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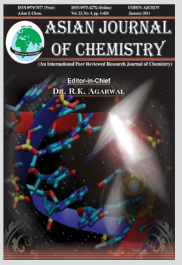

Reduction of 4-Nitrophenol Catalyzed by Platinum Nanoparticles Embedded into Carbon Nanocolloids†

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This paper reports the synthesis and characterization of a platinum nanoparticles catalyst supported on a carbon nanomaterial for the reduction of 4-nitrophenol. Platinum nanoparticles were deposited on the surface of carbon nanocolloids in an aqueous solution. The reduction of 4-nitrophenol in an aqueous solution containing platinum nanoparticles embedded into the carbon nanocolloids was examined by UV-vis spectroscopy and LC-MS. The catalytic activity was observed as a function of time. The fabricated carbon nanocolloids coated with platinum nanoparticles showed superior catalytic performance toward the reduction of 4-nitrophenol than the corresponding only platinum nanoparticles. The carbon nanocolloids acted as a support for the homogeneous dispersion of platinum nanoparticles in an aqueous solution. The order of catalytic effect according to the mole concentration of platinum nanoparticles was as follows: 0.50 mM > 0.25 mM > 0.13 mM > 0.06 mM > 0.03 mM. The nature of the resulting carbon nanocolloids coated with the platinum nanoparticles was characterized by X-ray diffraction and transmission electron microscopy.

Key Words: Nanomaterial, Catalyst, UV-vis spectra, TEM, LC-MS.

INTRODUCTION

Recently, the synthesis and application of metal nanoparticles have attracted considerable attention because of their unique properties compared to their bulk counterparts[1,2] as well as their potential as catalysts[3-5], sensors[6] and optical and electronic devices[7]. Therefore, a range of methods for the preparation of these metal nanoparticles have been developed[8].

Among the different metal nanoparticles, the preparation of platinum nanoparticles has attracted most attention because they can be used as metal colloids and applied as catalysis[9-11]. Most platinum colloids are prepared in aqueous solution with surfactants or hydrophilic polymers as stabilizing agents using chemical reductants[12]. The supporting materials adsorb to the surface of platinum nanoparticles, which stabilize them in the colloid state[13]. The supporting materials play an important role in obtaining a stable dispersion of platinum nanoparticles in solution[14].

Carbon nanocolloids (CNC) are colloidal solution that ranges between 10-50 nm in size. The carbon nanocolloids are stable enough that precipitation does not occur, even after a few months. The density of the carbon nanocolloids generally varies from 0.1 to 5.0 %. The characteristics of carbon nanocolloids include high heat and electrical conductivity as well as lubricous properties, which gives them a wide range of uses in different industries[15].

Metal nanoparticles have been used recently in the hydrogenation of aromatic compounds[16-19] on account of their higher catalytic efficiency than bulk metals from their large surface-to-volume ratios[20,21]. Metal nanoparticles are used as a catalyst to synthesize aromatic amine compounds. In addition, aromatic amines are used widely in industry as an intermediate for the synthesis of agrochemicals and dyes[22,23]. They are normally prepared by the reduction of aromatic nitro compounds through catalytic hydrogenation[24,25] and stoichiometric reduction[26]. Catalytic hydrogenation is a convenient method for reducing aromatic nitro compounds in high yield. This paper reports the reduction of 4-nitrophenol in an aqueous solution with sodium borohydride in the presence of platinum nanoparticles embedded into carbon nanocolloids as a catalyst.

EXPERIMENTAL

Potassium tetrachloroplatinate(II), 4-nitrophenol, $NaBH_4$ were purchased from Sigma-Aldrich. Carbon nanocolloids (CNC) was purchased from N-barotech.

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The synthesized platinum nanoparticles were analyzed using a transmission electron microscope (JEOL Ltd, JEM-2010) at an acceleration voltage of 200 kV. The TEM specimens were prepared by placing a few drops of sample solution on a carbon-coated copper grid. The UV-vis spectra were recorded on a Shimazu UV-1601PC spectrometer. The samples were also analyzed by X-ray diffraction (Rigaku, Rigaku DMAX PSPC MDG 2000). The 4-aminophenol was confirmed using an Agilent Technologies 1200 series HPLC system with a 6410 triple quad LC/MS detector.

