Template synthesis of transition metal nanoparticles and their applications as co-catalyst in TiO_2 photocatalytic reactions

A

Thesis submitted

In partial fulfillment of the requirement for the degree of

M.Sc. (Chemistry)

Submitted By

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Nidhi Badhwar

Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled "Template synthesis of transition metal nanoparticles and their application as co-catalyst in TiO_2 photocatalytic reactions", in the partial fulfillment of the requirements for the award of the degree of Masters in Chemistry, School of Chemistry and Biochemistry (SCBC), Thapar University, Patiala, is my own work during the period of January to July2011, under the supervision of Dr. Bonamali Pal. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Patiala

Data: 15 July, 2011

Nidhi

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This is to certify that the above statement made by cadidate is correct and true to the best of our knowledge.

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Certificate

This is to certify that the project entitled "Template synthesis of transition metal nanoparticles and their application as co-catalyst in TiO_2 photocatalytic reactions", being submitted by Ms Nidhi Badhwar in partial fulfillment of the requirement for the award of degree of Masters in Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonifide work carried out under the supervision of Dr. Bonamali Pal and that no part of this project has been submitted for the award of any other degree by me.

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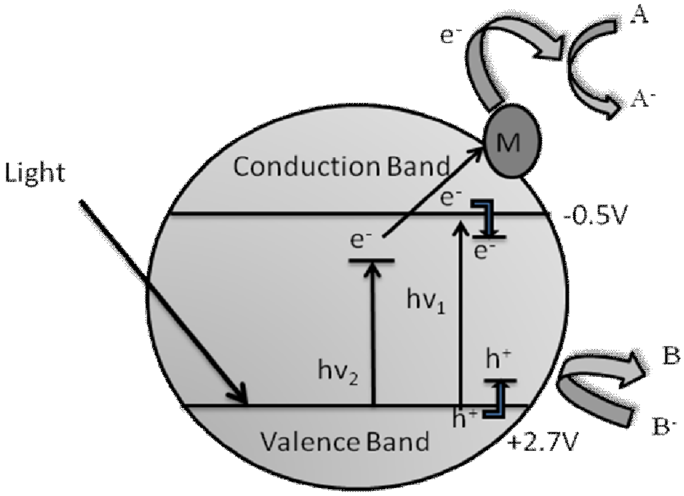
1. Introduction

Nanotechnology is the study of manipulating matter on an atomic and molecular scale. It deals with structures sized between 1 to 100 nm, an intermediate size range between molecular and bulk matter, called the nanoscale. In this range individual energy states of molecules and continuous energy bands of solids become discrete and their energy separations display an analytic dependence on the spatial dimension in at least one dimension and involves developing materials or devices possessing at least one dimension material. Nanoscale materials include semiconductor (SC) (e.g ZnS, CdS, PbS, CdSe, TiO_2, ZnO, SiC, PbS) and metal (M) nanoparticles (e.g Ag, Au, Pt, Pd, Rh) which are used in heterogeneous catalysis. On moving to nanoscale, surface area to volume ratio increases, and a greater amount of a substance comes in contact with surrounding material. This results in better catalysts, since the proportion of surface material exposed to potential reaction is larger. Further, stability reduces due to more charge on the surface, and obtaining their monodispersed colloidal solution becomes a challenge. Nanoparticles (NPs) hence may be coated with surface charge ligands or inert silica. Also a number of optical (color & transparency), electrical conductivity, physical (hardness & melting point), chemical reactivity/ properties changes as compared to macroscopic systems.

The surface coating of nanoparticles with different materials to form core-shell morphologies makes an important class of materials for developing catalysts and optoelectronic applications which manifest strong physical and chemical properties that is dependent on the relative dimensions of the core-shell constituents. During preparation of such core-shell morphology, firstly metallic nanoparticles are made by controlled chemical reduction with suitable stabilizer in surfactant assisted micelle solution and then this was surface modified with various materials (e.g. silica in most cases) for making the shell structure. This core-shell morphology was used in some cases for the synthesis of hollow metal oxide and/ or metal nanoparticles after removing the core material by chemical or thermal means. Specially, core-shell structure of silica coated Gold (Au) and Silver (Ag) has been studied owing to its potential optoelectronic applications. However, in such cases, core size of metal particles can not be regulated after the formation of silica shell structure. Furthermore, it would be of much interesting, if it is possible to make void space adjacent to the metal nanoparticles, encapsulated in silica shell besides the regulation of core size of metal particles. This kind of structures may have a broad range of potential uses in the field of pharmaceutics, catalysis, photonic and material science.

Considering these above facts, in the present study, silica coated Au, Ag and other transition metals nanocomposites containing void space will be synthesized by photoreduction of respective metals onto CdS core as an template. The CdS core can be selectively removed by chemical etching technique to modify the core size precisely after making silica shell. The formation of metal CdS composite NPs embedded in silica shell in which complete chemical etching of CdS after metal photodeposition may form a silica coated metal NPs having void space which can be used as a nanoreactor or nanovessel for the possible catalytic reactions. This technique can be used as an alternative synthetic route of silica coated other metal nanomaterials by the templating action of CdS and other photocorrosive semiconductors etc. the as-prepared colloidal metal NPs will be used as a co-catalyst in the TiO_2 photocatalytic reactions.

As reported in earlier studies, metal loading is mainly done in order to improve the photocatalytic activity of TiO_2. When metal like Au/Ag/Pt/Pd/Rh attach to the surface of the TiO_2 it scavenges the electron transferred from conduction band (CB) to valence band (VB) before the hole in the valence band can accept it, thus preventing recombination. On the other hand, the hole accepts electrons from the electron rich species and oxidizes it. The VB holes are powerful oxidant, while the CB electrons are good reductant. The redox power of the photocatalysts can be further improved by changing size from bulk to nanoscale. Therefore, careful consideration of both the oxidative and the reductive paths is required for desired applications. Hence, the photocatalytic activity of TiO_2 is affected by the nature, shape, size, amount and metal nanoparticles deposition techniques.



**Mechanism of TiO_2 photocatalysis:
$h\nu_1$: pure TiO_2; $h\nu_2$ metal-doped TiO_2**

2. Literature survey

Several approaches have been considered to synthesize NPs of transition metals in aqueous as well as nonaqueous media by adopting chemical, sonolytic, radiolytic and photolytic reactions [1-3]. Chemical reduction methods such as alcohol reduction [4, 5], hydrogen reduction [6-10], sodium borohydride reduction [11, 12] etc. have been the most common ways of synthesizing colloidal metal NPs. Other reduction methods such as electrochemical, photochemical and sonochemical [13, 14] reduction methods have also been used to a smaller extent. Furthermore, it is possible to control the size (particle diameter 2-30 nm) of the particle by varying [Au]/ [alkanethiol] ratio during the reduction step [15]. Metal NP having different shapes have also been prepared. Like, silver nanoprisms have been synthesized mainly through photochemically induced aggregation of small spheres [16, 17]. Although some procedures have been published for the production of gold nanoprisms [18, 19]. Choice of the reduction technique, time and capping material determines the size and shape of the NPs generated. Spheres [20], rods, cubes, disks [23], wires, tubes [22], branched [21], triangular prisms [21] and tetrahedral NPs have been generated in gold, silver and platinum with various reduction techniques and capping material. Among various systems, noble-metal nanostructures have received great interest primarily due to their unique properties and applications in catalysis, photonics, electronics, and information storage [24-28]. These metal NPs can be further used as co-catalyst to enhance the photocatalytic activity of semiconductors. Also, it been reported that M-SC junction can be formed by either direct addition of metal NPs or by supporting metal NP onto a SC.

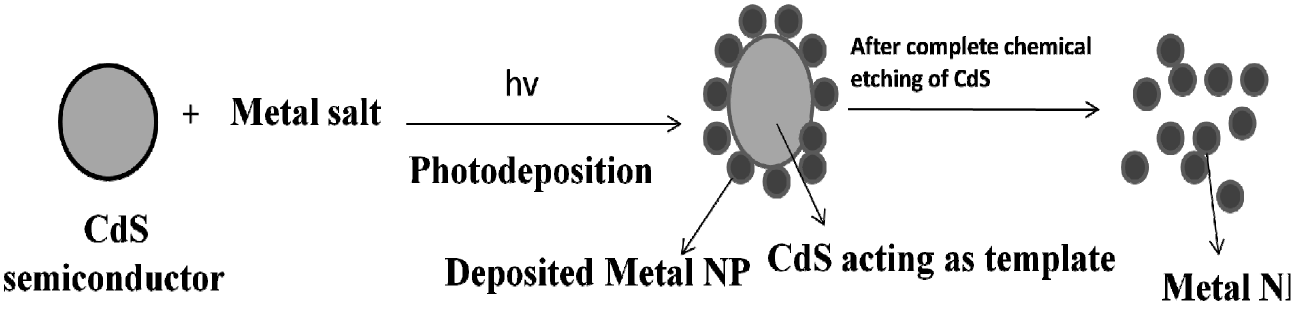
Supported metal nanocatalysts have been prepared by the adsorption of the colloidal metal nanocatalyst [29-32] and grafting of the nanoparticles onto the support [33-35]. Commonly, Au/TiO_2 supported catalysts has been prepared by co-precipitation and by deposition-precipitationmethods. In order to increase amount of gold loaded to prepare supported TiO_2 catalyst an alternative method has been suggested by Rodolfo Zanella [36]. Furthermore these supported catalysts can be used for various organic transformations. Thermocatalytically oxidation of benzyl alcohol to benzaldehyde using *tert*-butyl hydroperoxide over nanogold supported on TiO_2 has also been reported [37].

Template synthesis of nanostructures however is now a fast developing field. The most common templates are ion-track etched membranes [38] and anodized aluminium [39]. A number of hollow structures such as gold hollow microspheres [40], hollow silica spheres [41], Au @ hollow silica [42], hollow silver spheres [43] have been also prepared using template. However to our best of knowledge metal NPs synthesis has never being reported by template synthesis process. In this context, we aim to synthesize metal NP through template synthesis. CdS NPs have been extremely used for many applications. However, this material is photounstable due its self dissolution during light irradiation [44]. This photocorrosive action of CdS can be utilized as a template for the metal ions photoreduction into metal nanoparticles after removal of CdS template by simple chemical dissolution. With is concept, we have reported the silica coated CdS & Au NPs with varying core size controlled by size selective photoetching [45, 46]. It was found in preliminary experiments that isolated Au aggregates along with the small particles of size range (3-5 nm) are formed inside the silica spheres with core-shell morphology having void space. Furthermore, owing to higher electron density of Au and Ag, and unique size dependent electronic properties due to its surface plasmon resonance, that can be tuned easily in the Au/ or Ag-CdS absorption spectrum. This technique can be used as an alternative synthetic route of silica coated other metal nanomaterials by the templating action of CdS and other photocorrosive semiconductors etc.

