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Size-dependent work function and catalytic performance of gold nanoparticles decorated graphene oxide sheets

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ABSTRACT

We investigated the size-dependent work function and catalytic performance of gold nanoparticles (AuNPs) decorated graphene oxide (GO). The ultraviolet photoelectron spectroscopic analysis revealed that the work function decreased from 5.76 to 5.35 eV as the AuNP size was reduced from 40 to 5 nm. The catalytic performance of GO:AuNP hybrids was evaluated from the reduction of o-nitroaniline to 1,2-benzenediamine using sodium borohydride as a reducing agent. A considerable increase of the reaction rate constant with decreasing AuNP size is due to the enhanced surface interaction of AuNPs. Improved o-nitroaniline adsorption and electron transfer at the Au/GO interface leads to better catalytic activity, and this is more noticeable at an AuNP size of 5 nm. Our result indicates that GO:AuNP hybrids have considerable potential for use in industry wastewater treatment.

1. Introduction

In recent years, graphene, a two-dimensional (2D) honeycomb structure of carbon, has been known as a considerably interesting material in scientific research and technological applications because of its specified characteristic in mechanical, electric, optical, and thermal properties [1–7]. Chemically derived graphene oxide (GO) is a graphene sheet containing functional groups on its network such as hydroxyl, epoxide, carboxylic and carbonyl groups. The presence of these oxygen groups on 2D network of GO surface enhances its hydrophilic properties. Thus, GO is well dispersed in water and has excellent ability of attachments [8,9], which is regarded as the advantage of GO especially in the studies of the composite of GO with other nanomaterials.

Bulk gold is known to be a poor catalyst compared with other noble metals, however, there have been attempts to apply gold as a catalyst in the form of nanoparticles from 1980s. Up to now, gold nanoparticles (AuNPs) have been well-fabricated in different sizes and their unique properties were investigated from various approaches [10–13]. The AuNPs have different physical, chemical, and electrical properties from bulk Au because of the quantum confinement effect in small size and the large fractions of surface atom [14]. It was also found that the AuNPs have excellent catalytic activities on metal oxide or carbon supports [15–17].

In this work, we prepared AuNPs with various sizes of 5, 20, 40 nm and fabricated GO sheets decorated with AuNPs to study their size-dependent electrical and catalytic properties. The morphological properties of GO:AuNP hybrids were examined using transmission electron microscopy (TEM) and atomic force microscopy (AFM). The electrical properties of the GO:AuNP hybrids was analyzed from the Au size-dependent electron transfer at GO–Au interface using ultraviolet photoelectron spectroscopy (UPS). We also studied size-dependent catalytic performance by changing the Au size in GO:AuNP hybrids. The catalytic performance was investigated through the reduction of o-nitroaniline by sodium borohydride.

2. Experimental details

2.1. Synthesis of aqueous GO dispersion

1 g of graphite flake and 1 g of sodium nitrate were put into 50 mL of 96% sulfuric acid under stirring for 5 min, which was followed by a slow addition of 6 g of potassium permanganate and continuous stirring for 90 min [18]. After leaving the suspension at 45 °C for 2 h, 50 mL of water was gradually drop-casted under vigorous shaking. The suspension was diluted with additional 150 mL of water. Finally, 10 mL of 30% hydrogen peroxide was added to the diluted suspension, which underwent stirring for another 10 min.

