Research Paper

Kinetic Studies on Nanocatalysis by Iridium Nanoclusters in Some Oxidation Reactions

Goel Anjali *, Bhatt Ranjana, Neetu
Department of Chemistry, KGM, Gurukul Kangri University, Hardwar (U.K.), INDIA

Available online at: www.ijrce.org

Abstract- *The use of a catalyst is a common way to minimize energy use and less material waste formation by lowering the energy of activation for a reaction. With catalysts reactions can be more efficient and selective. This provides an enormous energy savings while reducing the risks of explosion or other high temperature hazards. The field of nanocatalysis has undergone an explosive growth during the past decades, both in homogeneous and heterogeneous catalysis. Since nanoparticles have a large surface-to-volume ratio compared to bulk materials, they are attractive to use as catalysts. With the improved developments in nano-chemistry, it is now possible to prepare soluble analogues of heterogeneous catalysts, materials that might have properties intermediate between those of the bulk metal and single metal-particle (homogeneous) catalysts. Noble metal nanoparticles with high specific catalytic activity are ubiquitous in modern synthetic organic chemistry during the recent decades. However how to reduce their dosage is one of the most exiting challenges due to the limited reserves of noble metals. In this study colloidal dispersion of iridium nanoparticles have been synthesized by wet reduction method using different polymers as protecting agent after the reduction of precursor salt by alcohol. The particle size has been effectively controlled in the range of 10 nm by the variation of solvent, reductant, temperature and polymer concentration. The synthesized iridium nanoparticles were characterized by UV-vis, XRD, FT-IR, TEM etc technique.*

The catalytic activity of colloidal iridium nanoparticles was evaluated in some oxidation reactions like amino acids- hexacyanoferrate (III) redox system in alkaline medium. These nanoparticles show a better catalytic activity than an equal amount of iridium precursor. Easy recovery of the catalyst from the reaction mixture shows another positive significance. Superior catalytic activities of nanoparticle-based catalytic systems than the corresponding bulk materials and recycling of metal nano particles are helpful in reducing the raw material costs and engineering a greener process via limiting the amount of waste chemicals for disposal.

Keywords: Iridium, Nanocatalyst, oxidation reaction.

Introduction

Catalytic reactions are preferred in environmental friendly green chemistry due to the reduced amount of waste generated. The field of nanocatalysis has undergone an explosive growth during the past decades, both in homogeneous and heterogeneous catalysis [1,2].zSince nanoparticles have a large surface-to-volume ratio compared to bulk materials, they are attractive to use as catalysts [3,4]. With the improved developments in nano-chemistry, it is now possible to prepare soluble analogues of heterogeneous catalysts that might have properties intermediate between those of the bulk metal and single metal-particle (homogeneous) catalysts. Noble metal nanoparticles with high specific catalytic activity are ubiquitous in modern synthetic

organic chemistry during the recent decades [5]. However how to reduce their dosage is one of the most exiting challenges due to the limited reserves of noble metals.

In this study colloidal dispersion of iridium nanoclusters have been synthesized by wet reduction method using polymer as protecting agent after the reduction of precursor salt by alcohol [6,8]. The particle size has been effectively controlled in the range of 0-10 nm by the variation of solvent, reluctant, temperature and polymer concentration used in synthesis. The synthesized Ir-nano were characterized by UV-vis, XRD, FT-IR, TEM etc techniques.

The catalytic activity of colloidal Ir-nano was evaluated in the oxidation of some amino acids / dyes-

hexacyanoferrate (III) redox system in alkaline medium. These nanoparticles show a better catalytic activity than an equal amount of iridium precursor. Easy recovery of the catalyst from the reaction mixture shows another positive significance. Superior catalytic activities of nanoparticle based catalytic systems than the corresponding bulk materials and recycling of metal nano particles are helpful in reducing the raw material costs and engineering a greener process via limiting the amount of waste chemicals for disposal.

Material and Methods

To make the kinetic studies on nanocatalysis in some oxidation reactions nanoparticles of iridium below size 10 nm were synthesized by wet chemical reduction method. The synthesized particles are used as catalyst in the oxidation of some amino acids and dyes.

All the chemicals and reagents used were of AR grade. All solutions were prepared with doubly distilled water. HCF (III) was recrystallized before use. Its solutions were kept in amber colored bottles to prevent photodecomposition. KCl (Merck) and NaOH (Merck) were used to provide the required ionic strength and alkalinity respectively of the reaction mixture. Some stabilizer as polyvinylpyrrolidone is used to stabilize the particles.

