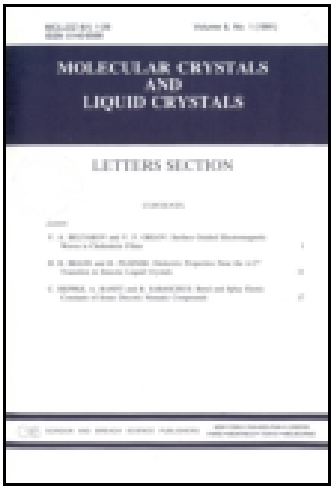

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Preparation of Highly Dispersed Gold Nanoparticles on Organosilane Modified Graphene Nanosheets

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Preparation of Highly Dispersed Gold Nanoparticles on Organosilane Modified Graphene Nanosheets

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In this study, we present a novel strategy for the immobilization of gold nanoparticles (AuNPs) on the surfaces of modified graphene oxide (MGO/Au) using (3-mercaptopropyl) trimethoxysilane as a bridging agent. In the fabrication process, the hydroxyl functionalized GO was covalently functionalized with (3-mercaptopropyl) trimethoxysilane through C−O−Si linkage and the terminal thiol groups were further used to fabricate MGO/Au hybrids via the specific interaction between −SH and Au. The degree of covalent functionalization and fabrication of MGO/Au hybrid materials were confirmed with Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, thermal gravimetric analysis and high resolution transmission electron microscopy (HRTEM) analyses. HRTEM images demonstrated that the AuNPs were homogeneously distributed on the surfaces of GO. The MGO/Au hybrid showed enhanced thermal stability due to the intrinsic properties of graphene and gold nanoparticles.

Keywords Graphene oxide; gold nanoparticles; covalent functionalization; silylation; self-assembly; GO/Au hybrid

Introduction

Metal nanoparticles have attracted great interest over the last decade owing to their wide range of applications in the fields of chemistry, physics, biology and medicine [1–3]. Among various metal nanoparticles, gold nanoparticles have been intensively studied since they exhibit peculiar optical and electronic properties such as surface plasmon resonance (SPR) by simple control of their size and shape. Therefore, gold nanoparticles are attracting increasing interest for use in photonics, catalysis, electronics, and biomedicine applications [4–6]. There are many methods available for the preparation of gold nanoparticles with various morphologies. In particular, the synthesis of gold nanoparticles in the aqueous

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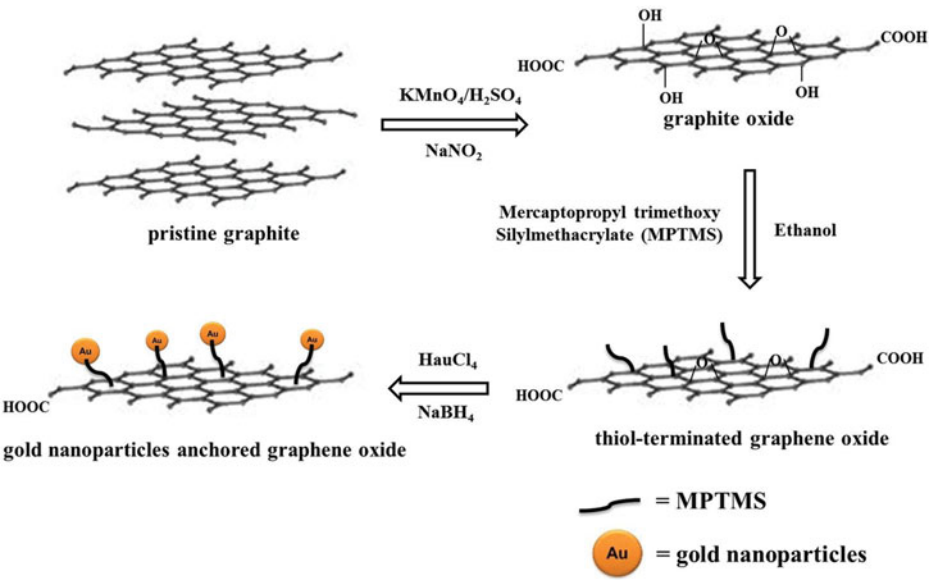
phase by the reduction of gold salts ($HAuCl_4$) using $NaBH_4$ is the simplest and most employed method [7].

