Supporting Information

The Direct Growth of Gold Rods on Graphene Thin Films
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Materials and Methods

Materials.
Natural graphite (FP 99.95 % pure) was purchased from Graphit Kropfmühl AG (Hauzenberg, Germany). Hydrogen tetrachloroaurate(III) hydrate was purchased from Kojima Chemicals Co.(Sayama, Saitama, Japan). Cetyl trimethyl ammonium bromide (CTAB) and di-tert-butyl dicarbonate were purchased from Across (New jersey, USA). Ethanol was purchased from Merck (Darmstadt, Germany). Potassium permanganate, 3-aminopropyltriethoxysilane, Sodium borohydride, anhydrous toluene, anhydrous dimethylformamide (DMF), ascorbic acid, pyrene butyric acid, diisopropylethylamine, dicyclohexylcarbodiimide, 1-hydroxybenzotriazole, trifluoroacetic acid and 1,2-Bis(2-aminoethoxy)ethane were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Hydrogen peroxide, sodium nitrate, trisodium citrate dehydrate and chloroform were purchased from Junsei Chemical Co. (Tokyo, Japan). Sulfuric acid was purchased from Samchun (Seoul, Korea). 500-nm SiO2/P++ Si substrates (500 μm in thickness) and 4 inch quartz wafers (500 μm in thickness) were respectively purchased from STC (Japan) and i-Nexus (Stamford, USA). All chemicals were used as received.

Synthesis of graphite oxide.

Synthesis of Au nanoparticles
20 ml of aqueous solution containing tri-sodium citrate (250 μM) and HAuCl4 (250 μM) was prepared in conical tube. 0.6 ml of ice cooled NaBH4 solution (0.1 M) was added to the solution at once with gentle shaking. The diameter of synthesized particles was approximately 5 nm. This gold nanoparticle solution was used as a seed for gold rod growth after 2 - 5 hours from synthesis.

Synthesis of graphene oxide (GO)
1.5 g of natural graphite and 0.5 g of NaNO3 were added in 23 ml of H2SO4 and stirred in an ice bath. Then, 3 g of KMnO4 was slowly added to the mixture with stirring while temperature was maintained below 20 °C. After addition, the reaction mixture was heated to 35 °C and stirred for an hour. Then, 40 ml of distilled water was added to the
mixture and stirred for 30 min. 100 ml of water was added to the reaction mixture in an ice bath to prevent rapid boiling of the reaction mixture. Finally, 3 ml of H₂O₂ (30 %) was dropwised to the reaction mixture. The mixture was filtered and thoroughly washed with copious water until the filtrate was neutralized. The filter cake was dried at room temperature under vacuum for 48 hours. The synthesized graphite oxide was exfoliated and dispersed in water by sonication for 30 min.

**Immobilization of GO on the substrate**

The 500-nm SiO₂/Si substrates were immersed in the piranha solution (hydrogen peroxide (30%): sulfuric acid = 1:3, WARNING: Piranha solution is highly corrosive and reactive. Handle with caution.) for 10 min at 125 °C, washed with water and ethanol and dried under a stream of nitrogen. The piranha treated substrates were immersed in the 10 mM anhydrous toluene solution of 3-aminopropyltriethoxysilane for 30 min, sonicated in toluene for 2 min, washed with water and ethanol and dried under a stream of nitrogen. After surface functionalization, the substrates were immersed in the graphene oxide suspension (1.5 mg/ml) for an hour, washed with water and ethanol and dried under a stream of nitrogen. The substrate was baked at 125 °C for 10 min under nitrogen atmosphere.

**Reduction of immobilized GO on the substrate**

The GO coated substrates were immersed in the 20 % hydrazine monohydrate solution in DMF at 80 °C for 24 hour, washed with water and ethanol and dried under a stream of nitrogen. The hydrazine treated substrates were further reduced by thermal annealing at 500 °C for an hour under argon atmosphere.

