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Synthesis and Characterization of Nanoscale Colloidal Iridium Metal Clusters by Chemical Reduction Method using Monohydric and Dihydric Alcohols

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Abstract

Chemistry plays an important role in the area of nanotechnology as it endeavor to prepare pure, crystalline, surface-derivatized nanoclusters, which can be processed in potential applications. Iridium metal is promising candidate for a wide range of applications due to its chemical stability, high melting point, high mechanical strength, superior oxidation resistance and high electrical conductivity. The present study involves the synthesis of iridium nanoclusters by the reduction of iridium chloride using polyvinylpyrrolidone (abbreviated as PVP) as protecting agent. This method is often called "alcohol reduction method", which is a very simple and convenient process for the production of metal nanoclusters, often stabilized by organic polymers. Synthesized nanoclusters were characterized by ultra violet spectroscopy (abbreviated as UV-vis spectroscopy), X-Ray diffractogram (abbreviated as XRD) and transmission electron microscopy (abbreviated as TEM) methods of analysis. The absorption spectra of all samples show an absorption peak at about 415nm. The intensity of this peak decreases with the increase of time. After about 25 minutes refluxing this absorption peak disappears and a new peak appears at about 235nm indicating the formation of Ir (0) nanoclusters. No further change was observed. During synthesis the colour of solution changes from yellow to black-brown. X-ray diffractrogram of these metallic clusters indicate that they are amorphous. The approximate cluster size from the X-Ray diffractogram was calculated using Scherrer equation. The cluster size ranges between 3.16 to 5.67 with methanol and 33.72 to 48.4 with ethanol (monohydric alcohols) while with ethylene glycol (dihydric alcohol) it ranges between 6 to 7nm. The average cluster size estimated by TEM was around 4.2

to7.01nm for the cluster prepared using methanol reductant, 27.8 to 33.5 using ethanol reductant, 9.6nm using ethylene glycol and 35nm using n-propanol reductant . TEM micrograph also shows that Ir-nano clusters are separated with no agglomeration tendency and spherical in size. The results of Fourier transmission electron microscopy (abbreviated as FTIR) indicate the presence of nanoclusters of Ir (0) which were stable in solution without precipitation for at least 180 days.

Keywords: Chemical reduction, Iridium, Nanoclusters, polymer.

Introduction

Nanoparticles posses many novel chemical and physical properties and have possible future application in ceramics, catalysis, optics[1]-[2], ferrofluids for biological applications[3], light-emitting diodes [4], chemical sensors [5], quantum computers [6], quantum dots [7], quantum devices[8],electronics and magnetic storage [9]-[10] and a new type of highly active and selective catalysts[11]. Nanoparticles of many metals, such as gold, platinum, palladium, cobalt, rhodium and silver have been synthesized with a wide variety of experimental techniques [12]-[15]. In this section a recently developed method of synthesis of nanoparticles is salt reduction-based synthesis, would be explained, as it was applied to the metal ruthenium, silver, gold [16]-[18] but it is scarcely discussed for synthesis of iridium nanoparticles from $IrCl_3$. Fievet et al [19]-[20] have successfully used this process for the synthesis of fine, highly pure, monodisperse, non-agglomerated particles of Cu. However, transition metal nanoclusters are only kinetically stable and thermodynamically unstable in solution to agglomerate into bulk metal. Therefore, special precautions have to be taken to avoid their aggregation or precipitation during the preparation of such nanoclusters in solution [21]-[22]. In the present investigation we have prepared metallic dispersions of finely divided Ir (particle size approximately 10 nm) in monohydric and dihydric alcohols. This serves both as solvent and reducing agent of metal species. Synthesis of these nanosize metals was achieved by varying the reaction temperature, the initial concentration of metal precursor, NaOH, and the mode and order of addition of reactants.

