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Sono-synthesis approach in uniform loading of ultrafine Ag nanoparticles on reduced graphene oxide nanosheets: An efficient catalyst for the reduction of 4-Nitrophenol

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ABSTRACT

In this research, a facile, one step and eco-friendly sonochemical rout was utilized to the synthesis of a new nanocomposite by Ag nanoparticle anchored on reduced graphene oxide (rGO-Ag-U). Sonication was carried out by using low frequency ultrasound (20 kHz) under ambient condition. In this way, graphene oxide and Ag^+ ions simultaneously reduced by polyol without using any additional reactants or capping agents. The polyol serves as both solvent and low toxic reducing agent. To achieve the best synthesis condition of rGO-Ag-U nanocomposite, the effects of irradiation time, ultrasonic amplitude and reaction temperature were investigated. In comparison, the synthesis of rGO-Ag was also carried out via reflux as a classical method (rGO-Ag-C). It was found that ultrasonic irradiation for 10 min at 70% amplitude was sufficient for the synthesis of rGO-Ag-U. Several analytical techniques were used to characterize the resulting nanocomposites such as UV–Vis spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The UV–Vis spectra show a shift of GO band to a higher wavelength which is due to the reduction of sp^3 sites. The results of TEM also confirm the smaller Ag nanoparticle (about 18 nm) which uniformly decorated on rGO nanosheets by sonochemical method than classical method. The experimental data suggest that among the synthesized nanocomposites, rGO-Ag-U exhibited better catalytic activity (k_{app} = 1.18 min^{-1}) towards the reduction of 4-Nitrophenol to 4-Aminophenol in the presence of sodium borohydride ($NaBH_4$).

1. Introduction

Graphene is a two-dimensional (2D) carbon material [1] that has rapidly become known as perfect candidate for application in various fields due to its unique properties such as mechanical, electrical, chemical, thermal, and optical properties [2–4]. Since its discovery in 2004, a lot of synthetic strategies have been developed, e.g. micromechanical exfoliation of graphite, chemical vapor deposition, epitaxial growth and solution-based chemical reduction of graphene oxide (GO) to reduced graphene oxide (rGO) [5,6]. Among these, the chemical reduction of GO to rGO is the most suitable and efficient route owing to its low cost and facile synthetic nature in a controlled, scalable, and reproducible manner. However, as-prepared reduced graphene sheets tend to form irreversible agglomerates or even restack to form graphite due to the van der Waals interactions [7]. Hence, researchers look for versatile methods to overcome the above shortcomings for obtaining non-agglomerated graphene.

Over the years, metal particles at nanolevel dimensional have attracted increasing attention because of their exclusive electronic, optical, magnetic and catalytic properties, which are totally different from those of bulk metals. These nanoparticles have been shown remarkable potential for numerous applications in electronic, chemical, biological, and medical fields and so on [8–11]. However, metal nanoparticles with small size are not at a thermodynamic stable state, so they are prefer to aggregate to minimize the total surface energy [12]. While, it has been proved that the physicochemical properties of metal nanoparticles are size and shape dependent [13].

Recently, enormous interests have been drawn for the development of reduced graphene oxide based nanoparticle composites. Since abundant functional groups on the surfaces of GO can act as nucleation centers or anchoring sites for the landing of nanoparticles, limiting the nanoparticles growth, improving the stability and dispersion of nanoparticles on rGO nanosheets. At the same time, these nanoparticles can aid to enlarge the interplanar spacing of the rGO especially when they are in solid state. Therefore, prevent the aggregating of rGO into graphitic structure, and maintain the excellent properties of individual rGO

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nanosheets [14–17]. However, the developed ways suffer from the employ of hazardous or toxic reducing agents such as $NaBH_4$ and formaldehyde to reduce both GO and Ag^+ ion, posing environmental and health risks, or the involvement of a surface modifier such as poly(N-vinyl-2-pyrrolidone) (PVP) [18].

Up to now, a variety of methods, such as electrochemical, chemical vapor deposition, ion exchange, hydrothermal, sol–gel, gamma irradiation and sonochemical methods have been applied to incorporate nanoparticles inside graphene sheets. Among the different approaches, sonochemistry has become an important method for the reduction of metal precursors and graphene oxide to rGO to get a homogeneous dispersion of exfoliated graphene sheets with metal nanoparticles [19–22]. The chemical effects of ultrasound irradiation is due to the acoustic cavitation phenomenon. When a liquid is irradiated with ultrasound, bubbles are created, growth and subsequent collapse, which leads to the release of the accumulated ultrasonic energy within a very short time. The extremely high local temperature (> 5000 K), pressure (> 20 MPa) and very high cooling rates ($> 10^{10}$ K s^{-1}) are suitable conditions for reducing GO and metal ions. Furthermore, the shear forces caused by acoustic cavitation are sufficient to overcome the van der Waals interaction between graphene sheets.

4-Nitrophenol (4-NP) is one of the most toxic and refractory pollutant in wastewater which derived from the industrial manufacturing processes of agrochemicals, pigments and pharmaceuticals. Instead, 4-aminophenol (4-AP) is very beneficial and important in many fields that include analgesic and antipyretic drugs, photographic developer, corrosion inhibitor, anticorrosion lubricant. Although there are many routes for removal of hazardous 4-NP but its catalytic reduction to 4-AP over appropriate catalyst (e.g. metal and metal oxide nanoparticle) has become a hot research topic [23–26].

