side literature reveals that nanorods (NRs) have lower quantum efficiencies with respect to nanospheres (NS) because of increased delocalization of charge carriers along the length, which reduces the e^- and h^+ overlap (Sitt et al. 2011).

Reports have substantiated that compared to zero dimensional NS, one dimensional NR has higher photon absorption cross sections (Protasenko et al. 2005; Htoon et al. 2003), larger per particle surface area and optical gain lifetimes. They have relatively strong permanent electric dipoles, enhanced photovoltaic efficiencies (Huynh et al. 2002), and size-dependent and polarized light absorption, scattering, and emission (Salant et al. 2012). CdS-NR of aspect ratio (> 100) displayed high luminescence efficiencies of $\sim 10.8\%$ quantum yield at RT (Saunders et al. 2008). Work on hybrid NP-polymer solar cells, reported that NRs exhibited improved characteristics compared with QDs (Huynh et al. 2003; Gur et al. 2005; Sun and Greenham, 2006; Wu et al. 2008). Pinna et al. observed red shifted emission spectra in CdS flat triangles compared to spherical QDs due to the trap emissions (Pinna et al. 2001). It has been detected that among different morphologies, lengthy one dimensional NRs are particularly interesting owing to its superior photoelectrochemical and nonlinear optical properties over spherical or other morphologies. This behavior is attributed to the delocalization of e^- and h^+ along the length, radial confinement and dimensionality effect. Furthermore, the surface area of NRs on a per particle basis is large compared to QDs, which may allow larger contact area and hence improve the interfacial contact between them and the surrounding electrolyte (Salant et al. 2012).

1.3 Stabilization of CdS nanoparticles

Literature reveals that the use of these particles is inadequate in spite of having an appropriate redox potential and numerous beneficial properties. Unfortunately, this SC is not stable in aqueous solution under irradiation. It undergoes anodic dissolution leading to the formation of sulphur and/or sulphate ions

through the following: $2h^+ + CdS \rightarrow Cd^{+2} + S$ photoinduced reaction (Dijken et al. 1998; Torimoto et al. 2001; Marandi et al. 2005). As a result, the photochemical activity deteriorates with illumination time and suffers a serious drawback of photostability. Another critical aspects of these NPs is their instability in nanorange due to high surface charge, lower zeta potential and high surface-to volume ratio. These factors result in agglomeration and thereby declines the photoactivity (Wei et al. 2004). Moreover, CdS-NPs cannot be used directly because of certain other limitations such as toxicity, hydrophobicity, interactions with oxygen etc. (Correa-Duarte et al. 1998).

In order to avoid the degradation of these active materials, they are usually loaded with metal particles or embedded into the host matrix to form composites. Surface passivation or functionalization has been recognized as a very advanced and convincing method to tailor the properties of nanomaterials. Modifiers are primarily used to stabilize the NPs and to avoid their permanent aggregation. Coating protects them from photo-initiated surface degradation and decrease the oxidation of NPs surface by limiting the transport of oxygen (Thangadurai et al. 2008; Aldana et al. 2001). Surface coating on nanostructured SC can alter the charge, functionality, and guarantees their site selective reactivity. As a consequence, surface coating enhance their functional properties due to localization of the e^-h^+ pairs (Datta et al. 2008). Many attempts have been taken care such as stabilizing CdS with aqueous solution of reducing agents acting as h^+ scavengers such as SO_3^{2-} and $S_2O_3^{2-}$ ions (Matsumura et al. 1983; Buhler et al. 1984). The use of SiO_2 , L-cys, polyphosphates, thiols, (Dollefeld et al. 2002; Hirai et al. 2001; Piven et al. 2008; Ryu et al. 2007; Barglik et al. 2004) clays, nafions, amines (Qi et al. 2001; Sapra et al. 2001; Marandi et al. 2005), carboxylic groups (Mansur et al. 2011) and surfactants were also considered (Mehta et al. 2009 and 2010). For instance, Naskar et al. compared the effect of two nonionic surfactant stabilized emulsions on ZnS-NPs size (Naskar et al. 2006). Shao et al. studied the role of oleic acid and TOP on growth and agglomeration behavior of Co-NPs synthesized via thermal decomposition (Shao et al. 2006).

Besides stabilization, various surface passivation treatments were explored to eliminate trap emission and increase the luminescence quantum yield. Saunders and group stated that both thiol and amine passivation significantly reduce the trap and enhance the band-edge emission. But the total luminescence quantum yields dropped significantly, with a maximum measured value of 1.5% for the amine-passivated

CdS-NR (Saunders et al. 2008). Emission efficiency of CdS QD's synthesized by aqueous route was found to increase by adding agents like hydrophilic thiols-thioglycolic acid, 3-mercaptopropionic acid, or thioglycerol (Vossmeier et al. 1994; Sooklal et al. 1998; Winter et al. 2001; Barglik et al. 2004; Chen et al. 2007). Recently, Aboulaich et al. reported that the PL quantum yield of CdS nanocrystals increased to 22–23% when coated with a ZnS shell using a mixture of zinc acetate and 3-mercaptopropionic acid (Aboulaich et al. 2012).

Surface coating in addition may lead to decrease in the activity of SC due to adsorption of reacting substrate on the shell surface that may block/reduce the incorporation of reactant into deep core. These problems can often be solved by making shells over such NPs. Therefore, derivatization by stabilizing the functional core is a pre-requisite for potential application of NPs. Thus, a thin layer of suitable coating material is favored to form active core-shell structures.

1.3.1 Core-shell structures

Core-shell or nanoshell particles constitute a special class of nanocomposite materials. They consist of two different materials in which one material is coated with a layer of another material. Core-shell material particles can be synthesized by using the combination of materials, like SC, metal (M) and insulators such as M-M; Ag (shell)@Au(core), Cu-Pt, Cu-Ag (Kumar and Zou, 2007; Bao et al. 2008; Zhang et al. 2009), M-SC; Au-CdS, Pt-CdS (Kim et al. 2005; Gu et al. 2009) and SC-SC; ZnS@CdS, CdS@CdSe, TiO₂@CdS (Marci et al. 2001; Wang et al. 2004; Yordanov et al. 2008; Vaidya et al. 2010), Cd(OH)₂@CdS composites (Kumar and Negi, 2000; Kumar and Jain, 2001) etc. These structures show continual tuning of optical properties from vis to infrared region of electromagnetic spectrum and/or geometric structure through changes in composition of core-shell ratio (Kalele et al. 2006). The properties of the core particle such as reactivity, stability and dispersibility can also be modified by varying the shell material. Such particles are found to be highly functional with tailored and improved properties than their single component counterparts. Also, from an economic point of view, a precious material can be coated over an inexpensive material to reduce the consumption of the expensive material compared with making the same sized pure material.

But such core-shell structures often could not retain the original crystal structure due to M-SC and M-M energy or electronic state intermixing. Thus, show properties different from the individual particle (Krishnan et al. 2004; Borys et al.

2010; Smyder and Krauss, 2011; Smith et al. 2011). It has been demonstrated that selective PbSe deposition on the tips of CdS and CdSe NRs provide further indication that the wurtzite CdS or CdSe (002) surface is the most reactive (Kudera et al. 2005). However, the fine tuning of the distinctive properties of an individual is difficult in these composites. The most substantial coating and stabilizing material studied is silica (SiO_2) that helps in preserving the individual characteristics of starting material. Moreover, the properties can be amended by changing either the constituting material or the core to shell ratio (Wei et al. 2010; Chaudhuri and Paria, 2012).

1.3.2 Silica as a shell material

SiO_2 (dielectric constant ~ 4.5 , $E_g = 9$ eV) as a coating material promises an unparalleled opportunity for the enhancement of colloidal properties and functions by using core-shell rational designs and proves profiting from its synthetic versatility. It is one of the most flexible and robust surfaces used for constructing shells over NP core. The use of SiO_2 as a coating material mainly lies in its anomalously high stability, especially in aqueous media. It reduces bulk conductivity and provides stability to the core material over a much wider range of solution conditions such as ionic strength, temperature and solvent polarity (Vigil et al. 1994; Arellano et al. 2000; Pal et al. 2004). Other reasons include easy regulation of the coating process, its chemical inertness, controlled porosity, process ability, and optical transparency. In general, it is a good insulator, chemically inert and does not affect redox reactions at the core surface. The main features favoring the noteworthy stability of SiO_2 sols are the low value of Hamaker constant. Which defines the Van der Waals forces of interactions among the particles and the medium; and the strong attachment of positively charged molecules to the polymeric silicate layer at silica-water interfaces under basic conditions. Thus, this silicate layer can confer both steric and electrostatic protection on different cores and act as dispersing agent of many electrostatic colloids (Vigil et al. 1994; Knopp et al. 2009).

Moreover, the SiO_2 shell is optically transparent to electromagnetic radiations in the visible region (300 to 800 nm) so that chemical reactions can be monitored spectroscopically and emitted light is not hindered (Ung et al. 1998; Holleman and Wiberg, 2001). Due to its high porosity, adsorption of reactant molecules can be increased for higher catalytic activity and products selectivity (Torimoto et al. 2003; Pal et al. 2007). SiO_2 coatings can also be used to modulate the position and intensity

of the SP band since SiO_2 is optically transparent. Furthermore, the ability to control the thickness of the SiO_2 shell implies that the separation between neighboring particles can be tuned, so that the collective behavior of the particles within a nanostructure can be tailored (Jankiewicz et al. 2012). SiO_2 as a shell material also helps in retaining the physical and the chemical properties of the core material. These aforementioned properties and advantages render SiO_2 an ideal and low-cost material to tailor surface properties (Martinez et al. 2010).

Many different methods for preparation were adopted, due to the different nature of the core particles (Hewa-Kobayashi et al. 2001; Shin et al. 2010). For example Liz-Marzán, Mulvaney, and co-workers have extensively studied M- SiO_2 core-shell particles prepared by a two-steps procedure. They used a silane coupling agent (a surface modifier) to provide the surface with silanol anchor groups (Marzan et al. 1996; Darbandi et al. 2012). Chang et al. prepared monodisperse colloidal SiO_2 -CdS by water-in-oil microemulsions for their use in non-linear optics (Chang et al. 1994a and b). SiO_2 (shell)@CdS (core) structure has been fabricated by Torimoto and group by using two steps method (Torimoto et al. 2002). Some others use single pot one step method for the synthesis of SiO_2 /CdS composites (Wuister and Meijerink, 2003; Wang et al 2008; Chu et al. 2008). Wang et al. have synthesized monodispersed CdS-NPs through γ -irradiating CdCl_2 , $\text{Na}_2\text{S}_2\text{O}_3$, and polyvinylpyrrolidone aqueous solution at RT and SiO_2 @CdS were prepared through the hydrolysis of TEOS (Wang et al. 2007).

The amazing physio-chemical properties of nanostructured matter were governed mainly by the core particle. SiO_2 coating endow the cores with several beneficial properties, such as the possibility of subsequent functionalization by decreasing the core size by using high energy light that creates void space inside the shell which act as nanoreactor. Torimoto et al. first time reported the size selective photoetching (PE) of SiO_2 coated CdS-NPs by controlling the wavelength of light source (Torimoto et al. 1998, 2000, 2003). The principle of the size-selective PE relies on the fact that metal chalcogenide SC particles get photocorroded in aqueous solution under irradiation. As a consequence, the E_g of size-quantized SC-NPs increases with a decrease in the particle size (Weller, 1993; Dijken et al. 1998). The great advantage of utilizing the photon is the one time synthesis of smaller particles of varied diameter with control ability of the etching energy. However, conventional

techniques require repetition of the same method for many times for the synthesis of different sizes which needs a huge amount of expensive chemicals.

In addition to the above mentioned benefits, SiO₂ coated structures of M and SC assists in fabricating hollow silica nanostructures by complete or partial chemical, thermal or photochemical treatment (Lin et al. 2009; Hui et al. 2010; Taniguchi et al. 2012). Thermal decomposition of an organometallic precursor in a core has also been utilized to prepare a M core with a surrounding void space (Lee et al. 2003). Recently, Yoon and co-workers synthesized hollow SiO₂ nanotubes by PE of CdS core in SiO₂ (shell)@CdS (core) structure (Yoon et al. 2006). As these hollow SiO₂ materials are light-weight, have low density, possess large surface area, and surface permeability, these can be suitable for efficient adsorption, separation, micro/nano-reactor, and targeted drug delivery applications (Bae and Shah, 2000; Teng et al. 2004; Liu et al. 2008).

1.4 Research gap and objectives

As found from the literature, the vast majority of studies on cadmium chalcogenides were devoted to QDs while the syntheses of one-dimensional structures and arrays were reported only in the past few years. Achieving well-defined size and shape distribution control in colloidal synthesis and the inherent manipulation of nanomaterial's properties are still challenging. Since their final shape and properties are sensitively inter-related. It has been substantiated that hexagonal NRs are more active than cubic spheres as a function of their geometry and radial confinement etc. Despite many investigations, some disagreement persists about the degree of delocalization of the electron wave function and how it depends on size/shape of the heterostructure.

Limited work has been done in the field of photocatalysis using CdS-NRs and other morphologies. Reports on the stabilization of different CdS morphologies other than nanospheres by SiO₂ coating is sparse. The effect of silica shell thickness and the control of core size by PE as a function of wavelength of light used was reported only to a limited extent. The influence of different metal loading in the void for effective M-SC junction and comparative study of different CdS morphologies for various photoredox reactions has not been reported considerably.

Keeping in view the above points, the following objectives have been designed

1) Synthesis of silica-coated CdS nanospheres and nanorods by reverse micelle method and their photoetching.

- 2) Photodeposition of various metal particles ($M = \text{Au, Ag, Cu, Pt, Pd}$ and Rh etc.) to make silica coated $M\text{-CdS}$ hybrid nanocomposite.
- 3) Spectroscopic and microscopic studies for determining size, shape and morphology.
- 4) Photocatalytic efficiency will be investigated for H_2 production as a test reaction and to verify nitroaromatic (Nitrophenol) photoreduction ability.

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2. Preparation and Characterization Techniques

2.1 Materials used

Cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), cadmium chloride (CdCl_2), sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), thiourea (NH_2CSNH_2), ethylenediamine (en), L-cysteine (L-cys), benzaldehyde, heptane, toluene, iso-propyl alcohol (IPA), acetone, methanol, tetraethoxysilane (TEOS), chloroauric acid ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$), silver nitrate (AgNO_3), cupric nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), nitric acid (HNO_3), methyl orange (MO), *m*-dinitrobenzene (*m*-DNB), barium sulphate (BaSO_4) were purchased from Loba Chemicals. Sodium di (2-ethylhexyl) sulfo-succinate (AOT) was purchased from Badrivishal Chemical Industry, Pune, India. Methyl viologen (MV^{2+}), 3-mercaptopropyltrimethoxysilane (MPTMS), chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$), rhodium chloride (RhCl_3), palladium chloride (PdCl_4), *m*-nitroaniline (*m*-NA) and *m*-phenylenediamine (*m*-PDA) were purchased from Sigma Aldrich. Sodium borohydride (NaBH_4), *p*-nitrophenol (PNP), *p*-aminophenol (PAP) were purchased from SD Fine Chemicals Limited. HPLC grade water and methanol were used for HPLC analysis. Millipore water ($35 \text{ ohm}^{-1} \text{cm}^{-1}$) was used for preparing solutions and washing samples.

2.2 Synthesis of CdS nanospheres

Three different methods were used for the synthesis of CdS nanospheres (NS) in order to obtain particles of different size and crystal structure. The obtained particles were represented as – CdS-NS1, CdS-NS2 and CdS-NSH as discussed below.

2.2.1 Method-I

CdS-NS were synthesized by using inverse micelle method (Torimoto et al. 2003). In a typical synthesis, 1.3 mL (1.0 M) aqueous solution of each $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added separately to 200 mL of heptane solution containing 14 g of AOT and 5.7 mL of water. After each of the solution had been stirred for 1 h, they were mixed together and stirred for another 3 h. An additional 260 μL of 1.0 M aqueous $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution was added to above solution and the solution was stirred for another 1 h to complete the growth of CdS particles. This resulted in the formation of *CdS-NS1*. The heptane was removed by evaporation to obtain thick solid *CdS-NS1* in AOT. Finally, it was washed repeatedly with methanol and dried at 70°C prior to use.

2.2.2 Method-II

CdS-NS were synthesized through a reverse-micelle-method (Wei et al. 2010). The solution of AOT (0.05 M) in *n*-heptane (100 mL) was prepared and aqueous solutions of (650 μ L, 0.2 M) each of Na₂S and Cd(NO₃)₂·4H₂O were separately added to two equal portions of the above AOT solution. Both solutions were then mixed together and stirred for another 1 h to obtain CdS-NP seeds. 130 μ L (0.2 M) of Na₂S solution was added and stirred for 3 h. An equal amount (130 μ L, 0.2 M) of Cd(NO₃)₂ solution was further added into this seed solution to obtain the desired CdS-NS2. These NPs (CdS-NS2) were washed repeatedly with methanol and dried at 70 °C.

2.2.3 Method-III

Hexagonal CdS-NS were synthesized (Zhao and Huang, 2008) by dissolving equivalent molar amounts (1.4 mmol) of Cd(NO₃)₂·4H₂O (432 mg) and L-cys (336.4 mg) into 70 mL of en. The solution was then stirred for about 10 min until a clear solution was gotten. It was then refluxed at 150 °C for 8 h in a round bottom flask. The reaction mixture was cooled to room temperature (RT) naturally. The product (CdS-NSH) was collected by centrifugation at 8000 rpm for 10 min and washed for several times with distilled water and methanol to remove the excess reactants and by-products. Finally, the product was dried in an oven at 70 °C.

2.3 Synthesis of spongy flower like CdS and CdS nanorods of different aspect ratio

The different CdS nanostructures were prepared by using a phase growth solution method (Yang, 2006). Typically, 123.2 mg of Cd(NO₃)₂·4H₂O and 60.8 mg of NH₂CSNH₂ were dissolved in 10 mL of en and refluxed at 120 °C for different time intervals (2, 6 and 10 h). The reaction mixture was cooled at RT (25 $\pm$ 5 °C) to stop the crystal growth. *Spongy flower like CdS* (SF-CdS-2h) were formed after refluxing the reaction for 2 h whereas prolonged refluxing of reaction to 6 and 10 h resulted in CdS nanorod (CdS-NR) of different aspect ratio denoted as *CdS-6 h* and *CdS-10 h/CdS-NR*. The obtained CdS crystals were washed with water followed by methanol for several times and dried at 70 °C for further use.

2.4 Surface modification

Surface modification of CdS nanoparticles (CdS-NPs) was done by different techniques such as metallization and silica (SiO₂) coating in order to improve their

activity and stability for longer light exposure.

2.4.1 Different metal (Cu, Ag, Au, Rh, Pd and Pt) loading

The deposition of different transition metals such as Au, Ag, Cu, Pt, Pd and Rh onto as-synthesized CdS nanostructures was carried out by using photodeposition technique. Typically, 50 mg of aqueous IPA (50 vol%) suspension of CdS powder and requisite amount (for 0.2-2 wt% loading) of 0.01 M aqueous metal salt solution of different metals was irradiated for 2-4 h under UV light (*LS-I, see section 2.8.1*). The deposition was carried out in an inert atmosphere (created by purging Ar for 20 min) in a glass test tube sealed with rubber cap under constant magnetic stirring. Finally, metal deposited CdS-NPs (M-CdS) were washed with methanol several times and dried at 70 °C to obtain powder.

2.4.2 Formation of core (CdS)-shell (SiO₂) structure

In order to stabilize the above synthesized CdS-NPs, silica coating was done by using MPTMS and TEOS as silica precursors (Torimoto et al. 2003). Briefly, CdS-NPs were dispersed homogeneously in 250 mL toluene using sonication and stirred continuously. Then 100 μ L of pure MPTMS was added to modify the CdS surface and solution was refluxed for 2 h at 80 °C. Later, 100 μ L of pure TEOS (0.7 mM) was added against above used MPTMS in order to increase the silica layer thickness. But for thin SiO₂ coating the amount of TEOS was reduced to 50 μ L (0.35 mM). The solution was again refluxed at 80 °C for another 2 h. Then after, hydrolysis was performed by drop wise addition of 250 mL of water resulting in the precipitation of SiO₂@CdS nanostructures. The solution was then allowed to stand undisturbed for 8-10 h in order to extract toluene and water layer. The two layers were separated by separating funnel and the SiO₂@CdS particles were washed repeatedly with water followed by methanol and vacuum dried.

2.5 Photoetching of CdS core

For photoetching (PE) of CdS core from SiO₂@CdS-NPs, 5 mg of the obtained SiO₂@CdS-NPs were dispersed in 10 mL of oxygen saturated solution containing 50 μ M MV²⁺ that act as electron relay from CdS particles to oxygen molecules. A monochromatic light of 488 and 458 nm from Ar ion laser (*section-2.7.12*) was continuously irradiated for different times- 3, 5 and 8 h. The characteristic dark yellow color of the solution gradually changes to light yellow after laser irradiation (Yoon et al. 2006; Dijken et al. 1998). Resultant particles were repeatedly washed with water and methanol to remove the photodissolved ions

(Cd^{2+} , SO_3^{2-} and S^{2-} etc.) and excess of MV^{2+} . The slurry was dried at 70 °C to obtain photoetched $\text{SiO}_2@\text{CdS}$ -NPs ($\text{SiO}_2@\text{CdS-NP(PE)}$).

2.6 Chemical etching of CdS core

Complete dissolution of CdS core from 50 mg of $\text{SiO}_2@\text{CdS}$ -NPs ($\text{SiO}_2@\text{CdS-NS1}$, $\text{SiO}_2@\text{CdS-NS2}$ and $\text{SiO}_2@\text{CdS-NR}$) and $\text{SiO}_2@\text{Au-CdS}$ nanocomposites was carried out by chemical etching with HNO_3 (2 M, 5 mL) under 15–20 h magnetic stirring. The process of CdS removal was monitored by the gradual disappearance of CdS absorption band, verified from the $\text{SiO}_2@\text{CdS}$ -NPs absorption spectra. The dissolution of CdS was also witnessed from the bad odor of H_2S gas formed after reacting CdS with HNO_3 . Complete removal of CdS from $\text{SiO}_2@\text{CdS}$ -NPs and $\text{SiO}_2@\text{Au-CdS-NR}$ nanocomposites led to the formation of hollow SiO_2 nanostructures and $\text{SiO}_2@\text{Au-NPs}$. These particles were washed with water (6–8 times) followed by methanol to remove unreacted HNO_3 and vacuum dried.

2.7 Characterization techniques

Evaluation of opto-electronic properties of semiconductor nanoparticles under ambient conditions using various instrumental techniques had been carried out through this research. The information obtained from these techniques can be processed to yield images or spectra which reveal the structural, chemical, geometric or physical details of the materials. Bare and surface modified (silica coated and metal loaded) CdS nanostructures were characterized by exploiting the following techniques.

2.7.1 UV-Vis Spectrophotometer

UV-Vis absorption is a very first characterization method for the NPs because the absorption features give information about the NP formation, the band gap and their size distribution. This instrument is based on the principle that when sample molecules are exposed to light having suitable energy for electronic transition within the molecule, required energy is absorbed and the electron is promoted to higher energy level. UV-Vis spectrophotometer (Analytic Jena, SPECORD 205) was used in this research in order to analyze the characteristic absorbance band of the synthesized CdS nanostructures. It detects the response of sample to UV and Vis range of electromagnetic radiation. Analysis was performed on the instrument by

taking 1mg/mL aqueous or acetone dispersion of the sample in 3.5 mL quartz cuvette. The detection range of 190-1100 nm was selected for analysis.

2.7.2 UV-Vis diffuse reflectance Spectrophotometer

The absorbance of solid powder was carried on Avantes diffuse reflectance spectrophotometer. This technique was used to understand the bandgap (E_g) between the valence band and conduction band of the powder samples. The E_g can be calculated for practical purposes by the equation, $E_g = 12400/\lambda$, (Lopez et al. 2001) where λ is the absorbance wavelength in nm. The adsorption shoulder can be found by extrapolating a straight line from the spectrum to x-axis. In UV-Vis spectroscopy the adsorption is carried out in the Vis as well as near the UV region of the spectrum. 2 mg of the sample was taken on a glass slide and the light source probe was placed over the sample to record the absorbance spectra and reflectance spectra. BaSO₄ was used as a reference and to dilute the solid sample.

2.7.3 Photoluminescence (PL) Measurement

PL is a very sensitive technique to understand the e^-h^+ recombination property of a particular substance. Perkin Elmer LS55 spectrofluorimeter was used to analyze the recombination properties of photogenerated species of synthesized compounds. For analysis, 1mg/mL acetone dispersion of as-prepared samples were photoexcited at 365 nm with the emission range of 350-900 nm and slit width of 2.5:5. A plot of emission against wavelength for given excitation wavelength is plotted to know the emission spectrum.

2.7.4 X-Ray Diffraction (XRD) Analysis

Powder X-ray diffraction is a primary tool for investigating the size and structure of crystal samples. This technique was used throughout the research to study the phase composition, structural variations and crystallinity. The working principle depends (Suryanarayana and Norton, 1998) on the fact that the sample is always equidistant to the source and the detector. At lower angles the sample receives only the part of the beam resulting in reduced beam intensity per unit area of sample. At higher angles the depth of penetration of the beam becomes deeper. Crystallite sizes can be calculated from the half widths according to the Scherrer's equation $D = k\lambda/\beta\cos\theta$, where D is the crystallite size; k is a constant; λ is the X-ray wavelength; β is full width at maxima of the diffraction line and θ is the diffraction angle. The intensity scale of the peak is critical because the relative intensity of a peak is a key in determining the structure due to difference in electron diffraction.

XRD analyses were performed on PANalytica X' pert PRO X-ray diffractometer with Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation. The powdered sample was pressed into a sample holder with a smooth plain surface. This analysis was done from Sophisticated Analysis Instrumentation Laboratory (SAI Lab), Thapar University, Patiala, India.

2.7.5 Scanning Electron Microscopy (SEM)

SEM was used to obtain information about the external morphology of the sample. The SEM images depend on the electron interactions at the surface rather than on transmissions so it can produce images that are good representation of 3D structure of the sample. SEM images are considered to provide information in terms of topography (surface skin), morphology (size, shape and arrangement), composition and crystallographic information about the sample surface.

During SEM analysis, a beam of electrons is focused on a selected area of a sample and there is therefore an exchange of energy from the electron beam to the sample surface. The electrons produced from electron gun at the top are referred to as primary electrons. These electrons are then amplified, analyzed and translated into images. In addition to the secondary electrons, there are reflected electrons that are referred to as backscattered electrons that carry more energy than the secondary electrons and also travel in a specific direction. These electrons cannot be collected by secondary electron detector (Zhou et al. 2007).

SEM was conducted by using JSM-7600F (0.1 to 30 kV) Field Emission Gun-Scanning Electron Microscope (FE-SEM). Samples were placed on a specimen stub which were lined with double side adhesive, conducting tape and was then coated with a thin layer of gold in order to reduce sample charging. SEM analysis was done from Sophisticated Instrumental Analysis Centre of Indian Institute of Technology (IIT)-Mumbai, India.

2.7.6 Energy Dispersive X-ray (EDX) Spectrophotometer Analysis

This technique was used to study and measure qualitatively and semi-quantitatively the chemical composition of the selected points or areas of the sample. It was also useful in identifying materials and contaminants and even in distinguishing their relative concentrations on the surface of the specimen. This technique was used as an attachment on SEM and utilizes the high-energy electrons that are ejected by an elastic collision of an incident electron, typically with sample's atom nucleus and are referred to as backscattered electrons. Yield of backscattered is in proportional to the atomic number of an elements in the sample. The sample

composition, elements and compounds, and their relative ratios in the area of one micrometer in diameter were determined using this technique. EDX analysis was carried on JEOL JSM-6510LB. At least three analyses at different spots were performed for each sample in order to obtain an average value.

2.7.7 Transmission Electron Microscopy (TEM)

TEM allows the imaging of individual particle and to some extent to evaluate the finest structural details and statistical distribution of sizes and shapes of the particles in sample. The possibility of high magnification has made the TEM a valuable tool to study the morphological and crystallographic structural details of the sample in this research. The electron diffraction can be described analogously with X-ray diffraction by Bragg's equation. The SAED reveals electron diffraction patterns of a sample area with the size in the order of 0.01 to $1\mu\text{m}^2$ and thus allowing a co-relation with the TEM images. The SAED patterns provide information about the lattice constants, crystallographic orientation and lattice type.

Unlike SEM, TEM works with the electrons that are transmitted through the electrons. An electron gun at the top produces a beam of monochromatic electrons and is focused to a small, thin coherent beam by use of condenser lenses. This beam is then restricted by a condenser aperture to strike the specimen. The beam transmitted through the specimen is passed through the intermediates and the projector lenses. Finally, the image strikes the phosphor image screen and light is generated thereby enabling the users to see the image (Williams and Carter, 2009).

A Hitachi-7500 transmission electron microscope at 120 KV was used to investigate the morphology. For the TEM studies, all of the samples were dispersed in methanol solution and then dropped on copper grid coated with carbon film. TEM analysis was done at Sophisticated Analysis Instrumentation Facility (SAIF) centre, Panjab University, Chandigarh, India; IIT-Mumbai, India and at Central Salt and Marine Chemicals Research Institute, Bhavnagar, Gujarat, India.

2.7.8 Surface Area Analysis

BET surface area analysis was performed in order to measure the surface area of the solids used in this research. Porosity is the element that panels the performance of the catalyst (Brunauer et al. 1938). The analysis of the porous texture was carried out by N_2 adsorption/desorption techniques at 77 K. Adsorption isotherms were determined using a Smartsorb 92/93 instrument where 50 mg of samples are pre-heated at 150°C for 1 h.

2.7.9 Langmuir Blodgett surface pressure film balance

This technique was used to measure the per particle surface area of the sample calculated from the surface–pressure isotherm. Surface pressure (Π) v/s surface area (A) of the CdS film was determined on KSV-NIMA minitrough model. Typically, 100 μL of chloroform dispersion of CdS particles (1mg/1 mL) was spread evenly on water in a trough and compacted to condensed state with 30 mN/m surface pressure.

2.7.10 Thermo Gravimetric Analysis (TGA)

TGA is the quantitative measurement of weight loss (weight gain) of a material as a function of temperature and time, in an inert atmosphere. It was useful in this research in order to investigate the thermal stability of materials in a controlled atmosphere. Their working is based on the fact that when material is heated they lose weight due to water release, phase changes, structural decomposition, carbonate decomposition and gas evolution. The thermal decomposition was carried out on Perkin Elmer-Diamond. Approximately 3 mg of the sample underwent thermal analysis with the heating rate of 5 $^{\circ}\text{C}/\text{min}$, and a temperature programming range from 0 to 1000 $^{\circ}\text{C}$.

2.7.11 Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy had been used to obtain information of the type of NPs and their binding to the surface after surface modification by silica layer. The working principle is based on the fact that bonds and groups of bonds vibrate at characteristic frequencies. When a sample is exposed with infrared radiations, absorbed infrared energy excites molecules into higher vibrational states, which is characteristic to that particular molecule (Atkins and Paula, 2006). All the FTIR measurements of the samples were carried out on Thermo Scientific, NICOLET S10 spectrometer. Solid sample was put on Attenuated Total Reflectance plate and the appearance or non-appearance of certain vibrational frequency in IR spectra of molecule gives valuable information about the structure of that particular molecule. The electromagnetic spectrum range used during analysis is 400 nm to 4000 nm.

2.7.12 Ar ion LASER

High energy laser was used to corrode the surface of photounstable semiconductor in order to reduce the dimensions of the semiconducting particles. In this research the dimensions of CdS core in silica coated core-shell structure of different shapes were reduced and controlled as a function of the wavelength of light

used. Ar ion continuous laser (Stellar-Pro, MODU LASER with multiline configuration) having energies in the range of 40-120 W and controllable monochromatic wavelengths i.e. 514, 488 and 458 nm was used for photoetching.

2.7.13 High Pressure Liquid Chromatography (HPLC)

HPLC is a powerful tool employed to analyze the formation of different compounds during the reaction process. In this research the analysis or the separation of the components of the reaction mixture were carried out by using Agilent technologies HPLC instrument equipped with stainless steel 5 micron C-18 column (250 mm length $\times$ 4.5 mm). The mobile phase used for the analysis was methanol and water (50:50 and 70:30) with a flow rate of 1 mL/min at 220 and 254 nm for the detection of *p*-nitrophenol and *m*-dinitrobenzene reduction products, respectively. 20 μ L of the reaction mixture was injected into the loop, after filtration by cellulose filter of 0.22 μ m. This technique is based on the principle of adsorption in which analyte molecules are separated on the basis of their interaction with the mobile and the stationary phase.

2.7.14 Mass Spectrophotometer (MS)

Mass spectrometry (Waters Micromass Q-TOF Micro) was performed using electro spray ionization (ESI) in positive ion mode. The technique is based on the principle that when molecules entered the mass spectrophotometer they are converted into charge particles by a beam of high energy electrons emitted from a filament. These charged particles were directed towards the accelerating plates which were directed to magnetic field in a uniform beam by focusing plates. Full scan mode was used for data collection. Scan range was set at 50–500 m/z. This technique was used to get the structural information of the various reaction intermediates and the products formed during the progress of the reaction. MS study was done from SAIF center, Panjab University, Chandigarh. Mass spectrometry was also performed by GC-MS spectrophotometer in chemical ionization mode (Shimadzu, GC-2010 and GC-MS- QP2010 Plus) with RTX- 5 Sil MS column. This study was done from Chemistry Department, Punjabi University, Patiala, India.

2.7.15 Gas Chromatography (GC) Measurements

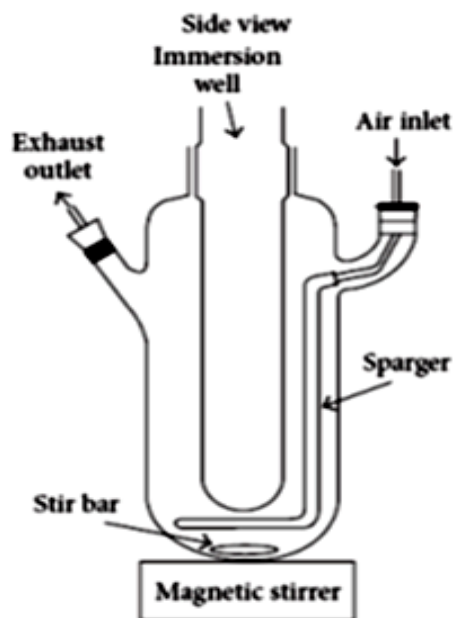
H₂ and CO₂ was measured using gas chromatography (NUCON 13 A) with a thermal conductivity detector (TCD). Due to similar conductivity values for He and H₂, nitrogen was used as a carrier gas. The separations were achieved with a molecular sieve column (30 m $\times$ 0.32 mm $\times$ 12.00 μ m) for H₂ analysis and the gas

chromatograph oven temperature was 30 °C, as this was found to be the best temperature for spatial resolution between N₂ (reactor purge gas) and H₂. Calibration curves were linear over a broad range of H₂ concentrations. The separation and the quantification of CO₂ were achieved with a Porapak-Q column (2 m × 3.17 mm). The gas chromatograph oven temperature was set at 40 °C, injector temperature at 70 °C and detector at 80 °C, as this was found to be the best temperature for spatial resolution between N₂ (reactor purge gas) and CO₂.

2.8 Photocatalytic reaction set ups

2.8.1 Photocatalytic reactor with Hg (UV) light source

The experiment was carried out in a photoreactor - a two glass tubes arranged concentrically, one having a larger diameter than the other. The inner channel contains an elongated light source, a bulb radiating light outwardly. There are two openings at the top, one for water inlet and the other for water outlet. On the sides, there is an air inlet and an exhaust outlet. A long thin capillary on the air inlet side helps in homogenizing air with the reaction mixture under magnetic stirrer. In the present case, the outer jacket of the reactor was removed and the sample is irradiated directly in a test tube surrounding the 125 W Hg (UV) lamp of intensity 10.4 mW/cm². The test tubes were kept at a distance of 2-3 cm from



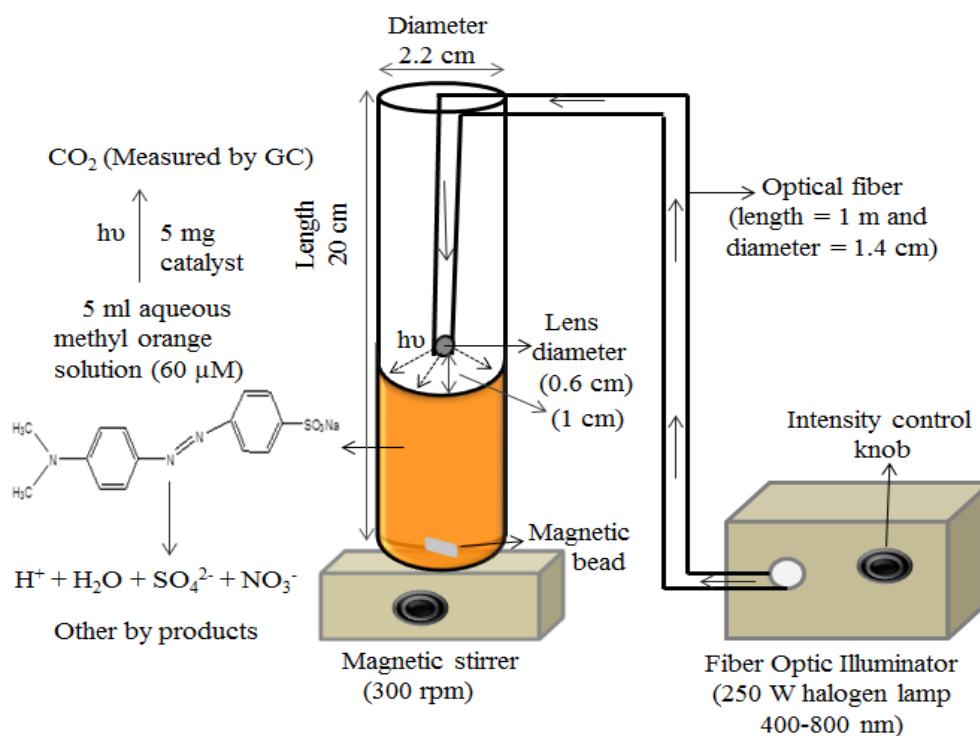
Scheme 2.1. UV light photoreactor.

light source and the reaction mixture was stirred constantly by magnetic stirrer with 300-400 rpm. The whole set up was placed in a wooden box to prevent the UV exposure as a safety measure and is denoted as *LS-I*

2.8.2 Photocatalytic reactor with visible light source

A 250 W halogen (tungsten-iodine) lamp was served as the light source. The lamp has high stability and an intense coverage of wide spectrum in the range of 380-780 nm. The experiments were carried out in a pyrex glass test tube of L = 20 cm and D = 2.2 cm. The source set up was extended with a thin probe of L = 1 m and D =

1.4 cm terminated with a lens of $D = 0.6$ cm. Light source (*LS-II*) was constructed with a knob to control the intensity of light (0.8 to 3.4 mW/cm^2) and cooled by the fans to keep it at RT. The probe was inserted into the wide pyrex test tube containing reaction solution and assembled above the solution at 1 cm height. The intensity level of the light is controlled by fixing the distance between the source of light and the reaction solution. The halogen radiations above reaction sample were measured by Lux meter.



Scheme 2.2. Photoreaction set up for photodegradation of methyl orange.

Another visible light set-up (*LS-III*) was used as a light source for photochemical reactions. In this system, a direct halogen light (250 W tungsten-iodine lamp) of a particular intensity was allowed to irradiate on the test tube after detaching the extended probe of *LS-II*.

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3. Effect of Silica Coating on the Optical and Photocatalytic Properties of Different Shapes of CdS

3.1 Introduction

Chapter - 1 mentioned that CdS is a promising material studied for practical applications because of its suitable band gap energy in the visible region of solar light (Wang et al. 2005; Romano and Alves, 2006; Acevedo, 2006). It shows tunable optochemical properties with change in size and morphology. But it undergoes anodic dissolution; as a result its photochemical activity deteriorates with illumination time (Matsumura et al. 1983). Moreover, it easily coalesces into larger particles owing to their large surface-to-volume ratio. Recently, surface passivation of CdS nanostructures by SiO₂ shell coating over CdS nanoparticles (NPs) has been demonstrated (Vigil et al. 1994; Pal et al. 2004; Arellano et al. 2000) to improve the photostability and photoactivity due to its various properties mention in chapter-1 (*section-1.3.2*). It has been demonstrated that the core-shell structure of spherical SiO₂@CdS (< 5 nm) nanocomposite is more photostable than bare CdS-NPs. They exhibit improved photoactivity for methanol dehydrogenation (Pal et al. 2004) and nitrobenzene reduction to azoxybenzene (Pal et al. 2007) under visible light (436 nm) illumination up to 80 h. It has also been proved that the SiO₂ shells are thin enough to allow penetration of small molecules and act as a photocatalyst without their coalescence.

Since, the redox ability of a photocatalyst is highly dependent on size, shape and surface modification. CdS nanorod (NR) gained special interest owing to its beneficial advantages over spherical shape in optoelectronic and photovoltaic applications. However, there are few reports available in the literature (Torimoto et al. 2009) about the preparation of core-shell morphology of SiO₂@CdS-NR and its opto-chemical properties. In this perspective, the effect of SiO₂ coating over CdS-NS and NR on the optical properties in correlation to their surface structural morphology was investigated. The photocatalytic activity of SiO₂@CdS nanocomposites for the oxidation of benzaldehyde was also studied.

