Ni/reduced graphene oxide nanocomposite as a magnetically recoverable catalyst with near infrared photothermally enhanced activity

Chun-Chieh Yeh, Dong-Hwang Chen*

Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan

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ABSTRACT

A nanocomposite of nickel nanoparticles/reduced graphene oxide (Ni/rGO) has been developed as a magnetic recoverable catalyst with near-infrared (NIR) photothermally enhanced activity owing to the magnetic and catalytic properties of Ni nanoparticles as well as the large specific surface area and excellent NIR photothermal conversion property of rGO. By the hydrazine reduction in ethylene glycol, Ni ions, and graphene oxide were reduced simultaneously to form the Ni/rGO nanocomposite. The resulting Ni/rGO nanocomposite with about 62 wt.% of Ni nanoparticles was nearly superparamagnetic and possessed good catalytic activity toward the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) with sodium borohydride. The corresponding pseudo-first-order rate constants increased with increasing the temperature and 4-NP concentration, revealing activation energy of 43.7 kJ/mol and the synergistic effect of rGO. Furthermore, under NIR irradiation, it was demonstrated that the Ni/rGO could efficiently enhance the reduction rate via the photothermal conversion which might induce the heating of local environment around the Ni nanoparticles and reaction medium. Such a nanocomposite was expected to be helpful in the development of NIR or solar photothermally enhanced catalytic systems.

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1. Introduction

4-Nitrophenols (4-NP) is a common organic pollutant in wastewater. A lot of processes have been developed for its removal, such as adsorption, microbial degradation, photocatalytic degradation, electro–Fenton method, electrocoagulation, electrochemical treatment, and so on [1]. Moreover, 4-NP is also a common precursor of 4-aminophenol (4-AP) which is renowned as a kind of useful material in many applications that involve corrosion inhibitor, analgesic/antipyretic drugs, photographic developer, anticorrosion lubricant, hair-dyeing agent [2–4]. So, considerable efforts have been made on the reduction of 4-NP to 4-AP. In the past two decades, the borohydride reduction of 4-NP to 4-AP by metal nanoparticles such as Au, Ag, Pt, Pd, Pt–Ni, and Ni has received increasing attention because this reaction can be performed in aqueous solution under mild condition [5–11].

On the other hand, graphene which is a single or few layer of 2-dimensional graphite carbon sheets has attracted great interest recently in various fields of science and engineering owing

to its high surface area, unique optical property, and good electrical, thermal and mechanical properties [12–16]. Although a lot of methods have been developed for the preparation of graphene sheets, the most suitable and efficient approach was the solution-based chemical reduction of exfoliated graphite oxide to reduced graphene oxide (rGO) because of its low-cost and facile synthetic nature in a controlled, scalable, and reproducible manners [17,18]. Graphite oxide can be readily dispersed in water to yield the stable dispersions of graphene oxide (GO) by simple sonication owing to the presence of oxygen-containing functional groups such as hydroxyl, epoxide, and carboxyl moieties [19]. Furthermore, these oxygen functional groups can act as nucleation centers or anchoring sites for the attachment of nanoparticles [20], which limited the growth of nanoparticles and improved the stability and dispersion of nanoparticles on GO or rGO. These nanoparticles can also help to enlarge the interplanar spacing of the GO or rGO in solid state, maintain the excellent properties of individual GO or rGO sheets, and avoid the aggregation of GO or rGO sheets into graphitic structure [11,21]. On the basis of the above advantages, GO and rGO have been widely used as the supports for the attachment of nanoparticles to yield the nanocomposites for various applications, particularly in the catalysis [22–24].

It was mentionable, recently we demonstrated that LaB_6 nanoparticles possessed excellent near infrared (NIR) photothermal conversion property and could be used in the NIR photothermal

* Corresponding author at: National Cheng Kung University, Department of Chemical Engineering, No 1, Ta-Hsueh Rd, Tainan 701, Taiwan.
Tel.: +886 6 2757575x 6268; fax: +886 6 2344496.
E-mail address: chendh@mail.ncku.edu.tw (D.-H. Chen).

therapy of cancer therapy and the photothermal ablation of bacteria [25–27]. Also, after silica coating and Au nanoparticles deposition, the resulting $LaB_6@SiO_2/Au$ composite nanoparticles were efficient for the catalytic reduction of 4-NP with $NaBH_4$ and the reduction rate of 4-NP could be enhanced by NIR irradiation because they not only induced the heating of reaction medium but also provided hot spots on the catalyst surface via the photothermal conversion [28]. Graphene and rGO also possess the excellent NIR photothermal conversion property and have been used in NIR photothermal therapy [29–31]. Although graphene-based sheets have been widely used as the catalyst supports, their application in the photothermally enhancement of catalytic reaction rate by NIR irradiation has not been reported.

According to the above, the nanocomposite of Ni nanoparticles and rGO (Ni/rGO) was fabricated for the catalytic reduction of 4-NP to 4-AP in this work. Ni nanoparticles were chosen because they were cheaper as compared to other noble metal catalysts Au, Ag, Pt, and Pd. Also, the magnetic property of Ni nanoparticles could make the nanocomposite magnetically recoverable. The rGO was used as the support because of its large surface area, suitability for the deposition of nanoparticles, and excellent NIR photothermal conversion property. Such a catalyst with NIR photothermally enhanced activity might be helpful for the development of more efficient catalytic systems with less electrical thermal input. Moreover, although the synthesis of Ni/rGO nanocomposite has been reported, longer reaction time, higher reaction or heat treatment temperature, and/or inert atmosphere were usually required [11,32–36]. Also, only quite few effort has been made on its use in the catalytic reduction of 4-NP [11]. In this work, by the hydrazine reduction in ethylene glycol at a relatively low temperature (i.e., 70 °C), Ni ions and graphene oxide were reduced simultaneously to form the Ni/rGO nanocomposite within 30 min without the input of an extra inert gas. It was demonstrated that the Ni/rGO nanocomposite was magnetically recoverable and efficient for the catalytic reduction of 4-NP to 4-AP with $NaBH_4$. Also, the rGO not only enhanced the catalytic activity via a synergistic effect but also could enhance the reduction rate by NIR irradiation.

