

# Synthesis of Colloidal Iridium Nanoparticles and Their Role as Catalyst in Homogeneous Catalysis – An Approach to Green Chemistry

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## Abstract

*The formation of colloidal iridium nanoparticles has been carried out by the chemical reduction of  $H_2IrCl_6$  with methanol using polyvinyl-pyrrolidone as protecting agent. The synthesized iridium nanoparticles were characterized by IR, UV-vis Spectrophotometer, XRD, TEM and XPS methods of analysis. The catalysis by iridium nanoparticles was studied kinetically using the oxidation of amino acid – hexacyanoferrate(III) (abbreviated as AA & HCF(III) respectively) reaction in alkaline medium. The colloidal iridium nanoparticles were found to be more effective catalyst for oxidation of AA. The catalytic system could be recycled and reused without loss of activity.*

## Introduction

Colloidal transition metal nanoparticles are recently receiving increased attention since they hold promise for use as advanced materials with new electronic, magnetic, optical, and thermal properties[1]. In addition to their interesting physical properties exhibited due to quantum size effect, they also have applications in catalysis due to their large surface area and special morphologies. With the improved developments in nanochemistry, it is now possible to prepare soluble analogues of heterogeneous catalysts, which might have properties intermediate between those of the bulk metal and single metal-particle (homogeneous) catalysts. The nanoparticle-based catalytic systems generally exhibit superior catalytic activities than the corresponding bulk materials<sup>2-9</sup>. The recycling of both ligand and metal is highly desirable for reducing raw material costs and engineering a greener process via limiting the amount of waste chemicals for disposal. In this study, we have synthesized colloidal iridium nanoparticles by chemical reduction method. The catalysis by these iridium nanoparticles was studied kinetically using the oxidation of some amino acids (like glycine and alanine)- hexacyanoferrate(III) reaction in alkaline medium.

## Experimental Section

### Chemicals

All the reagents used were of AR grade. All solutions were prepared with doubly distilled water.  $K_3[Fe(CN)_6]$  was recrystallized before use. Its solutions were kept in amber colored bottles to prevent photodecomposition. Catalyst was prepared by the reduction of  $H_2IrCl_6$  (Merck). Polyvinyl-pyrrolidone (SRL) and Methanol (Merck) was used as stabilizing agent and reducing agent respectively. KCl (Merck) and NaOH (Merck) were used to provide the required ionic strength and alkalinity respectively.

### Preparation of Colloidal Iridium Nanoparticles

In the present work colloidal iridium nanoparticles were synthesized by reduction of dihydro-hexachloroiridic acid (Merck) with methanol using polyvinyl-pyrrolidone as protecting agent. PVP-stabilized nanoparticles were obtained. These nanoparticles were dried at 50°C temperature and analyzed by UV-vis spectrophotometer, IR, XRD, XPS and TEM.

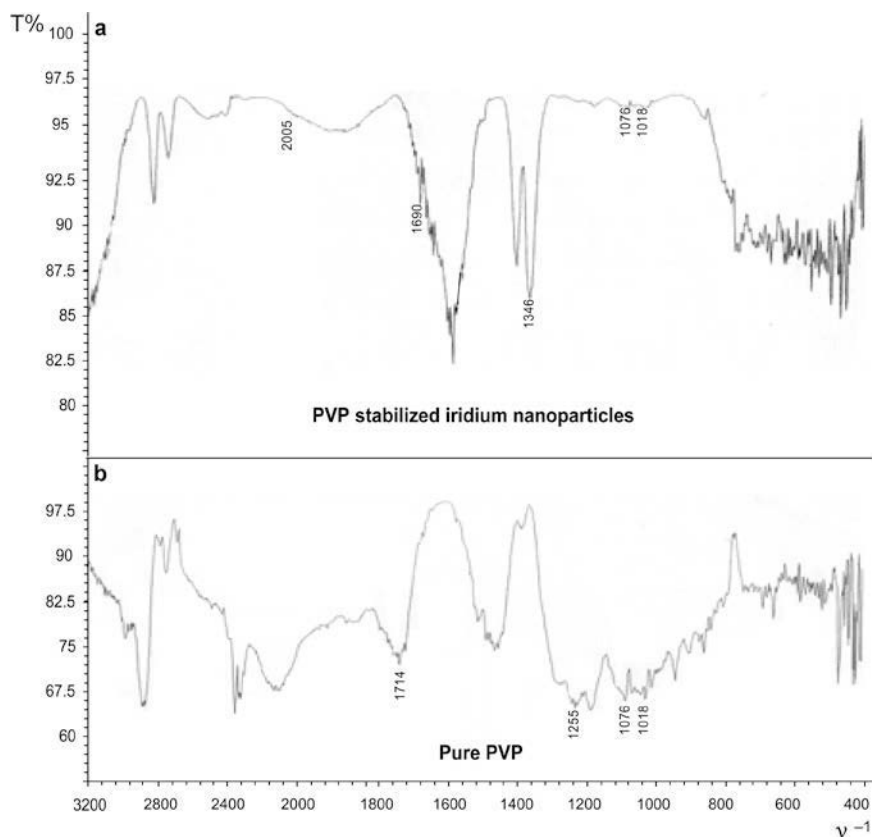
### Characterization of the Iridium Nanoparticles