3.2 Experimental section

3.2.1 Preparation of bare and SiO₂@CdS nanospheres and nanorods

Bare CdS nanospheres (CdS-NS1) were synthesized by *method-I* (*section-2.2.1*) and CdS nanorods (CdS-NR) were prepared as discussed in chapter- 2,

section- 2.3. SiO₂ coating on both of these structures was done using MPTMS and TEOS as per the procedure mentioned in section- 2.4.2 (chapter-2).

3.2.2 Photodeposition of Au nanoparticles

Deposition of Au-NPs onto bare and SiO₂@CdS-NR was done by using photodeposition technique as mentioned in section- 2.4.1

3.2.3 Photocatalytic activity study

Photocatalytic oxidation of 5 mL (10 μ M) benzaldehyde with 10 mg of CdS catalyst (bare, SiO₂@CdS-NS1, SiO₂@CdS-NR and 1 wt% Au loaded onto CdS-NR and SiO₂@CdS-NR) was carried out in an oxygen saturated atmosphere in a test tube under UV irradiation (*LS-I*) for 5 h. The reaction aliquots were taken from the test tube at regular interval of 1 h. Samples were filtered by cellulose filter (0.22 μ m) and analyzed by UV–Vis spectrophotometer at $\lambda_{\text{max}} = 252$ nm.

3.2.4 Characterization

Crystal structures of the synthesized samples were investigated using XRD. The absorbance and emission spectra were recorded by diffuse reflectance and photoluminescence (PL) spectrophotometer, respectively. FT-IR measurements were done to know the binding surface of NPs. The size and shape analysis were done by SEM, TEM, elemental analysis was done by EDX and BET surface area was measured by N₂ adsorption technique.

3.3 Results and discussion

Fig. 3.1a shows the UV–Vis absorbance spectra of small bare and SiO₂@CdS-NS1 in methanol and CdS-NR in ethylenediamine. The characteristic

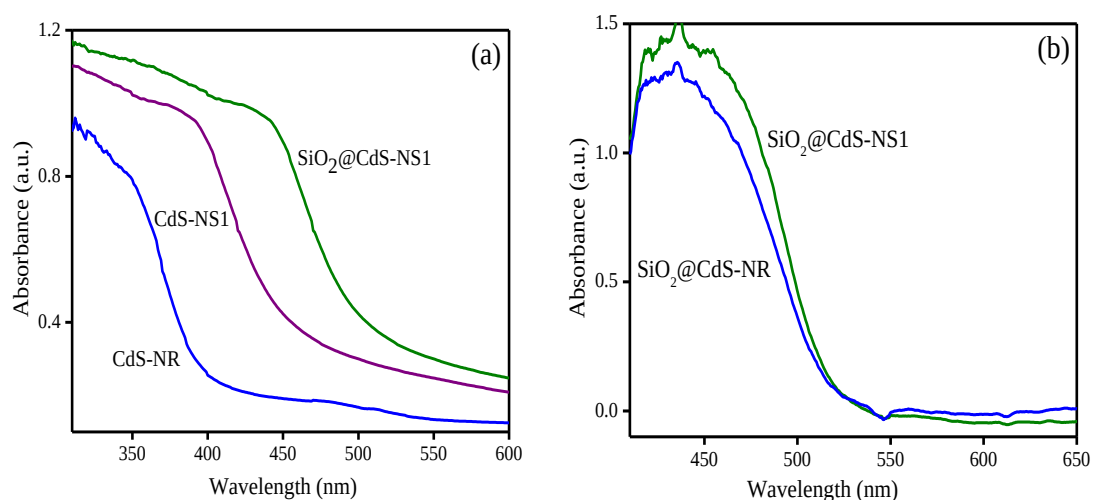


Figure 3.1 (a) Absorption spectra of CdS-NS1 and SiO₂@CdS-NS1 in methanol and CdS-NR in ethylenediamine and (b) diffuse reflectance spectra of SiO₂@CdS-NS1 and SiO₂@CdS-NR.

absorbance onset of bare CdS-NR and NS1 appeared at ~ 400 and 445 nm, respectively. After SiO_2 modification, the absorbance band of CdS-NS1 was red-shifted to 495 nm because of the growth of cluster size and confinement effect into SiO_2 matrix (Chang et al. 1994). Thus, it was evident that the band gap (E_g) of CdS-NR crystallite was higher than CdS-NS1 nanocrystals. The diffused reflectance spectra (Fig. 3.1b) of powder SiO_2 @CdS-NR and NS1 nanocomposites exhibited same band edge at ~ 520 nm due to agglomeration on drying process. In addition, some scattering was observed at shorter wavelengths i.e. below 460 nm due to SiO_2 content.

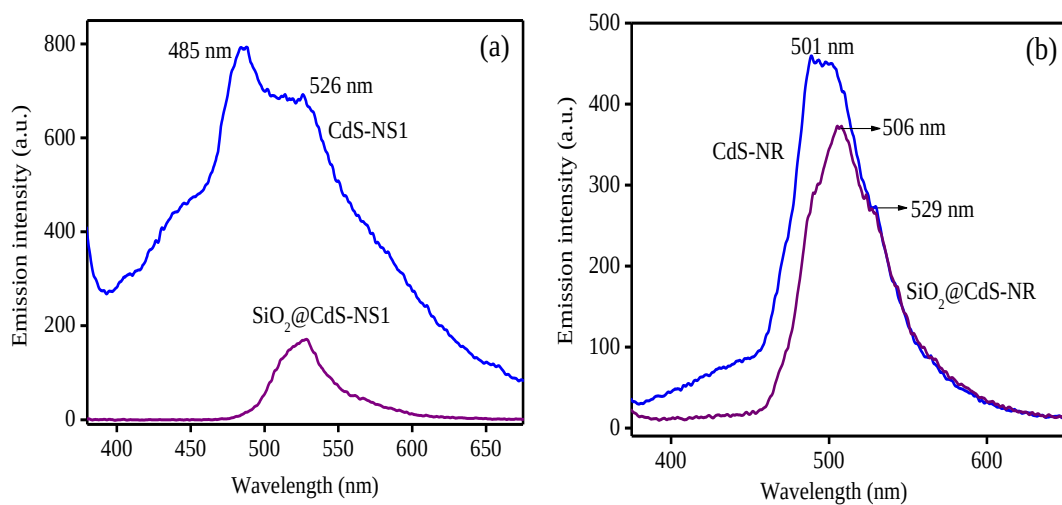


Figure 3.2. Photoluminescence spectra of (a) CdS-NS1 and SiO_2 @CdS-NS1 and (b) CdS-NR and SiO_2 @CdS-NR in acetone (1mg/mL) at $\lambda_{\text{ext}} = 365$ nm.

PL spectra (Fig. 3.2a) of bare and SiO_2 @CdS-NS1 nanocrystals (1 mg/mL dispersion in acetone at $\lambda_{\text{ext}} = 365$ nm) consisted of one sharp emission at 485 nm and a weak band at 526 nm. The fluorescence emission at 485 nm was attributed to the excitonic fluorescence (band edge emission) most likely occurred due to the radiative recombination of thermally detrapped e^- with valence band h^+ . Light absorption lead to an e^-h^+ pair or exciton that either undergoes radiative band gap or near band gap recombination with a characteristic intensity. However, the weak emission band at 526 nm occurred due to the radiationless recombination of the charge species at the surface defect sites (Mathew et al. 2011; Resch et al. 1992). It was observed that the emission intensity of CdS-NS1 get highly quenched due to thick SiO_2 matrix. The effect originated from the blocking of superficial surface traps of the CdS-NS1 by the $-\text{SH}$ groups (MPTMS) attachment and thick silica oxide layer formation. The conversion of Cd-SH to Cd-SR (Si-O-Si) bond formation and the

accumulation of excess Cd^{2+} on the surface thus seemed to destroy the sites where radiationless recombination of the charge carriers occur (Wuister and Meijerink, 2003). In fact, EDX elemental analysis confirmed the presence of large amount of Si (43.79 at%) along with Cd (2.62 at%) and S content (2.33 at%) in $\text{SiO}_2\text{-CdS}$ nanocomposites. In addition to Cd, S and Si, various other elements like O (40.76 at%), C (1.60 at%) and Cu (8.91 at%) were also detected. Moreover, S-H band at 2560 cm^{-1} for MPTMS was found absent in $\text{SiO}_2@\text{CdS}$ composites. A broad band at ca. 904 cm^{-1} and 1040 cm^{-1} was observed in FT-IR spectra due to Si-O-Si linkage (Torimoto et al. 2006). This suggested the surface modification of CdS with MPTMS via Cd-SR bond formation.

It is well known that NRs have higher photon absorption cross-section, size dependent and polarized light absorption and emission in comparison with spherical CdS-NPs. Therefore, the optical properties of high aspect ratio CdS-NRs are particularly attractive because the e^- and h^+ are delocalized along the length of the NRs (Saunders et al. 2008). A broad emission band for bare CdS and $\text{SiO}_2@\text{CdS}$ -NR (1 mg/ mL in acetone, $\lambda_{\text{ext}} = 365\text{ nm}$) was observed at 496-529 nm (Fig. 3.2b). The intense peak at 501 nm in bare CdS-NR was ascribed to the band gap emission that arises from recombination of e^-h^+ pairs. On silica coating, this band gap emission was again shifted to 506 nm. Another weak emission band at 529 nm was ascribed to the recombination of trapped charge carriers at the CdS defects sites. The emission of CdS-NR gets quenched when its surface was modified with amorphous silica. This effect suggested that the number of surface emissive defect sites were largely reduced after surface capping with MPTMS and subsequent silica shell coating (Chang et al. 1994; Yoon et al. 2006). Interestingly, it was also noted that the extent of fluorescence quenching in case of $\text{SiO}_2@\text{CdS}$ -NS was quite higher than $\text{SiO}_2@\text{CdS}$ -NR because of their different surface structural morphology and silica (thickness) content.

Fig. 3.3 shows the XRD patterns of bare and $\text{SiO}_2@\text{CdS}$ -NS1 and $\text{SiO}_2@\text{CdS}$ -NR. The broad peaks of CdS-NS1 (Fig. 3.3a) at 26.77° , 43.97° and 51.28° were in good agreement with (111), (220) and (311) planes of cubic CdS crystal structures, respectively, in accordance with the JCPDS data cards (No. 80-0019). The diffraction lines of the XRD planes were seemed to be broadened. This broadness was because of the fact that as the size of a crystal decreases, the number of its lattice planes and thus the extent of orderly arrangement also decrease. After

SiO₂ coating, the intensity of diffraction peaks was greatly reduced because of the

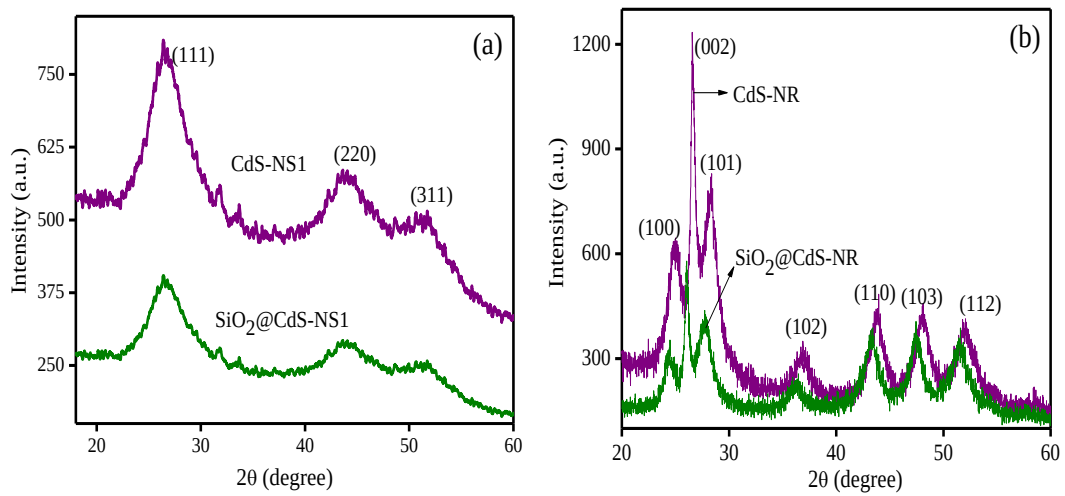


Figure 3.3. X-ray diffraction patterns of (a) CdS-NS1 and SiO₂@CdS-NS1 and (b) CdS-NR and SiO₂@CdS-NR.

hindrance of light scattering from CdS-NPs encapsulated into thick SiO₂ matrix (Chang et al. 1994). Fig. 3.3b shows a typical hexagonal crystalline structure of CdS-NR having characteristic lattice planes as detected in SAED pattern (*shown in TEM images below*). The (002) diffraction peak was found to be more intense and narrower than the peaks from other planes. This pattern evidenced the consistent growth of rod-shaped crystals along the crystallographic *c*-direction of the hexagonal structure. It has been reported (Manna et al. 2002; Jun et al. 2001) that surface modifiers such as alkyl phosphonic acid greatly bound to Cd sites on cadmium chalcogenides crystal surface and change the relative growth rate of individual crystal face. As a consequence, SiO₂ growth on CdS-NR could prevent the relative growth of (002) plane along *c*-axis as compared to other planes. Upon SiO₂ coating, the peak intensity of (100), (002) and (101) plane was greatly reduced as compared to negligible changes of other lattice planes. However, no characteristic peaks for amorphous SiO₂ was identified. This intensity suppression was probably due to the surface passivation of CdS planes that were directly exposed or connected with Si-O-Si linkage of amorphous SiO₂ matrix (Torimoto et al. 2009).

The morphological study of synthesized nanostructures of CdS was carried out using SEM and TEM analysis (Fig. 3.4). SEM images in Fig. 3.4 (a and b) reveals that CdS particles had almost similar surface morphology. They formed irregular clusters containing agglomerated particles in the size range of few nanometers to micrometres. The aggregation of the particles could occur due to

drying process. The TEM images of CdS-NS1 (Fig. 3.4 (c and d)) shows the monodispersion of small spherical particles of almost uniform size ca. 10-12 nm.

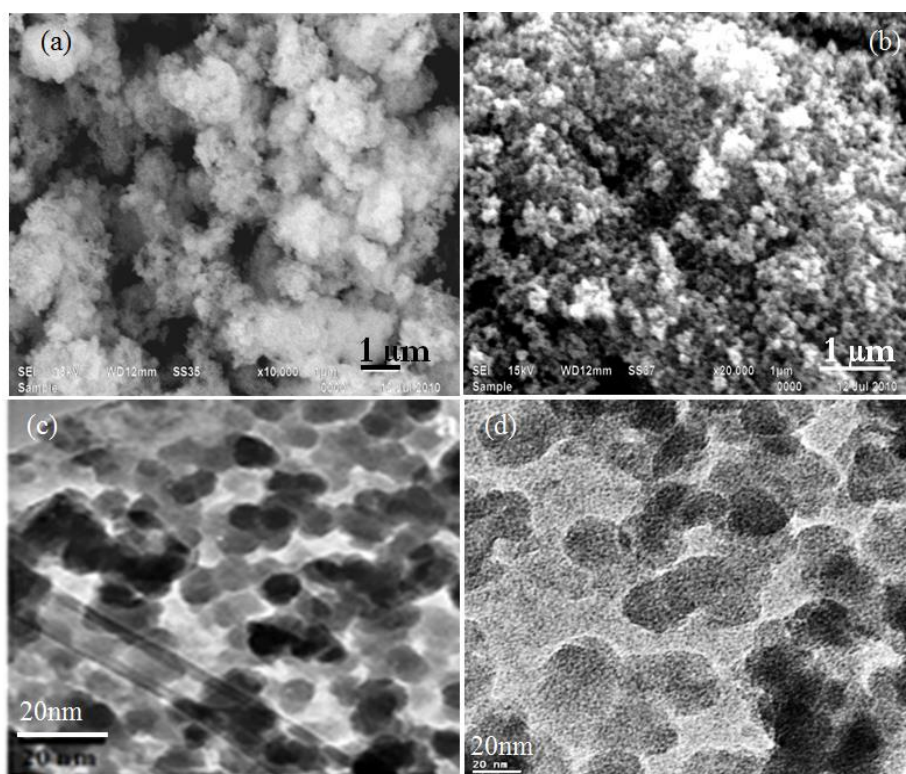


Figure 3.4 (a and b) SEM and (c and d) TEM micrographs of bare CdS-NS1.

The TEM micrographs of $\text{SiO}_2@\text{CdS-NS1}$ (Fig. 3.5a and b) shows that many individual CdS-NS (*light black*) of size 9–10 nm were found to be entrapped into thick silica matrix (*gray support*) and the most of the CdS-NPs were separated from each other by a certain distance. The HR-TEM image (Fig. 3.5c) of $\text{SiO}_2@\text{CdS-NS1}$ reveals that CdS-NS had well defined lattice fringes with interplanar spacing of 0.33 nm correspond to (111) plane of cubic structure. This confirmed the growth of cubic crystal structure of CdS-NS1 in conformity with the XRD pattern. The SAED pattern (Fig. 3.5d) displayed the characteristic diffraction rings of cubic CdS and relatively few diffused rings resulted from very small dimensions and grain size. Another probable reason of diffused rings could be the random orientation of crystallites as amorphous sample contains randomly distributed scattering units. The concentric rings with some bright spots in SAED patterns were assigned to the diffractions from (111), (220) and (311) planes of fcc-CdS as measured from the radius of these concentric rings. Although no definite thickness of silica shell was measured. But the EDX analysis (Fig. 3.5e) showed relatively higher amount of Si (43.79 at%) in

comparison with very less amount of Cd (2.63 at%) and S (2.33 at%) contents. This indicated the encapsulation of CdS-NS in thick SiO₂ enriched matrix as evident from TEM images. Moreover, the increased surface area ca. 51 m²g⁻¹ of SiO₂@CdS-NS1 as compared to bare CdS-NS1 ca. 18 m²g⁻¹ of size 9–10 nm further confirmed the immobilization of CdS-NS1 in thick SiO₂ support.

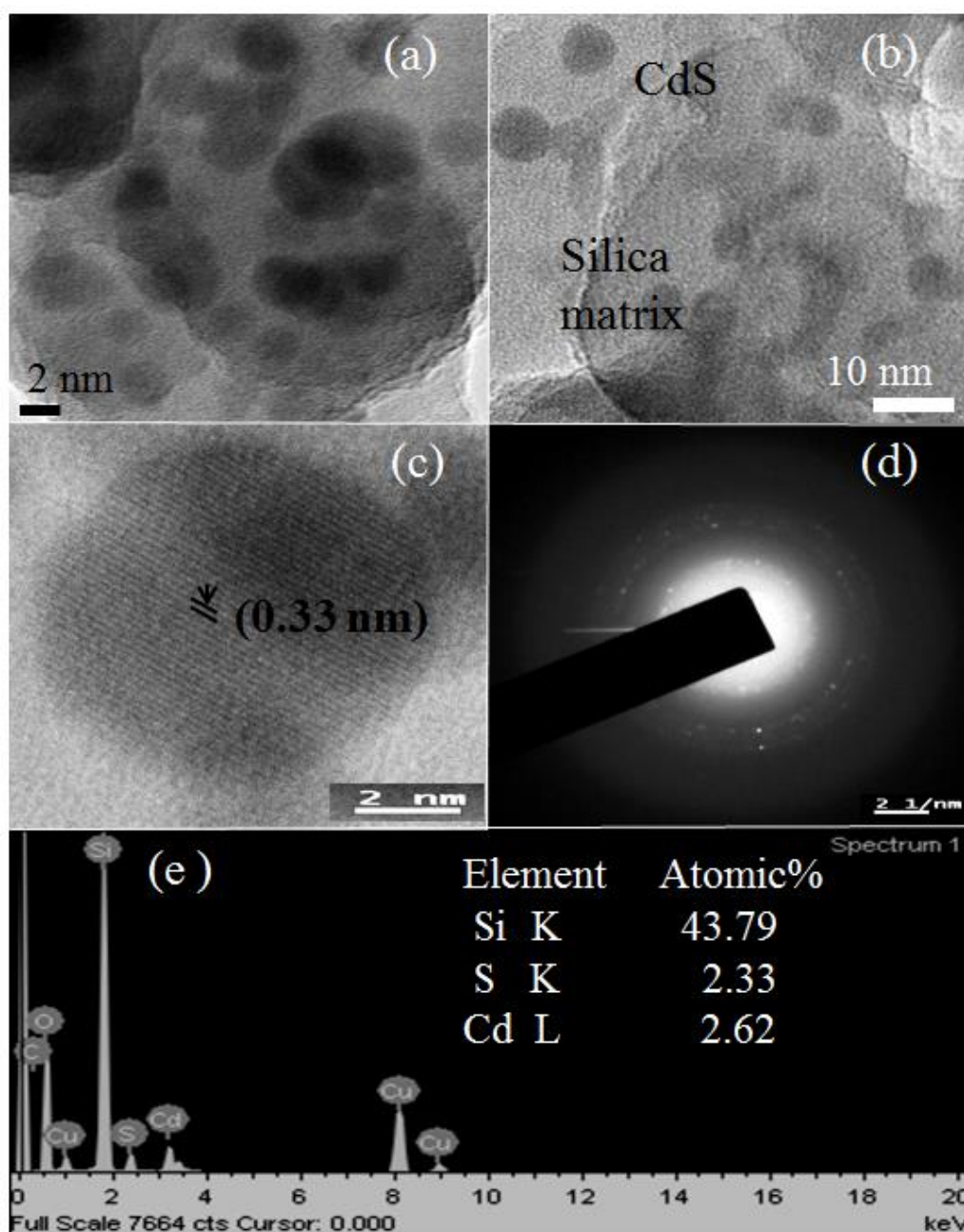


Figure 3.5. TEM images (a and b) of SiO₂@CdS-NS1, (c) HR-TEM image, (d) selected area diffraction pattern and (e) EDX elemental analysis.

The FE-SEM surface analysis (Fig. 3.6) showed the uniform growth of CdS-NR along radial as well as longitudinal facets. The aspect ratio (length (L)/width (W)) of

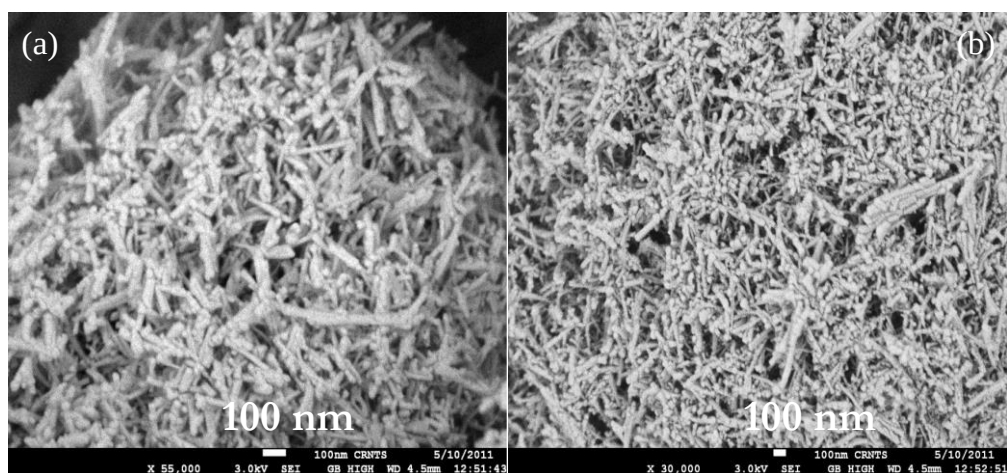


Figure 3.6. FE-SEM images of bare CdS-NR.

as-synthesized CdS-NR under SEM analysis consistently well matched with TEM micrographs. The TEM images (Fig. 3.7) shows the size and shape of bare and SiO₂@CdS-NR. The CdS-NR with an average D of ~ 6 nm and L of ~ 126 nm (ca. from 20 particles) correspond to aspect ratio = 21 were formed (Fig. 3.7a). The core-shell structure of SiO₂ (thickness 1.3 nm) coated CdS-NR was clearly observed (Fig. 3.7b), where two NRs were found to be attached as per the sketch (*inset*) in the TEM image. The entire CdS surface was seen to be completely covered with a thin silica layer of uniform thickness. An enlarged view (*inset*) of the marked area depicts the clear contrast of two unlike materials of CdS (core)-SiO₂ (shell) morphology.

Moreover, a cluster of four to five CdS-NRs was found to be coated together with a thin silica shell as per the scheme in Fig. 3.7c. A large number of CdS-NRs (*black color*) were found to be individually embedded into thin silica (*light gray*) shell (Fig. 3.7d). The EDX elemental analysis (Fig. 3.7e) of SiO₂@CdS-NR also confirmed the presence of lesser amount (12.81 at%) of Si as compared to thick SiO₂ matrix of SiO₂@CdS-NS1 (43.79 at%). The amount of Cd and S present were 19.79 at% and 22.90 at% (O = 17.81 at% and Cu = 26.69 at% from sample grid), respectively, which were quite higher than SiO₂@CdS-NS as discussed in Fig. 3.5e. The BET surface area of bare and SiO₂@CdS-NR was measured to be 21.2 and 42.3 m²g⁻¹, respectively.

The SAED patterns (Fig. 3.7f) exhibited a number of characteristic diffraction rings for a typical hexagonal CdS-NR of polycrystalline nature. From the radius of all these concentric rings, the lattice spacing analyzed for different planes were; d₁₀₀ = 0.358 nm, d₀₀₂ = 0.332 nm, d₁₀₁ = 0.314 nm, d₁₀₂ = 0.244 nm, d₁₁₀ =

0.208 nm, $d_{103} = 0.190$ nm and $d_{112} = 0.175$ nm. These indexed planes and their interplanar spacing were exactly consistent with the XRD diffraction (Fig. 3.3b) peaks of CdS-NR as measured from the Bragg's equation, $n\lambda = 2d_{hkl} \sin\theta$. In order to further elucidate the structural morphology of CdS crystal structure, HRTEM images were taken.

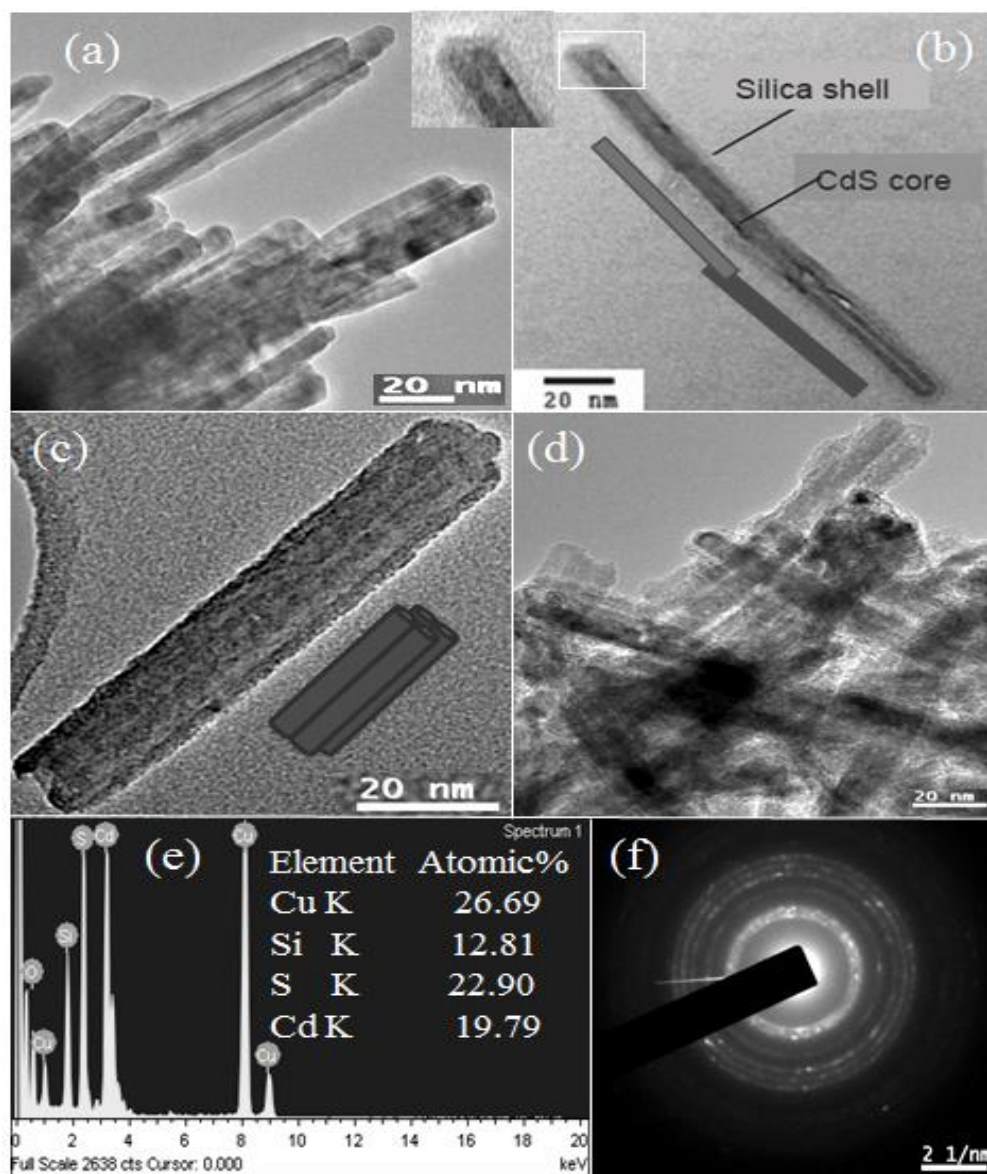


Figure 3.7. TEM images of (a) bare CdS-NR, (b, c and d) SiO₂@CdS-NR, (e) EDX elemental analysis and (f) selected area diffraction patterns.

Fig. 3.8 shows few identified unique lattice fringes of CdS nanocrystals being covered by amorphous silica matrix. The measured interplanar spacing (*from enlarged view of TEM images*) as 0.18, 0.23, 0.34 and 0.36 nm was assigned to (112), (102), (002) and (100) planes, respectively, of hexagonal (wurtzite) crystal

structure (Torimoto et al. 2009). Thus, the observed lattice spacing was in accordance with the SAED patterns. It was evident that the lengthwise growth of CdS-NRs occurred preferentially both along the (crystallographic *c*-axis) parallel (002 and 112) and perpendicular (102 and 100) direction, and there was a little variation in diameter of CdS-NRs as noticed under restricted preparative conditions (Yang, 2006).

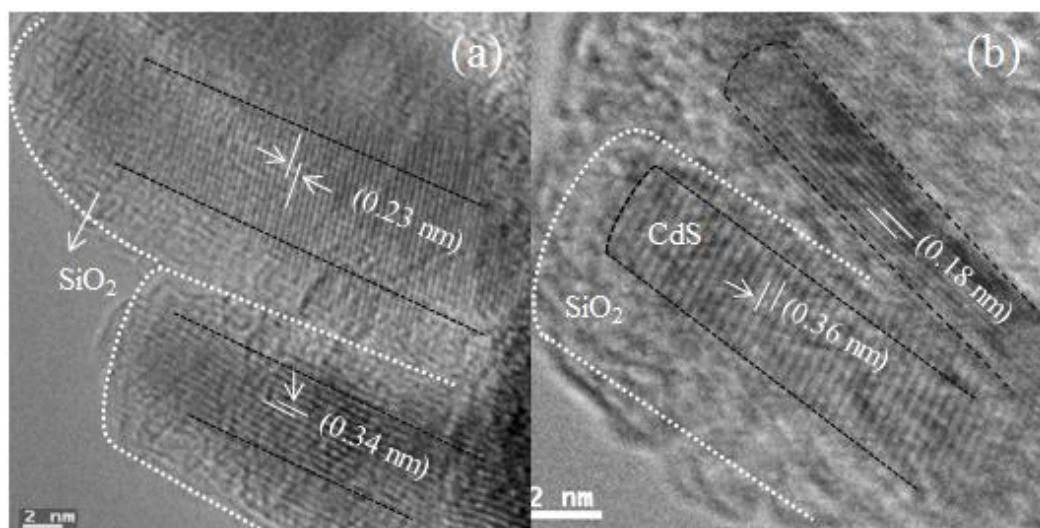


Figure 3.8. HR-TEM images of SiO₂@CdS-NR with well resolved lattice fringes.

Photochemical reactions at the semiconductor–electrolyte interface occur if charge carriers generated by absorbed light reach the interface during their life time and find suitable reaction partners. The photoexcited e^- and h^+ induce reduction and oxidation of chemical substances adsorbed on the surface of the photocatalyst. The extent of desired photoreduction and photooxidation of chemical reactions largely depends on the position of conduction band (CB) and valence band (VB) edges as a function of the size of the photocatalysts (Chen and Mao, 2007; Kamat, 2002). Hence, the size-dependent photoactivity of CdS has been extensively studied because of its visible light ($E_g = 2.42$ eV) photoactivity and suitable CB (-0.4 V vs. NHE) position. Recently, Pal et al. reported the high photocatalytic activity for nitrobenzene reduction and methanol dehydrogenation reactions by core–shell structure of SiO₂@CdS nanocomposites under 436 nm light irradiation (Pal et al. 2004 and 2007). This was attributed to the execution of stable photoactivity of smaller (< 5 nm) CdS core due to the prevention of coalescence by a thin layer of silica shell. The photoactivity of as-synthesized SiO₂@CdS nanocomposites for the oxidation of benzaldehyde under UV light irradiation was investigated.

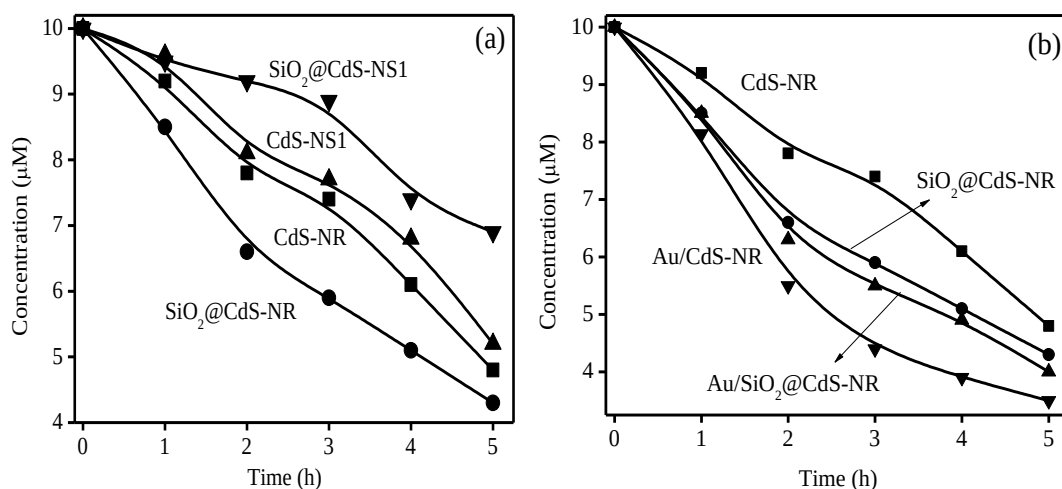


Figure 3.9. Photocatalytic oxidation of 5 mL (10 μM) benzaldehyde: comparative photoactivity of (a) bare and SiO_2 @CdS-NS1 and CdS-NR and (b) bare, SiO_2 @CdS-NR, Au loaded CdS-NR and Au loaded SiO_2 @CdS-NR.

Fig. 3.9a shows that although the bare CdS-NS1 (48%) and CdS-NR (52%) displayed almost similar photoactivity, but a large difference in photocatalytic activity was observed after silica coating over the respective CdS-NPs. As it is difficult to stabilize small CdS particles without any surface passivation, the observed low photoreactivity of bare CdS-NS1 and CdS-NR can be attributed to the aggregation effect. The SiO_2 coating prevents the agglomeration of CdS NPs; hence, the photoactivity was enhanced to 57% due to quantum size effect of CdS-NR core protected by thin (1–1.3 nm) SiO_2 layer. Moreover, the silica surface helps in superior adsorption of benzaldehyde molecules owing to higher surface area ($42.3 \text{ m}^2\text{g}^{-1}$) than that ($21.2 \text{ m}^2\text{g}^{-1}$) of bare CdS moiety. Thus, the reactant molecules can easily access the photoexcited CdS particles through porous silica layer and thereby improve the photooxidation rate, whereas SiO_2 @CdS-NS1 showed poor activity because the reactant species cannot access the irradiated CdS core through thick silica matrix as seen in TEM images of Fig. 3.5. Fig. 3.9b shows that the rate of benzaldehyde degradation was highly enhanced ($\sim 65\%$) when 1 wt% Au was photodeposited on bare CdS-NR. It is well known that the M deposition onto photocatalysts always enhance the photoactivity (Choi et al. 2004, Subramanian et al. 2004; Bellardita et al. 2007) via preventing e^-h^+ recombination. Due to direct electrical link between deposited Au and bare CdS-NR surface, access of photogenerated electrons by Au deposits was more. However, 1 wt% Au

photodeposition onto SiO₂@CdS-NR did not improve the photooxidation rate because of the poor electrical contact between Au and CdS core due to the presence of silica barrier at their interface.

3.4 Conclusion

The encapsulation of CdS-NS1 (size 9-10 nm) in thick (43.79 at%) SiO₂ matrix and long CdS-NR (aspect ratio = 21) coated with thin (12.81 at%) SiO₂ layer was found. The core-shell morphology having CdS-NR core and thin SiO₂ shell (thickness = 1-1.3 nm) was exclusively formed as noticed in the HR-TEM images. Accordingly, the BET surface area of CdS nanostructures was found to increase as a function of SiO₂ content and CdS morphology. The SAED patterns and HR-TEM images displayed a number of characteristic diffraction rings and unique lattice fringes of CdS-NR crystals being covered by silica shell. The measured interplanar spacing, ca. 0.18 nm, 0.23 nm, 0.34 nm and 0.36 nm was assigned to (112), (102), and (002) and (100) planes, respectively, for hexagonal CdS-NR crystals in accordance with the XRD patterns. Although the advantage of thin SiO₂ coating was tested by the improved photoactivity of CdS (core)-SiO₂ (shell) structure yet the photostability needs to be investigated for longer exposure to light irradiation.

3.5 References

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4. Photoluminescence and Photocatalytic Activity of CdS (Core)–SiO₂ (Shell) Morphology Prepared by CdS Photoetching

4.1 Introduction

As mentioned in chapter-1 (section-1.3.2), silica (SiO₂) coating prevents the coalescence and provides the stability to CdS particles from photocorrosion. In this chapter the discussion is extended about the other positive benefits delivered by SiO₂ coating for photocatalytic reactions. Concisely, it enhances the dispersion of CdS in aqueous media which can be easily regained by sedimentation and filtration of the reaction mixture. It also provides more specific surface for adsorption of the reactants due to its porosity thus enhance the reaction rate of photocatalyst. Since the described photocatalytic effects mainly concern the surface of the catalyst, the SiO₂@CdS core-shell system is highly advantageous and inexpensive (Wilhelm et al. 2007; Zhang et al. 2011). Moreover, core-shell structures help in preparing smaller nanoparticles (NPs) by photoetching (PE) and create void space inside the SiO₂ shell which may act as nanoreactors. These photoetched NPs are expected to show better photoemission properties compared to unetched particles where surface adsorbed species may quench the fluorescence emission. Also, they exhibit better photoactivity due to the shift in their redox potential to higher values on decreasing particle size and other properties. For example, Torimoto et al. first time reported the size selective PE of SiO₂@CdS-NPs by controlling the wavelength of light source (Torimoto et al. 2003). Pal et al. reported the enhanced photoproduction of H₂ by SiO₂@CdS PE particles under visible light (Pal et al. 2004). Li and co-workers reported 126% enhanced H₂ evolution by PE Pt loaded CdS particles in comparison to the original unetched Pt-CdS (Li et al. 2008).

Considerable research has been done on core-shell structure of SiO₂@CdS-NS (Teng et al. 2004; Wei et al. 2010). Up to date, there are few reports (Yoon et al. 2006; Torimoto et al. 2009) about the synthesis and PE of core-shell structure of SiO₂@CdS-NR and their application in photochemical reactions. *In continuation to the previous work (discussed in chapter 3), in this study the effect of CdS core size of various SiO₂@CdS-NR and SiO₂@CdS-NS nanocomposites as a function of wavelength of light irradiation from Ar ion laser is discussed.* As metal loading in void assists in creating effective metal (M)- semiconductor (SC) interface in

restricted SiO₂ boundaries and will mend the photocatalytic efficiency of SC particle by effective separation of photogenerated species. The influence of PE and M loading onto PE SiO₂@CdS samples on the optical absorption, emission and photocatalytic properties was also discussed.

4.2 Experimental details

4.2.1 Preparation of SiO₂@CdS-NPs, their photoetching and metals (Au, Ag, Cu, Pt, Pd and Rh) photodeposition

Synthesis of SiO₂@CdS-NPs (SiO₂@CdS-NS1 and SiO₂@CdS-NR) and their photoetching was performed as per the procedure discussed in *section 2.4.2 and 2.5, respectively of chapter 2*. Metal loading onto these particles was done by using photodeposition technique mentioned in chapter- 2 (*section- 2.4.1*).