Synthesis

Synthesis of platinum nanoparticles by sodium borohydride in carbon nanocolloids: Various concentration of K_2PtCl_4 (0.50, 0.25, 0.13, 0.06 and 0.03 mM) were dissolved in carbon nanocolloids (10 mL), respectively. The resulting solution was stirred at room temperature until complete dissolution of the metal salts. An appropriate amount of sodium borohydride was added to the aqueous solution and the solution was stirred for 10 min at room temperature.

Catalytic efficiency of platinum nanoparticles for the reduction of 4-nitrophenol: The catalytic efficiency of platinum nanoparticles for the reduction of 4-nitrophenol was analyzed. In a typical experiment, a solution containing 0.1 M $NaBH_4$ as a hydrogen source and 0.005 M 4-nitrophenol was mixed with various concentration of platinum nanocolloids (1 mL). The UV-vis spectra of the mixture were recorded continuously upon the addition of platinum nanoparticles. The product of the reduction of 4-nitrophenol *i.e.*, 4-aminophenol was confirmed by the UV-vis spectrum.

Confirmation of 4-aminophenol reduced from 4-nitrophenol by triple quadrupole LC-MS: The HPLC system was an Agilent Technologies 1200 series with a 6410 triple quad LC/MS detector. The mobile phase was acetonitrile and ammonium acetate at the ratio (v/v) of 8:2. The column used was a YMC hydrosphere C_{18} (2.0 mm I.D. × 50 mm) with a particle size of 3 μm. The injection volume was 3 μL and the flow rate was 0.2 mL/min. The column and gas temperature was at 25 ºC and at 300 ºC. The gas flow was 10 L/min (N_2) and Nebulizer was at 20 psi.

RESULTS AND DISCUSSION

The platinum nanocolloids obtained by chemical reduction of their salts in solution can be stabilized by carbon nanocolliods to prevent the aggregation of the platinum nanoparticles. Fig. 1 shows the TEM image of Pt nanoparticles embedded into carbon nanocolloids. The image shows that Pt nanoparticles are well dispersed, embedded and stable in carbon nanocolloids (CNC). The carbon nanocolloids are spherical shape with an average diameter of 10~50 nm. All Pt nanoparticles have quasi-spherical shapes. The average size of the Pt nanoparticles is < 5 nm and the Pt nanoparticles are not aggregated.

Fig. 2 shows the XRD pattern of the canbon nanocolloids. This spectra indicates that dried carbon nanocolloids particles are a mixture of polycrystalline and amorphous structures[15]. The formation of Pt nanoparticles-embedded into carbon nanocolloids was also confirmed by powder X-ray diffraction (XRD). Fig. 3 shows the typical XRD pattern of Pt nanoparticles obtained in the carbon nanocolloids using $NaBH_4$ as a reducing agent. The characteristic peaks for Pt (2θ = 40.0, 46.5, 67.8, 81.5) marked by the indices [(111), (200), (220), (311)] showed that the resulting Pt was essentially a lattice plane[27], respectively. This demonstrates that the platinum precursor had been reduced successfully.