Typical transmittance FTIR spectra of the PVP stabilized iridium nanoparticles and the pure PVP employed in the synthesis are shown in Fig. 1a and 1b respectively. The peaks were identified by comparing with literature value [10, 11]. Fig 1(a) shows that there is no peak due to precursor under the region  $2550\text{cm}^{-1}$ . The peak at  $1690$  (Fig. 1a) is due to red shift of resonance peak of pure PVP at  $1714\text{cm}^{-1}$  (Fig. 1b) indicating the interaction of  $>\text{C}=\text{O}$  group of PVP with nanoparticles. The appearance of a new weak peak at  $2005\text{cm}^{-1}$  due to iridium (PVP- stabilized) shows formation of iridium nanoparticles from  $\text{H}_2\text{IrCl}_6$ . UV-vis Spectrophotometer is a convenient technique for monitoring the progress of metal colloid formation. A PVP-  $\text{H}_2\text{IrCl}_6$ - methanol-water solution kept in an oil bath was sampled at different time and then the samples were characterized by UV-vis Spectrophotometer. As can be seen from Fig. 2  $\text{IrCl}_6^{2-}$  shows an absorption peak at  $487\text{nm}$ , the intensity of

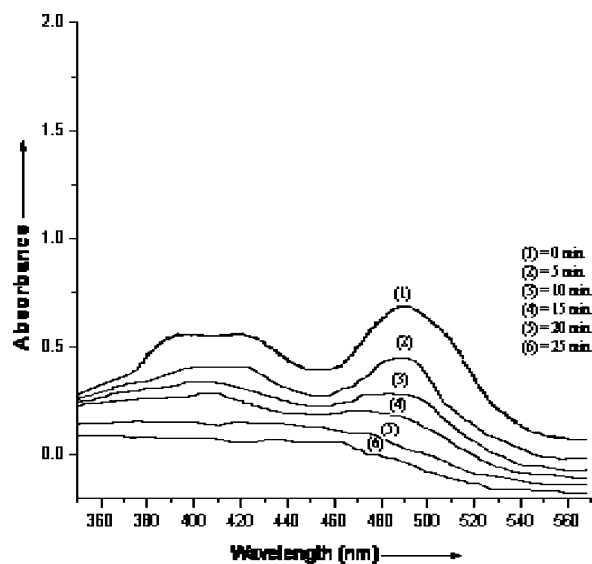
this peak decreases with the passage of time. After about 15 minutes the absorption peak starts disappearing indicating the reduction of  $\text{IrCl}_6^{2-}$ . After 25 min no peak was observed showing that  $\text{IrCl}_6^{2-}$  has completely reduced. XRD was performed on the dry powders obtained after the evaporation of solvent using Bruker Axs D-8 Advance diffractometer with a scan rate  $1^\circ\text{min}^{-1}$  and a  $\text{Cu K}_\alpha$  X-ray source ( $\lambda = 0.154\text{nm}$ ).

The XRD analysis (Figure 3) shows the presence of very small particles. The diffraction peaks were assigned as correspond to the iridium colloidal particles at  $2\text{-theta}$   $34.4$ ,  $35.3$ ,  $38$ ,  $40$  and  $42$  for iridium and iridium oxide. Analysis of the peaks broadening using the Scherrer equation gives an estimate of particle diameter. The X-ray diffractograms of these metallic particles show broad peaks characterization of materials with a small size.

