Catalytic and co-catalytic activity of different shapes and sizes of platinum nanostructures

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in partial fulfillment of the requirements for the award of the degree of
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IN
CHEMISTRY

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Candidate Declaration

I hereby declare that the work being presented in the dissertation entitled, "Catalytic and co-catalytic activity of different shapes and sizes of platinum nanostructures" in partial fulfilment of the requirements for the award of the degree of Masters in Chemistry, being submitted to School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of January to July 2014, under the supervision of Dr. Satnam Singh and Dr. Bonamali Pal. I have not submitted the matter embodied in this dissertation for the award of any other degree.

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

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This is to certify that the project entitled Catalytic and co-catalytic activity of different shapes and sizes of platinum nanostructures", being submitted by Ms Madhuri in partial fulfilment of the requirements 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. Satnam Singh and Dr. Bonamali Pal and that no part of this project has been submitted for the award of any other degree.

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ABSTRACT

Pt nanostructures of different shapes (PtNS, PtNP-1, PtNP-2) have been synthesized. During characterization**,** it is observed that PtNP-2-TiO_2 addition exhibits the highest photo activity as compared to lowest photo activity by other shapes of Pt nanostructures. The same amount of PtNPs addition in Pt-TiO_2 composite always enhanced the degradation rate of reacting substrates. The nanoparticle’s surface morphology and surrounding adsorbed contaminants have vital role for exhibiting optimum activity for a catalysis reaction.

Introduction:

Metallic nanostructures of different shapes and sizes have great potential for homogenous and heterogeneous catalysis that ensure green chemistry. The quantum sized metal nanoparticles (NPs) possess unique optical, electronic, chemical, and magnetic characteristics which are neither of bulk metal nor those of molecular compounds [1-2]. Metallic nano colloids show more reactivity than bulk materials as the percentage of atoms on the surface become much significant in relation to the number of atoms in the bulk of material and thus results in higher activity. The high surface area to volume ratio of NPs provides unexpected optical properties as NPs are small enough to confine their electrons and produce quantum effects.

Nanostructures have gained profound interest in catalysis. One reason for this is perhaps that these structures of well controlled size and shape possess different surface areas and crystallographic facets which could fine-tune both the selectivity and reactivity for many major catalytic reactions [3]. As a result, determination of the influence of size and shape of nanostructures on both catalytic and co-catalytic performance has been the aim of several recent studies. Even though this area has undergone explosive growth during the past decade, most of the studies deal with size dependent catalytic activity of spherical nanoparticles and very little work on non-spherical particles or anisotropic shapes currently exist[4-8].

Among various metallic nanostructures, platinum has been selected for the investigation of their shape-dependent reactivity, for many reasons[9]. Platinum is chemically stable, it has good resistance to oxidation. Interestingly, Pt especially in the form of small particles on a support, plays an outstanding role as a multifunctional catalyst for many industrial reactions. Similarly, it is the only efficient fuel cell electrocatalyst (which is very hard to replace) for many reactions, irrespective of the nature of the reaction, i.e., oxidation or reduction[10]. Platinum nanostructures are subject to dissolution and poisoining under fuel cell reaction conditions, thus reducing both the active catalyst surface area and catalytic efficiency, which leads to an undesired increase in over potential especially for oxidation reaction. However, the high cost of platinum remains a challenge that demands its full or partial replacement without affecting the performance for commercial applications. It has been established that the catalytic reactivity of platinum nanostructures depends highly on their morphology, and therefore the design and synthesis of well controlled shapes and sizes of platinum nanostructures is crucial for their applications, especially in the field of catalysis and photocatalysis[11].

Photocatalysis on semiconductor surfaces, mainly titanium dioxide (TiO_2), has attracted considerable attention in recent years as a potential means for the mineralization of organic pollutants present in water. TiO_2 characterized by undesired electron/hole recombination in the absence of a proper electron acceptor or donor represents energy-wasting step, thus limiting the quantum yield. Therefore, it is necessary to develop new composite materials based on noble-metal-functionalized semiconductors for use in electrochemical, homogeneous and heterogeneous catalysis [12]. The efficiency of the photocatalytic process is measured in terms of quantum yield which is defined as the number of events occurring per photon absorbed. The ability to measure the actual absorbed light is very difficult in heterogeneous systems due to scattering of light by the semiconductor surface. It is usually assumed that all the light is absorbed and the efficiency is quoted as an apparent quantum yield. If several products are formed from the photocatalytic reaction then the efficiency is sometimes measured as the yield of a particular product. To determine the efficiency or quantum yield, a combination of all the pathway probabilities for the electron and hole must be considered. Without recombination the quantum yield would take on the ideal value for the photocatalytic process. Modifications to semiconductor surfaces such as addition of metals or combinations with other semiconductors are beneficial in decreasing the electron and hole recombination rate and thereby increasing the quantum yield of the photocatalytic process [13].

2. Literature survey:

Many experiments have been approached for the synthesis of Platinum nanostructures of different shapes and their optical properties has been reported in the literature[14]. Teranishi et al. and Song et al.[15,16] observed that PVP-protected Pt nanoparticles specific band comes in the range of 268–270 nm due to the ligand-to-metal charge-transfer transition of [PtCl6]−2 ions of N and/or O atoms of PVP to Pt4+ ions. It was concluded that there was a narrow and strong band cantered at 400– 405 nm for Ag nanoparticles protected by polyvinyl pyrrolidine (PVP). On the other hand, these silver species seem to be preferentially adsorbed on more active tetrahedral surfaces of Pt nanoparticles than cubic surfaces. It was observed that pure Pt nanoparticles with PVP were obtained by centrifugation step using an ethanol/hexane mixture with a volume ratio of 1:3. TEM images of the major polyhedral Pt nanoparticles and various shapes with a good particle size distribution and an average particle size of about 7 nm- 10 nm nanosize range. In this case, PVP-protected Pt nanoparticles were successfully synthesized by the polyol method at 160 ˚C with the addition of 0.0002 AgNO3. It was found that the silver cation has been a structure-directing agent in controlling the formation of stable polyhedral Pt nanoparticles from polyhedral seeds.Pt nanoparticles were produced in the well-controlled size range of 5-7 nm in diameter. These Pt nanoparticles are very useful in catalytic reactions.

