

Supplementary Information

Layer-by-Layer Assembly of Graphene and Gold Nanoparticles by Vacuum Filtration and Spontaneous Reduction of Gold Ions

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Experimental details

1. General

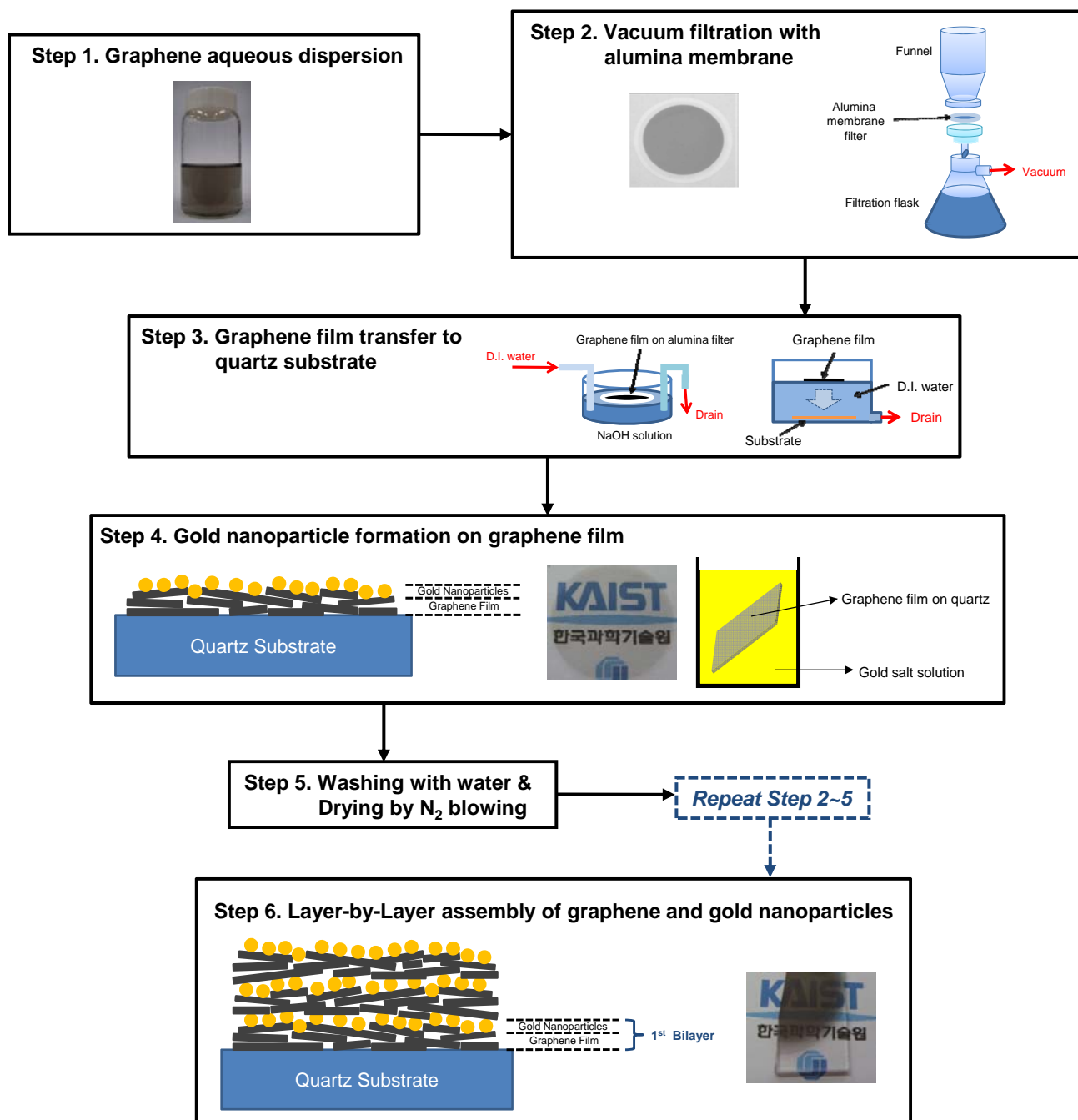
All chemicals were used without purification or treatment and deionized water (18 M Ω ·cm) purified by an ultra-pure water system (Milli-Q, Millipore) was used in all experiments. All procedures were performed under ambient temperature in air.