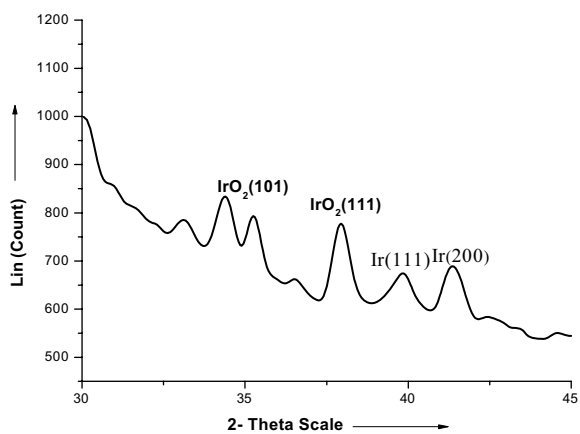
Nanoparticles were also characterized by Transmission Electron Microscope (Philips). Fig. 4 shows a representative TEM image of iridium colloidal particles. It appears that the Ir (nano) particles are sepa-



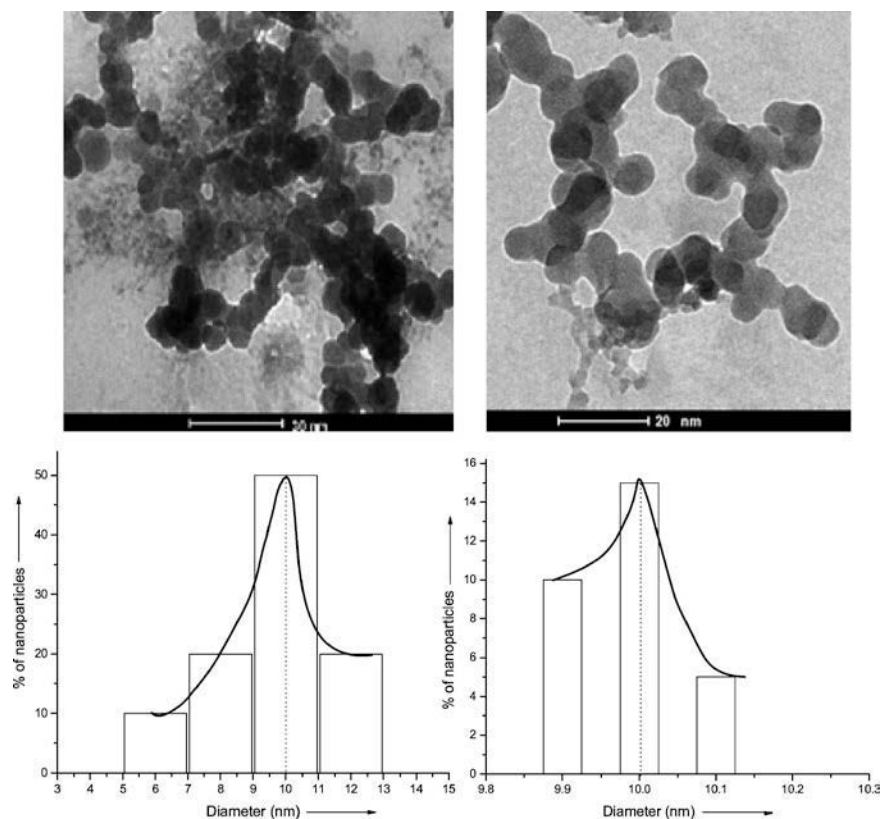
**Fig. 1:** FT-IR spectra of (a) PVP- stabilized iridium nanoparticles (b) Pure PVP



**Fig. 2:** Ultraviolet absorption spectra during the formation of iridium nanoparticles in the PVP-  $\text{H}_2\text{IrCl}_6$  –methanol – water system after different irradiation time



**Fig. 3:** XRD pattern of Ir (nano) particles



**Fig. 4:** TEM micrograph and corresponding particle size distribution histogram of iridium Nanoparticles

rated with no agglomeration tendency. Representative TEM micrograph shows that individual iridium nanoparticle is similar to spherical. The particle size distributions obtained from TEM images were fairly narrow and an average particle size was estimated to be around 10 nm.