**The synthesis of pyrene ethyleneglycol amine**

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\begin{align*}
1 & \quad \text{H}_2\text{N-O-O-NH}_2 \\
2 & \quad \text{O} \quad \text{O} \\
3 & \quad \text{Boc} \quad \text{O} \\
4 & \quad \text{O} \\
5 & \quad \text{O} \\
\end{align*}
\]
**Synthesis of compound 2**

1,2-Bis(2-aminoethoxy)ethane 1 (12.2 g, 83 mmol) was stirred with diisopropylethylamine in 50 mL of chloroform (CH$_2$Cl$_2$) (4.8 mL, 28 mmol), then di-tert-butyl dicarbonate (6 g, 27 mmol) in 30 mL of CH$_2$Cl$_2$ was added for 30 min. The reaction mixture was stirred overnight at R.T., then solvent was removed. The mixture was dissolved in CH$_2$Cl$_2$ and washed with H$_2$O twice. Organic layer was taken and dried. It was used for next step without further purification.

**Synthesis of compound 4**

Compound 2 (431 mg, 1.74 mmol), pyrene butyric acid 3 (500 mg, 1.73 mmol), 1-hydroxybenzotriazole (234 mg, 1.73 mmol), and dicyclohexylcarbodimide (358 mg, 1.74 mmol) were dissolved in 20 mL of CH$_2$Cl$_2$ at 0°C. The reaction mixture was stirred at R.T. for 24 hours. H$_2$O was poured into the flask, and the reaction mixture was extracted with CH$_2$Cl$_2$ and purified by column chromatography to obtain the product 4 (670 mg, 75%).

1H NMR (CDCl$_3$) $\delta$ 1.41 (s, 9H), 2.18-2.29 (m, 6H), 3.22-3.25 (m, 2H), 3.35-3.53 (m, 10H), 7.85 (d, J=0.03 Hz, 1H), 7.94-8.16 (m, 7H), 8.29 (d, J=0.03 Hz, 1H)

**Synthesis of compound 5**

Boc-protected compound 4 (500 mg, 0.94 mmol) was dissolved in 30 % TFA solution in CH$_2$Cl$_2$. The reaction mixture was stirred overnight at R.T. Solvent was removed and the reaction mixture was purified by column chromatography (silica, CH$_2$Cl$_2$: MeOH=10:1) to obtain the compound 5 (360 mg, 92%).

1H NMR (CDCl$_3$) $\delta$ 2.11-2.15 (m, 4H), 2.25-2.30 (m, 2H), 2.85 (t, J=0.017 Hz, 2H), 3.29-3.38 (m, 4H), 3.42-3.53 (m, 6H), 6.57-6.59 (m, 1H), 7.81 (d, J=0.03 Hz, 1H), 7.91-8.12 (m, 7H), 8.25 (d, J=0.03 Hz, 1H)

**Seedless growth of gold rods on the reduced GO (RGO) surface**

The RGO coated substrates were immersed aqueous growing solution containing 9 ml of 100 mM CTAB, 450 μl of 10 mM hydrogen tetrachloroaurate and 50 μl of ascorbic acid for an hour, washed with water and ethanol and dried under a stream of nitrogen.

**Seed mediated growth of gold rods on RGO surface**

The RGO coated substrates were immersed in the 1 mM ethanolic solution of pyrene ethylene glycol amine for 12 hours, washed with water and ethanol and dried under a stream of nitrogen. The surface modified RGO substrates were immersed in the prepared gold seed solution for 20 min, washed with water and ethanol and dried under a stream of nitrogen. The seed adsorbed RGO substrates were respectively immersed in the aqueous growing solution containing 9 ml of 100 mM CTAB, 110, 225, 450 and 560 μl of 10 mM hydrogen tetrachloroaurate and 50 μl of ascorbic acid for an hour, washed with water and ethanol and dried under a stream of nitrogen.

