Electronic Supplementary Material (ESI) for Lab on a Chip
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Supplementary information

Synthesis of a 3D graphite microball based on a microfluidic droplet generator and its polymer composite with core-shell structure

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Chemicals and materials

Graphite flakes, $KMnO_4$, ammonium persulphate, pyrrole monomer were purchased from Sigma-Aldrich (USA). Extra pure H_2O_2 (30 %) and H_2SO_4 (95 %) were ordered from JUNSEI (Japan) and OCI Company Ltd (Korea), respectively. HCl (35~37%) and iron oxide nanoparticles (10-15 nm diameter) were obtained from SAMCHUN CHEMICLAS (Korea) and SkySpring Nanomaterials, Inc. (USA).

Synthesis of a GO solution

A suspended GO solution was synthesized by using a modified Hummers method. Briefly, 1g of graphite flakes was added into a mixture solution of H_2SO_4 (34 mL) and $NaNO_3$ (0.75 g) in a 250 mL flask, kept in an ice-water bath, and vigorous stirred with a magnetic bar. Then, $KMnO_4$ (5 g) was slowly added, and the temperature increased to 35 ºC. After stirring for 2 h, distilled water (50 mL) was supplemented to the mixture in an ice bath. After 1 h, a 30 % H_2O_2 (4 mL) solution was added dropwise to the mixture, and then transferred to a 1:10 aqueous HCl (500 mL) solution. Graphite oxide was recovered by using a cellulose acetate membrane filter (pore size: 200 nm) at room temperature. The graphite oxide was washed with DI water several times under the centrifugation at 4000 rpm to reach pH 7. The graphite oxide solution was dispersed by ultrasonication for 5 h. After centrifugation at 4000 rpm, the GO sheets were obtained which were present in the supernatant.

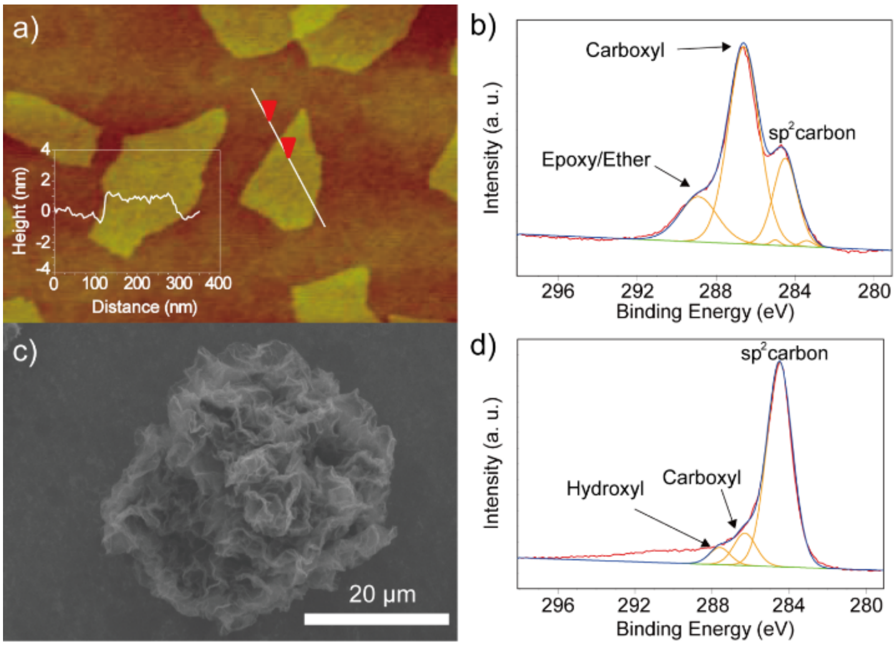

Fig. S1 a) AFM and b) XPS data of the 2D GOs. c) SEM image and d) XPS data of the 3D GMs.