Experimental Materials and Methods

All chemicals used in this research work were of reagent grade. Ethylene glycol, ethanol, methanol, n-propanol served as reducing agent as well as solvent. polyvinylpyrrolidone (abbreviated as PVP) were used as protective agent. iridium trichloride is used as metal precursor. The colloidal iridium nanoclusters were synthesized by reduction of $IrCl_3.xH_2O$ with monohydric and dihydric alcohols using polyvinylpyrroliodone as protecting agent. For this preparation 7.9×10^{-4} mol of $IrCl_3.3H_2O$ were dissolved in 25 ml of solvent. In another beaker 3.78×10^{-6} mol of polyvinylpyrrolidone was added in 18.4 ml of water. Both the solutions were mixed slowly at room temperature by stirring magnetically. Then 1 ml of an aqueous

solution of NaOH (0.2M) was added dropwise with vigorous stirring. Now the solution was transferred in a three naked round bottom flask and heated in oil bath for 1-2 hrs. At that time the temperature was noted until the color of the solution was changed from brown to black. PVP stabilized nanoparticles were obtained. These nanoparticles were dried at 70^0C temp, and analysed by ultra violet spectroscopy (abbreviated as UV-vis spectroscopy), X-Ray diffractogram (abbreviated as XRD) Fourier transmission electron microscopy (abbreviated as FTIR) and transmission electron microscopy (abbreviated as TEM) techniques**.**

Results and Discussion

Various methods [23]-[27] have been reported in the literature for preparing Iridium nanocrystals. We have prepared iridium nanoclusters by reducing iridium trichloride with monohydric and dihydric alcohols at 180^0C temperature. The data are presented in Table 1. The average particle size of the best method among all the methods used was calculated to be nearly 3.16 to 5.17 nm and matches well with the 4.2, 4.5 and 7.01nm average diameter determined from TEM (Fig3).

UV-vis spectrophotometry is a convenient technique for monitoring the progress of metal colloid formation [28]. A PVP- $IrCl_3$- alcohol-water solution exposed in an oil bath was characterized by Backman Coulter UV-visible spectrophotometer as can be seen from fig 1 $IrCl_3$ shows an absorption peak in UV-region at 240nm, the intensity of this peak in different solvents is nearly same as wavelength increases the peak starts disappearing indicating the reduction of $IrCl_3^{3-}$. After 300nm no peak was observed showing that $IrCl_3^{3-}$ has been completely reduced.

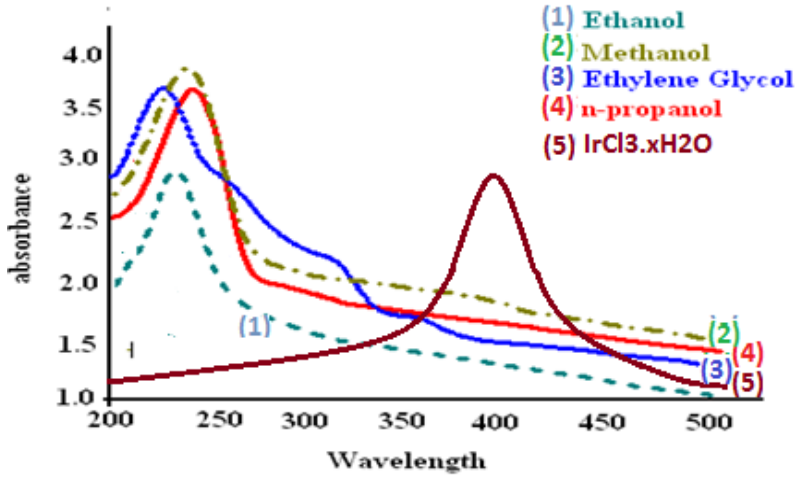


Figure 1: Uv-absorption peak indicating the reduction of $IrCl_3^{3-}$

X-Ray-diffraction was performed on the dry powders using Bruker Axs D-8 Advance diffractometer with a scan rate 10 min^{-1} and Cu K_α(λ=0.154 nm).