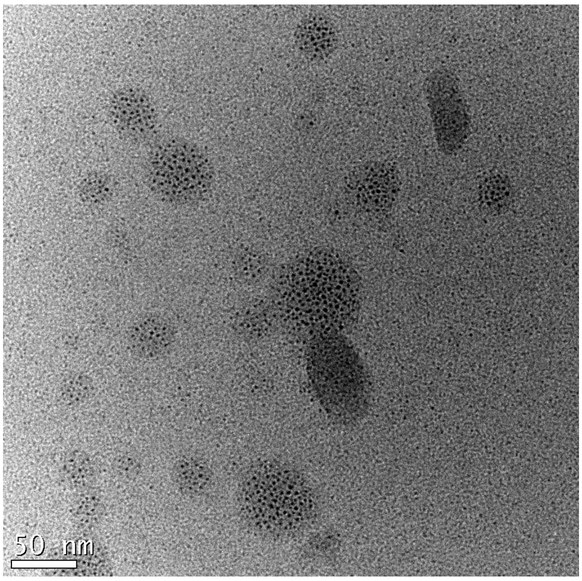


Fig. 1. TEM image of Pt nanoparticles embedded into carbon nanocolloids

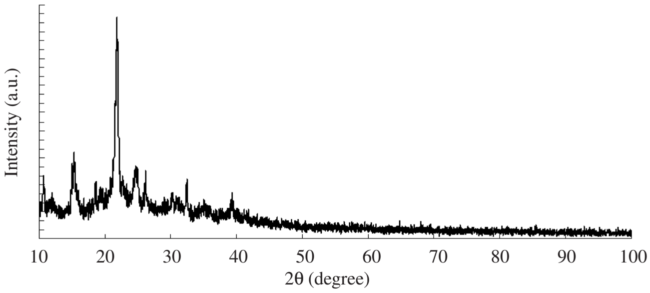


Fig. 2. XRD spectra of carbon nanocolloids

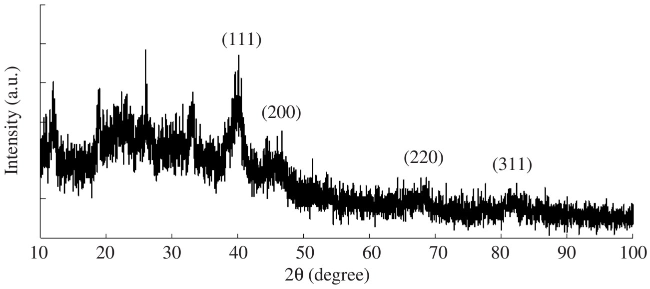


Fig. 3. XRD spectra of Pt nanoparticles embedded into carbon nanocolloids

The catalytic effect of the platinum nanoparticles was examined using the reduction of 4-nitrophenol (4NP) at room temperature as a substrate. Fig. 4 shows the reduction of 4-nitrophenol to 4-aminophenol[28].

For the investigation, the UV-vis spectrum of the 4-nitrophenol in water was examined. A red shift of the peak due to 4-nitrophenol from 320 to 400 nm was observed immediately after the addition of $NaBH_4$. This is because of the formation of 4-nitrophenolate ion in alkaline condition caused by $NaBH_4$. In the absence of a catalyst, the absorbance

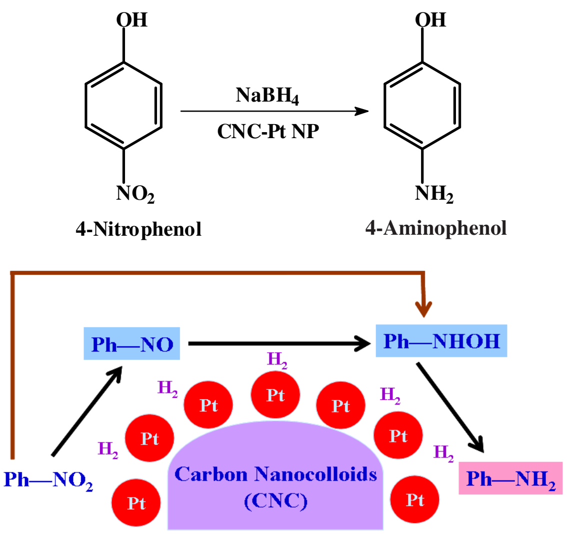
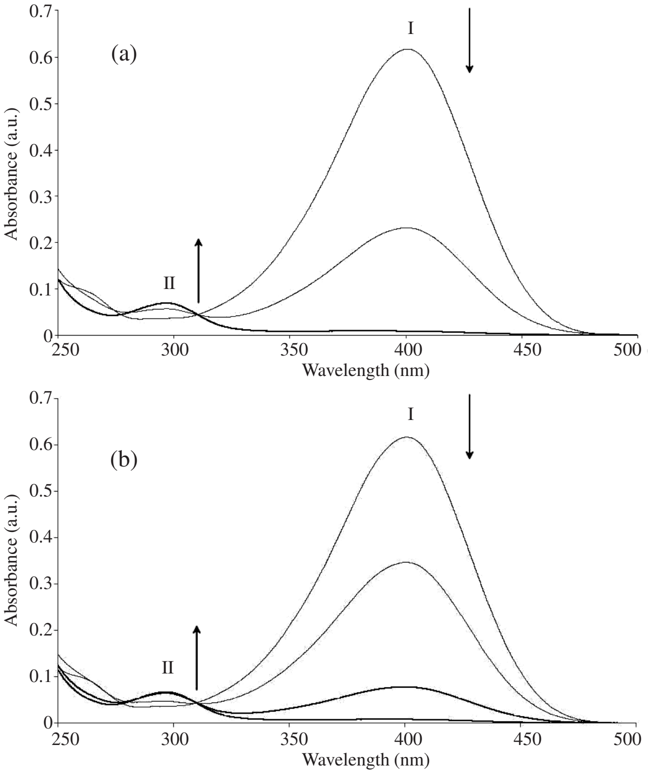