4.2.2 Photocatalytic reactions

4.2.2.1 Benzaldehyde photooxidation

Photocatalytic efficiency of as-synthesized catalysts was examined by oxidative degradation of 10 μ M benzaldehyde aqueous solution. 5 mL of benzaldehyde solution containing 10 mg of catalyst was irradiated under UV light (*LS-I*) for different time intervals up to 5 h. The reaction samples were taken out from the test tube at fixed interval of 1 h. The reaction mixture was then filtered by 0.22 μ m cellulose filter and analyzed using UV-Vis spectrophotometer.

4.2.2.2 Methyl orange photodegradation

The photocatalytic activity of as synthesized CdS nanocomposites was further evaluated at room temperature for the photodegradation of methyl orange (MO) under visible light. A 250 W halogen (tungsten-iodine, $\lambda = 656.28$ nm) lamp extended with a thin probe was served as the light source (*LS-II*) mentioned in *section- 2.8.2 and shown in scheme- 2.2*. The reaction system was guaranteed an oxygenation from atmospheric air by a simple air pump. The aliquots were withdrawn from the test tube periodically, and the photocatalyst was separated from the suspension by centrifugation followed by filtration with 0.22 μ m cellulose filter. The photodegradation process was monitored by the characteristic absorbance band of MO at 465 nm using a UV-Vis spectrophotometer and the intermediates formed were analyzed by GC-MS spectrophotometer. The photodegradation efficiency of MO was defined as

$$\eta = (C - C_0)/C_0 \times 100\%$$

where η is the degradation efficiency of MO, C is the concentration of MO at reaction time t , and C_0 is the initial concentration of MO. It is well known that photocatalytic oxidation of organic pollutants follows Langmuir-Hinshelwood kinetics. This kind of reaction can be represented as follows:

$$\ln(C/C_0) = -kt$$

where k is the pseudo-first-order rate constant (min^{-1}) determined by using the expression, $\text{Rate } (k) = 2.303 \times \text{slope}$

4.2.3 Characterization

The resulting $\text{SiO}_2@\text{CdS}$ nanostructures were characterized by absorption and PL spectrophotometer, XRD, TEM, SEM and EDX. BET surface area (SA) was measured by N_2 adsorption technique. SA per particle of CdS-NR, $\text{SiO}_2@\text{CdS}$ -NR and $\text{SiO}_2@\text{CdS}$ -NR(PE) was measured by LB film balance. Surface pressure (Π) v/s surface area (A) of the CdS film was determined. The reaction intermediates were analyzed by GC-MS spectrophotometer. Amount of CO_2 produced on mineralization was measured by GC with a TCD detector. All the analysis were done as per the conditions mentioned in *section 2.7.14 and 2.7.15*.

4.3 Results and discussion

4.3.1 Optical and structural analysis

The absorbance onset of $\text{SiO}_2@\text{CdS}$ -NR (Fig. 4.1a) was around 505 nm which was blue shifted to 488 and 458 nm after irradiation with monochromatic light of 488 and 458 nm wavelengths for 3 and 5 h, respectively. The size of these particles was such that the band gap (E_g) was larger than the photon energy and further etching would not occur because of the limitation of light absorption by this particle size. It is well-known that semiconductor exhibit quantum size effect when the size of the solid particle is smaller than the bulk exciton radius as a result of the spatial confinement of the charge carriers (Dijken et al. 1998). Thus, the blue shift in the absorbance onset could be attributed to quantum confinement of CdS-NR core or decomposed CdS particles of smaller dimension formed by PE with laser light having diameter < 8 nm (equivalent to Bohr's radius).

Diffuse reflectance spectra of bare and $\text{SiO}_2@\text{CdS}$ -NR exhibited an absorbance onset ~ 520 nm and photoetched sample exhibit at ~ 500 nm which was red shifted in comparison to absorbance spectra of aqueous dispersion of these nanocomposites due to agglomeration on drying process (Fig. 4.1b). The quantum confinement of CdS core in present case could be justified by the evolution of a

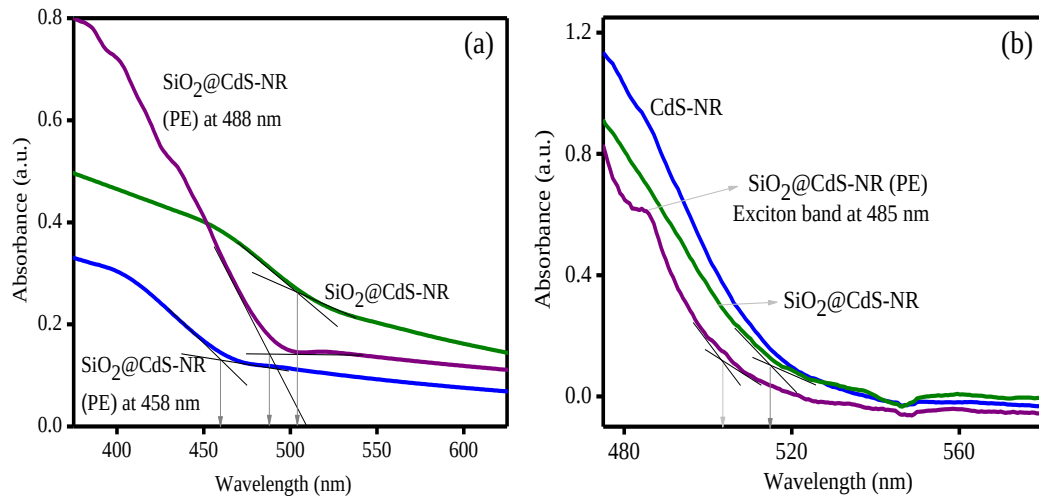


Figure 4.1. Absorbance spectra of (a) SiO₂@CdS-NR, SiO₂@CdS-NR(PE) photoetched at 488 and 458 nm dispersed in water and (b) solid state absorbance spectra of CdS-NR, SiO₂@CdS-NR and SiO₂@CdS-NR(PE).

characteristic exciton band at 485 nm in the absorbance spectra of photoetched SiO₂@CdS-NR (SiO₂@CdS-NR(PE)) composites (Fig. 4.1b) (Vossmeier et al. 1994; Zhang et al. 2003). The E_g was calculated (ca.) by using Tauc's relation: $\alpha h\nu = A(h\nu - E_g)^{n/2}$ where α , h , ν , E_g , and A are absorption coefficient, Planck's constant, frequency of light, band gap, and proportionality constant, respectively. The E_g of CdS-nanostructures was obtained by plotting $(\alpha h\nu)^2$ versus photon energy ($h\nu$). This relationship gave the E_g by extrapolating the straight portion of $(\alpha h\nu)^2$ against $h\nu$. The E_g of SiO₂@CdS-NR, ca. 2.4 eV, and SiO₂@CdS-NR(PE), ca. 2.6 eV, (Fig. 4.2a) was in good agreement with the blue shift in the absorbance spectra.

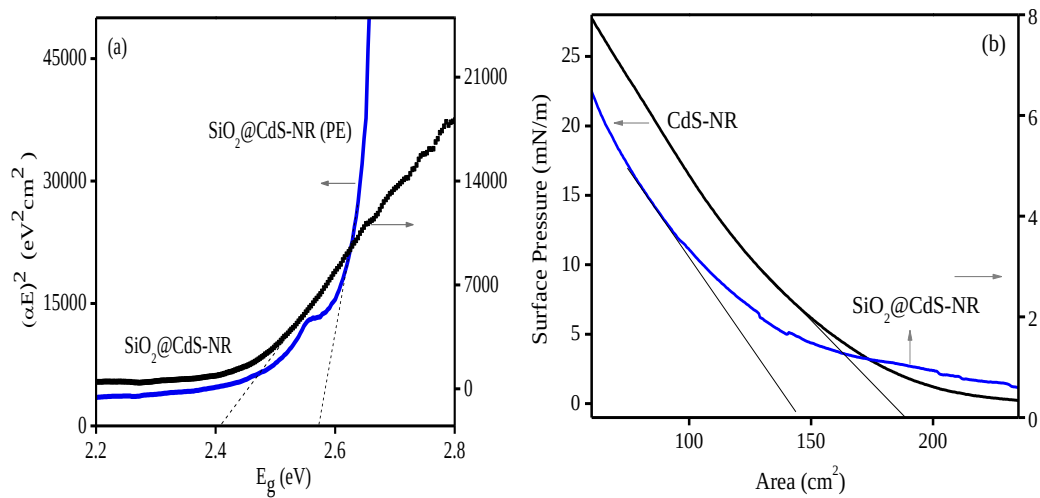


Figure 4.2 (a) Band gap energy of SiO₂@CdS-NR and SiO₂@CdS-NR(PE) and (b) surface pressure-area isotherm of CdS-NR and SiO₂@CdS-NR dissolved in chloroform.

The SA per particle of bare and SiO₂@CdS-NR was ca. from regular Π v/s A isotherm (Fig. 4.2b). 100 μ L of chloroform dispersion of CdS particles was spread evenly on water in trough and chloroform was allowed to evaporate for 20 min. Surface-pressure measurement was initiated by compression of barrier at a fixed rate of 5 cm²/min. It was observed from the surface-pressure isotherm (Fig. 4.2b) that CdS-NR particles formed a stable monolayer at Π below 15 mN/m and changed to condense state at Π above it. But for SiO₂@CdS-NR dispersion the stable surface pressure was found below 9 mN/m. This could be attributed to the hydrophilic nature of SiO₂ shell that could easily spread as thin film over polar water molecule through OH⁻ linkage. SiO₂@CdS-NR required less surface pressure for compression because of non-aggregated nature of CdS particles encapsulated in SiO₂ shell. Moreover in bare CdS-NR, free CdS particles might overlap and form agglomerated stacks that result in the formation of thick film. Area occupied by single molecule of CdS was measured by extrapolating from the condensed portion of Π v/s A isotherm and was found to be 44.7×10^{-3} nm². After SiO₂ coating the area was increased to 49×10^{-3} nm², although no substantial change was noticed. This result did not provide much information about the increase in SA due to silica coating. However, LB film SA of a particle for CdS-NR and SiO₂@CdS-NR was ca. to be 2125 and 2591 nm², respectively and was closely comparable with (CdS-NR area = 2319 nm² and SiO₂@CdS-NR = 2877 nm²) the estimated TEM size analysis. Tian and Fendler ca. the area occupied by a single CdS spherical particle capped by different surfactants using LB technique. They estimated that area after capping of CTAC was 11.7 nm² and on DODAB capping area was increased to 58 nm² (Tian and Fendler, 1996).

The TEM micrographs of various CdS nanostructures (Fig. 4.3a) showed the formation of CdS-NR (yellow) of length (L) = 100-120 nm and diameter (D) = 5–6 nm. After SiO₂ deposition onto CdS-NR, the color was changed to light yellow due to thin transparent covering of SiO₂ layer. Fig. 4.3b illustrates the core-shell morphology consisting of relatively dark colored CdS-NR core uniformly entrapped in gray colored amorphous SiO₂ shell (thickness 1-1.5 nm). SAED patterns (*inset* of Fig. 4.3a and b) of CdS-NR exhibited characteristic diffraction rings with bright spots for typical hexagonal crystal having polycrystalline nature and small grain size of CdS. Different lattice planes ca. by reciprocating the radius of diffraction ring corresponds to the planes that obtained from XRD confirmed wurtzite structure (Kang et al. 2007). SiO₂ deposition relatively decreased the intensity of SAED rings

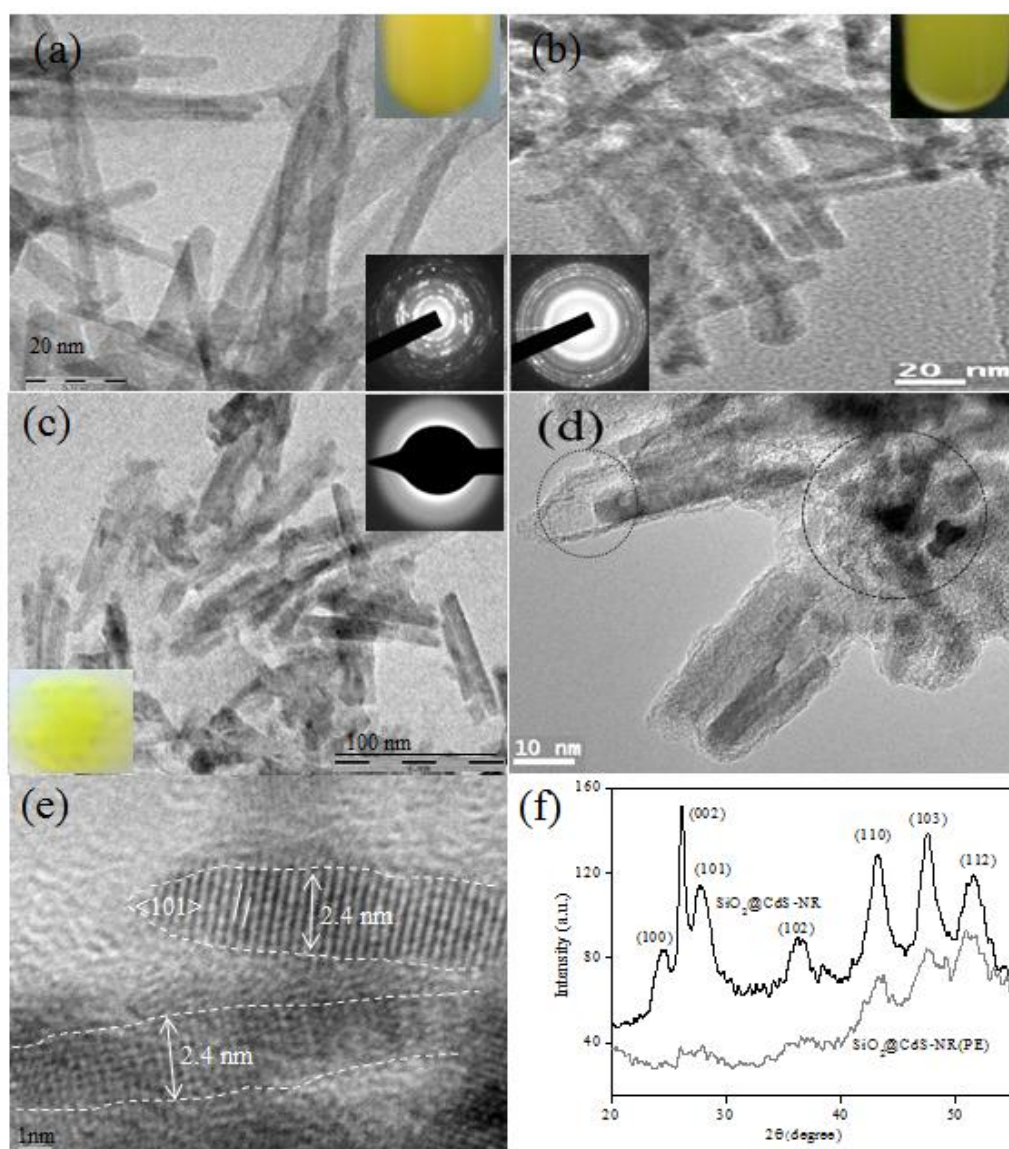


Figure 4.3. TEM images and SAED diffraction pattern of (a) CdS-NR, (b) SiO₂@CdS-NR, (c and d) SiO₂@CdS-NR(PE) photoetched, (e) enlarged view of SiO₂@CdS-NR(PE) and (f) XRD patterns of SiO₂@CdS-NR and SiO₂@CdS-NR(PE).

due to obstacle of electron scattering from heavier CdS core. After PE of CdS core with 488 nm laser irradiation, fragmented smaller CdS-NPs (*greenish- yellow*) of relatively shorter dimensions ($L \sim 79$ nm and $D \sim 2.4$ nm) compared to unetched SiO₂@CdS-NR ($L \sim 120$ nm and $D \sim 6$ nm) were seen to be encapsulated in SiO₂ shell (Fig. 4.3c). They appeared like a decomposed CdS-NR having no definite shape with no significant change in SiO₂ shell structure. After PE of CdS-NR core, the Debye rings (*inset Fig. 4.3c*) became more diffuse and fuzzy as compared to unetched SiO₂@CdS-NR which showed relatively clear contrast of concentric rings for crystalline CdS-NR. This fact indicated that crystallinity and grain size of CdS-

NR gets affected due to PE of CdS particles. An enlarged view of the TEM image (Fig. 4.3d) revealed the formation of many CdS-NR-(core) and SiO₂-(shell) morphology with ~ 1.8 nm of SiO₂ layer thickness though not homogeneous. After PE, many decomposed smaller CdS cores as compared to unetched SiO₂@CdS (Fig. 4.3b) were found to be entrapped in SiO₂ matrix (marked area Fig. 4.3d). Also, the void space (*top left circled area in Fig. 4.3d*) created due to CdS photoetching was an indication of CdS dissolution inside the silica matrix. EDX elemental analysis confirmed the presence of thin SiO₂ shell containing 12.81 at% Si and 17.81 at% O along with 19.79 at% Cd and 22.90 at% S for CdS core.

HR-TEM image (Fig. 4.3e) of SiO₂@CdS-NR(PE) sample displayed clear lattice planes of CdS-NR(PE) encapsulated in SiO₂ matrix with reduced width, ca. 2.4 nm, from the original CdS-NR (~ 6 nm). It was also investigated from TEM images that PE did not lead to any change in the interplanar spacing, ca. 0.317 nm, for (101) plane which was almost equal to spacing for unetched particles, ca. 0.314 nm. Fig. 4.3f shows the XRD pattern of SiO₂@CdS before and after PE. It had been evident that the diffraction peaks due to (100), (002), (101) and (102) planes of hexagonal CdS-NR crystal were almost disappeared after CdS PE, whereas the intensity of the peaks for (110), (103) and (112) planes was relatively decreased after photodissolution. This proved the directional etching of lattice planes of CdS-NR. The decreased intensity of XRD peaks for (101) indexed to D and (002) planes correspond to L were in good agreement with the reduced dimensions of CdS after PE (Fig. 4.3e). Similar study was done by Torimoto et al. who reported the effect of PE on the dimensions of surface modified CdS-NR at different wavelengths. They found that most of the PE was done along the length of rod (Torimoto et al. 2009). Yoon et al. also reported the formation of hollow silica nanotubes after PE of CdS core from SiO₂@CdS-NR nanocomposites by Q-switched Nd:YAG laser (Yoon et al. 2006).

Fig. 4.4(a) shows more representative TEM images of SiO₂@CdS composites having average aspect ratio = 21 that were coated uniformly with a thin SiO₂ shell. TEM micrograph (Fig. 4.4b) depicted the high crystallinity of CdS from the presence of well-defined lattice fringes. Some much smaller CdS-NRs (Fig. 4.4c and d) of L ~ 30 nm and D ~ 2.4 nm compared to those shown in Fig. 4c were also obtained. The decrease in the D of CdS-NR to 2.4 nm as a function of wavelength used (488 nm) was well consistent with the earlier reports (Torimoto et al. 2003). All the small PE

CdS-NR of almost uniform size were seemed to be embedded within a SiO₂ matrix. The interplanar distance (Fig. 4.4f) ca. 0.25, 0.20, and 0.34 nm characteristic of (102), (110), and (002) planes, respectively again confirmed the retention of hexagonal phase of CdS-NR.

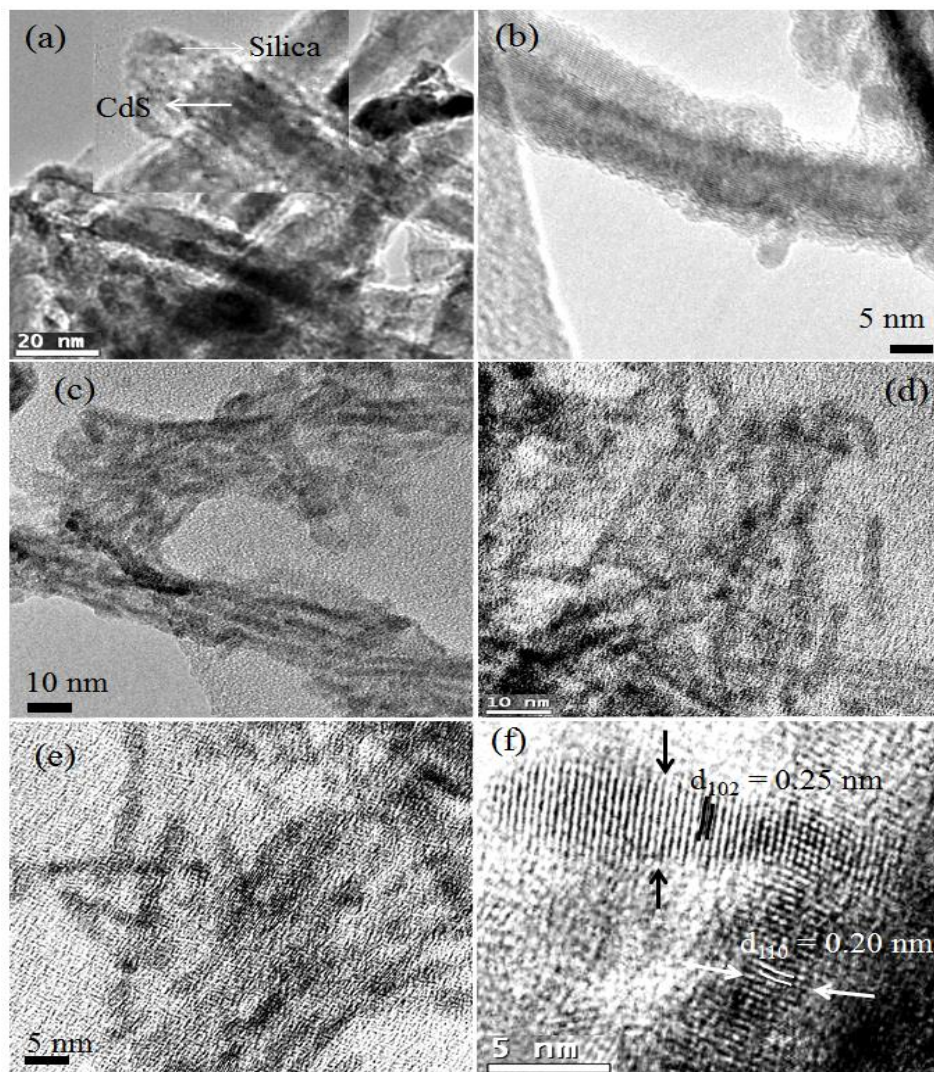


Figure 4.4. TEM images of (a and b) SiO₂@CdS-NR, (c-e) SiO₂@CdS-NR after photoetching at 488 nm and (f) their HR-TEM.

Fig. 4.5 shows the TEM images of 0.5 wt.% Au photodeposited SiO₂@CdS-NR(PE) nanostructures and the color change from light yellow (Fig. 4.3c) to dark green after Au deposition onto SiO₂@CdS-NR(PE) (*inset of Fig. 4.5a*). Such color change could be attributed to electronic interactions between SP band of Au-NPs and CdS-NR excitons. Small dark spherical Au nanodeposits of size $\sim$ 2-3 nm were found to be entrapped in the SiO₂ shell (Fig. 4.5a) in addition to few aggregates of Au deposits residing on the outer surface of SiO₂ shell. At high resolution in Fig.

4.5b, many spherical black colored Au deposits ($\sim 2\text{-}3\text{ nm}$) were observed onto CdS-NR of $\text{SiO}_2\text{@Au-CdS-NR(PE)}$. Although SiO_2 shell was not distinctive, but it was believed that Au^{3+} ions diffuse to CdS surface through porous silica layer and get reduced by photoexcited electrons of CdS, thus deposited on its surface. EDX analysis (Fig. 4.5c) confirmed the presence of Au - 0.53 at%, Cd - 21.57 at%, S - 23.45 at%, Si - 5.04 at% and O - 49.41 at% in $\text{SiO}_2\text{@Au-CdS-NR(PE)}$. Due to

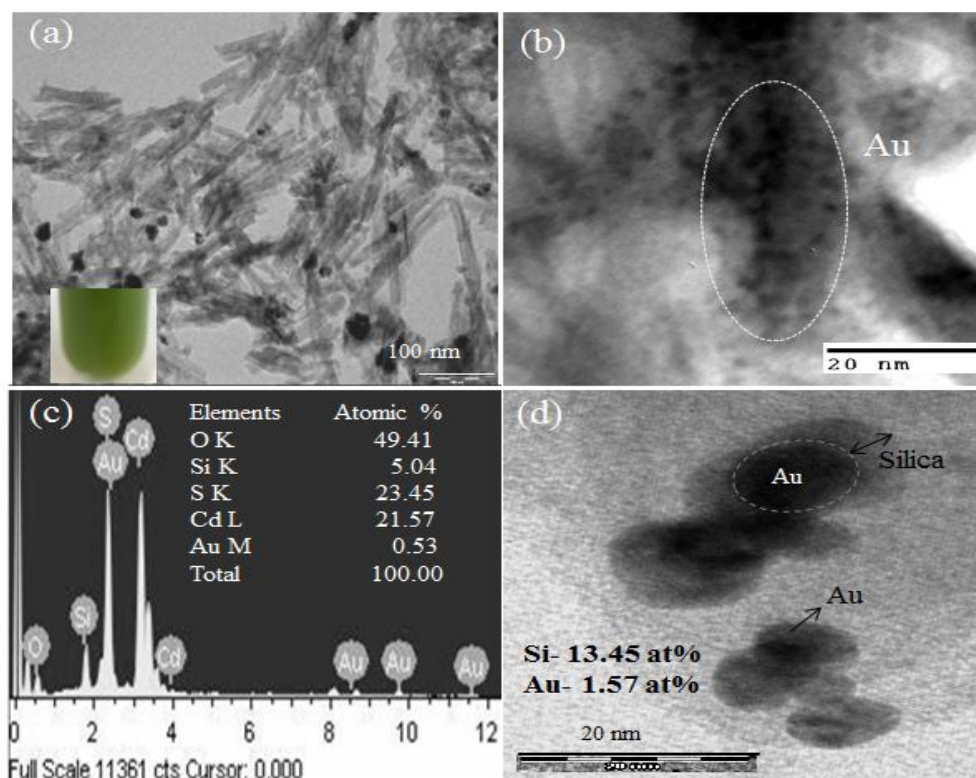


Figure 4.5. TEM images of (a) 0.5 wt.% Au photodeposited on $\text{SiO}_2\text{@CdS-NR(PE)}$, (b) enlarged view, (c) EDX analysis and (d) $\text{SiO}_2\text{@Au-NPs}$ after chemical etching of (a).

presence of SiO_2 , Au and CdS, it was difficult to distinguish these materials by TEM images. In order to confirm the presence of Au deposition in the interior of silica shell, CdS was chemically removed by etching with 2 M HNO_3 under stirring for 12 h to get $\text{SiO}_2\text{@Au-NPs}$ having core-shell structure. The TEM image (Fig. 4.5d) confirmed the incorporation of Au (*black color*) nanodeposits into thicker SiO_2 (*gray*) matrix. Smaller Au-NPs get agglomerated after CdS removal leading to the formation of bigger Au particles of an average size $\sim 10\text{ nm}$. EDX analysis confirmed the removal of Cd due to the absence of its characteristic peak and presence of 13.45 at% Si, 1.5 at% Au, 11.24 at% S and 20.5 at% O.

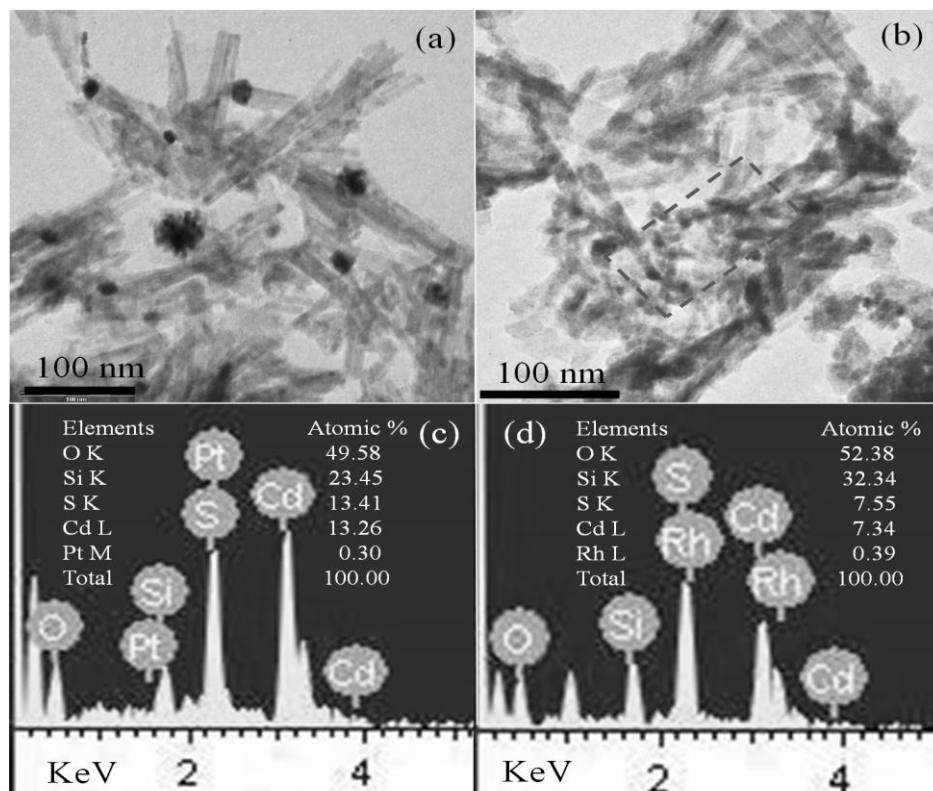


Figure 4.6. TEM images of 0.5 wt% (a) Pt, (b) Rh loaded photoetched $\text{SiO}_2\text{@CdS}$ nanorod and (c and d) their respective EDX spectras.

TEM micrographs of other metal loaded $\text{SiO}_2\text{@CdS}$ -NR(PE) (Fig. 4.6a) illustrate the attachment of very small Pt particles (size 2-3 nm) and Rh metal of size ~ 5 nm on CdS-NR (Fig. 4.6b). Many large aggregated particles were observed where some of the particles get incorporated inside the SiO_2 shell and few were attached over the SiO_2 shell. Though, we did not get very clear images but EDX analysis (Fig. 4.6c and d) confirmed the presence of respective elements. The at% of different elements were found to be - Cd-13.6 at%, S-13.41 at %, Si- 23.45 at%, O- 49.58 at%, Pt- 0.30 at% and Rh – 0.39 at% in their respective metal loaded samples. Similar kind of TEM images were obtained for other metal loaded $\text{SiO}_2\text{@CdS}$ -NR(PE) particles.

The photoemission of various CdS morphologies was measured using 1mg/mL acetone dispersion and photoexcited at 365 nm. The synthesized CdS samples displayed a wide emission band from 404 to 530 nm. Fig. 4.7a shows that bare CdS-NR exhibited a strong emission band at ~ 500 nm due to band gap emission and evolution of a weak band at 529 nm could be ascribed to surface trap emissions (Mathew et al. 2011). The emission intensity was reduced to certain extent

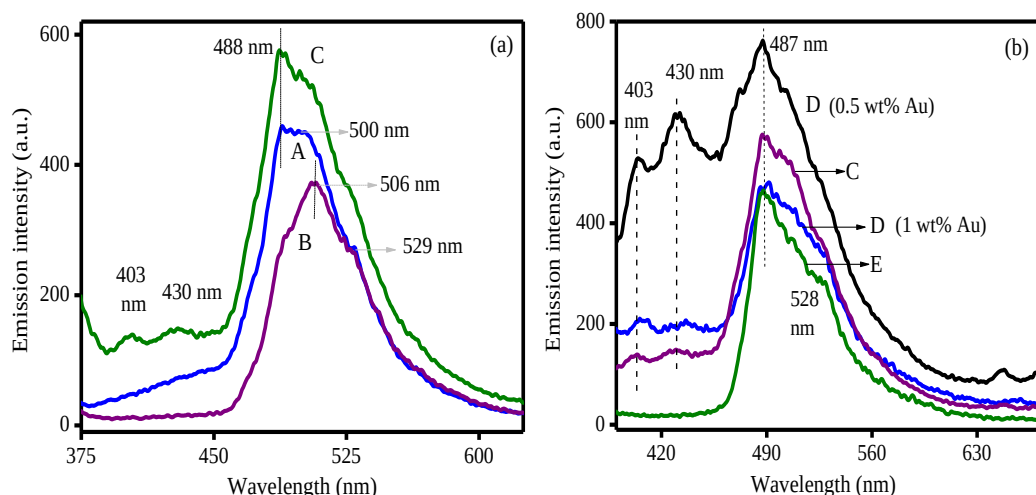


Figure 4.7. Photoluminescence spectra of (a) CdS-NR (A), SiO₂@CdS-NR (B) and SiO₂@CdS-NR(PE) photoetched (C) and (b) C, SiO₂@Au(0.5 wt%)-CdS-NR(PE) (D), SiO₂@Au(1 wt%)-CdS-NR(PE) (D) and SiO₂@Ag(0.5 wt%)-CdS-NR(PE) (E) in acetone ($\lambda_{\text{ex}} = 365 \text{ nm}$).

in SiO₂@CdS-NR with a red shift of 5 nm as *discussed earlier in chapter 3 (section-3.3)*. After PE by 488 nm irradiation, SiO₂@CdS-NR(PE) displayed highly enhanced emission intensity compared with unetched SiO₂@CdS-NR and emission peak gets blue shifted to 488 nm corresponding to its band edge emission. This improvement of emission intensity could be accounted to the formation of quantum size CdS particles having new surface and to more exposed surface of CdS molecules in the interior of silica shell. The other two peaks at 404 nm and 430 nm arose probably due to electronic emission from silica-CdS matrix (Lu et al. 2003).

Fig. 4.7b illustrates the effect of Au and Ag deposition on the emission intensity of SiO₂@CdS-NR(PE). This photo-physical process happened due to electronic interaction and energy transfer between surface plasmon resonance (SPR) band of deposited Au nanoparticles and CdS exciton. As Au SPR band has lower energy than band gap emission of SiO₂@CdS-NR(PE), during irradiation, energy of CdS-NR gets transfer to Au SPR. This plasmon-exciton interaction led to the emission quenching of CdS-NR on 1 wt% Au loading as reported by Mokari (Mokari et al. 2004). But on 0.5 wt% loading, enhancement in the emission intensity might be due to non-effective interaction of Au and CdS or due to the resonance effect of Au emission with that of CdS. As Au-NPs itself shows photoluminescence so they might add their effect to the emission intensity of CdS-NR. Lin et al. reported the enhanced emission intensity in Au (core)-CdS (shell) nanostructures. They assumed that the

excited e^- on Au surface by SP wave transferred to CB of the CdS shell and recombined with h^+ in VB. In their case, the internal Au core was the key factor of the energy transfer (Lin et al. 2006). However, more quenching was noticed in case of 1 wt% Ag than Au loading onto $\text{SiO}_2\text{@CdS-NR}$ (PE) because of the difference in the nature of metal (M) and their electronic property. Effect of different metals on the emission intensity of $\text{SiO}_2\text{@CdS-NS(PE)}$ was reported by Pal et al. They found that direct contact of M to CdS surface may lead to some surface defects that depends on the nature and the amount of M loaded, as a result emission occurred at higher wavelengths (Pal et al. 2005). This characteristic should be helpful for tuning the band gap of metal-semiconductor composites and controlling their optical property. Similarly effect of silica coating and photoetching on the optical and structural properties of CdS-NS was also investigated.

PE of $\text{SiO}_2\text{@CdS-NS1}$ with 488 and 458 nm laser light led to blue shift in the absorbance onset to ~ 483 and 455 nm from initial value of 500 nm due to decrease in the CdS core size. The E_g ca. using Tauc's equation was found to be 2.5 eV, for $\text{SiO}_2\text{@CdS-NS1}$ and 2.67 and 2.72 eV for $\text{SiO}_2\text{@CdS-NS1(PE)}$ at 488 and 458 nm,

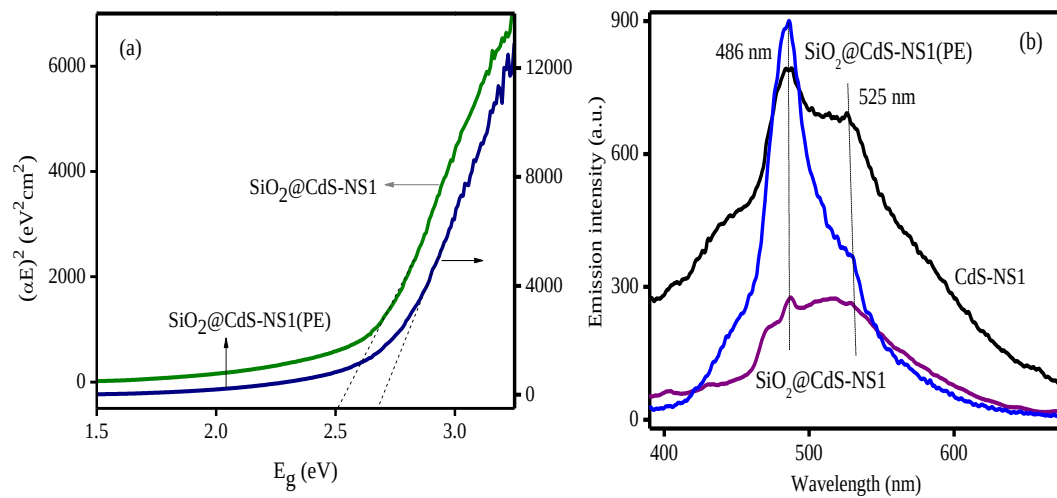


Figure 4.8 (a) Band gap energy of $\text{SiO}_2\text{@CdS-NS1}$ and $\text{SiO}_2\text{@CdS-NS1(PE)}$ photoetched and (b) photoluminescence spectra of CdS-NS1, $\text{SiO}_2\text{@CdS-NS1}$ and $\text{SiO}_2\text{@CdS-NS1(PE)}$ in acetone ($\lambda_{\text{ex}} = 365$ nm).

respectively, which was in good agreement with their difference in particle size (Fig. 4.8a). Fig. 4.8b shows the photoluminescence (PL) spectra (1mg/mL dispersion in acetone, excited at 365 nm) of bare CdS-NS1 and $\text{SiO}_2\text{@CdS-NS1}$ before and after PE. PL emission of CdS-NS1 consisted of two peaks - one sharp peak at 485 nm and another weak peak at 526 nm. The emission at 486 nm was attributed to the excitonic

fluorescence, most likely occurred from the radiative recombination of thermally detrapped e^- with VB h^+ . The weak emission band at 526 nm occurred due to the radiationless recombination of the charge species at the surface defect sites. It was observed that the emission intensity of CdS-NS1 was highly quenched on silica coating due to blocking of superficial surface traps of the CdS-NS by the $-SH$ groups (from MPTMS) attachment and thick SiO_2 layer formation. On photoetching by 488 nm irradiation, band gap emission intensity gets intensify whereas emission due to surface defects was reduced which proved that photoetching improved the CdS surface morphology.

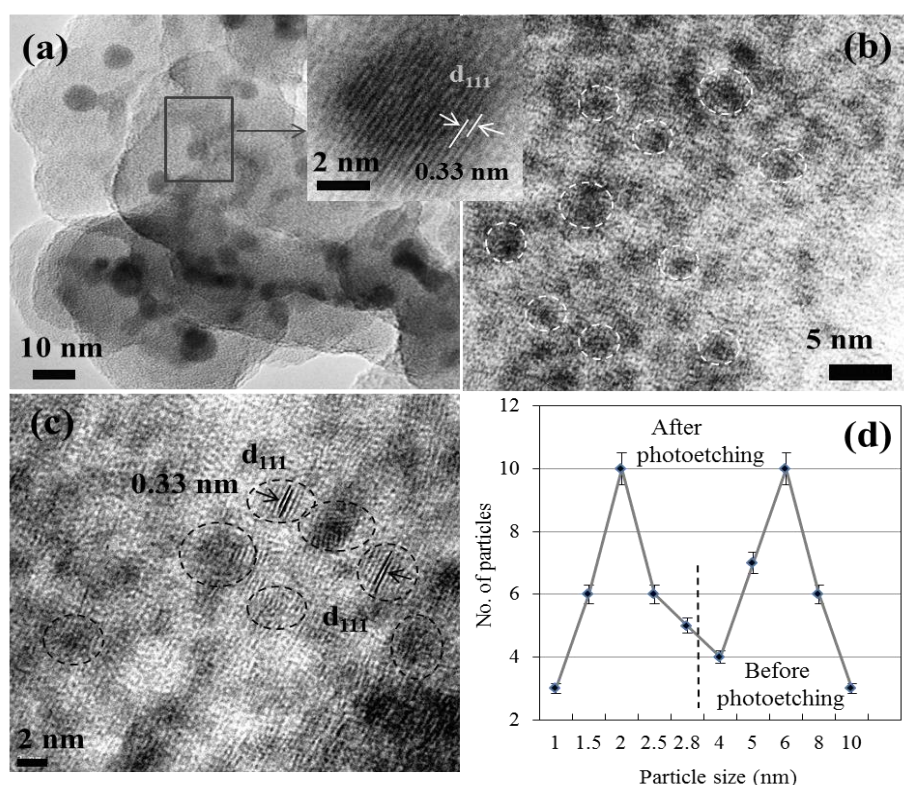


Figure 4.9. TEM images of (a) $SiO_2@CdS$ -NS1 (*Inset-lattice fringes*), (b) and (c) HR-TEM of $SiO_2@CdS$ -NS1 after photoetching and (d) particle size distribution of $SiO_2@CdS$ -NS1 before and after photoetching.