Narayanan et al.[17] reported that the predominantly cubic polyacrylate-stabilized Pt nanoparticles have an average size 7-10 nm. The predominantly near-spherical PVP-capped Pt nanoparticles have an average size of 4.90 nm by using another stabilizer as the polyacrylate and the H_2 reduction method (Petroski et al.) [18] as well as a study of the adsorption of the polyacrylate to cap Pt nanoparticle shapes . It is observed that Pt nanoparticles usually lie in an ordered way of oriented attachment and there may be a trend of combination among them to form bigger irregular nanoparticles in a small area. the so-called van der Walls force. In the case of the absence of PVP stabilizer, Pt nanoparticles attract each other and tend to coagulate. Metal nanoparticles are necessarily stabilized by means of electrostatic and steric stabilization[19]. Therefore, the irregular shapes of Pt nanoparticles have been formed due to the aggregation and clustering of Pt nanoparticles if the PVP stabilizer of Pt nanoparticles was removed.

Somorjai et al.[20] in the case of the benzene hydrogenation reaction observed that Pt nanocubes comprising only the (100) plane yield solely cyclohexane. More importantly, the apparent activation energy for cyclohexane formation on these cubic nanostructures is less than that on single crystalline facets. This is attributed to an increase in the ratio of corner and edge atoms to terrace atoms with the decrease of crystal domains. In another example, El-Sayed’s group has observed shape-dependent catalytic activity for tetrahedral, cubic and spherical Pt structures, where tetrahedral shape is more active than spherical or cubic for electron-transfer reactions between hexacyanoferrate(III) ions and thiosulfate ions, especially because it contains a larger percentage of surface atoms on corners and edges compared to spherical and cubic structures[21].

3.Research gap

Most of the work on photocatalysis has been studied by loading of noble metals via various techniques (wet impregnation, doping and photodeposition). All these methods result in the formation of spherical aggregated nanodeposits on TiO_2 surface and hence, restrict the shape and size dependent co-catalytic effect. However, every shape has its own uniqueness and can be characterized by unlike surface to volume ratio, number of atoms on the corners and edges, exposed crystallographic facets and varying per particle surface area. Different shapes (such as spheres, nanorods, wires, anisotropic particles, etc.) of Pt NPs would interact with semiconductor (TiO_2) in a varied way and would result in dissimilar photocatalytic activity. Therefore, the size and shape of the Pt nanoparticles can influence the electronic properties of the Pt-TiO_2 composites and thereby photocatalytic activity.

4. Objectives:

1. Synthesis and characterization of Pt nanoparticles of various shapes and sizes.
2. Comparative study of catalytic activity of Pt nanoparticles on decomposition of H_2O_2.
3. To study the effect of shape and size dependent catalytic activity of these prepared Pt NPs as co-catalysts on TiO_2 for the photocatalytic oxidation of organic compounds e.g. salicyaldehyde and o-nitrobenzaldehyde.

5. Experimental Section:

(i)Material:

Hydrogen chloroplatinate (H_2PtCL_6), silver nitrate ($AgNO_3$), o-Nitrobenzaldehyde, Salicyaldehyde (o-CHO-C_6H_4OH), Polyvinyl pyrrolidine (PVP), HCl and H_2SO_4 were purchased from Loba Chemie Pvt. Ltd. CTAB (cetyl trimethyl ammonium bromide) was purchased from Central Drug Pvt. Ltd. $NaBH_4$ was purchased from Spectrochem Pvt. Ltd., Mumbai. L-Ascorbic acid was purchased from SD Fine-Chem Ltd.

(ii) Synthesis of Platinum Nanostructures:

Platinum nanospheres (Pt NS)

Pt nanospheres were prepared by the addition of 10 ml CTAB (10 mM) with 600µl $NaBH_4$ (100 mM) and 250µl H_2PtCl_6 (10mM).After the addition of these above solution, the blackish colour was obtained. It means that the Pt NS were formed having size(≈2-5nm)

Anisotropic shape (Pt NP-1): Pt NP-1 were prepared by mixing 10 ml CTAB (10 mM) solution, 88µl L-ascorbic acid (100 mM), 100µl $AgNO_3$ (10Mm) followed by addition of 20µl seed solution (prepared above) resulting in the formation of brownish yellow colour.

Anisotropic shape (PT NP-2): Pt NP-2 were synthesized by mixing 0.066g of Polyvinylpyrrolidine dissolved in 33ml distilled water, in the PVP solution then add four drops of 1M HCl,3ml of (0.01M) H_2PtCl_6 solution and heat the solution.When the solution was heating, 14 ml ethanol was added. After sometime, the colourless solution turns into dark black. The solution was left overnight in the dark.

Preparation of metal(Pt-TiO_2) nanostructure composite:

For preparation of Pt-TiO_2 composite, 100mg TiO_2 and required amount of different shapes of platinum nanostructure (400µl to 3500µl) in 10 ml of distilled water were taken in a beaker, stirred and heating at 100c for 2h. After 2h stirring and heating,the composites were dried in oven for 4h.

Catalytic activity of Platinum nanoparticles catalyst for the H_2O_2 decomposition

100ml N/100 H_2O_2 solution was taken in a conical flask and diluted with distilled water. Added the platinum catalyst (300µl to700µl) to the conical flask. The mixture was shaken vigorously. 10ml portion was withdrawn after every 2min in the initial stage (upto about 15 min from the start of the reaction) and after every 5/10 min at longer periods of intervals. Pipetted out 10 ml of the reaction mixture into a conical flask and added excess of dilute (2N) sulphuric acid to arrest the progress of the reaction. Titrated the mixture against N/100 $KMNO_4$.