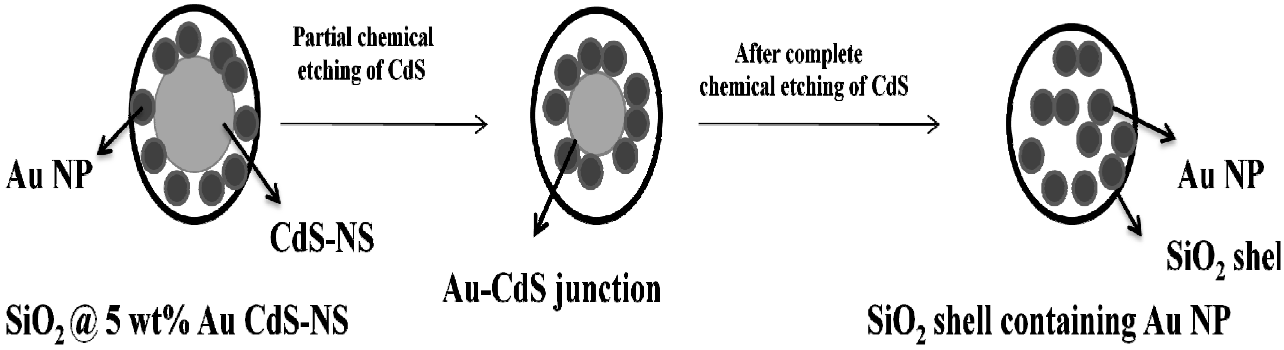
3. Objective

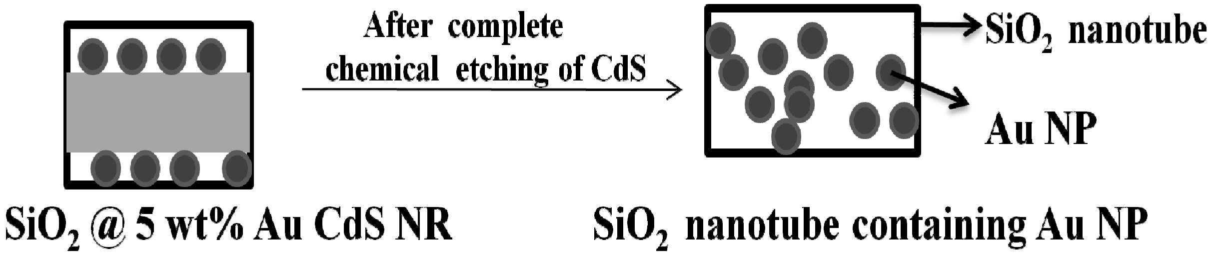
(i) To synthesize CdS nanosphere (NS) & nanorod (NR) and its surface modification by metal (Au, Ag, Pt, Pd and Rh) deposition through photochemical reduction of respective metal ions.

(ii) Complete chemical dissolution of CdS after metal photodeposition to obtain metal NPs and their characterization.

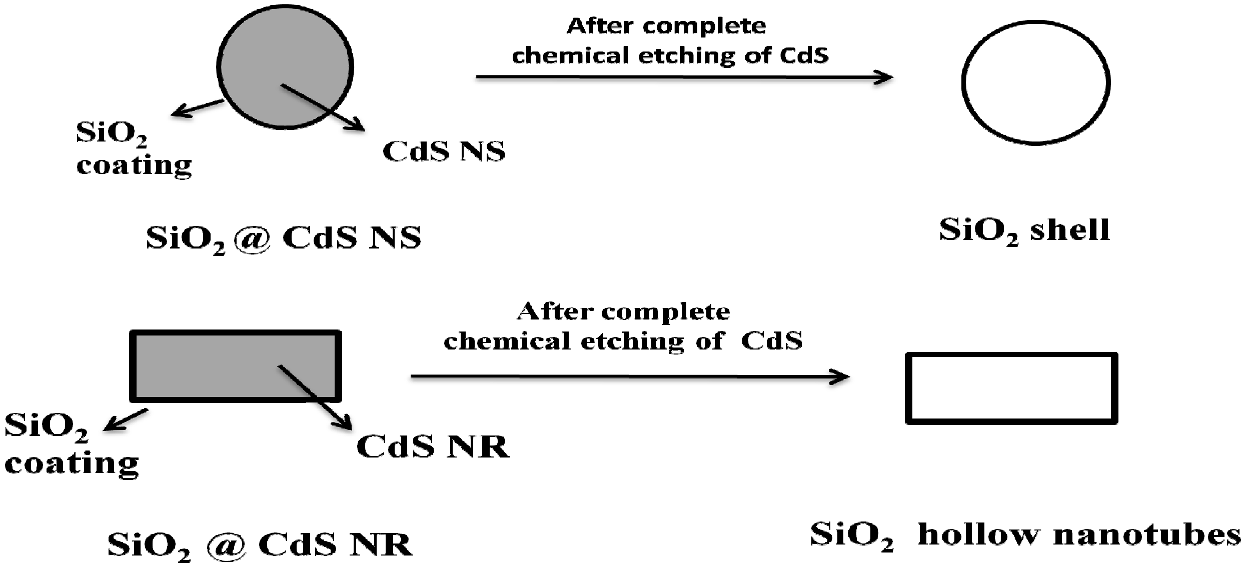


(iii) Preparation and characterization of core-shell (spherical & rod shape) structure of silica-coated metal NPs.

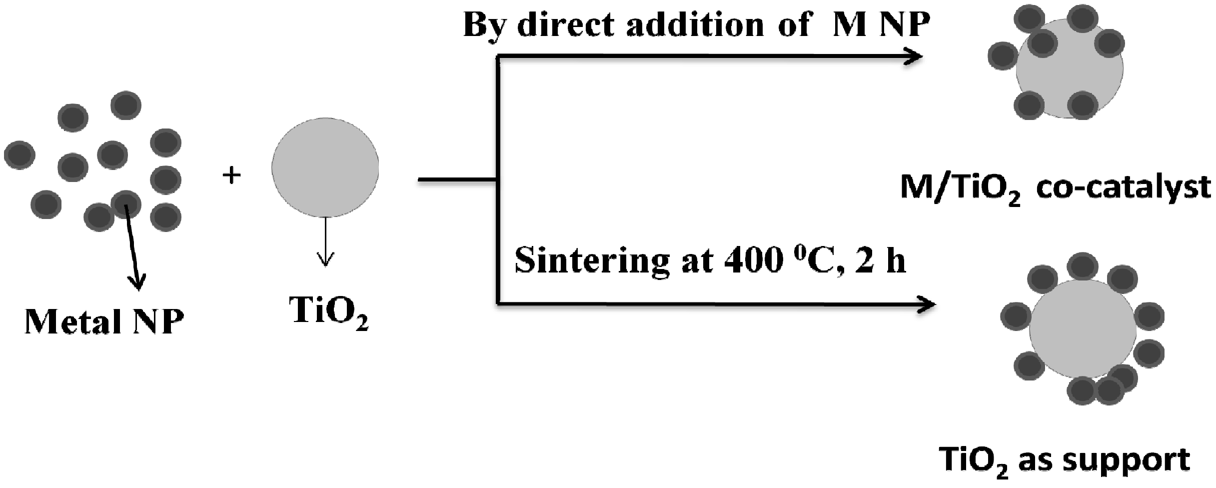




(iv) Preparation of hollow silica NS & NR after complete chemical etching of CdS template and their characterization.



(v) Applications of these bare and silica-coated metal NPs as co-catalysts to the TiO_2 photocatalytic reactions.



4. Experimental section

4.1 Materials: Cadmium chloride ($CdCl_2$), cadmium nitrate ($CdNO_3$), sodium sulphide (Na_2S), thiourea (NH_2CSNH_2), ethylenediamine ($C_2H_4(NH_2)_2$), toulene ($C_6H_5CH_3$), platinium chloride ($PtCl_2$), chloroauric acid ($HAuCl_4 \cdot aq$), rhodium chloride ($RhCl_3$), palladium chloride ($PdCl_2$), silver nitrate ($AgNO_3$), methanol (CH_3OH), AOT ($C_{20}H_{37}NaO_7S$), heptane ($CH_3(CH_2)_5CH_3$), TEOS ($Si(OC_2H_5)_4$) and MPTS ($(CH_3O)_3SiCH_2CH_2CH_2SH)$) were purchased from loba chemie. Salicylic acid ($2\text{-}(HO)C_6H_4CO_2H$), and nitric acid (HNO_3) was purchased from Sd Fine limited. P25 TiO_2 was obtained as a gift sample from Degussa, Germany.

4.2 Procedure:

Synthesis of various nanostructures

CdS nanosphere: CdS nanocrystals were synthesized through AOT/heptane/H_2O reverse micelle method. The solution of AOT (0.005 M) in *n*-heptane (100 mL) was prepared by stirring for half an hour. The aqueous solutions of $Cd(NO_3)_2$ (0.2 M) and Na_2S (0.2M) were separately added to the two equal portions of AOT containing *n*-heptane solution. The mixed solutions were stirred for two hours until optical transparency was achieved. Then both solutions were mixed together and stirred for another 1 h for obtaining CdS nanoparticles. Now a certain amount of Na_2S was further added into the reverse micelle solution containing these seeds of CdS. After stirring for 3 h, equal amount of $Cd(NO_3)_2$ solution was added into the reverse micelle solution to obtain CdS nanoparticles.

CdS nanorods: CdS nanorods were synthesized by taking $Cd(NO_3)_2$ (0.4 mmol) and NH_2CSNH_2 (0.8 mmol) to which ethylene diamine (10 ml) was poured and then refluxed for 10 h. The reaction mixture was allowed to cool at room temperature followed by washing with distilled water and methanol. It was then subjected to drying to get powder.

Metal deposition: Metal (Au, Ag, Pt, Pd & Rh) photodeposition was carried out in a test tube using argon purged isopropyl alcohol (50 vol%, 10 ml), CdS nanoparticles (100 mg), and requisite amount of metal salts ($HAuCl_4$, $AgNO_3$, $PtCl_2$, $PdCl_2$ & $RhCl_3$) under UV irradiation (2 h) and magnetic stirring. Finally, metal deposited CdS-NS and NR were washed with methanol and dried to use.

Silica coating: CdS nanoparticles (100 mg) was suspended in toluene (250 ml) and stirred by addition of MPTS (103 µl) and TEOS (100 µl) and then the mixture was refluxed for 2 h at 80-100 °C and then hydrolyzed by addition of water. It was washed repeatedly with methanol and water. Similarly, Au photodeposited CdS nanostructure was also coated with silica using the above procedure to obtain core shell structure of silica coated Au-CdS composites.