Preparation of colloidal iridium nanoparticles: In the present work Ir-nano were prepared by chemical reduction of two precursors- $IrCl_3.3H_2O$ and $H_2IrCl_6.6H_2O$ to study the effect of precursor on particles size [9]. Methanol (Merck) was used as reducing agent. NaOH (Merck) was used to make medium alkaline. Some stabilizer as polyvinylpyrrolidone, is used to stabilize the particles. For their preparation required amount of precursor was dissolved in 25 ml of methanol. A solution of stabilizer in water was mixed slowly at room temperature by stirring magnetically. After that 1.6 ml of an aqueous solution of sodium hydroxide (0.2 M) was added drop wise with vigorous stirring. Now the solution (in a three necked round bottom flask) was heated in oil bath over 1 hr with a heating rate of 4^0/min. Polymer stabilized nanoparticles were obtained. These nanoparticles were dried at 50^0C and analyzed by UV-vis, IR, XRD and TEM methods of analysis. Size controlled synthesis was carried out by varying the amount of precursor, NaOH, stabilizer and methanol as described in Table 1. TEM micrograph shows that Ir-nano particles were separated by no agglomeration tendency and are similar to spherical with narrow size distribution. Ir-nano particles synthesized by method "a" and "c" are used in the oxidation of glycine and methyl orange.

Evaluation of catalytic activity: The catalytic activity of Ir-nano synthesized by method 'a' has been studied in the oxidation of glycine while the catalytic activity of Ir-nano synthesized by method 'c' has been studied in the oxidation of methyl orange by hexacyanoferrate (III) ions in aqueous alkaline medium.

The kinetic measurements were performed at constant at constant temperature the requisite amount of each reactant was thermostated to attain thermal equilibrium. The appropriate quantities of reactants were mixed in a 100 ml iodine flask. The progress of reaction was measured by

injecting a solution of glycine / methyl orange into the reaction mixture at λ_{max} 420/465 nm corresponding to the HCF(III)/ methyl orange respectively. It was verified that there is negligible interference from other species present in the reaction mixture at these wavelength.

Results and Discussion

For characterization of colloidal iridium nanoparticles: UV-vis spectroscopy is a convenient technique for monitoring the progress of metal colloid formation [10]. A PVP- H_2IrCl_6-methanol-water solution kept in an oil bath was sampled at different time & the samples were characterized by UV-vis spectrophotometer. Initially $IrCl_6^{-2}$ and $IrCl_3$ show an absorption peak at about 487 nm. The intensity of this peak decreases with the increase of time. After about 25 minutes refluxing this absorption peak disappeared completely and a new peak appeared at about 235 nm indicating the formation of Ir (0) nanoparticles. No further change was observed. The colour of solution changes from yellow to black-brown.

The XRD spectra of the Ir-nano shows two broad peaks at 2-theta about 40^0 and 48.5^0 at reflection plane Ir (111), Ir (200) respectively Figure 1. Which are the characteristic of isolated Ir(0) nanoparticles Analysis of the peaks broadening using the Scherrer equation gives an estimate of particle diameter. Diameters of particles calculated by Scherrer equation are given in Table 1. The particle size ranges between 10.55 nm by method 'a', and 42.50nm and 3.91to 4.46nm by method 'a' to 'c' respectively. The X- ray diffractogram of these metallic particles indicate that X they are amorphous and show broad peak characterization of materials with a small size [11].

The IR spectra of Ir-nano show a new band near the frequency 2015 cm^{-1} indicates the formation of Ir(0) [12]. In method a, b and c which are stabilized by steric stabilization using PVP as protecting agent. These large adsorbates provide a steric barrier which prevents close contact of metal nanoclusters to each other as demonstrated in (Figure 2) [13]**.**

Detailed characterization studies of the adsorbed polymer have demonstrated that the polymers can coordinate to the metal forming rather strong chemical bonds. The polymer molecule can coordinate to the metal particle at multiple sites [14].

The red shift of resonance peak of pure PVP at 1700 cm^{-1} to 1664 indicates the interaction of >C=O group of PVP with Ir-nano[15] The presence of same bands at about 1500 cm^{-1},1461 cm^{-1} (aromatic C-C str, N-H bending) in spectra shows that these groups do not interact with Ir-nano [16].TEM micrographs confirms the particle size as 10, 50 and 4.5 nm by method a, b and c respectively Figure 3. Nanoparticles in the range of size 1-10 nm are good catalyst [17]so nanoparticles synthesized by method 'a' and 'c' are used in the oxidation of glycine (amino acid) and dye (methyl orange) respectively.

