Supporting Information

UV Protection of Reduced Graphene Oxide Films by TiO$_2$
Nanoparticle Incorporation

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Materials and methods

Materials. Natural graphite (FP 99.95% pure) was purchased from Graphit Kropfmühl AG (Hauzenberg, Germany). Sodium nitrate, sodium sulphate, hydrazine monohydrate, N’N-dimethylformamide (DMF) and hydrogen peroxide (30% in water) were purchased from Junsei (Japan). Potassium permanganate, 3-aminopropyltriethoxysilane (APTES), anhydrous toluene, acetic acid and titanium isopropoxide (99.99%) were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Nitric acid, hydrochloric acid and sulfuric acid were purchased from Samchun (Seoul, Korea). Ethanol was purchased from Merck (Darmstadt, Germany). Si substrates (500 µm in thickness) and quartz substrates (500 µm in thickness) were purchased from STC (Japan) and i-Nexus (Stamford, USA), respectively. All chemicals were used as received.

Preparation of GO. 3 g of natural graphite and 1 g of sodium nitrate were added in 46 mL of sulfuric acid and stirred. 6 g of potassium permanganate was slowly added to the acid mixture with stirring in an ice bath. After the addition, the mixture was moved to a water bath at 35 °C and the mixture was stirred for an hour. 40 mL of water was gradually added to the mixture, further stirred for 30 min and diluted with 100 mL of water in an ice bath to prevent rapid boiling because this process is extremely exothermic. Finally, 6 mL of hydrogen peroxide (30%) was slowly added to the mixture with color change to bright yellow. The final mixture was filtered with filter paper (Number 3, Whatman) and washed with copious water until the filtrate was neutralized. The filtered solid was dried under reduced pressure for 48 h.

Preparation of colloidal TiO₂ suspension. Colloidal TiO₂ suspension in ethanol was prepared by dropwise addition of 2.97 mL of titanium isopropoxide into 250 ml of ethanol solution (1.5% acetic acid) with vigorous stirring and the mixture was then stirred for 24 h. The TiO₂ powder was obtained by evaporation of the solvent. The powder was stored in a desiccator. 50 g of TiO₂ powder was then dispersed into 100 ml of aqueous solution (hydrochloric acid (4.5%)) by sonication for 10 min. The resulting colloidal TiO₂ sol in water was transparent in the visible light, and used as a stock solution.

Preparation of APTES modified glass substrates. The Si and glass substrates were immersed in Piranha solution (sulfuric acid: hydrogen peroxide (30 %) = 3:1, WARNING: Piranha solution is extremely explosive and corrosive.) for 15 min at 125 °C, washed with water and ethanol, and dried under a stream of nitrogen. The cleaned substrates were immersed in a 10 mM toluene solution of APTES for 30 min, briefly sonicated in toluene for 1 min, rinsed with ethanol and water and dried under a stream of nitrogen.

Preperation of RGO films. To fabricate GO films on glass substrates, APTES-treated glass substrates were immersed in the GO suspension (1.5 mg/mL) for 1 h, washed with water and ethanol,
dried under a stream of nitrogen and baked at 150 °C under a stream of nitrogen. The GO films coated on substrates were reduced by immersing in hydrazine monohydrate solution (20% in DMF) for 24 h at 80 °C, washed with DMF, water and ethanol and dried under a stream of nitrogen. The RGO film coated substrates were annealed at 500 °C under nitrogen atmosphere.

**Preparation of TiO$_2$/RGO films.** The RGO coated substrate was immersed in the TiO$_2$ sol for 1 h under UV irradiation (254 nm, 8 W). The distance between TiO$_2$ sol and light source was 1 cm. Then, the film was washed with water and ethanol and dried under a stream of nitrogen. As a control sample, the RGO substrate was immersed in the TiO$_2$ sol for 1 h without UV irradiation, washed with water and ethanol and dried under a stream of nitrogen.

**UV exposure of RGO, TiO$_2$/RGO and control TiO$_2$/RGO films.** RGO, TiO$_2$/RGO and control TiO$_2$/RGO films were exposed to UV light (254 nm, 8 W) for 1, 3, 6 and 9 h. The distance between the films and light source was 1 cm. After UV exposure for certain time period, the films were characterized to obtain the average sheet resistance and $I_D/I_G$ value.

**Characterization.** The surface morphologies of RGO based films were observed by S-4800 FE-SEM (Hitach, Japan). Atomic force microscopy (AFM) images, line-profiles and center-line average surface roughness of the substrates were acquired with an XE-100 (Park System, Korea) with a backside gold-coated silicon SPM probe (M to N, Korea). High resolution XPS measurements were carried out with SIGMA PROBE (ThermoVG, U.K) with monochromatic Al-K$\alpha$ (1.5 kV). The UV-vis spectra were recorded with a UV-2550 (Shimadzu, Japan). Raman characterization was carried out by LabRAM HR UV/vis/NIR (Horiba Jobin Yvon, France) using an Ar ion CW laser (514.5 nm) as an excitation source focused through a BXFM confocal microscope equipped with an objective (50×, numerical aperture=0.50). FT-IR spectra measurements of graphite oxide were performed with an EQUINOX55 (Bruker, Germany) using the KBr pellet method. The measurement of average sheet resistances of RGO, TiO$_2$/RGO films was conducted by standard 4 probe method with a CMT-SR2000 (Changnam Tech, Korea).
Figure S1. a) The AFM image and line profile showed broad lateral size distribution of GO sheets (0.2 – 3 µm) with 0.93 nm thickness, corresponding to single layered GO sheets. b) UV-vis absorption spectrum of GO showed absorption peak at 230 nm from π-π* transition of aromatic C-C bond. c) The FT-IR spectrum showed typical peaks from oxygen containing functional group GO at 1079 cm⁻¹ from C-O stretching, at 1400 cm⁻¹ from O-H deformation, at 1627 cm⁻¹ from C=C skeletal vibrations of the oxidized graphitic carbon, at 1716 cm⁻¹ from C=O stretching and at 3415 cm⁻¹ from O-H vibrations. d) Raman spectrum of GO showed D- and G-peak at 1343 and 1595 cm⁻¹ derived from the defected graphitic structure and graphitic structure, respectively. All of the characterization results indicated that the GO was successfully synthesized.
Figure S2. TEM image (a) and UV-vis spectrum (b) of TiO$_2$ nanoparticle respectively showed that the diameter of TiO$_2$ nanoparticles was 5-8 nm with strong absorption in UV region 190 – 350 nm.
**Figure S3.** The cross sectional SEM images of TiO$_2$/RGO film coated Si substrate with different magnifications. Although the resolution of SEM is not enough to precisely define the thickness of the incorporated TiO$_2$ layer, it is clear that the thickness of incorporated TiO$_2$ layer is less than 20 nm.
**Figure S4.** a) C1s XPS spectrum of GO films showed several peaks at 284.5, 286.7 and 288.5 eV from graphitic C–C, C=O and O–C=O bonds, respectively. b) The oxygenated C bonds were significantly decreased after chemical reduction.