Fig. 4.9 displays the TEM micrographs of $SiO_2@CdS$ -NS1 before and after photoetching. Fig. 4.9a reflects microscopic image of many CdS-NS1 particles (*relatively dark contrast*) incorporation in thick silica matrix (*gray*) with an average size of ~ 8 nm (calculated from 20 particles). The magnified view of HR-TEM image of CdS-NS1 (*inset Fig. 4.9*) revealed well resolved lattice fringes having interplanar spacing of 0.33 nm corresponding to (111) crystallographic plane of cubic crystal structure of CdS-NS1. PE of CdS core from $SiO_2@CdS$ -NS1 led to reduction of CdS

core size in the range of 1.5-3 nm as compared to 6-8 nm of unetched CdS-NPs embedded into SiO₂ matrix. Well resolved lattice fringes with interplanar spacing of 0.33 nm corresponding to (111) lattice plane of CdS (Fig. 4.9b and c) were identified that evidenced the retention of crystal structure. The particle size distribution (considering 20 particles) before and after PE of SiO₂@CdS-NS1 particles is shown in Fig. 4.9d. It was found that most of the particles were in the size range of 6-8 nm before etching which reduced to 1.5- 2.8 nm after PE. Repetitive calculation for particle size distribution considering different particles was done and an error bar was fixed by considering $\pm 5\%$ error.

It is well known that CdS undergoes photodissolution on long exposure to UV light. To prevent it from photodissolution silica coating was found to be the superior coating agent due to its physico-chemical properties. In this context, effect of thin layer of silica coating on the photostability of CdS-NS was tested by UV light irradiation (LS-I) of bare CdS-NR and SiO₂@CdS-NR(PE) for 2-4 h is shown in Fig. 4.10. It revealed that upon UV irradiation, optical density of bare CdS-NR gradually decreased (Fig. 4.10a) and no characteristic absorbance onset of CdS was observed because of the complete photodissolution of CdS particles after 2-3 h UV irradiation. Whereas absorbance spectra of SiO₂@CdS-NR(PE) underwent no change even after 3 h UV exposure (Fig. 4.10b) because of thin SiO₂ shell deposited over CdS surface that prevents the direct light incidence and slowed down the photocorrosion process. Hence, this kind of nanostructures will be suitable for stable catalytic activity in photochemical reaction. Similar report on the stability of SiO₂@CdS-NS on longer

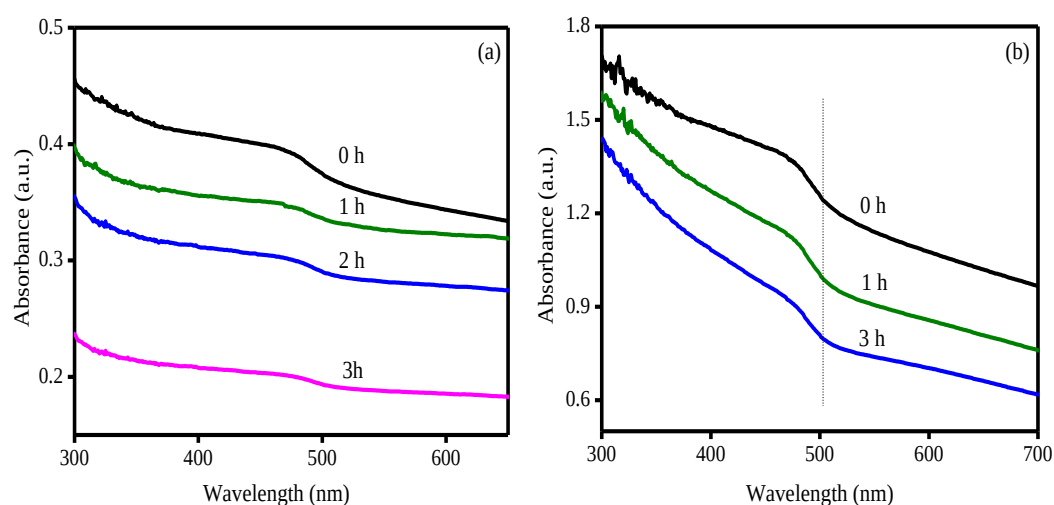


Figure 4.10. Photostability of (a) CdS-NR and (b) SiO₂@CdS-NR under UV irradiation.

exposure of light was demonstrated by various researchers (Pal et al. 2004; Wei et al. 2010). The $\text{SiO}_2@\text{CdS-NS}$ photocatalyst exhibited linear increase of H_2 production and nitroaromatic reduction up to 80 h light irradiation without any deterioration in photoactivity of CdS-NPs.

4.3.2 Photocatalytic oxidation of benzaldehyde under UV light

Along with high reduction potential (- 0.4 eV) CdS has good oxidation power with high positive VB position of + 2.0 eV. Photocatalytic efficiency of the synthesized catalysts was examined by oxidative degradation of 5 mL (10 μM) benzaldehyde aqueous solution with 10 mg of CdS catalyst under UV light irradiation for different time intervals. The photocatalytic activity (Fig. 4.11a) of $\text{SiO}_2@\text{CdS-NR}$ was found to be higher in contrast to bare CdS-NR because of the non-aggregation of CdS particles after silica coating and as a result, effective participation of smaller CdS particles led to the increased photoactivity. Another probable reason for the higher activity of $\text{SiO}_2@\text{CdS-NR}$ was high SA, ca. $42.4 \text{ m}^2\text{g}^{-1}$ compared to $21.2 \text{ m}^2\text{g}^{-1}$ of bare CdS-NR and silica layer may provide the better adsorption of substrate than bare CdS-NR surface. The $\text{SiO}_2@\text{CdS-NR(PE)}$ displayed improved photocatalytic degradation rate of benzaldehyde as compared to unetched $\text{SiO}_2@\text{CdS-NR}$ catalyst because of the smaller CdS-NPs of new surface atom formed in the interior of silica matrix after PE. It was found that after 0.5 wt% Au deposition, $\text{SiO}_2@\text{Au-CdS-NR(PE)}$ exhibit an enhanced photoactivity than $\text{SiO}_2@\text{CdS-NR(PE)}$ indicated that deposited Au particles efficiently captured the

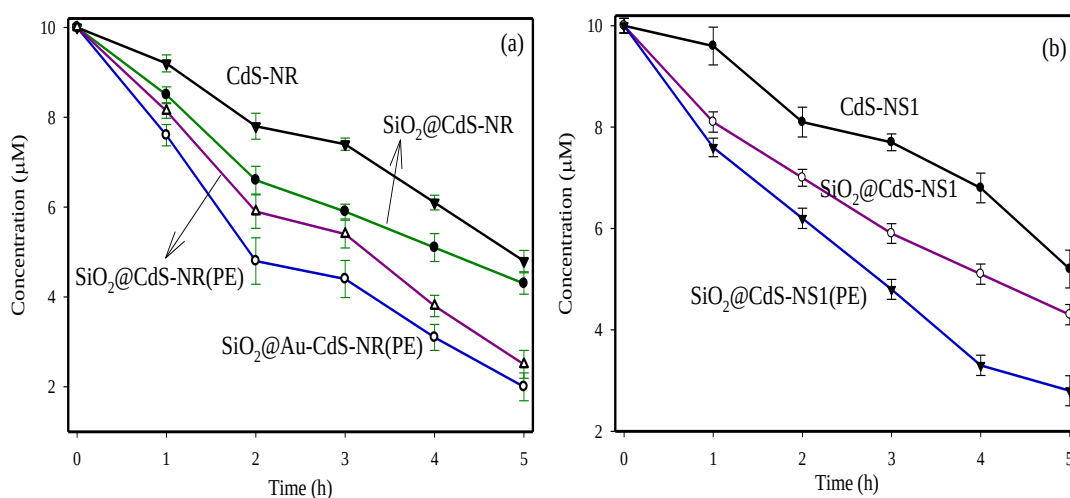


Figure 4.11. Photocatalytic degradation of benzaldehyde with 10 mg of (a) $\text{SiO}_2@\text{CdS-NR}$ and (b) $\text{SiO}_2@\text{CdS-NS1}$ composites under UV light irradiation.

photogenerated e^- from CdS-NR leaving the h^+ for oxidation process. However, Au deposition onto unetched $SiO_2@CdS$ -NR nanocomposites barely show any change in the photoactivity in comparison to $SiO_2@CdS$ -NR because of silica barrier as proved in chapter 3 (Fig. 3.9b).

Photooxidation of benzaldehyde follows the first order kinetics and the rate of degradations was best fitted to exponential decay curve. An error was found in the range of ± 0.3 which was fixed as error bar. $SiO_2@Au$ -CdS-NR(PE) exhibited the highest photooxidation efficiency of 80% followed by $SiO_2@CdS$ -NR(PE) (75%) than $SiO_2@CdS$ -NR (57%) and the lowest rate was exhibited by bare CdS-NR (52%). $SiO_2@CdS$ -NS1(PE) displayed (Fig. 4.11b) highest activity with photooxidation efficiency of 72%. The smaller NPs and new surface achieved after PE accounts the high activity. $SiO_2@CdS$ -NS1 exhibited superior efficiency of 57% than bare CdS-NS1 (48%) due to the prevention of agglomeration of NPs and more adsorption of the reactant species due to higher BET SA, ca. $51\text{ m}^2\text{g}^{-1}$ of $SiO_2@CdS$ -NS1 discussed in section-3.3 (chapter 3).

After deliberating the effect of as-synthesized different $SiO_2@CdS$ nanocomposites on the photooxidation of benzaldehyde under UV light, in the next section we will discuss the effect of same nanostructures loaded with 0.5 wt% of different metals mentioned in section-4.2.1 on the *photodegradation of MO under visible light (LS-II)*. A rate expression for the photocatalytic degradation of MO as a model compound in the visible/CdS process was developed, and various operational parameters such as CdS loading, initial dye concentration, intensity of light, pH variation were inserted into the rate equation. MO was selected for this study, as it is a water-soluble, highly stable and simplest azo dye and is used extensively as a coloring agent in textile industries.

4.3.3 Photodegradation of methyl orange under visible light

Fig. 4.12a shows the change in the absorbance spectra of 60 μM aqueous solution of MO (pH = 7.3) during photocatalytic decolorization performed by using 5 mg of $SiO_2@CdS$ -NR photocatalyst in the absence and presence of light. The suspension was magnetically stirred in the dark for 30 min to ensure the establishment of adsorption equilibrium between the photocatalyst and MO. A very little loss of MO due to the adsorption property of $SiO_2@CdS$ -NR was observed. However, on visible light irradiation, when the cleavage of the $-C-C-$ and $-N=N-$ bonds and the aromatic rings occurred, the intensity of the absorbance peak (465 nm)

of the MO solution decreased with increasing irradiation time. The absorbance onset shifted to lower wavelength indicated the breakage of MO to lighter compounds (Abdelmalek et al. 2006). The solution became colorless, indicated that the $\text{SiO}_2@\text{CdS}$ -NR completely decolorized the MO solution according to the UV-Vis spectroscopy.

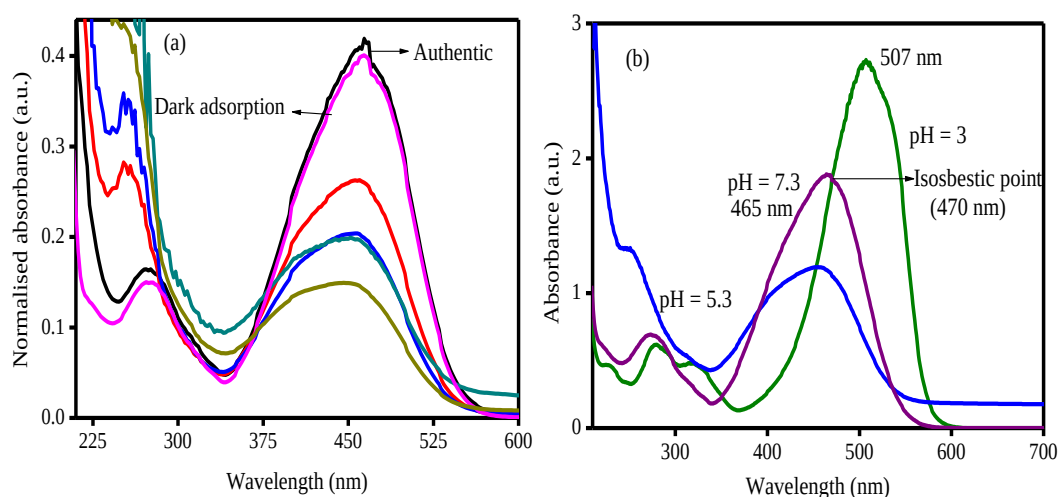


Figure 4.12 (a) Absorbance spectra of methyl orange (MO) after reacting with $\text{SiO}_2@\text{CdS}$ for different time intervals and (b) effect of pH on the absorbance spectra of MO.

4.3.3.1 Effect of pH

In general, pH change affects the surface properties of catalyst, such as surface charged properties and the absorption behavior for target organic materials. The UV-Vis spectrum of MO exhibited a broad peak at 465 nm typical of a substituted azobenzene. As the pH was reduced below 5, dye protonates and the spectrum shifted to longer wavelength (507 nm) via an isosbestic point at 470 nm (Fig. 4.12b) whereas no shift in wavelength was observed at pH- 5.3. The decolorization rates of MO were found to decrease with the increase in the pH value ca. 73.3% (pH 3) and 67.34 % (pH 5.3) after 45 min whereas 57.9% and 38.6 % at pH 7.3 and 9 after 1 h of irradiation, respectively. This fluctuation could be explained on the fact that in acidic solution, a strong adsorption of MO on the $\text{SiO}_2@\text{CdS}$ particles was observed as a result of the electrostatic attraction of the positively charged CdS particles with the anion dye. In alkaline solution, the MO molecules were negatively charged and their adsorption was also expected to little extent. Moreover, at high pH values the hydroxyl radicals were so rapidly scavenged that they did not have the opportunity to react with dyes.

4.3.3.2 Effect of $\text{SiO}_2@\text{CdS}$ concentration on photodegradation of methyl orange

The effect of photolysis (Fig. 4.13a) was examined using 5 mL of MO solution in the absence of catalysis. It was found that the concentration of MO changes very little after light irradiation thus indicated that the photoinduced self-sensitized photolysis can be neglected in comparison with the photocatalysis caused by catalyst particles. It was found that the rate of photodegradation increased linearly with increasing SiO₂@CdS-NR dosage from 2 to 10 mg and decreased or showed negligible effect on 20 mg loading. The increased degradation rate was probably due to an increased number of available active sites on the SiO₂@CdS-NR surface, which in turn increased the number of hydroxyl and superoxide radicals. Whereas 20 mg of SiO₂@CdS loading might cause the aggregation of free catalyst and decrease the visible light penetration as a result of the increased scattering effect (Hua et al. 2012; Gupta et al. 2012). Moreover, the monolayer coverage of the catalyst for the effective adsorption of the dye molecule decreases.

Rate constant, k (Fig. 4.13b) was determined from the slope of the linear relationship of the natural logarithm of the ratio between the initial concentration of dye (C_0) and the concentration after photocatalytic degradation (C) versus the corresponding irradiation time. The results showed that the photocatalytic decolorization of MO followed the first order kinetic model, $\ln(C_0/C) = kt$. The plots of the concentration data gave a straight line. The correlation constant for the fitted line was ca. to be $R^2 = 0.989, 0.968, 0.979, 0.953$ and 0.945 for catalyst concentrations 2, 3, 5, 10 and 20 mg respectively. The k values ca. were 0.1918, 0.2860, 0.4988, 0.6709 and 0.7565 min^{-1} , respectively.

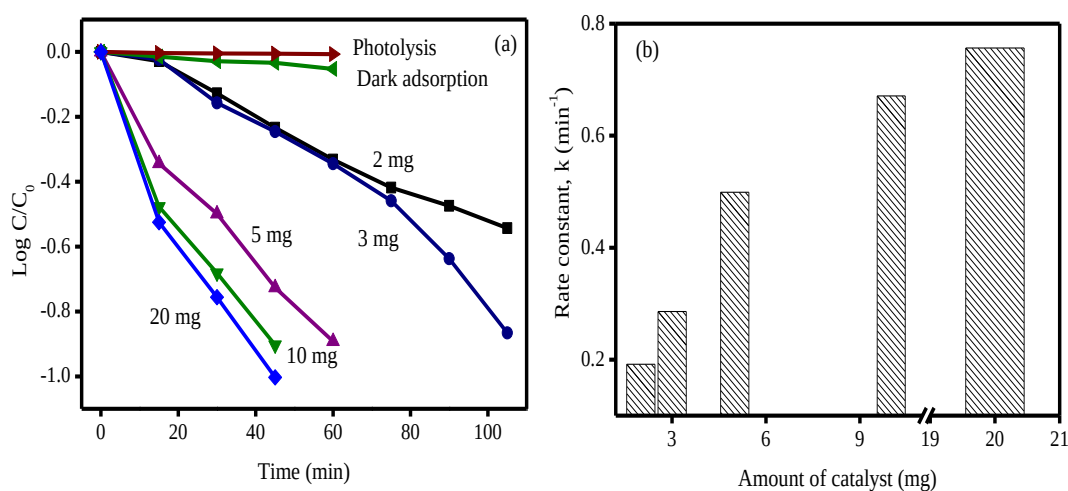


Figure 4.13. Time course of methyl orange photodegradation (a) catalyst concentration and (b) variation of rate constant at pH 7.3 at different catalyst concentration.

4.3.3.3 Effect of methyl orange concentration

The photocatalytic degradation of different concentrations of MO (30 to 120 μM) using 5 mg of $\text{SiO}_2\text{@CdS}$ ($\text{pH} = 7.3$) was investigated as a function of irradiation time (Fig. 4.14a). It is generally noted that the degradation rate of the dye increases with the increase of dye concentration to a certain extent and a further increase leads to a decrease in the dye degradation rate. In present case the degradation rate was found to be almost same for 30 and 60 μM concentration but with an increase in the concentration of dye to 120 μM , the degradation efficiency decreased to 23.3% from 92.6% (for 60 μM) in 75 min. This decrease was accounted to the lesser generation of $\text{OH}^\cdot$ radicals on the catalyst surface. Since the active sites of catalysts get covered by dye ions and the intermediates thus resulted in the lesser photon absorption by the catalyst (Li et al. 2005; Kansal et al. 2006; Rashed and El-Amin, 2007). Gupta and co-workers postulated that the high molar extinction of the dye is another probable cause, as a rise in dye concentration induces an inner filter effect and hence the solution becomes more and more impermeable to light radiation (Gupta et al. 2012). The k value (Fig. 4.14b) was found to decrease linearly with increase in the MO concentration indicated the lower reaction rate.

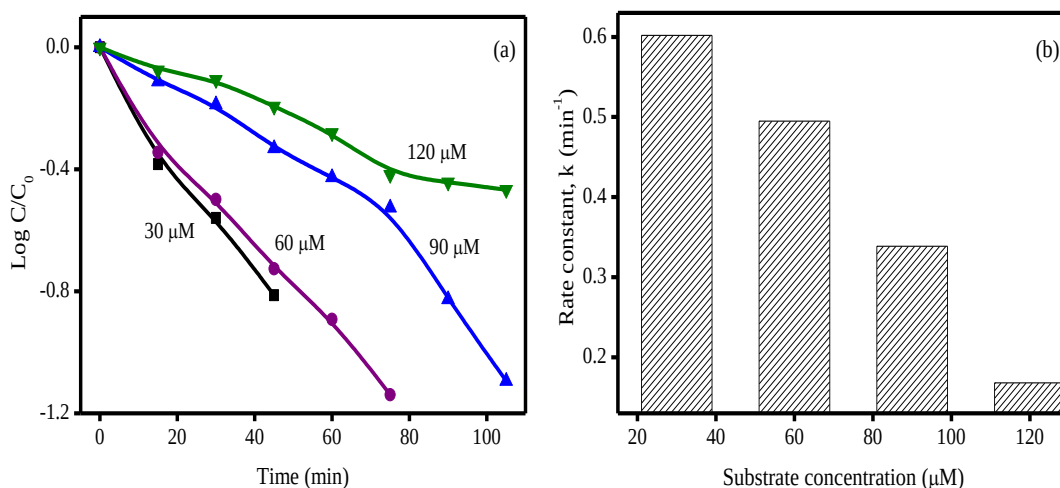


Figure 4.14 (a) Time course of photodegradation of methyl orange by 5 mg $\text{SiO}_2\text{@CdS}$ -NR and (b) variation of the rate constant with different substrate concentration at $\text{pH} 7.3$.

4.3.3.4 Effect of light intensity

Light intensity is a major factor in the photocatalytic process because electron (e^-)-hole (h^+) pairs are generated by light energy. Fig. 4.15a shows a linear increase in the rate of decolorization as a function of light intensity. It is reported that at lower light intensities ($0\text{--}20 \text{ mW/cm}^2$), the rate increased linearly with increasing intensity

(first order) and at higher light intensities, the rate is independent of light intensity (Ollis et al. 1991; Konstantinou and Albanis, 2004). Because at high light intensity, e^-h^+ pair separation competes with their recombination thereby cause a decrease effect on the reaction rate. Whereas in low light intensity reactions, e^-h^+ formation is predominant and their recombination is negligible. It was evident that the percentage of decolorization and photodegradation increased with the increase in light intensity and followed first-order kinetics (Fig. 4.15b). The correlation constant for the fitted line was calculated to be $R^2 = 0.964$, 0.998 and 0.9865 for light intensity 0.8 , 2.1 and 3.4 mW/cm^2 , respectively.

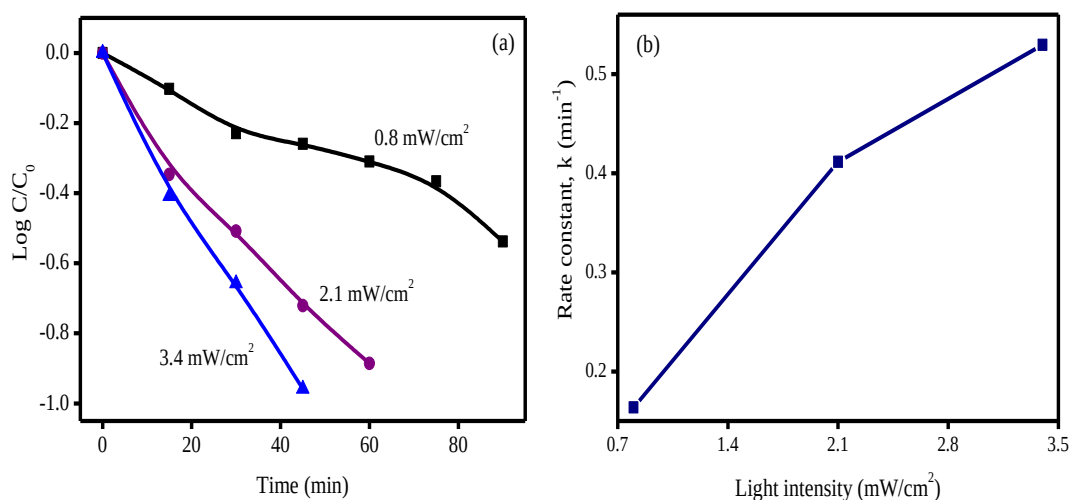


Figure 4.15. Photocatalytic degradation of methyl orange (a) effect of light intensity and (b) variation in the rate constant with different light intensities at pH 7.3.

4.3.3.5 Effect of nature of catalysts and noble metal loading on methyl orange photodegradation

Fig. 4.16a shows that for all the catalysts, almost linear photodegradation of MO was observed with time. It was found that SiO₂@CdS-NR exhibited better activity ($k = 0.3166 \text{ min}^{-1}$) in contrast to bare CdS-NR ($21 \text{ m}^2\text{g}^{-1}$, $k = 0.256 \text{ min}^{-1}$) due to its high specific surface area ($42 \text{ m}^2\text{g}^{-1}$) that played the key factor of photocatalytic activity. Also, smaller bare CdS-NR particles agglomerate into larger particles due to high surface charge, resulted in an adverse effect on catalyst performance. Furthermore, photoetching of SiO₂@CdS-NR (SiO₂@CdS-NR(PE)) resulted in improved photodegradation efficiency (72.2%, $k = 0.431 \text{ min}^{-1}$) due to their small core size, more number of effective surface atoms and large band gap of 2.6 eV (i.e. high oxidation potential) compared to 2.4 eV of SiO₂@CdS-NR. Metal loading (0.5 wt%) onto PE particles highly enhanced the photodegradation rate and

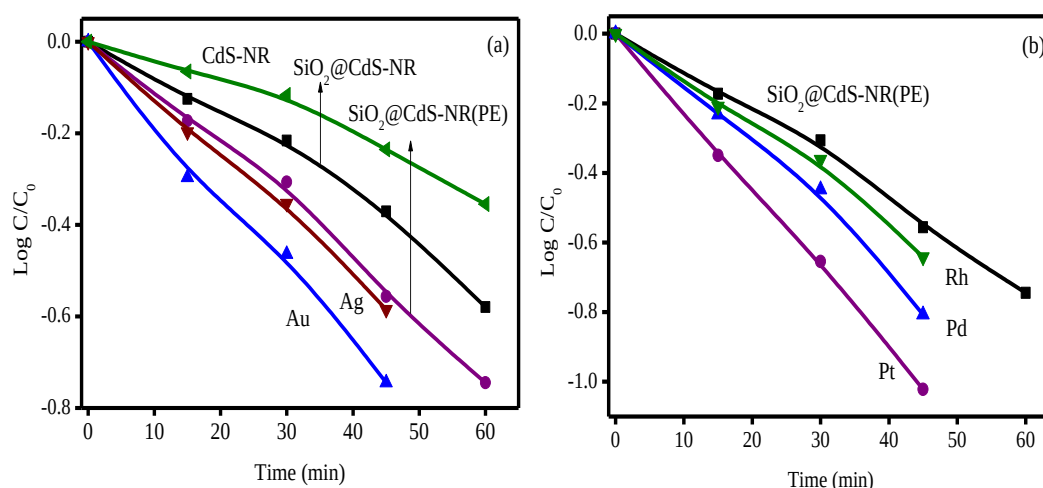


Figure 4.16. Time course photodegradation of methyl orange by (a) different as-prepared catalysts and 0.5 wt% photodeposited Ag and Au on photoetched $\text{SiO}_2@\text{CdS-NR(PE)}$ and (b) effect of 0.5 wt% photodeposited noble metals on $\text{SiO}_2@\text{CdS-NR(PE)}$.

showed complete degradation in 45 min. Au loading displayed high co-catalytic activity with $k = 0.553 \text{ min}^{-1}$ in contrast to Ag and Cu loading ($k = 0.44 \text{ min}^{-1}$). This behavior can be explained on the fact that conduction band (CB) of CdS is located (-0.4 V vs NHE) higher in the energetic state than the Fermi level/work function of Au (0.5 V) and Ag (0.15 V). Consequently, the photo excited free e^- would preferentially transfer to Au, leading to depletion of free e^- in CdS domain and avail the h^+ for photooxidation. Fig. 4.16b illustrates the comparative effect of 0.5 wt% loading of platinum group metals where Pt loading exhibited the highest co-catalytic activity and follows the order $\text{Pt} (k = 0.776 \text{ min}^{-1}) > \text{Rh} (k = 0.5015 \text{ min}^{-1}) > \text{Pd} (k = 0.471 \text{ min}^{-1})$.

The deposition of noble metal serves as a reservoir for photogenerated e^- and promotes interfacial charge-transfer processes by Fermi-level equilibration (Subramanian et al. 2003; Pal et al. 2003; Li et al 2008) at the metal (M)-semiconductor (SC) interface and thereby, enhances the photocatalytic activity. The photoinduced e^- and h^+ in the CdS nanocrystals migrate to the NPs surface easily, and they were effectively trapped at the M-CdS interface. As a result, strongly oxidizing h^+ could be available for photooxidation of adsorbed MO effectively in a better rate. On the other hand, the incorporation of M-NPs onto the CdS surface resulted in a substantial decrease in work function (Sykes et al. 2002; Wang et al. 2009). The observed variance in the co-catalytic activity of different metals could be explained on the difference between CB of CdS and Fermi level energy of different metals, their work function and electron capturing capacity etc. The size of M

deposited onto CdS also influence the photocatalytic activity because Fermi energy equilibration is size dependent i.e. smaller the size of the metal deposit earlier is the Fermi level equilibration (Lee and Choi, 2005; Hidalgo et al. 2007). The comparative degradation efficiency of all the as-synthesized catalysts and highest active co-catalysts i.e Au and Pt was observed (Fig. 4.17a). It was found that Pt loading exhibited the highest degradation efficiency of (90.8%) compared to Au (82%),

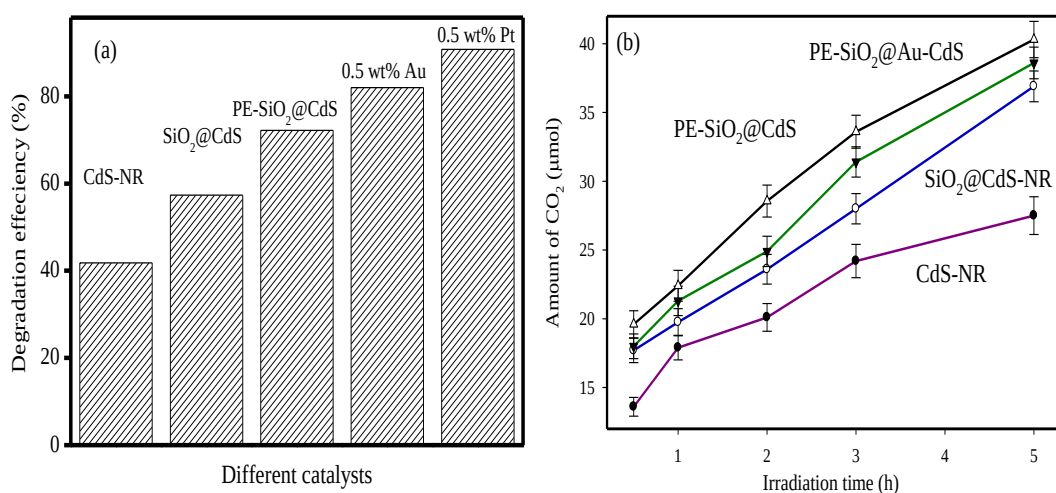
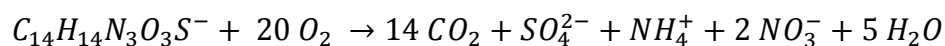


Figure 4.17 (a) Comparative degradation efficiency of SiO₂@CdS composites and highest active Au and Pt metal co-catalysts and (b) amount of CO₂ formed by different CdS-NR, SiO₂@CdS-NR, SiO₂@CdS-NR(PE) and 0.5 wt% Au deposited on SiO₂@CdS-NR(PE).

SiO₂@CdS-NR(PE)- 72.2%, SiO₂@CdS-NR- 66.17% and CdS-NR- 57.9%. The ease of electron transfer from CdS-NR to Pt metal could be ascribed to its higher reduction potential ca. 0.72 eV than that of ca. 1.5 eV for Au co-catalyst. Furthermore, quick Fermi level equilibration of Pt owing to its lower work function (4.2 eV) than Au (5.5 eV) with the CB of CdS could be responsible for superior migration of charge carriers. The comparative photodegradation efficiency of all the loaded co-catalysts as the redox potential and work function is given in table 4.1.

It was proposed that if the MO molecule gets completely photodecomposed, then species like NO₃⁻, SO₄²⁻, NH₄⁺, H₂O and CO₂ would form according to the equation-



In order to ensure the complete mineralization of MO, the CO₂ measurement was done at different time intervals using GC spectrophotometer. Fig. 4.17b shows the linear increase in CO₂ formation depending on the extent of photocatalytic activity of different CdS catalysts. It was found that PE-SiO₂@Au-CdS produced the highest

Table 4.1: Co-relation of photodegradation efficiency with work function and redox potential of different metals.

Metal (M)	Work function (eV)	Redox potential (E°)	Photodegradation efficiency (%) of M-CdS composites
Au	5.32	1.00	82
Ag	4.30	0.799	74
Cu	4.70	0.52	73
Pt	5.40	1.188	90.8
Pd	5.00	0.951	84.4
Rh	4.98	0.758	77.4

amount of CO₂ i.e. ~ 40 µmol (74%) in 5 h in contrast to 38.6 µmol (71.9%), 37 µmol (68.7%) and 27.5 µmol (51.2%) by PE-SiO₂@CdS, bare SiO₂@CdS and CdS-NR, respectively, indicating that MO photomineralization was not cent percent completed because a maximum of 53.68 µmol CO₂ could form after complete mineralization of 60 µM MO. This suggested that M loading enhanced the mineralization of MO to large extent (~ 75%) in 5 h of irradiation light.

4.4 Conclusion

The formation of core-shell structure of SiO₂@CdS-NR and CdS-NS1 embedded in silica matrix was noticed. It was found that PE by monochromatic light of higher energy helped in selective control of size and shape with the retention of lattice parameters. Blue shift in the absorbance spectra after PE confirmed the quantum confinement. Fluorescence emission intensity was enhanced after the reduction of core size and could be tuned by depositing different nature of metals at various concentrations. CdS-NS1 were found to be more fluorescent than CdS-NR due to their difference in the geometry and the path of electron delocalization. Photoetching of CdS core improved the photocatalytic activity in both cases by providing smaller particles and new reaction surface. Photoactivity was further improved by loading metal after PE. Stabilization of CdS-NPs on longer light exposure verified the assistance of SiO₂ coating.

4.5 References

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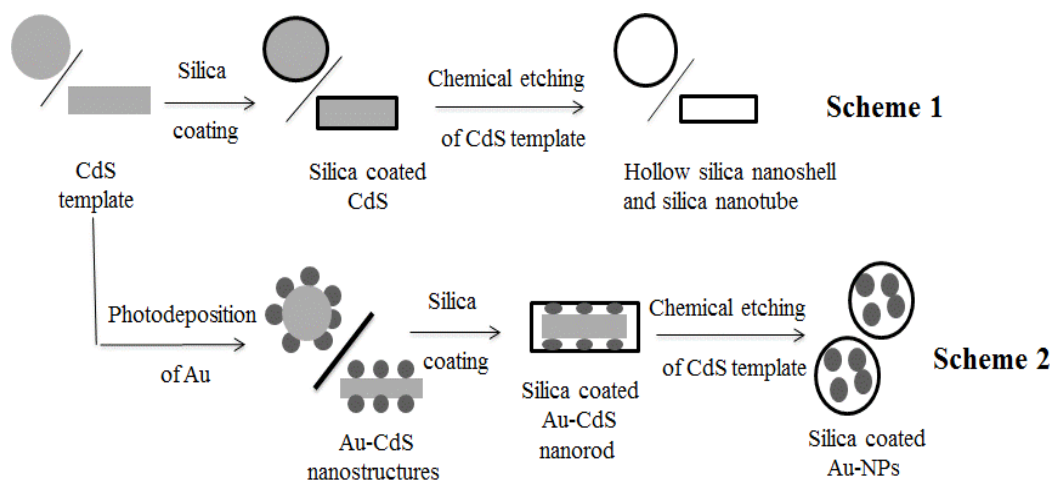
5. Preperation of Hollow and Au (core)–SiO₂ (shell) Nanostructures by CdS Template Dissolution

5.1 Introduction

Chapter-1 (section 1.3.2) highlighted the advantages and applications of core-shell structures of silica coated materials. For instance, the fabrication of hollow nanostructures of different metal and semiconducting materials having desired components through the complete or partial removal of core material by calcining (Taniguchi et al. 2012), chemical dissolution and photoetching (PE) methods etc. (Chah and Fendler, 2002; Teng et al. 2004; Hui et al. 2010). Recent progresses (Sardar et al. 2009; Tao et al. 2008) in synthetic control of size, shape and surface modification of various nanoparticles (NPs) make them interesting and potentially useful in optical and catalytic applications. Many synthetic techniques (Wu et al. 2011; Park and Song, 2011; Pal et al. 2005a and b) have been developed for encapsulating Au nanospheres (NS) in various inorganic oxides. However, the reactivity and surface structure of Au-NPs is somewhat degraded by encapsulation, thus hinder the advantage of nanoscale optical properties. In order to avoid the degradation of these active materials and to improve their dispersibility in water, they are usually embedded into thin SiO₂ shells. SiO₂ coating not only prevents their coagulation but also improve the optical, catalytic activity and photostability of metal (M) and semiconductor (SC) NPs (Pal et al. 2005a and b; Wei et al. 2010).

Highly photoactive light sensitive CdS (core)–SiO₂ (shell) structure incorporating void space was generated by partial PE of the CdS template using Ar ion laser light (Pal et al. 2007; Torimoto et al. 2009). The SiO₂@Au nanostructure was also prepared by complete removal of the CdS template from SiO₂@Au–CdS core material via chemical dissolution. Except in a few reports (Liu et al. 2008; Teng et al. 2004) hollow silica nanospheres (HSNS) and hollow silica nanotubes (HSNT) were fabricated by CdS–NS or microemulsion templating (Lin et al. 2009; Yoon et al. 2006). *In chapter-3 we have demonstrated the formation of SiO₂@CdS–NR* composites for improved photocatalytic activity. If this CdS–NR core could be selectively removed by controlled chemical etching, one may obtain desired HSNT of different dimensions as a function of CdS–NR aspect ratio. Depending on the extent of CdS dissolution and the nature of M deposition onto the CdS surface, a wide variety of SiO₂ nanostructures can be tailored as a function of CdS template

size and shape as shown in schemes 5.1 and 5.2. With the perspective, in this study HSNS, HSNT nanostructures and $\text{SiO}_2\text{@Au}$ -NPs by chemical treatment were synthesized and their utilization in catalytic reaction.



Scheme 5.1. and 5.2. Preparation of $\text{SiO}_2\text{@CdS}$ -NS and NR and bare SiO_2 and $\text{SiO}_2\text{@Au}$ nanostructures obtained after complete removal of CdS templates.

5.2 Experimental details

5.2.1 Synthesis of CdS nanoparticles and their surface modification

CdS-NS1, CdS-NS2 and CdS-NR were synthesized as discussed in *section-2.2.1(method-I)*, *2.2.2 (method-II)* and *2.3*, respectively. Their surface was then modified by 2 wt% Au deposition and silica coating as mentioned in *section- 2.4* (chapter- 2).

5.2.2 Removal of CdS core

CdS core was removed from different $\text{SiO}_2\text{@CdS}$ nanostructures i.e. NS1, NS2, NR and $\text{SiO}_2\text{@Au-CdS}$ -NR using 2 M HNO_3 as per the procedure discussed in *section- 2.6* (chapter- 2).

5.2.3 Catalytic reduction of *p*-nitrophenol

The catalytic efficiency of $\text{SiO}_2\text{@Au}$ -NPs synthesized by chemical etching (CE) was examined by reduction of 90 μM *p*-nitrophenol (PNP) to *p*-aminophenol (PAP). The reaction was carried out in a beaker containing 5 mL PNP, 660 μL NaBH_4 (0.65 M) and 20 μL of $\text{SiO}_2\text{@Au}$ -NPs dispersion (1.5 mg in 200 μL water). After regular intervals, the absorbance spectrum of the reaction mixture was recorded using a UV-Vis spectrophotometer.

5.2.4 Characterization

The prepared nanostructures were characterized using a UV-Vis

spectrophotometer. The size, shape and composition of the powders dispersed in methanol were analyzed by TEM and EDX. BET surface area was measured by N₂ adsorption.

5.3 Results and discussion

5.3.1 Optical and structural characterization

Fig. 5.1a presents the absorbance spectra of CdS–NS2, SiO₂@CdS–NS2 and HSNS powder obtained after complete dissolution of CdS–NS2 core. The characteristic absorbance onset of bare CdS–NS2 appeared at ~ 495 nm. After SiO₂ coating (using 50 μ L TEOS), the absorbance band of CdS–NS2 did not show any significant shift and appeared at ~500 nm because of the increase in cluster size and confinement effect within the SiO₂ matrix (Chang et al. 1994). The absorbance onset of CdS–NR (Fig. 5.1b) appeared at 500 nm and did not show significant change after SiO₂ modification. After complete chemical etching (CE) of the CdS–NS2 and CdS–NR cores from SiO₂@CdS–NS2 and SiO₂@CdS–NR, the absorbance due to CdS was eliminated. However, a featureless spectrum (Fig. 5.1a and b) except for high absorbance at wavelengths below 300 nm due to the presence of SiO₂ nanostructure (Chang et al. 1994) was observed indicated the complete removal of CdS particles. It was also noticed that the optical density gradually decreases because of gradual bleaching of the yellow color as a result of CdS dissolution. As the SiO₂ shell is amorphous, thin and porous in nature, the dissolved species, e.g., Cd²⁺ and S²⁻ within the interior of the SiO₂ sphere, get readily diffuse into the water solution (Henglein, 1982; Dijken et al. 1998).