For evaluation of catalytic activity:
Nanocatalysis by Ir-nano in the oxidation of glycine (α-amino acids)by hexacyanoferrate(III) in alkaline medium: In the first series of experiments Ir-nano are used as catalyst for studying its catalytic effect on the rate of oxidation of amino acids namely glycine kinetically. All kinetic runs were

followed as described in foregoing section. The concentration of Ir-nano used in the experiments is of the order of 10^{-6} mol dm^{-3}. The effect of Ir-nano concentration on the rate of oxidation of glycine has been studied by varying its concentration from 1.23×10^{-6} mol dm^{-3} to 6.14×10^{-6} mol dm^{-3}. The concentration of other reactants was as follows:

[HCF (III)] = 3×10^{-4} mol dm^{-3}, [Glycine] = 3×10^{-3} mol dm^{-3}, [NaOH] = 0.4 mol dm^{-3}, μ = 0.5 mol dm^{-3}, Temp. = 35 $\pm$ 0.1^0C, λ_{max} = 420 nm.

The experimental results are presented in Figure 4, 5 for the oxidation of glycine. The graphical representation of absorbance vs time shows that the rate of reaction catalysed by iridium nano ($\approx$10 nm) is more than that of precursor iridium. The initial rate of the reaction has been calculated by the slope of the curve between absorbance vs time (Figure 5). The graphical representation between reaction rate and [Ir-nano] (Figure 3), r $\geq$ 0.96, S.D. $\leq$ 0.008 and 04, r $\geq$ 0.97, S.D. $\leq$ 0.006) clearly reveals that the reaction follows first order kinetics with respect to Ir-nano concentration. The effect of particle size on oxidation rate was studied by studying the effect of precursor iridium (H$_2$IrCl$_6$), [Ir-nano] ($\approx$50nm) and [Ir-nano] ($\approx$10nm) as catalyst keeping the concentration of all other reactants constant. A graph plotted between rate vs concentration of precursor iridium/Ir-nano ($\approx$50nm)/Ir-nano ($\approx$10nm) shows that reaction rate of Ir-nano ($\approx$10 nm) catalyzed reaction are more than that of precursor iridium and Ir-nano ($\approx$50 nm) [18,19]. This shows that the catalytic activity of Ir-nano is two to three times more than that of precursor iridium due to large surface area to volume ratio. It also shows that the catalytic activity of small particles is more than that of larger particles.

PVP plays an important role in the present system. The present colloidal dispersion was stable in air under the protective action of polymers. No precipitation had occurred after storing the dispersion in air for month. Figure 5 shows a small effect of PVP concentration on the rate of oxidation it may be due to the steric effect and chemical bonding [20].

To calculate the thermodynamic parameters the effect of temperature on the oxidation of glycine with alkaline Hexacyanoferrate (III) has been studied in the presence of Ir-nano particles at four temperatures (30^0, 35^0, 40^0 & 45^0). The data presented in Table 2 shows that presence of Ir- nano decreases the activation energy as compared to bulk iridium making the reaction rate fast in presence of nanoparticles. Large negative entropy values suggest formation of more ordered and polar complex formation during the reaction [21].

Stoichiometry of the reaction was determined by making different sets of reaction mixtures containing an excess [Hexacyanoferrate (III)] over [substrate] at 0.4 mol dm^{-3} NaOH, same concentration of Ir-nano at constant ionic strength was allowed to react. This mixture was analyzed by titrating against Ce (IV) solution. The results indicated that two moles of hexacyanoferrate (III) were reacted with one mole of glycine. After completion of the reaction, the amount of hexacyanoferrate (II) formed (which is equal to the amount of hexacyanoferrate (III) consumed) was determined by measuring the absorbance of the reaction mixture.

The main oxidative products were submitted to spot tests. The product was extracted with ether and purified. The IR spectrum of the compound revealed the presence of one carboxylic group and one keto group. It was observed that, the products do not undergo further oxidation under prevailing kinetic conditions. The stoichiometry and the products of Ir-nano catalysed oxidation are same as reported for catalysed reaction by bulk iridium [22].

