Supporting information

A Route to Superhydrophobic Graphene Surfaces: Surface-Treated Reduced Graphene Oxide Spheres

Jung-Soo Lee, Jong-Chul Yoon, and Ji-Hyun Jang*

Interdisciplinary School of Green Energy, Low Dimensional Carbon Materials Center, UNIST, Korea

Synthesis of graphene oxide

GO was prepared from graphite (Bay-carbon, sp-1) via the Hummers method.[40] All chemicals were used without any further purification. First, 23 ml of H_2SO_4 was added into a 250 ml 2-neck flask filled with graphite (0.5g) and $NaNO_3$ (0.5g) at ambient temperature. Next, 3 g of $KMnO_4$ was slowly added to the mixture to prevent abrupt reaction in an ice bath. The solution was stirred at 35 °C for 2 hrs, and 40 ml of deionized water was slowly added and stirred for 1 hr while the reaction temperature was kept at 90 °C. Then, 100 ml of deionized water was added, and the solution was cooled to room temperature. Finally, the prepared graphite oxide was purified via filtration using a glass fibre membrane (pore size 1 um), followed by rinsing with 1 wt% HCl and deionized water. The graphite oxide solution was centrifuged several times at 4,000 rpm for 10 min until the pH of the supernatant was nearly neutral. To obtain graphene oxide, the prepared graphite oxide was exfoliated in a sonication bath for 1 hr. The concentration of the GO solution was 1 mg/ml with water.

Synthesis of SiO_2 particle and preparation of amine-functionalized SiO_2 (NH_2-SiO_2)

SiO_2 particles were prepared by mixing 40 ml of aqueous ammonia (NH_4OH, 28 wt%) with a solution containing 1000 ml of absolute ethanol (EtOH) and 80 ml of deionized water (H_2O). After stirring for 30 min, 60 ml of Tetraethyl orthosilicate (TEOS, 98 %, Aldrich) was added to the solution and stirred for 6 hrs at room temperature. The prepared silica particle suspension was purified by filtration with

ethanol several times and dried in a vacuum oven. Surface modification was conducted with 3-aminopropyl-trimethoxysilane (APTMS). The SiO2 particles (1g) were dispersed into 3 % APTMS solution in ethanol (20 ml) and this solution was stirred for 3 hrs at ambient temperature. Amine-functionalized SiO_2 was washed via a centrifugation technique and dried in a vacuum oven overnight.

Preparation of nano-rGO (rGO spheres)

Thin layers of graphene films were pre-coated with prepared GO solutions on the SiO_2/Si substrate. Separately, GO@NH_2-SiO_2 solutions were prepared by mixing 0.5% aqueous NH_2-SiO_2 solutions and as-prepared GO solutions. The mixture solutions were dropped and spin-coated onto the GO-coated SiO_2/Si wafer. Chemical bonds between the functional groups on the surface of the GO film and the GO spheres were created during subsequent thermal processes, securing firm binding/stability at the interface between GO spheres and the graphene-coated Si substrate. To reduce the graphene oxide, the sample was thermal-treated in a tube furnace under an H_2/Ar atmosphere at 1,000 ^{o}C for 30min. The rGO@NH_2-SiO_2 was spin-coated with a PMMA solution (Mw = 350,000, 1,4 wt% in toluene) and dried at 120 ^{o}C for 5min. PMMA/rGO@ NH_2-SiO_2 on a 300 nm SiO_2/Si substrate was then floated on HF (5%) for 5 hrs to remove the SiO_2 substrate and particles simultaneously, and then PMMA/nano-rGO was transferred onto PET. Finally, we obtained the nano-structure rGO by removing the PMMA layer in acetone for 4hrs. For silane-treated rGO film, Trichloro(1H,1H,2H,2H-perfluorooctyl)silane was vaporized under a sealed container for 30 min at room temperature.