Synthesis of the 3D GM and 3D GM-Fe_3O_4 NP composite

For the 3D GM synthesis, a GO solution and n-hexadecane with 2 wt% Span-80 were used an aqueous and oil phase, respectively. They were injected in the designated inlets on the microfluidic droplet generator device. At the flow-focusing region, homogeneous droplets were generated and passed through the passive mixing channel. The flow rate of the GO solution was fixed at 1.0 μl/min, while that of the oil phase was changed with 10.0, 25.0, 50.0, and 75.0 μl/min to control the droplet size. The produced droplets containing 2D GO sheets were collected on a silicon wafer (1.5 cm × 1.5 cm) from an outlet. Then, the wafer was incubated in the tube furnace at 900 ^oC with 10% H_2 gas (100 cc/min) for 3 hrs. The capillary compression process proceeded to result in the 3D GMs. The 3D GMs were detached from the wafer by ultrasonication (100 W) for 30 min, and purified by centrifugation at 4000 rpm for 30 min. To synthesize the 3D GM-Fe_3O_4 NP hybrid, we loaded a water-dispersible Fe_3O_4 NP (0.05 mg/ml) in a GO solution. Following the same procedure as above, the GO and Fe_3O_4 NP were physically adsorbed to form the 3D GM-Fe_3O_4 NP.

Synthesis of the 3D GM-Ppy composites

The 3D GM-Ppy with core-shell structure was synthesized as follows. One mL of an aqueous 3D GM-Fe_3O_4 NP solution was mixed with 10 μL of a pyrrole monomer solution for 3 h to immobilize pyrrole on the GM by π- π stacking between the graphene and pyrrole. After removing excess monomers using an external magnet, a solution of ammonium persulphate (0.17 mmol in 0.25ml water) was added to initiate polymerization, and stirred for 1 h. After washing with water under the centrifugation at 4000 rpm, the resultant 3D GM-Ppy composites were obtained.

Characterization Instruments

The shape and morphology of the 3D GMs and their nanocomposites were investigated by Field Emission Scanning Electron Microscope (FE-SEM, HITACHI S-4800) and Field Emission Transmission Electron Microscope (FE-TEM, Tecnai G^2 F30 S-TWIN). Raman characterization was conducted by a high resolution dispersive Raman microscope with an Ar ion CW laser at 514.5 nm (Horiba Jobin Yvon, France). X-Ray Photoelectron Spectroscopy (XPS) analysis was performed by a Thermo VG Scientific Sigma Probe system. Fourier Transform Infrared Spectroscopy (FT-IR) was characterized by IRPrestage-1 (Dong-Il SHIMADZU Corp.) over the range from 600 to 4000 cm^{-1}.

SEM and TEM analysis for the 3D GM and 3D GM-Ppy composites

After synthesizing the 3D GM and 3D GM-Ppy composites, we cut them by focused ion beam, and investigated the difference of the inner structure of the 3D GM (Fig. S1a) and 3D GM-Ppy composites (Fig. S1b) by SEM and TEM. The top panel of Fig. S1 shows the SEM images of the cross-section. The samples (the 3D GM and 3D GM-Ppy composites) were cut into thin slices for TEM analysis, and the low magnification TEM (the middle panel) and the high magnification TEM at the edge part (the bottom panel) were taken for comparison. Although the inner structure was not clearly shown in the SEM images, the low-magnification TEM images revealed the difference in that the dark spots were dispersed in the core due to the presence of Fe3O4 nanoparticles in the 3D GM-Ppy composites. The high-magnification TEM images at the edge part obviously demonstrated the structural difference between the 3D GM and 3D GM-Ppy composites (the bottom panel). While the packed graphene sheets were shown in the 3D GM, the 3D GM-Ppy composites displayed the graphite-Fe3O4 composite in the core and the polypyrrole in the shell. Thus, we believe that the spherical 3D GM serves as a polymer support to generate the 3D GM-Ppy composites with unique core-shell structure.