Regarding the above description, the present research focuses on the use of ultrasonic irradiation to achieve the uniform loading of Ag nanoparticles on rGO nanosheets. Ag nanoparticles were chosen because among various kinds of noble metal such as Au, Pt, and Pd, they are low cost. In this work, a mild, inexpensiveness and environmental friendly reductant, diethylene glycol (DEG), was used as both reductive and dispersing agent. To the best of our knowledge, there has been no report on the sonochemical synthesis of Ag-rGO nanocomposites using DEG that does not involve chemical reducing and/or stabilizing agents. In comparison, the formation of rGO-Ag nanocomposite was accomplished by reflux precursor solution (classical method). Finally, catalytic activity of desired nanocomposites were investigated by reduction of 4-Nitrophenol in the presence of sodium borohydride ($NaBH_4$) as a model reaction.

2. Experimental

2.1. Materials

Graphite powder (purity 99%, mesh 325), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl, 37%), ethanol (96%), silver nitrate ($AgNO_3$, 99%), 4-nitrophenol ($C_6H_5NO_3$, 99%) and sodium borohydride ($NaBH_4$, 98%) were provided from Merck. Diethylene glycol ($(HOCH_2CH_2)_2O$, 99%) and phosphoric acid (H_3PO_4, 85%) from Riedel, hydrogen peroxide (H_2O_2 30%) from Fluka company. All reagents were used directly without any further purification. Deionized water (DI) was used in the synthesis process.

2.2. Synthesis of graphene oxide (GO)

GO was obtained from the oxidation of graphite with the improved Hummers method [27]. Briefly, 1 g of graphite powder was mixed with a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (120/13.3 mL). Then 6 g $KMnO_4$ was added gradually under vigorous stirring, while temperature was kept below 20 °C to control the exothermic reaction. The reaction was oxidized for 12 h at 50 °C. Next, the mixture was cooled to room temperature and then 133 mL DI and 1 mL H_2O_2 was added to end the reaction. GO was collected by centrifuging the mixture and rinsed with 10% HCl and H_2O several times and then dried under vacuum.

2.3. Synthesis of rGO-Ag-C nanocomposite

First, 15 mg of graphene oxide was dispersed in 15 mL of DEG to form a stable GO colloid solution and 2.5 mL DI water was added to it (solution 1). Different amount of $AgNO_3$ (0.025–0.125 g) was dissolved in 7.5 mL DEG and then mixed with solution 1. After that, the mixture was stirred for 30 min to ensure the adsorption of Ag^+ ions on the surface of GO sheets. The reduction reactions were then performed at 150 °C for 3.5 h under constant stirring. At the end of the reactions, the mixture was cooled and products (rGO-Ag-C) were finally separated by centrifugation. Then the sample was washed with deionized water several times, and dried at 80 °C overnight. Following the above procedures, rGO nanosheets and Ag nanoparticles (Ag NPs) were prepared separately under the same conditions.

2.4. Synthesis of rGO-Ag-U nanocomposite

The solutions for the ultrasonic reduction were produced by the similar way with classical method. After magnetic stirring the mixture for 30 min, the resulting suspension was exposed to sonication using an ultrasonic horn (20 kHz, Branson Digital Sonifier-USA, W-450D) in a Rosset cell. Various amplitudes (50%, 60% and 70%) for 10 min were applied to deliver different acoustic power of 20.1 W, 24.5 W and 29.9 W, respectively. Ultrasonic waves applied in pulse mode with a 3-s pulse and 3-s relaxation cycle. Finally, the samples (rGO-Ag-U) were separated, washed with DI water and dried at 80 °C overnight. The ultrasonic process was conducted without any cooling. Therefore, a temperature of about 40 °C was reached after 10 min at the end of the reactions. The fabrication process for rGO-Ag-C and rGO-Ag-U nanocomposites are outlined in Fig. 1.

2.5. Analysis instruments

To investigate the optical properties of the samples, UV–Vis spectra were collected on a Unico 2800 spectrophotometer with 1 cm quartz cells. Fourier transform infrared (FT-IR) spectrum was done on a Thermo Nicolet 370 spectrometer in KBr medium in the region of 500–4000 cm^{-1}. The crystal structure of the as-prepared powders were determined by X-ray diffractometer (XRD, Explorer, JNR) equipped with Cu Kα radiation ($\lambda = 0.15406$ nm) over 2θ range of 5–90° at a scanning rate 0.05° s^{-1}. The morphology and structure of as-prepared particles were examined by transmission electron microscopy (TEM, Philips BioTwinCM120). Samples for TEM analysis were prepared by depositing a single drop of diluted sample dispersion in ethanol on carbon-coated grids. Energy dispersive X-ray spectroscopy (EDX) analysis coupled to the SEM instrument was carried out to study the elemental composition of the nanocomposites. The Raman spectra was recorded using a Teksan Takram P50C0R10 spectrometer with a 532 nm YAG laser as the excitation source. The specific surface area of the products were investigated by the Brunauer–Emmett–Teller (BET) method on the basis of nitrogen adsorption-desorption isotherms measured at 77 K using a BELSORP-mini analyzer.

2.6. Catalytic reduction of 4-NP

Catalytic efficiency of the resultant nanocomposites were evaluated by employing the reduction of 4-nitrophenol to 4-aminophenol in the presence of excess $NaBH_4$, which is a well-known model reaction. Briefly, 0.05 g $NaBH_4$ was added to 25 mL of 0.2 mM 4-NP aqueous solution with continuous stirring in a 50 mL beaker under ambient conditions. And then, special amount of the rGO-Ag-C and rGO-Ag-U powders (1–4 mg) were added to above mixture in different series of