(Fig.2a)The X- ray diffractogram of these metallic particles indicate that they are amorphous and show broad peak characterization of materials with a small size [29]. Using the Scherrer Formula, we found the approx crystal size of the iridium nanoclusters. Increasing digestion period there is no effect on the size of nanoclusters. (Fig 2b) shows two broad peaks at 2 theta 30 and 45^0 by increasing OH^- with methanol there is no effective change in the broadening of peaks but with ethanol sharp and narrow peaks are shown at 2-theta 30, 35 and 40^0 which indicates crystalinity of nanoclusters increases with increasing OH^-. (Fig 2c.) shows sharp and narrow peaks with ethanol at 2-theta 35 and 45^0 sharpness of peak indicates crystalinity of nanoclusters as time period of digestion increases sharpness of peaks increases which indicates the crystalinity of nanoclusters increases with increasing digestion period. Fig (2d) shows sharp peaks with n-propanol and broad peak with ethylene glycol which indicates the presence of crystallinity with n-propanol and but broad peak with ethylene glycol indicates amourphous nature of nanoclusters.

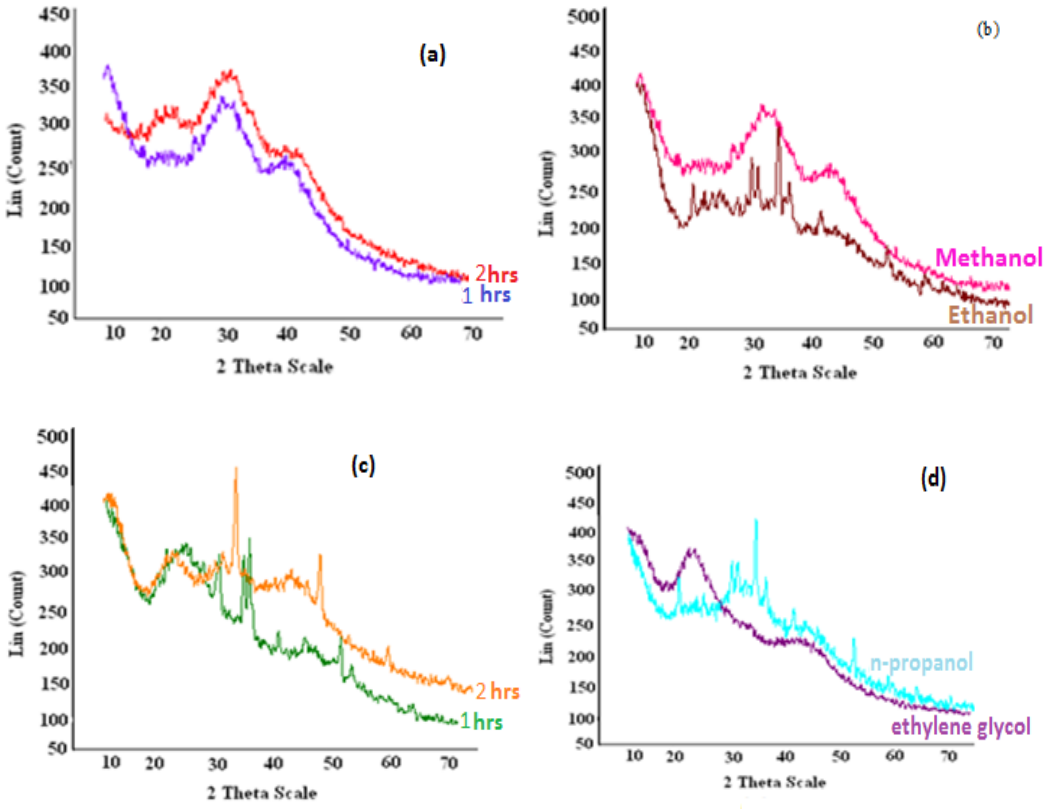
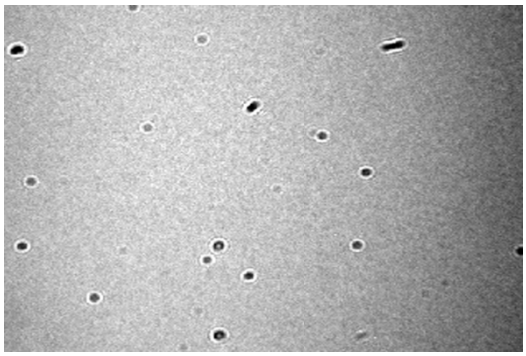


