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Synthesis of Platinum Nanoparticles Using Pluronic® F108NF and Catalytic Effect

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This study examined the efficient preparation of platinum nanoparticles using pluronic® F108NF and $K_2[PtCl_4]$ in water under non-classical condition. The nanoparticles were characterized by transmission electron microscopy and ultraviolet-visible spectroscopy. The platinum nanoparticles were used as a catalyst to reduce 4-nitrophenol to 4-aminophenol with $NaBH_4$. The resulting product was confirmed by UV-vis spectroscopy and liquid chromatography-mass spectroscopy.

Key Words: Platinum nanoparticles, Pluronic® F108NF, UV-Vis spectra, TEM, Catalyst.

INTRODUCTION

Metal nanoparticles have attracted considerable research interest because of their potential as catalysts[1-3], sensors[4] and optical and electronic devices[5]. Therefore, a range of methods for the preparing these metal nanoparticles have been developed[1,6]. Among the methods for synthesizing metal nanoparticles, the preparation of platinum nanoparticles[7] has received much attention[8] because they can be used as metal colloids and applied to catalysis[9]. Most of the preparation of platinum colloids has been carried out in aqueous solutions with surfactants or hydrophilic polymers as stabilizing agents using chemical reductants[10]. The supporting materials become adsorbed on surface of platinum nanoparticles which stabilize them in the colloid state[11]. Supporting materials play an important role in obtaining a stable dispersion of platinum nanoparticles in solution[12]. Many colloidal metal nanoparticles can be prepared by the reduction of various metal ions using a non-classical method[13]. Recently, a simple and potentially cost effective microwave irradiation approach was reported[14]. Microwave irradiation is a simple, rapid and efficient heating method that has been used widely in synthetic research[7,15,16]. The reduction of platinum nanoparticles occurs by the species generated in an aqueous solution with pluronic® F108NF as a surfactant. Metal nanoparticles have been used recently in the hydrogenation of aromatic compounds[17-20] on account of their higher catalytic efficiency than bulk metals from their large surface-to-volume ratios[21,22]. Platinum 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[23,24]. They are normally prepared by the reduction of aromatic nitro compounds through catalytic hydrogenation[25,26] and stoichiometric reduction[27]. Catalytic hydrogenation is a convenient method for reducing aromatic nitro compounds in high yield. This paper reports the preparation of platinum nanoparticles in aqueous solution with pluronic® F108NF and the reduction of 4-nitrophenol in an aqueous solution with sodium borohydride in the presence of platinum nanoparticles as a catalyst.

EXPERIMENTAL

Pluronic® F108NF was purchased from BASF corporation. $K_2[PtCl_4]$, 4-nitrophenol and $NaBH_4$ were purchased from Sigma-Aldrich.

The morphology and crystallite size of the Pt(0) nanoparticles synthesized were analyzed by transmission electron microscopy (TEM, Philips CM-30) at an acceleration voltage of 50-300 kV. The TEM specimens were prepared by placing a few drops of the sample solution onto a copper mesh coated with a carbon film. The UV-vis spectra were recorded on a Shimadzu UV-1601PC spectrometer. The samples were also analyzed by X-ray diffraction (XRD, Rigaku, Rigaku DMAX PSPC MDG 2000). Microwave irradiation was carried out in multimode with continuous heating with a domestic oven at full power (2450 MHz, 700 W). 4-Aminophenol was confirmed using an Agilent Technologies 1200 series HPLC system with a 6410 triple quad LC/MS detector.

Synthesis of platinum nanoparticles with pluronic® F108NF under microwave irradiation: In the experiments, 0.014 mM of $K_2[PtCl_4]$ was added to 10 mL of a 1 wt % pluronic® F108NF aqueous solution followed by microwave irradiation.

The colour of the solution turned from yellow brown to black after 20 s, indicating the formation of platinum nanoparticles.

Catalytic efficiency of platinum nanoparticles for the reduction of 4-nitrophenol: The catalytic efficiency of the platinum nanoparticles for the reduction of 4-nitrophenol was analyzed. In a typical experiment, a solution containing 0.1 M of $NaBH_4$ as a hydrogen source and 0.005 M of 4-nitrophenol was mixed with 0.014 mM of Pt nanoparticles. The UV-vis spectra of the mixture were recorded continuously after a constant Pt nanoparticle concentration was added to the 4-nitrophenol aqueous solution. The reduced product of the catalytic reaction was confirmed with UV-vis spectroscopy.