On the other hand, hybrids containing carbon nanomaterials and gold nanoparticles combine the advantages of two kinds of materials, and have many potential applications in sensors [8], optical electronics [9] and electrocatalysis [10]. More specifically, graphene, planar monolayers of sp^2 bonded carbon atoms tightly packed into a two-dimensional honeycomb lattice, has gained significant interests because of their excellent optical, mechanical, electronic and biological properties [11–13]. This unique nanostructure is emerging as a versatile material for applications in nanoscience and nanotechnology. One of the most common preparation method of graphene starts from the oxidation and exfoliation of graphite to graphene oxide (GO).

It is well known that, GO consists of several oxygen-containing groups such as hydroxyl, epoxy, carbonyl and carboxyl groups. The presence of these functional groups makes GO strongly hydrophilic, which allows GO to readily disperse in water. The reactive functional groups situated at the edges of GO can facilitate not only their dispersion in a range of solvents but also their further modification with polymers or metal nanoparticles [14]. Various methods have been reported to modify the surface of GO. Among them, covalent and noncovalent modifications have been extensively studied [15]. Based on this concept, a mild covalent functionalization of GO with organosilane is developed in this study.

Herein, we describe a facile approach for the deposition of AuNPs on the surface of modified GO nanosheets (MGO/AU) via covalent approach using (3-mercaptopropyl) trimethoxysilane (MPTMS) as a crosslinker. Two-step procedure is demonstrated to obtain MGO/Au hybrid, as shown in Scheme 1. First step involves the covalent functioanlization of GO with MPTMS and the second step involves the attachment of virgin AuNPs on the surface of functionalized GO via gold-thiol linkage.



Scheme 1. Schematic illustration of the synthesis of MGO/Au composites.

Experimental

Materials

Graphite powder, MPTMS, hydrogen tetrachloroaurate $HAuCl_4$ (gold solution; 30 wt.% in dilute HCl) and sodium borohydride ($NaBH_4$) were obtained from Sigma–Aldrich (Korea) and used as received. Conc. sulfuric acid (H_2SO_4) and hydrochloric acid (HCl), potassium permanganate ($KMnO_4$), Sodium nitrate ($NaNO_3$) and hydrogen peroxide (H_2O_2) were purchased from Junsei chemicals (Japan) and used without further purification.

Preparation of GO

GO was synthesized from natural graphite according to the previously reported method [16]. Typically, 1 g of graphite, 0.5 g of $NaNO_3$ and 23 mL of H_2SO_4 were mixed in an ice bath. Subsequently, 3 g of $KMnO_4$ was slowly added. The mixture was stirred at 35°C for 30 min. Then, 46 mL of water was added and the mixture was heated at 98°C for 30 min. The reaction was terminated by addition of 170 mL of aqueous solution of H_2O_2 (0.05 wt%), resulting in a yellow brown mixture. The as-obtained GO was centrifuged, washed with 10% of HCl followed by water and dried under a vacuum at 40°C for 24 h.

Covalent Modification of GO with (3-Mercaptopropyl) Trimethoxysilane

The covalent functionalization of GO with MPTMS was carried out as follows. Briefly, 0.1 g of GO was dispersed in 25 mL of ethanol with ultrasonication for 30 min. Then, 10 mL of MPTMS was added to the dispersion and the reaction mixture was stirred at 70°C for 24 h. The black precipitate was separated by centrifugation, washed thoroughly with water and absolute ethanol to remove any impurities, and then dried under vacuum at 50°C for 24 h.

Synthesis of Modified Graphene Oxide/AuNPs Composites (MGO/Au)

The virgin AuNPs were anchored on the MGO as follows. Briefly, 0.1 g of MGO was dispersed in 25 mL of DI water and ultrasonicated for 30 min. 100 mL of 10^{-4} M aqueous solution of $HAuCl_4$ was added to the dispersion and stirred for 10 min. Then, 0.01 g of $NaBH_4$ was added to the reaction mixtures and stirred at 25°C for 2 h. The resultant product was filtered and washed several times with DI water and dried under vacuum at 40°C. The entire synthesis from covalent functionalization to formation of the MGO/Au hybrid is illustrated in Scheme 1.