2. Materials and methods

2.1. Materials

Graphite powder (99.9%) was a product of Bay Carbon. Nickel chloride was obtained from Riedal-de Haën. Ethylene glycol and sodium hydroxide were supplied by J. T. Baker. Hydrazine hydrate solution (80%) was purchased from Sigma–Aldrich. 4-Nitrophenol and sodium borohydride were obtained from Alfa Aesar and Aldrich, respectively. The above and other chemicals were all of guaranteed or analytical grade reagents commercially available and used without further purification. The water used throughout this work was reagent grade, produced by a Milli-Q SP Ultra-Pure-Water Purification System of Nihon Millipore Ltd., Tokyo.

2.2. Preparation of GO

GO was prepared from purified natural graphite by a modified Hummers' method [11,37]. The graphite powder (1.5 g) and $NaNO_3$ (0.75 g) were added to the concentrated H_2SO_4 (18 M, 37 mL) in an ice-bath. $KMnO_4$ (4.5 g) was added gradually under stirring. The mixture was then stirred at 35 °C for 24 h. Then the deionized water (70 mL) was slowly added to the mixture, followed by stirring the mixture at 98 °C for 15 min. The suspension was further diluted to 110 mL and stirred for another 30 min. The reaction was terminated by adding H_2O_2 (3.7 mL, 35 wt.%) under stirring at room temperature, followed by washing with the deionized water several times.

2.3. Preparation of Ni/rGO nanocomposite

Ni/rGO nanocomposite was synthesized according to our previous work on the synthesis of Ni nanoparticles [38]. Typically, firstly, GO (5 mg) was dispersed in ethylene glycol (7.5 mL) with ultrasonication for 30 min and then mixed with the ethylene glycol of $NiCl_2$ (100 mM, 7.5 mL) to yield a homogeneous brown solution. Secondly, an appropriate amount of NaOH (1.0 M) was added to adjust the pH to about 10.5 and then hydrazine solution (80%, 0.7 mL) was added under continuous stirring. Finally, the reaction was conducted at 70 °C for 30 min to yield a homogeneous black solution. The product was recovered magnetically by a magnet, washed with ethanol for three times, and then dried in an oven at 40 °C. For comparison, Ni nanoparticles and rGO were prepared according to the above procedures in the absence of GO or $NiCl_2$, respectively.

2.4. Characterization

The particle size and composition were determined by transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy on a high-resolution field emission transmission electron microscopy (HRTEM, JEOL Model JEM-2100F). The high-resolution TEM (HRTEM) image and selected area electron diffraction (SAED) pattern were obtained by a JEOL Model JEM-2100F electron microscope at 200 kV. The crystalline structures were characterized by X-ray diffraction (XRD) analysis on a Shimadzu model RX-III X-ray diffractometer at 40 kV and 30 mA with Cu Kα radiation ($\lambda = 0.1542$ nm). Raman scattering was performed on a Thermo Fisher Scientific DXR Raman Microscopy using a 532 nm laser source. The XPS measurements were performed on a KRATOS AXIS Ultra DLD photoelectron spectrophotometer with an achromatic Mg/Al X-ray source at 450 W. Magnetic measurement was performed on a superconducting quantum interference device (SQUID) magnetometer (MPMS7, Quantum Design). The absorption spectra were analyzed using a JASCO V-570 UV–vis spectrophotometer.

2.5. Catalytic reduction of 4-nitrophenol

For the catalytic reduction of 4-NP, typically, an appropriate amount of Ni/rGO nanocomposite was added to the aqueous solution containing 4-NP and $NaBH_4$ at the desired temperature to start the reaction. The bright yellow color of solution gradually vanished, indicating the reduction of 4-NP. The variation of 4-NP concentration with time was monitored spectrophotometrically at a wavelength of 400 nm. Unless specified otherwise, the initial concentration of 4-NP was 0.05 mM and the reaction temperature was 25 °C. The initial concentration ratio of $NaBH_4$ to 4-NP was fixed at 100 so that the concentration of $NaBH_4$ could be considered as a constant during the reaction. The concentration of Ni/rGO nanocomposite in the reaction solution was 0.01 mg/mL and the solution volume was 3.0 mL throughout this work. For comparison, the catalytic reduction of 4-NP with $NaBH_4$ by rGO or Ni nanoparticles was also examined. For the NIR photothermally enhanced catalytic reduction of 4-NP, the reaction was performed under NIR irradiation by a CW 808 nm diode laser at a power density 5.42 W/cm^2. During the reaction, the temperature was also detected with a thermal couple to examine the temperature variation. To demonstrate the adsorption of 4-NP on rGO, an adsorption experiment was conducted in the solution (3 mL) containing 4-NP (0.05 mM) and rGO (0.01 mg/mL) in the absence of $NaBH_4$ at 25 °C. After about 25 min, the 4-NP concentration in the solution was determined spectrophotometrically at a wavelength of 317 nm.