Confirmation of 4-aminophenol from 4-nitrophenol by triple quadrupole LC-MS: An Agilent Technologies 1200 series HPLC system with a 6410 triple quad LC/MS detector was used. The mobile phase was the mixture of acetonitrile and ammonium acetate, (v/v) 8:2. The used column was YMC hydrosphere C_{18} (2.0 mm i.d. × 50 mm) with a 3.0 μm particle size. The injection volume was 3.0 μL and the flow rate was 0.2 mL/min. The column and gas temperature were 25 and 300 ºC, repsectively. The flow rate of the gas was 10 L/min (N_2) and the Nebulizer was at 1.38 atm.

RESULTS AND DISCUSSION

Microwave irradiated synthesis of platinum nanoparticles was performed with pluronic® F108NF and $K_2[PtCl_4]$ in an aqueous solution and observed at reaction time. The colour of the solution changed from yellow brown to black within 20 s under microwave irradiation, indicating the formation of platinum nanoparticles. Fig. 1(a) shows the absorption peak of the non-reduced platinum salt in aqueous solution at λ_{max} = 217 nm due to the presence of complex ions of $[PtCl_4]^{2-}$. However, the absorption peak at λ_{max} = 217 nm decreased after the platinum salt was reduced by pluronic® F108NF because $[PtCl_4]^{2-}$ was reduced by pluronic® F108NF under microwave irradiation. In addition, platinum nanoparticles could also be stabilized by adsorbed non-ionic surfactant, such as pluronic® F108NF.

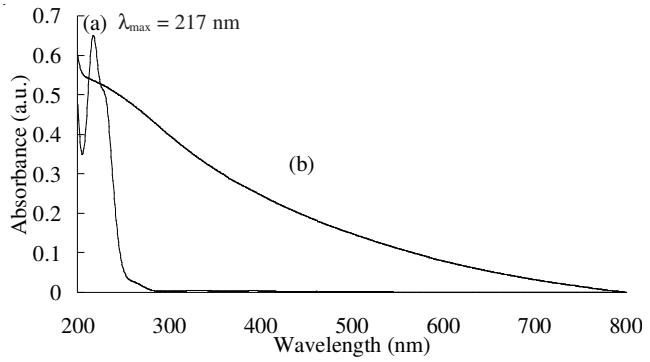


Fig. 1. UV-vis absorption of (a) K_2PtCl_4 and (b) pluronic® F108NF-protected Pt nanoparticles

In Fig. 2, repulsive forces separate the Pt nanoparticles bearing adsorbed pluronic® F108NF. Surfactants, such as pluronic® F108NF, are needed to both reduce the ionic platinum and stabilize the resulting nanoparticles.

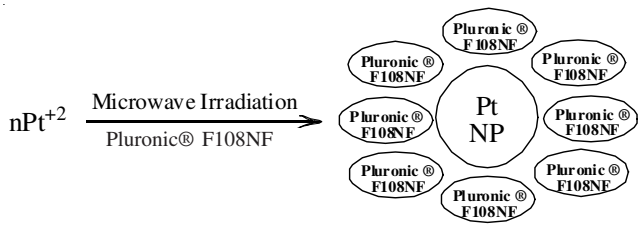


Fig. 2. Repulsive forces separate the Pt NP (nanoparticles) bearing the adsorbed pluronic® F108NF

Fig. 3 shows a TEM image of the Pt(0) nanoparticles synthesized in the pluronic® F108NF solution under microwave irradiation. All the nanoparticles had quasi-spherical shapes. The size of the platinum nanoparticles is ranging less than 5 nm. Non-ionic surfactant such as pluronic® F108NF prevents the platinum nanoparticles from aggregation and helps reduce the Pt^{2+}-Pt(0) nanoparticles by acting as a precursor for the reducing agent under microwave irradiation. In addition, the stability of colloidal nanoparticles might be achieved by overcoming attractive interactions such as van der Waals forces with a repulsive barrier by capping with a surfactant. It is suggested that non-ionic surfactant induce the reduction of the platinum salt through involvement of the repeat unit (-CH_2-CH_2-O-) depicted in Fig. 4. In the reaction with platinum nanoparticles, the oxyethylene group (-CH_2-CH_2-O-) of pluronic® F108NF was an efficient reducing agent for the non-ionic surfactant.

