

One-pot Fabrication of Au/graphene Nanocomposites from Graphite Using Polyethylene Glycol

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Graphene, a one atom-thick 2D honeycomb-structured carbon compound, has a remarkable electric conductivity even at room.^{1,2} Owing to these properties, it is being studied for a wide range of applications such as for supercapacitors, solar cells, batteries, transparent conductors and catalysts.³ There are many ways to obtain graphene, such as the peel-off method, chemical exfoliation of graphite, and chemical vapor deposition (CVD).⁴ The most common exfoliation method was introduced by Ruoff group who synthesized graphene oxide (GO) based Hummers and Offeman's method using strong oxidizing reagents such as sulfuric acid and potassium permanganate.⁵ The oxygen molecules attached to the graphite layers cause them to repel each other and exfoliate into thin sheets. However, this oxidation and the following reduction process results in defects of the reduced graphene oxide (rGO) due to hazardous chemicals. In addition, the use of hazardous chemicals such as hydrazine makes this method problematic for large-scale manufacturing. In this sense, it is important to develop a simple, realistic technique to exfoliate graphite. Sonication seems to have potential for the scalable production of graphene, and exfoliation in various solvents such as *N,N*-dimethylformamide (DMF),⁶ *N*-methylpyrrolidone (NMP),⁷ *ortho*-dichlorobenzene (oDCB)⁸ and benzylamine⁹ has been previously reported.

Recently, there have been studies on graphene and metal nanoparticle composites aiming to enhance the catalytic activity of the metal nanoparticles. The GO attracts metal salts or nanoparticles due to its oxygen-containing functional groups. The synthesis of nanoparticle/graphene composites using surfactants such as sodium dodecyl sulfate (SDS)¹⁰ and cetyltrimethyl ammonium bromide (CTAB) has been reported.¹¹

In previous studies, the exfoliation process had the drawback of using GO, toxic materials, and requiring a separate solvent and surfactant. In this communication, we report a new simple, one-pot exfoliation method using polyethylene glycol (PEG) as a solvent that initially adheres to the surface of graphene flake after ultrasonication. PEG also acts as reducing agent for the gold (Au) ions that form the nanoparticles. Moreover, this method does not require an oxidation/reduction process for graphene, which we believe, will result in fewer defects on the resulting products.

In the experiment, we used 3 mg of graphite powder and 10 mL of PEG (Mn = 400). The graphite powder was provided

by Samchun Chemicals and PEG by Sigma-Aldrich. Sonication was conducted for 40 min using a 600 W horn sonicator from SonicTopia. Then, graphene layers dispersed in the PEG solvent were observed. After adding 0.5 mL of 5 mM HAuCl₄, the solution was subjected to white light for 1 h, leading to the photo-assisted fabrication of Au nanoparticles. During the experiment, the temperature was maintained between 60-70 °C. When we increased the temperature to 200 °C, which means the decrease of PEG viscosity, the results were not satisfactory (Supporting information).

Figure 1(a) and 1(b) show the transmission electron microscopy (TEM) images of the solution after the sonication of graphite in PEG solvent. The dark areas, indicated by the arrow in Figure 1(b), represent the graphites still stacked in many layers. In our experiment, after Au ions infiltrated between the graphene flakes with PEG, Au nanoparticles were synthesized by photo reaction, which caused the pre-exfoliated graphite into graphene. Au nanoparticles with two different sizes of about 10 nm and 2 nm on the graphene are shown in Figure 1(c) and 1(d). In addition, a great decrease in the thickness of the graphene layers is observed. The X-ray diffraction (XRD) pattern shown in Figure 2 confirms the synthesis of Au nanoparticles which can be indexed to <111>, <200>, <220> and <311> of Au. (face-centered cubic,

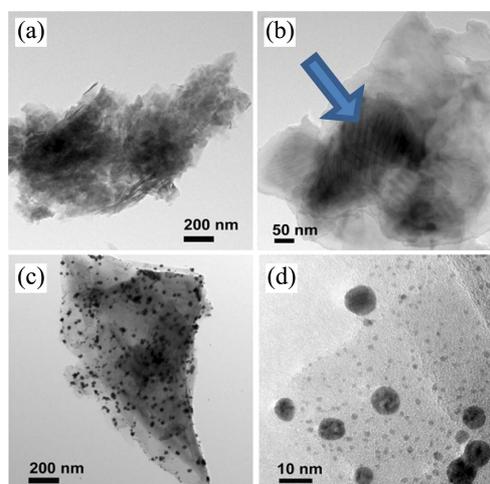


Figure 1. TEM images of graphene flakes functionalized with PEG (a), their magnified image (b) and Au/graphene nanocomposites (c), (d).

