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Synthesis and characterization of ultrafined palladium nanoparticles decorated on 2D magnetic graphene oxide nanosheets and their application for catalytic reduction of 4-nitrophenol

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ABSTRACT

In this study, Pd NPs/Fe_3O_4/PEI/RGO nanohybrids were synthesized by dispersion of ultrafined Pd nanoparticles and the subsequent assembly of coupled Fe_3O_4 nanoparticles on polyethyleneimine-functionalized graphene oxide sheets. Transmission electron microscopic images showed that Pd nanoparticles were ultrafined and well-dispersed on the reduced graphene oxide nanosheets, and the mean particle size of Pd is around 2.2 nm. The nanohybrids were found to exhibit high catalytic activity toward the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in aqueous solution, which is attributed to the effects of ultrafined Pd nanoparticles decorated on the reduced graphene oxide nanosheets. More importantly, the Pd NPs/Fe_3O_4/PEI/RGO catalyst could be conveniently separated from the reaction mixture by a magnet, and the catalyst was recycled over ten times without a significant loss in its activity. Therefore, the promising nanocatalyst might have wide applications in catalysis, environment, biotechnology and new energy fields in the future.

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1. Introduction

Nanohybrids based on the ultrafined noble metal nanoparticles (NPs) have increasingly attracted considerable attention in the past few decades owing to their unique properties, such as distinctive optical [1], magnetic [2], electronic [3], biomedical [4] and especially their catalytic activities in a number of the degradation reactions of the industrial dyes wastewater treatment, which are often stronger than those of the bulk metal materials [5,6]. Therefore, various noble metal nanoparticles at the ultrafine particle sizes have been prepared by using various physical and chemical methods recently [5–15]. However, these nanoparticles with the ultrafine sizes easily tend to aggregate and lose their catalytic activities [16,17]. Meanwhile, these nanoparticles in the industrial applications are also hindered because of their high cost and difficult separation from the reaction mixture. To overcome these problems, numerous efforts have been made to construct novel noble metal NPs catalysts with high dispersion, good stability and rapid separation from the reaction medium during the catalytic reactions in recent years. Therefore, introducing noble

metal nanoparticles with various shapes and sizes on/into various solid supports [18] to form the nanohybrids is regarded as an effective strategy [16,19–21]. Among many solid supports studied thus far, magnetic materials and graphene have attracted great research interests [22] all over the world because magnetic materials have efficient magnetic separation capacity from the reaction solution by an external magnetic field and graphene with a high surface area possess unique electronic and optoelectronic properties [23–26], which can enhance the dispersibility and catalytic activity [2,17,27–29]. In many cases, there exists a strong synergistic interplay between the nanoparticles and the supports, which can further improve the activity and stability of the catalysts [30]. However, to the best of our knowledge, the in situ growth of Pd NPs on magnetic graphene nanosheets by using HCHO as reducing agent has been rarely reported in the previous literature [11].

In this paper, we fabricated Pd NPs/Fe_3O_4/PEI/RGO nanohybrids through the in situ growth of Pd NPs and the subsequent assembly of Fe_3O_4 NPs on reduced graphene oxide (RGO) by using HCHO as reducing agent and polyetheylenimine (PEI) as the coupling linker among the components. The morphology, structure and compositions of the as-prepared nanohybrids were characterized by various techniques. Moreover, the catalyst showed superior catalytic performance for the degradation of the 4-NP aqueous

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solution in the presence of NaBH$_4$ [31,32]. To obtain information about the catalytic activity, the effects of the catalyst dosage and NaBH$_4$ concentration on the degradation of 4-NP were tested. In addition, the kinetic analyses and reusability involved in the degradation process were also investigated.

2. Experimental

2.1. Materials

Graphite powder, Polytheylenimine (PEI, MW: 20000), 2,4-dihydroxybenzaldehyde (DIB), Palladium acetate (Pd(OAc)$_2$), iron (III) acetylacetonate ([Fe(acac)$_3$]), benzyl ether, oleylamine, and formaldehyde (HCHO, 40%) were purchased from Sigma-Aldrich (USA); Potassium permanganate (KMnO$_4$), sulfuric acid (H$_2$SO$_4$, 98%), hydrogen chloride (HCl, 37%), sodium hydroxide (NaOH), hydrogen peroxide (H$_2$O$_2$, 30%), sodium borohydride (NaBH$_4$), and 4-nitrophenol (4-NP, C$_6$H$_5$NO$_3$) were purchased from Tianjin Med (Shanghai, China). Dialysis bags (MWCO 8000-14000) were purchased from Shanghai Med (Shanghai, China). All reagents and solvents were obtained commercially and were used without further purification unless otherwise noted. Deionized water was used throughout the entire experimental process.

2.2. Instrumentations

The crystal structure of the as-prepared nanoparticles were determined using a Bruker AXS D8 Advance diffractometer with Cu$_{K\alpha}$ radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI-5702 multifunctional spectrometer with Al$_{K\alpha}$ radiation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were examined with a JEM-2100 system under an accelerating voltage of 200 kV through the deposition of hexane or ethanol dispersions of the nanomaterials on amorphous carbon-coated copper grids at room temperature. Energy dispersive X-ray spectroscopy (EDX) analysis was used to identify the elemental composition of the composite. The contents of the Pd and Fe in the sample were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using PerkinElmer OPTIMA 3300DV analyzer. UV–vis absorption spectra were measured with a UV-lambda 800 spectrophotometer (PerkinElmer, USA) by using a 1.0 cm quartz cell.