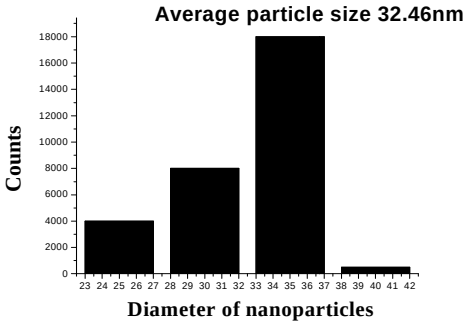
Figure 2: (a) X-Ray diffraction pattern when methanol used as solvent and heated for 1 and 2 hrs respectively. (b) Ethanol and methanol are used as solvents with increasing 0.2M NaOH and heated for 1 hrs respectively. (c) Ethanol used as solvent and heated for 1 and 2 hrs respectively.(d) Ethylene glycol and n–Propanol used as solvent and heated for 2hrs respectively.

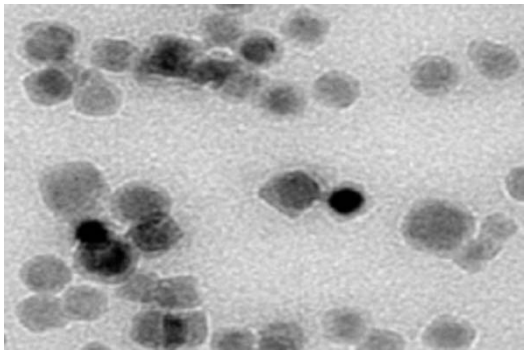
Table I: Synthesis conditions and diameter of iridium nanoclusters

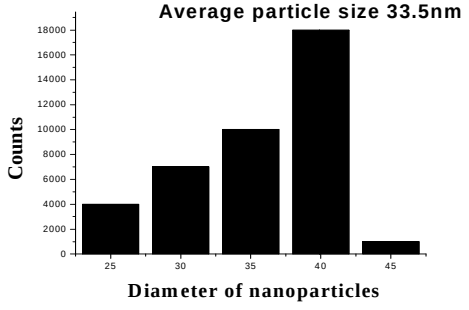
S. No	Solvent	Amount of Solvent	Amount of NaOH	Amount of water	Time	Colour	Diameter	
							By XRD	TEM
1.	Ethanol	25 ml	2ml	18.4	1 hrs.	Brown to Black	40.7,33.72,42.14,43.34	32.5nm
2.	Ethanol	25 ml	1 ml	18.4	1hrs.	Brown to Black	43.6,42.1,48.4	33.5nm
3.	Ethanol	25 ml	1 ml	18.4	2hrs.	Brown to Black	14.0,20.65,21.76,22.12	27.8nm
4.	Methanol	25 ml	1 ml	18.4	1hrs.	Brown to Black	3.16,5.67	7.01nm
5.	Methanol	25 ml	1 ml	18.4	2hrs.	Brown to Black	4.12,4.23	4.5nm
6.	Methanol	25 ml	2 ml	18.4	1hrs.	Brown to Black	3.91,4.46	4.2 nm
7.	n –Propanol	25 ml	1 ml	18.4	2hrs.	Brown to Black	41.2, 42, 43	35nm
8.	Ethylene Glycol	25 ml	1 ml	18.4	2hrs.	Brown to Black	6.20,7.0	9.6nm

It can be revealed from the data presented in Table 1 that the size of iridium nanoclusters ranges between 4.2 to 7.01 with methanol and 27.8 to 33.5 with ethanol (monohydric alcohols) while with ethylene glycol (dihydric alcohol) it ranges 9.6nm by TEM.