Oxidative degradation of methyl orange (dye) using hexacyanoferrate (III) ions

In the second series of experiments the effect of Ir-nano prepared by method 'c' are studied on the rate of oxidation of methyl orange an azo dye. Azo dye methyl orange creats environmental pollution problems by releasing toxic and potential carcinogenic substances in to the aqueous phase [23]. The experimental conditions set are as follow:

[HCF (III)] = 3×10^{-6} mol dm^{-3}, [Methyl Orange] = 3×10^{-5} mol dm^{-3}, μ = 0.3 mol dm^{-3}, [NaOH] =0.25 mol dm^{-3} λmax = 465, Temp. = 40 $\pm$ 0.1^oc.

Under the above experimental conditions the reaction rate of uncatalysed and catalysed oxidation was determined. For catalysis iridium nanoparticles of size 4.5nm are used as catalyst. Figure 6 and 7 shows that rate of catalysed reaction is more than the rate of uncatalysed reaction. The effect of PVP on the oxidation is also studied. Figure 6 show a negligible effect of PVP on the reaction rate. Thus the overall effect is only due the Ir-nano. The reaction was also studied at four different temperatures to calculate the thermodynamic parameters. The results in Table 2 show that the presence of Ir-nano increases the oxidation rate many times by decreasing the energy of activation from 18.9 to 8.6 kcal mol^{-1}. The stoichiometry and oxidation product are studied by the above mentioned method as for glycine oxidation. Stoichiometry of glycine is 2:1whereas methyl orange is 1:1 [24].

For recycling of Ir-nano from reaction mixture after kinetic study of reaction, solution was carried out for centrifugation. The obtained residue was dried at 75^0C temperature and analyzed by XRD technique. XRD pattern was presented in Figure 8 and Figure 9. The results in Table 3 shows that the size of particles increases from 10.55 to 12.63 with glycine and 4.5 to 6.51 with methyl orange due to the distortion and agglomeration of the particles. The recovery of Ir-nano is good though the colloidal PVP-Pd nanoparticle were found to have poor recycling potential [24].

Conclusion

PVP stabilized colloidal iridium nanoparticles with an average particle size of 10 nm and 4.5 nm, respectively, can be generated easily from the reduction of precursor materials H$_2$IrCl$_6$ and IrCl$_3$.3H$_2$O with methanol which remain stable even after several months. TEM analyses of the PVP stabilized colloidal iridium (0) nanoparticles indicated that all of the nanoparticles are in spherical shape with narrow particle size distributions. XRD patterns of PVP stabilized colloidal iridium (0) nanoparticles showed that these nanoparticles are existed in amorphous phase. The attachment of PVP on the surface of the metal (0) nanoparticles through

the C=O groups was concluded from the observation of change in C=O strecthing frequency of PVP in the FT-IR spectra. PVP stabilized colloidal iridium (0) nanoclusters were highly active catalysts in oxidation of amino acids (glycine) and dye (methyl orange). The kinetic study on nano catalysis show that iridium (0) nanoparticles act as good catalyst than the bulk Ir (III). It also shows a remarkable effect on degradation of methyl orange azo dye than rather glycine oxidation. Thus the study shall be helpful in making the environment green. Recovery of the catalyst from the reaction mixture shows another positive significance. Recycling of metal nano particles are helpful in reducing the raw material costs and engineering a greener process via limiting the amount of waste chemicals for disposal.