Co-catalytic activity of Pt nanoparticles for Pt-TiO_2 Photocatalysis

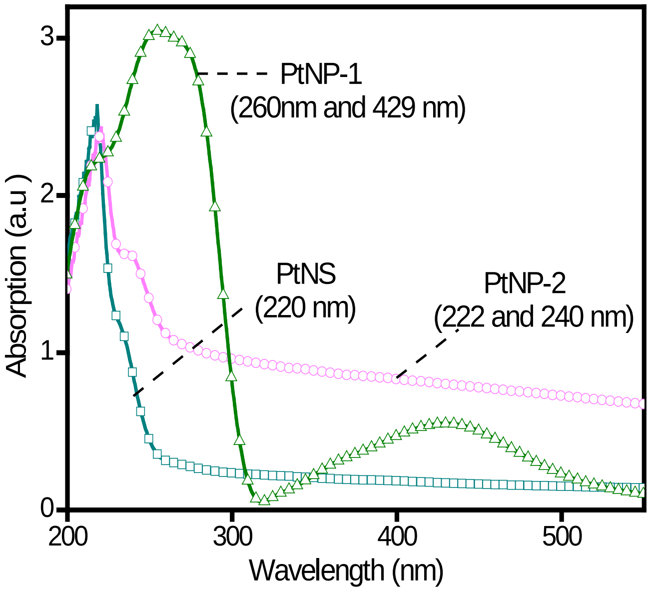
In the first test tube 30mg TiO_2 and 5ml nitrobenzaldehyde (0.2mM), and in other three test tubes 30mg of different shape of platinum nanoparticle composites and 5ml solution of (0.2mM) nitrobenzldehyde were taken. These mixtures were UV-light irridated under magnetic stirring for various time periods. The reaction product was analysed on UV spectrophotometer.

6. Characterization:

The different nanostructures of platinum (PtNS, PtNP-1,PtNP-2) were analyzed by UV-Vis spectrophotometer, HRTEM-NIPER(SAS),200Kv. The oxidation of salicyaldehyde and nitrobenzaldehyde to its main product, was monitored using UV-Vis spectrophotometer. The study of decomposition of H_2O_2 was performed using volumetric method. The another method for analysed different shapes pf platinum nanoparticle i.e. Surface Plasmon band. SPR band is the preliminary characterisation of metal nanoparticles. We can estimate the shape of platinum nanoparticles from the position of SP band. If SP band of platinum nanoparticles of different shape comes at(218 nm, 235nm, 432nm) , the size range of platinum nanoparticle (2-200nm) , as the size of platinum nanoparticles increases, the SP band shift from higher wavelength i.e.red shift takes place. For measurement of platinum nanoparticles size, Transmission electron microscope images were taken having power 200 Kv.

7. Results and discussion:

7.1 Optical properties of platinum nanoparticles of different shapes:



[Figure 1]. (Surface plasmon resonance bands for different shape and sizes of Pt nanoparticles).

The surface Plasmon Resonance band(SPR) for aqueous colloidal solution of PtNPs as a function of their particle size is shown in figure 1. The light yellow colored particles (PtNS) displayed their SPR band at 220 nm that corresponds to spherical shape. The SPR band observed at 260nm and 429 nm of PtNP-1 corresponds to transverse and longitudinal bands, respectively. These two bands originate due to the change in the morphology. According to Mie’s theory, single SPR band is observed for the nanospheres, while anisotropic particles display more than one SPR band. PtNP-2 particles displayed band at 222 nm and also a little elevation has been seen at 240 nm which may be due to the difference in the light scattering behavior owing to the modification in morphology of NPs. Sujin et al.[25] reported that change in the particle size distribution and surface morphology of NPs causes changes in light scattering and plasmon.

Transmission Electron Microscopy (TEM)

The TEM images in Fig. 2a reveal that the average size of the monodisperse PtNS of size range ≈ 2-5 nm corresponds to sharp SPR band at 220 nm. Martin and Moskovits et al.[22,23] observed spherical Pt nanoparticles with a diameter of ca. 73 nm which showed a characteristic broad extinction feature over 200-800 nm with a peak maximum at 400 nm. TEM images for