Characterization

Fourier transform infrared spectra (FTIR) were recorded on a Perkin-Elmer FTIR spectrometer in the range 4000–400 cm^{-1}. For FTIR analysis, the samples were finely ground with KBr powder and pressed into a pellet using a hydraulic press. X-ray photoelectron spectroscopy (XPS) measurements were obtained with an ESCA 2000 XPS (Thermo VG Scientific) spectrometer using a monochromatic MgKα ($h\nu = 1253.6$ eV) X-ray source. Thermal gravimetric analysis (TGA) was conducted on a Perkin–Elmer Pyris 1 TGA under nitrogen flow from 50 to 850°C at a heating rate of 10°C/min. X-ray diffraction (XRD) patterns of the samples were carried out by using Rigaku X-ray diffractometer with Cu Kα

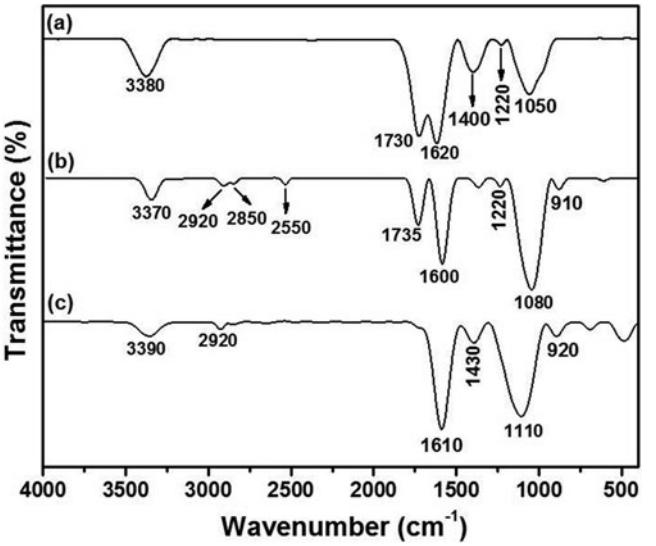


Figure 1. FTIR spectra of (a) GO (b) MGO and (c) MGO/Au composites.

radiation ($\lambda = 0.15418$ nm) under a voltage of 40 kV and a current of 40 mA. Samples were scanned over the range of diffraction angle $2\theta = 5$–80°, with a scan speed of 2°/min at room temperature. High resolution transmission electron microscopy (HRTEM) images were obtained using a Hitachi JEOL-2100 (Japan) microscope with an accelerating voltage of 200 kV. Samples for the HRTEM analysis were prepared by dropping the sample dispersion on a carbon coated copper grid and allowed them to dry in air before analysis.

Results and Discussion

The covalent functionalization of GO was confirmed by the FTIR spectroscopy. Fig. 1 shows the FTIR spectra of GO, MGO and MGO/Au hybrids. For the pristine GO, the broad band at 3380 cm^{-1} is attributed to O—H stretching vibration, while the strong band at 1620 cm^{-1} is assigned to the skeleton vibration of unoxidized graphitic domain. In addition, the characteristic bands at 1730, 1400 and 1220 cm^{-1} are associated with C=O, C—O and epoxy C—O stretching vibrations, respectively. In the case of MGO (Fig. 1b), the peaks at 2920 and 2850 cm^{-1} are associated with the symmetric and asymmetric CH_2 stretching vibrations of MPTMS attached to the GO surface. The broad peak in the range from 1180 and 1080 cm^{-1} is assigned to the stretching vibration of Si—O—C/Si—O—Si bonds, while the weak band at 2550 cm^{-1} is attributed to the —SH group. Furthermore, the weak band is observed at 910 cm^{-1} due to the free Si—OH groups. These bands suggested that MPTMS molecules are successfully bound to the surface of GO. However, the spectrum of the MGO/Au hybrid displays a similar spectrum to that of MGO. After deposition of AuNPs on the surface of MGO, the weak band at 2550 cm^{-1} completely disappeared, suggesting the AuNPs were covalently attached to the MGO surface via S–Au linkage.

To further determine whether AuNPs are anchored on the surface of MGO and to get information on the intensity of crystallization, XRD measurements were performed. The XRD patterns of natural graphite, GO, MGO and MGO/Au hybrids composites are displayed in Fig. 2. It can be seen that, a sharp diffraction peak is present at $2\theta = 26.68^\circ$

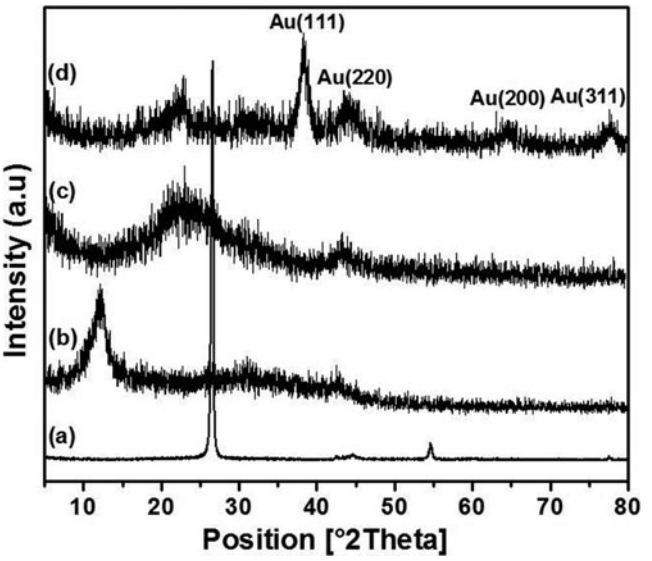


Figure 2. XRD patterns of the (a) pristine graphite (b) GO (c) MGO and (d) MGO/Au composites.