**Characterization.**
Size of gold nanoparticles was determined by Tecnai G2 F30 Field Emission TEM (FEI company, The Netherlands). S-4800 Field emission SEM (Hitachi, Japan) was used to observe heterogeneous interfacing system of RGO and gold rod on SiO$_2$/Si substrates. AFM image and profile of graphene oxide were taken with an XE-100 (Park system, Korea) with a backside gold coated silicon probe (M to N, Korea). Raman spectra of the GO, RGO and heterogeneous interfacing system of RGO and gold rod on SiO$_2$/Si substrates were obtained by HORIBA LabRAM (jobin Yvon, France) using an air-cooled He/Ne laser (632.8 nm) as an excitation source focused through an integral microscope (Olympus BX 41). Raman scattering signal was detected with 180° geometry using and air-cooled 1024 x 256 pixel CCD detector. The UV-vis spectra were recorded with a UV-2550 (Shimadzu, Japan) using quartz substrate. FT-IR spectrum of graphite oxide was obtained with an EQUINOX55 (Bruker, Germany) using the KBr pellet method. Ellipsometric analysis was carried out with a L116S (Gaertner Scientific Coorporation, USA)
Fig. S1. The FT-IR spectrum of graphite oxide showed several characteristic absorption peaks derived from oxygen containing functional groups such as alcohol at 3415 and 1400 cm\(^{-1}\) from O-H vibration and deformation, carboxylic acid at 1716 cm\(^{-1}\) from C=O stretching and epoxy at 1079 cm\(^{-1}\) from C-O stretching. This result suggested that graphite was successfully oxidized under our experimental conditions (a). The graphite oxide was exfoliated in water by sonication for 30 min for preparation of GO suspension. A drop of this suspension was spread onto mica surface and analyzed by AFM to reveal the monolayer isolation of graphite oxide. The thickness of GO sheets in AFM image was about 1 nm, which is comparable to that of monolayered GO sheets (b).
**Fig. S2.** FETEM image shows the uniform gold nanoparticles (5 nm in diameter) were synthesized. The gold nanoparticles were used as a seed for gold rod growth.
Fig. S3. AFM image and profile of bare RGO substrate after immersing into gold seed solution showed seed nanoparticles adsorbed on bare RGO surface (a). After immersing the RGO substrate into growing solution, the surface morphology of the RGO substrate characterized with FESEM (b). The FESEM image shows that gold nanostructures grown on bare RGO surface after seed immobilization without surface modification using pyrene EG amine were mostly irregular shapes.
Fig. S4. UV-vis spectra of GO showed the characteristic absorption at 245 nm, corresponding to π-π transitions of aromatic C-C bonds. After reduction, the characteristic absorption band was shifted to 277 nm and overall absorption in visible region increased due to restoration of π-conjugation (a). Pyrene butyric acid (PBA) showed strong absorption bands at 244, 268, 279, 332 and 349 nm. Those absorption bands of PBA were no longer clearly resolved after adsorption on the surface of RGO but ambiguous shoulder peaks appeared around 244 and 349 nm, which means large aromatic ring of PBA strongly interacts with RGO sheet (b). RGO decorated with Au seeds showed negligible absorption at typical surface Plasmon band of gold nanoparticle and broadening of the shoulder peaks around 244 and 349 nm, which means gold nanoparticles on RGO surface were well adsorbed but the immobilization density was relatively low.1 After growing, the noticeable surface Plasmon (SP) band at 540 nm appeared because the small Au particles were grown into long rod and larger particles. The SP band from RGO/Au rod heterogeneous system prepared by seed mediated approach was stronger than that prepared by seedless approaches due to the large number of gold nanostructures. This result is consistent with SEM observation in main text (c).
Fig. S5. Size distribution of the synthesized gold rods on RGO surface by seed mediated (a) and seedless (b) approaches.
**Fig. S6.** Energy dispersive spectrometer (EDS) spectra of RGO/gold rod heterogeneous interfacing system prepared by seed mediated (a) and seedless (b) approaches.
Fig. S7. UV-vis spectrum of the growing solution was recorded immediately after surface confined growth experiment. There was no characteristic absorption band of gold nanostructure in visible region, which means that there was no or negligible nucleation of gold nor desorption of surface adsorbed gold seed particles.

Reference