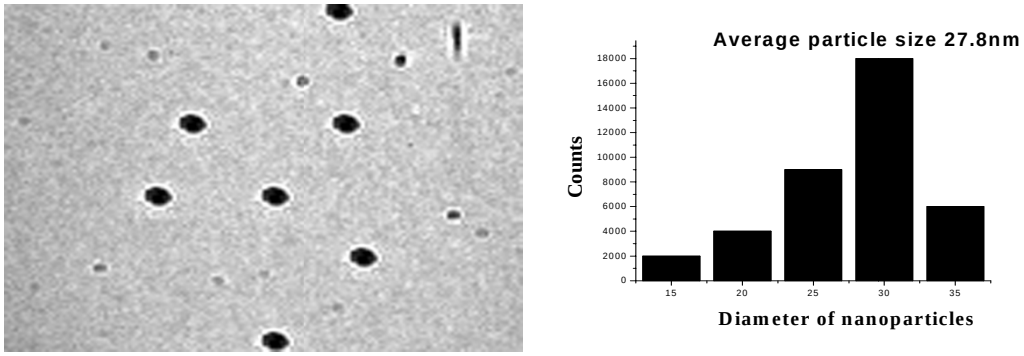


Figure 3: TEM pictures of the iridium nanoclusters prepared by reduction method using ethanol reducatnt. (a)on increasing OH^-. (b)digested for 1 hrs. (c) digested for 2.hrs.