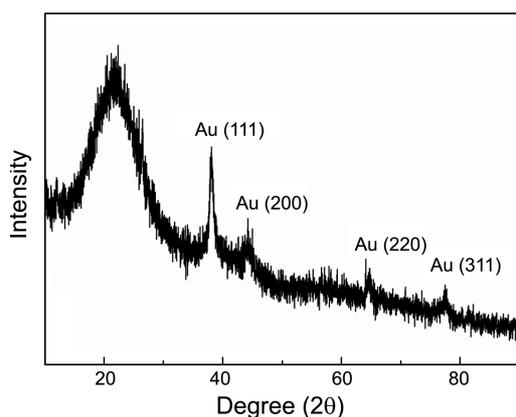


Figure 2. XRD Pattern of Au/graphene.

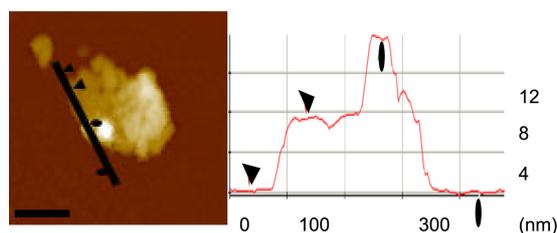


Figure 3. AFM image of Au/graphene nanocomposite.

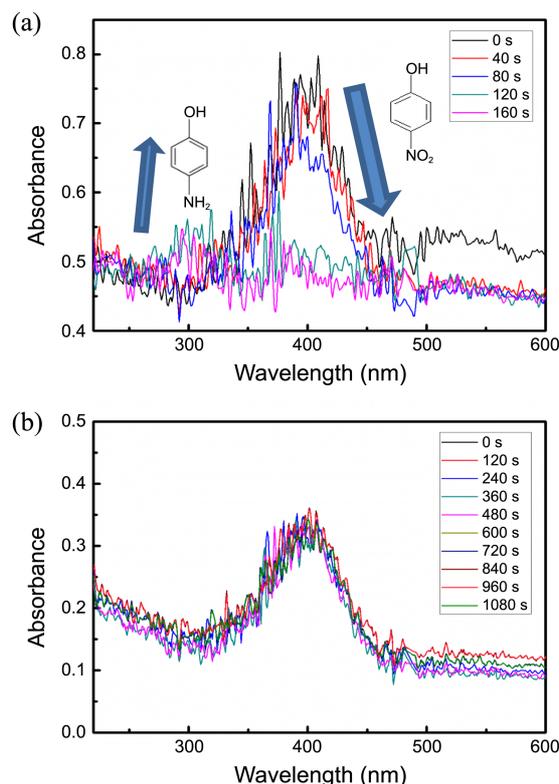


Figure 4. UV-vis absorption spectra of the reduction of 4-nitrophenol by NaBH_4 in the presence of Au/graphene (a) and Au/rGO (b).

JCPDS 4-0783). We could not observe the graphite peak at 26° . To check the thickness of graphene synthesized from graphite, we use atomic force microscopy (AFM). The data in Figure 3 shows that the graphene has a thickness of 7 nm.

The catalytic activity of the Au/graphene nanocomposite

was tested using reduction reaction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH_4 as a hydrogen source. (Figure 4) The reaction was investigated with UV-vis absorption spectroscopy. The peak at 400 nm corresponding to the absorption of 4-NP decreases as the peak at 300 nm of 4-AP peak increases. It is well known that the catalytic activity of Au/rGO is better than that of Au nanoparticles.^{12,13} Therefore, we tested Au/graphene from graphite and Au/rGO from reduction of GO with ascorbic acid as a reducing agent. In the case of Au/graphene as a catalyst, the reaction proceeded rapidly and the peak at 400 nm was almost negligible after 2 mins, while in the case of Au/rGO, the peak slightly decreased even after 18 mins; Au amounts in Au/graphene and Au/rGO are 70.07 and 82.25 wt %, respectively. The reason is not much convincing, however, we guess remained oxygen in Au/rGO affect the reduction reaction.

In conclusion, Au/graphene nanocomposites from graphite were fabricated directly using polyethyleneglycol. PEG acted as a solvent to initially exfoliate graphite under sonication and as a reducing agent for the Au ions to produce the nanoparticles. It is thought that the viscosity of PEG hinders the restacking of graphite during the intercalation of Au nanoparticles. This method is time-efficient compared to the synthesis of rGO and it is simple because separation of the surfactant is not required.

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