characterized as the crystalline structure of natural graphite. With the oxidation treatment, the original diffraction peak of the natural graphite disappeared, and a small peak at $2\theta = 12.98^\circ$ appeared, corresponding to the (001) reflection of GO. However, after functionalization with MPTMS, the diffraction of peak of GO disappeared and a new peak was observed at 24.5°, indicating the restoration of graphene network by the functionalization procedure. However, the X-ray pattern of the MGO/Au composites presents both the characteristic peaks of AuNPs and graphene. The weak diffraction peak at $2\theta = 26.5^\circ$ corresponding to the (002) planes of the graphite like structure and the strong diffraction peaks at $2\theta = 39.1$, 44.1, 64.6 and 77.4° can be assigned to the characteristic (111), (200), (220) and (311) crystalline planes of AuNPs, respectively, which possesses face-centered-cubic (fcc) structure. This indicates the presence of metallic AuNPs in the composites. This result was further confirmed by the XPS analysis.

The core-level XPS spectrum of the MGO/Au composites is displayed in Fig. 3. The spectrum of the composites shows major peaks at 284.5 and 533.5 eV, corresponding to the carbon atoms (C1s) and oxygen atoms (O1s) respectively. The O1s signal can be derived from the various oxygen-containing functional groups such as C=O, C−O and OH. In addition, the composites exhibits a sulphur region at 165 eV and silica region at 101.5 eV, indicating the GO has been successfully functionalized by MPTMS with free SH groups. It is worth noting that the weak peak at 83.5 eV corresponds to the Au bonded sulphur matrix, presumably suggesting that the interaction between S and Au through S−Au chemistry.

The successful deposition of AuNPs on the modified GO was confirmed by HRTEM measurements. Fig. 4 presents the typical HRTEM micrographs of the as-prepared MGO and MGO/Au under different magnifications. The HRTEM image of MGO shows the curled and transparent morphology. The HRTEM images of the composites (Fig. 4c and d) under different magnifications clearly indicate AuNPs are homogeneously dispersed on the surface of the MGO sheets without any significant agglomeration.

The TGA thermograms of pristine graphite, GO, MGO and MGO/Au composites are presented in Fig. 5. The pristine graphite exhibits little weight loss until 700°C. As shown

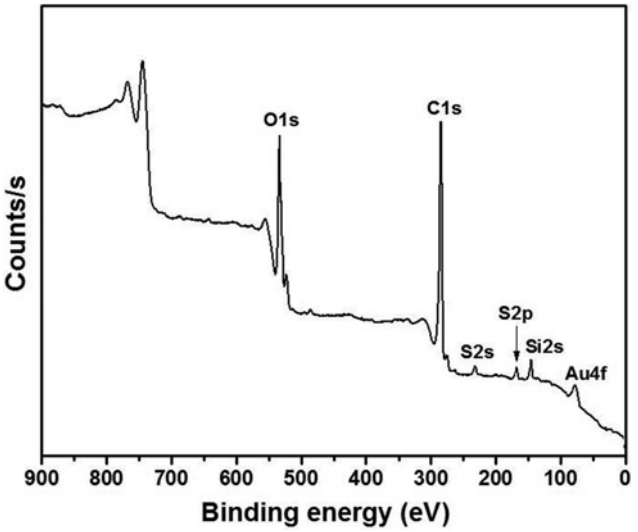


Figure 3. XPS spectrum of MGO/Au composites.