Chemical etching: The photodeposited Au (1, 2 & 5 wt%), Ag (1, 2, 5 wt%), 2 wt% Pt, 2 wt% Pd and 2 wt% Rh deposited CdS-NS and CdS-NR (50 mg) were chemical etched with HNO_3 (5M, 5 ml) under stirring for 12-14 h till complete removal of CdS. The composite color of the metal CdS samples was changed with etching time due to chemical dissolution of CdS.

Silica coated metal nanoparticles: The metal photodeposited CdS-NS and CdS-NR were silica coated as above and then it was washed and dried followed by complete removal of CdS by chemical etching to get the silica coated metal nanoparticles.

Hollow silica nanosphere and nanorods: Complete chemical etching of CdS from silica coated CdS-NS and CdS-NR (50 mg) with HNO_3 (5 M, 5 ml) under 20 h stirring will lead to hollow SiO_2 nanosphere and nanotubes. These were then washed with methanol and water to remove unreacted nitric acid.

Catalytic activity of as prepared metal nanoparticles as co-catalysts for TiO_2 photocatalysis

100 mg TiO_2, salicylic acid (0.35 mM, 20 ml) and 1 ml aqueous dispersion of various metal NPs mixture was irradiated (125 W Hg lamp) in a beaker for different time periods under magnetic stirring. At the end of every 1 h, the solutions were filtered using a cellulose filter, until a clear solution was obtained which was then analyzed by taking their UV spectra, the same was returned back in the beaker after analysis and the reaction was continued till complete photodegradation of salicylic acid.

4.3 Characterization

The prepared nanostructures were characterized using UV spectrophotometer (model name-specord 205) of analytic jena and fluorescence spectroscope (PTP-1) from perkin elmer. TEM facility (20-200 KV) was provided by sophisticated analytical instrument facility of IIT-Bombay. Scanning electron microscopy (SEM) and energy-dispersive X ray analysis (EDX) were performed on JEOL JSM-6510LB. The intermediates involved in the photocatalytic reaction was analysed with high performance liquid chromatography, HPLC chromatogram, from Agilent technologies. The chromatographic conditions were: column (C-18 column); mobile phase (methanol : water-50:50) with a flow rate 1 mL/min; UV detector at 254 nm; injection volume: 20 µl and column temperature: 25°C.

5. Result and Discussion

5.1 Optical and photocatalytic activity of synthesized metal nanoparticles

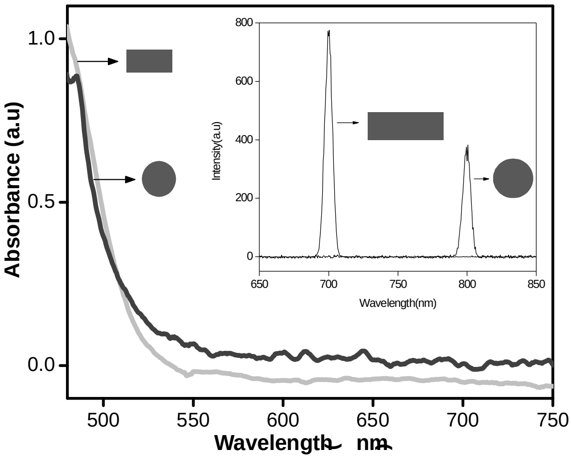


Figure 1. Absorbance and Fluorescence spectra of CdS NS and NR

Figure 1 showed the characteristic absorption and fluorescence spectra of CdS-NS and NR. The absorption onset appears at ~520 nm and strong emission peak at 800 nm for CdS-NS and 700 nm for CdS-NR are seen during excitation at λ_{ex} = 350 nm. The emission spectra of CdS NP may be due to electron-hole recombination and due to cation (Cd^{2+}) or anion (S^{2-}) vacancy defects[47]. This CdS nanosphere and nanorod were then subjected to surface modification by Au (1, 2 & 5 wt%) photodeposition. It has been found that the yellow color of bare CdS nanoparticles changed to greenish colored after Au deposition. Their spectral changes in absorbance spectra as well as emission spectra are in shown in Figure 2 and 3. It can be seen (*fig.2 inset*) that the nature of absorption spectra gradually changed due to Au deposition as compared to bare CdS-NR. After complete removal of CdS template by HNO_3 etching from Au-CdS composite, a broad absorption band centered at 400-800 nm of aggregated Au NPs is seen in Figure 2 where CdS absorbance band disappeared. This absorption band represents the characteristic surface plasmon band of Au NPs in visible region. The fluorescence emission (fig. 3) of bare CdS-NR at 700 nm is quenched after Au photodeposition onto CdS [48], since the metal accepts the photoexcited electrons from the CdS at the time of photodeposition and thereby, emission due to recombination of e^- - h^+ pairs is prevented. After CdS removal, an emission band at 600 nm is seen, probably due to the presence of trace amount of smaller CdS NPs /or Au NPs aggregation in the Au-CdS nanocomposites.

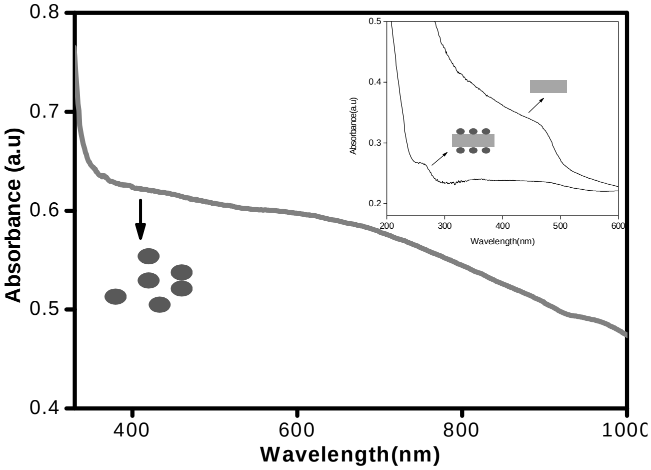


Figure 2. SP band of Au NP obtained by CE of 5 wt% Au CdS-NR, Inset- bare and 5 wt% Au CdS-NR.

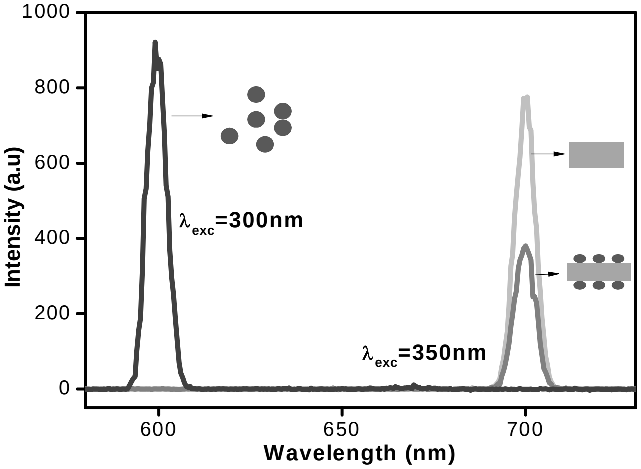


Figure 3. Fluorescence of bare CdS NR, 5 wt% Au CdS-NR and Au NP from CE of 5 wt% CdS-NR.

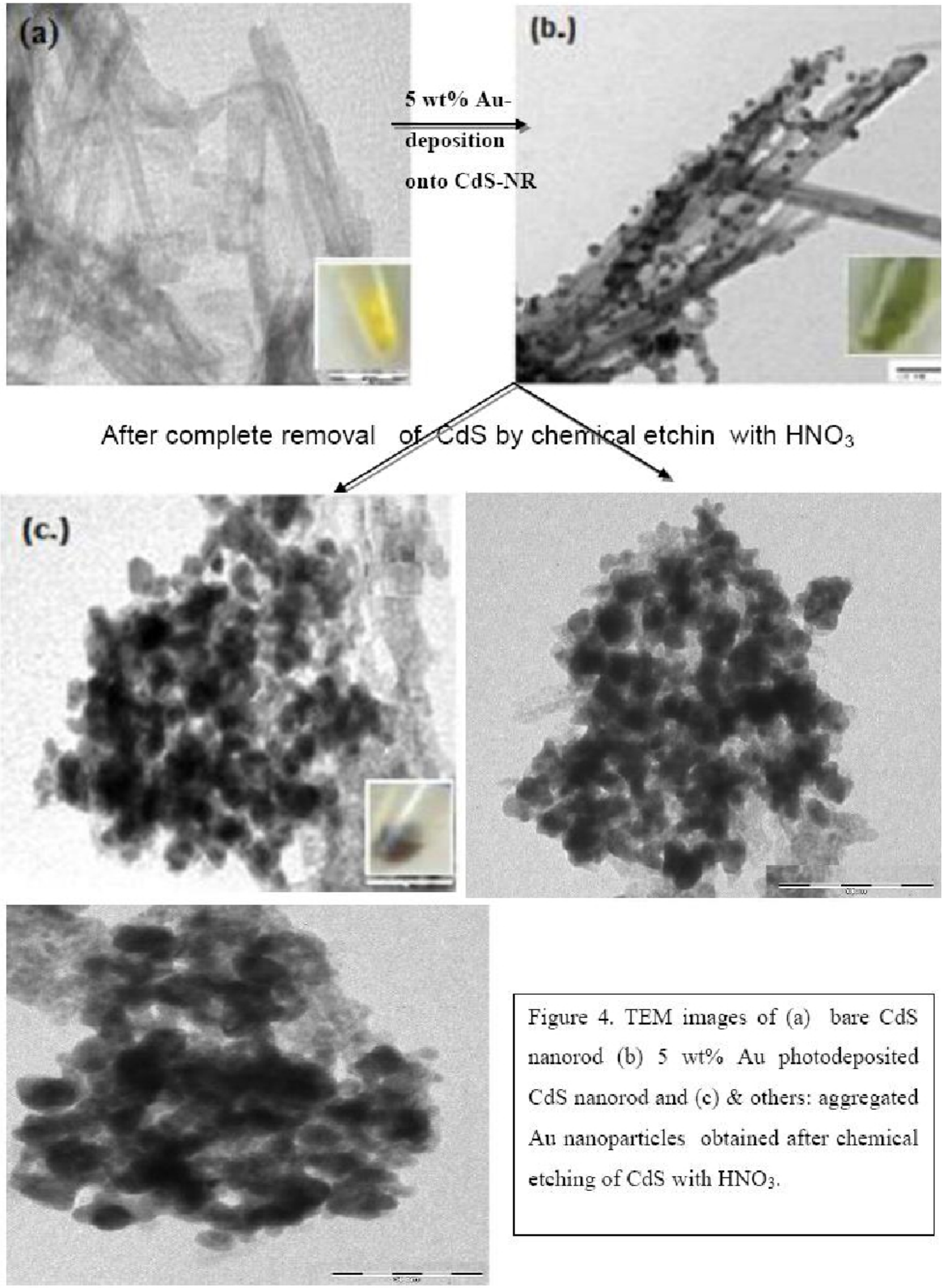
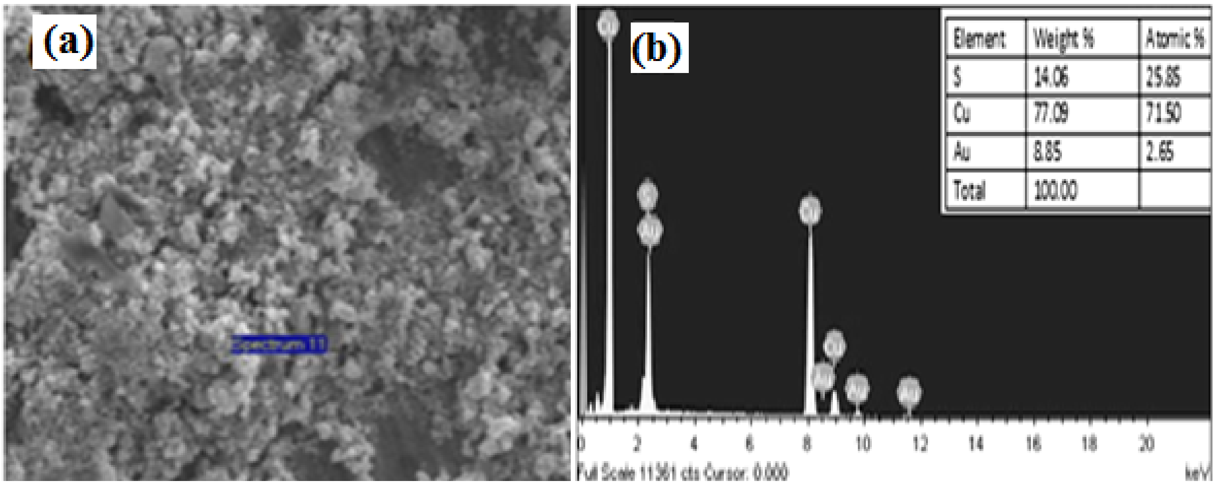