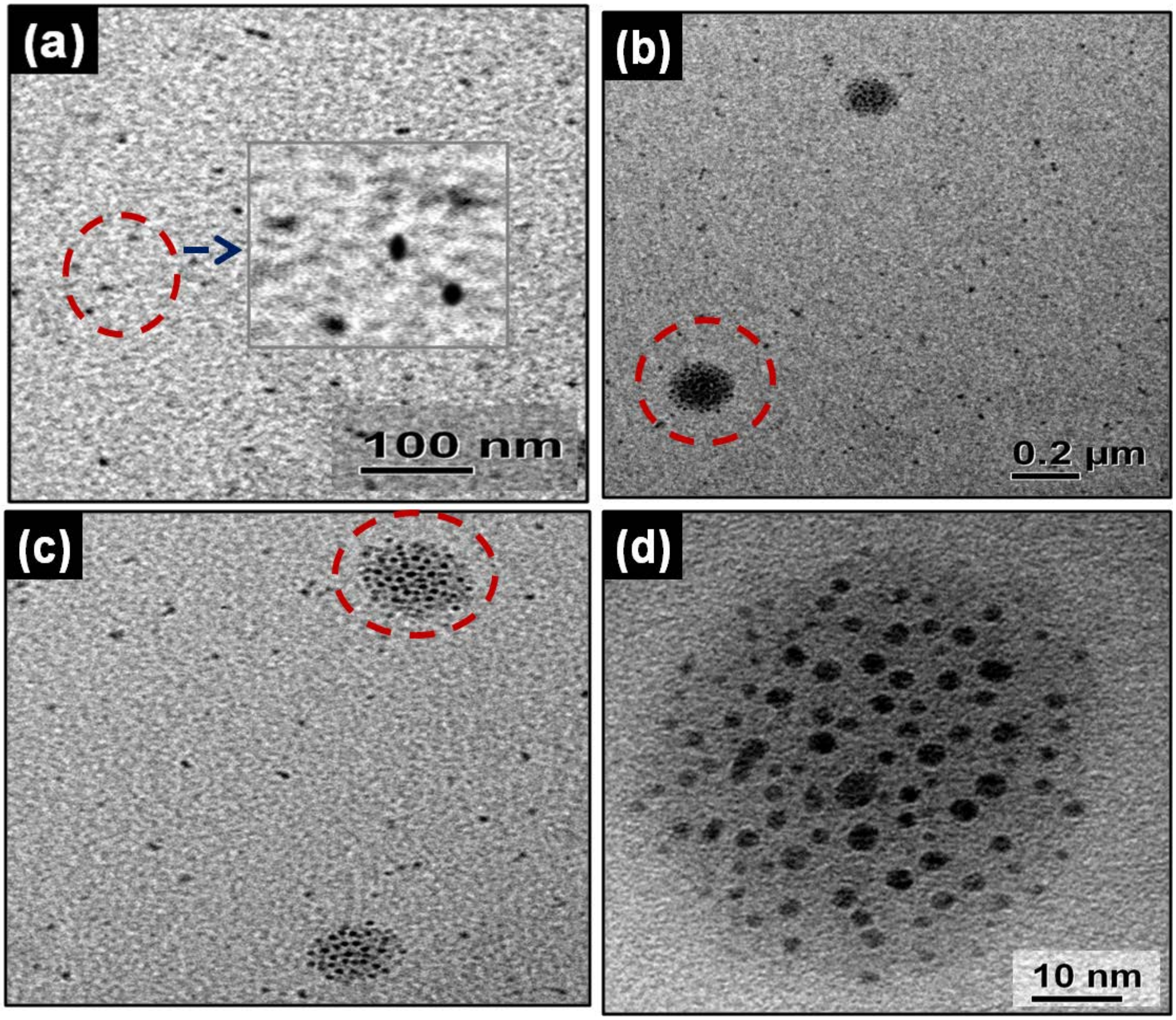


Figure 2. TEM images of platinum nanosphers (PtNS).

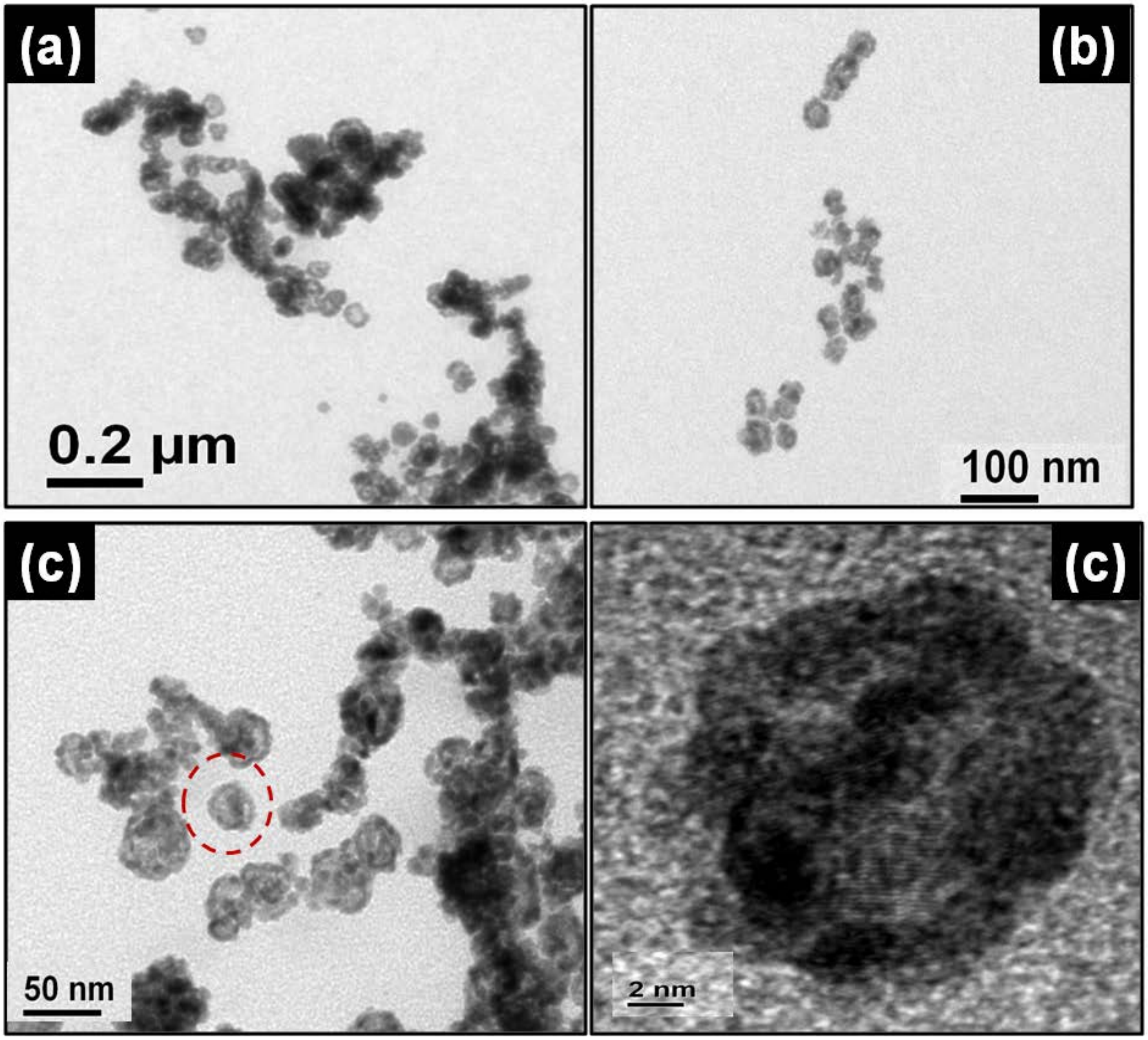
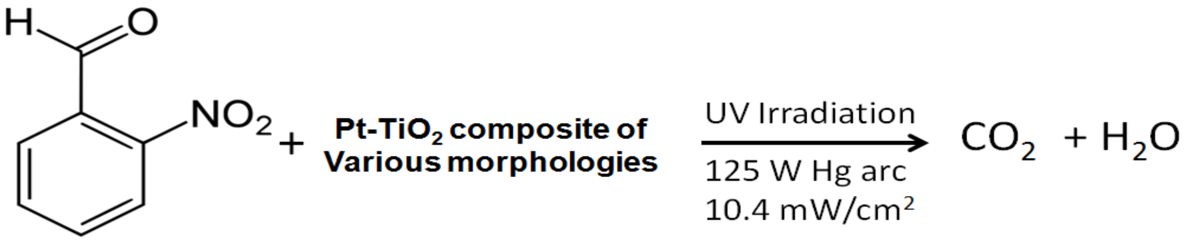


Figure 3. TEM images of platinum nanoparticle (PtNP-2).