Characterization

The morphology of the samples were observed by Field-Emission SEM (Nova Nano-SEM 230, 15 kV). The quality of graphene oxide and thermal reduced graphene was confirmed by Raman

spectroscopy (WITec, alpha300R, excited by a 532nm laser). The variation of the chemical composition was analyzed by FT-IR (Agilent, USA, ATR mode) and XPS (Thermo Fisher, UK). The contact angle was measured by a Drop Shape Analysis System DSA100 (Kruss, Germany). Zeta potentials of the samples were measured using an electrophoretic light scattering spectrophotometer (ELS-8000). The roughness of rGO spheres was captured by atomic force microscope (AFM, Digital Instruments, Nanoscope III) in the tapping mode. The sheet resistance of rGO sphere films (both film and powder type) was characterized by 4 point-probe (Dasol Eng, FPP-RS8, pin-spacing 1 mm, pin-radius 100 μm).
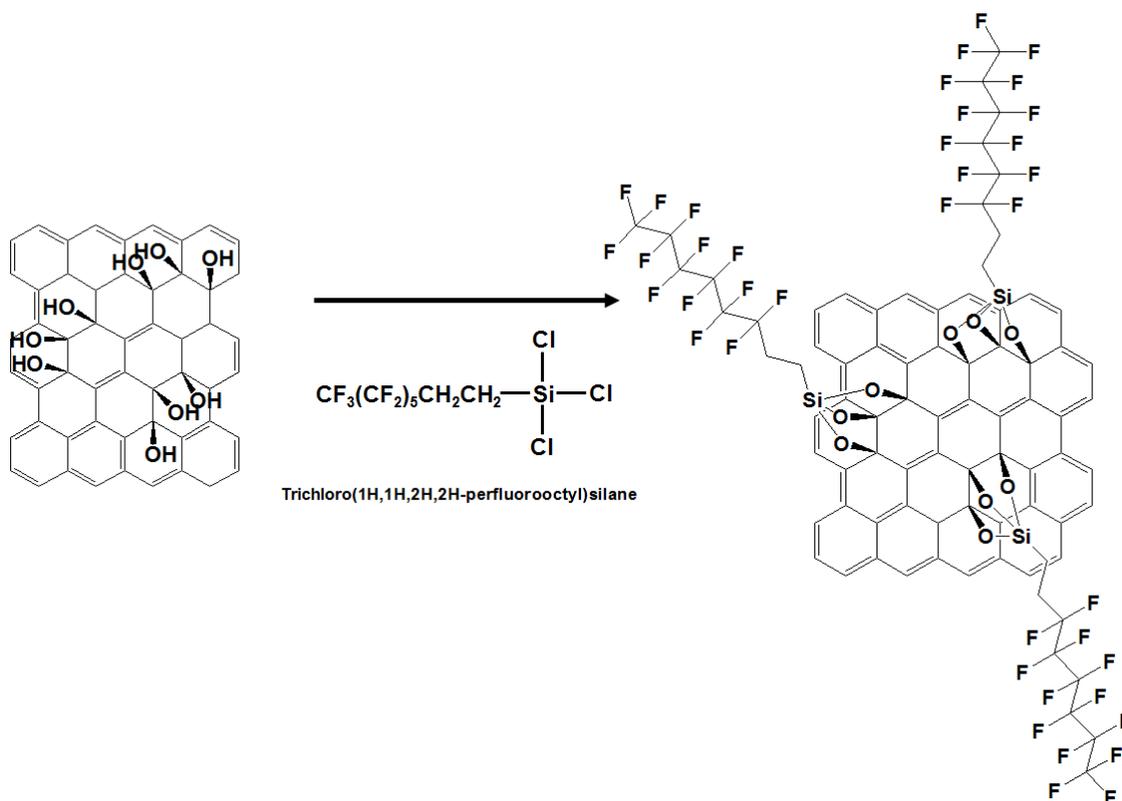
Scheme S1. Schematic illustration of reactions during the silane-treatment process.
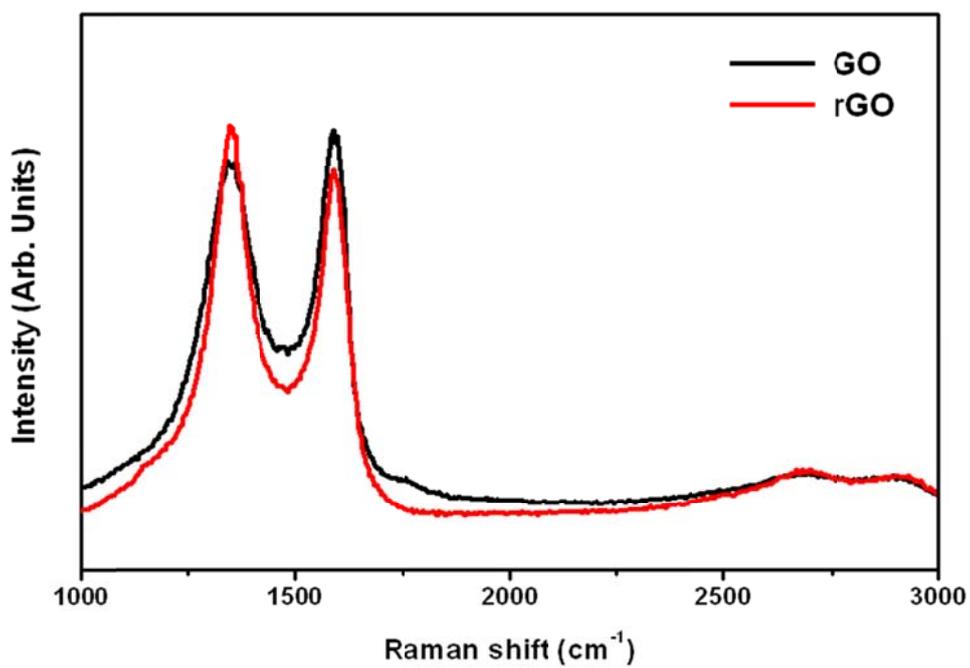
Figure S1. Raman spectra of GO and thermal reduced GO
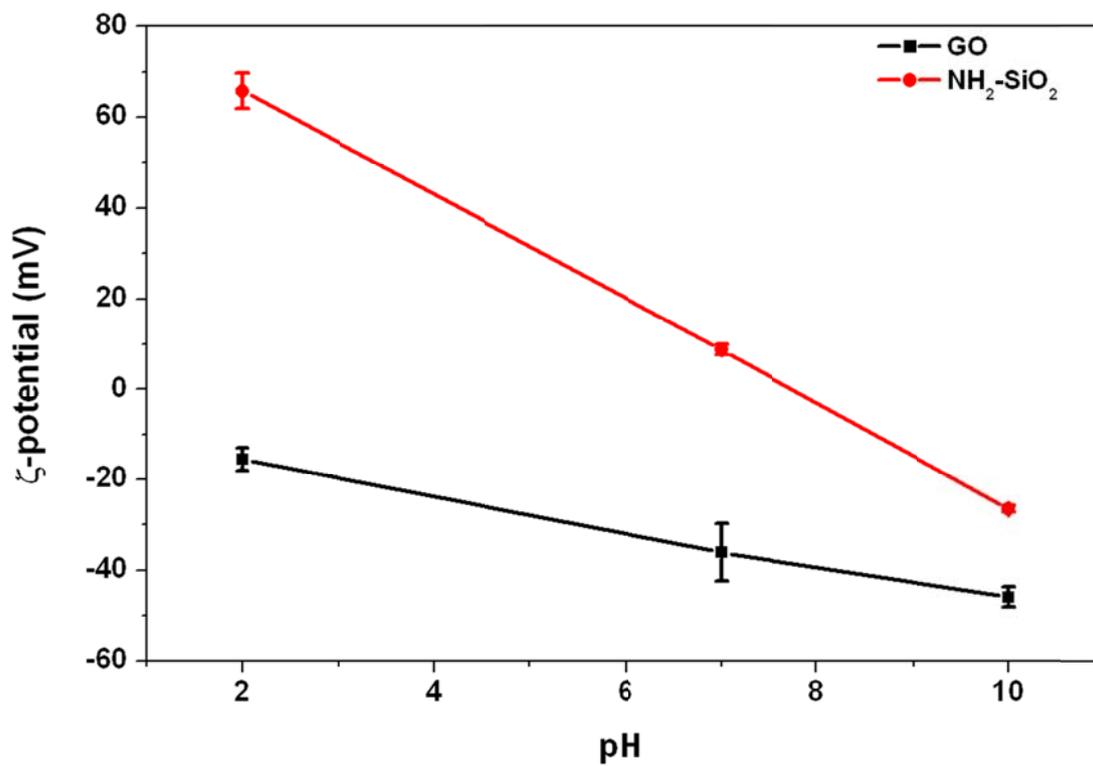
Figure S2. Zeta-potential of GO and NH_2-SiO_2 with a variety of pH
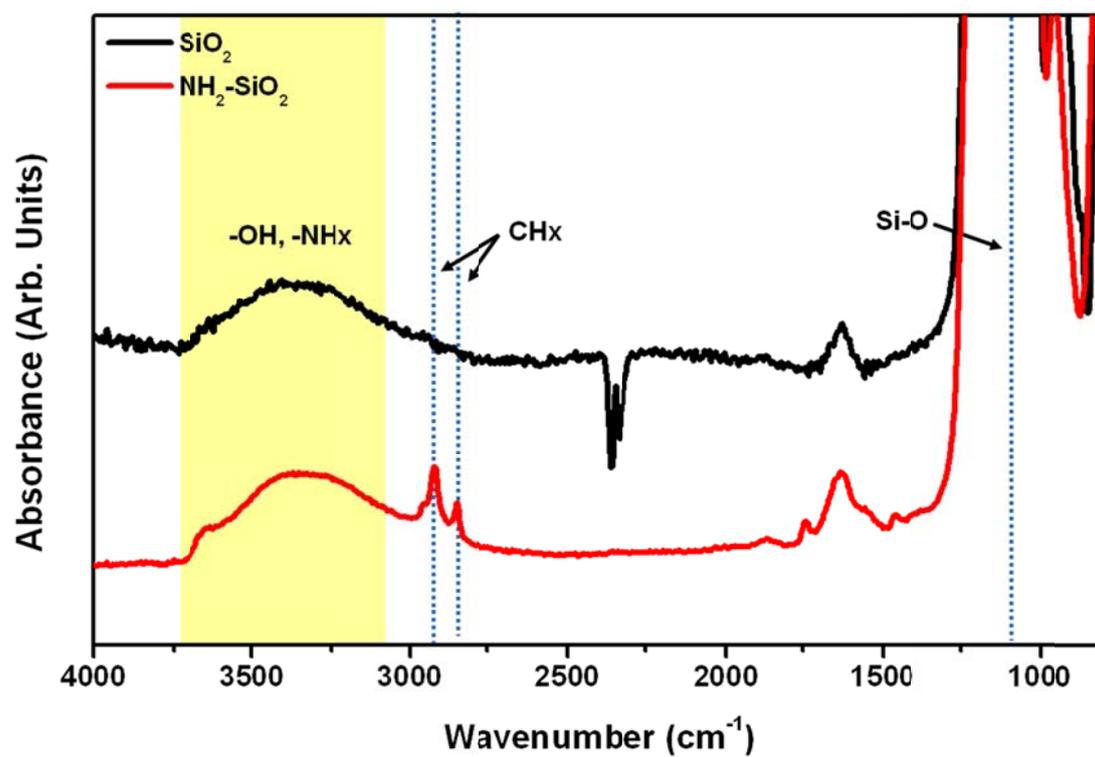