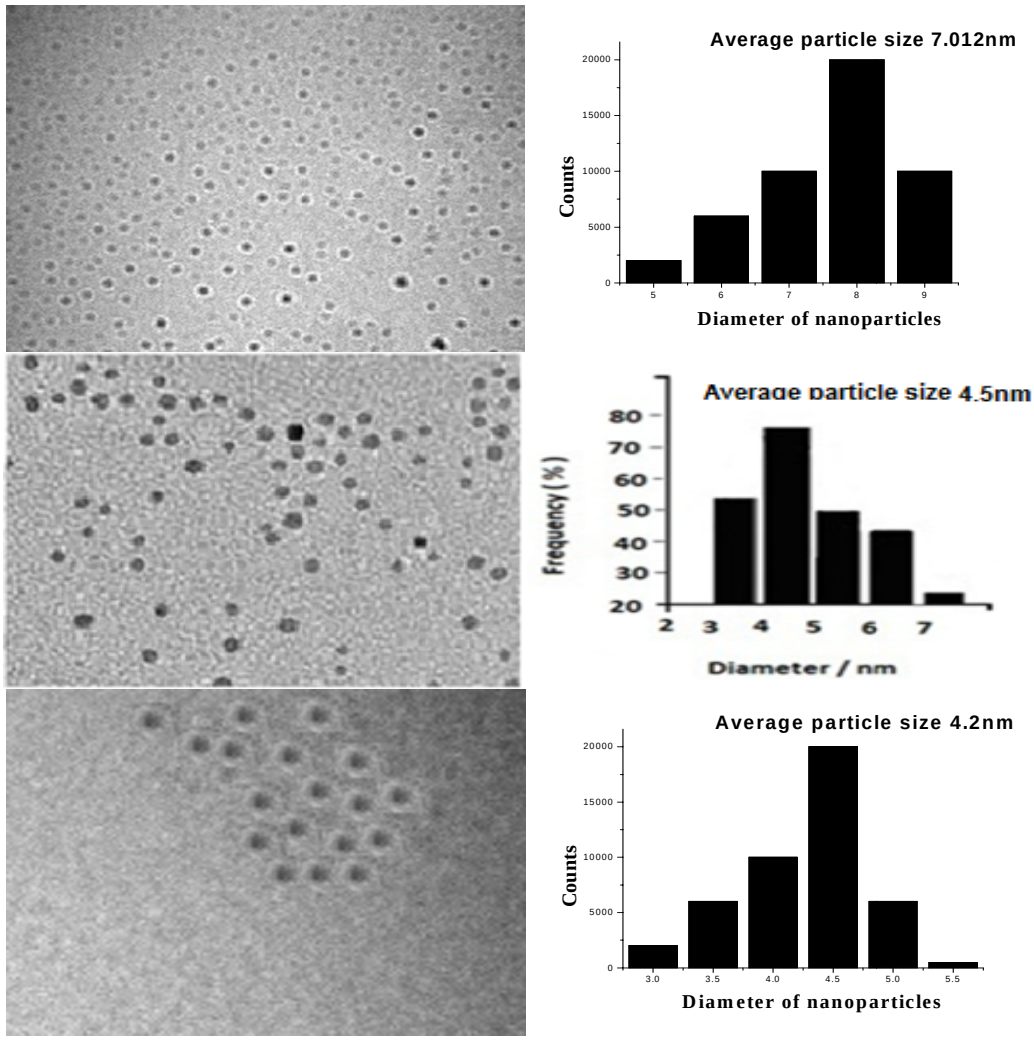


Figure 4: TEM pictures of the iridium nanoclusters prepared by reduction method using methanol reductant. (a)digested for 1hrs. (b) digested for 2hrs. (c) digested on increasing OH^-.

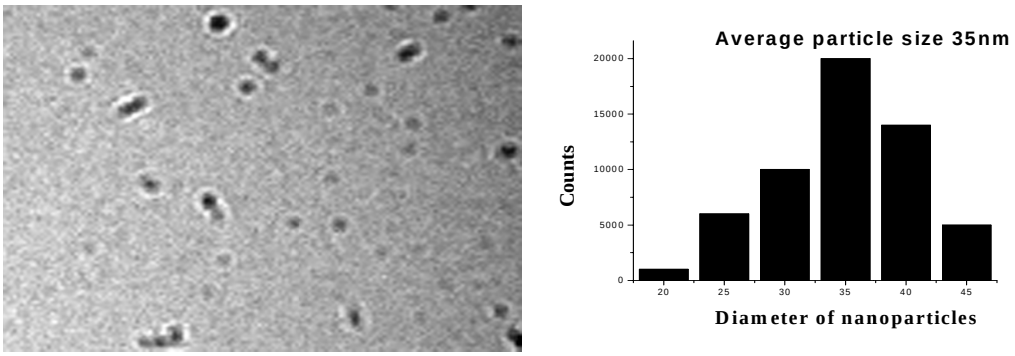


Figure 5: TEM pictures of the iridium nanoclusters prepared by reduction method using n-propanol reductant.