Figure 4. TEM images of (a) bare CdS nanorod (b) 5 wt% Au photodeposited CdS nanorod and (c) & others: aggregated Au nanoparticles obtained after chemical etching of CdS with HNO_3.

Figure 4 showed the TEM images of bare CdS-NR (yellow) and 5 wt% Au photodeposited CdS-NRs (greenish color). It is revealed that there is a wide distribution in size of bare CdS-NR (length 110-125 nm) but the average aspect ratio (length/width) of 50 particles is 13.8 and the Au nanoparticles uniformly deposited on CdS-NR by photodeposition method has an average size of 4 nm. After complete chemical dissolution of CdS template from these Au-CdS composites, the obtained Au NPs (black) of aggregated size *ca.* ~6-12 nm are seen in the TEM images. These obtained Au NPs are then characterized by their broad absorbance band corresponding to its characteristic surface plasmon band (SP band), which appears around 520 nm. However, a broad absorption band at ~ 600 nm due to their large particle size is seen in the absorption spectra. Again the shift in the fluorescence (fig. 3) band confirms template dissolution (fluorescence for CdS appear at 700 nm at $\lambda_{ex} = 350$ nm) and appearance of a peak at 600 nm for $\lambda_{ex} = 300$ nm might be due to Au NP. Figure 5 showed the SEM images of Au NPs and the absence of CdS is further confirmed by the EDX-DATA from Figure 5(b). It is observed that there is a strong peak for Au and no Cd peaks and presence of S (soft base) is possibly due to strong affinity of Au (soft acid) for S. Thus by using above template synthesis procedure 1, 2 and 5 wt% Au NPs were prepared by chemical etching (CE) of CdS template from various wt% Au photodeposited CdS-NS and NR and characterized. It is a proven fact that transition metal loading onto TiO_2 photocatalysts highly improved the photocatalytic activity. Hence, the as-prepared Au NPs are used as co-catalyst to TiO_2 photocatalytic degradation of salicylic acid (SA) to measure their co-catalytic activity. Figure 6 showed the comparative rate of photocatalytic oxidation of SA by bare TiO_2 and 1, 2 & 5 wt% Au NPs added TiO_2 suspension.



Element	Weight %	Atomic %
S	14.06	25.85
Cu	77.09	71.50
Au	8.85	2.65
Total	100.00	

Figure 5. SEM image of 1wt% Au NP obtained after chemical etching of CdS from Au deposited CdS-NR and EDX - elemental analysis of chemically etched 1 wt% Au NP.

This Au NPs are obtained by CE from Au deposited CdS nanosphere and nanorod. It is found that the photooxidation rate of SA is highly improved by the addition of Au NPs to TiO_2 suspension and with increasing amount of Au NPs loading on TiO_2 from 1 wt% to 2 wt% to 5 wt% the photocatalytic activity of Au-TiO_2 increased gradually in which 5 wt % Au NPs addition exhibited highest co-catalytic efficiency. It was observed that Au NPs obtained from CE of Au photodeposited CdS nanosphere and nanorod have similar co-catalytic activity under given experimental conditions. Hence, the nature of the Au NPs obtained is independent of the shape of the CdS template. Similarly 2 and 5 wt% Ag-CdS NS and NR were prepared by photodeposition

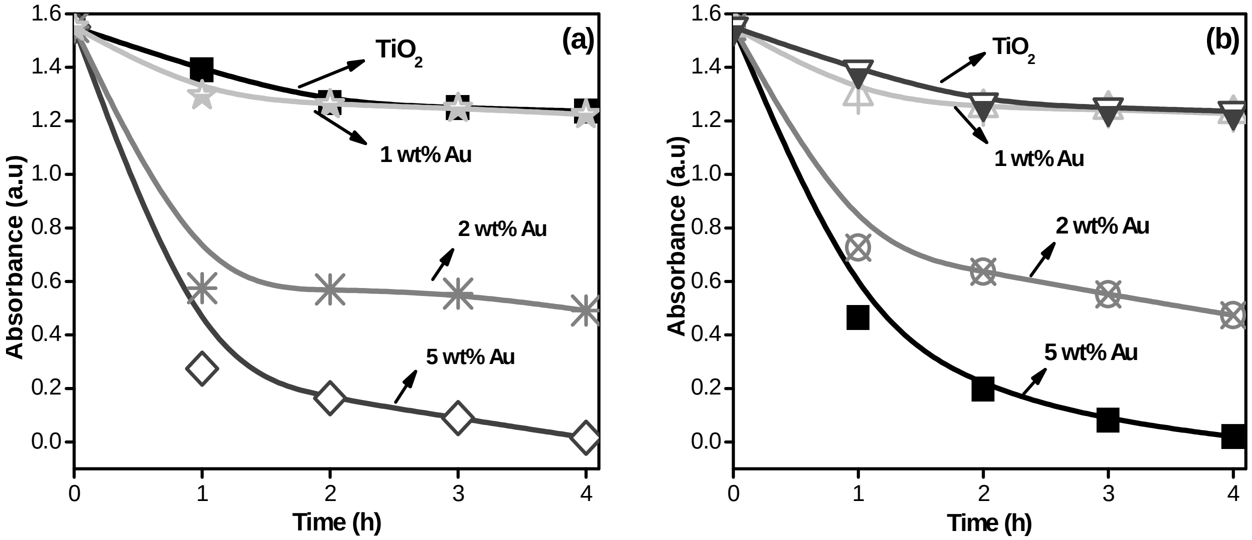
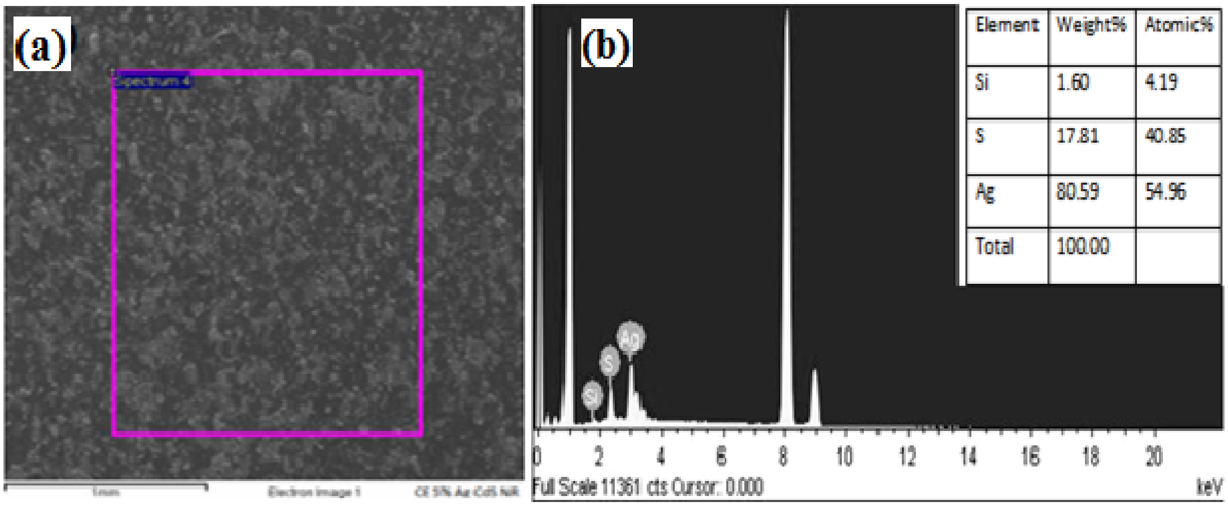


Figure 6. Photocatalytic oxidation rate of salicylic acid by bare and Au loaded TiO_2 : Au NPs obtained from CE of Au photodeposited onto (a) CdS-NS and (b) CdS-NR.



Element	Weight%	Atomic%
Si	1.60	4.19
S	17.81	40.85
Ag	80.59	54.96
Total	100.00	

Figure 7. SEM image and EDX elemental analysis of Ag NPs obtained after CdS dissolution from 5 wt% Ag photodeposited CdS-NR.

followed by CE to get Ag NPs. The complete dissolution of CdS template was again confirmed from the absence of Cd peak in the EDX elemental analysis (fig. 7b) and CdS absorption onset (fig. 8a). Although the characteristic surface plasmon band due to Ag NP did not appear but there is a strong evidence of Ag along with adsorbed S peak in EDX analysis. Other metal NPs such as Pt, Pd and Rh are also prepared after chemical dissolution of CdS from metals photodeposited CdS NS and NR. Their absorption spectra in Figure 8a exhibited characteristic broad absorbance band without CdS absorption indicating the complete removal of CdS template.