PtNS (Fig. 2b-d) showed some close arrangement of particles at regular intervals. All the particles seem to enclosed in an assembly consisting of around 30-40 nm size and composed of 60-80 particles of size 2-5 nm each. Figure 3 showed the formation of some irregular shaped PtNP-2 particles of size in the range of 10-15 nm. It is clearly depicting that the morphology of PtNP-2 particles is not exactly spherical; some uneven or curved surfaces has been observed which give them polygonal appearance. The magnified image in fig. 3d clearly highlights the highly asymmetrical morphology of PtNP-2 particles[24]. These variations in the morphological aspects of PtNPs are highly dependent on the synthesis technique and nature of the interactions among reducing entity and precursor salt.

7.2 Co-catalytic activity of Pt nanoparticles for Pt-TiO_2 Photocatalysis



Scheme 1. Diagrammatic representation for the photodegradation of nitrobenzaldehyde using various Pt-TiO_2 composites under UV light irradiation.

The co-catalytic activity of as synthesized Pt nanostructures of different morphology was evaluated by mixing 30 mg Pt-TiO_2 composite for the photooxidation of 5 ml nitrobenzaldehyde and salicylaldehyde separately. Semiconductor nanostructures (such as TiO_2) have significant application in photocatalysis due to their characteristic filled valence band (VB) and empty conduction band (CB) in the ground state. Photocatalytic reaction takes place when photocatalyst

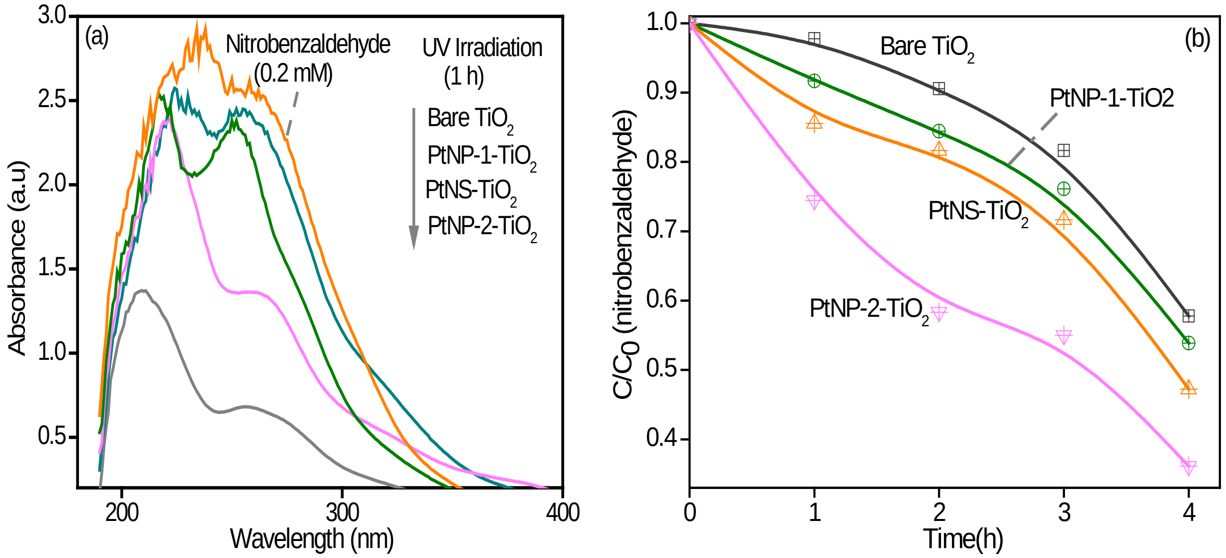
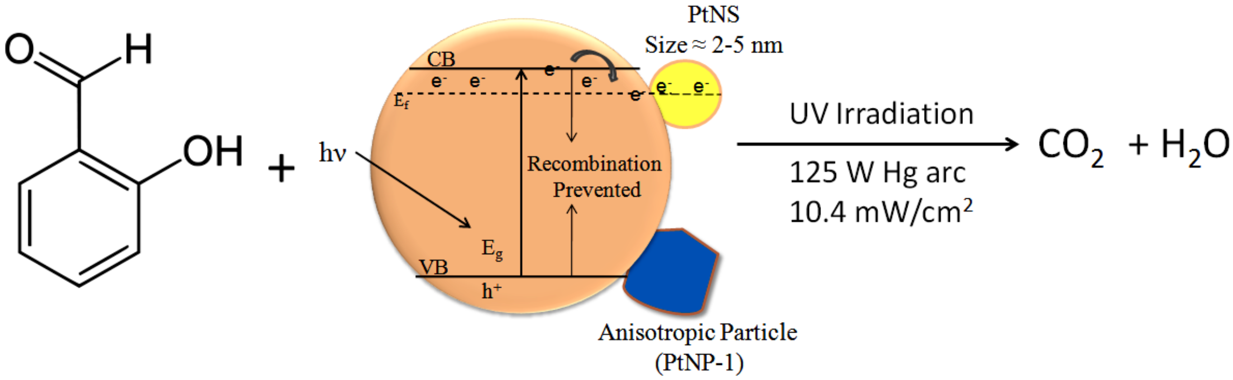


Figure 4. Changes in absorption spectra of nitrobenzaldehyde (0.2 mM) after 1 hr irridation (b) time course for the photooxidation of nitrobenzaldehyde using various Pt–TiO_2 composites under UV light irradiation.

is excited by energy equals to or more than the band gap of the catalyst, resulting in the formation of excitons, i.e., electrons at the CB and holes at the VB, which may recombine within



Scheme 2. Various morphologies of Pt-TiO_2 for photodegradation of salicylaldehyde under UV light irradiation.

an instant of time and this recombination results in the low quantum yield.