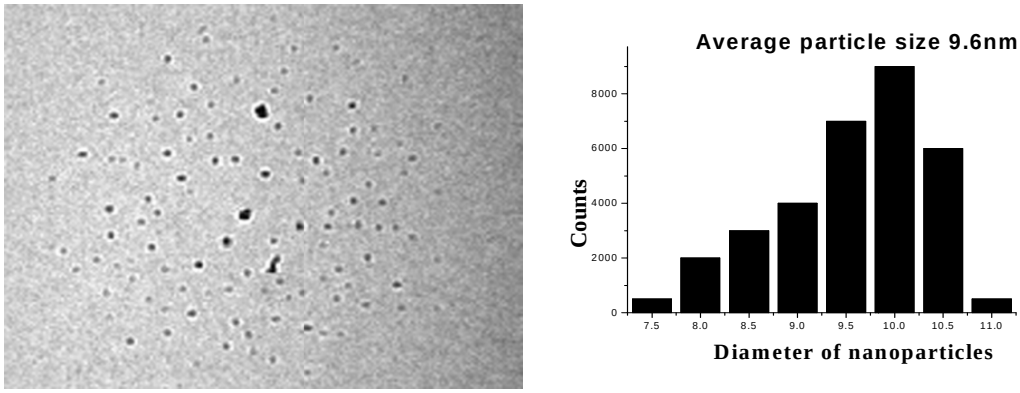
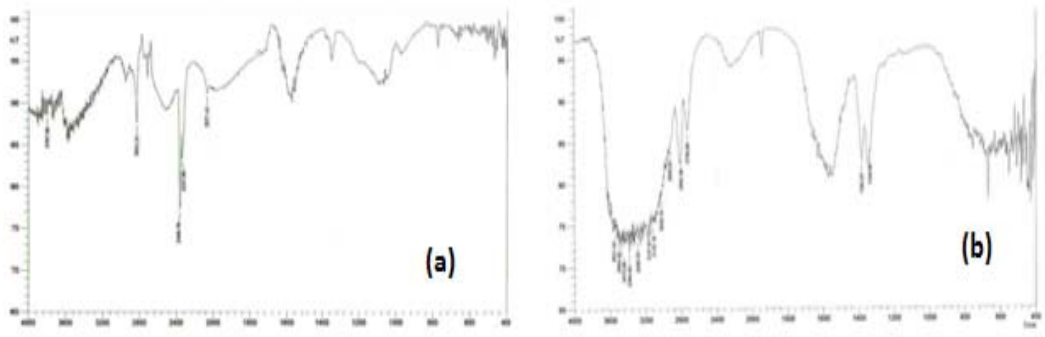


Figure 6: TEM pictures of the iridium nanoclusters prepared by reduction method using ethylene glycol reductant.

Infrared spectroscopy determines the position and relative sizes of all the absorption, or peaks in the infra red region. Fig (7) shows the IR spectra of precursor iridium and Ir-nano-clusters synthesized in different solvents. The peaks under the region 2665 cm^{-1} and 2773 cm^{-1} [Fig 7] may be due to precursor iridium but a new band near the frequency 2015 cm^{-1} indicates the formation of Ir (0) [30].



