Preparation of Palladium-Graphene Nanocomposites and Reduction of Nitrophenols

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Palladium nanoparticles were synthesized from palladium(II) chloride, trisodium citrate dihydrate and sodium borohydride with constant stirring. Palladium-graphene nanocomposites were prepared from the resulting palladium nanoparticles and graphene, which were reacted with polyallyamine with constant stirring for 1 h followed by ultrasonic irradiation for 3 h. The palladium-graphene nanocomposites were heated in an electric furnace at 700 °C for 2 h and characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. UV-visible spectrophotometry was used to evaluate the palladium-graphene nanocomposites as a catalyst to reduce 2-nitrophenol, 3-nitrophenol and 4-nitrophenol to 2-aminophenol, 3-aminophenol and 4-aminophenol with sodium borohydride.

Keywords: Palladium-graphene nanocomposites, Reduction of 2-nitrophenol, 3-Nitrophenol, 4-Nitrophenol, UV-vis spectrophotometry.

INTRODUCTION

Palladium is a soft silver-white metal that is the least dense and has the lowest melting point of the platinum group metals[1]. Palladium is a well-known metal with high catalytic activity and promising potential applications owing to its hydrogen adsorption properties[2].

Graphene is a new type of carbon material that was first prepared by the mechanical exfoliation from graphite in 2004 and has attracted particular attention because of its extra-ordinary nanostructure[3,4]. Graphene is a free-standing, two-dimensional substance with a single layer structure that has become hottest topics in the fields of physics, chemistry, nanotechnology and materials science. Graphene-based nanocomposites have stimulated intense research over the last decade because of their novel optical, electronic, mechanical and catalytic properties[5]. Graphene has also attracted increasing attention as a zero band gap, sp^2-hybridized carbon material[6]. Among the nanocomposites available, graphene can serve as a high-performance supporting material because of its ideal two-dimensional structure, good chemical stability, excellent electrical conductivity and large surface area[4,6-10].

Metal oxides can be dispersed uniformly on the plane of graphene and charge transfer at the interface of these hybrid materials can show a synergistic effect in inducing properties that are different from those of each individual components[11-15]. Therefore, in the present study, palladium-graphene nanocomposites were prepared and evaluated as catalysts for palladium-graphene nanocomposites using a UV-visible spectrophotometer by the reduction of several nitrophenol compounds to aminophenol compounds with sodium borohydride.

EXPERIMENTAL

Graphene-polyallylamine hydrochloride (PAH): 0.5 g of polyallylamine hydrochloride and a 0.5 M NaCl solution were added to a beaker, which contained 50 mL of distilled water. The pH of the above solution was adjusted to 9.5 by adding a 0.5 M NH_4OH solution. 10 mg of graphene was added to the above polyallylamine hydrochloride solution with constant stirring for 1 h, followed by ultrasonication for 3 h. The graphene-polyallylamine hydrochloride in the distilled water mixture was prepared by stirring and ultrasonication.

Preparation of palladium nanoparticles: 10 mL of 0.1 M trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, 0.029 g) and 0.05 M palladium chloride ($PdCl_2$, 0.088 g) as aqueous solutions were mixed in a beaker. Subsequently, 0.015 M sodium borohydride ($NaBH_4$, 0.014 g) was added to the above mixture solution with constant stirring. The molar ratio of the chemicals in solution, $Na_3C_6H_5O_7/PdCl_2/NaBH_4$, was 2:1:0.3 and palladium nanoparticles were obtained in the solution after stirring for 10 min.

Preparation of palladium-graphene nanocomposites: 20 mL of a graphene-polyallylamine hydrochloride solution was added to 20 mL of a Pd nanoparticles suspension. After leaving the mixture solution to stand for 1 h, the suspension was centrifuged to separate the product as a precipitate from the solution. The precipitated product was dried at 60 °C in a drying oven. The synthesized product was confirmed by X-ray

diffraction (XRD, Bruker, D8 Advance). The surface shape of the palladium-graphene nanoproduct was observed by scanning electron microscopy (SEM, JEOL Ltd, JSM-6510) at an accelerating voltage of 0.5 to 30 kV. The morphology and crystallite size of the product was confirmed by transmission electron microscopy (TEM, JEOL Ltd., JEM-2010) at an acceleration voltage of 200 kV.

Evaluation of catalytic activity of palladium-graphene nanocomposites in the reduction of nitrophenols: The prepared palladium-graphene nanocomposites were used as a catalyst to reduce nitrophenols to aminophenols with $NaBH_4$. The reduction of nitrophenols in an aqueous solution with the palladium-graphene nanocomposites were examined by UV-visible spectroscopy (Shimazu UV-1691PC).