The produced nanoparticles were analyzed by X-ray photoelectron spectroscopy (Fig. 5). The XPS spectrum shows typical Ir(0), IrO<sub>2</sub> absorption at 60.7 eV, 65.0 eV and 63.0 eV, 67.5 eV for f<sub>7/2</sub> and f<sub>5/2</sub>. This absorption is consistent with those reported in the literature [12,13].

### Kinetic Study

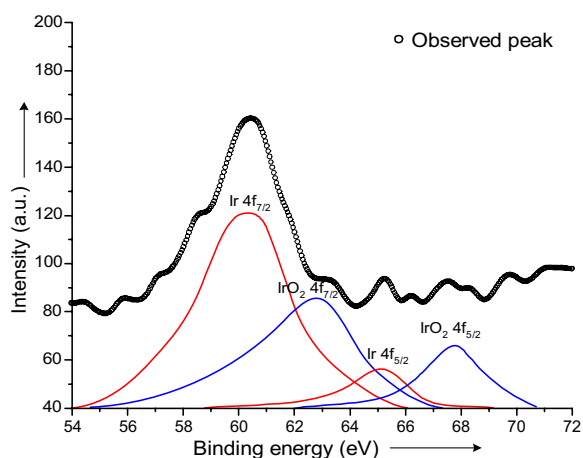
The kinetic measurements were performed at constant ionic strength of 0.50 mol dm<sup>-3</sup> and at constant temperature 35.0 ± 0.1 °C. The requisite amount of each reactant was thermostatted at 35 °C to attain thermal equilibrium. The appropriate quantities of reactants were mixed in a 100 ml iodine flask. The progress of reaction was measured by injecting a solution of amino acid into the reaction mixture at λ<sub>max</sub> 420 nm corresponding to the [Fe(CN)<sub>6</sub>]<sup>3-</sup>. It was verified that there is negligible interference from other species present in the reaction mixture at this wavelength.

The kinetic study reveals that the oxidation of AA by HCF(III) in aqueous alkaline medium catalyzed by

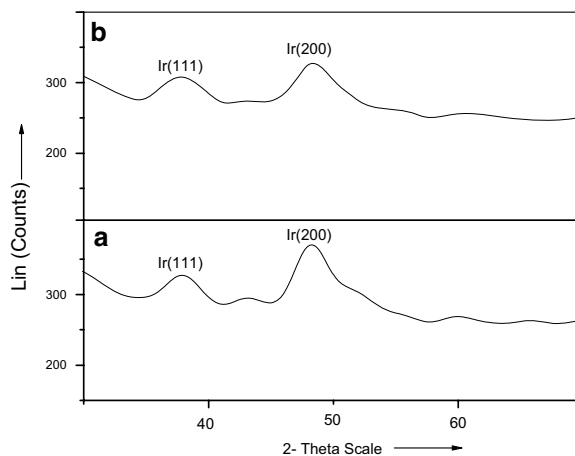
Ir-nano are same as catalyzed by bulk iridium [14,15]. The comparisons of results show that Ir-nano is more effective catalyst as compared to bulk iridium. They have the advantage of being recyclable and reusable but the recycled particles are agglomerated (Fig. 6). The catalyst was isolated via centrifugation and analyzed by XRD and TEM.

### Conclusion

The present study shows that iridium nanoparticles acts as effective catalyst in the oxidation of AA by HCF(III) ions and the reaction proceeds through an electron transfer process. The data shows larger negative value of entropy of activation and a low value of energy of activation. A large -ive value of ΔS<sup>#</sup> shows that the complex formed is more ordered and polar. Iridium nanoparticles, which were prepared by reduction of H<sub>2</sub>IrCl<sub>6</sub>, remain stable after several months. The X-ray diffractograms of these metallic particles show broad peaks characterization of materials with a small size. TEM micrograph shows that iridium nanoparticles were separate by no agglomeration tendency and are similar to spherical with narrow size distribution. The kinetic study on the oxidation of AA by HCF(III) shows that iridium nanoparticles act as good catalyst in the above said reaction.



**Fig. 5:** X-ray photoelectron spectra of the PVP stabilized Ir(0) and IrO<sub>2</sub> nanoparticles



**Fig. 6:** XRD pattern of Ir(0)-nano obtained by recovery. (a) For recovered Ir-nano after completion of reaction with glycine (b) For recovered Ir-nano after the completion of reaction with alanine

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