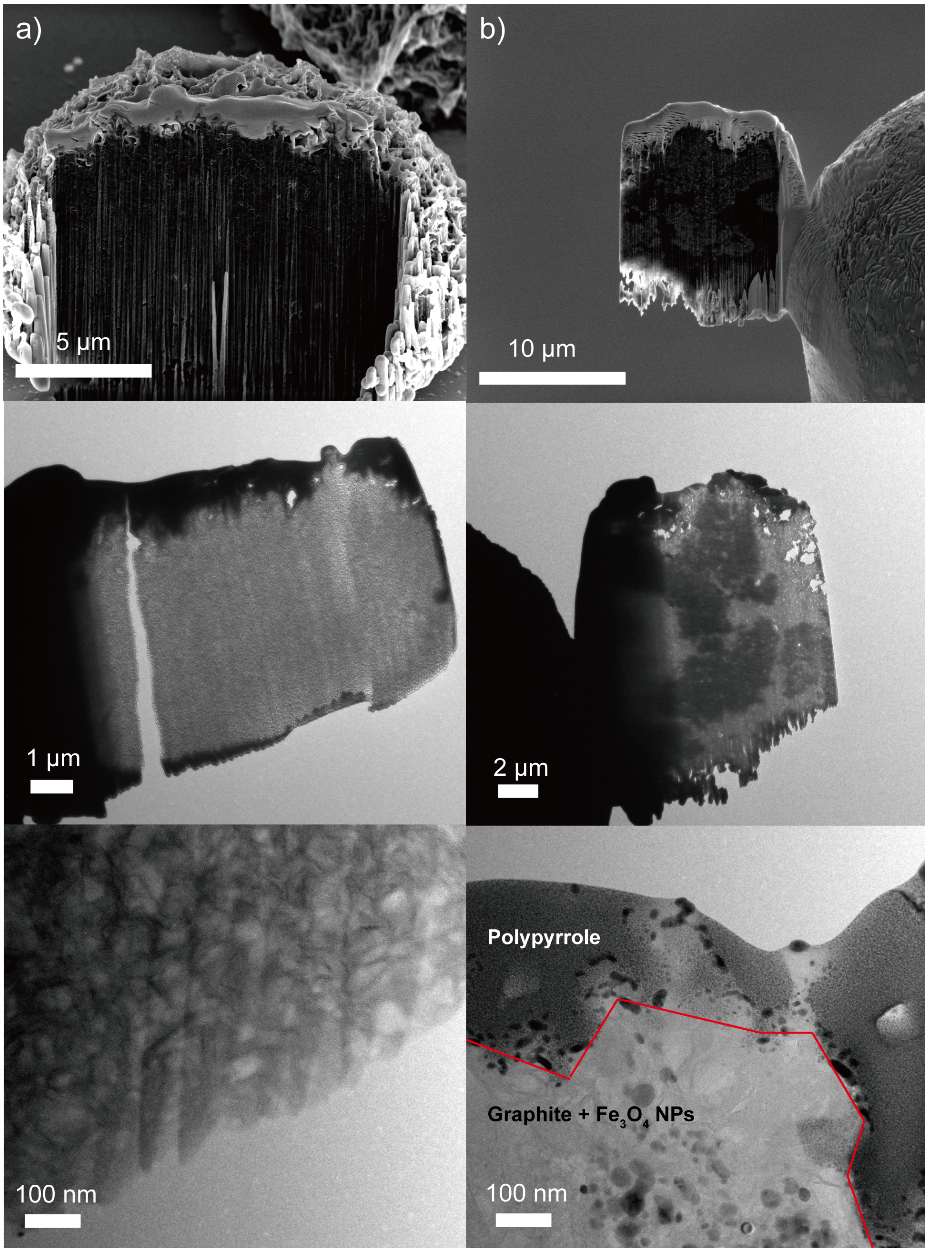

Fig. S2 SEM and TEM data for a) a cross-section of the 3D GM (left panel) and b) the 3D GM-Ppy composite (right panel). The top panel is for the SEM analysis, the middle panel is for the low magnification TEM analysis, and the bottom panel is for the high magnification TEM analysis at the edge part.