RESULTS AND DISCUSSION

SEM and TEM analysis: Fig. 1 presents a typical SEM image of the palladium-graphene nanocomposites. The image revealed salt-like particles with a hexahedron shape. TEM showed that the palladium-graphene nanocomposites were spherical with a mean diameter of 50 nm (Fig. 2).
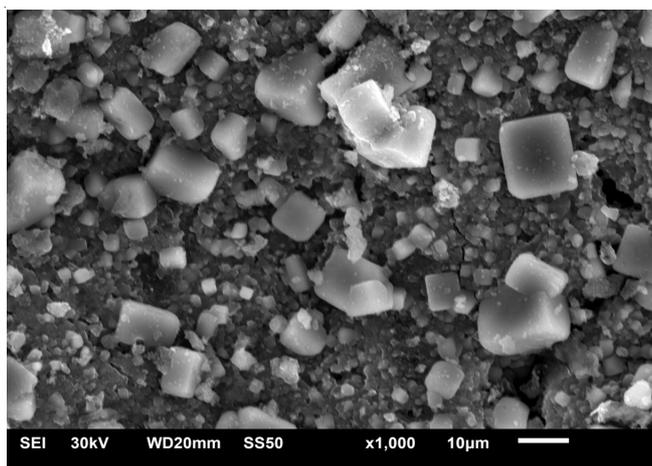
Fig. 1. SEM images of the Pd-graphene nanocomposites
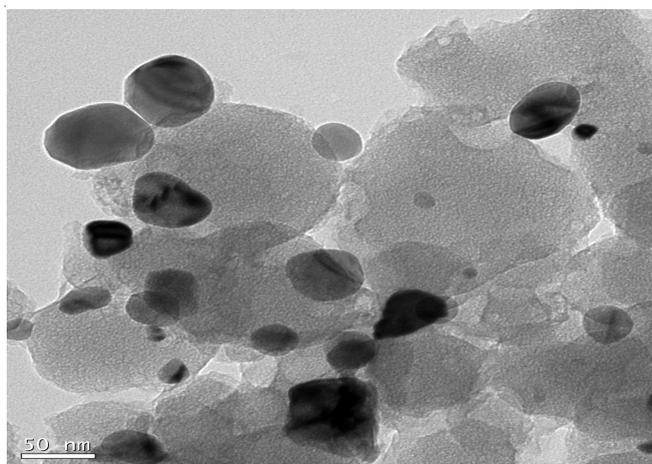
Fig. 2. TEM images of the Pd-graphene nanocomposites

XRD analysis: The palladium-graphene nanocomposites were analyzed by XRD (Fig. 3). The palladium-graphene nanocomposites were heated by calcining the as-prepared
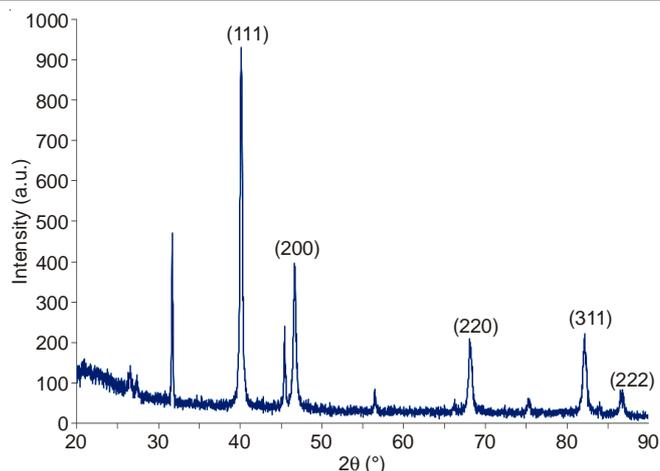
Fig. 3. XRD images of the Pd-graphene nanocomposites

sample at 700 °C for 2 h in an electric furnace. Five obvious diffraction peaks located at 40.12°, 47.56°, 68.48°, 82.59° and 87.68° 2θ, were assigned to the (111), (200), (220), (311) and (222) plane indices, respectively, for palladium (JCPSD44-1159).

UV-Visible spectroscopy analysis of palladium-graphene nanocomposites as a catalyst: Fig. 4 shows the reduction of nitrophenols to aminophenols with $NaBH_4$ using the palladium-graphene nanocomposites as a catalyst. In the present study, the UV-visible spectra were used to examine the reduction of nitrophenols to aminophenols. In this reaction, $NaBH_4$ was used as a reducing agent. As soon as $NaBH_4$ was added, the palladium-graphene nanocomposites began the catalytic reaction by relaying electrons from the donor BH_4^- to the nitrophenol substrate. A red shift in the peak due to 2-nitrophenol from 280 to 294 nm, a blue shift in the peak for 3-nitrophenol from 291 to 287 nm and from 252 to 238 nm, a red shift in the peak due to 4-nitrophenol from 320 to 400 nm were observed immediately after adding $NaBH_4$ in the presence of palladium-graphene nanocomposites as a catalyst. This was attributed to the formation of a nitrophenolate ion under alkaline conditions caused[16] by $NaBH_4$. The color of the solution also changed from yellow to colorless due to the conversion from 2-nitrophenol, 3-nitrophenol, 4-nitrophenol to 2-aminophenol, 3-aminophenol and 4-aminophenol. According to Fig. 4, the absorbance peak at 400 nm decreased gradually and disappeared with the reduction of 4-nitrophenol. At the same time, new peaks at 294, 287 and 300 nm appeared and increased due to the production of 2-aminophenol, 3-aminophenol and 4-aminophenol, respectively.