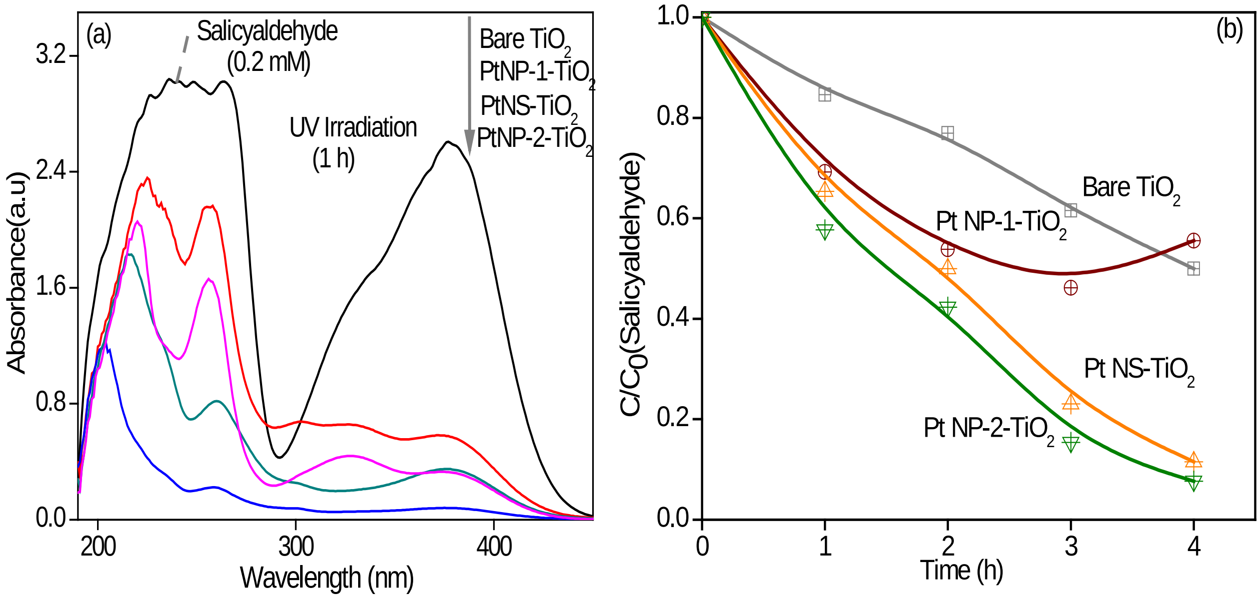


Figure 5. Changes in absorption spectra of salicyaldehyde (0.2 mM) after 1 hr irridation (b) time course for the photooxidation of salicyaldehyde using various Pt–TiO_2 composites under UV light irradiation.

Whereas, Pt-TiO_2 nanocomposite interactions accelerate the photocatalytic reactions by promoting the charge separation (e^--h^+) as metal co-catalyst serve as the sink for storing and shuttling of photogenerated electrons from the semiconductor to metal that resulted in better separation of charge carriers (e^--h^+). The different shapes and sizes of PtNPs led to generate electron accepting ability in a different extent that assist the photooxidation of adsorbed reactants at PtNPs-TiO_2 interface to a varied extent. Figure 4a and 5a displayed the changes in the absorption intensity of nitrobenzaldehyde and salicylaldehyde during its photo-oxidation on mixing with 30 mg Pt-TiO_2 composites of different sizes and shapes under 1 h UV light irradiation**.** It is observed that PtNP-2-TiO_2 addition exhibits the highest photoactivity as compared to lowest photoactivity by AgNP-1 because of their dissimilar co-catalysis effects. Figure 4b and 5b showed the influence of Pt nanopartiles co-catalysts shapes on the photooxidation rate of substrates at various time intervals of UV light irradiation. Both the reactants are exponentially decreased with increase in the UV irradiation time, indicating the first order reaction kinetics as $C_t = C_o e^{-kt}$, where C_t is the amount degraded at time t, C_o is the initial concentration of reactant and k (min^{-1}) is the first order rate constant. The same amount of PtNPs addition in Pt-TiO_2 composite always enhanced the degradation rate of reacting substrates in a varied extent as a function of their size and shape. The PtNP-2-TiO_2 composite exhibits the highest photoactivity ($k = 2.3\times10^{-1}$ min^{-1}) for nitrobenzaldehyde degradation as compared to the lowest $k = 1.27\times10^{-1}$ min^{-1} obtained by PtNP-1-TiO_2 due to the significant variation in interfacial properties which are responsible for charge transfer processes at the PtNPs-TiO_2 heterojunction.

7.3 Catalytic Activity of Pt nanoparticles for H_2O_2 decomposition

$$H_2O_2 + H_2SO_4 \xrightarrow[\text{Different Morphologies}]{\text{Pt Nanoparticles of}} H_2O + O_2$$

(i)Effect of different shapes of platinum nanoparticles for the decomposition of H_2O_2

Fig.6 shows the effect of Platinum catalyst of different shapes and size (PtNS, PtNP-1, PtNP-2) on the decomposition of H_2O_2. It was found that on the addition of different shapes of Platinum catalyst in the H_2O_2(0.01N) solution and titrated with (0.01N) KMnO4 solution, we had seen that the PtNP-2 shape more effective in the decomposition of H_2O_2 due to their different shapes and size(≈10-15nm).Because the every shape has different surface area, so the effect of every shape should be different.The result further confirmed by the addition of Platinum catalyst, KMnO4 gradually decreases with time , these changes can be seen in the Fig6.

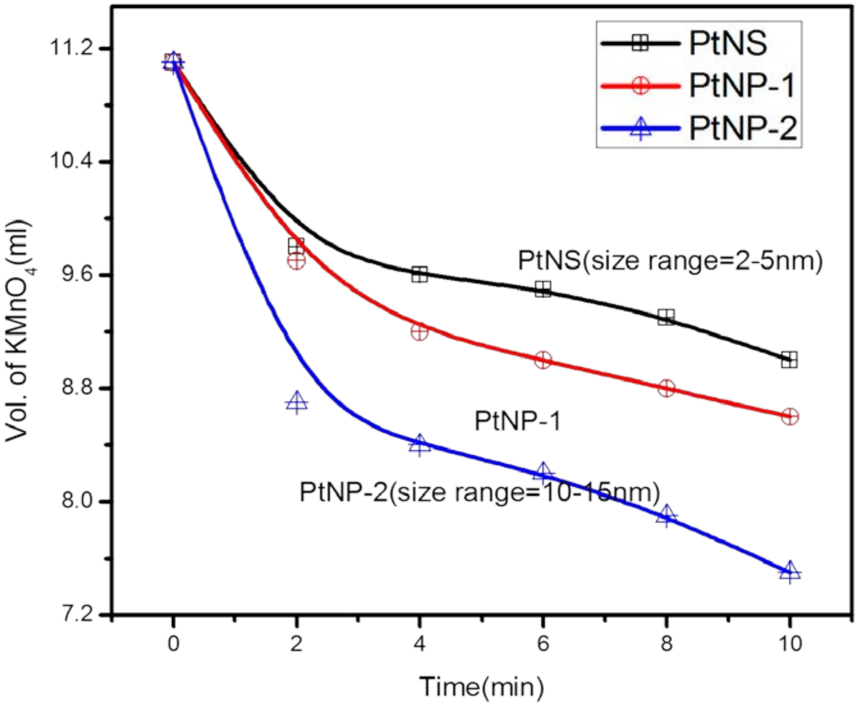


Figure6 . Influence of Pt nanoparticle morphology on the decomposition of H_2O_2

(ii)Effect of different concentration (300 µl,500 µl,700 µl) of Platinum catalyst on the decomposition of H_2O_2