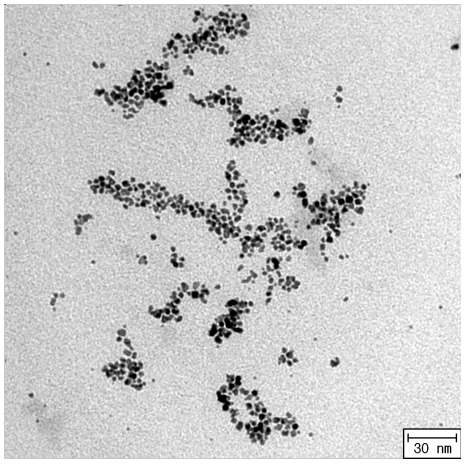
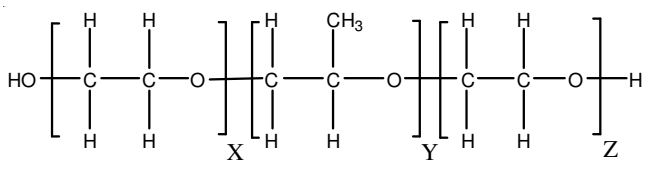


Fig. 3. TEM image of the platinum nanoparticles produced in water under microwave irradiation using pluronic® F108NF



X = 114, Y = 44, Z = 141

Fig. 4. Chemical structure of pluronic® F108NF

Fig. 5 shows the XRD patterns of the typical Pt nanoparticles. The characteristic peaks for Pt (2θ = 40.0, 46.5, 67.8, 81.5, 85.9), marked by the indices [(111), (200), (220), (311), (222)] showed that the resulting Pt was essentially a lattice plane[28], respectively.

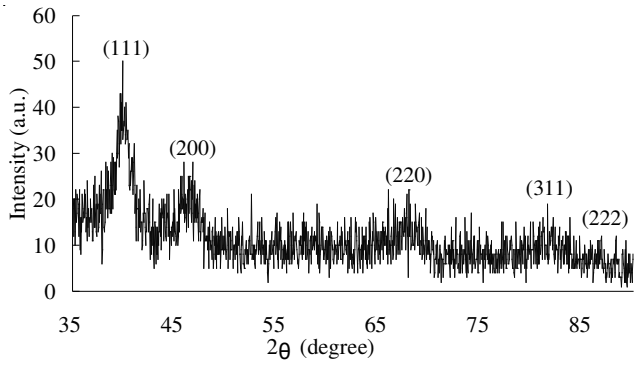


Fig. 5. XRD image of the platinum nanoparticles

The catalytic effect of the Pt nanoparticles was examined using the reduction of 4-nitrophenol (4NP) at room temperature as a substrate. Fig. 6 shows the reduction of 4-nitrophenol to 4-aminophenol[29]. After adding the $NaBH_4$, the 4-nitrophenol peak showed an immediate red shift from 317 to 400 nm, indicating the formation of 4-nitrophenolate ions by $NaBH_4$ under alkaline conditions. The colour of the solution changed from yellow to colourless due to the reduction of 4-nitrophenol to 4-aminophenol. The absorbance of the peak at 400 nm decreased gradually over time with the reduction of 4-nitrophenol in Fig. 7. This reduction is denoted by the disappearance of the peak(a) at 400 nm with the concomitant appearance of a new peak (b) at 300 nm due to 4-aminophenol.

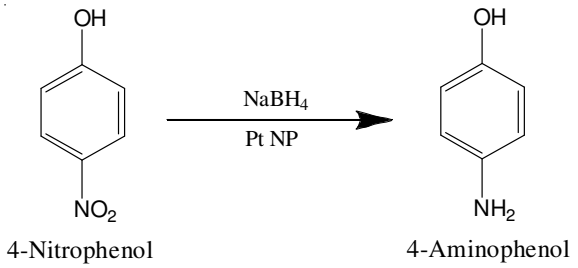


Fig. 6. Reduction of 4-nitrophenol to 4-aminophenol

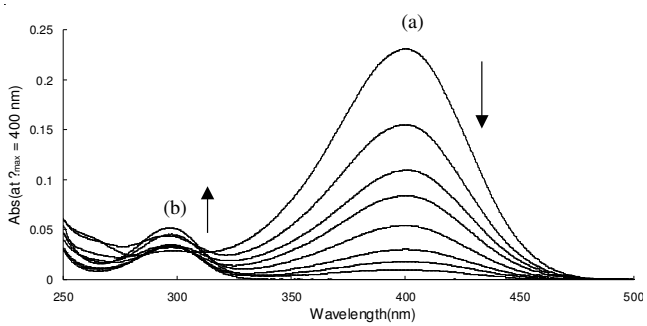


Fig. 7. UV-vis spectra of the reduction of 4-nitrophenol to 4-aminophenol with NaBH4 with 0.01 M Pt nanoparticles as a catalyst for 9 min; the interval between each peak is 1 min