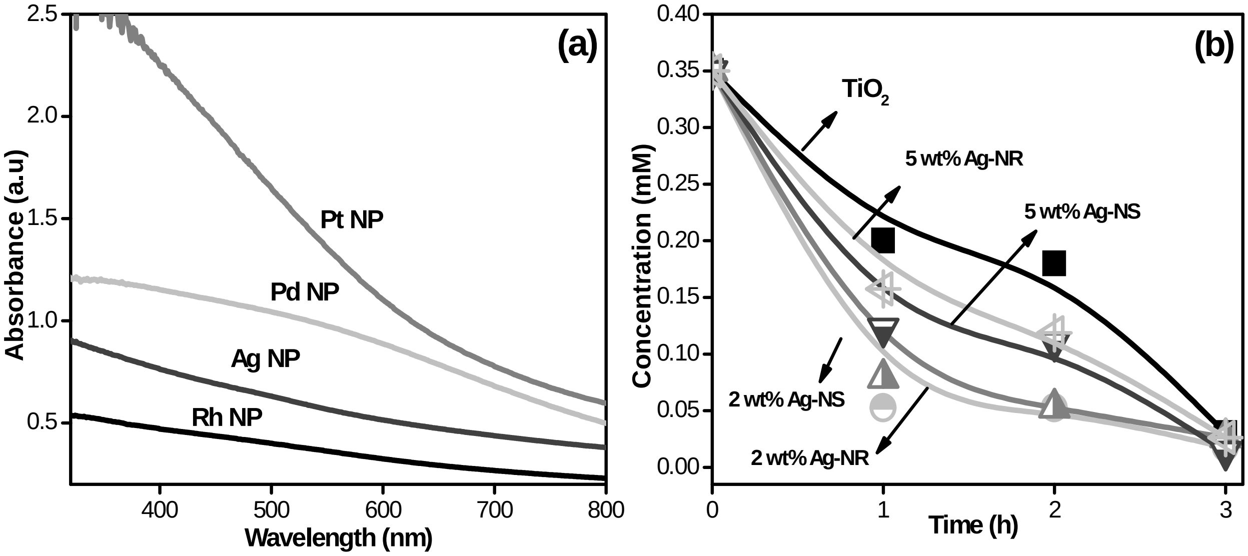


Figure 8. (a) Absorption spectra of Pt, Pd, Ag and Rh NPs obtained from CE of respective metals (2 wt%) photodeposited CdS-NR and (b) co-catalytic activity of as-prepared Ag NPs imparted to TiO_2 during photocatalytic oxidation of 0.35 mM SA under light irradiation.

The co-catalytic activities of as-prepared Ag NPs are measured by the photocatalytic oxidation of SA with this Ag NPs loaded TiO_2. It is found (fig. 8b) that after 2 wt% Ag loading, the photocatalytic degradation rate of SA by Ag-TiO_2 is highly enhanced which is decreased with the increasing amount of Ag loading from 2 to 5 wt%. It is shown in Figure 9 that as-prepared 2 wt% Pd loaded TiO_2 greatly increased the photooxidation rate of SA as compared to bare TiO_2 and 2 wt % Pt and Rh does not significantly improved the photoactivity of TiO_2. Moreover, all the metals-NPs obtained from CE of CdS template from photodeposited CdS nanosphere and nanorod exhibited same activity irrespective of preparation conditions. The different photoactivity of TiO_2 by various metals NPs loading can be explained on the basis of their dissimilar co-catalytic ability of Au, Ag, Pt, Pd and Rh NPs due to the difference in their electronegativity, work function and electron accepting capacity. The photoenergetics of variousM-TiO_2 junction and the photoexcited electron rates varied in a large extent during irradiation, hence, the recombination rate of electron-hole pairs and thereby change the photoactivity of TiO_2.

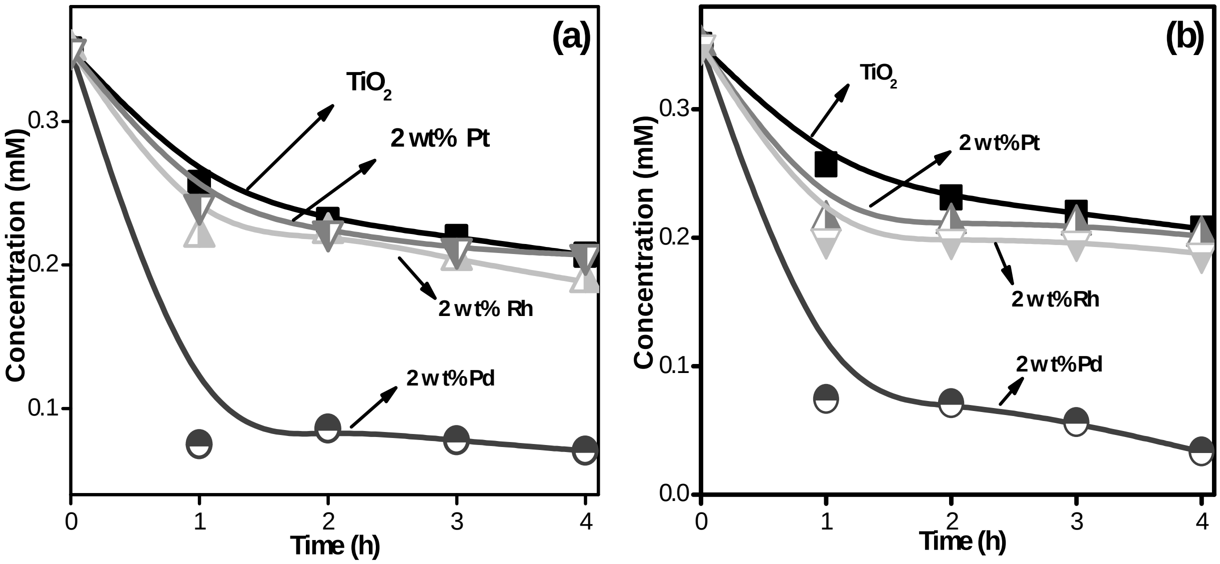


Figure 9. Photocatalytic oxidation rate of SA by various metal NPs (2 wt%) loaded TiO_2 suspension: As-prepared metals NPs obtained from metal deposited (a) CdS nanosphere and (b) CdS nanorod.

The reaction intermediates involved for SA oxidation reaction were analysed by HPLC (λ = 254 nm). The peaks corresponding to retention time 2.5, 2.8 and 3 min are believed to be due to oxidation intermediates i.e 2,5-dHBA, catechol and 2,3-dHBA [49] etc.

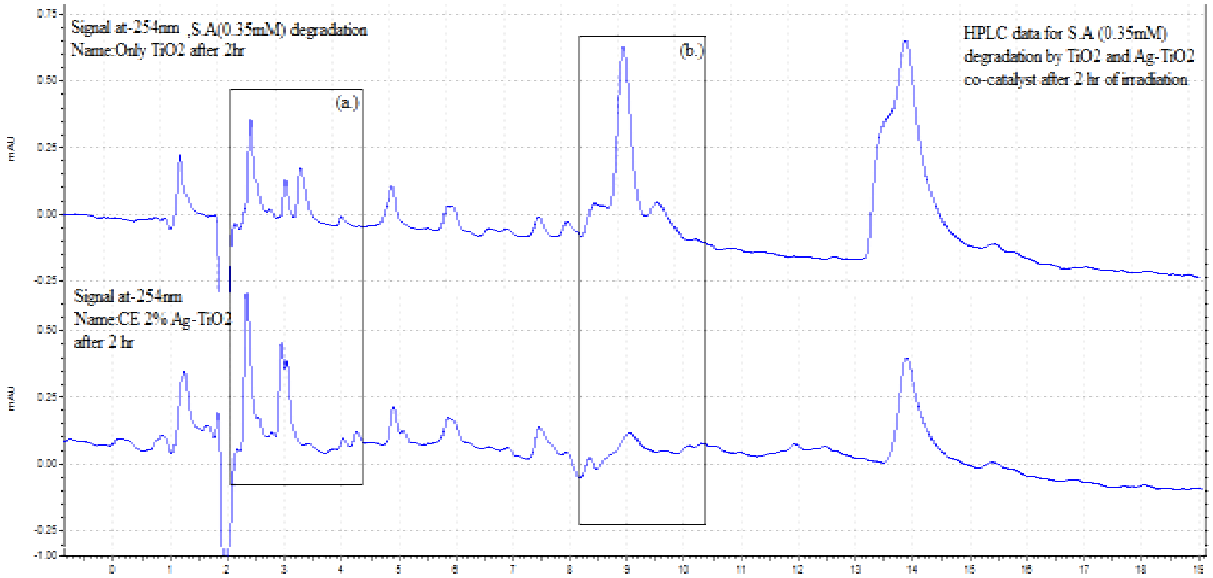


Figure 10. HPLC chromatogram of salicylic acid photooxidation at various time. Peaks in region-a and b are expected to be due to 2,5- dHBA, catechol, 2,3-dHBA and salicylic acid, respectively.

It was very interesting to observe the color change of the CdS template on photodeposition of different metals islands onto it. Bare CdS is yellow and after metal deposition, the color of metal-CdS changes to greenish and light yellowish etc. When the CdS template was completely removed, the characteristic color of the various aggregated metals NPs are seen in Figure 11.