Fig. 4. Reduction of 4-nitrophenol to 4-aminophenol

and peak position remained the same, even for a couple of days. $NaBH_4$ served as the reducing agent for 4-nitrophenol to produce the 4-aminophenol. As soon as $NaBH_4$ was added, the Pt nanoparticles began the catalytic reaction by relaying electrons from the donor BH_4^- to the 4-nitrophenol substrate. The colour of the solution changed from yellow to colourless due to the reduction of 4-nitrophenol to 4-aminophenol. The discolouration was monitored and it has been noted as a successive decrease of the peak height by UV-vis spectroscopy. The absorbance of the peak at 400 nm decreased gradually with the concomitant reduction of 4-nitrophenol in Fig. 5. This reduction is indicated by the disappearance of the peak at 400 nm with the concomitant appearance of a new peak at 300 nm due to 4-aminophenol.



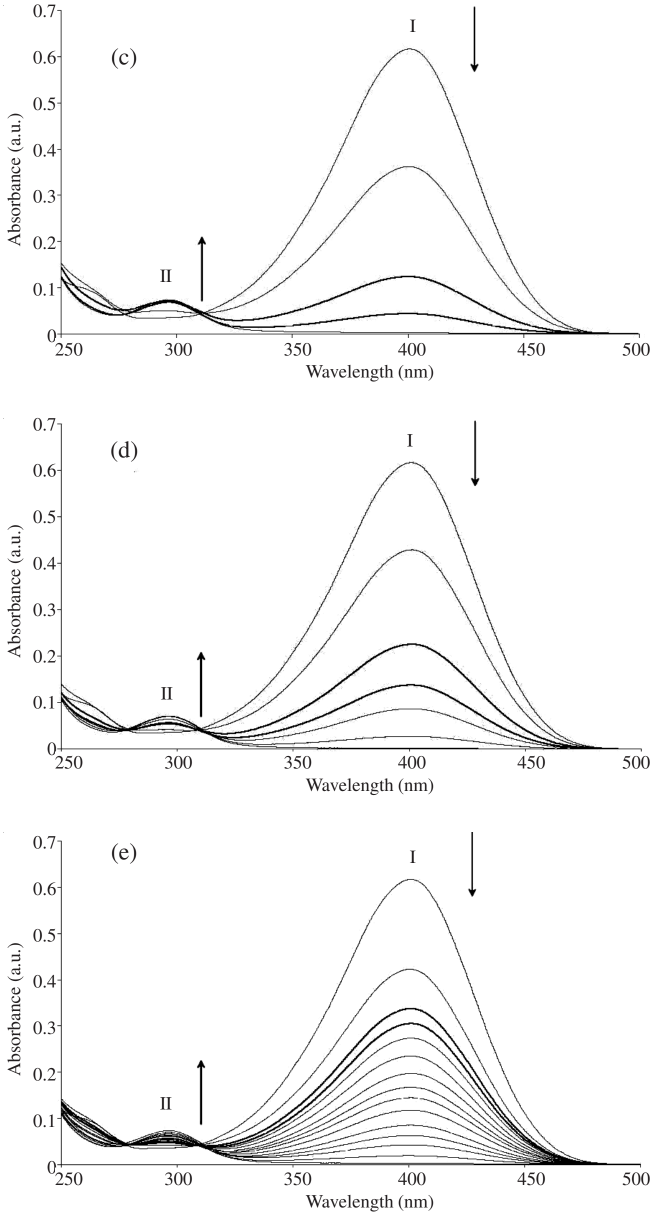


Fig. 5. UV-vis spectra of reduction of (I) 4-nitrophenol to (II) 4-aminophenol with $NaBH_4$ by (a) 0.50 mM, (b) 0.25 mM, (c) 0.13 mM, (d) 0.06 mM and (e) 0.03 mM of CNC-Pt nanoparticles as a catalyst; an interval of each peak is 1 min