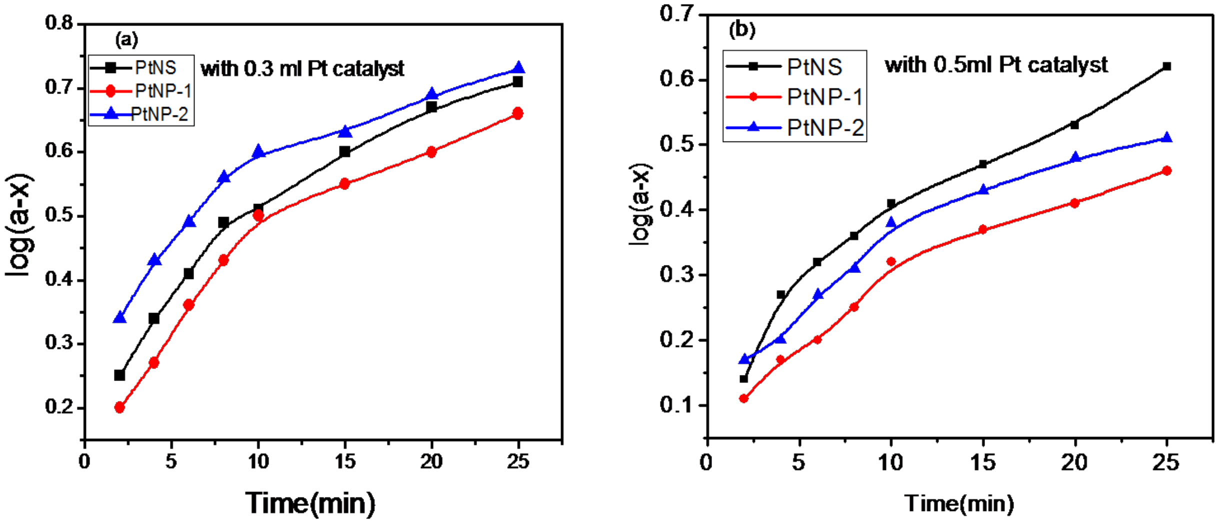


Figure7 .. Effect of shape of platinum catalysts for the decomposition of H_2O_2 of different concentrations (a) 0.3 ml and (b) 0.5 ml.

Fig 7(a)(b)(c) shows the effect of platinum catalyst concentration on the decomposition of H_2O_2.It was found that when we add different concentration (300 µl,500µl,700µl) of the platinum catalyst in the H_2O_2 solution and titrated with (0.01N)KMnO4 solution , we have seen that the final concentration(a-x) of the platinum nanoparticles of the

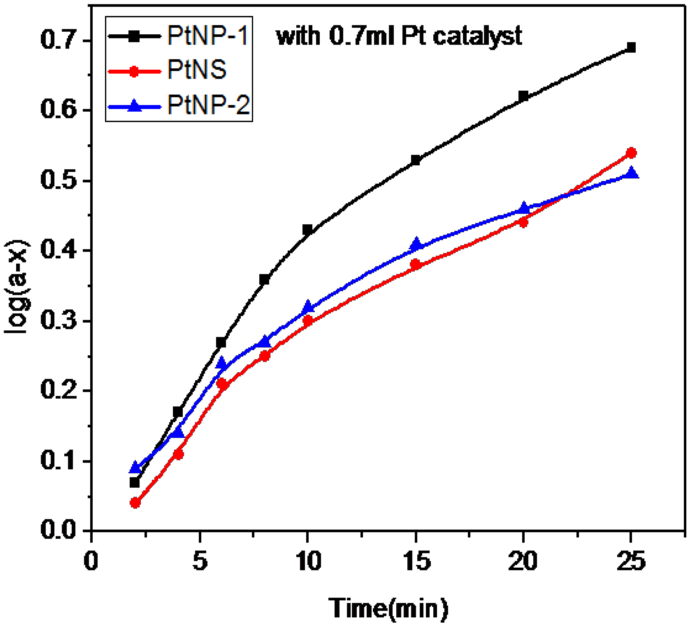


Figure7(c).. Decomposition of H_2O_2 using 0.7 ml Pt catalyst of various shapes and sizes.

different shapes should be different. Then we take the log of the final concentration. The value of log(a-x) should be calculated by the first order reaction which should be written as below:

$$K= 2.303/t \log(a/a-x)$$

$$Kt=2.303\log(a)-2.303\log(a-x)$$

$$\log(a-x)= 2.303/2.303 \log a-kt/2.303$$

$$\text{i.e. } (y= c - mx), (m= k/2.303)$$

With the help of this equation, we can easily find out the log(a-x).Log(a) is the initial concentration of the volume of KMnO4 used, log(a-x) is the final concentration of the volume of $KMnO_4$ used , which shows that how much amount of H_2O_2 decomposed by the addition of (300µl,500µl,700µl)platinum catalyst. The volume of KMnO4 gradually decreases with increase in the value of log(a-x). The result confirmed by the addition of (300 µl,500µl,700µl) Platinum

Table 1. Physical parameters and rate constants for the co-catalytic and catalytic activity mediated by Pt nanoparticles