References

1. Bradley J. S., Scmided G., Clusters and Colloids: From Theory to Application VCH, New York *"Cluster Colloids".,* 459 (**1994).**
2. Thomas J. M., Johnson B. F. G., Raja R., Sankar G., Midgley P. A., Acc. Chem. Res., 36(1), 20(**2003**).
3. Bruss A.S., Gelesky M.A., Machado G., Dupont. J.,"*J. of Molecular Catalysis A".,* 252, 212-218 (**2006**).
4. Firooz A.A., Mahjoub A.R., and Khodadadi A.A., World Academy of Science, Engineering and Technology 76, 138-140(**2011**).
5. Jansat S., Gomez M., Philippot K., Muller G., Guiu E., Claver C., Castillon S., Chaudret B., "*J. Am. Chem. Soc".,* 126, 1592 (**2004**).
6. Faraday M., Philos. Trans. R. Soc. London, 147, 145 – 153 (**1857**).
7. Turkevich J., Gold Bull., 18, 86-91(**1985**).
8. Hashemipour H., Zadeh M. E., Pourakbari R., and Rahimi P., "*International Journal of the physical sciences*", 6(18), 4331-4336 (**2011**).
9. Creighton J.A.; Eadon D.G., *J. Chem. Soc. Faraday Trans.*, 87, 3881 (**1991**).
10. Wechuysen B.M., In-situ spectroscopy of Catalysts, American Scientific Publishers, CA, USA, (**2004**).
11. Tu W., Liu H. and Liew K., J. Colloid Interf. Sci., 229, 453 (**2000**).
12. Hirai H., Toshima N., *In Catalysis by Metal Complexes: Tailored Metal Catalyst*, Iwasawa Y (Ed.), Reidel Publishing Company, Dordirect, (**1986**).
13. Toshima N., *Macromol. Symp.*, 156, 45 (**2000**).
14. Hirai H., Chawanya H., N. Toshima, React. Polym., 3,127(**1985**).
15. Zuo Xiao-bin and Liu Han-fan, *Chinese Journal of Polymer Science Vol. 26, No. 1, 23-29* (**2008**).
16. Bell A.T., Science, 299, 1688 (**2003**).
17. Tsunoyama H., Sakurai H., Tsukuda T., "*Chem. Phys. Lett*"., 429, 528(**2006**).
18. Somorjai G.A., Bratlie K.M., Montano M.O., Park J.Y., *"J. Phys.Chem. B".*, 110, 2014, (**2006**).
19. Zhang Z. T., Zhao B. and Hu L. M., *J. Solid State Chem.,* 105,121 (**1996**).
20. Goel A., Sharma S., "*Trans. Met. Chem".*, 35, 549-554 (**2010**).
21. Goel A., Sharma S., Shakunj., "*Int. J. Chem. Sci*"., 6(4), 1891-1899 (**2008**).
22. Meena V.K., Meena R.C, "*J. Ind. Council Chem*",27(2),180-184(**2010**),
23. Narayan R., and El-Sayed M. A., "*J. American Chemical Soc*"., 125(27), 8340 (**2003**).
24. Fu X., Wang Y., Wu N., Gui L., Langmuir, 18, 4619(**2002**).
25. Narayanan R., El-Sayed M.A., J. Phys. Chem. B, 108, 5726 (**2004**).
26. Crooks R.M., Zhao M., Sun L., Chechik V., Yeung L.K. Acc. Chem. Res., 34, 181(**2001**).
27. Bönneman H., Richards R.M., Eur. J. Inorg. Chem., 10, 2445(**2001**).

Table 1: Effect of reactant concentration on Nanocluster size

Met hod	Precursor (mol dm^{-3})		Stabilizer (mol dm^{-3})		Reductant (ml)	NaOH (ml)	Diameter (nm)	
	Iridium	Concentration	Polymers	Concent-ration	Methanol	(0.2M)	XRD	TEM
a.	$H_2 IrCl_6.6H_2O$	$2.83 *10^{-5}$	PVP	$1.4*10^{-4}$	25 ml	1.6 ml	10.55	10.00
b	$H_2 IrCl_6.6H_2O$	$1.54*10^{-5}$	PVP	$1.4*10^{-4}$	25 ml	1.6 ml	42.50	50.00
c.	$IrCl_3.3H_2O$	$7.07*10^{-4}$	PVP	$8.69*10^{-5}$	25 ml	1 ml	3.91,4.46	4.00

Table 2: Kinetic parameters for oxidation of glycine and methyl orange by HCF (III) in the presence of Ir-nano catalyst

Parameter/ Substrate	E_a (k cal mol^{-1})	A (l mol^{-1} sec^{-1})	$-\Delta S^{\#}$ (E.U.)	$\Delta H^{\#}$ kcal / mol	$\Delta F^{\#}$ kcal / mol
Glycine (Ir-precursor)	13.8	1.65 x 10^{-8}	23.03	13.2	20.4
Glycine (Ir-nano catalysed)	12.2	6.89 x 10^{-6}	29.3	11.6	20.7
Methyl Orange (uncatalysed)	18.9	7.36 x 10^{-12}	11.4	18.3	14.6
Methyl Orange (catalysed)	8.6	1.56 x 10^{-6}	20.0	7.9	1.6