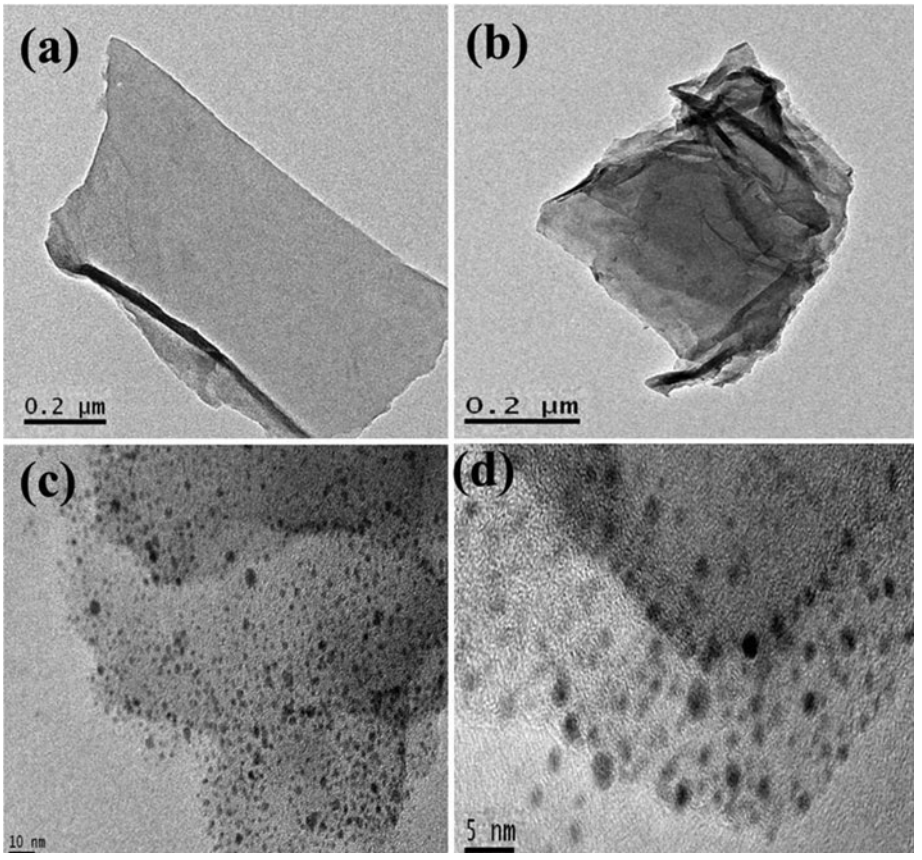


Figure 4. HRTEM images of the (a) MGO and (b) MGO/Au composites under different magnifications.

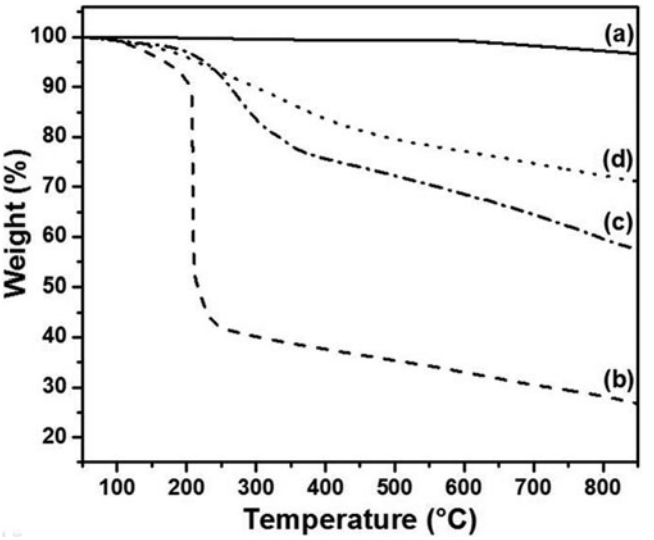


Figure 5. TGA curves of the (a) pristine graphite (b) GO (c) MGO and (d) MGO/Au composites.

in Fig. 5a, the mass loss of GO before 100°C is attributed to the evaporation of the absorbed water and the major mass loss occurs at ∼190°C can be assigned to the pyrolysis of the labile oxygen-containing functional groups. For MGO, the total weight loss is 25%, which is related to the pyrolysis of MPTMS, indicating a successful grafting of MPTMS onto GO. The TGA thermogram of MGO/Au composites presents a two stage weight loss profile. The weight loss below 350°C is associated with the decomposition of MPTMS and the main one, above this temperature, is due to the carbon skeleton degradation. However, the composites displays an increased stability which may be attributed to the presence of well-dispersed AuNPs on the surface of MGO.

Conclusions

The MGO/Au nanohybrid was prepared by the chemical reduction method using MPTMS as a bridging agent. The nanostructure was chemically and morphologically evaluated by FTIR, XRD, XPS and HRTEM measurements. HRTEM micrographs confirmed that AuNPs were homogeneously dispersed on the surface of the functionalized GO sheets. Furthermore, the nanohybrids exhibited the enhanced thermal stability due to the intrinsic properties of MGO and AuNPs.

Funding

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