2.3. Synthesis of PEI/RGO

Graphene oxide (GO) was firstly obtained by the modified Hummer method [33]. PEI/RGO was prepared according to the literature with a little modification [15]. In brief, 20 mg of GO was dispersed into deionized water (200 mL) to form a light brown dispersion by sonication for about 30 min. Subsequently, a solution containing 2 g of PEI (MW 20000) in distilled water (200 mL) was added slowly into the above dispersion. PEI/RGO was prepared by heating the solution in an oil bath at 60 °C for 12 h. After that, the product was collected by centrifugation and washed with mixture of ethanol and diethyl ether (v/v 1:4) to remove the free PEI. The product was then redispersed into 200 mL of ethanol.

2.4. Synthesis of DIB/PEI/RGO

To prepare DIB/PEI/RGO, 110 mg DIB in 40 mL of ethanol was added dropwise into the PEI/RGO dispersion. After stirring for 15 h at room temperature, DIB/PEI/RGO was separated by centrifugation and washed thoroughly with mixture of ethanol and diethyl ether (v/v 1:4). The product was then redispersed into 30 mL of ethanol as a stock solution.

2.5. Synthesis of Pd NPs/DIB/PEI/RGO

To prepare Pd NPs/DIB/PEI/RGO, 4.48 mg Pd(OAc)$_2$ (0.02 mmol) in 10 mL of ethanol was added dropwise into DIB/PEI/RGO solution (2 mg GO) in 40 mL of ethanol, and stirred for 2 h at room temperature to ensure the metal ions thoroughly bind to N atoms of PEI. Then, 15 mL HCHO was added dropwise under N$_2$ atmosphere into the above solution within 10 min and stirred for another 2 h. Finally, the product was centrifuged and washed with mixture of ethanol and hexane to remove the remaining reagents. The product was redispersed into 40 mL mixture of ethanol and chloroform (v/v 2:1).

2.6. Synthesis of Pd NPs/Fe$_3$O$_4$/PEI/RGO

Fe$_3$O$_4$ nanoparticles (NPs) were obtained according to the literature [34]. Fe$_3$O$_4$ NPs (4 mg) in a fresh mixture of ethanol and chloroform (2 mL, 1:2 v/v) was added into Pd NPs/DIB/PEI/RGO stock solution (20 mL) and was maintained at room temperature for 24 h with vigorous stirring. The black solid was collected by an exogenous magnet and washed with hexane. Finally, the solid product was dried under a vacuum at room temperature. The final product was denoted as Pd NPs/Fe$_3$O$_4$/PEI/RGO.

2.7. Catalytic activity measurement

The reduction reactions of 4-nitrophenol in the presence of NaBH$_4$ were performed to investigate the catalytic activity of Pd NPs/Fe$_3$O$_4$/PEI/RGO nanocomposites at room temperature. Firstly, Stock solutions of 4-NP (50 μM) and Pd NPs/Fe$_3$O$_4$/PEI/RGO (2 mg/mL) were obtained in ultrapure water. A total of 2.0 mL ultrapure water was mixed with 100 μL 4-NP stock solution and 30 μL of freshly prepared NaBH4 aqueous solution (1 mM) in a standard quartz cuvette with a 1 cm path length. Subsequently, 10 μL of the catalyst stock solution was added to the above resulting mixture and the conversion of 4-NP was in situ recorded using a UV-lambda 800 spectrophotometer with the scanning range of 200–700 nm at a regular internal of time to obtain the successive changes of the reaction at room temperature. As the reaction proceeded, it could be observed that the solution color gradually changed from yellow to colorless. The concentration of 4-NP was measured by the absorption peak at 400 nm, and the 4-NP reduction conversion efficiency was usually determined using the following reduction efficiency equation. Reduction efficiency (%) = 100 (C$_0$ − C$_t$)/C$_0$, C$_0$ is the initial concentration of 4-NP, C$_t$ is the concentration of 4-NP during reaction at a given time (t).

3. Results and discussion

3.1. Structural characteristics

The overall synthetic strategy of Pd NPs/Fe$_3$O$_4$/PEI/RGO nanohybrids is vividly mirrored in the Scheme 1. First, graphene oxide (GO) with a high surface area and Fe$_3$O$_4$ NPs with an average diameter around 6.0 nm were successfully prepared according to the previous work with a little modification [15]. Second, PEI/RGO were obtained by an amidation reaction between PEI and GO, and further treated with DIB to form DIB/PEI/RGO for the coordination assembly of Fe$_3$O$_4$ NPs. Subsequently, HCHO was added to the solution of Pd(OAc)$_2$ and DIB/PEI/RGO to form Pd NPs/DIB/PEI/RGO. Finally, Pd NPs/Fe$_3$O$_4$/PEI/RGO was obtained by adding the as-synthesized Fe$_3$O$_4$ NPs to the solution of the Pd NPs/DIB/PEI/RGO. The formation of the Pd NPs/Fe$_3$O$_4$/PEI/RGO was firstly ascertained by the X-ray photoelectron spectroscopy (XPS). The survey spectra show the existence of C, N, O, Pd, and Fe elements in the hybrid materials, suggesting that Pd NPs/Fe$_3$O$_4$/PEI/RGO was successfully