



One pot *in situ* growth of gold nanoparticles on amine-modified graphene oxide and their high catalytic properties



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ABSTRACT

In this work, one pot strategy was proposed for *in situ* growth of Au nanoparticles (Au NPs) on the surface of amine-modified graphene oxide (GO@NH₂) nanosheets. Au NPs were generated via an *in situ* reduction of Au³⁺ by Cu⁺ which was linked to the surface of GO@NH₂ nanosheets through inorganic grafting. The initial Au NPs then served as seed for subsequent particle growth. The as-obtained GO@NH₂-Au nanocomposites (GO@NH₂-Au NCs) exhibited high catalytic activity for the degradation of 4-nitrophenol, which was a refractory pollutant that occur in industrial waste water. The catalytic efficiency was examined by turnover frequency (TOF). It was calculated to be 595 h⁻¹, which was higher than that of other Au catalysts. Furthermore, the as-prepared catalyst showed high cycle stabilization during the catalytic reduction.

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1. Introduction

Noble metal particles of nanosized have attracted widespread attentions because of their unusual physicochemical properties, such as electronic [1,2], optical [3], biomedicine [4] and especially their catalytic activity [5–8] in a number of chemical reactions, which are totally different from those of bulk metals. As one of the most promising nanocatalysts, gold nanoparticles have been extensively explored for a variety of catalytic reactions in recent years [9,10]. Nevertheless, smaller Au NPs easily aggregate to minimize their surface area due to their higher surface energy, which lead to the decrease in their catalytic activity. To overcome this problem, numerous methods have been utilized to fabricate different Au NPs with tunable sizes and dimensions [11,12] or introduce Au NPs on/into less expensive solid supports, such as carbon spheres, carbon nanotubes [13], metal oxides [14,15], polymers [16,17], SiO₂ [9], and Fe₃O₄ to form composite catalysts [18–21]. In many cases, there exists a strong synergistic interaction between Au NPs and supports, which can greatly enhance the catalytic activity and selectivity [22].

Among them, graphene has been used as an outstanding support due to its two-dimensional plate-like structure and huge specific surface area [23,24]. It exhibits a number of intriguing properties, such as low manufacturing cost, excellent conductivity and good mechanical flexibility [25,26]. Thus considerable efforts have been made to incorporate graphene into composite materials and explore their applications in all kinds of fields [27–29]. Up to now, many kinds of graphene-based composites, such as, metal/graphene, metal oxide/graphene, polymer/graphene, and biomolecular/graphene have been reported and used in batteries [30], fuel cells [31], chemical sensors [32,33], electrocatalysis [34], and biosensors [35]. Meanwhile, graphene oxide (GO) sheets are generally used as raw materials or precursors of graphene sheets because of their good dispersibility, which have received a great attention in various applications, such as electrochemical energy storage, sensor, target delivery and photocatalysis [36–40]. Thus GO sheets exhibit a lot of advantages over their counterparts. Loading metal nanoparticles onto GO sheets not only prevent GO sheets from restacking but also obviously improve the catalytic activity owing to the strong synergistic interaction between the two components [41,42]. In addition, the introduction of GO sheets makes the materials easily separate from the reaction system [8]. To date, there have been a lot of reports on the preparation of 2D metal/GO (Au, Pd, Pt) composites nanosheets, for example, Zhang et al. prepared Au/GO nanocomposites without the addition of reductant [23]. He et al. synthesized Au/graphene nanosheets by one-pot

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solution method [43]. Shang et al. fabricated Pd supported on polyamine-modified graphene oxide [44]. Although some of these experimental procedures are simple, however, the resulting catalysts prepared by these approaches still suffer from more or less drawbacks, such as the uneven distribution and limit loading of the metal NPs, low catalytic activity of the catalysts and the cause of environmental pollution. Compared with the traditional preparation method, *in situ* synthesis method is a distinguished method which can better control of the metal loading and effective dispersion [29,45,46]. In the past, Zhong et al. reported an *in situ* method to reduce Pd²⁺ by Sn²⁺ and subsequently deposit highly dispersed palladium (Pd) NPs onto the surface of hydroxyl-group-rich TiO₂ precursor [47]. Zheng et al. developed an approach for *in situ* catalyzing Au NPs loaded in Fe₃O₄@SiO₂ magnetic nanospheres via Sn²⁺ linkage and reduction [7]. These researches may provide a feasible approach for *in situ* assembling of well-dispersed Au NPs on other activated supports.

However, as far as we know, few studies have been reported about *in situ* growth of 2D Au/GO nanocomposites. Therefore, it is urgent to develop a reliable *in situ* synthesis method for immobilizing noble metal NPs on the surface of the GO supports. Herein, we developed a novel strategy to fabricate GO@NH₂-Au nanocomposites through *in situ* growth method and subsequently deposit well-dispersed Au NPs on both sides of 2D amine-modified graphene oxide nanosheets (Fig. 1). In this designed approach, the economical synthesis route of GO@NH₂-Au NCs via a one pot reduction of Au³⁺ by Cu⁺ was first achieved. The Cu⁺ species which were linked to the surface of GO@NH₂ nanosheets were used as a reducing agent to localize Au NPs on GO@NH₂ nanosheets. Sodium citrate was also added into the reaction system to control the growth of Au NPs. The as-prepared GO@NH₂-Au NCs exhibited excellent activity in catalyzing the reduction of 4-nitrophenol (4-NP) and other nitrophenols by NaBH₄ in aqueous phase at room temperature. In addition, the as-obtained GO@NH₂-Au NCs catalyst was recycled nine times and showed high stability due to its heterogeneous composite structure.