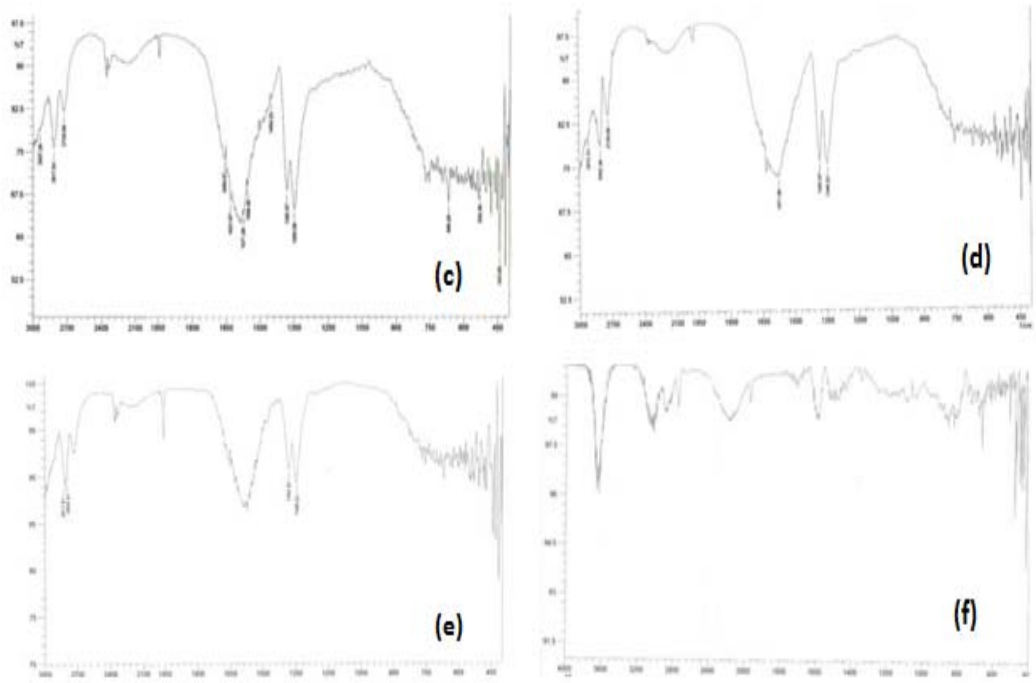


Figure 3: (a.) FTIR spectra of $IrCl_3$ salt. (b) Nanoclusters synthesized by using methanol as solvent. (c) Nanoclusters synthesized by increasing NaOH using ethanol as solvent and (d) using methanol as solvent. (e) Nanoclusters synthesized by using n-propanol as solvent and (f) using ethylene glycol as solvent.

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 (fig.08) [31**].**

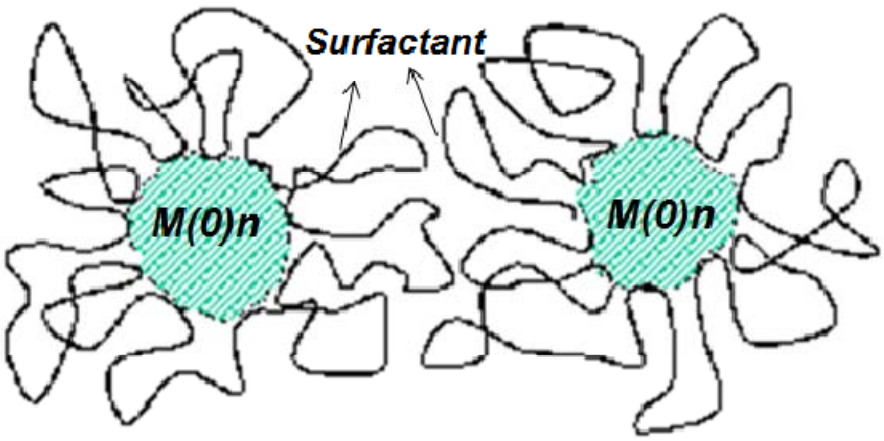


Figure 8: The schematic representation of the steric stabilization of transition metal

Nanoclusters

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[32].

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[33] 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.[34].

Conclusion

PVP stabilized colloidal iridium nanoclusters with an average particle size ranges from 35 nm to 4.2 nm, can be generated easily from the reduction of precursor material $IrCl_3.3H_2O$ with monohydric and dihydric alcohols which remain stable even after several months. TEM analyses of the PVP stabilized colloidal iridium(0) nanoclusters indicated that all of the nanoclusters are in spherical shape with narrow particle size distributions and separated by no agglomeration tendency. XRD patterns of PVP stabilized colloidal iridium (0) nanoclusters showed that these nanoclusters 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. According to literature nanoclusters < 10 nm size works as good catalyst. Iridium(0) nanonoclusters size ranges from 27.8 to 33.5nm with ethanol, 35nm with n-propanol which is quite large but colloidal iridium(0) nanocluster size ranges from 4.2 nm to 7.01 nm with methanol and 9.6nm with ethylene glycol. During synthesis I observed that it is complicated to synthesize iridium nanoclusters with ethylene glycol so the method in which methanol is used as solvent and reducing agent is the best method for synthesis of nanoclusters because of narrow size distribution and these are used in catalysis of many chemical reactions and further used as catalyst for oxidation of some reacti**ons.**

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