Table 3: Diameter of nano-particles before and after recovery

S. No.	Diameter of the particles (nm) before starting of the reaction	Diameter of the particles (nm) after completion of the reaction
1.	10.55	12.63 $\pm$ 0.34 with glycine
2.	4.5	5.70 with methyl orange
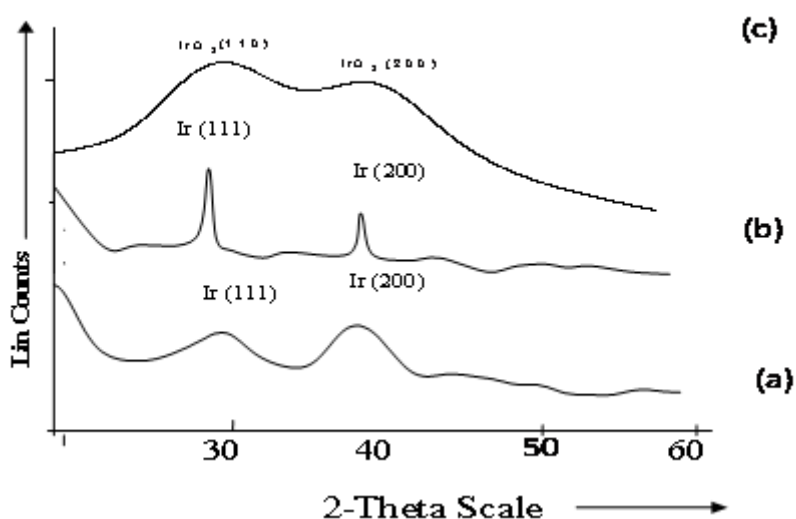
Figure 1: XRD Spectra of Ir-nano prepared by Method 'a', 'b' and 'c'
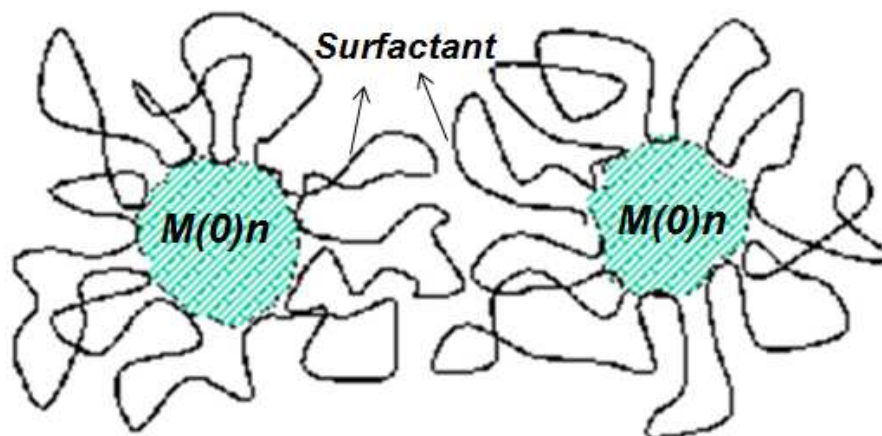
Figure 2: The schematic representation of the steric stabilization of transition metal Nanoclusters
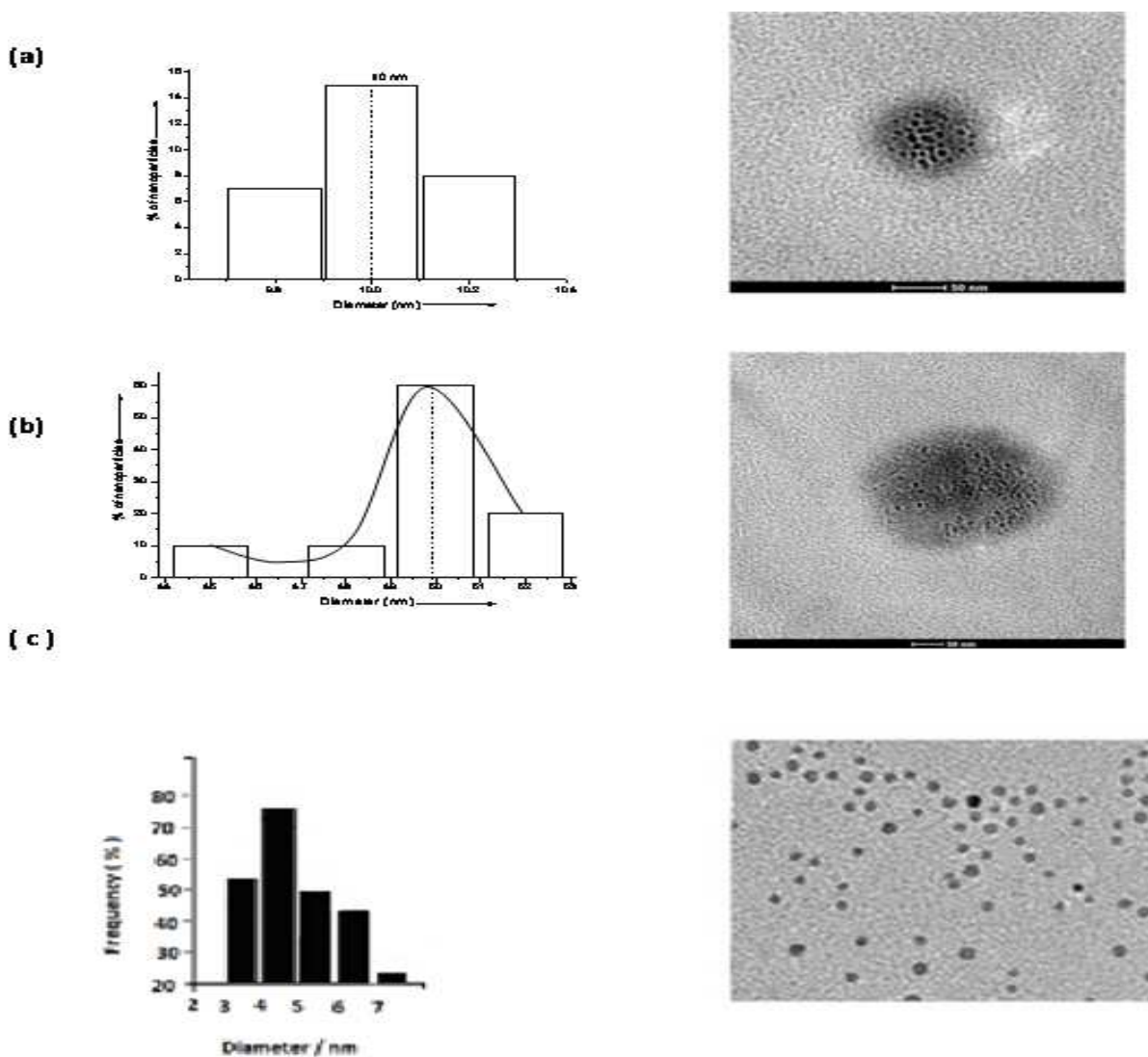
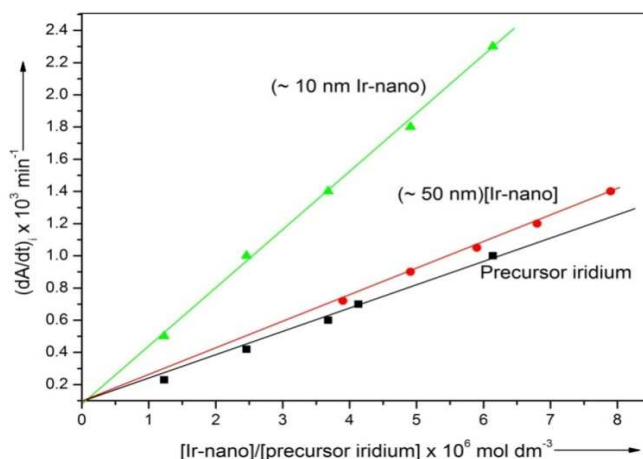**Figure 3: TEM Micrograph (a), (b) and (c) of Ir-nano Synthesized by method a, b, and c respectively**