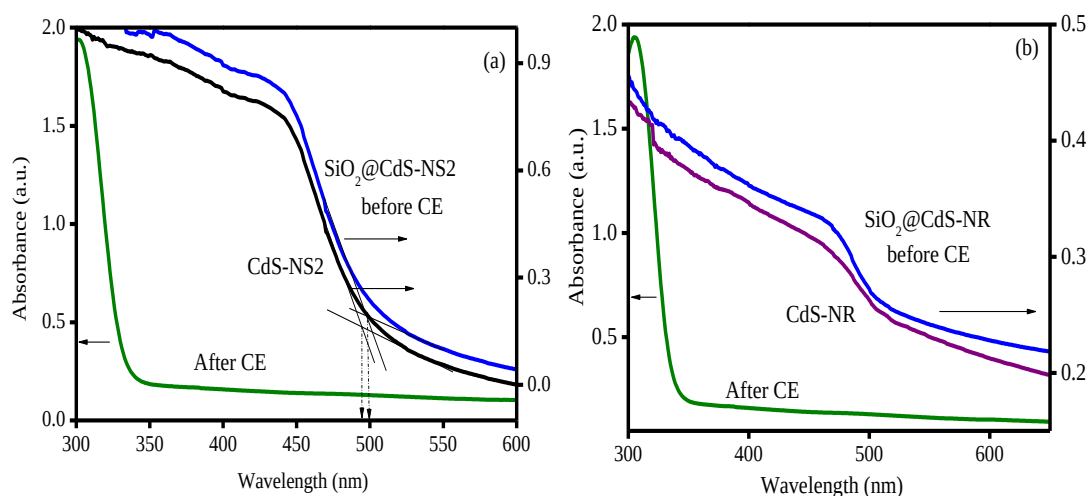


Figure 5.1. Absorbance spectra of (a) CdS–NS2, SiO₂@CdS–NS2 (before) and after chemical etching (CE) and (b) CdS–NR, SiO₂@CdS–NR (before) and after CE.

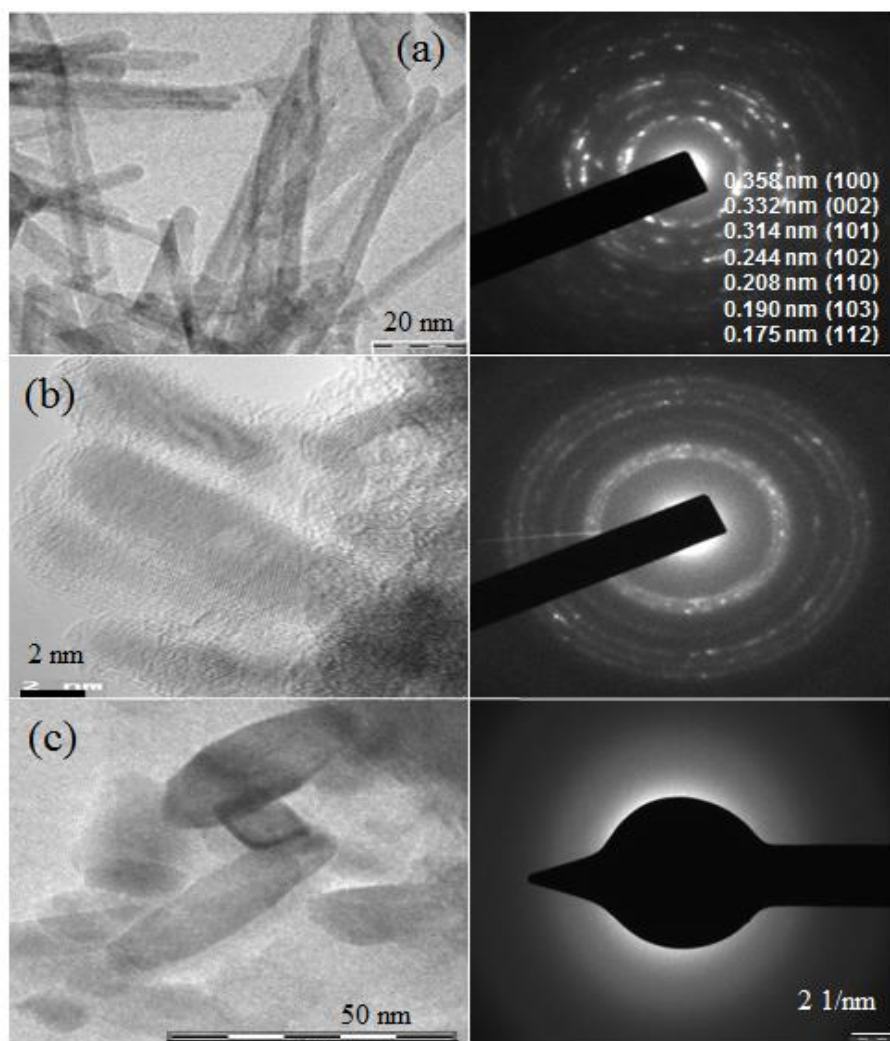


Figure 5.2. TEM images and SAED patterns of (a) bare CdS-NR, (b) SiO₂@CdS-NR and (c) hollow silica nanotubes obtained after CdS removal.

Fig. 5.2 shows the comparative surface morphology analyzed by TEM and SAED pattern, of bare CdS-NR, SiO₂@CdS-NR and close ended hollow silica nanotubes (HSNT) obtained after complete dissolution of CdS template from SiO₂@CdS-NR by HNO₃ treatment. The average length, width and aspect ratio of CdS-NR (Fig. 5.2a) were found to be 126 nm, 6 nm and 21, respectively. The SAED pattern exhibited well-defined diffraction rings with bright spots, reflecting the polycrystallinity of CdS-NR due to their small size. The interplanar spacing ca. from the radii of these circular rings match the characteristic lattice planes indexed to (100), (002), (101), (102), (110), (103) and (112) of hexagonal CdS-NR, as confirmed by X-ray diffraction analysis in our recent report (Gupta and Pal, 2012). CdS-NR was found to be embedded in a thin (1–1.6 nm) SiO₂ matrix to form a core-

shell nanostructure as shown in Fig. 5.2b. The SAED pattern suggested that after SiO₂ coating; the diffraction rings became more diffuse due to the amorphous nature of the SiO₂ layer over the CdS nanocrystals as amorphous sample contains randomly distributed scattering units. Although the interplanar spacing *ca.* from the diffuse rings were similar to those obtained for bare CdS–NR.

The surface area (SA) of bare CdS–NR, calculated (*ca.*) 21 m²g⁻¹, was found to increase to *ca.* 42 m²g⁻¹ after deposition of a thin layer of SiO₂. When SiO₂@CdS–NR was treated with 2 M HNO₃ under magnetic stirring, tube-like, closed-end SiO₂-NPs of shorter length (L), *ca.* 45 nm, and larger diameter (D), *ca.* 13 nm, were obtained (Fig. 5.2c) in comparison to the longer and thinner CdS–NR template (L - 126 nm and D - 6 nm). The decrease in the dimensions might be resulted from the breakage of SiO₂@CdS–NR due to magnetic frictions (stirring) during chemical treatment. The other reason could be the compression of the space inside the amorphous SiO₂ nanotubes during repeated washing, centrifugation and vacuum drying. The formation of broad hollow silica nanotube (HSNT) could be explained on the basis of silica coating over aggregated CdS–NR. The SAED pattern exhibits no characteristic diffraction ring due to CdS, whereas the diffuse fuzzy rings for SiO₂ confirmed the complete removal of CdS core (Fig. 5.2c). During chemical dissolution of CdS–NR by HNO₃, formation of H₂S gas was indicated by its characteristic odor. Whereas the characteristic yellow color of SiO₂@CdS–NR gradually changed to light-white, as expected for SiO₂ particles. The measured SA of these SiO₂ particles (HSNT) was found to be significantly larger (~ 94 m²g⁻¹) than that of SiO₂@CdS–NR particles because of CdS removal.

Fig. 5.3 shows some representative TEM images of various bare CdS–NR, SiO₂@CdS–NR and HSNT. The bare CdS–NR (Fig. 5.3a) of L = 120–128 nm and D = 8–11 nm when coated with SiO₂ using MPTMS and TEOS forms the core–shell structure of SiO₂@CdS–NR. Uniform silica shell (*light gray*) of thickness *ca.* 1–1.4 nm (Fig. 5.3b) covered the entire CdS–NR surface and each CdS–NR (*light black contrast*) seemed to be encapsulated in SiO₂ matrix separately. As CdS core possesses higher electron density than SiO₂, the CdS core in many SiO₂@CdS samples were observed clearly in the TEM images. The presence of Cd–19.79 at%, S–22.90 at%, Si–17.81 at% and O–12.81 at% (*obtained by EDX analysis*) confirmed the coating of SiO₂ over CdS–NR. When CdS core was completely removed from SiO₂@CdS–NR (Fig. 5.3b) by HNO₃ dissolution, a rice shaped HSNT of L = 30–45

nm and $D = 9\text{--}13$ nm along with few smaller SiO_2 structure was obtained as shown in Fig. 5.3c. The TEM image shows hollow structures with closed ends which implied that acid treatment selectively removed the core CdS template only without decomposing the SiO_2 layer on CdS-NR surface. The size of resultant HSNT was again found to be compressed to ~ 37 nm as compare to the $L = 120\text{--}128$ nm of CdS in $\text{SiO}_2\text{@CdS-NR}$ and became broader relative to CdS-NR width. This HSNT shrinkage and enlargement probably happened due to the compression of vacuum

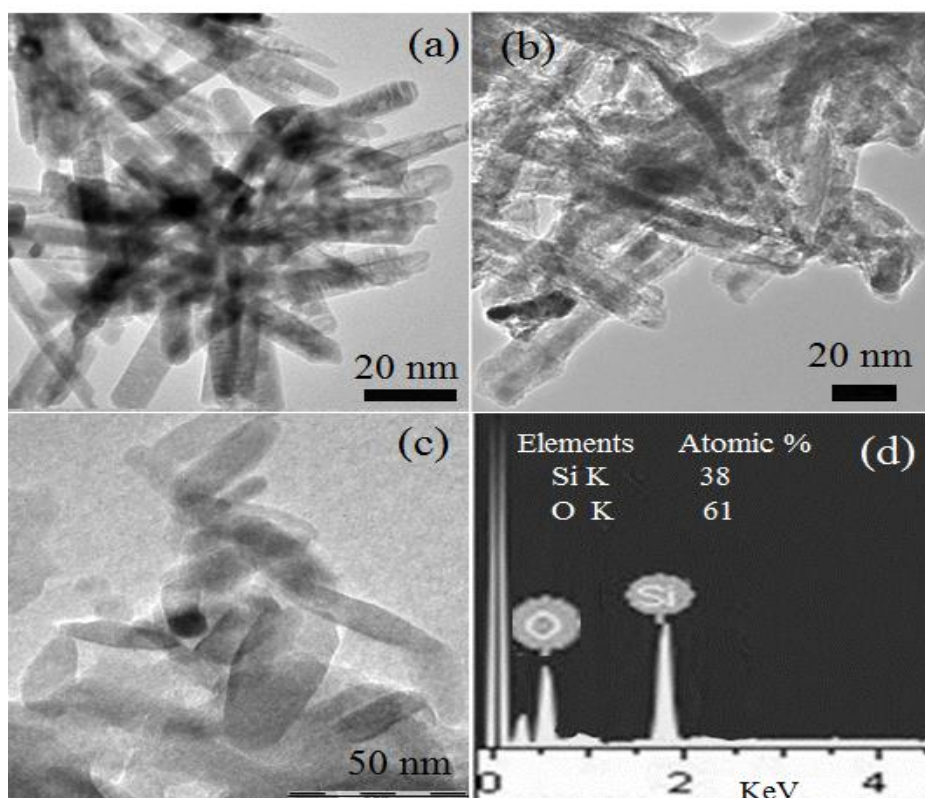


Figure 5.3. TEM images of (a) bare CdS-NR, (b) $\text{SiO}_2\text{@CdS-NR}$, (c) hollow silica nanotube (HSNT) obtained after CdS dissolution and (d) EDX elemental analysis of HSNT.

space inside the amorphous $\text{SiO}_2\text{-NT}$ during repeated washing and centrifugation followed by drying. Yoon and group reported the formation of long close ended $\text{SiO}_2\text{-NT}$ of $L = 300\text{--}500$ nm and $D = 8\text{--}15$ nm by CdS photoetching with monochromatic light using Q-switched Nd:YAG laser (Yoon et al. 2011). Recently, Chen et al. synthesized HSNT of $L \sim 9.5$ μm by templated thermolysis of silicon tetraacetate using anodic aluminium oxide as hard templates (Chen et al. 2011). EDX analysis confirmed the presence of Si-15.08 at%, S-10.56 at%, O-24.30 at% and Cu-50.06 at% and the complete removal of CdS. Some S particles were probably trapped to the porous silica shell during leaching out from the interior or a part of S

may accumulate from MPTMS usage. Then after, these samples were purified by dispersing in methanol followed by sonication and repetitive washing. The EDX analysis (Fig. 5.3d) confirmed the presence of high content of Si (37.7 at%) and O (60.8 at%) and the removal of impurities like S and Cu.

Fig. 5.4a shows TEM images of CdS–NS1 (size 9–10 nm) homogeneously embedded throughout the thick silica (100 μ L, 0.7 mM–TEOS used) matrix. EDX

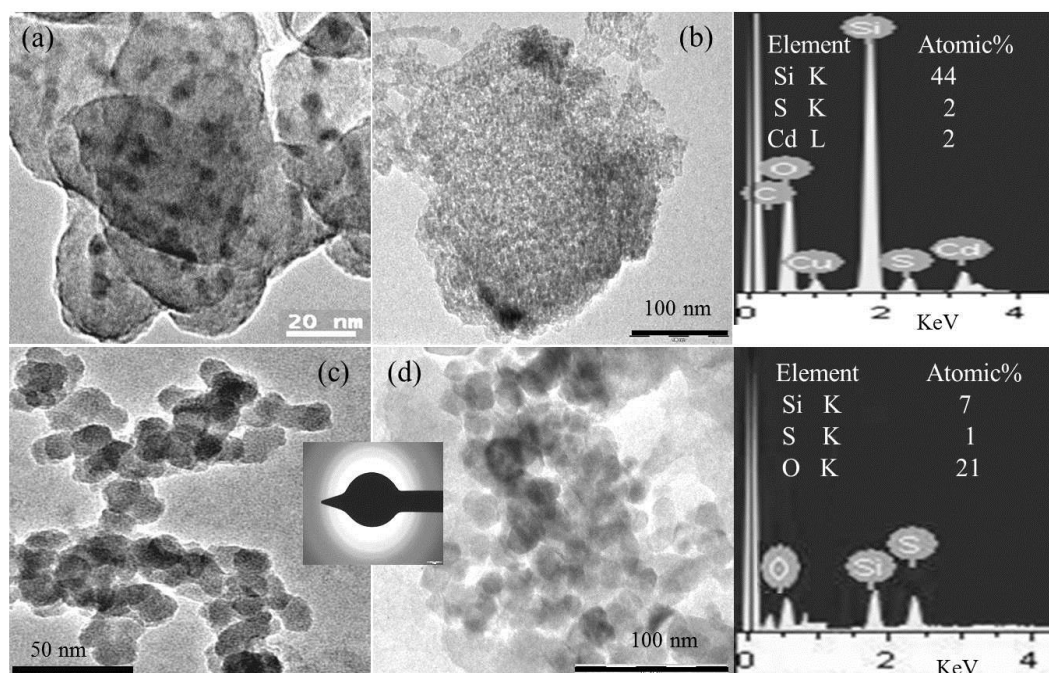


Figure 5.4. TEM images of (a) CdS–NS1 incorporated in thick SiO₂ matrix, (b) nanoporous silica matrix formed after chemical etching (CE); EDX spectra of (a), (c) thin SiO₂@CdS–NS2 and (d) hollow silica nanospheres obtained after CE of CdS–NS2 and its EDX spectra.

analysis revealed the high percentage of Si–43.79 at% as compared to presence of less CdS (Cd–2.62 at% and S–2.33 at%) content which was similar to the findings of Wei and group (Wei et al. 2010). Moreover, increased SA *ca.* 51 m²g^{−1} of SiO₂@CdS–NS1 relative to bare CdS–NS1 *ca.* 18 m²g^{−1} of size 9–10 nm further established the encapsulation of CdS–NS in thick silica support. A spongy, porous mass of SiO₂ cluster (Fig. 5.4b) was formed after complete CE of CdS–NS template by HNO₃. As visible, the sample depicts a lamellar structure with nanopores originated from the voids created by removal of small CdS–NS from silica matrix. The BET SA *ca.* 112 m²g^{−1} of porous SiO₂ support was highly increased as compared to 51 m²g^{−1} thick SiO₂@CdS–NS1 composite, indicated the removal of CdS–NS template. This kind of porous silica materials could be useful for making efficient

catalysts support/host for various metal co-catalysts (Bergbreiter, 1999). Due to thick silica matrix, we were not able to get homogeneous/separated HSNS after CdS core removal.

Hence, the amount of silica precursor TEOS addition (50 μ L, 0.35 mM) was reduced during SiO₂@CdS-NS2 synthesis and nearly spherical SiO₂@CdS-NS2 composites of an average size 12 nm were obtained as depicted in Fig. 5.4c. After removal of single core from thin (thickness 1–1.6 nm) SiO₂@CdS-NS2, a variety of deformed hollow SiO₂ spherical particles with an average $D \sim 12$ nm was formed (Fig. 5.4d). The average size of these SiO₂ nanostructures was found to be nearly identical to the size of SiO₂@CdS nanocomposites indicating no etching, damage or dissolution of silica layer during HNO₃ treatment. Similar hollow silicon NS of thickness 30 nm were recently prepared by Mg reduction of silica spheres using CTAB as a template (Liu et al. 2012). Low silica content (Si-7.11 at%) compared to thick silica cluster (Si-23.65 at%) without any presence of Cd peak in EDX analysis revealed the complete removal of CdS template and the formation of hollow and thin SiO₂ nanostructure. Although perfect SiO₂-NS were not formed (due to washing, centrifugation and drying process), little distorted structures can be seen in Fig. 5.4d. The featureless diffused diffraction rings characteristic to amorphous SiO₂ and absence of any notable X-ray scattering due to presence of CdS lattice plane in this SiO₂ mass was evidenced by the SAED pattern. The increased BET SA of SiO₂ particles (*obtained after CdS removal*) from 29 m²g⁻¹ of SiO₂@CdS-NS2 to 134 m²g⁻¹ indicated hollow morphology of SiO₂ nanostructures. Liu et al. (Liu et al. 2008) prepared hollow SiO₂ mesostructures by using octylamine as a template and investigated the effect of TEOS concentration and the thermal treatment on the mesostructures. Lamellar SiO₂ structures were formed on high concentration of TEOS which was very much similar to our results. Table 5.1 shows the comparative dimensions, specific SA and Si content of as prepared samples.

Fig. 5.5a displays the absorbance spectra of silica coated 2 wt% Au photodeposited CdS-NR (SiO₂@Au-CdS-NR) and after removal of CdS-NR from SiO₂@Au-CdS-NR composites. The absorbance onset of SiO₂@Au-CdS-NR appeared at ~ 500 nm without any evolution of SP band due to Au nanodeposits onto CdS surface. It was reported (Saunders et al. 2006) that such type of Au-CdS-NR junctions promotes the mixing of electronic states at M-SC interfaces, which causes a significant suppression of both plasmon and excitations of carriers. A femtosecond

Table 5.1: Comparative data of dimensions, silica content and surface area of all synthesized CdS and SiO₂ nanostructures.

Sample	Dimensions (nm)	Si at%	Surface area (m ² g ⁻¹)
CdS-NR	L = 126, D = 6	-	21
SiO ₂ @CdS-NR	L = 126, D = 6 Thickness = 1-1.6	17.81	42
HSNT	L = 45, D = 13	37.7	94
CdS-NS1	9-10	-	18
SiO ₂ @CdS-NS1 (thick)	9-10	43.78	51
NPSM	-	23.65	112
SiO ₂ @CdS-NS2 (thin)	~12	20.41	29
HSNS	~12	7.11	134

absorption spectroscopy revealed that the electron transfer from CdS to Au domain occurs at a rate which is slower than quenching of CdS–NR emission. This was attributed to mixing of M and SC electronic states and charging of Au nanodeposits under illumination effectively decrease the quantum confinement of CdS–NR (Khon et al. 2011). Interestingly, when the CdS–NR support was completely removed from the SiO₂@Au–CdS–NR by etching with HNO₃, the appearance of a sharp and distinct SP band at 550 nm for Au deposits was noticed (Fig. 5.5a). This fact was again well correlated with the gradual bleaching of *green* color of SiO₂@Au–CdS–

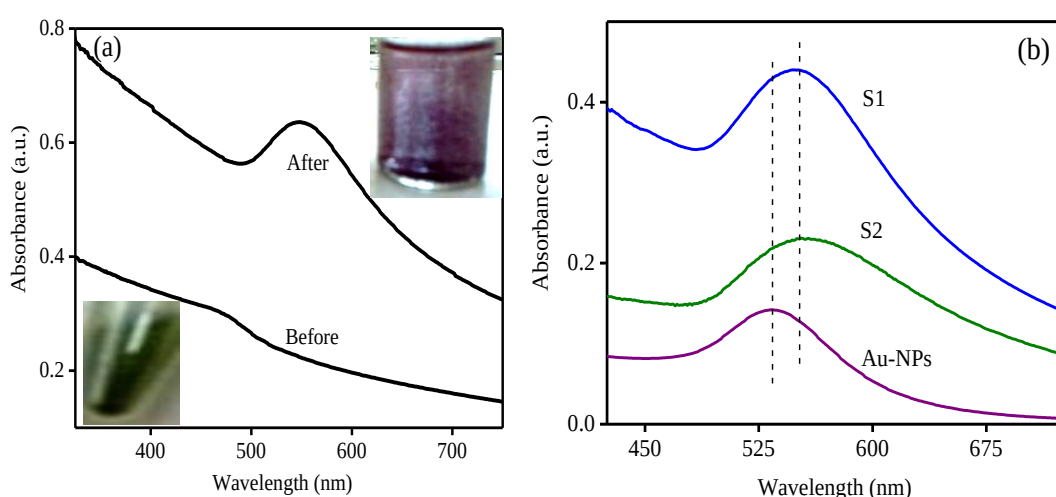


Figure 5.5. The absorbance spectra of (a) SiO₂@Au–CdS–NR before and after chemical etching (CE) of CdS–NR core (SiO₂@Au–NPs), (b) comparative absorption of SiO₂@Au composites obtained after CE of CdS core from SiO₂@Au–CdS–NS (S1) and SiO₂@Au–CdS–NR (S2) and bare Au–NPs (size 3–5 nm) synthesized by conventional method.

NR and appearance of *dark pink* color typically for small Au nanocrystals of size range 3 to 5 nm. Fig. 5.5b represents the comparative SP band of SiO₂@Au-NPs obtained after removal of CdS template from SiO₂@Au-CdS-NS2 (S1) and SiO₂@Au-CdS-NR (S2) and separately synthesized Au-NPs of size ~ 3 nm. It was noticed that SiO₂@Au-NPs obtained from different shape of CdS template of SiO₂@Au-CdS composites displayed their SP band at 550 nm irrespective of the size and shape of CdS support. The observed 20 nm red shift of the SP band as compared to 530 nm of synthesized (Kaur and Pal, 2012) bare Au-NPs (~ 3 nm) occurred due to the surface capping of Au-NPs with silica.

The TEM images of SiO₂@Au-CdS-NR (Fig. 5.6a) shows that quite smaller spherical Au nanodeposits (*black contrast*) of size range 3–5 nm were attached on the surface of CdS-NR that were incorporated into silica matrix. The SiO₂@Au-CdS, where Au deposited CdS-NR surrounded by silica mass according to the sketch (*inset*) in the TEM image (Fig. 5.6b) and small black dots of Au deposits was visualized inside silica support.

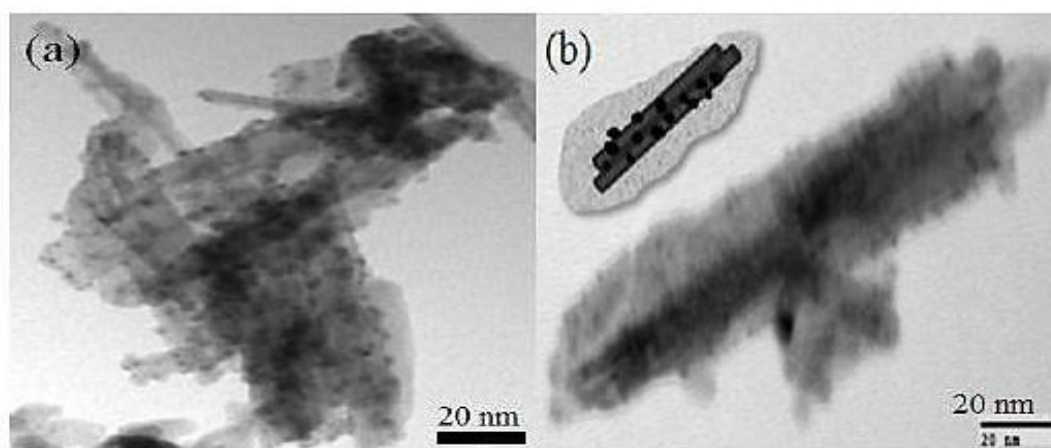


Figure 5.6. TEM images of 2 wt% Au photodeposited CdS-NR encapsulated in SiO₂ matrix of two different composites and *inset* is the sketch of Au-CdS-NR surrounded by silica mass.

Fig. 5.7 displays the TEM images of SiO₂@Au-NPs obtained after complete removal of CdS-NR template from SiO₂@Au-CdS by HNO₃ treatment. Many Au-NPs (*black dots, see marked area*) of size range between 3–5 nm were found to be incorporated into silica nanoshell (*gray contrast*) having thickness 1–2 nm (Fig. 5.7a and b). Fig. 5.7c revealed that many Au-NPs (2–6 nm) got incorporated into a large (~100 nm) spherical thick silica matrix. Thus, the attempt to get the Au-NPs core in hollow SiO₂-NT after dissolution of CdS-NR template was not successful. However,

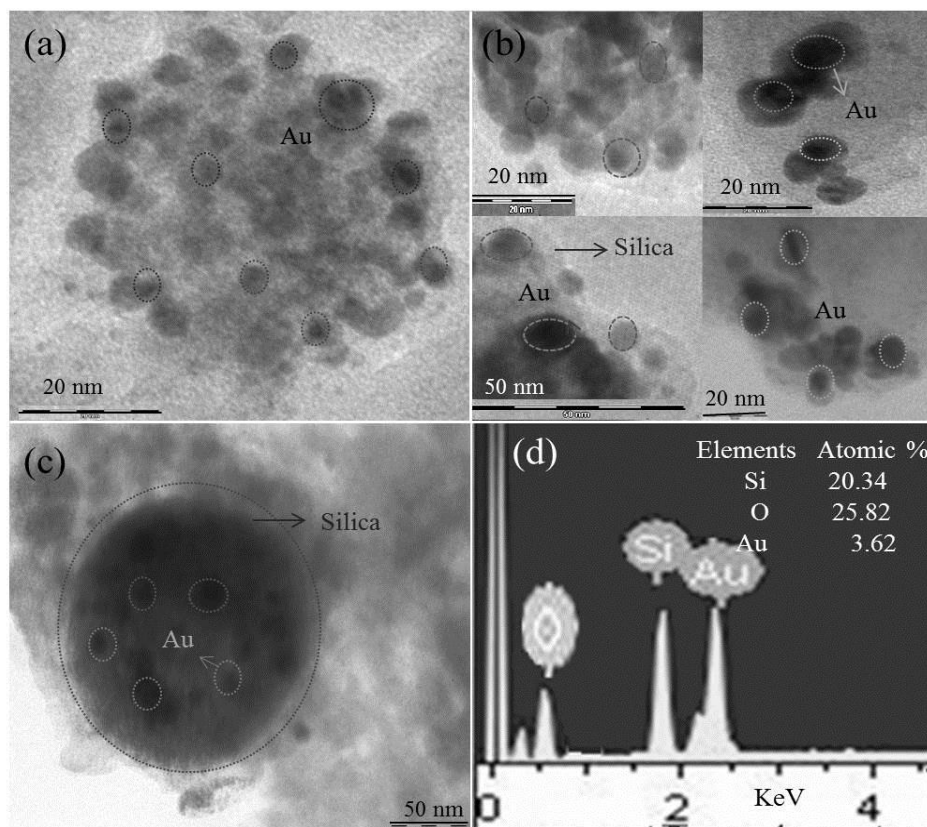


Figure 5.7. TEM images of (a–c) $\text{SiO}_2\text{@Au}$ -NPs formed after complete removal of CdS core from $\text{SiO}_2\text{@Au}$ -CdS-NR and (d) their EDX elemental analysis.

this core-shell $\text{SiO}_2\text{@Au}$ structure has many advantages as a heterogeneous catalyst since it ensures a homogeneous environment around metal core. This deformation of morphological shape could probably be explained on the basis of geometric criteria resulting in least surface energy to grow spherical particles. Moreover, owing to amorphous and wetted nature of long tube like SiO_2 mass, the surface morphology of SiO_2 particles was collapsed after drying process because of the heavier Au islands without any supported matrix inside lengthy SiO_2 tubular mass. The EDX analysis (Fig. 5.7d) of the purified samples confirmed the presence of Si- 20.34 at%, O- 25.82 at% and Au- 3.62 at% and the complete removal of CdS with no Cd and S content.

Similar morphology of thin and thick $\text{SiO}_2\text{@Au}$ -NPs by chemical dissolution of previously PE (by Ar laser light) CdS spherical NPs core was also reported by Pal et al. (Pal et al. 2005a and b). Recently, Park et al. (Park and Song, 2011) synthesized $\text{SiO}_2\text{@Au}$ -NPs with core size 120 ± 10 nm and shell thickness of 32 ± 2 nm and studied the effect of SP band position on the Au core size by etching with KCN. The effect of thick silica shell on the optical property of Au-NS and NR embedded in

silica matrix was also investigated (Kobayashi et al. 2001; Cong et al. 2010). Though optical properties were studied as a function of SiO₂ shell thickness and Au core size, few reports (Wu et al. 2011; Park and Song, 2011) were available regarding the catalytic properties of such type of SiO₂@Au nanostructures.

5.3.2 Catalytic activity of SiO₂@Au nanoparticles

The reduction of PNP by NaBH₄ in the presence of noble M-NPs catalyst has been widely studied for the efficient production of PAP (Pradhan et al. 2001; Zhang et al. 2011). Therefore, the reduction of PNP to PAP was carried out as a model system to evaluate the catalytic activity of SiO₂@Au nanocomposites. Fig. 5.8a shows that in the absence of SiO₂@Au-NPs, the mixture of PNP and NaBH₄ exhibited a strong absorbance peak at 400 nm, corresponding to the PNP ions under alkaline conditions (Chang et al. 2012). After addition of 20 μ L of SiO₂@Au-NPs dispersion (1.5 mg in 200 μ L H₂O), the reduction process was monitored by measuring the time-dependent absorbance spectra. It was found that the absorbance intensity of PNP at 400 nm decreases quickly with time and follows the pseudo-first order kinetics with a rate constant of 0.792 min⁻¹ (Fig. 5.8b). The appearance of a new peak at 300 nm due to formation of PAP reflected the conversion of PNP (0.45 μ mol) to PAP with $\sim$ 76.8% efficiency in 50 min which was lower than the findings of Wu et al. (Wu et al. 2011) and Zhang et al. (Zhang et al. 2011). The difference in the efficiency of the synthesized catalysts in both cases could be explained on the basis of the synthesis technique, silica thickness and size distribution of Au-NPs. Thin SiO₂@Au-NPs showed good catalytic activity compared to thick SiO₂@Au-

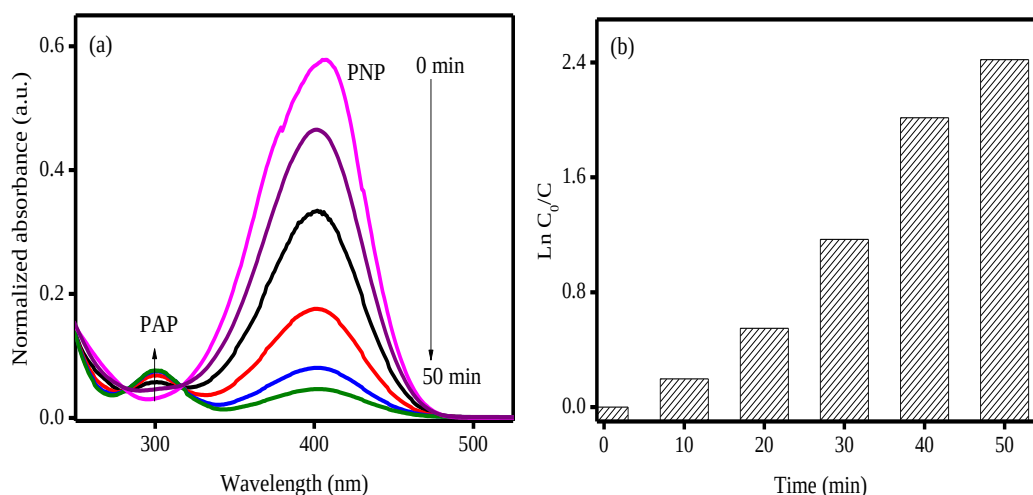


Figure 5.8 (a) Time course (10 min interval) of changes in the spectrum of *p*-nitrophenol (PNP) during its catalytic reduction to *p*-aminophenol (PAP) by SiO₂@Au-NPs (1.5 mg in 200 μ L H₂O) and (b) Ln C₀/C for PNP as a function of time.

NPs (~ 35%) due to easy access of the reactant through pores of silica shell. The thick silica shell SiO₂@Au nanocomposites might reduce the catalytic activity because of the silica barrier that may hinders the penetration of reactant into the core.

5.4 Conclusion

In this study the core-shell structure of SiO₂@CdS–NS and NR as a function of semiconductor template was synthesized. Chemical dissolution of CdS core from SiO₂@CdS–NS and SiO₂@CdS–NR led to the formation of HSNS of size 10–12 nm and close ended HSNT of L = 45 nm and D = 13 nm. Highly porous mesostructure SiO₂ matrix can also be prepared by the removal of CdS dispersion from thick SiO₂@CdS–NS composites. The Au deposition over CdS followed by SiO₂ coating and subsequent chemical etching of CdS template resulted the formation of core–shell morphology of SiO₂@Au–NPs. These particles displayed excellent optical absorption and catalytic activity for the reduction of PNP to PAP.

5.5 References

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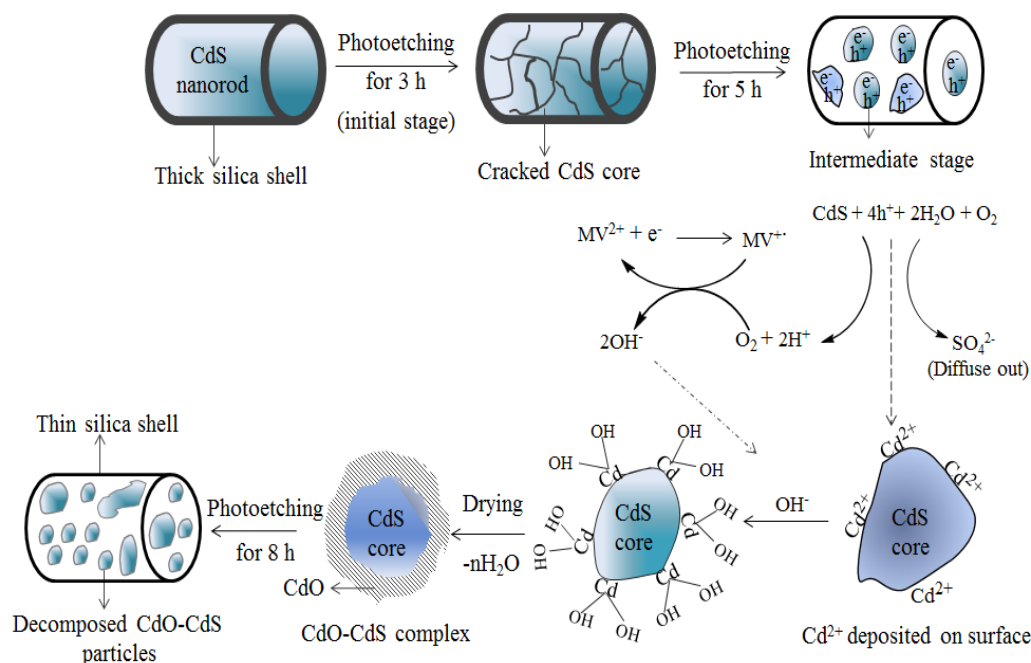
6. Fabrication of Movable CdO@CdS Nanocomposites Enclosed in Tubular SiO₂ Matrix for Superior Photoactivity and Stability

6.1 Introduction

Chapter-1 (section-1.3.1) focused on the properties of core-shell structures of bimetallic, metal (M) - semiconductor (SC) and SC-SC materials. Concisely, core-shell materials such as Ag (shell)@Au (core) (Guzel et al. 2010; Sun and Xia, 2004; Rodriguez-Gonzalez et al. 2005), ZnS@CdS (Ethayaraja et al. 2007), CdS@CdSe (Luo and Wang, 2010) exhibit enhanced catalytic activity, selectivity and photostability as compared to their monometallic counterparts. This enhancement can be probably due to their bifunctional or synergistic effects, electronic and geometric or ensemble effect (Moskovits et al. 2002; Srnova-Sloufova et al. 2004). For instance, bimetallic Ag@Cu composites showed higher selectivity (76.6%) for styrene epoxidation in contrast to monometallic Ag (65.6%) and (20.4%) Cu nanoparticles (NPs) (Wang et al. 2011). Ag@Au nanostructure exhibits improved catalytic activity (rate constant, $k = 0.18 \text{ min}^{-1}$) for the reduction of *p*-nitrophenol to *p*-aminophenol than the respective monometallic Au ($k = 0.019 \text{ min}^{-1}$) and Ag-NPs ($k = 0.069 \text{ min}^{-1}$) (Zhang and Su, 2012). CdS-ZnO hetero-array displayed high visible light sensitivity and enhanced photodegradation (85%) of organic II dye in contrast to 31% of bare ZnO nanowires (Tak et al. 2008). The resultant properties of these nanocomposites were altered owing to their band energy mixing and interfacial interaction between different M and SC having diverse work functions or Fermi energies (Kambhampati, 2011 and 2012; Grünwald; 2013).

But the fine tuning of observed photochemical and opto-electronic properties is sometimes difficult in these composites owing to their similar atomic structure, band energy and chemical activity of respective core and shell materials. However, if an inert shell like a thin layer of SiO₂ as coating material is employed, it preserves the chemical identity and properties of core material. Incorporation of movable Au core in polymer shell (Kamata et al. 2003) and nano-rattle of hollow SiO₂@Au showed better catalytic activity for *p*-nitrophenol reduction (Wu et al. 2011). Torimoto had demonstrated superior photoproperties (Torimoto et al. 2009) and photoactivity of laser photoetched SiO₂@CdS nanospheres (NS) (Pal et al. 2004 and 2007). *In this chapter we discussed about the synthesis of one such type of composite*

i.e. CdO@CdS coated with SiO₂ which was formed by the laser treatment of silica coated CdS nanorod (SiO₂@CdS-NR). Their effect photocatalytic application to the decomposition of organic pollutant was also studied.



Scheme 6.1. Schematic representation of SiO₂ coated CdO@CdS morphology formed by photoetching of SiO₂@CdS-NR with 458 nm laser beam irradiation.

In this study it is demonstrated that as-prepared SiO₂@CdS-NR when instantly used for photoetching (PE) without drying, CdS core gets cracked during initial hour (3 h) of 458 nm laser irradiation and gradually split into a number of smaller asymmetric CdS particles. These particles were slowly converted into spherical morphology with increasing (> 5 h) laser exposure time. This occurrence resembled the photothermal melting of Au and Ag-NPs into a variety of irregular Au nanostructures by different laser energies as reported recently (Badr et al. 2006; Bueno-Alejo et al. 2012). During PE of SiO₂@CdS, the photoexcited CdS assisted the formation of Cd²⁺ and OH⁻ ions that combine to form Cd(OH)₂ layer over partly etched CdS surface. This resulted in movable Cd(OH)₂@CdS morphology which on drying converted into CdO@CdS nanostructure entrapped in tubular SiO₂ matrix as shown in scheme 6.1. With further laser irradiation (> 8 h), Cd(OH)₂@CdS morphologies were finally decomposed into smaller CdS particles entrapped in soft-gel like SiO₂ nanotube that resembles bacterial cell morphology. Such CdO@CdS composite obtained after gradual removal of CdS layer possessed high surface area.

It showed high photoactivity due to superior adsorption of reacting species, mixed cubic (CdO) and hexagonal (CdS) crystal phase and new interfacial energy owing to (CdO (2.16 eV) and CdS (2.4 eV)) band mixing.

6.2 Experimental details

6.2.1 Preparation of core-shell structure and its photoetching

Synthesis of CdS-NR and SiO₂@CdS-NR were done using the procedure discussed in *section- 2.3 and 2.4.2*, respectively of *chapter- 2*. In this study little modification compared to earlier procedure (*section- 2.4.2*) was done during hydrolysis of silica precursor. In this study hydrolysis of the trimethoxysilyl group was done by instant addition of hot water (150 mL) for the growth of silica shell without further refluxing at 80 °C. The obtained core-shell structure was then subjected to photoetching without drying using the same procedure discussed in *section 2.5 (chapter- 2)*.

6.2.2 Photodegradation of methyl orange

The photodegradation of 5 mL (60 µM) methyl orange (MO) using 5 mg of catalysts was carried out in a test tube under 250 W tungsten-iodine halogen lamp (*LS-II*) using a lengthy probe as shown in (*scheme 2.1*). The solution was constantly stirred in an oxygen saturated atmosphere under magnetic stirring at 300 rpm.