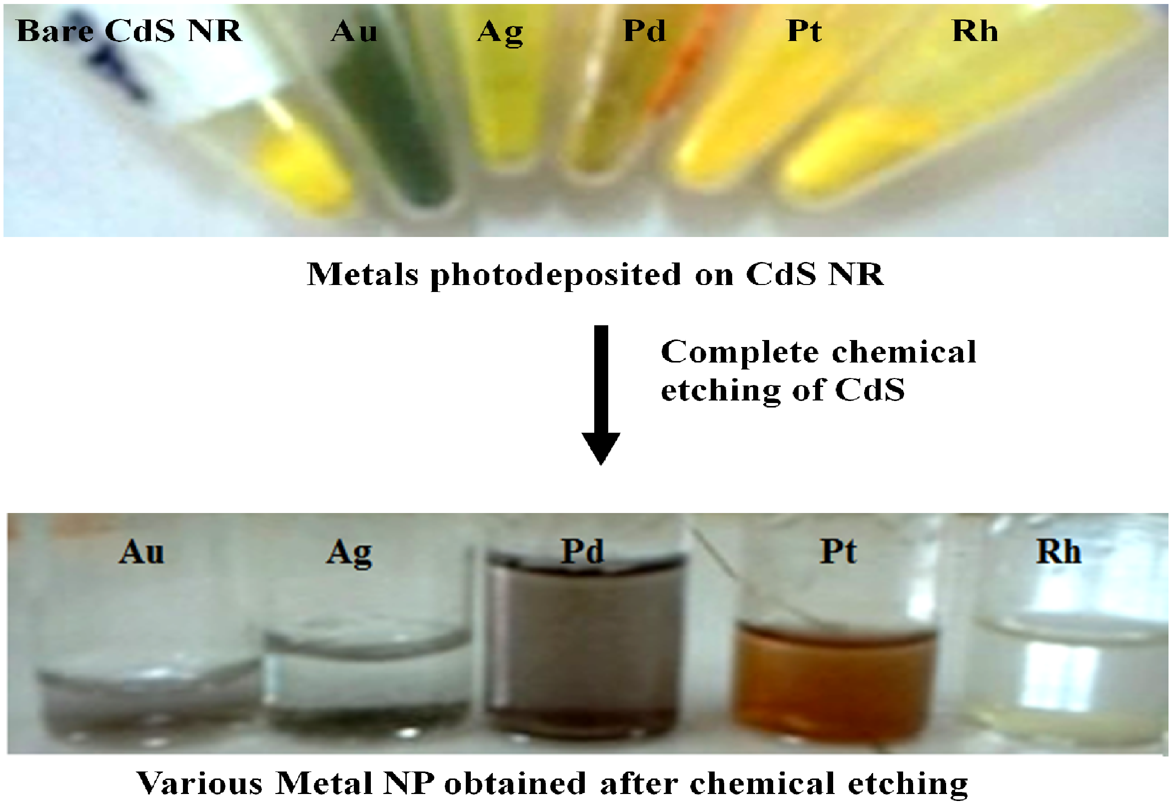


Figure 11. Various colors of different metal-CdS-NR composites and bare metal nanoparticles

5.2. Template synthesis and characterisation of advanced nanostructures

A. Hollow Silica Shell

To obtain hollow silica shell, CdS-NS and NR were coated with silica and characterized by UV and fluorescence spectroscopy. Their absorbance and fluorescence (λ_{exc}=350nm) was found to be quenched (fig. 12) after silica coating in comparison to bare CdS-NS and NR. This emission change is due to reduction in the number of the surface defect sites after surface capping with the mercaptopropyl trimethoxysilane (MPTS) and the subsequent silica shell coating [50]. Complete dissolution of CdS template using nitric acid it is expected to obtain hollow silica tube and silica sphere. It can be seen (fig 12b, inset) that after complete removal of CdS, the absorption due to CdS is disappeared in the absorption spectra of hollow silica nanostructures as compared to silica coated CdS (SiO_2@CdS) or bare CdS. Dissolution of CdS is being confirmed experimentally from the EDX elemental analysis (fig. 13) which showed absence of Cd peak, however, presence of S can be justified by the fact that S may have diffused into the pores of silica matrix during leaching through silica shell at the time of CdS dissolution.

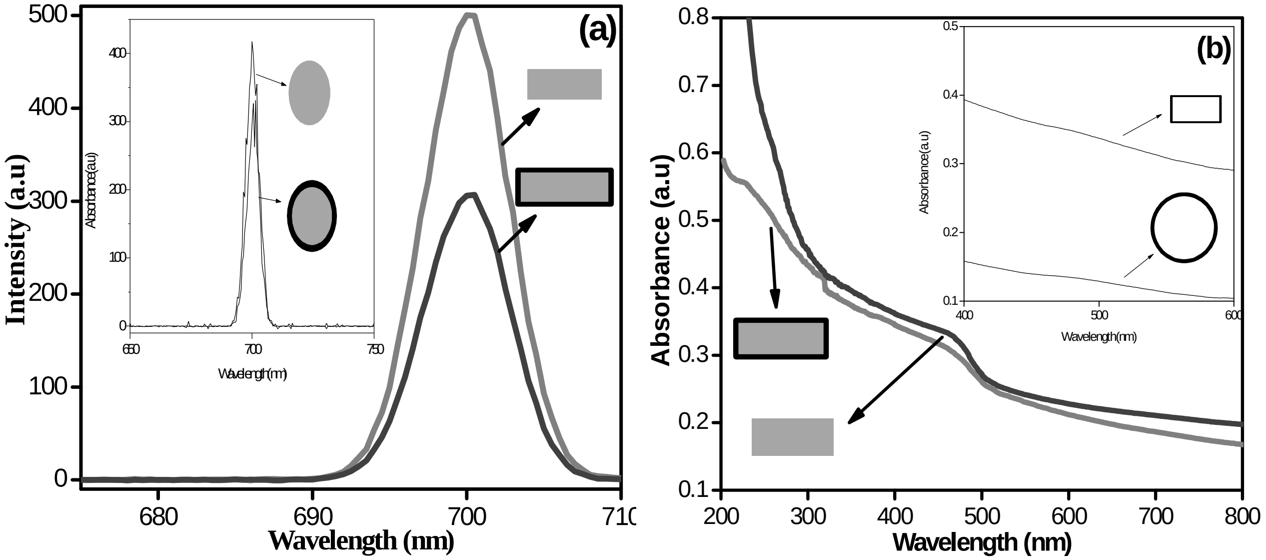
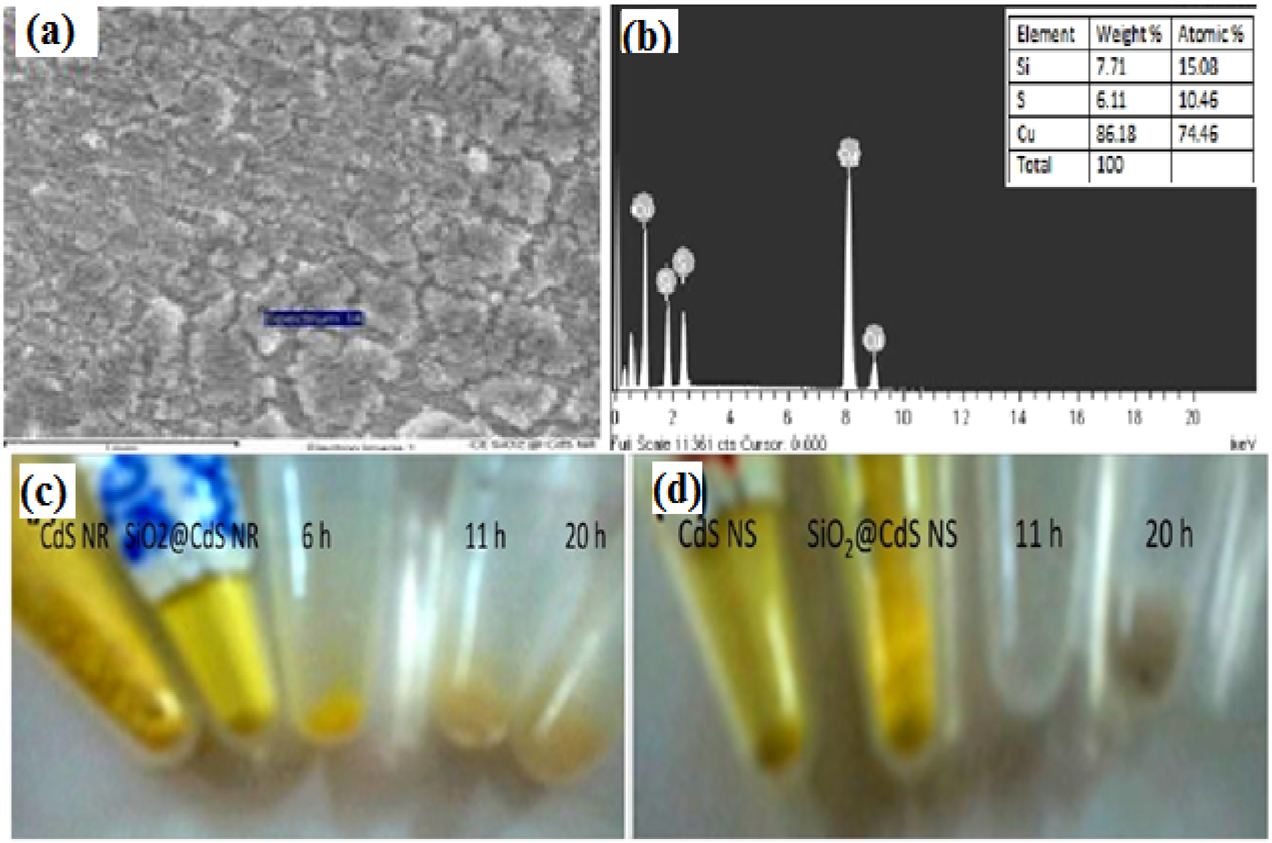


Figure 12. (a) Fluorescence and (b) absorbance spectra of various bare & silica coated CdS and hollow silica nanosphere & nanorod.



Element	Weight%	Atomic%
Si	7.71	15.08
S	6.11	10.46
Cu	86.18	74.46
Total	100	

Figure 13. SEM images and EDX analysis of hollow silica nanotube after CE of SiO_2 coated CdS-NR. Gradual color change during chemical etching of SiO_2 @ CdS-NR and SiO_2 @ CdS-NS.

The color of bare CdS is yellow which changed to pale yellow after silica coating onto CdS and after chemical etching the color changes gradually and the pale yellow color almost disappeared with CdS dissolution time as seen in Figure 13. The formation of silica coated CdS nanorod and hollow silica nanotube after CdS dissolution can be further confirmed from the TEM size and shape analysis. Figure 14 showed the silica coated CdS nanorod consists of light black colored CdS core entrapped in grey colored silica matrix and hollow silica nanotube of different length obtained after complete removal of CdS core by chemical etching with HNO_3 for 20-22 h under magnetic stirring.

