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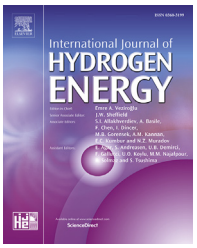

In situ synthesis of gold nanoparticles on N-doped graphene quantum dots for highly efficient catalytic degradation of nitrophenol

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ABSTRACT

In our work, a simple and green method of in situ synthesis of Au nanoparticles (Au NPs) on graphene quantum dots doped with nitrogen (NGQDs) was reported. Construction of the nanocomposite was accomplished through mixing the NGQDs and $HAuCl_4 \cdot 4H_2O$ with no additional reductant and surfactant. The as-obtained Au NPs-NGQDs nanocomposite exhibited high catalytic activity in its application in the degradation of p-nitrophenol (4-NP), a pertinacious pollutant occuring in industrial wastewater. Characterization results indicated that Au NPs were well distributed upon the surface of NGQDs and Au NPs-NGQDs nanocomposites were formed. Such Au NPs can provide high catalytic activity due to its naked catalytic surface with no surfactant capping. Turnover frequency (TOF) was used to examine the catalytic efficiency and its value was obtained to be 12 h^{-1}. Furthermore, the as-obtained catalyst exhibited high reusability in the catalytic process of the degradation of 4-NP. This study indicates that such novel nanocomposite is promising for catalytic degradation of 4-NP.

Introduction

p-Nitrophenol (4-NP) is the by-product of the processes of manufacturing pharmaceuticals, pesticides and pigments in industry and regarded as one of the most venenous and hazardous pollutants [1,2]. It has been widely spread in the environment due to the wastewater discharged from industries. 4-NP can enter the food chain and cause irreversible damage to the organs of humans and animals [3]. 4-aminophenol (4-AP) has lower toxic and important applications in hair-dyeing agent, antipyretic drugs, and anticorrosion-lubricant [4]. Therefore, it is significant to change 4-NP to 4-AP. One of the notable methods to remove 4-NP is to convert 4-NP to 4-AP through catalytic reduction by borohydride ions (BH^{4-}) with metal nanocatalysts [5]. Different kinds of metal nanocomposites have been synthesized and investigated due to their unusual physicochemical properties [6–11]. Compared with other metal catalysts, Au NPs are one of the most promising nanocatalysts due to their chemical stability and unique structure dependent optoelectronic properties [12,13].

However, the catalytic activity of Au NPs could be decreased due to the aggregation and minimization of their surface area caused by their high surface energy. The synthesization of metal nanoparticles on a stable substrate, such as carbon family, magnetic nanoparticles, polymers and metallic oxides provides a potential method to solve the problem [14]. For instance, Pd/CuO nanomaterial was synthesized and applied in the conversion of 4-NP [15]. Pd

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nanospheres was decorated on reduced graphene oxide and their catalytic activity was investigated [16]. Pd monometallic/bimetallic nanoparticles was immobilized on carbon nanotubes to catalyze the reduction of 4-NP [17]. Au@AuPt nanoparticles was embedded in B-doped graphene as an electrocatalyst for the determination of rutin [18]. An efficient and recyclable catalyst was also introduced by immobilizing Pd nanoparticles on magnetic fibers [19].

Graphene quantum dots (GQDs), a new member of the carbon family, with both the outstanding properties of quantum dots and graphene, are gaining enormous attraction because of their peculiar features like high accessible surface area, high chemical stability, less cytotoxicity, marvellous biocompatibility and outstanding water solubility [20]. The surface activities, electronic properties and local chemical characteristics of GQDs could be effectively modified by doping with heteroatoms (such as sulfur, boron, nitrogen atoms) [21–23]. Especially, graphene quantum dots doped with nitrogen (NGQDs) can attune their electronic, physical and chemical properties resulting in remarkable features such as tunable luminescence, excellent biocompatibility and electrocatalytic activity [24–27].

Therefore, the synthesis of Au NPs on NGQDs substrate may exhibit excellent catalytic activity and accelerate the degradation of 4-NP to 4-AP mediated by $NaBH_4$.