6.2.3 Characterization

The resulted SiO₂@CdS nanostructures were characterized by XRD, TEM and EDX analysis, absorption and PL spectrophotometer, TGA and BET surface area was measured by N₂ adsorption. The progress of the reaction was monitored by a UV-Vis spectrophotometer and reaction intermediates were analyzed by GC-MS spectrophotometer. Amount of CO₂ produced was measured by GC with TCD as per the conditions mentioned in chapter-2 (*section-2.7.15*).

6.3 Results and discussion

An absorbance spectrum (Fig. 6.1) shows that the bare SiO₂@CdS (1 mg/mL water dispersion) exhibited an absorbance onset around 515 nm which was comparable to the bulk particles. During PE of 3-8 h there was a gradual blue-shift in the absorbance onset which ultimately shifted to ~ 458 nm after 8 h laser exposure. Further dissolution of CdS-NPs was not occurred due to an increase in energy gap (2.45 eV to 2.7 eV) with a decrease in the particle size (Van Dijken et al. 1998). A broad emission band of CdS-NR (1mg/mL acetone, $\lambda_{\text{ext}} = 365$ nm) was observed at 496–529 nm (Fig. 6.1). An intense peak at 501 nm accounted for the e⁻-h⁺

recombination and other weak emission at 528 nm was ascribed to the recombination of trapped charge carriers at the CdS defects sites. On silica coating, the band edge emission of CdS-NR shifted to 506 nm and gets quenched due to the reduced number of surface defects, such as dangling bonds as discussed in chapter 3 (section 3.3). However, the intensity of band edge emission was highly enhanced ($\sim 175\%$) as compared to $\text{SiO}_2\text{@CdS}$ and gets shifted to ~ 458 nm after PE. A weak shoulder at

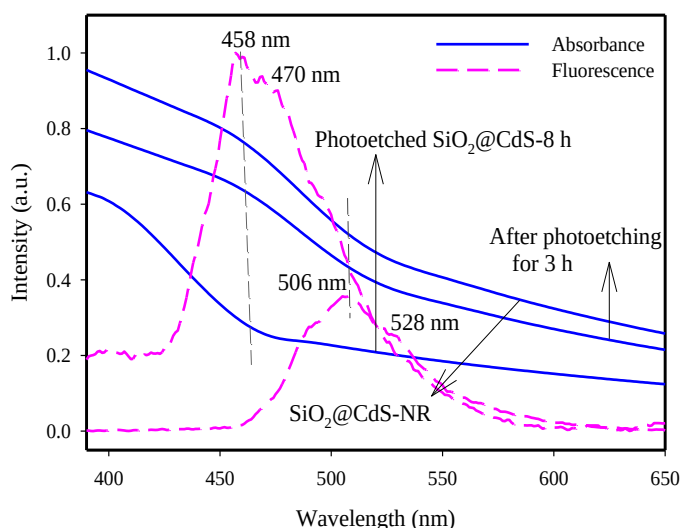


Figure 6.1. Absorbance and photoluminescence spectra of $\text{SiO}_2\text{@CdS}$ -NR and photoetched $\text{SiO}_2\text{@CdS}$ -8 h.

472 nm arose due to formation of defect sites on decreasing the particle size. The enhanced luminescence intensity on PE signified the decreased radiationless recombination sites of bare $\text{SiO}_2\text{@CdS}$ because of the gradual photoanodic dissolution of CdS layer i.e. decreased particle size (Torimoto et al. 1998). The formation of fresh $\text{Cd}(\text{OH})_2$ layer on partly etched CdS could be the another probable reason (Dannhauser et al. 1986) as per the mechanism discussed in scheme 6.1. It was reported that CdS stabilized by surface passivating agents had weak fluorescence which could be enhanced by adding NaOH and excess Cd^{2+} ions (Torimoto et al. 1998).

Fig. 6.2a shows the changes in XRD peaks occurred during photoetching of 3-8 h as compared to bare $\text{SiO}_2\text{@CdS}$ -NPs. A typical hexagonal crystal structure of CdS-NR with characteristic intense peaks for (100), (002) and (101) along with broad peaks due to SiO_2 coating for (102), (110), (103) and (112) lattice planes were observed in bare $\text{SiO}_2\text{@CdS}$ (Chang et al. 1994; Gupta and Pal, 2012). The sharp (002) diffraction peak for the growth of hexagonal CdS particle along

crystallographic *c*-axis was gradually reduced because of the consistent dissolution of CdS in longitudinal direction with (5 h) laser exposure indicated the distortion of cylindrical symmetry. Whereas the broadening of other high index peaks occurred owing to the smaller and inhomogeneous particle size. The broad diffuse high index peaks relative to unetched SiO₂@CdS could be attributed to the difference in the electron scattering because of surface roughness and adsorbed chemical species e.g., Cd²⁺, SO₃²⁻ and MV²⁺ etc. On prolonged irradiation for 8 h, (100), (002) and (101) peaks were almost disappeared relative to (110), (103) and (112) planes due to vigorous dissolution of CdS-NR core. They appeared to be more non-crystalline and amorphous owing to formation of many anisotropic CdS-NPs having many rough faces of broken edges and corners.

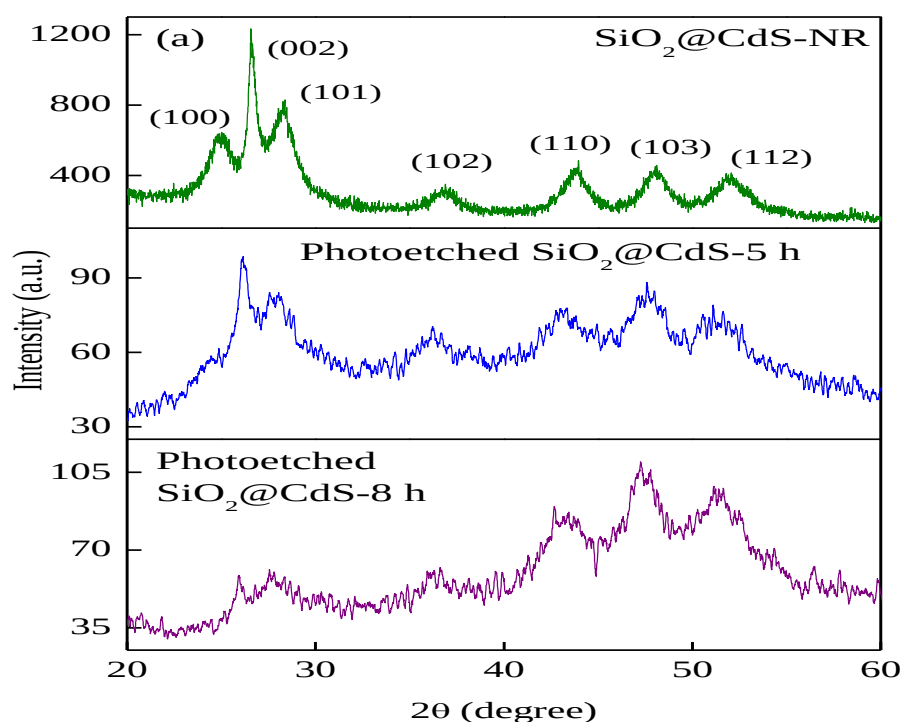


Figure 6.2a XRD patterns of SiO₂@CdS-NR before and after photoetching with 458 nm laser irradiation for different times.

Fig. 6.2b depicts the thermal gravimetric weight loss graph of bare and photoetched SiO₂@CdS (SiO₂@CdS(PE)) which were heated at the rate of 20 °C/min in nitrogen atmosphere. A continuous weight loss had taken place with increasing temperature and revealed the loss at three major steps. In SiO₂@CdS, weight loss ca. 24.4% observed between 303.5 and 488.6 °C (first step) was related to phase transformation at 350 to 400 °C. A small decrease of 11.7% between 488.6 and 886.3 °C (second step) could be due to some sulfur deficiency (Nirmala Jothi et

al. 2011). At the third stage, after 886 °C the weight loss was accounted to the thermal decomposition of CdS particles. In contrast, SiO₂@CdS-8 h (PE) samples showed a small weight loss between 182.4 and 234.3 °C related to decomposition of water and unreacted organics (TEOS and MPTMS) adsorbed over CdS surface. A large decrease (~ 30%) from 234.3 to 552.9 °C occurred probably due to decomposition of some adsorbed MV²⁺ (carbon source) to carbon dioxide, phase transformation, and dehydroxylation of Cd(OH)₂ to CdO after 350-400 °C etc. At the third stage, after 747.9 °C the weight loss arose due to complete decomposition and sublimation of CdS in SiO₂@CdS-8 h (PE) sample (Pan et al. 2005). Thus, higher total weight loss of 55.4% for SiO₂@CdS-8 h (PE) powder than 43.6% for bare SiO₂@CdS before laser exposure evidenced the creation of void space inside SiO₂ matrix. The void created thus offers more surface area for better adsorption in photoreaction.

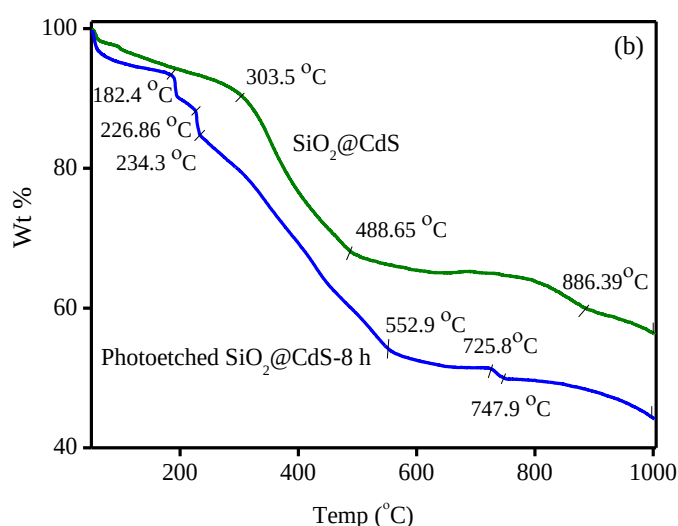


Figure 6.2b TGA graph of bare and photoetched SiO₂@CdS with 458 nm laser beam for 8 h (SiO₂@CdS-8 h (PE)).

TEM micrographs (Fig. 6.3a) of bare SiO₂@CdS illustrates that the lengthy CdS-NR (*dark gray*) of aspect ratio = 21 coated with SiO₂ layer (*light gray*) of thickness ~ 1.4 nm formed a clear core-shell structure. A distinct CdS-NR core (diameter (D) ~ 26.6 nm) was found to be uniformly coated with transparent SiO₂ shell layer of thickness ~ 3.7 nm (*color*). The increased D might be resulted from the fusion of some NRs during SiO₂ coating. Likewise, bundle of few (3-4) CdS-NRs were also found to be coated with thin SiO₂ shell (Fig. 6.3b) as observed in chapter 3 (Fig. 3.7c). After initial 3 h of laser exposure, one such bundle of aggregated CdS-NRs (D ~ 100 nm) was seemed to be cracked into smaller pieces in a tubular SiO₂

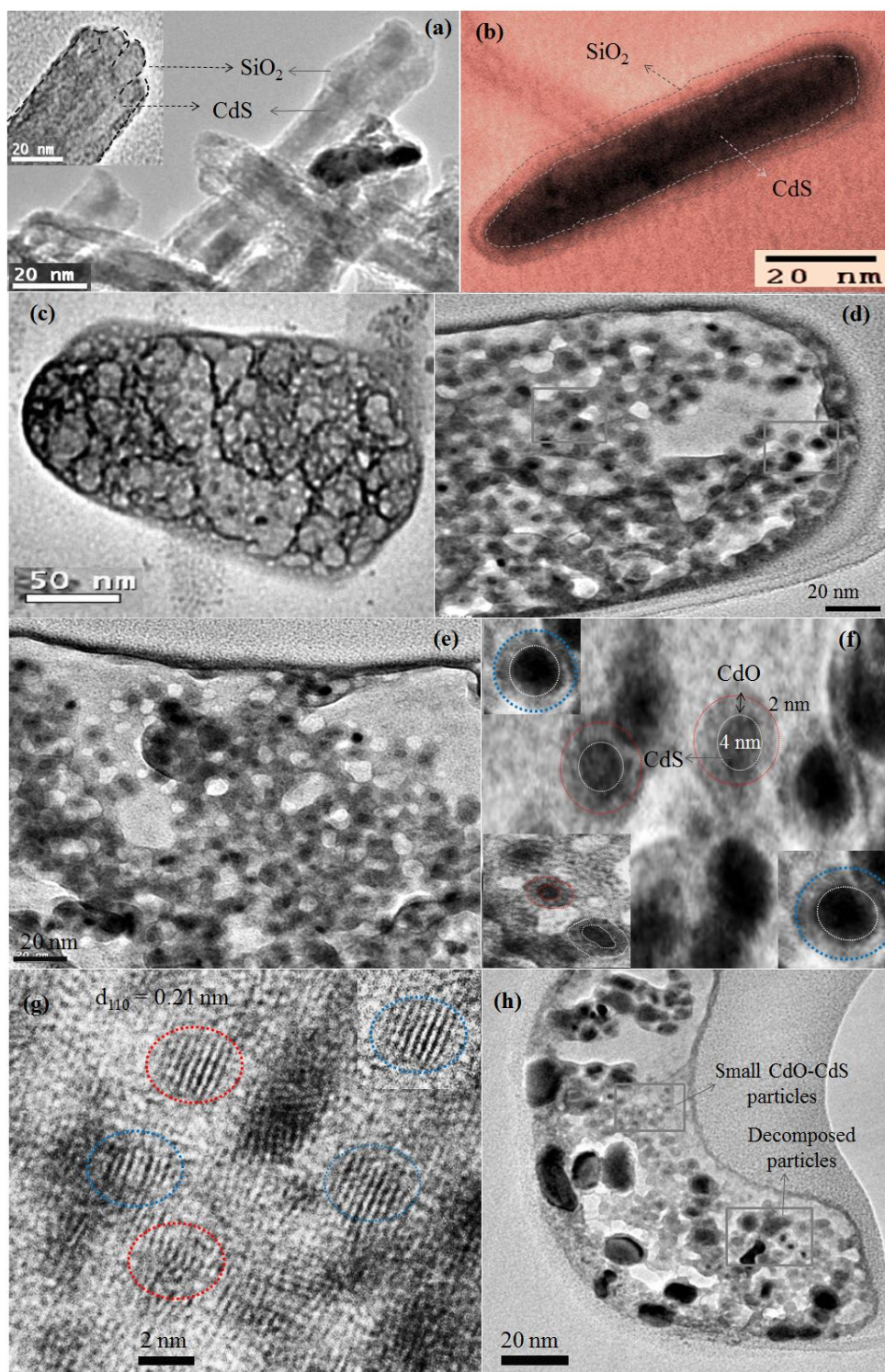


Figure 6.3. TEM micrographs of (a and b) $\text{SiO}_2\text{@CdS-NR}$; inset: an enlarged view, photoetched $\text{SiO}_2\text{@CdS}$ after (c) 3 h, (d and e) 5 h, (f) enlarged view of (d), (g) HR-TEM of (d) and (h) after 8 h of photoetching by 458 nm laser beam.

matrix. On further laser exposure for 5 h, CdS core was ultimately decomposed into almost monodisperse spherical CdS particles homogeneously spotted inside cylindrical SiO_2 matrix. A void space thus created due to breakdown of lengthy CdS-

NR by laser induced dissolution was distinctly evident in the TEM image (Fig. 6.3d). A close look at TEM image (Fig. 6.3e) revealed that many core-shell morphologies consisting of spherical CdS core (size $\sim 4.5 \pm 1$ nm) with relatively dark contrast were seem to be embedded in a gray colored shell of thickness $\sim 2.3 \pm 0.5$ nm. It was proposed that each dark CdS core surface was simultaneously deposited with Cd(OH)₂ layer during oxidative etching of CdS surface to Cd²⁺ ions and *in-situ* formation of HO⁻ ion by photoexcited charge species upon laser illumination. The Cd(OH)₂ layer got converted to CdO shell on drying which was further confirmed by EDX elemental analysis at various stages of CdS dissolution discussed in table 6.1.

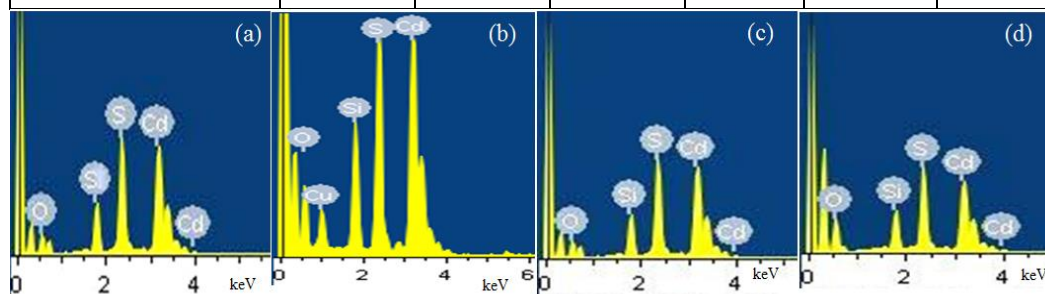
An enlarged view (Fig. 6.3f) from the marked area of TEM images (Fig. 6.3d and e) showed distinctive formation of many core-shell nanomorphology consisting of relatively darker CdS core (size ~ 4 nm) and grayish CdO shell layer (thickness ~ 2 nm) resembling movable composites encapsulated into tubular SiO₂ matrix. Higher electron density of CdS core made it less transparent (dark) than lighter CdO shell (gray) for electron transmission in TEM picture. The HR-TEM (Fig. 6.3g) depicted the formation of small isolated CdS-NPs of an average size 3.5 ± 0.5 nm. The interplanar spacing ca. 0.21 nm for (110) plane of hexagonal CdS was found to be nearly equal to the spacing (0.208 nm) for the bare SiO₂@CdS particle, confirming the retention of crystal structure after laser fragmentation. Prolonged laser irradiation up to 8 h resulted in vigorous decomposition of CdO@CdS core-shell structure into many larger and smaller irregular CdS or CdO clusters. These clusters were found to be entrapped in a thin amorphous SiO₂ membrane, resembling the bacterial cell morphology having various organelles enclosed in cell membrane. Enlarged surface area ($123.7 \text{ m}^2\text{g}^{-1}$) measured for SiO₂@CdS-8 h (PE) samples in comparison to $42.4 \text{ m}^2\text{g}^{-1}$ of bare SiO₂@CdS composites further confirmed the creation of void space inside silica tube by photofragmentation of CdS-NR into small CdS-NPs.

EDX analysis (Table 6.1 and spectra) revealed the variation in at% of elements present in different SiO₂@CdS nanostructures before and after laser exposure. EDX spectra showed that although Cd/S ratio (0.85-0.90) did not varies much, but the absolute amount (at%) of both Cd and S was drastically decreased with subsequent dissolution of CdS by laser etching at different time (3-8 h) periods. The stoichiometric decrease in Cd and S content suggested (Torimoto et al. 2003) the leaching out of Cd²⁺ (ionic radii = 140 pm) and SO₄²⁻ (ionic radii = 240 pm) ions through pores of SiO₂ shell layer. At the same time, oxygen (O) content was

concurrently enhanced (2-3 times) to 49.47 at% from 5.07 for CdS-NR and 17.81 at% for SiO₂@CdS, respectively. This fact proved the formation of CdO layer surrounding CdS core or isolated CdO particles during various stages (3-8 h) of laser etching of SiO₂@CdS particles, where SiO₂ content (12.81-7.47 at.%) did not alter much indicated that SiO₂ matrix remain intact after laser exposure.

Table 6.1: EDX elemental analysis of bare CdS-NR and SiO₂@CdS-NR (before) and after photoetching for different time intervals.

Sample	Cd (at%)	S (at%)	Si (at%)	O (at%)	Cu (at%)	Total
(a) CdS-NR	36.63	40.57	-	5.07	17.73	100.00
(b) Bare SiO ₂ @CdS	19.79	22.90	12.81	17.81	26.69	100.00
(c) Photoetched SiO ₂ @CdS-5 h	14.62	17.12	9.57	38.15	20.54	100.00
(d) Photoetched SiO ₂ @CdS-8 h	8.77	11.61	7.47	49.47	22.68	100.00



The photocatalytic performance was examined by degrading 5 mL (60 μ M) of MO with 2-10 mg of various CdS catalyst under visible light (250 W tungsten-

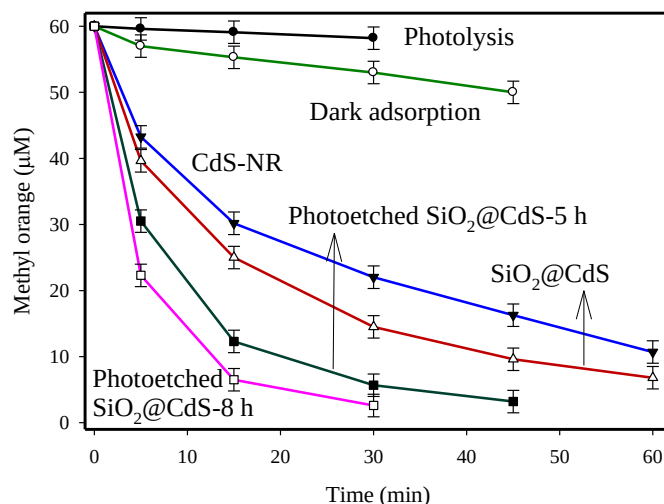


Figure 6.4. Photocatalytic degradation of 60 μ M methyl orange by different CdS catalysts under visible light irradiation.

iodine, $\lambda = 656.28$ nm) irradiation through an optical fiber probe (diameter 1.4 cm) for 60 min as shown in *scheme 2.2*. The reaction mixture was stirred in the dark for 30 min for attaining adsorption equilibrium and direct photolysis of MO oxidation was verified to be none. It was found that the MO degradation was enhanced significantly by increasing the CdS catalyst dosage from 2 to 5 mg and thereafter catalytic activity decreases beyond 5 mg catalyst usage. An exponential decrease ($C_t = C_0 e^{-kt}$) in a concentration of MO by different catalysts as a function of irradiation time followed the 1st order kinetic law as shown in Fig. 6.4. It was observed that MO degradation efficiency was gradually improved as: 82.2% for CdS-NR ($k = 0.781$ min⁻¹) < 88.7% bare SiO₂@CdS ($k = 1.032$ min⁻¹) < 95-98% for photoetched SiO₂@CdS-5 h and 8 h samples by 60 min visible light exposure. This could be ascribed to the formation of many hybrid CdO-CdS interface, creation of new surface

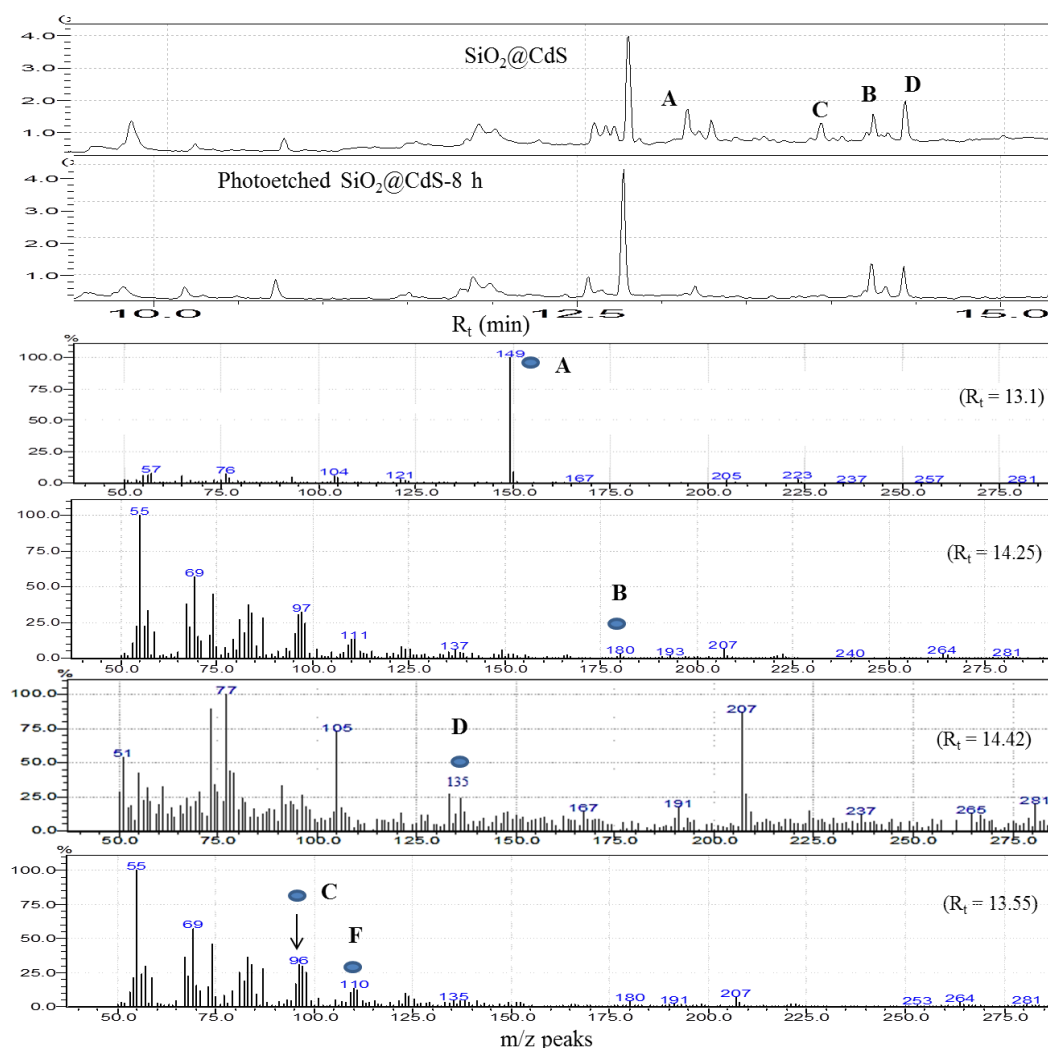
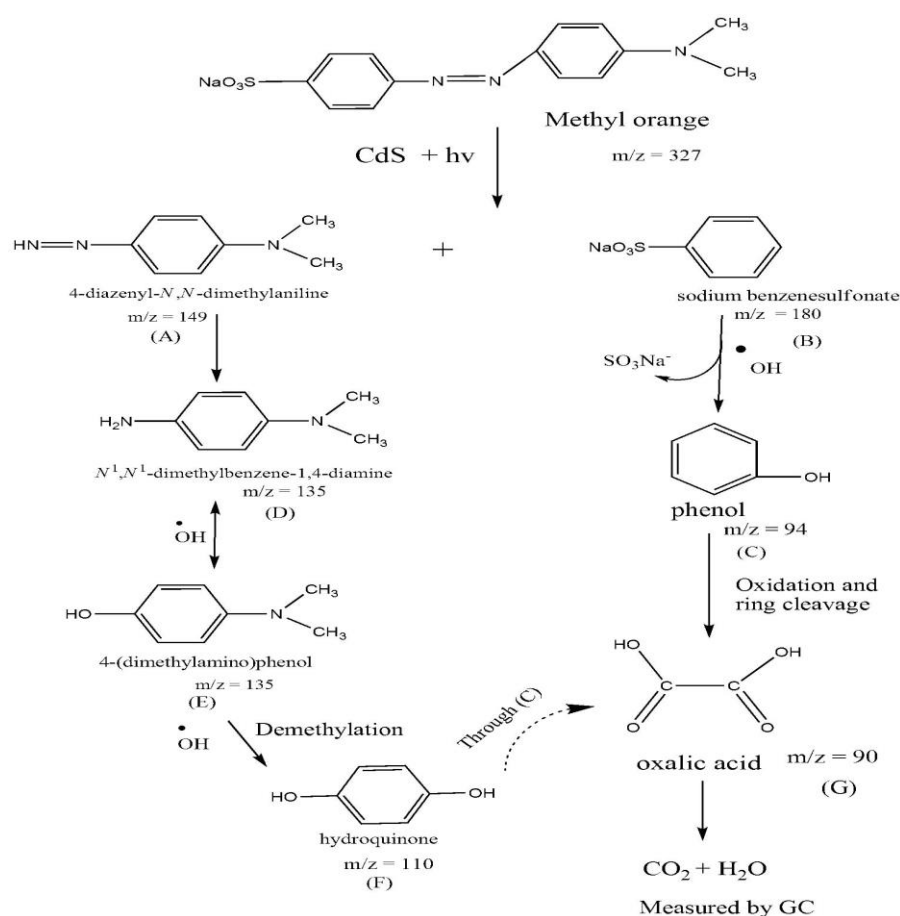


Figure 6.5. GC chromatogram of methyl orange after 1 h reaction with SiO₂@CdS and photoetched SiO₂@CdS-8 h and the mass spectra of possible intermediates formed.

facets, larger specific surface area due to the porous nature of silica and void space thus created acts as nanoreactors in contrast to bare $\text{SiO}_2\text{@CdS-NR}$ particles. Moreover, higher surface to volume ratio, 0.857 nm^{-1} (relative to ~ 0.6824 of bare CdS-NR) of smaller spherical CdS ($\sim 7 \text{ nm}$) possessing higher percentage of fresh surface exposed CdS molecules obtained from $\text{SiO}_2\text{@CdS-NR}$ fragmentation could be the plausible cause for superior photodegradation of dye after laser treatment. The breakdown of CdS-NRs crystal by laser treatment led to new surface facets and creates an imbalance force on the surface atoms whose dangling bonds became highly energetic and satisfied them by forming better chemisorption of MO molecules for higher photooxidation rate.



Scheme 6.2. Proposed reaction pathway for the photo-mineralization of methyl orange.

The GC-MS analysis further confirmed the difference in MO oxidation process between bare and laser etched $\text{SiO}_2\text{@CdS-8 h}$ samples after 60 min light irradiation. GC chromatograms showed that more intermediate products were formed by $\text{SiO}_2\text{@CdS}$ in contrast to laser etched $\text{SiO}_2\text{@CdS-8 h}$. This dissimilarity was evident from the appearance of several GC peaks (Fig. 6.5) at retention time > 10

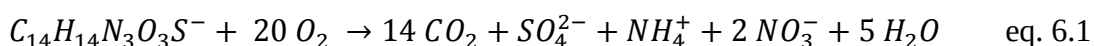
min (between 12.5-14.5 min) as compared to reduced number of peaks for intermediates due to rapid mineralization of MO by SiO₂@CdS-8 h (PE). Various intermediates (table 6.2) with corresponding m/z values were identified in accordance with some reported results (Telke et al. 2010; Abdelmalek et al. 2006). Their respective mass spectras and a plausible degradation pathway are shown in Fig. 6.5 and scheme 6.2, respectively. The photodegradation mechanism of MO involved two steps:

Table 6.2: Intermediates products formed after 1 h photodegradation of methyl orange by laser etched SiO₂@CdS-8 h composites.

Intermediates formed	Code	m/z value
Sodium - benzenesulfonate	B	180
4-diazenyl-N,N-dimethylaniline	A	149
N'-N'-dimethylbenzene-1,4-diamine	D	135
Hydroquinone	F	110
Phenol	C	78

the first step in the decolourisation of the azo dyes was due to asymmetric cleavage occurred due to lower bond energy of -C-N- (305 KJ/mol) than -N=N- (418 KJ/mol). This led to the formation of highly reactive carbocations that react with OH radical resulted in the formation of several intermediates such as 4-diazenyl-N,N-dimethylaniline (A) and sodium benzenesulphonate (B) having molecular weights (m/z = 149 and 180, respectively) lower than MO dye (m/z = 327) were detected. The diazine intermediate was presumably unstable in the presence of molecular oxygen and OH radical, and got converted to N',N'-dimethylbenzene-1,4-diamine (D). In the second step, hydroxylated products such as 4-(dimethylamino)phenol (E) with m/z = 135 formed which gets converted to hydroquinone (F, m/z = 110) on reacting with OH radical and form 4-nitrocatechol, *p*-nitrophenol etc. as identified by other groups (Joseph et al. 2000). The other fragmented part of MO dye i.e. sodium benzenesulphonate (B, m/z = 180) gets converted to phenol (C, m/z = 94) when reacted with OH radical and finally degraded to oxalic acid (F, m/z = 90) and further to formic acid, a well-known organic by-product of aromatic ring opening reactions (Abdelmalek et al. 2006; Oturan et al. 2001).

If the MO molecule gets completely photodecomposed, then NO₃⁻, SO₄²⁻, NH₄⁺, H₂O and CO₂ has to be formed according to the equation-



Although species like nitrate, sulphate and ammonium ions were not measured but the measured CO₂ formation confirmed the complete degradation of MO dye by laser

etched $\text{SiO}_2@\text{CdO}@\text{CdS}$ -8h catalyst under visible light irradiation. Fig. 6.6 shows the linear increase of CO_2 formation depending on the extent of photocatalytic activity of different CdS catalysts. It was found that $\text{SiO}_2@\text{CdO}@\text{CdS}$ -8h (PE) catalyst produced the highest amount of CO_2 i.e. $\sim 40 \mu\text{mol}$ (74%) in 5 h in contrast to 37 (68.7%) and 27.5 (51.2%) μmol by bare $\text{SiO}_2@\text{CdS}$ and CdS-NR, respectively. This indicated that MO photomineralization was not cent percent completed because a maximum of 53.68 μmol CO_2 could be formed after complete mineralization of 60 μM MO as per above equation.

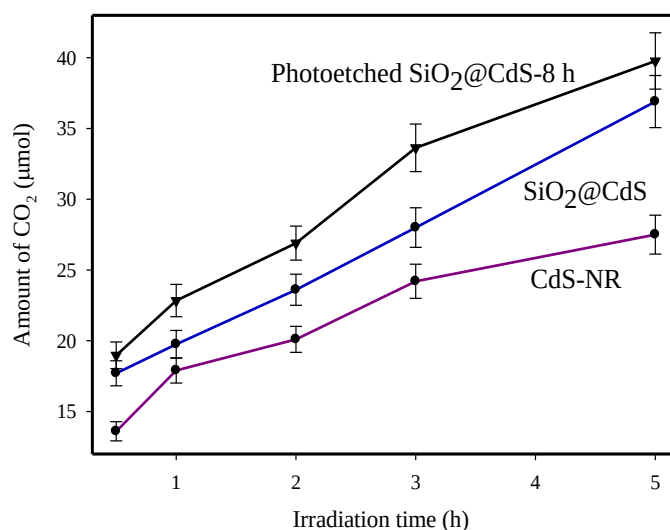


Figure 6.6. Time course of CO_2 formation by various CdS catalysts on photodegradation of methyl orange.

The stability and recyclability of a catalyst is a very important issue in CdS photoactivity. Absorbance spectra (Fig. 6.7) of aqueous dispersion (1 mg/mL) of

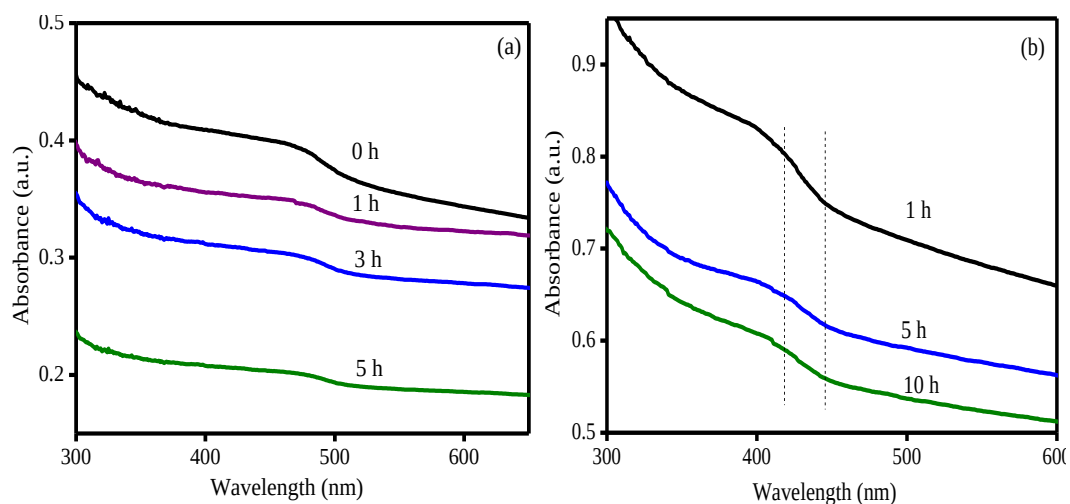


Figure 6.7. Photostability graph of (a) CdS-NR and (b) photoetched $\text{SiO}_2@\text{CdS}$ -8 h under visible light.

CdS-NR and SiO₂@CdS-8 h (PE) reveals that optical density of CdS-NR (Fig. 6.7a) decreased sharply and the band onset levels off within 5 h of visible light irradiation whereas SiO₂@CdS-8 h (PE) (Fig. 6.7b) showed almost no change in the absorbance band onset on longer light exposure, thus verified their photostability. To examine the recyclability, CdS-NR and SiO₂@CdS-8 h (PE) was repeatedly used for MO degradation during longer light exposure. Fig. 6.8 illustrates a linear increase in its activity up to 10 h photodegradation of MO (0.6 mM-5 mL), whereas CdS-NR photoactivity starts decreased after 6 h light irradiation. In second cycle, CdS-NR exhibited low catalytic activity in contrast to SiO₂@CdS-8 h (PE) samples because bare CdS was very prone to photodissolution as confirmed from the resultant remaining CdS (~ 2.5 mg) of bare CdS and 4.1 mg of photoetched SiO₂@CdS obtained from initially used 5 mg CdS catalyst after the first cycle of photoreaction. This fact suggested that the SiO₂ coating imparted considerable stability to CdS core during dye degradation under longer duration of visible light exposure.

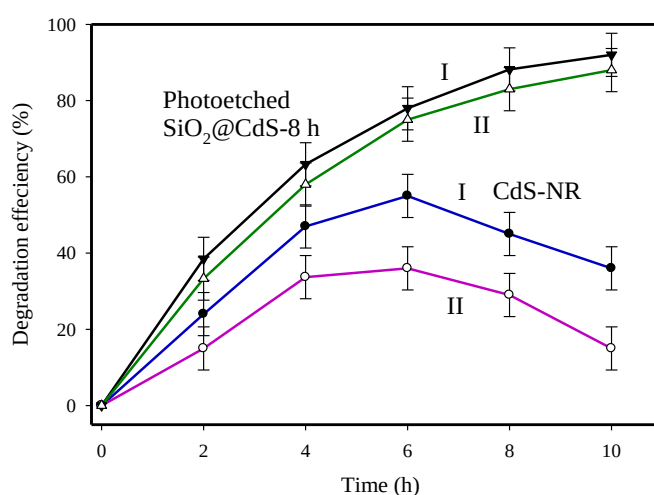


Figure 6.8. Stability and recyclability of CdS-NR and photoetched SiO₂@CdS-8 h for photodegradation of 0.6 mM (5 mL) of MO under visible light exposure.

6.4 Conclusion

The synthesis of multiple-movable core-shell structures of CdO@CdS enclosed in a SiO₂ tubular matrix having voids was done for the first time by controlling laser exposure time over SiO₂@CdS-NR composites. These SiO₂@CdO@CdS structures were found to be highly photoluminescent (~ 175%) due to possession of fresh surface active CdO or CdS molecules that displayed good photostability and improved photocatalytic activity (~ 98%) for MO degradation

under specifically visible light illumination. Such core-shell composites may be more useful in many optoelectronic applications than traditional CdS particle morphology.

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7. Selective Photoreduction of p-Nitrophenol to p-Aminophenol by CdS Nanostructures of Different Shapes

7.1 Introduction

As discussed in chapter-1, the opto-chemical properties of CdS nanoparticles (NPs) vary with size, shape and crystal structure. It has been proposed that there are many factors such as surface area, size, crystallinity, and active sites etc. that are taken into account for the optical and photocatalytic properties of semiconducting NPs. CdS nanorods (NRs) located between spherical particles and one dimensional nanowires have been investigated extensively because of its superior properties that are attributed to the size confinement and dimensionality effect (Kan et al. 2003; Adachi et al. 2004; Liu et al. 2008; Krahne et al. 2012). The band gap energy (E_g) of rod, and consequently its emission wavelength are strongly dependent on the diameter (D) as well as on the length (L) of the nanorod (Hu et al. 2002; Persano et al. 2010; Zhang et al. 2008). Although contradicting results of optical and electronic properties have been reported but little work has been done on the effect of morphology and crystal structure on the photoreductive activity of cylindrical nanocrystals. *In order to understand the fact closely, in this chapter different shape and size of CdS particles were synthesized and investigated their effect on the optochemical properties.*

CdS is considered as a potential candidate for the photoreduction reaction due to its high negative conduction band (CB) position and visible light absorption. Their redox potential can be further tuned depending upon the size of particles, because band edge position shift towards negative and positive potential with alternation in size and shape (Murray et al. 2000; Parak et al. 2004). But if the size of particle is reduced to large extent then its band gap will shift to UV region which will end to a notable disadvantage. So controlling the suitable dimensions of CdS for efficient reductive reaction under light irradiation will be beneficial. Furthermore, coinage metal loading onto such nanostructures will improve their photoactivity and visible light sensitivity. Many reports (Yang, 2006; Li et al. 1998; Cheng et al. 2009; Shen et al. 2010) found that CdS-NRs loaded with Au, Ag and Pt displayed superior photocatalytic activity for H_2 production, dye degradation and functional group transformations etc.