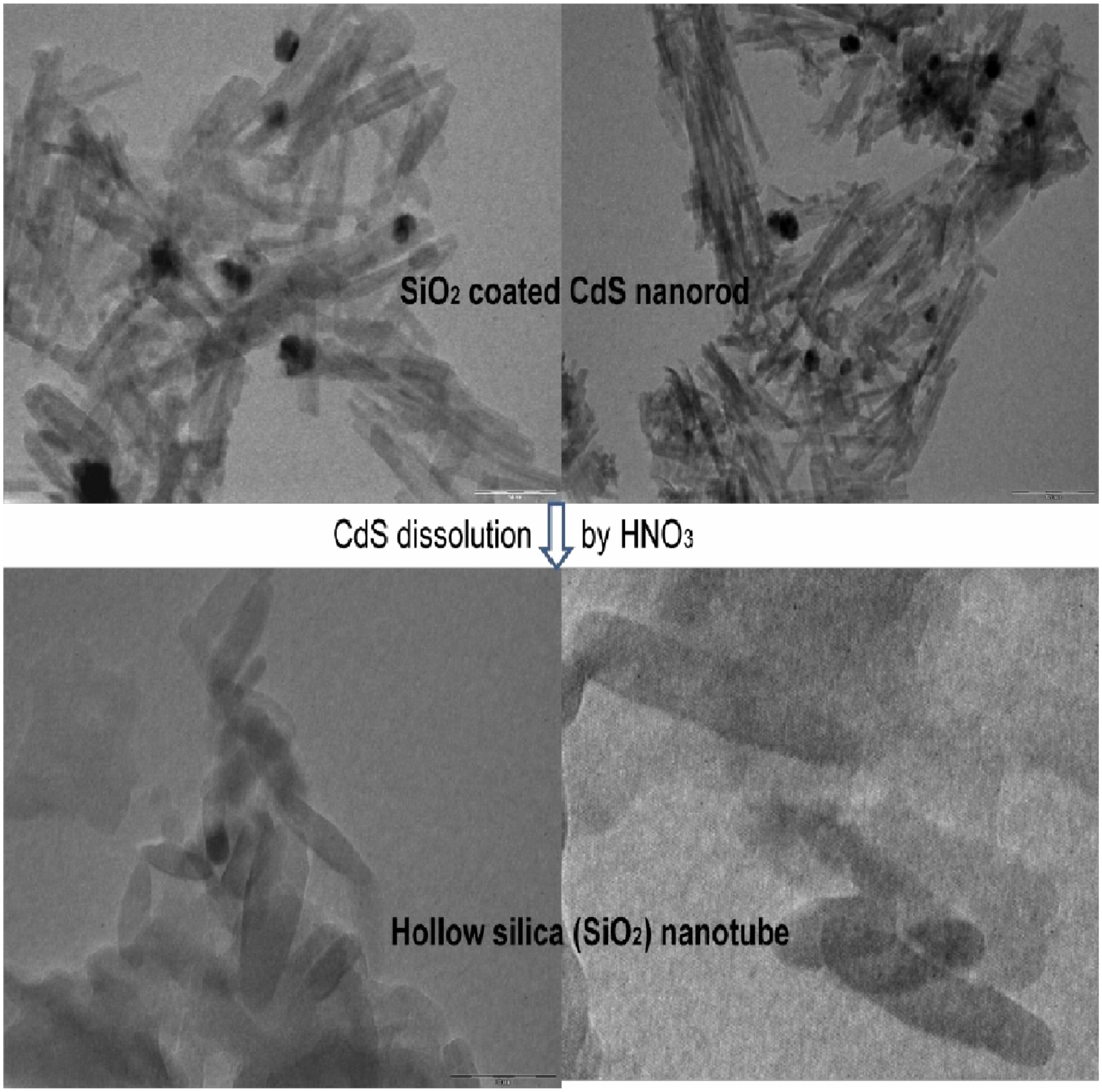


Figure 14. TEM images of silica coated CdS nanorod and hollow silica nanotube obtained after CdS removal by chemical etching.

B. Silica (SiO_2) coated Au nanoparticles

The CdS-NS and NR were first loaded with 5 wt% Au by photodeposition followed by silica coating. The absorption spectra and fluorescence emission are quite different for various nanostructures of bare CdS, Au-CdS, SiO_2 coated CdS & Au-CdS, bare Au NPs and SiO_2 coated Au NPs as shown in Figure 15. The fluorescence of CdS-NR was found to be quenched when deposited with 5 wt% Au and by silica coating on 5 wt% Au CdS-NR. When silica coated 5 wt% Au CdS-NS is subjected to chemical etching, we expect to obtain silica coated Au NPs. Analysis of UV spectra confirms the dissolution of CdS template and it is expected that we have obtained silica coated Au nanostructures, where Au NPs are entrapped in hollow silica sphere and nanotube. Change in color with increasing etching time and EDX elemental analysis supporting the

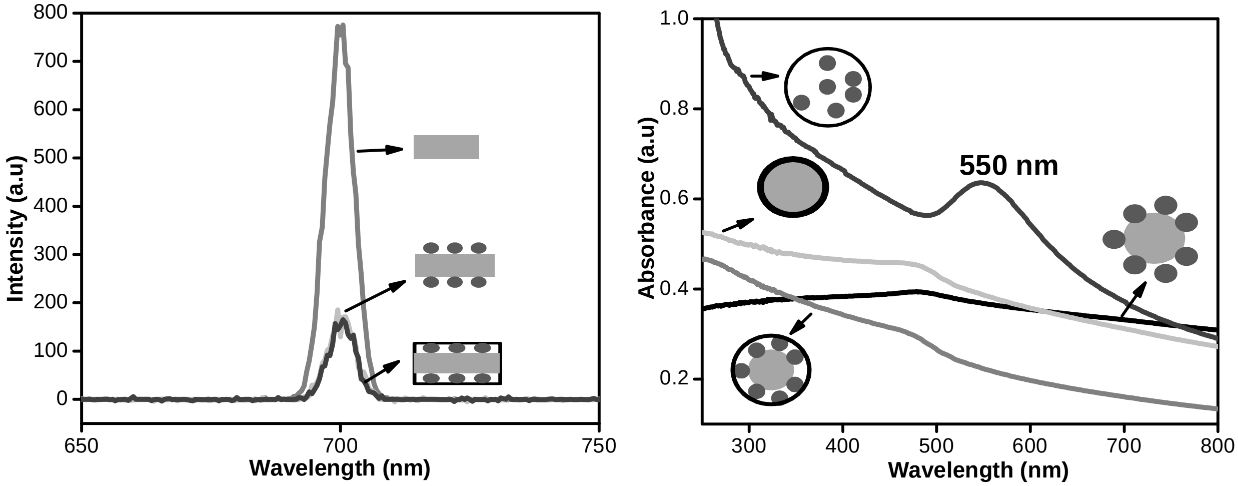
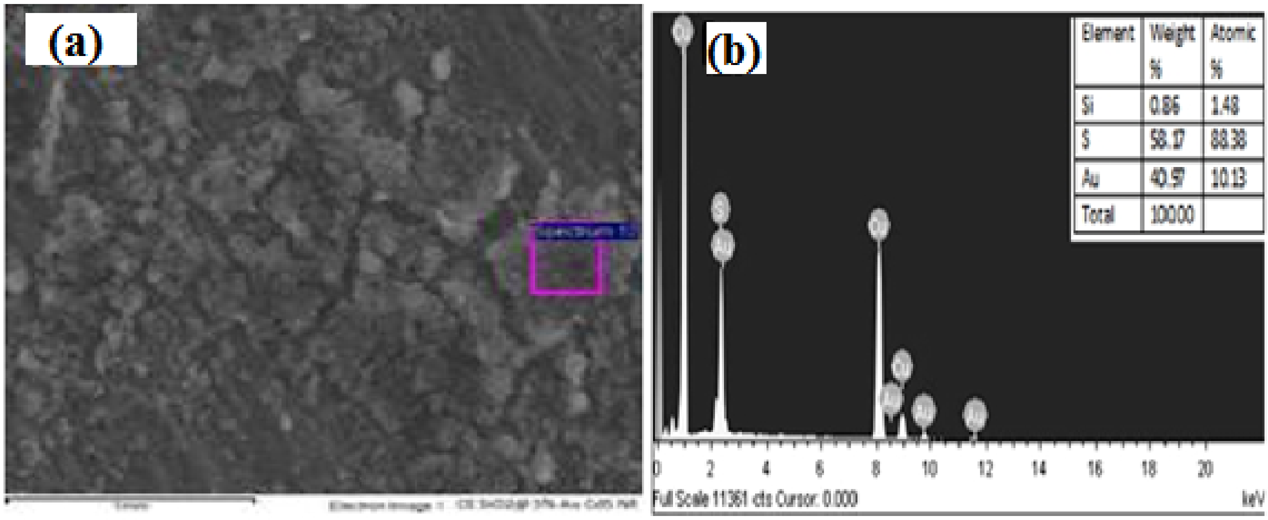


Figure 15. The fluorescence emission and absorption spectra of bare CdS, Au-CdS, SiO_2 coated CdS & Au-CdS and SiO_2 coated Au NPs where CdS nanosphere and nanorod are shown pictorially.



Element	Weight %	Atomic %
Si	0.86	1.48
S	58.17	88.38
Au	40.97	10.13
Total	100.00	

Figure 16. SEM image and EDX analysis of SiO_2 @ 5 wt% Au CdS-NR.

evidence for CdS dissolution and presence of Au and Si in the SiO_2 @ Au composites as shown in Figure 16. When SiO_2 coated 5 wt% Au CdS-NS is subjected to chemical etching for complete CdS removal, SiO_2 coated Au NPs is found to formed as evident from the appearance of characteristic intense surface plasmon (SP) band (fig. 15) due to non-aggregated Au NPs formation. The appearance of this sharp SP band at ~ 550 nm of SiO_2 @ Au NPs (pink colored) rather than a broad absorption band (400-900 nm) as found in aggregated (black colored) bare Au NPs (obtained from Au-CdS composites) is due to the prevention of coagulation of Au NPs by thin silica shell/layer and thereby stabilized the smaller size Au NPs as compared to without silica coating of bigger size of Au NPs as shown in Figure 17. The TEM images (fig. 18) of this silica coated Au NPs (SiO_2 @ Au NPs) clearly displayed the formation of black colored Au NPs entrapped inside spherical silica matrix after complete removal of CdS template. This core-shell structure of Au-SiO_2 can be applied for the improved activity of many heterogeneous catalytic reactions owing to high surface area and adsorption capacity of porous spherical SiO_2 matrix.

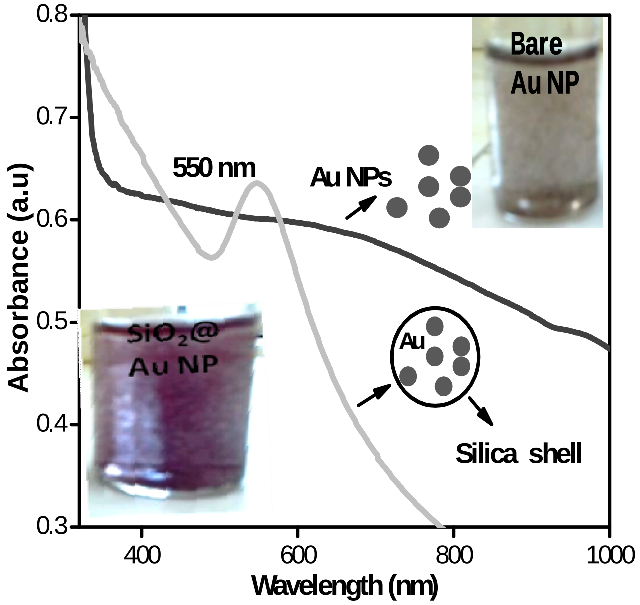


Figure 17. Comparative surface plasmon band of SiO_2@ Au NPs and bare Au NPs.