2. Experimental

2.1. Materials

Graphite (99.95%) with an average particle diameter of 4 mm, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) were all purchased from J&K scientific Ltd. (Beijing, China). Copper (I) chloride, sodium borohydride (96%) and sodium formate were bought from Sinopharm Chemical Reagent Company (Shanghai, China). Hydrogen tetrachloroaurate (III) tetrahydrate (HAuCl₄·4H₂O) was obtained from Shanghai Sijun Chemical Reagent Co., Ltd. Ethylenediamine was purchased from Tianjin Guangfu Chemical Reagent Factory (Tianjin, China). A dialysis chamber with a molecular weight cut-off of 8000–14,000 g mol⁻¹ was purchased from Beijing Ding-guo Biotechnology Co. (diameter 1/4 36 mm). All solvents and reagents were of analytical grade and directly used without further purification. Ultrapure water from an AXLM 1820-V AXL water system (Aoyunda) was used throughout the experiments.

2.2. Synthesis of GO sheets

Graphene oxide (GO) sheets were first synthesized according to the modified Hummer's method [48]. Graphite (1 g) was ground with NaCl (50 g) for 10 min. Then the NaCl was dissolved in ultrapure water and removed by filtration. The remaining graphite powder was stirred in 23 mL of concentrated H₂SO₄ for 8 h. After that, KMnO₄ (3 g) was gradually introduced into the mixture in

an ice bath. Subsequently, the mixture was stirred at 35–40 °C for 30 min and at 65–80 °C for another 45 min. Next, ultrapure water (46 mL) was added and the mixture was heated at 98–105 °C for 30 min. Finally, the reaction was terminated by the addition of ultrapure water (140 mL) and 30% H₂O₂ solution (10 mL), causing the color of the suspension to turn bright yellow. The product was collected by centrifugation and washed repeatedly with 5% HCl aqueous solution. The resultant product was suspended in ultrapure water to give a brown dispersion and subjected to dialysis to completely remove the residual salts and acids. The last suspensions were dried to get GO sheets for further usage.

2.3. Synthesis of the GO@NH₂ nanosheets

Thirty five milligram of the obtained GO sheets was dissolved in 30 mL ultrapure water. Then, the solution was initially ultrasonicated for 20 min with the addition of 42 mg EDC and 38 mg NHS. After magnetic stirring for 30 min at room temperature, 1.8 mL of ethanediamine was added and kept stirring for 2 h at 80 °C. The final stable black dispersion was centrifuged and washed with ultrapure water to neutral. The GO@NH₂ suspensions were dried to get the GO@NH₂ powder.

2.4. Synthesis of the GO@NH₂-Au NCs

Sixteen miligram GO@NH₂ was dissolved in 24 mL ultrapure water by ultrasonicated until GO@NH₂ was homogeneously dispersed in the solution. The mixture was followed by nitrogen bubbling for 10 min to remove the free oxygen in the solution, then 21 mg copper (I) chloride was added to the mixture under stirring and N₂ atmosphere for 20 min. Then, 0.48 mL HAuCl₄ solution (0.0485 M) was added to the activated solution under vigorously stirring for about 30 min. Finally, 20 mg sodium formate was added to the mixture. After stirring for 5 h at room temperature, the obtained mixture was separated by centrifugation and completely washed with ultrapure water, and then dried at 50 °C for further use. The final product was denoted as GO@NH₂-Au NCs. The GO@NH₂-Cu²⁺ nanocomposites (GO@NH₂-Cu²⁺ NCs) were synthesized with the same above method, without the addition of HAuCl₄ solution.

2.5. Catalytic reactions of GO@NH₂-Au NCs

The reduction of 4-NP with NaBH₄ was conducted to investigate the catalytic activity of GO@NH₂-Au NCs. Firstly, 2.70 mL ultrapure water, 20 μL 4-NP (10 mM) solution, and 160 μL of freshly prepared NaBH₄ (0.1 M) aqueous solution were added into a standard quartz cuvette, respectively. The color of the mixture turned to bright yellow rapidly. Subsequently, 120 μL GO@NH₂-Au NCs (0.1 mg mL⁻¹) was added to the above solution and the conversion of 4-NP was monitored by UV-vis absorption spectra at a short interval of time at room temperature. The rate constants of the reduction process were determined through measuring the change in absorbance at 400 nm as a function of time. As a control, gold nanoparticles with diameter of 13 nm were synthesized according to the literature [49]. The molar ratio of Au:4-NP:BH₄⁻ in the catalytic reaction was about 1:22:1753.

2.6. Apparatus and characterization

All the characterization and the experiment were carried out by GO@NH₂-Au NCs with Au content of 14.98 wt% at room temperature, unless otherwise stated. The morphologies and sizes of the as-prepared samples were characterized by a Hitachi-600 transmission electron microscope (TEM, Hitach, Japan) equipped

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