The HPLC chromatogram in Fig. 8(a) shows a retention time of 0.55 min. MS analysis in Fig. 8(b) shows the formation of 4-aminophenol because the LC-MS spectrum shows the peak for 4-aminophenol at m/z = 110, which corresponds to 4-aminophenol in an aqueous solution[30].

Conclusion

The synthesis of platinum nanoparticles was demonstrated with pluronic® F108NF and K_2PtCl_4 in an aqueous solution under microwave irradiation. Pluronic® F108NF acted as both a reducing and stabilizing agent. The resulting platinum nanoparticles 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 followed with UV-vis spectroscopy. In addition, in order to show a 4-aminophenol produced by the catalytic reaction, liquid chromatography-mass spectroscopy was used to analyze the product of the reductive reaction for 4-nitrophenol.

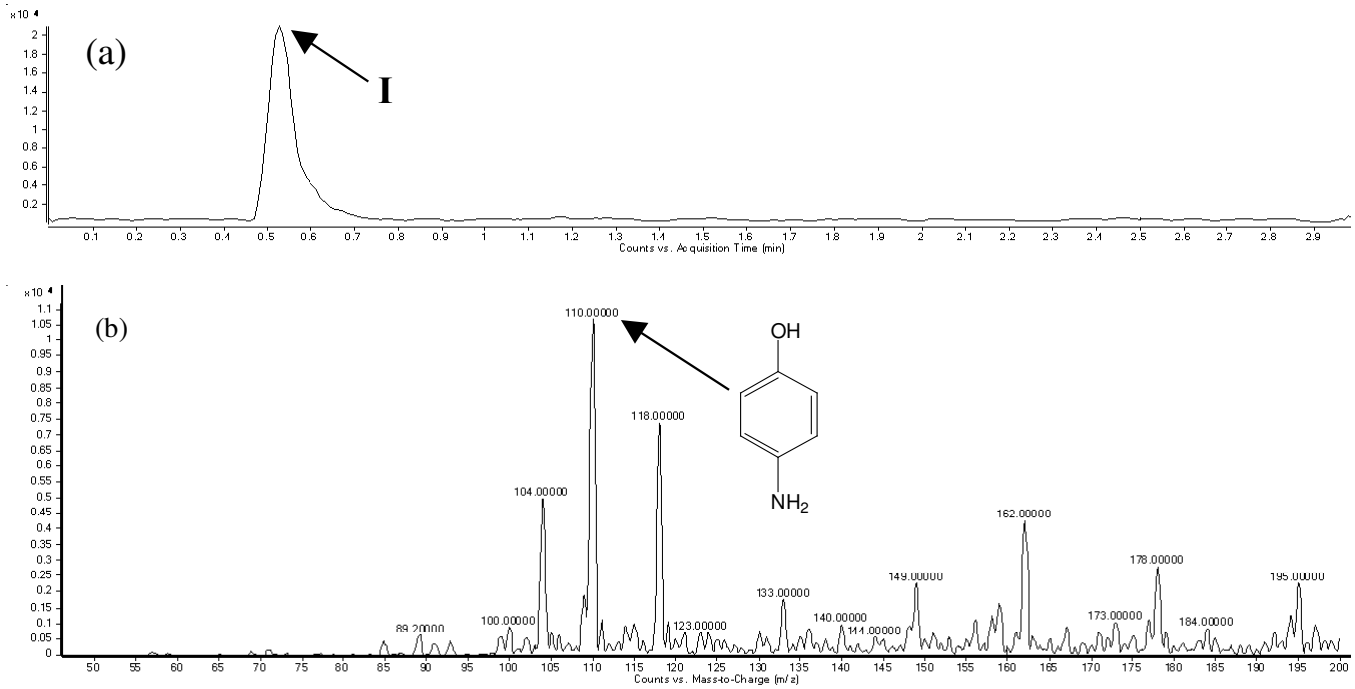


Fig. 8. LC-MS chromatogram: (a) total ion chromatogram (peak identification: I = 4-aminophenol); (b) mass spectrum of 4-aminophenol

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