2. Preparation of graphene-gold nanohybrid films

Graphite oxide, was prepared from natural graphite (FP 99.95 % pure, Graphit Kropfmühl AG) by using a modification of the method described by Hummers.[1-3] For the exfoliation of graphite oxide, sonication by bath sonicator (FS140H, 135 W, 42 kHz; Fisher Scientific) was carried out for 30 min to yield a 0.5 mg/mL graphene oxide aqueous dispersion. The procedure reported by Li et al.[4] was used for the reduction of graphene oxide to graphene. The homogeneous graphene oxide dispersion (5.0 mL) was mixed with 5.0 mL of water, 5.0 μ L of hydrazine solution (35 wt% in water, Aldrich), and 100.0 μ L of ammonia solution (28 wt% in water, Junsei Chemical). The hydrazine to graphene oxide weight ratio is 7:10, which was suggested to be optimal by Li et al.[4] The mixture was stirred at 95 °C for 1 h. The dispersion was centrifuged at 15000 rpm for 30 min to remove flocculated graphene using a Sorvall Biofuge Stratos centrifuge with #3335 rotor (Step 1 in Scheme 1).

The graphene films were prepared on a quartz substrate by using the vacuum filtration method described previously.[5] The vacuum filtration of graphene dispersion was performed using a porous alumina membrane filter (200 nm pore size, 25 mm diameter; Whatman) (Step 2). The graphene film was placed directly into a bath of 3 M NaOH. The alumina membrane was then dissolved, and the thin graphene film was floated on the surface of the NaOH solution. The NaOH solution was exchanged with deionized water by recirculation until the pH was *ca.* 7. A piece of the quartz substrate was immersed into the water and allowed to sink to the bottom of bath. As the water was drained, the floating graphene film slowly descended and attached onto the quartz substrate. The graphene film on the quartz was dried in an oven at 60 °C for 12 h (Step 3). To form gold nanoparticles on the graphene

films, the graphene film was immersed in a 1 mM solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ($\geq 99.9\%$ pure, Aldrich) in 50 vol% ethanol for 10 min. The sample was rinsed extensively with deionized water and dried under nitrogen gas (Steps 4-5).



Scheme 1. Schematic of the steps involved in fabrication of layer-by-layer assembled films consisting of graphene sheets and gold nanoparticles.

3. Characterization

Images of graphene films after formation of gold nanoparticles were taken at various magnifications using a Sirion field emission scanning electron microscope (SEM; FEI). The gold nanoparticles on the graphene films were analyzed using a JEM-2100F HR field emission transmission electron microscope (TEM; Jeol). The structure of the gold particles was analyzed by TEM performed in bright field mode at 200 keV. TEM samples were prepared by detaching graphene films from quartz substrates.[5] The graphene film was covered with a 25 % aqueous solution of poly(acrylic acid) (PAA; Aldrich). After drying in air, the PAA/graphene film composite was easily peeled off of the quartz substrate and then floated on deionized water PAA-side down for several hours. When the PAA layer was completely dissolved in the water, the floating graphene film was recovered on a copper TEM grid. TEM sample of the LbL film was prepared by cross sectioning by the focused-ion beam (FIB; FB-2100; Hitachi) with the thickness of 100 nm. Energy-dispersive X-ray spectroscopy (EDS) mode of TEM and ESCA 2000 X-ray photoelectron spectrophotometer (XPS; VG) with a monochromated Mg K α radiation (1253.6 eV) were used for elemental analyses of graphene films. The optical absorbance of graphene films was measured by a V-570 UV/VIS/NIR spectrophotometer (JASCO) and a quartz sheet was used for the reference. The resulting data represent the transmittance of a graphene film excluding the transmittance of a quartz substrate. The topologies of graphene oxide and reduced-graphene oxide were measured by using non-contact mode of atomic force microscope (AFM; SPA 400; Seiko Instruments Inc.) with specimens prepared by depositing each dispersion on a mica surface (Muscovite Mica; Electron Microscopy Sciences). The work function of reduced-graphene oxide films was measured by using an ultraviolet photoelectron spectroscopy (AC-2; RKI Instruments) in the air. It was determined by using gold metal (4.75 eV) as a reference. This reference value is measured with an e-beam evaporated gold thin film on glass substrate and very similar to the previous results (4.78 eV).[6] The reduction potential versus the standard hydrogen electrode (SHE) is converted into the energy relative to the vacuum level (E_{abs}), i.e. work function, using the relation: $E_{\text{abs}}(\text{eV}) = -4.50 - E_{\text{SHE}}(\text{V})$. [7]

References for Supplementary Information

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