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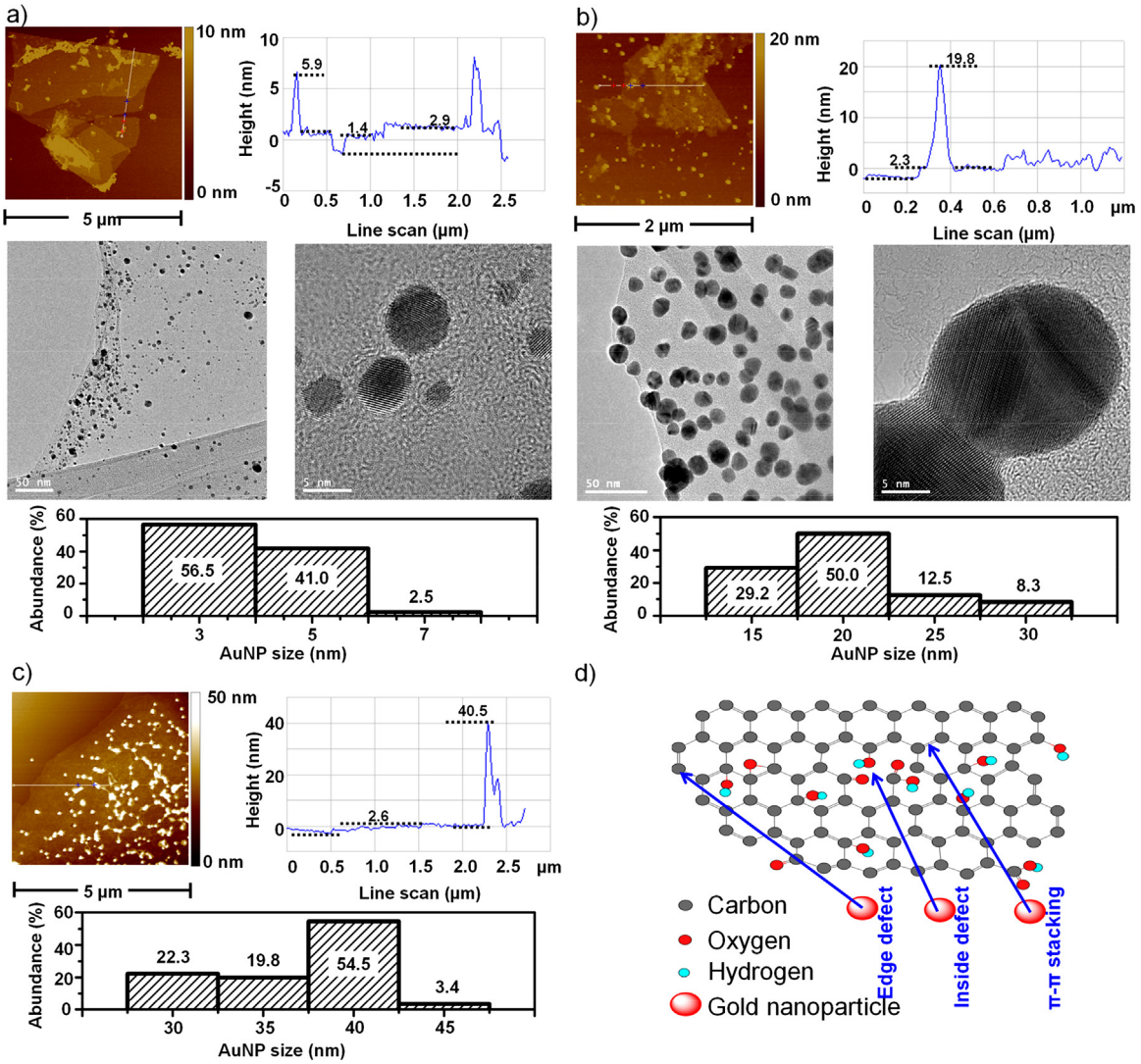

Fig. 1. The morphological surface of GO:AuNP hybrids with 5 nm (a); 20 nm (b); 40 nm (c) AuNPs performed by AFM, TEM, and HR-TEM measurements. (d) Illustrates Au decorated GO monolayer.

The centrifugation was performed at 5000 rpm for 5 min to remove the remained graphite. The GO was further washed using centrifugal at 7000 rpm for 5 min and this process was repeated until pH became 7. The colloidal GO was dried at 50 °C and then 0.3 g of the dried GO was dispersed with 1 L of deionized water.

2.2. Synthesis of GO:AuNP hybrids

To synthesize 5 nm AuNPs, 1 mL of 38.8 mM trisodium citrate (Na_3-citrate) was added to 10 mL of 1 mM $HAuCl_4$ and vigorously stirred for 15 min. 0.4 μg of sodium borohydride ($NaBH_4$) dissolved in 0.4 mL of 38.8 mM Na_3-citrate was slowly added dropwise to the Au precursor solution, which was followed by stirring for 120 min. To synthesize 20 nm AuNPs, 10 mL of 1 mM $HAuCl_4$ was vigorously stirred on a hot plate at 150 °C for 15 min. 1 mL of 38.8 mM Na_3-citrate was immediately introduced and continually stirred for 15 min [19]. 0.45 mL of 38.8 mM Na_3-citrate was introduced in the case of synthesizing 40 nm AuNPs. The deionized water was added to the AuNP sample to make 30 mL. To obtain GO:AuNP hybrids, 1 mL of GO solution (0.3 g L^{-1}), 1 mL of water, and 1 mL of AuNPs solution (0.333 μmol) were mixed together and stirred for 12 h.

2.3. Catalytic activity measurement

The catalytic performance of GO:AuNP hybrids was examined by applying them in the reduction reaction of o-nitroaniline which is known as a harmful material usually found in industry waste water. $NaBH_4$ was used as a hydrogen generation source in water. 0.3 mL of $NaBH_4$ (1.2 M), and 0.2 mL of GO:AuNPs (0.022 μmol of Au) were mixed in 4 mL of deionized water and stirred for 30 min. After 2 mL of mixture was put into the quartz cuvette, 0.3 mL of o-nitroaniline aqueous (3.4×10^{-3} M) was immediately added to initiate the reduction process. The color change of o-nitroaniline during reaction was monitored using a spectrophotometer (HP8453) by measuring the absorbance intensity at 410 nm.

2.4. Characterization

AFM and TEM measurements were performed to study the morphological surface of GO:AuNPs. To prepare the samples for AFM measurement, 0.2 mL of GO:AuNP hybrids was diluted with 4 mL of ethanol. 0.1 mL of the solution was drop-casted on 1 cm × 1 cm of silicon substrate and dried in ambient environment. AFM images