Figure S3. FT-IR analysis of SiO_2 and NH_2-SiO_2
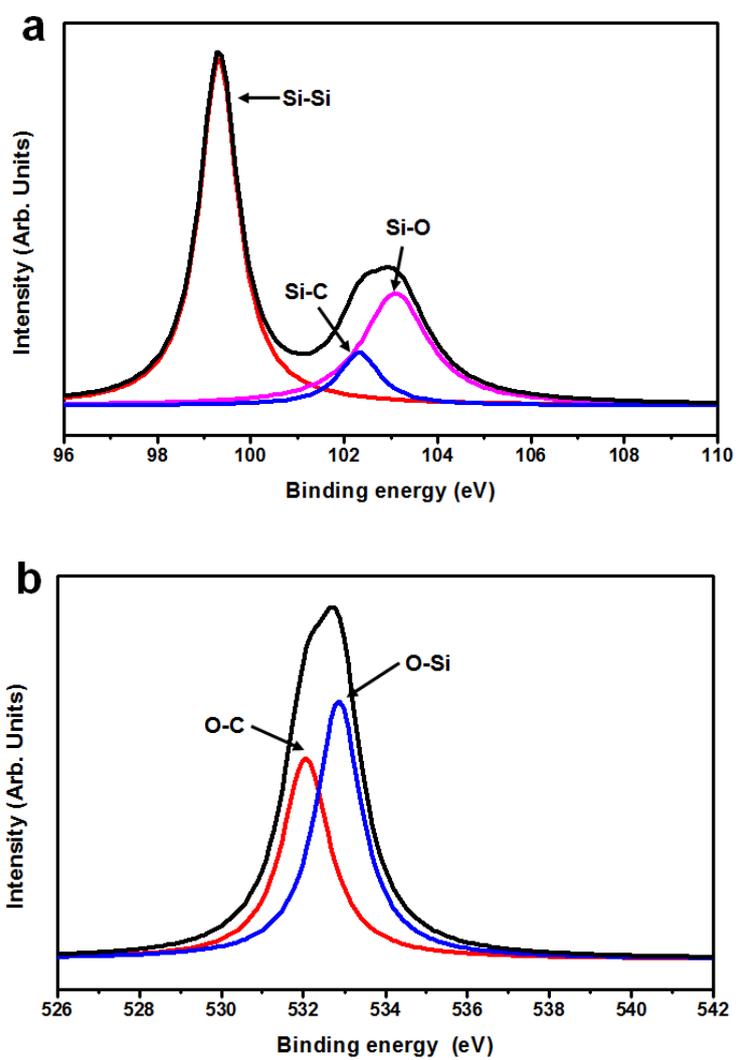
Figure S4.XPS analysis of silane treated nano-rGO for (a) Si2p, (b) O1s.
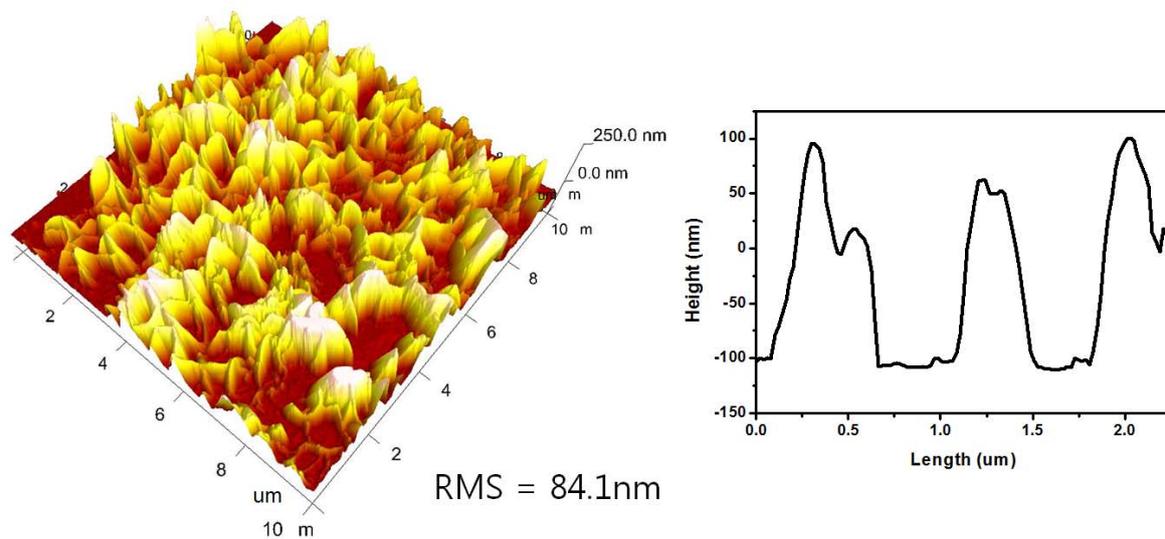
Figure S5.AFM analysis of rGO spheres.
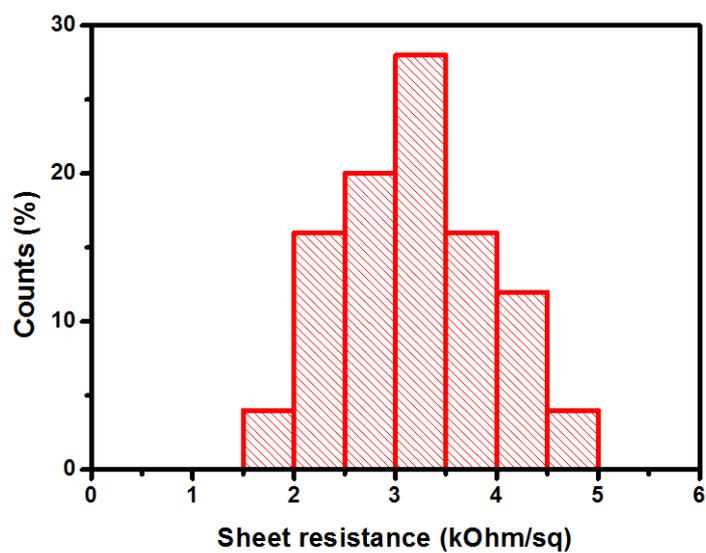
N total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
25	3.1596	0.75183	78.99	1.567	3.113	4.62

Figure S6. Conductivity analysis of rGO spheres.