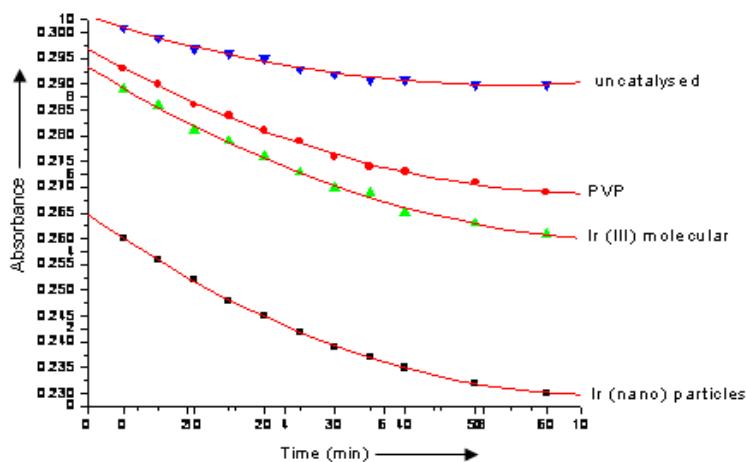**Figure 4: Plots between rate vs concentration of precursor iridium/≈10nm Ir-nano/ ≈50nm Ir-nano for the oxidation of glycine.**