Extensive research for fabricating new nanocrystals for exhibiting best photoactivity is yet to achieve. Herein, spongy flower or cotton bun like CdS (SF-CdS-2 h) morphology possessing much larger surface area than spherical and rod like CdS-NPs was prepared. The effect of Au deposition and a thin layer of SiO₂ coating for the stable photocatalytic activity for the reduction of *p*-nitrophenol (PNP) to *p*-aminophenol (PAP) were also studied. Nitroaromatic reduction is emphasized due to the selective reduction of nitro group over other functional groups such as esters, cyano and aldehydes groups because of their reduction potential lies below the CB position of CdS-NPs (Piccinini et al. 1997). Moreover, PAP is a useful raw material for many analgesic and antipyretic drugs (Rana and Parida, 2012; Komatsu and Hirose, 2004; Vaidya et al. 2003); hence, their production employing light energy and SC-NPs will be highly enviable as compared with cumbersome synthetic techniques.

7.2 Experimental details

7.2.1 Preparation of bare, Au deposited and SiO₂ coated CdS nanostructures

Synthesis of different morphologies such as- *CdS-NS1*, spongy flower like CdS (*SF-CdS-2 h*) and CdS-NR of different aspect ratio (i.e. *CdS-6 h* and *CdS-10 h*) were done as discussed in *section- 2.2.1 and 2.3*, respectively. Photodeposition of various (0.2-1) wt% of Au-NPs onto different as-synthesized CdS morphologies were carried out as per the procedure discussed in *section- 2.4.1*. SiO₂ coating was done to form *core-shell structure* as mentioned in *section- 2.4.2*.

7.2.2 Photocatalytic reduction of *p*-nitrophenol to *p*-aminophenol

The hydrogenation of PNP to PAP was carried out in a test tube containing 5 mL, 50 vol% aqueous-IPA (act as hole scavenger) solution of 1mM PNP and 20 mg CdS catalysts in an argon atmosphere (purged for 20 min) under visible light (150 W halogen lamp, *LS-III*) irradiation for 1-4 h. The test tube was sealed with a rubber cap in order to prevent the leakage of gas and the reaction mixture was stirred constantly by magnetic stirrer.

7.2.3 Characterization

CdS nanostructures were characterized by diffuse reflectance spectrophotometer and photoluminescence study. Structural analysis was done by XRD, TEM and BET surface area (SA) was measured by N₂ adsorption technique. The progress of the reaction was monitored from the decrease in the PNP absorbance peak at $\lambda = 400$ nm and simultaneous increase in the PAP absorbance peak at $\lambda = 298$

nm using a UV-Vis spectrophotometer and HPLC (Mobile phase: 1:1 methanol and water with a flow rate of 1 mL/min at 220 nm) analysis after filtration by cellulose filter (0.22 μm). Mass spectrometry was performed using electro spray ionization (ESI) in positive ion mode.

7.3 Results and discussion

The TEM images (Fig. 7.1a and b) revealed the formation of a spongy flower or cotton bun like amorphous CdS morphology (SF-CdS-2 h) having diameter in the range of 200-300 nm. These structures were obtained during refluxing of Cd and S precursors in ethylenediamine at 120 $^{\circ}\text{C}$ for 2 h. Fig. 7.1c depicts a star fish or brush like microstructure formed at the same time. A close view of the same particle (*marked area*) at higher magnification depicts the formation of a very thin (1-3 nm) and lengthy grass or ribbon like CdS-NPs (Fig. 7.1d). The SA of SF-CdS-2 h was ca. to be 119 m^2g^{-1} , indicated its porous surface structure. TEM micrograph of 1 wt% Au

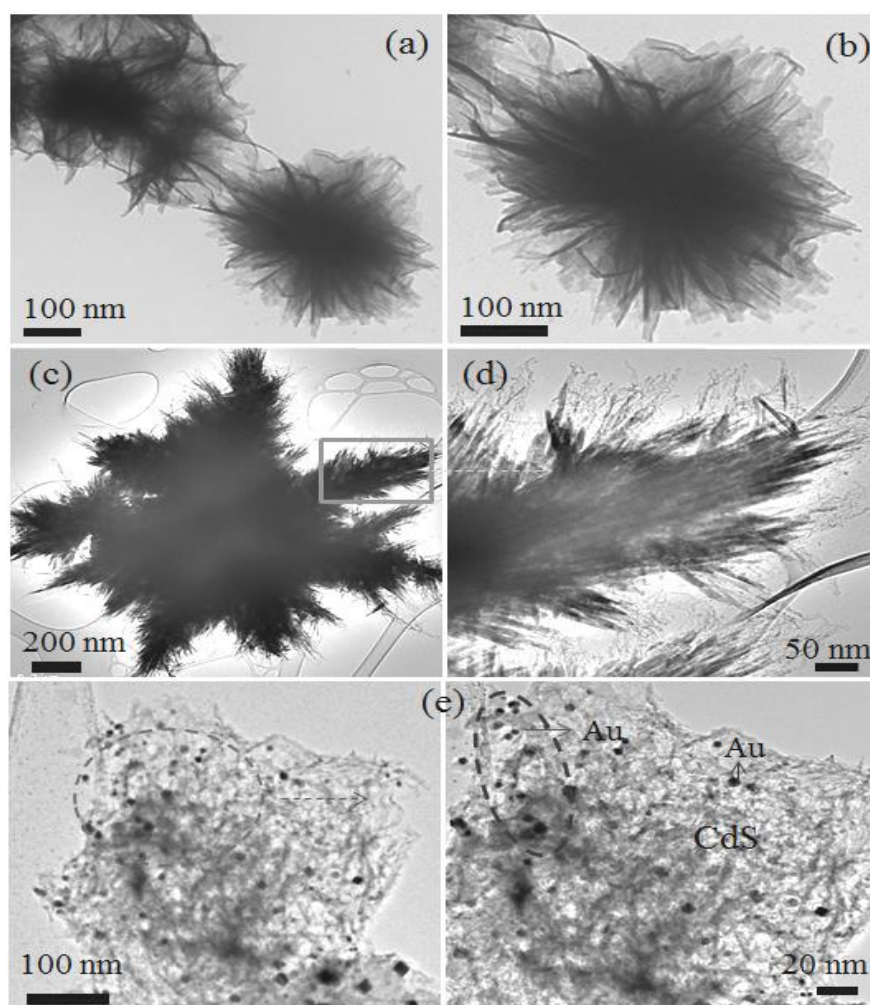


Figure 7.1. TEM micrographs of (a-d) flower like spongy CdS-2 h (SF-CdS-2 h) and (e) 1 wt% Au photodeposited SF-CdS-2 h at different magnifications.

deposited SF-CdS-2 h (Fig. 7.1e) depicted the uniform dispersion of small Au nanodeposits (*black dots*) in the size range of 3-6 nm over the entire CdS morphology (*marked area*). Au-NPs were found to be embedded in the cotton bun like porous CdS nanostructure.

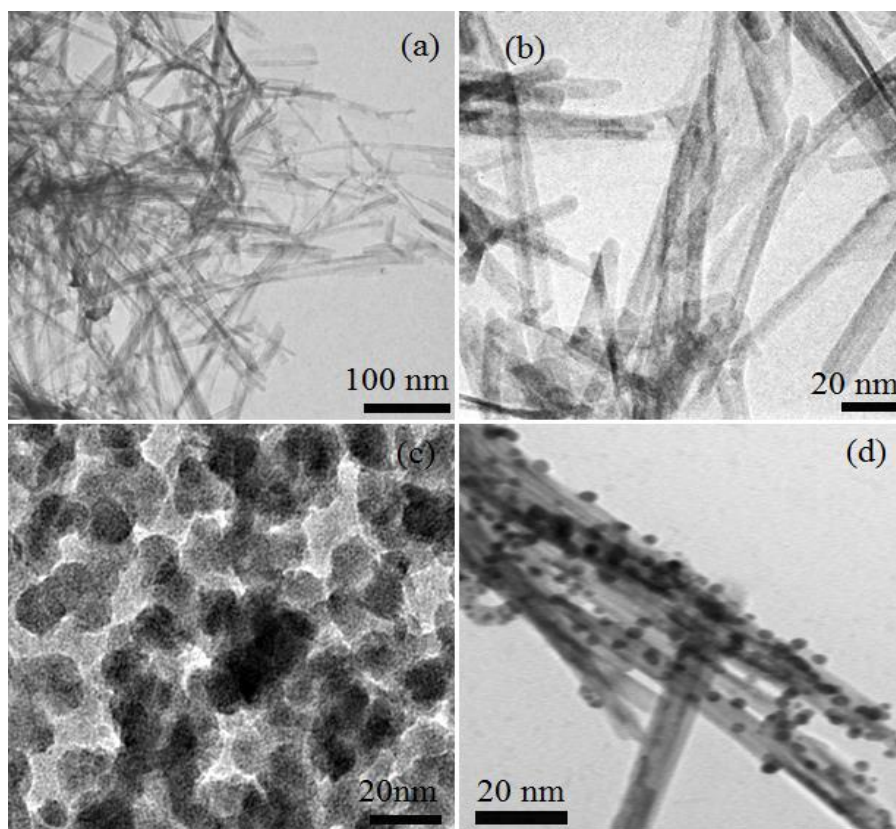


Figure 7.2. TEM micrographs of (a) CdS-6 h, (b) CdS-10 h, (c) CdS-NS1 and (d) 1 wt% Au photodeposited CdS-10 h nanostructures.

With the increase in refluxing time to 6 h, the lengthy rod like crystalline CdS-NPs of $L \sim 106$ nm and $D \sim 5$ nm was obtained (Fig. 7.2a). Their BET SA ca. $77 \text{ m}^2\text{g}^{-1}$ was found to be lower than the amorphous SF-CdS-2 h. When the refluxing was prolonged to 10 h, a distinct crystalline CdS-NR (CdS-10 h) of an average $L = 126$ nm and $D = 6$ nm were largely formed. The decreased BET SA to $21 \text{ m}^2\text{g}^{-1}$ in comparison to $77 \text{ m}^2\text{g}^{-1}$ of CdS-6 h indicated its high crystallinity. Increased crystallinity was also evident from the SAED pattern. The concentric rings were found to be more diffused and less intense because of the polycrystalline nature of SF-CdS-2 h and CdS-6 h as compared with clear contrast and brighter diffraction rings of CdS-10 h (Gupta and Pal, 2012; Singh and Pal, 2012). Smaller CdS-NS of size 10-12 nm (Fig. 7.2c) were synthesized and its BET SA was ca. $18 \text{ m}^2\text{g}^{-1}$ (*mentioned in chapter-3*). Fig. 7.2d displays the TEM micrographs of 1 wt% Au

deposited CdS-10 h. A well dispersed and uniform distribution of small spherical Au nanodeposits (black dots) having size 3-5 nm could be seen on CdS-NR surface.

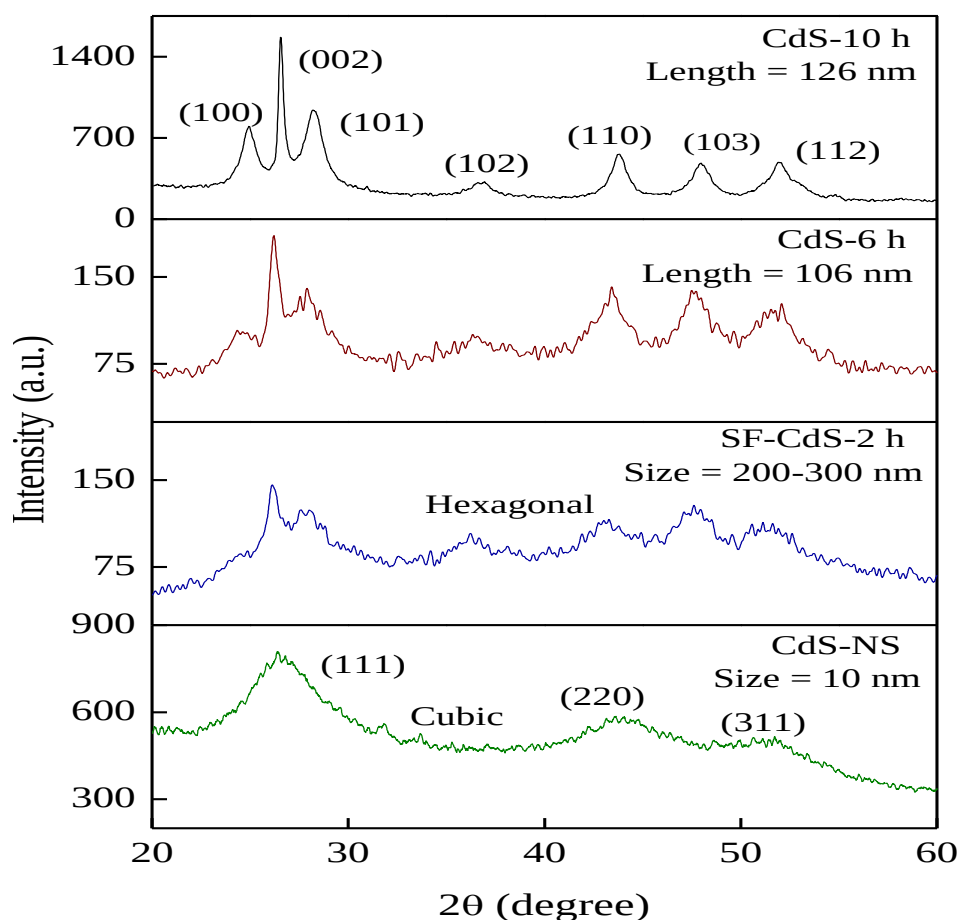


Figure 7.3. XRD patterns of CdS nanospheres (CdS-NS1), spongy flower like CdS (SF-CdS-2 h), CdS nanorods (CdS-6 h and CdS-10 h)

The characteristic X-ray diffraction peaks for (111), (220) and (311) planes of cubic crystal of CdS-NS1 having lattice constant $a = 0.582$ nm (JCPDS NO. 80-0019) were seen to be relatively broad (Fig. 7.3). The broadness could be explained due to the small size of CdS-NS1. XRD patterns evident that the crystal phase of SF-CdS-2 h nanostructure subsists between the intermediate phases of cubic and wurtzite structure with broad and less intense (002) peak. The lesser intensity of (002) peak was due to incomplete growth of regular lattice planes during early hours of refluxing. The intensity of (002) peak was gradually increased and became sharper with the increasing (2 to 10 h) reaction time, evidencing the growth of CdS-NR along c -axis with the concurrent formation of better crystalline phases. The XRD peaks of CdS-NR showed characteristic peaks for (100), (002), (101), (110), (103) and (112)

lattice planes of hexagonal crystal phase of wurtzite structure. The lattice parameters of CdS-10 h, *ca.* $a = b = 0.404$ nm and $c = 0.674$ nm (JCPDS No. 41-1049) were in accordance to the literature value (Lee et al. 2009).

The red shift in the absorbance edge (Fig. 7.4a) from 485 nm of SF-CdS-2 h to 515 nm of CdS-10 h evidenced the increase in size of the CdS-NPs. The corresponding E_g , *ca.* 2.55 and 2.35 eV for SF-CdS-2 h and CdS-10 h, respectively,

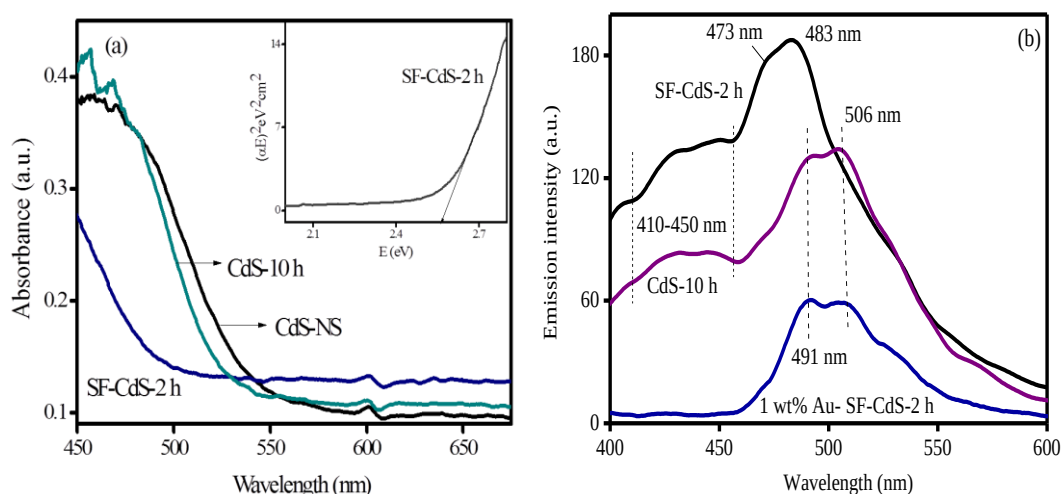


Figure 7.4 (a) Absorbance spectra of SF-CdS-2 h, CdS-10 h, CdS-NS1, Inset: band gap energy of SF-CdS-2 h and (b) photoluminescence of SF-CdS-2 h, CdS-10 h and 1 wt% Au deposited SF-CdS-2 h.

were higher than 2.33 eV of CdS-NS as determined by Tauc's equation (Sobhana et al. 2011). The higher E_g led to the shift in the position of CB and VB (valence band) in varied extent leading to alternation in their electrochemical properties. The broad emission peaks (Fig. 7.4b) at 410-450 nm of CdS nanocrystallites (1 mg/mL in acetone, $\lambda_{\text{ex}} = 365$ nm) corresponds to the bluish-green emission might arise due to interstitial S (Singh and Chauhan, 2009) in SF-CdS-2 h, CdS-6 h and CdS-10 h. No such peak was observed in Au loaded SF-CdS-2 h due to the strong interaction of Au with S^{2-} ions. A weak hump at 473 nm evolved due to band-edge emission of amorphous structure and a more intense peak at 483 nm probably occurred due to the radiative recombination from the large number of surface defect sites (Nirmala Jothi et al. 2011). The surface state is generally localized within the band gap of the semiconductor and they can trap the excited state electrons and led to red-shifted emissions. The band edge emission intensity was reduced with increasing dimensions of crystalline CdS-NR formed by 6 and 10 h refluxing. Relatively intense peaks at 491 nm (band edge emission) and 506 nm (reduced number of defect sites) in

crystalline CdS-10 h and Au loaded SF-CdS-2 h were appeared. In general, increased delocalization of charge carriers along the length of cylindrical shape reduce the e^-h^+ overlap, thus decreases the radiative decay rate with increasing length of CdS-NR (Saunders et al. 2008; Sun et al. 2011). Au (1 wt%) deposition appreciably quenched (69%) the CdS emission intensity due to the interaction between surface plasmon band of Au deposits and excitons of CdS-NR that cause a significant suppression of CdS luminescence (Khon et al. 2011; Yang et al. 2011).

Fig. 7.5a shows the effect of SF-CdS-2 h photocatalyst concentration (10-80 mg) on the PNP conversion to PAP during 4 h visible light irradiation (*LS-III*). The preliminary experiment on the hydrogenation of PNP showed that no reduction

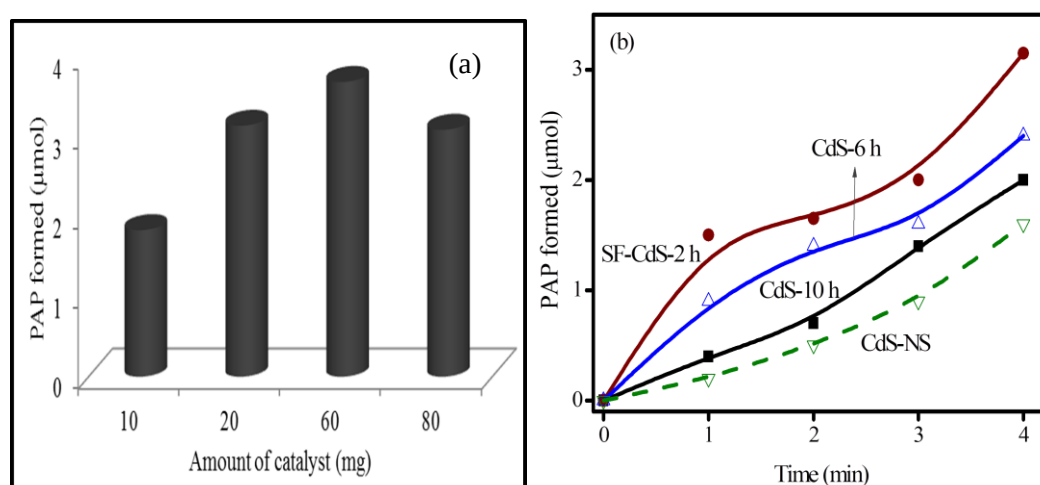


Figure 7.5 (a) Effect of amount of SF-CdS-2 h on *p*-aminophenol (PAP) production and (b) time course of PAP formation by the reduction of *p*-nitrophenol (PNP) with different CdS catalysts under 4 h visible light irradiation.

reaction was occurred by CdS in dark, which verified the photoactive nature of CdS NPs. It was found that PAP conversion rate increases (37% to 74%) with increase in SF-CdS-2 h dosage from 10-60 mg and thereby efficiency gets reduced to 62% on further dose up to 80 mg. This could be explained on the fact that higher amount of CdS beyond the optimum concentration decrease the light penetration thus limits the formation of photoexcited e^- and h^+ to react with the adsorbed PNP and deteriorate the photoreactivity (Gupta et al. 2012). Therefore, 20 mg of CdS photocatalyst was used for the maximum reactivity throughout the experiment. Fig. 7.5b shows the amount of PAP formed by the reduction of 5 μmol PNP with different CdS morphologies under visible light irradiation at different time. It was found that the amount of PAP increased linearly with irradiation time as a function of the increased

SA of CdS obtained at different refluxing time, where CdS-NS exhibited the lowest and SF-CdS-2 h displayed the highest photoactivity for PNP photoreduction. The yield of PAP by CdS-NS and SF-CdS-2 h had increased from 32% to 62% with improved selectivity from 51% and 81%, respectively, after 4 h of light irradiation.

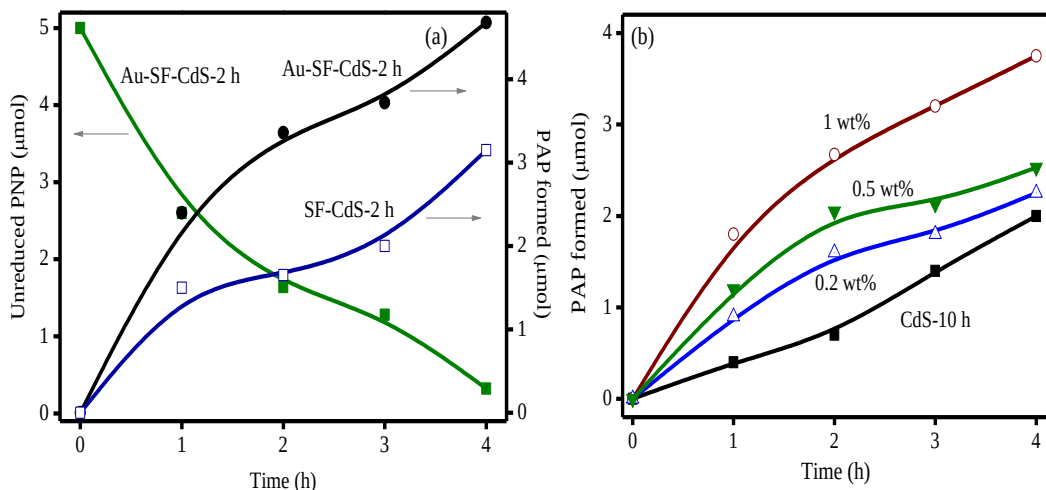


Figure 7.6 (a) Time course reduction of *p*-nitrophenol (PNP) reduction to *p*-aminophenol (PAP) formation by SF-CdS-2 h and 1 wt% Au loaded SF-CdS-2 h and (b) effect of amount (0.2-1 wt%) of Au deposition onto CdS-10 h for the PNP reduction.

The high yield and selectivity of PAP production was further verified by HPLC analysis. HPLC chromatograms (Fig. 7.7) confirmed the nature and amount of the products formed by PNP photoreduction with bare SF-CdS-2 h and 1 wt% Au loaded SF-CdS-2 h during 2-4 h light irradiation. The HPLC peak for PAP at $R_t = 3.2$ min was increased gradually when reacted with 1 wt% Au loaded-SF-CdS-2 h (Fig. 7.7b) in comparison to bare SF-CdS-2 h (Fig. 7.7a) during 2-4 h irradiation. The simultaneous reduction of PNP peak at $R_t = 6.4$ min was also noticed during the same hours of irradiation. It was noted that the absorbance intensity of the peak at $R_t = 3.2$ min for PAP was significantly enhanced by Au loaded SF-CdS-2 h as compared with bare catalyst after 4 h light irradiation under similar experimental condition. A major peak (Fig. 7.7a) at $R_t = 2.3$ min corresponds to 4-hydroxylaminophenol (Chen et al. 2007) was observed during PNP reduction by photoirradiated SF-CdS-2 h catalyst. But absence of such HPLC peak by Au loaded SF-CdS-2 h showed the selective reduction of PNP to PAP. The LC-MS analysis (Fig. 7.7c and d) confirmed that the intensity of $M+1$ peak at 110 m/z value correspond to PAP (Khan et al. 2012) formation was gradually increased from ~36% to ~92% after 2 to 4 h light irradiation and was in good agreement with the HPLC results.

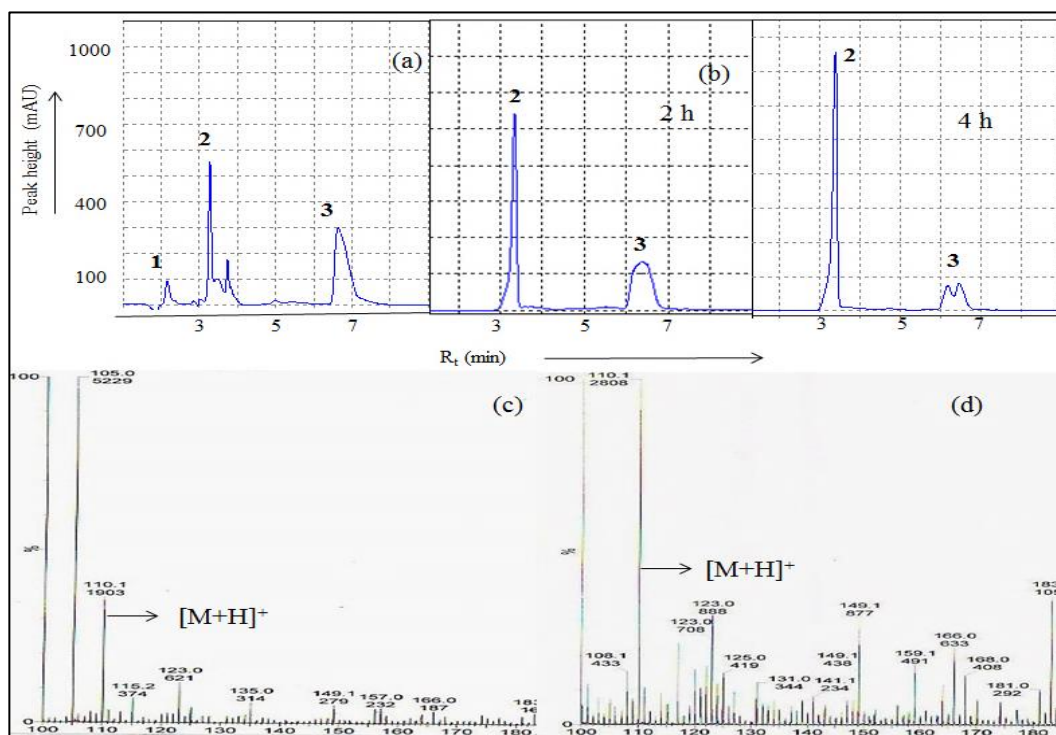


Figure 7.7. HPLC chromatogram of PNP reduction reaction with (a) SF-CdS-2 h for 4 h, (b) 1 wt% Au loaded SF-CdS-2 h for 2 h and 4 h light irradiation and the peaks (1) 4-hydroxylaminophenol, (2) PAP, (3) PNP. Mass spectra of PNP reduction to PAP formation with Au loaded SF-CdS-2 h after (c) 2 h and (d) 4 h light irradiation.

It is well known that CdS undergoes photodissolution on long exposure of light and various surface coating agents like thiols, clay, nafion and silica have been used for making stable photoactive CdS. Silica being inert is advantageous because of its better transparency for light penetration, easy access of reactants molecules through its porous surface, it prevents coagulation of catalyst powder, makes stable dispersion through surface hydroxyl groups (Arellano et al. 2000) and provides larger surface area for better adsorption and catalysis effect.

When aqueous-iso-propanol dispersion of bare SF-CdS-2 h (20 mg) and 25 μ mol PNP under argon atmosphere was illuminated with visible light for 30 h, the initial PAP yield due to PNP reduction increases linearly up to 10 h photoreaction and thereby PAP formation rate does not change and levelled-off with further irradiation up to 30 h (Fig. 7.8a). However, SiO₂ coated SF-CdS-2 h showed an almost steady increase in the PAP yield ($\sim$ 18 μ mol) by PNP (25 μ mol) reduction after 30 h irradiation, evidencing superior photostability and photoactivity of SiO₂@SF-CdS-2 h than bare SF-CdS-2 h nanostructure. The apparent reason can be

explained by the differences in surface structural morphology between bare and $\text{SiO}_2@\text{CdS}$ catalyst.

Generally, silica shell prevents coalescence of CdS-NPs and also avoids direct light exposure over CdS surface thus slowed down the photodissolution process. Consequently, these relatively smaller, isolated and photostable CdS particles improved the PNP photoreduction in a better extent. Beyond that, a layer of silica deposition over CdS surface drastically enhanced the specific surface area, ca. $158 \text{ m}^2\text{g}^{-1}$, as compared with $119 \text{ m}^2\text{g}^{-1}$ of bare SF-CdS-2 h morphology. As a result, better adsorption of PNP over porous and amorphous SiO_2 layer attached to SF-CdS-2 h surface led to much higher activity than bare CdS morphology.

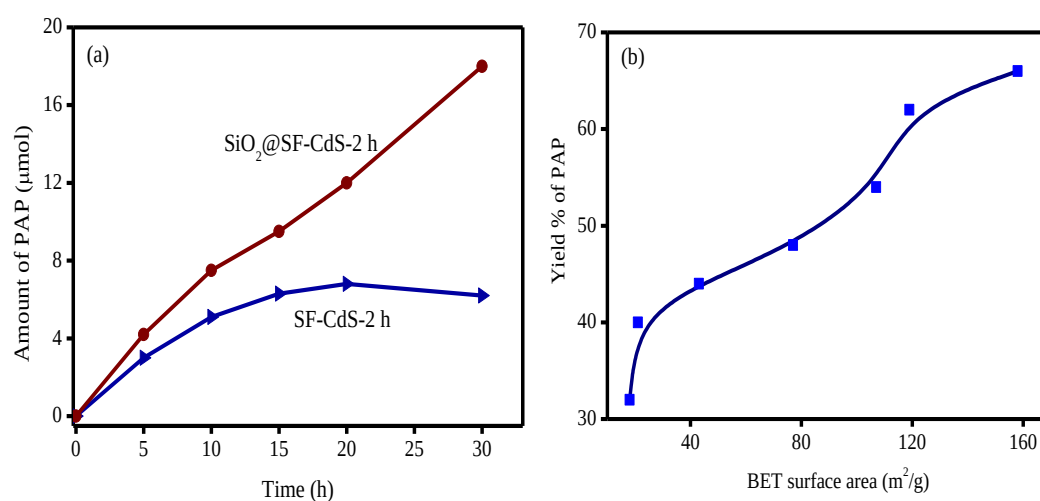


Figure 7.8 (a) Comparative rate of PNP (25 μmol) photoreduction by bare and SiO_2 coated SF-CdS-2 h on prolonged (30 h) irradiation and (b) PAP yield (%) versus BET surface area co-relation of various CdS catalysts.

Similar increase in the BET surface area of CdS-NS, CdS-6 h and CdS-10 h from 18 to $51 \text{ m}^2\text{g}^{-1}$, 77 to $109 \text{ m}^2\text{g}^{-1}$ and 21 to $43 \text{ m}^2\text{g}^{-1}$, respectively, was found when coated with a thin layer of silica shell. Fig. 7.8b demonstrates the correlation between the BET SA and their photocatalytic activity of all CdS samples for the reduction of PNP to PAP. Almost a linear increase in PAP yield (%) with surface area concluded that BET SA was primarily responsible for the observed catalytic activity. As large SA helps in better adsorption of PNP and accessibility of more active sites to react with the photoexcited electrons of CdS having different surface structures. In quantum sized nanocrystals, the effect of SA is less significant in comparison to surface to volume ratio. As increased surface to volume ratio guarantees a high density of active sites available for surface reactions as well as a high interfacial charge carrier transfer rate. This could partially compensate for the

occurrence of surface trap states and ensure a more efficient charge separation. Less crystalline CdS-6 h having large surface area ($77 \text{ m}^2\text{g}^{-1}$) was found to display more reactivity than CdS-10 h of less surface area $21 \text{ m}^2\text{g}^{-1}$ which opposes the general trend of higher activity due to increased crystallinity (Yun et al. 2009; Sun and Li, 2007). Despite being micrometer size ($0.2\text{-}0.3 \text{ }\mu\text{m}$) and amorphous nature of SF-CdS-2 h morphology, its highest reductive activity could be ascribed to the larger surface area and spongy surface texture for better adsorption of PNP molecules. Moreover, many thin surface exposed bunches consisting of SF-CdS-2 h nanostructures possess large number of surface active atoms for efficient reactivity than other compact shapes. The higher photoactivity for CdS-NR as compared to CdS-NS ($18 \text{ m}^2\text{g}^{-1}$) could be attributed to the increased delocalization of charge carriers along the length axis that reduces the $\text{e}^- \text{-h}^+$ recombination in contrast to quick recombination of charged species in spherical particles. Time resolved emission decay analysis results also confirmed that relaxation time of photoexcited charge carriers is much more for lengthy CdS nanorod than spherical NPs. Consequently, larger number of e^- and h^+ exist on the active sites of the nanocrystals surface, resulting in higher photoactivity. This is in accordance with the results of higher photocatalytic activity by hexagonal CdS-NR of different aspect ratio than cubic CdS NPs (Sathish et al. 2006).

7.4 Conclusion

Spongy cotton like CdS particles differ from the perfect spherical and rod shaped morphology having intermediate crystal phase between cubic and hexagonal structure were synthesized. Structural and physicochemical characterization revealed the dependence of photocatalytic activity of CdS on different surface morphologies. This amorphous CdS having large surface area exhibits highest photoactivity for PNP reduction among the mostly studied spherical and rod shaped CdS due to an increase in the number of adsorption sites. Au deposition considerably improved the yield and selectivity of PAP formation because of the efficient charge separation. Silica coating considerably improves the surface area and photo stability of CdS nanoparticles without hampering their photoactivity during longer light exposure.

7.5 References

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8. Photocatalytic Reduction of *m*-Dinitrobenzene and Methanol Dehydrogenation by Metal Deposited CdS Nanostructures

8.1 Introduction

Chapter-1 mentioned that II-VI group semiconducting materials capable of splitting water and reducing organic compounds has been developed. The production of CdS nanoparticles (NPs) is focused because of its narrow band gap (2.4 eV) and a flat-band potential at -0.66 V (pH 7), which satisfy the energy requirements set by the reduction potential for H₂O and nitro compounds with visible light (Pedone et al. 2005). But their application in “selective” organic transformations is relatively uncommon (Fox, 1983; Tada et al. 2009; Zhang et al. 2012). Maldotti et al. reported the increase in the azoxybenzene selectivity (11 to 41%) from nitrobenzene by simply varying the photocatalyst from WO₃ to CdS (Maldotti et al. 2000). Selective reduction of various nitrocompounds using CdS nanowire-reduced graphene oxide nanocomposite is recently reported (Liu et al. 2013).

The effective utilization of nanomaterials indeed require sufficient control of their structures and assembly systems. Because the intrinsic properties of the nanomaterials are determined by their structures, including size, shape, and dimension (Cao et al. 2006). Matsumura and co-workers found that 2% Pt-loaded CdS hexagonal crystal structure is more efficient than that of cubic crystal structure (Matsumura et al. 1985). Bao et al. observed the increased H₂ evolution rate from hexagonal, to the mixture of hexagonal and cubic, and to cubic CdS nanocrystals (Bao et al. 2007). On the contrary, higher H₂ generation by mixed cubic and hexagonal phase of CdS particles than the hexagonal bulk particle was also reported (Satish et al. 2006). Moreover, Janet and Viswanath reported the superior activity of cubic CdS-NR for H₂ production (Janet and Viswanath, 2006). Low photodegradation of RhB by hexagonal CdS nanorod (NR) of high aspect ratio and strong surface-trap emission is also reported recently (Zhang et al. 2012). In our previous study (*chapter- 7*), we addressed the role of surface area of CdS nanoparticles (NPs) on the photocatalytic reduction of *p*-nitrophenol.

It is commonly accepted that photogenerated e⁻ plays a key role in the photocatalytic selective reduction reaction (Tada et al. 2000). Thus, improving the utilization efficiency of photogenerated e⁻ and prolonging its lifetime are expected to

enhance the photoactivity for selective reduction of nitro organics and H₂ production. Tada et al. reported photocatalytic 2e⁻ reduction of azobenzene to hydrazobenzene using TiO₂ while Pt loading on TiO₂ induces N=N bond cleavage via 4e⁻ reduction (Tada et al. 2000). Pal et al. reported the highly selective (68%) reduction of nitrobenzene to azoxybenzene using SiO₂@Rh-CdS NS (Pal et al. 2007). The reduction of *m*-dinitrobenzene (*m*-DNB) to *m*-phenylenediamine (*m*-PDA) (yield 60%) by using Pt loaded titania catalyst is also reported (Rojas et al. 2011).

In spite of enormous literature on the effect of crystal structure, morphology, crystallinity, and the available surface area for reaction still many discrepancies persist. The reports on the effect of the morphology of CdS attaining same crystal structure are sparse. *In this chapter we lightened up the effect of different morphologies having similar hexagonal structure but dissimilar optoelectronic properties, onto selective reduction of m-DNB and methanol dehydrogenation.* In the second part, the effect of different metal loading onto different CdS nanostructures is discussed. As in photocatalysis, effective separation of photogenerated species is essential and assemblies of metal (M) loading with semiconductor have been demonstrated to separate the charge efficiently.

8.2 Experimental details

8.2.1 Synthesis of hexagonal CdS nanospheres, spongy flower like CdS and CdS nanorod

Hexagonal CdS nanospheres (CdS-NSH), spongy flower like CdS (SF-CdS-2 h) and CdS nanorod (CdS-NR) were synthesized using phase growth solution method as per the procedure discussed in *section- 2.2.3 and 2.3*, respectively of chapter- 2.

8.2.2 Photodeposition of different metals (Au, Cu, Pt and Rh)

The deposition of different transition metals such as Au, Cu, Pt and Rh onto different CdS nanostructures were carried out via photodeposition technique using light system *LS-I* discussed in *section- 2.4.1 (chapter- 2)*.

8.2.3 Photocatalytic reaction

8.2.3.1 Photocatalytic reduction of *m*-dinitrobenzene

Reduction of (5 mM) *m*-dinitrobenzene (*m*-DNB) was carried out using 50% alcoholic *m*-DNB solution. 5 mL of the solution and 10 mg of SF-CdS-2 h, CdS-10 h and CdS-NSH and their respective 2 wt% Au loaded composites were irradiated in an inert atmosphere (created by purging Ar gas for 30 min) under visible light (*LS-III*) irradiation. The aliquots were taken at fixed interval and were filtered by using

0.22 μm cellulose filter to get a clear solution. The reaction samples were then characterized and quantified by HPLC and GC-MS spectrophotometer. The mobile phase used for HPLC analysis was methanol and water (70:30) with a flow rate of 1 mL/min at 254 nm. 20 μL of the filtered reaction mixture was injected into the loop. GC-MS study was performed as per the conditions mentioned in *section- 2.7.14 (chapter-2)*.

8.2.3.2 Methanol dehydrogenation

Dehydrogenation of 5 mL of methanol (50 vol%) for the estimation of H_2 production in an inert atmosphere was carried out by using 10 mg of CdS-NR and CdS-NSH under visible light irradiation (*LS-III*). The effect of 1 and 2 wt% loading of noble metals like Ag, Cu, Pt and Rh onto the H_2 evolution was also examined.

8.2.4 Characterization

The prepared nanostructures were characterized using a diffuse reflectance spectrophotometer and spectrofluorimeter. Structural characterization was done using XRD, TEM and elemental analysis by EDX extended with TEM. The reaction samples of *m*-DNB were analyzed using HPLC and GC-MS. The H_2 production from methanol dehydrogenation was detected and quantified using GC with a TCD detector as per the conditions mentioned in chapter- 2 (*section- 2.7.15*).

8.3 Results and discussion

8.3.1 Optical and structural characterization

The structure, phase and the purity of the synthesized CdS-NPs were confirmed by XRD patterns. Fig. 8.1 suggests that all the CdS morphologies owned wurtzite structure having hexagonal phase which was in good agreement with the standard data from JCPDS card 41-1049. No additional peak of any impurity was detected, indicated the high purity of CdS-NPs. The strong, intense and sharp diffraction peaks indicate their high crystallinity whereas broadening of the peaks referred to their small particle size. Au and other M loading onto CdS-NR substantially lowered the intensity of CdS-NR diffraction peaks. Lowering of peak intensity was probably because of the suppression of electron scattering of CdS by heavy M attached to its surface. But no additional peak corresponding to the loaded M was observed which might be due to their low content. Absence of additional metallic peak also signified the nano size deposition of M that did not affect the CdS lattice. However, EDX analysis confirmed the presence of different metals discussed in Fig. 8.5.