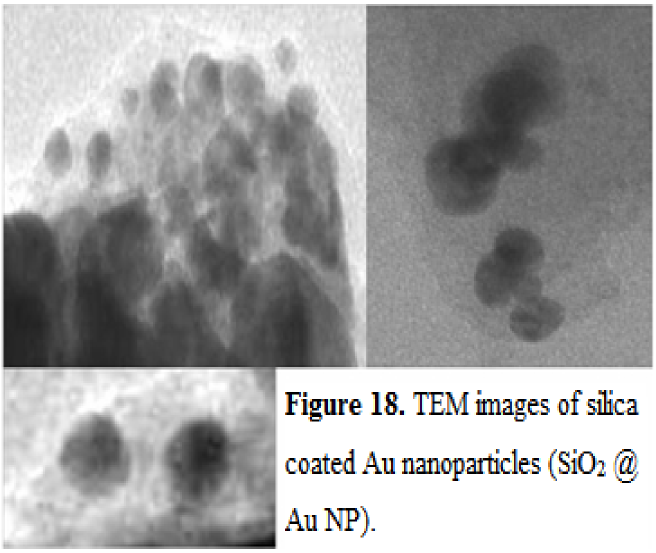


Figure 18. TEM images of silica coated Au nanoparticles (SiO_2 @ Au NP).

6. Conclusions

Like, other conventional techniques of metal NP synthesis, template synthesis has been found to be successful for preparation of wide variety of nanostructures. CdS proves to be a promising candidate as template. Metal photodeposition followed by dissolution of CdS yielded various transition metal NPs. The metal NPs obtained are however aggregated, and have large size, whose perfect spherical shape could not be controlled. The obtained Au, Ag, Pt, Pd and Rh NPs could be used to prepare M-TiO_2 composite photocatalysts of improved reactivity and all of them are found to be highly active as co-catalysts and showed better photocatalytic activity of TiO_2 when these metal NPs are loaded. Different M-TiO_2 photocatalysts showed different photocatalytic activity for salicylic acid oxidation reaction due to different co-catalytic activity depending on the nature of metals, electronegativity difference and work functions. The 2 wt% Pd-TiO_2 co-catalyst is found to be more effective in comparison to 2 wt% Rh-TiO_2 and 2 wt% Pt-TiO_2 co-catalyst under given experimental conditions. It was also observed that the catalytic activity of metal NPs obtained from CdS nanosphere as well as from CdS nanorod behave more or less similarly. Thus shape of the metal nanoparticles is independent of the different shape of the CdS template. It has been found that silica coating gave smaller non-aggregated Au NPs distribution which exhibited sharp surface plasmon absorption band as compared to broad absorption band of large aggregated Au NPs obtained by chemical etching of CdS from bare Au-CdS nanocomposites of without silica coating. Advanced nanostructures such as small core size metal-CdS junction, hollow silica nanosphere, silica nanotube and silica coated Au NPs are synthesized successfully. These hollow particles could be used as fillers, coatings, nanoreactor and catalyst supports because they possess lower density, higher surface area, higher adsorption capacity and excellent optical properties.

Reference:

(1) Turkevich, J., Stevenson, P.L., Hillier, *J. Discuss. Faraday Soc.*, 1951, **11**, 55.

(2) Henglein, A., *J. Phys. Chem. B,* 2000, **104**, 6683.

(3) Templeton, A.C., Wuelfing, W.P., Murray, R.W., *Acc. Chem. Res.*, 2000, **33**, 27.

(4) Li, Y., Boone, E., El-Sayed, M.A., *Langmuir*, 2002, **18**, 4921.

(5) Li, Y., El-Sayed, M.A., *J. Phys. Chem. B,* 2001, **105**, 8938.

(6) Yu, Y., Xu, B., *Chin. Sci. Bull.*, 2003, **48**, 2589.

(7) Narayanan, R., El-Sayed, M.A., *J. Phys. Chem. B,* 2004, **108**, 5726.

(8) Narayanan, R., El-Sayed, M.A., *Nano Lett.*, 2004, **4**, 1343.

(9) Narayanan, R., El-Sayed, M.A., *J. Am. Chem. Soc.*, 2004, **126**, 7194.

(11) Narayanan, R., El-Sayed, M.A., *Langmuir*, 2005, **21**, 2027.

(12) Sau, T. K., Pal, A., Pal, T., *J. Phys. Chem. B* , 2001, **105**, 9266.

(13) Narayanan, R., El-Sayed, M.A., *J. Phys. Chem. B,* 2004, **108** , 8572.

(14) Caruso, R.A., Kumar A.M., Grieser, F., *Colloids Surf., A*, 2000, **169**, 219.

(15) Fujimoto, T., Terauchi, S., Umehara, H., Kojima, I., Henderson, W., *Chem. Mater.*, 2001, **13**, 1057.

(16) Hostetler, M.J., Wingate, J.E., Zhong, C.J., Harris, J.E., Vachet, R.W., Clark, M.R., Londono, J.D., Green, S.J., Stokes, J.J., Wignall, G.D., Glish, G.L., Porter, M.D., Evans, N.D., Murray, R.W., *Langmuir*, 1998, **14**, 17.

(17) Jin, R., Cao, Y.C., Hao, E., Metraux, G.S., Schatz, G.C., Mirkin, C.A., *Nature,* 2003, **425**, 487.

(18) Callegari, A., Tonti, D., Chergui, M., *Nano Lett.*, 2003, **3**, 1565.

(19) Shankar, S.S., Rai, A., Ankamwar, B., Singh, A., Ahmad, A., Sastry, M., *Nat. Mater.*, 2004, **3**, 482.

(20) Millstone, J.E., Park, S., Shuford, K.L., Qin, L., Schatz, G.C., Mirkin, C.A., *J. Am. Chem. Soc.,* 2005, **127**, 5312.

(21) Daniel, M.C., Astruc, D., *Chem. Rev.*, 2004, **104**, 293.

(22) Hao, E., Schatz, G., Hupp, J., *J. Fluoresc.*, 2004, **14**, 331.

(23) Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., Gates, B., Yin, Y., Kim, F., Yan, H., *Adv. Mater.*, 2003, **15**, 353.

(24) Pileni, M.P., *Nat. Mater.*, 2003, **2**, 145.

(25) Ghosh, S.K., Pal, T., *Chem. Rev.*, 2007, **107**, 4797.

(26) Lee, J.S., Ulmann, P.A., Han, M.S., Mirkin, C.A., *Nano Lett.*, 2008, **8**, 529.

(27) Hirsch, L.R., Stafford, R.J., Bankson, J.A., Sershen, S.R., Rivera, B., Price, R.E., Hazle, J.D., Halas, N.J., West, J.L, *Proc. Natl. Acad. Sci. U.S.A* , 2003, **100**, 13549.

(28) Murphy, C.J., Gole, A.M., Hunyadi, S.E., Orendorff, C.J., *Inorg. Chem.*, 2006, **45**, 7544.

(29) Zeng, J., Huang, J., Lu, W., Wang, X., Wang, B., Zhang, S., Hou, J., *Adv. Mater.*, 2007, **19**, 2172.

(30) Chen, S., Kucernak, A., *J. Phys. Chem. B,* 2004, **108**, 3262.

(31) Liu, Z., Ling, X.Y., Lee, J.Y., Su, X., Gan, L.M., *J. Mater. Chem.*, 2003, **13**, 3049.

(32) Lang, H., May, R.A., Iversen, B.L., Chandler, B.D., *J. Am. Chem. Soc.*, 2003, **125**, 14832.

(33) Bianchini, C., Santo, D.V., Meli, A., Moneti, S., Moreno, M., Oberhauser, W., Psaro, R., Sordelli, L., Vizza, F., *J. Catal.*, 2003, **213**, 47.

(34) Yoo, J.W., Hathcock, D.J., El-Sayed, M.A., *J. Catal.,* 2003, **214**, 1.

(35) Yoo, J.W., Hathcock, D., El-Sayed, M.A., *J. Phys. Chem. A,* 2002, **106**, 2049.

(36) Marconi, G., Pertici, P., Evangelisti, C., Caporusso, A.M., Vitulli, G., Capannelli, G., Hoang, M., Turney, T.W., *J. Organomet. Chem.*, 2004, **689**, 639.

(37) Zanella, R., Giorgio, S., Henry, C.R., Louis, C., *J. Phys. Chem. B*, 2002, **106**, 7634..

(38) Choudhary, V.R., Dumbre, D.K, Bhargava, S.K, *Ind. Eng. Chem. Res*., 2009, **48**, 9471.

(39) Chakarvarti, S.K., *J. Vetter Radiat. Meas.*, 1998, **29**, 149.

(40) Thompson, G.E., *Thin Solid Films*, 1997, **192**, 297.

(41) Chah, S., Fendler, J.H, Yi, J., *J. Colloid and Interface Sci.*, 2002, **250**, 142.

(42) Shiquan, L., Jiancun, R., Xueye, S., Pegie, C., Vansant, E.F, Tendeloo, G.V., Cheng X., *J. Non-Cryst. Solids*, 2008, **354**, 826.

(43) Wu, S., Tseng, C., Lin, Y., Lin, C., Hung, Y., Mou, C.Y, *J. Mater. Chem.,* 2011, **21**, 789-794.

(44) Wang, A., *Appl. Surf. Sci.*, 2010, **256**, 2611.

(45) Ashok, M.K., *Int. J. Hydrogen Energy.*, 1988, **23**, 427.

(46) Torimoto, T., Reyes, J.P., Murakami, S., Pal, B., Ohtani, B., *J. Photochem. and Photobiol. A: Chemistry,* 2003, **160**, 69.

(47) Torimoto, T., Reyes, J.P., Iwasaki, K., Pal, B., Shibayama, T., Sugawara, K., Takahashi, H., Ohtani, B., *J. Am. Chem. Soc., 2003*, **125**, 316.

(48) Mathew, S., Santhi, J.A., Radhakrishnan, P., Nampoori, V.P.N., Vallabhan, C.P.G., *J. Fluoresc.,* PACS Code 78.67.

(49) Kumar, A., Janata, E., Henglein, A., *J. Phys. Chem.*, 1988, **92**, 9.

(50) Mrowetz1, M., Villa, A., Prati, L., Selli, E., *Gold Bull.,* 2007, **40**, 2.

Template synthesis of transition metal nanoparticles and their applications as co-catalyst in TiO_2 photocatalytic reactions

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