Hereinafter, in this work, the construction of the Au NPs-NGQDs nanocomposites was successfully attempted through in situ synthesis. This method was simple and facile, and did not need addition reductant and surfactant. The combination of Au NPs with NGQDs efficiently improved the catalytic capability of 4-NP conversion. Furthermore, the as-obtained Au NPs-NGQDs nanocatalyst could be reused for nine times and still show excellent stability because of the heteroatoms-doped composite structure.

Experimental section

Chemicals

Citric acid and dicyandiamide were bought from J&K Chemicals. (Beijing, China). Hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$), sodium borohydride and 4-NP were obtained from Shanghai Sijun Chemical Reagent Co., Ltd. All the chemicals were analytically pure and used without purification. Ultrapure water was used throughout the experiments which was obtained through an AXLM 1820-V AXL water equipment (Aoyunda).

Apparatus

Hitachi-600 transmission electron microscope (Hitach, Japan) was used to record transmission electron micrographs (TEM) and energy dispersive X-ray (EDX). Nicolet Nexus 670 Perkin-Elmer spectrometer was used to collected fourier transform infrared (FTIR) spectra. Agilent 5500 AFM was used to investigate atomic force microscopy (AFM) images. X-ray diffraction (XRD) were conducted by an X-ray diffractometer (X′ Pert Pro Philips, Cu Kα radiation, $\lambda = 0.154{,}056$ nm, $2\theta = 5°–80°$). Composition analysis of the Au NPs-NGQDs nanocomposites were proceeded on a Thermo Elemental IRIS Intrepid (USA) with a 4300 DV inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Absorption spectra was recorded by a TU-1901 UV–Vis spectrophotometer (double beams, 1.0 cm quartz cell) (Purkine General Instrument Co. Ltd., Beijing, China). A PHI-5702 multifunctional spectrometer with Al Kα radiation was used to measure X-ray photoelectron spectroscopies (XPS).

Synthesis of NGQDs

NGQDs were synthesized according to reference [28], which utilize hydrothermal method to treat citric acid and dicyandiamide. Citric acid (2 g) and dicyandiamide (1 g) were mixed with ultrapure water (5 mL). The mixed reactants were dissolved completely by ultrasonic and then poured into a 25 mL autoclave lined with Teflon and heated for 12 h at 180 °C. When the reaction was completed, cooled down the reactor in the air to room temperature. The product with dark brown color was transferred to 100 mL ultrapure water and centrifugated for 10 min at 10 000 rpm. Then, the NGQDs were obtained by discharging the black residue and large dots on the bottom. The concentration of N-GQDs' aqueous solution was around 20 mg/mL.

Synthesis of the Au NPs-NGQDs nanocomposites [28]

Au NPs-NGQDs were prepared by refluxing: 2 mL 20 mg/mL synthesized NGQDs coupled with 2 mL ultrapure water were mixed in a dual-port flask (25 mL), then the aqueous solution was reacted at 100 °C for 10 min under stirring. After that, added 0.5 mL 0.1 M $HAuCl_4 \cdot 4H_2O$ and stirred the above solution for 20 min. Then Au NPs-NGQDs nanocomposites formed and the solution color also turned from yellow to black. Cooled down the solution to room temperature naturally and centrifuged for 10 min at 10 000 rpm. The product was dried at 60 °C for 12 h.

Nanoparticle-catalyzed reduction of 4-NP

The conversion of 4-NP to 2-NP with $NaBH_4$ was proceeded to investigate the catalytic property of Au NPs-NGQDs. First, ultrapure water (2.70 mL), 4-NP solution (10 mM, 20 μL), and fresh-prepared $NaBH_4$ aqueous solution (0.1 M, 160 μL) were added into a standard quartz cell, respectively. Then, Au NPs-N-GQDs solution (0.4 mg mL^{-1}, 120 μL) was added into the same quartz cell. The reduction reaction was then recorded at room temperature by a UV–vis spectrophotometer (250–500 nm). The rate constants of the reduction reaction were calculated by measuring the time-dependent changes in absorbance of the solutions at 400 nm.

Results and discussion

Morphological and compositional characterization

TEM (Fig. 1) was used to examine the morphology and size of the NGQDs. The TEM image showed the well dispersion of NGQDs with homogeneous sizes at about 2 nm (see inset of

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