The effect of various concentration (0.50, 0.25, 0.13, 0.06 and 0.03 mM) of Pt nanoparticles embedded into carbon nanocolloids on the catalyzed reduction was also studied. In a typical set of experiments, the amount of $NaBH_4$ addition was kept constant and the Pt nanoparticles-embedded into carbon nanocolloids concentration was changed. Fig. 6 shows plots of the absorbance *versus* time with different concentrations of Pt nanoparticles. The reduction time decreased with increasing concentration of Pt nanoparticles embedded into carbon nanocolloids. The Pt nanoparticles acted as a catalyst for the reduction of 4-nitrophenol to 4-aminophenol.

The HPLC chromatogram in Fig. 7(a) shows a retention time of 0.55 min. LC-MS analysis in Fig. 7(b) confirmed the formation of 4-aminophenol by the appearance of the peak for 4-aminophenol at m/z = 110, which corresponds to 4-aminophenol in an aqueous solution[29].

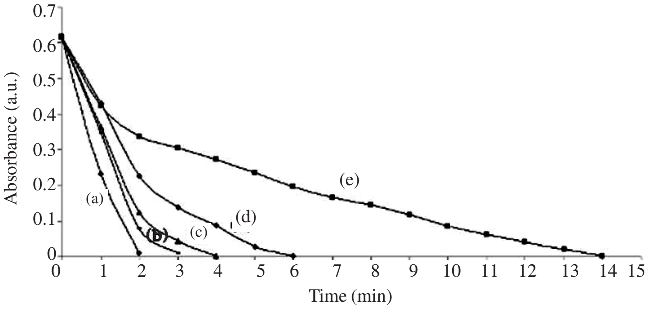
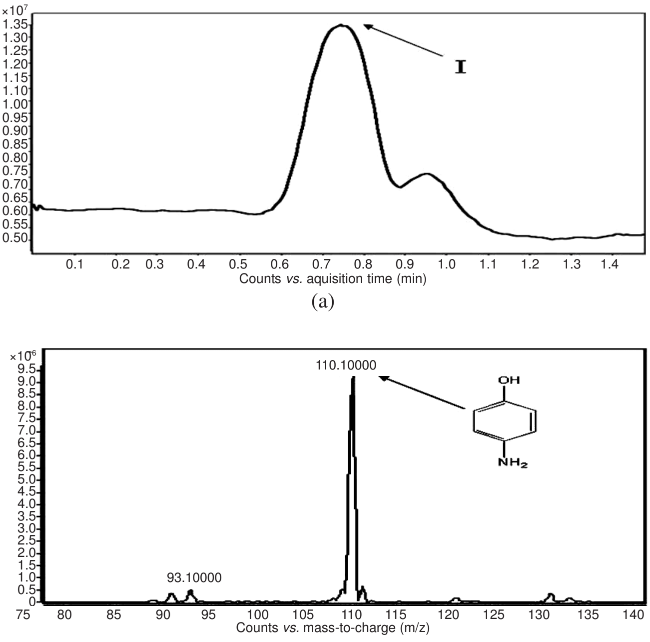


Fig. 6. Plot of absorbance against time for the reduction of 4-NP by (a) 0.50 mM, (b) 0.25 mM, (c) 0.13 mM, (d) 0.06 mM and (e) 0.03 mM of CNC-Pt nanoparticles as a catalyst



(a)

(b)

Fig. 7. LC-MS spectra; (a) Total ion chromatogram (peak identification: I = 4-aminophenol), (b) Mass spectrum of 4-aminophenol

Conclusion

The preparation of platinum nanoparticles-embedded into carbon nanocolloids was investigated. The platinum nanoparticles-embedded into carbon nanocolloids were characterized by TEM and XRD.

The carbon nanocolloids could act as both a dispersing agent and stabilizing agent in the synthesis of platinum nanoparticles-embedded into carbon nanocolloids with $NaBH_4$ as a reducing agent. The synthesized platinum nanoparticles-embedded into carbon nanocolliods were used as a catalyst for the reduction of 4-nitrophenol to 4-aminophenol with $NaBH_4$. The reduction of 4-nitrophenol to 4-aminophenol was confirmed by UV-vis spectroscopy and liquid chromatography-mass spectroscopy.

ACKNOWLEDGEMENTS

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