Conclusion

Palladium-graphene nanocomposites were synthesized from graphene-polyallylamine hydrochloride and palladium nanoparticles. The palladium-graphene nanocomposites were dehydrated in a drying oven at 60 °C. XRD confirmed five obvious peaks of palladium-graphene nanocomposites were observed at 40.12°, 47.56°, 68.48°, 82.59° and 87.68° 2θ. SEM showed that the palladium-graphene nanocomposites were in the form of salt like particles with a hexahedron shape. TEM showed that the palladium-graphene nanocomposites had a spherical shape with a mean size of 50-70 nm. In addition, the
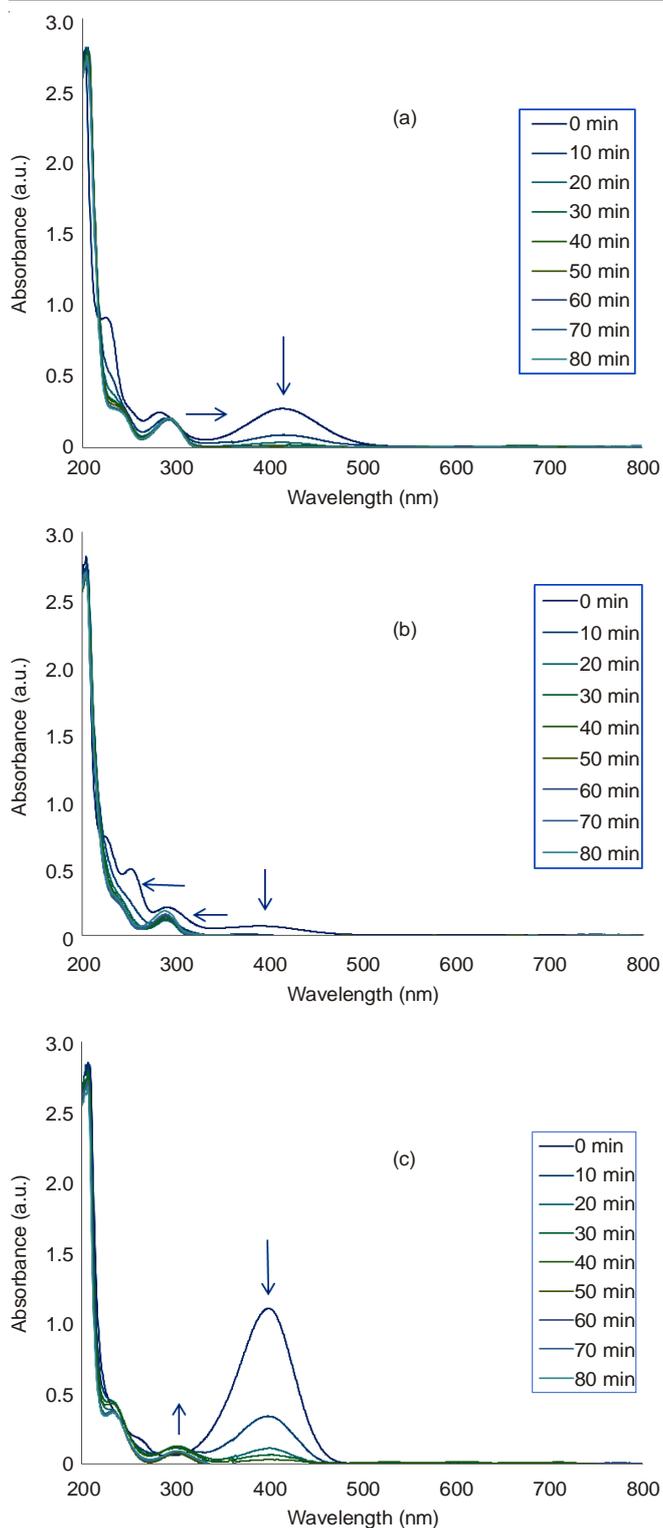
Fig. 4.　UV-visible spectra of the reduction in (a) 2-nitrophenol, (b) 3-nitrophenol and (c) 4-nitrophenol

palladium-graphene nanocomposites, as a catalyst, could promote the reduction of 2-nitrophenol, 3-nitrophenol, 4-nitrophenol to 2-aminophenol, 3-aminophenol, 4-aminophenol, respectively in the presence of sodium borohydride.

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