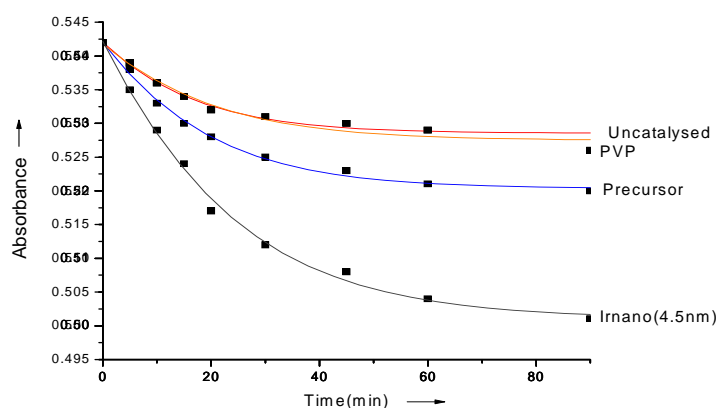**Figure 5: Plots between absorbance and time for the effect of uncatalysed, PVP, Ir (III) bulk and Ir-nano on the rate of oxidation of glycine.**
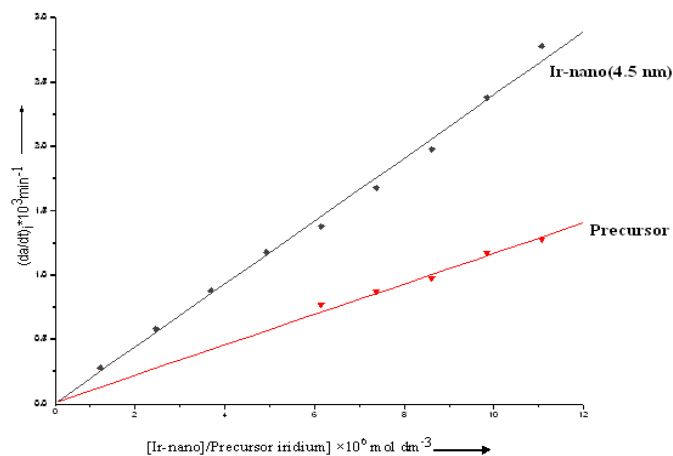

Figure 6: Plot between absorbance and time for the effect of uncatalysed, PVP, Ir (III) bulk and Ir-nano on the rate of oxidation of methyl orange.

Figure 7: Plots between absorbance and time for the effect of uncatalysed, PVP, Ir (III) bulk and Ir-nano on the rate of oxidation of methyl orange.
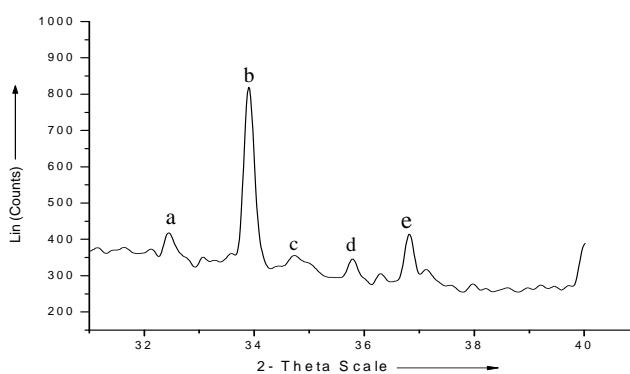

Figure 8: XRD spectra of Ir- nano particles after recovery with glycine amino acid.
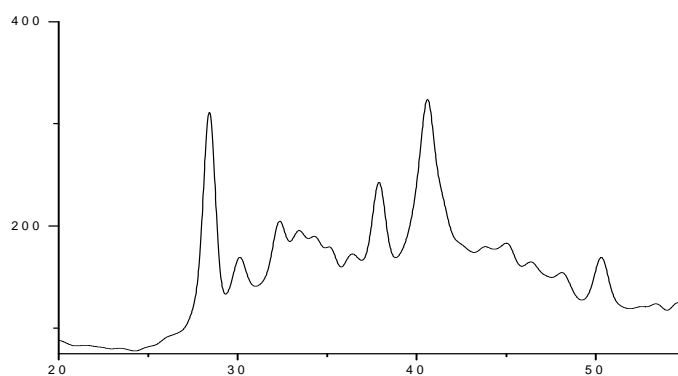

Figure 9: XRD spectra of Ir-nano particles after recovery with methyl orange dye.

217