Catalysts	SPR band/ TEM shape and size	Rate constant (k, h^{-1})		
		Nitrobenzaldehyde	Salicylaldehyde	Decomposition of H_2O_2
TiO_2	-----	1.1×10^{-1}	1.64×10^{-1}	---
PtNS	220 nm/ spheres and 2-5 nm	1.49×10^{-1}	4.4×10^{-1}	6.7×10^{-1}
PtNP-1	222 and 429 nm	1.27×10^{-1}	1.98×10^{-1}	7.0×10^{-1}
PtNP-2	222 and 240 nm/ irregular shape and 10-15 nm	2.3×10^{-1}	5.3×10^{-1}	7.7×10^{-1}

catalyst in the H_2O_2 solution ,the value of log(a-x) should be different at every shape of platinum catalyst. The value of rate constant should also be different for different concentration. For(300µl) concentration, the value of rate constant should be different for differentshape of platinum(PtNS,PtNP-1,PtNP-2) which is shown in the table 1. In addition of (300 µl)Platinum catalyst ,the value of log(a-x) is different(PtNS=0.71,PtNP-1=0.69,PtNP-2=0.75) at the interval of 25min, for different shapes of platinum nanostructures. In addition of (500µl), (700µl) Platinum catalyst, the value of log(a-x) is(PtNS=0.54,PtNP-1=0.69,PtNP-2=0.80),(PtNS=0.68, PtNP-1=0.62,PtNP-2=0.51). The value of log(a-x) is so much important, because the graph plot between log(a-x) versus time.

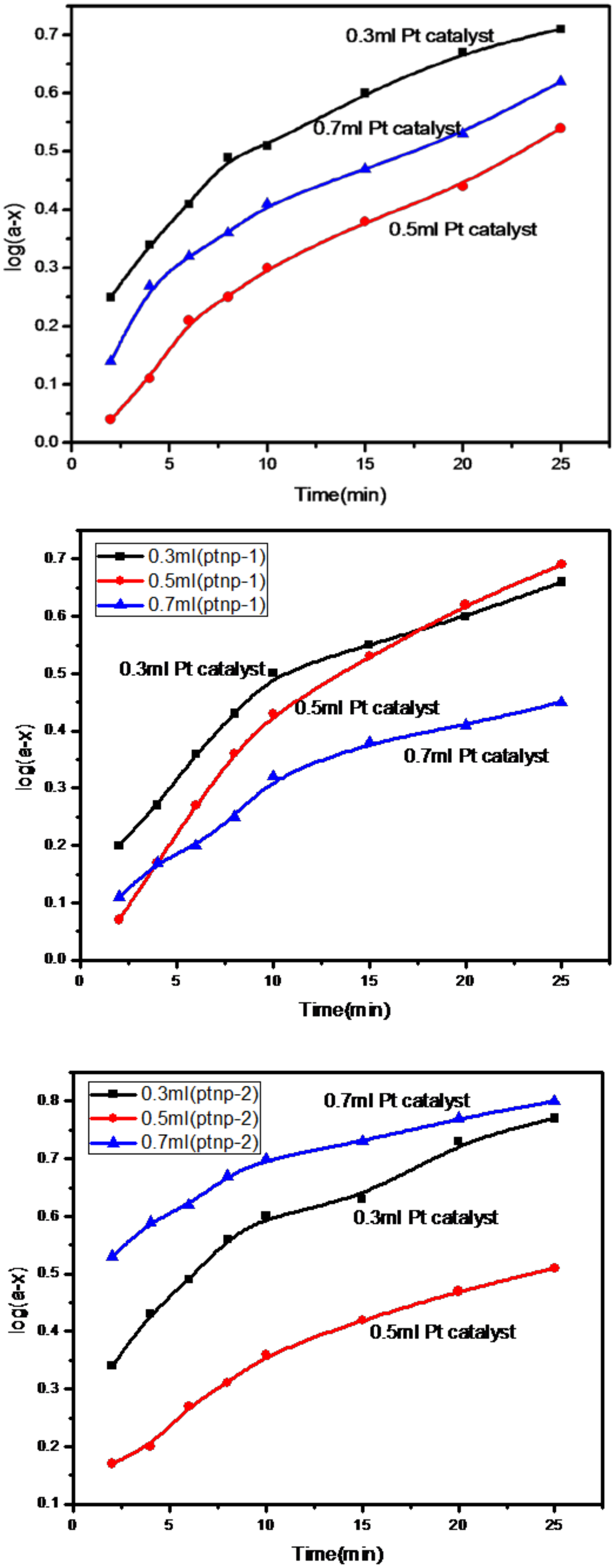


Figure8. Effect of different concentration on the similar shape of Pt nanoparicle**.**

(iii)Effect of different concentration of Platinum catalyst on the similar shape of platinum nanoparticle(PtNS, PtNP-1,PtNP-2)

Fig8(a)(b)(c) shows that the effect of different concentration of Platinum catalyst on the similar shape of platinum nanoparticle (PtNS). Different morphologies of PtNPs have been utilized for the decomposition of H_2O_2 as shown in Fig. 8a. The plot of log(a-x) versus time indicated that PtNP-2 showed highest rate constant value relative to other nanostructures. The rate of H_2O_2 decomposition was further examined by varying amount of PtNPs (300-700 μl) as a function of time as shown in Fig. 6b. It has been observed that the 500 μl addition of PtNS enhanced the decomposition rate of H_2O_2, while on increasing the amount to 700 μl does not much effect the catalytic rate. It is assumed that the increasing catalyst amount (700 μl) of PtNS catalyst causes interruption for efficient transfer of electrons to the reacting substrate and hence the decomposition proceeds at a slower rate. Therefore, an optimum amount of PtNS was needed to complete the H_2O_2 decomposition\

8. **Conclusion:**

In summary, Pt nanostructures of different shapes (PtNS, PtNP-1, PtNP-2) has been synthesized, characterized and compared their various co-catalytic and catalytic activity. It is observed that PtNP-2-TiO_2 addition exhibits the highest photoactivity as compared to lowest photoactivity by AgNP-1 because of their dissimilar co-catalysis . The same amount of PtNPs addition in Pt-TiO_2 composite always enhanced the degradation rate of reacting substrates in a varied extent as a function of their size and shape.

The difference in the catalytic and co-catalytic activity of various Pt nanostructures could be attributed to the unlike dimension, surface to volume ratio, geometric facets, atomic arrangement, and alternation in surface exposed atoms. The highest catalytic and co-catalytic activity of PtNP-2 can be explained on the basis of highly asymmetric shape , more surface atoms and rough surface that results in better catalytic activity. It has been reported that particles possess more steps, edges and kinks on their geometric shape could have higher catalytic efficiency. Thus, the nanoparticles surface morphology and surrounding adsorbed contaminants have vital role for exhibiting optimum activity for a catalysis reaction.

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