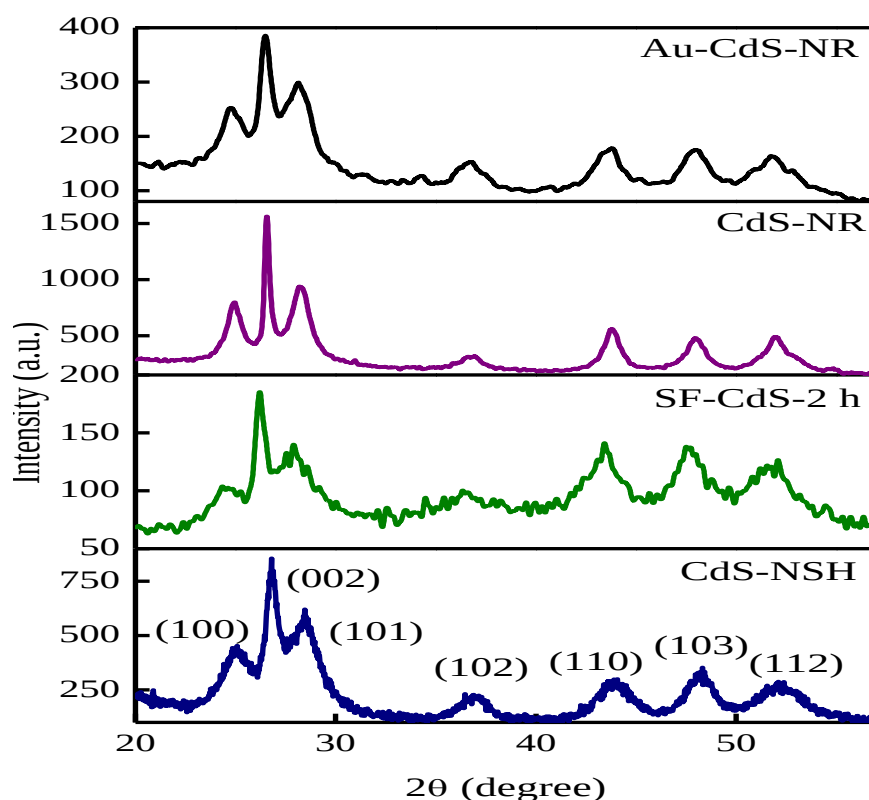


Figure 8.1. XRD patterns of different CdS morphologies and 2 wt% Au loaded CdS-NR.

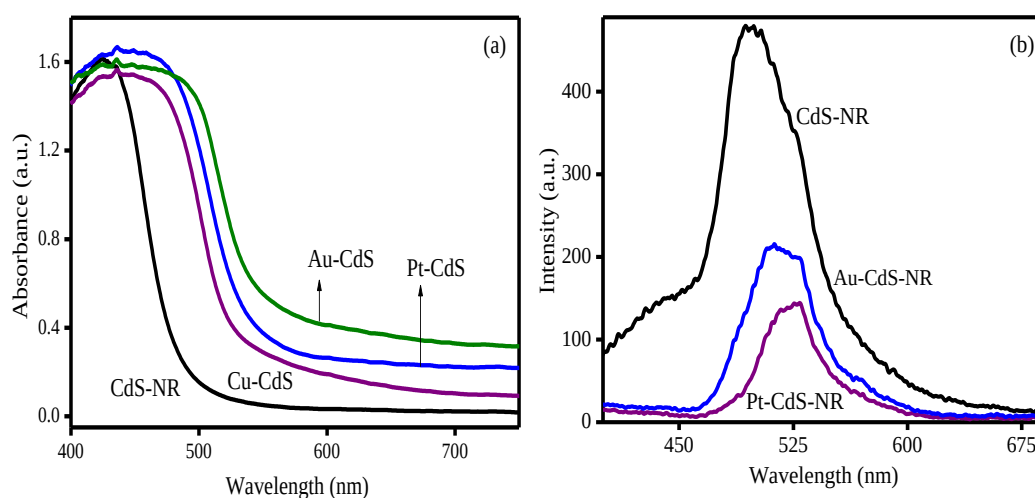


Figure 8.2 Effect of 1 wt% metal loading on (a) solid state absorbance spectra and (b) photoluminescence spectra of CdS nanorod.

The UV-Vis diffuse reflectance spectra of CdS-NR and M-CdS-NR composites (Fig. 8.2a) displayed an intense absorbance band from 420 to ca. 550 nm. This could be primarily ascribed to e^- promotion of CdS from the valence band (VB) to the conduction band (CB). The red-shifted absorbance onset was observed but the appearance of any SPR peak characteristic of different metals was not observed. As discussed in previous chapters that such type of M-CdS-NR junction promotes the

mixing of electronic states at metal-semiconductor interfaces, which cause a significant suppression of both plasmon and excitations of carrier's. Moreover, the SPR peak of Pd at ~ 300 nm (Xiong et al. 2005) gets shielded by the strong absorption of CdS and Pt-NPs have no characteristic peak in the region of 300 to 800 nm (Johnson et al. 2002). The estimated band gap energy (E_g) of Au-CdS, Pt-CdS, and Cu-CdS nanocomposites were found to be in the range of 2.29-2.37 eV that clearly showed a band gap narrowing compared to the bare CdS (2.54 eV). Thus, conclude the crucial effect of M loading on the optical properties of CdS which can be tuned by the incorporation of different metals.

A broad emission band for bare CdS-NR (1 mg/ mL in acetone, $\lambda_{\text{ext}} = 365$ nm) was observed at 496-529 nm (Fig. 8.2b). The intense peak at 501 nm was ascribed to the band gap emission and another weak emission band at 529 nm was ascribed to the recombination of trapped charge carriers at the CdS defects sites. On M loading the emission of CdS-NR was quenched because of the intimate contact of the CdS-NR with different metals that dramatically alter the energy flow across M-CdS interface. Thus facilitates the transfer of photogenerated e^- from the CdS to M, and reduce the charge recombination (Kumar and Chaudhary, 2009; Khon et al. 2011; Yang et al. 2011). The PL peak position was red-shifted to 526-529 nm as compared to bare CdS-NR (515 nm) because of the electronic interactions between SP band of Ag (420 nm) and Au (540 nm) nanodeposits with CdS exciton. In case of CdS-NSH, one sharp emission at 488 nm (exciton emission) and a weak band at 528 nm correspond to the radiationless recombination of the charge species at the surface

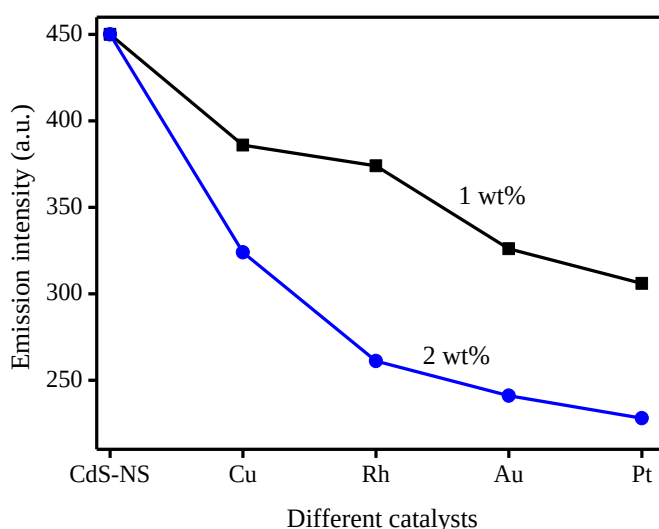


Figure 8.3. Effect of different amount of metal loading onto the emission intensity of hexagonal CdS nanospheres.

defect sites appeared. The large extent of exciton quenching by 1-2 wt% Au, Cu, Rh and Pt photodeposited CdS-NSH was observed (Fig. 8.3). It was found that the intensity of band edge emission (488 nm) of the M-CdS-NSH hetero-composites was significantly reduced as compared to bare CdS-NSH. The percentage of PL quenching increased on increasing the amount of M loading. This behaviour could be explained on the fact that higher the M loading, more is the number of M atoms that can interact with CdS surface and hence led to more quenching.

TEM images (Fig. 8.4a) of bare CdS-NSH illustrated the homogeneous dispersion of CdS-NSH of an average size = 12 nm. Fig. 8.4b-d elucidates that numerous M particles with an ultrafine size and a very narrow size distribution were decorated on the surface of CdS-NSH. It was observed that the distribution of different metals onto CdS-NSH was different. The size of M-NPs varied in the range of 4.5 to 7.5 nm depending on the type and the nature of M loaded. Fig. 8.4c-d reveals that Pt-NPs were largely dispersed over CdS particles compared to other

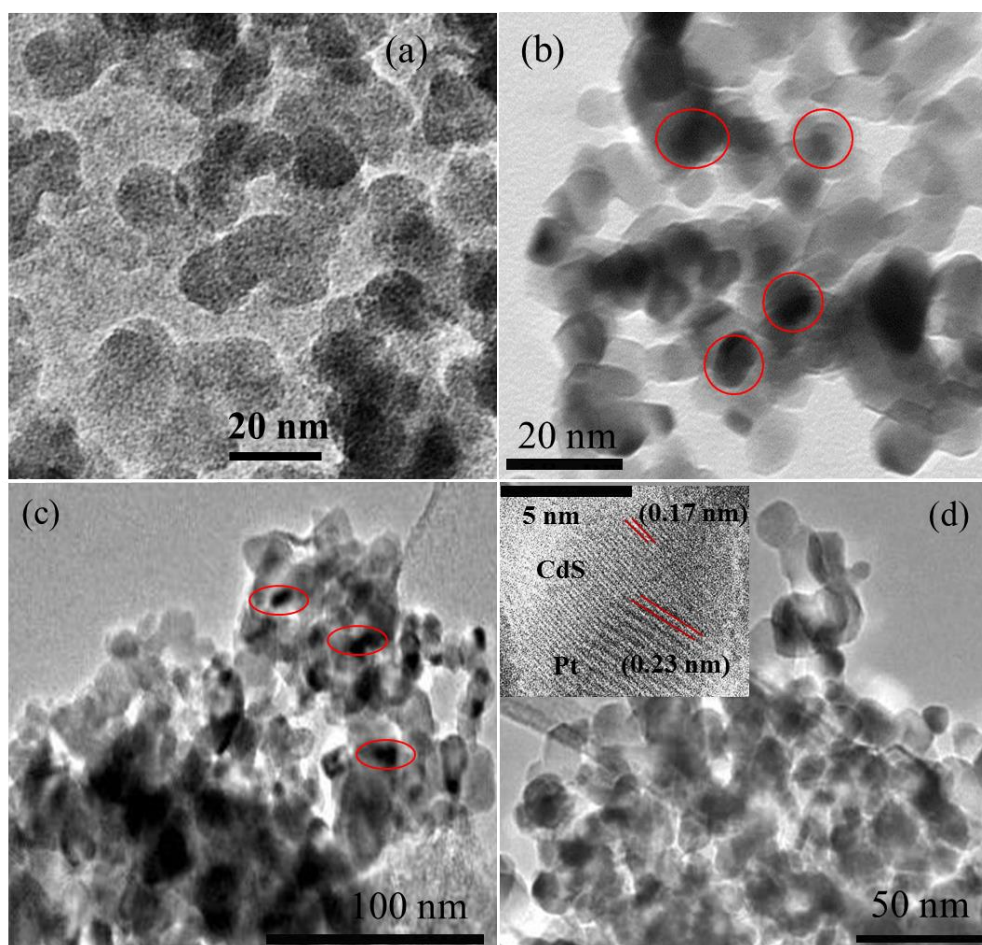


Figure 8.4. TEM micrographs of (a) CdS-NSH, (b) Au loaded CdS-NSH and (c and d) Pt loaded CdS-NSH; Inset: HR-TEM of Pt-CdS-NSH.

metals, thus formed higher M-CdS interfaces with size smaller than Au (Fig. 8.4b). HR-TEM image of Pt-CdS-NS (*Inset*, Fig. 8.4d) clearly demarcated its crystalline nature due to the presence of well-defined lattice fringes. Interplanar spacing (d) = 0.17 nm corresponding to (112) of hexagonal CdS and 0.23 nm of (111) plane confirmed the cubic structure of Pt (Peng and Yang, 2009).

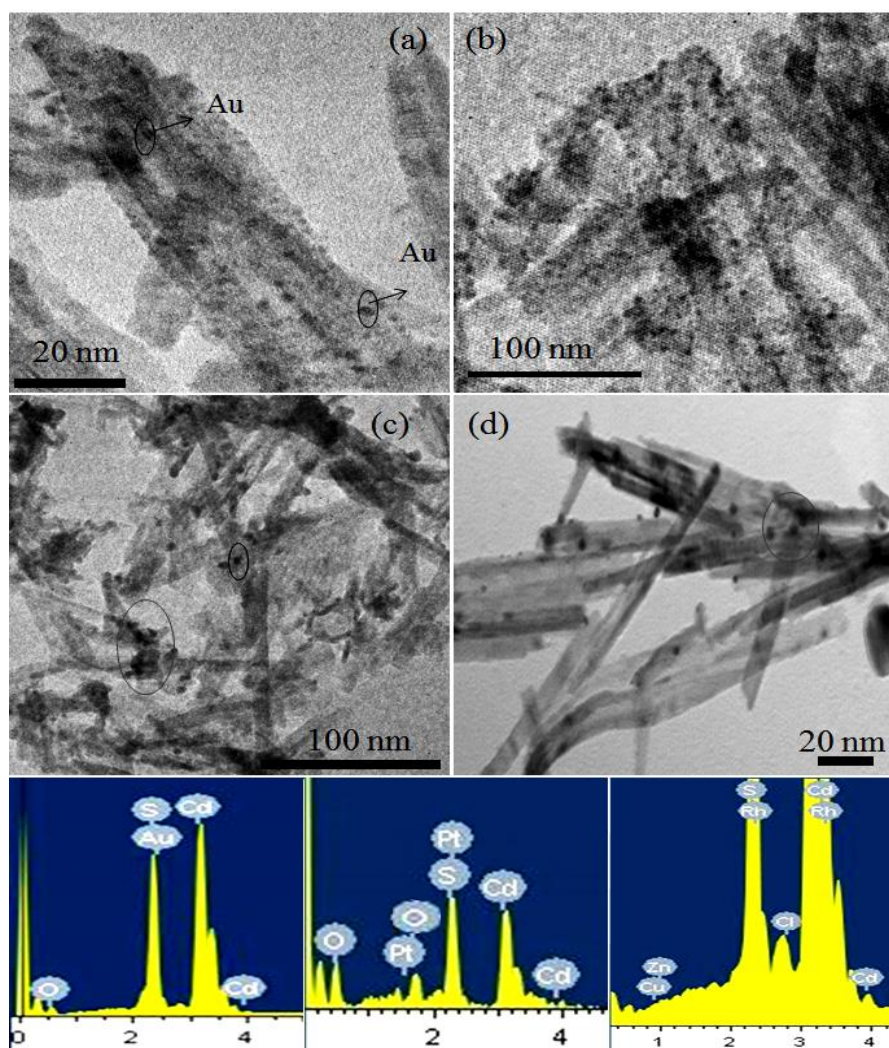


Figure 8.5. TEM micrographs of Au (a) 1 wt%, (b) 2 wt%; 1 wt% (c) Pt and (d) Rh loaded CdS-NR and their EDX spectra.

Fig. 8.5 shows the TEM micrographs of different M loaded CdS-NR where the surface of lengthy CdS-NR (length = 100-110 nm and diameter = 5-6 nm) were found to be covered with small NPs (*black dots*) of size range 3-5 nm depending on the nature and amount of M. After comparing Fig. 8.5a and b, we clearly observed that the number and the size of the M particles present on the CdS surface increased with the amount of M loading. EDX data showed the presence of Au - 1.76 at%, Pt - 1.07 at% and Rh- 1.51 at% over CdS-NR.

8.3.2 Photocatalytic reduction of *m*-dinitrobenzene

Fig. 8.6a shows the time course graph of the amount of *m*-nitroaniline (*m*-NA) formed by the selective photoreduction of *m*-DNB by as-prepared CdS morphologies under visible light irradiation (*LS-III*). It was observed that *m*-NA formation increased linearly with irradiation time as a function of the increased surface area and small particle size of CdS nanostructure. High surface area provides more reaction sites for the adsorbed species whereas benefits of small particle size arose from its more surface to volume ratio. Moreover, increased surface to volume ratio guarantees a high density of active sites available for surface reactions as well as a high interfacial charge carrier transfer rate. This could partially compensate for the occurrence of surface trap states and ensure a more efficient charge separation. CdS-NSH and CdS-NR exhibited the highest and lowest photoactivity, respectively, for *m*-DNB photoreduction. The yield of *m*-NA by CdS-NR and CdS-NSH was increased from 36% to 58%, respectively and a considerable yield $\sim 53\%$ was produced by bare CdS-SF-2 h after 7 h irradiation. On 1 wt% Au loading, the yield of CdS-NSH was further improved to ca. 90% whereas Au-SF-CdS-2 h resulted in comparable increase of $\sim 86\%$ yield with cent percent (100%) selectivity.

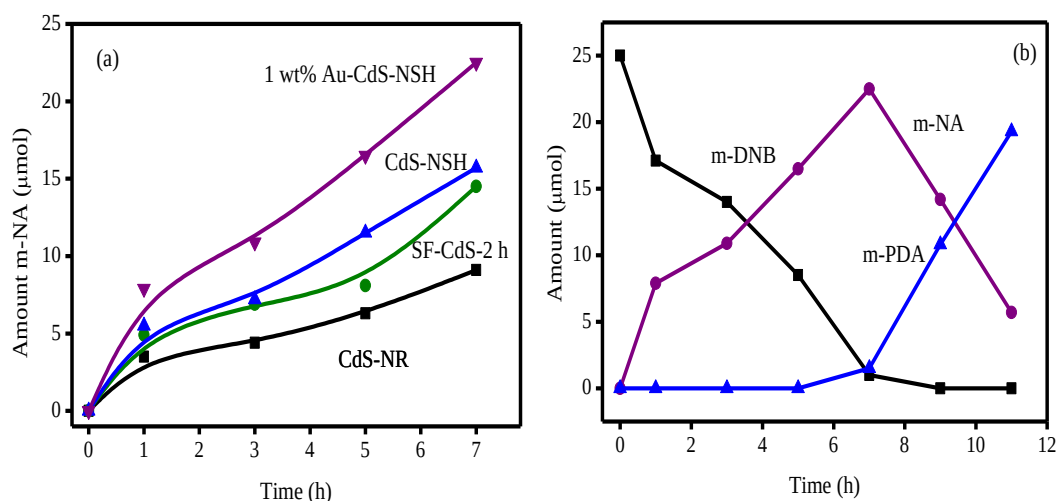


Figure 8.6 (a) Time course of *m*-NA by selective reduction of *m*-DNB with different catalysts under visible light irradiation and (b) conversion of *m*-DNB to *m*-NA and *m*-PDA by 1 wt% Au-CdS-NSH with irradiation time.

Fig. 8.6b shows the effect of prolonged irradiation up to 11 h on the product distribution of 5 mM *m*-DNB reduction by Au-CdS-NSH. It was observed that the reduction products i.e. *m*-NA and *m*-phenylenediamine (*m*-PDA) were selectively formed as a function of time. Linear production of *m*-NA was observed up to 7 h of

light irradiation whereas prolonged irradiation resulted in decreased *m*-NA concentration which itself gradually converted to *m*-PDA. The amount of *m*-PDA formed after 11 h of irradiation was ca. 19.3 μmol ($\sim 77\%$) from 25 μmol of *m*-DNB.

The high yield and selectivity of *m*-NA production was further verified by HPLC and GC-MS analysis (Fig. 8.7). The HPLC peak (Fig. 8.7a) for *m*-NA at $R_t = 3.6$ min was increased gradually from CdS-NR to SF-CdS-2 h to CdS-NSH whereas 1 wt% Au-CdS-NSH produced the highest peak with the simultaneous reduction of *m*-DNB peak at $R_t = 4.5$ min. However, no peak at $R_t = 2.9$ min corresponding to *m*-PDA was observed indicated the selective conversion of *m*-DNB to *m*-NA in 7 h. Single peak (Fig. 8.7b) in GC chromatogram at $R_t = 8.2$ min correspond to *m*-NA confirmed the selectivity of *m*-NA. The GC-MS analysis (Fig. 8.7c) confirmed that the abundance of m/z peak at 138 value correspond to *m*-NA formation was gradually increased from 53% to 80% on reaction with CdS-NSH and Au-CdS-NSH, respectively which was in good agreement with the HPLC results.

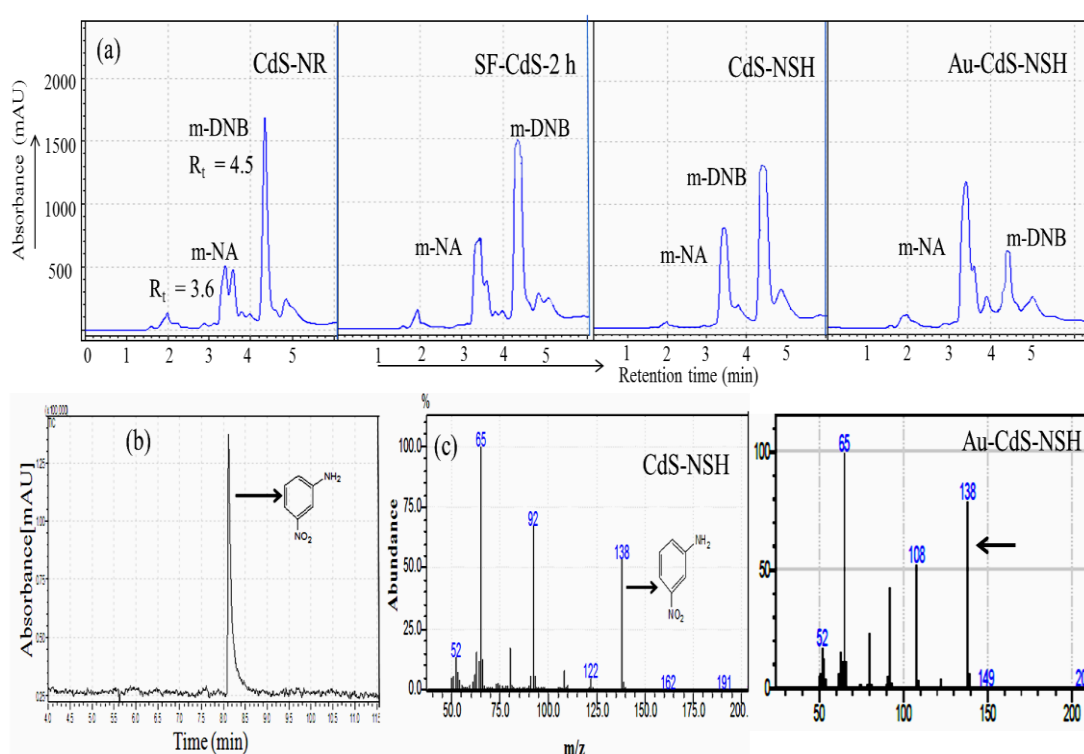


Figure 8.7 (a) HPLC chromatograms of *m*-DNB reduction by different CdS morphologies, (b) GC chromatogram of *m*-NA obtained after reaction with Au-CdS-NSH and (c) mass spectra of (b) after reaction with CdS-NSH and Au-CdS-NSH for 7 h of light irradiation.

8.3.3 Methanol dehydrogenation

To compare the effect of substrate on different CdS morphologies i.e. CdS-NSH and CdS-NR having same crystal structure, photocatalytic methanol

dehydrogenation was performed using 50 vol% (5 mL) of methanol. Fig. 8.7 shows the linear increase in the H_2 production with the irradiation time up to 8 h and 1 wt% Au loading enhanced the production rate. On comparing Fig. 8.7a and b, it was observed that the amount of H_2 produced by CdS-NR ($21 \text{ m}^2 \text{ g}^{-1}$) was higher, ca. $\sim 173 \text{ } \mu\text{mol}$ than CdS-NSH ($126 \text{ m}^2 \text{ g}^{-1}$), ca. $155 \text{ } \mu\text{mol}$. The probable reason for the higher photoactivity of CdS-NR was the high crystallinity of CdS-NR in contrast to CdS-NS. It is known that sulphides with small surface areas of $< 10 \text{ m}^2 \text{ g}^{-1}$ showed good photocatalytic efficiency because of their good crystallinity and less crystal defects that can largely reduce the bulk e^-h^+ recombination during the migration of e^- and h^+ to the surface of CdS. Matsumura reported that high yields of hydrogen

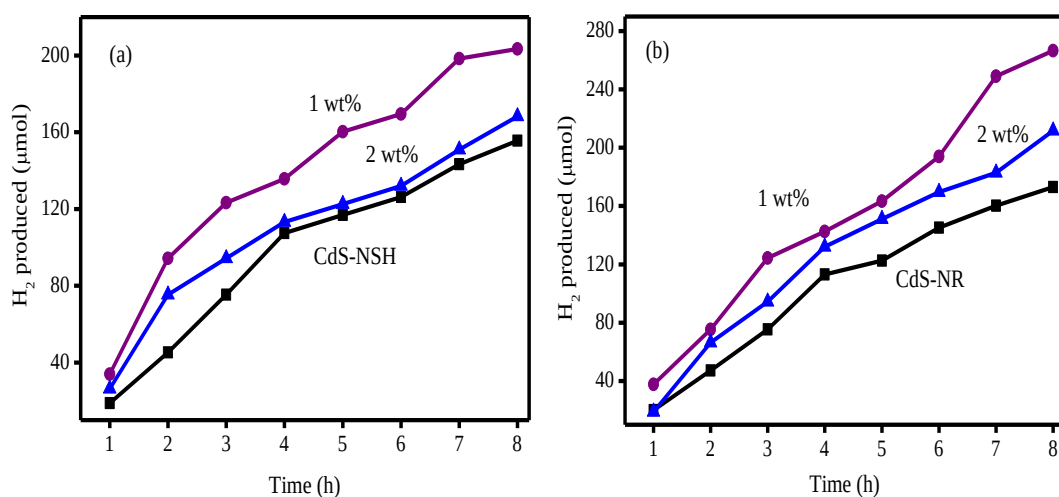


Figure 8.7. Comparative amount of H_2 produced with irradiation time by (a) CdS-NS and 1-2 wt% Au loaded CdS-NS and (b) CdS-NR and 1-2 wt% Au loaded CdS-NR.

(Matsumura et al. 1985) could be obtained with CdS samples with very low specific surface areas and high crystallinity. Moreover, the role of surface area predominates in the adsorption reactions such as organic transformations and dye degradation etc. whereas H_2 production requires high crystallinity. This relation of surface area and photoactivity suggested that the improved crystallinity and rapid delocalization of photogenerated charge carriers along the length of CdS-NR probably slow down the e^-h^+ recombination and hence, increased the photocatalytic efficiency. 1 wt% metal loading onto both morphologies enhanced the H_2 production rate linearly as a function of time. Whereas photocatalytic efficiency declined on higher loading (2 wt%) due to inactive participation of optimum number of M-CdS composites in

photoinduced charge transfer processes. As on higher loading, more of the M particles cover the surface of CdS (verified from TEM images) which inhibit the penetration of light to semiconductor for the effective photogeneration of charged species. Also, the particle size of the deposited M increased probably due to aggregation which lowered down the Fermi level equilibration and hence the co-catalytic activity.

Fig. 8.8a shows the comparative effect of 1 wt% loading of different metals onto CdS-NR and CdS-NSH for H₂ production. It was perceived that M loading

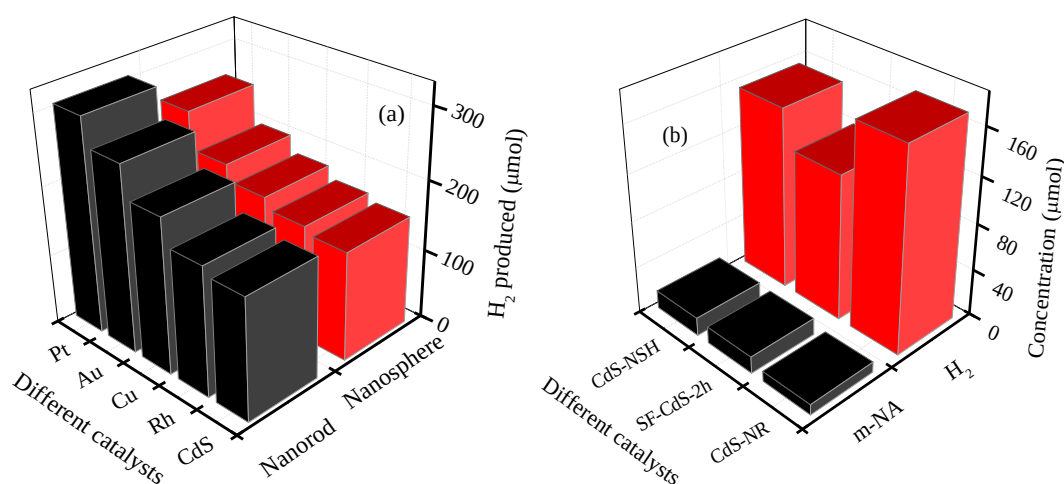


Figure 8.8 (a) Effect of 1 wt% loading of different metals onto CdS nanoparticles for H₂ production and (b) comparative effect of all the catalysts on selective reduction of *m*-DNB to *m*-NA and H₂ production.

always improves the production rate and follows the order - Pt > Au > Cu > Rh in both the morphologies. Pt-CdS heterocomposites produced the highest amount ca. 306 μmol (CdS-NR) and 257 μmol (CdS-NSH) whereas Rh loading produced lowest ca. 184 and 165 μmol by NR and NSH, respectively. The significantly improved activity after M loading resulted from the strong synergy between the nanostructured CdS support and tiny M particles. The enhanced performance of M-CdS could be partly attributed to the capability of trapping electrons by Au, Cu, Pd, or Rh, verified by PL spectra analysis (Fig. 8.2b and 8.3) that suggested the reduced charge carrier's recombination. As a result strongly reducing e⁻ could be available for photoreduction of methanol effectively in a better rate.

The discrepancy on the co-catalytic activity of different metals could be explained on the basis of their work function and redox potential etc. The difference in size of deposited metals i.e. Au (~ 3.5 nm) and Pt (~ 1.8 nm) could be the other

probable reason because Fermi energy equilibrium is size dependent which alter the ease of electron transfer. The conduction band (CB) of bulk CdS is located at ~ -0.4 V vs. NHE, significantly negative compared to the Fermi energy/work function of bulk metals (Au-5.32 eV, Cu- 4.70 eV, Pt- 5.40 eV and Rh- 4.98 eV). As the Fermi level of Pt lies closer to the CB of CdS, the electron transfer occurs more rapidly from CdS to Pt than Au, thus exhibits improved co-catalytic activity.

Fig. 8.8b shows the effect of morphology on the photoconversion of different substrates to their respective products. It was observed that small sized, less crystalline and high surface area attaining CdS-NSH were more active for *m*-DNB reduction whereas highly crystalline lengthy CdS-NR with low surface area produced more H₂. It could be concluded that many factors, including the light absorption intensity, e^- - h^+ pairs life, morphology, crystallinity, crystallite size, etc. play an important effect in affecting the photocatalytic performance. In other words, the overall photocatalytic performance resulted from a synergistic effect of several key factors. However, the surface morphology is the most key factor contributing to the photocatalytic activity when the photocatalyst possess similar crystal geometry.

8.4 Conclusion

It was noticed that the activity of CdS nanoparticles depend on the surface morphology, specific surface area and the crystallinity. Metal loading affects the opto-electronic properties of CdS and helped in improving the reduction ability for all the reactions. As-synthesized morphologies selectively reduce *m*-DNB to *m*-NA and *m*-PDA as a function of time where the effect of surface area predominates. 2 wt% Au loading onto CdS-NSH highly enhance the yield of *m*-NA to 92%. However, the role of crystallinity was found to be more pronounced in H₂ production. In addition, metal co-catalysts size, specific wavelengths of light and suitable solvent are needed to control high product selectivity and yield.

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Summary and conclusions

In summary, the present research work involved the preparation and detailed characterization of various shapes of CdS nanostructures such as nanospheres, nanorods of different aspect ratio, spongy flower like CdS nanoparticles, core (CdS)-shell (SiO_2) and SiO_2 coated movable CdO@CdS morphology by UV-Vis absorption and photoluminescence spectroscopy, XRD, SEM, TEM, BET surface area, LB film and TGA etc. Their relative optical absorption, band position, photoluminescence, and photocatalytic redox properties both under UV and visible light illumination, and the photostability by SiO_2 coating were investigated elaborately in correlation to their size, shape, effect of metal loading, impact of laser exposure, crystal structure, crystallinity, band gap energy, surface area etc. Furthermore, CdS morphologies were also stabilized against its photodissolution by SiO_2 coating which results in the formation of core-shell structures that improved the photochemical activity and stability of CdS nanoparticles during longer light exposure. Multiple-movable core (CdS)-shell (CdO) structures enclosed in lengthy SiO_2 matrix were synthesized by photoetching of CdS core using monochromatic light irradiation from Ar ion laser. Different transition metals (Au, Ag, Cu, Pt, Pd and Rh) were loaded on the synthesized CdS nanostructures for finding the best and effective photocatalytic activity of metal-CdS heterocomposite.

Chapter-1 deals with a general introduction of photocatalysis, an outline on size quantization and the effects of the particle shape and composition on the optical and electronic properties. The potential properties such as inertness, transparency, porosity, stability etc. that make SiO_2 as a suitable shell material are also discussed. A short overview of the various studies carried out earlier in the field of presented work is also delivered. A short description of used experimental methods and techniques for the determination of opto-chemical and photophysical properties are presented in chapter-2.

Chapter-3 defines the synthesis of core-shell structure of different morphologies such as nanospheres (NS) and nanorods (NR) of $\text{SiO}_2\text{@CdS}$ with uniform SiO_2 shell thickness. Such nanocomposites were found to be highly stable for long exposure of light (30 h) and beneficial for various photochemical reactions compared to bare CdS as a function of their increased surface area. The effect of silica shell thickness was investigated and it was found that thick $\text{SiO}_2\text{@CdS}$

imparted low activity because of poor access of the reactant species. $\text{SiO}_2@\text{CdS}$ -NS and NR displayed different activity because of their dissimilar surface morphology, geometry and per particle surface area etc. SiO_2 coating quenches the photoluminescence intensity of CdS nanoparticles by reducing the number of surface emissive defect sites. The enhanced colloidal stability of silica encapsulated particles allows the preparation of very concentrated dispersions without loss of stability.

Chapter-4 describes that photoetching of $\text{SiO}_2@\text{CdS}$ nanocomposites by monochromatic Ar ion laser light of higher energy assisted in selective control of core diameter as a function of the wavelength of light used without affecting the crystal structure. The quantized particles obtained after photoetching exhibit improved opto-electronic and photochemical activity for benzaldehyde photooxidation and methyl orange photodegradation. Because of their small particle size and increased band gap energy. Metal loading onto these structures further improve their photocatalytic efficiency depending upon the type of metal loaded.

Chapter-5 mentions that subsequent chemical dissolution of CdS core from $\text{SiO}_2@\text{CdS}$ nanocomposites result in the formation of hollow silica nanostructures such as hollow silica nanospheres, close ended hollow silica nanotubes and silica coated Au nanoparticles. These structures possess high surface area and displayed excellent optical absorption and catalytic activity for the reduction of *p*-nitrophenol to *p*-aminophenol. These hollow nanoporous silica materials having large surface area can be potentially used as novel supporting materials and nanoreactors in catalytic reaction. Moreover, selective etching of CdS template led to the form silica spheres/tubes with complex cavities and porosities.

Chapter-6 delivers the synthesis of multiple-movable core-shell structures of $\text{CdO}@\text{CdS}$ enclosed in a SiO_2 tubular matrix by photoetching of $\text{SiO}_2@\text{CdS}$ -NR using high energy Ar ion laser light (458 nm). Such structures were found to be highly photoluminescent and displayed good photostability. $\text{CdO}@\text{CdS}$ composites having fresh CdS obtained after gradual removal of CdS layer showed superior photoactivity under visible light illumination. Due to large adsorption of reacting species, mixed cubic (CdO) and hexagonal (CdS) crystal phase, new interfacial energy owing to (CdO (2.16 eV) and CdS (2.4 eV)) band mixing. Such metal oxide coated metal sulphide (core-shell) composites can be more useful for effective

utilization of solar illumination in greener environmental clean-up processes and in many optoelectronic applications than traditional CdS particle morphology.

Chapter-7 describes the synthesis of a new spongy flower like morphology of CdS particles different from the spherical and rod shaped morphology having intermediate crystal structure between cubic and hexagonal. This amorphous CdS displayed different optical properties and exhibited high yield and selective photoreduction of *p*-nitrophenol to *p*-aminophenol than mostly studied spherical and rod shaped CdS due to their high surface area. Such nanostructures are advantageous for adsorption processes, catalysis, for water purification, contaminated soil remediation, and heavy metal adsorption. The effect of different morphologies having hexagonal crystal structure for the photoreduction of *m*-dinitrobenzene (*m*-DNB) and methanol dehydrogenation was closely investigate as discussed in chapter- 8. It was found that different structures behave differently depending on the nature of the reactant. Smaller hexagonal CdS-NS having large surface area was proficient for *m*-DNB reduction whereas lengthy crystalline rods were more efficient for H₂ production. Metal loading in all the as-synthesized morphologies affect their opto-chemical properties and displayed superior photocatalytic properties up to optimum loading as a function of their different chemical properties. Moreover, metal co-catalysts size, specific wavelengths of light and suitable solvent are needed to control for high product selectivity and yield.

List of publications:

1. **N. Gupta** and B. Pal (2012) *The synthesis, structure, optical and photocatalytic properties of silica-coated cadmium sulfide nanocomposites of different shapes.* **Journal Colloidal and Interface Science** **368**: 250-256.
2. **N. Gupta** and B. Pal (2013) *Superior Photoluminescence and Photocatalytic Activity of CdS (Core)-SiO₂ (Shell) Nanostructures Obtained by CdS Photoetching and Au Deposition,* **Journal of Nanoscience and Nanotechnology** **13**: 5069-5079.
3. **N. Gupta** and B. Pal (2013) *Selective photoreduction of p-Nitrophenol to p-Aminophenol by Au deposited CdS nanostructures of different shapes having large surface area.* **Journal of Nanoscience and Nanotechnology** **13**:4917-4924.
4. **N. Gupta**, N. Badhwar and B. Pal (2013) *High surface area possessing hollow SiO₂ nanostructures and Au (core)–SiO₂ (shell) nanocomposites fabricated by CdS template dissolution.* **Journal of Sol-Gel Science and Technology** **68**:284-293.
5. M. Rani, **N. Gupta** and B. Pal (2012) *Superior photodecomposition of pyrene by metal ion-loaded TiO₂ catalyst under UV light irradiation.* **Environmental Science and Pollution Research** **19**:2305–2312.
6. **N. Gupta** and B. Pal (2013) *Photocatalytic activity of transition metal and metal ions impregnated TiO₂ nanostructures for iodide oxidation to iodine formation.* **Journal of Molecular Catalysis A: Chemical** **371**:48-55.
7. **N. Gupta** and B. Pal (2013) *Photoformation of phenol from benzene and cycloalkanones from cycloalkanols by the metal ion-TiO₂ nanocomposites.* **Journal of Experimental Nanoscience**, DOI:10.1080/17458080.2013.807938
8. N. Badhwar, **N. Gupta** and B. Pal (2013) *Photochemical fabrication of transition metal nanoparticles using CdS template and their co-catalysis effect for TiO₂ photocatalysis.* **International Journal of Nanoscience** **12**:1350020.
9. **N. Gupta** and B. Pal (2013) *Superior Photoactivity and Stability of Movable CdS (core)-CdO (shell) Nanostructures Formed in Tubular SiO₂ by Laser Etching of SiO₂@CdS Nanorod.* **Langmuir** (communicated).
10. **N. Gupta** and B. Pal, *Core-Shell Structure of Metal Loaded SiO₂-CdS Hybrid Nanocomposites for Complete Photomineralisation of Methyl Orange by Visible Light.* **Journal of Hazardous Materials** (communicated).

11. **N. Gupta** and B. Pal, *Selective photoreduction of m-dinitrobenze and methanol dehydrogenation by different metal loaded CdS nanostructures*. **International Journal of Hydrogen Energy** (communicated).

Papers published in conference proceedings:

1. **N. Gupta** and B. Pal, *Study of optical property and photocatalytic activity of silica coated CdS nanorods* in National symposium on nanoscience and nanotechnology (Nanotech 2011), Benchmarking – Science and Society.
2. **N. Gupta** and B. Pal, *Effect of CdS core photoetching on optical and photoactivity of SiO₂@CdS nanocomposites* in International conference on frontiers in nanoscience, nanotechnology and their applications (NanoSciTech 2012).
3. **N. Gupta** and B. Pal, *Effect of Laser Irradiation on the Optical and Photocatalytic Activity of SiO₂ Coated CdS Nanorod* in International conference on Emerging Technologies: Micro to Nano 2013 (ETMN-2013).