Supplementary Information

Aggregation-mediated assembly of graphene oxide on amine-functionalized poly(glycidyl methacrylate) microspheres for core-shell structures with controlled electrical conductivity

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Experimental details

Materials

All chemicals were purchased from Sigma-Aldrich and used without additional purification: glycidyl methacrylate (GMA), polyvinylpyrrolidone (PVP, *M*w~40,000), azobisisobutyronitrile (AIBN), methanol, ethylenediamine (EDA), graphite powder (particle size less than 150 μm, product number: 496588), nitric acid (68%, HNO_3), sulfuric acid (95 - 97%, H_2SO_4), phosphoric acid (85%, H_3PO_4), hydrogen chloride (HCl), hydrogen peroxide (30%, H_2O_2), potassium permanganate ($KMnO_4$), and hydrazine monohydrate ($N_2H_4 \cdot H_2O$). Deionized water was used throughout the experiments.

Preparation of poly(glycidyl methacrylate) (PGMA) microspheres and amine-functionalization

Dispersion polymerization of the glycidyl methacrylate was conducted to produce uniform-sized polymer microspheres. GMA (40 g) and PVP (8 g) were dissolved in methanol (180 ml) with nitrogen purging. The solution was heated to 65 ^{o}C with stirring, and an AIBN solution (0.4 g AIBN pre-dissolved in 25 ml methanol) was added to this solution. The reaction was conducted at 65 ^{o}C for 12 h followed by washing with methanol and DI water using centrifugation. Then, the poly(glycidyl methacrylate) microspheres (PGMA) were dispersed in DI water with sonication, and 30 ml of EDA was added to the dispersion. The reaction was conducted at 70 ^{o}C for 12 h to functionalize the PGMA microspheres (PGMA-ed). Then, the microspheres were washed several times with methanol and water by centrifugation and collected by freeze-drying

Preparation of GO suspension

Graphite oxide was prepared by the improved Hummers method. A mixture of H_2SO_4 (360 ml) and H_3PO_4 (40 ml) was added to the graphite flakes (10 g), and $KMnO_4$ (40 g) was added to the mixture with mild stirring. The mixture was then heated to 50 °C, and the oxidative reaction of graphite was conducted for 3 hours. After the reaction, deionized water (2000 ml) with H_2O_2 (100 ml) was added to the mixture and stirred for 30 min to remove impurities. Afterwards, the oxidized graphite flakes were collected by filtration, and the filtrate was washed several times with 10% HCl solution and deionized water. Finally, the graphite oxide flakes were freeze-dried. The graphite oxide (0.05 g) powder was added to deionized water (50 ml) and exfoliated by sonication for 4 h followed by centrifugation of the suspension for 15 min at 4000 rpm to remove precipitates and used to obtain a stable GO suspension.

Preparation of GO-coated core-shell microspheres (GO/PGMA-ed) and reduction of GO shell (RGO/PGMA-ed)

The PGMA-ed microspheres (100 mg) were dispersed in the GO dispersion (50 ml) with sonication at pH 10 and stirred for 10 min to form GO/PGMA-ed core-shell microspheres. Then, the pH of the solution was gradually decreased to pH 3, 5, and 7 with 0.25 M HCl. Then, the GO/PGMA-ed microspheres were thoroughly washed with DI water and collected by centrifugation. In order to reduce the GO shell, the GO/PGMA-ed microspheres were dispersed in DI water, and 5 ml of hydrazine was added. The suspension was heated to 100

°C, and the reduction was carried out for 1 hour. They were thoroughly washed with water using centrifugation and collected by freeze-drying.

Characterization

The morphology of the samples was characterized by scanning electron microscopy (SEM, JEOL JSM 7000F) and transmission electron microscopy (TEM, JEOL JEM-1010) at 80 kV. For the TEM observation, the samples were molded with epoxy and then microtomed with a diamond knife. The polymer microspheres were characterized using Fourier transform infrared (FTIR) spectroscopy (Bruker IFS-66/S). The zeta potential of the GO and PGMA-ed dispersions were measured using a Zetasizer Nano ZS instrument (Malvern). The Raman spectra were obtained with RXN1 (Kaiser) using 633 nm Ar^+ laser excitation. X-ray photoelectron spectroscopy (XPS) (ESCA 2000, VG Microtech) was performed with a monochromatic Al Ka X-ray source. To investigate the electrical properties of the RGO/PGMA-ed microspheres, the core-shell particles were placed in a cylindrical tube and compressed by two stainless steel plungers located at each open end using a universal testing machine (UTM, LLOYD LR30K plus), from which the electrical resistance of the microsphere powder pack was measured using a digital multimeter (Agilent U1252A). The electrical resistances were recorded as a function of the volume changes of 0, 15, 30, 45, and 60%. The electrical conductivity was calculated using the equation $\sigma = L/RA$, where R is the measured resistance, L is the distance between the electrodes (m), and A is the area of the electrode (πr^2, 9.6 mm^2 in this study).

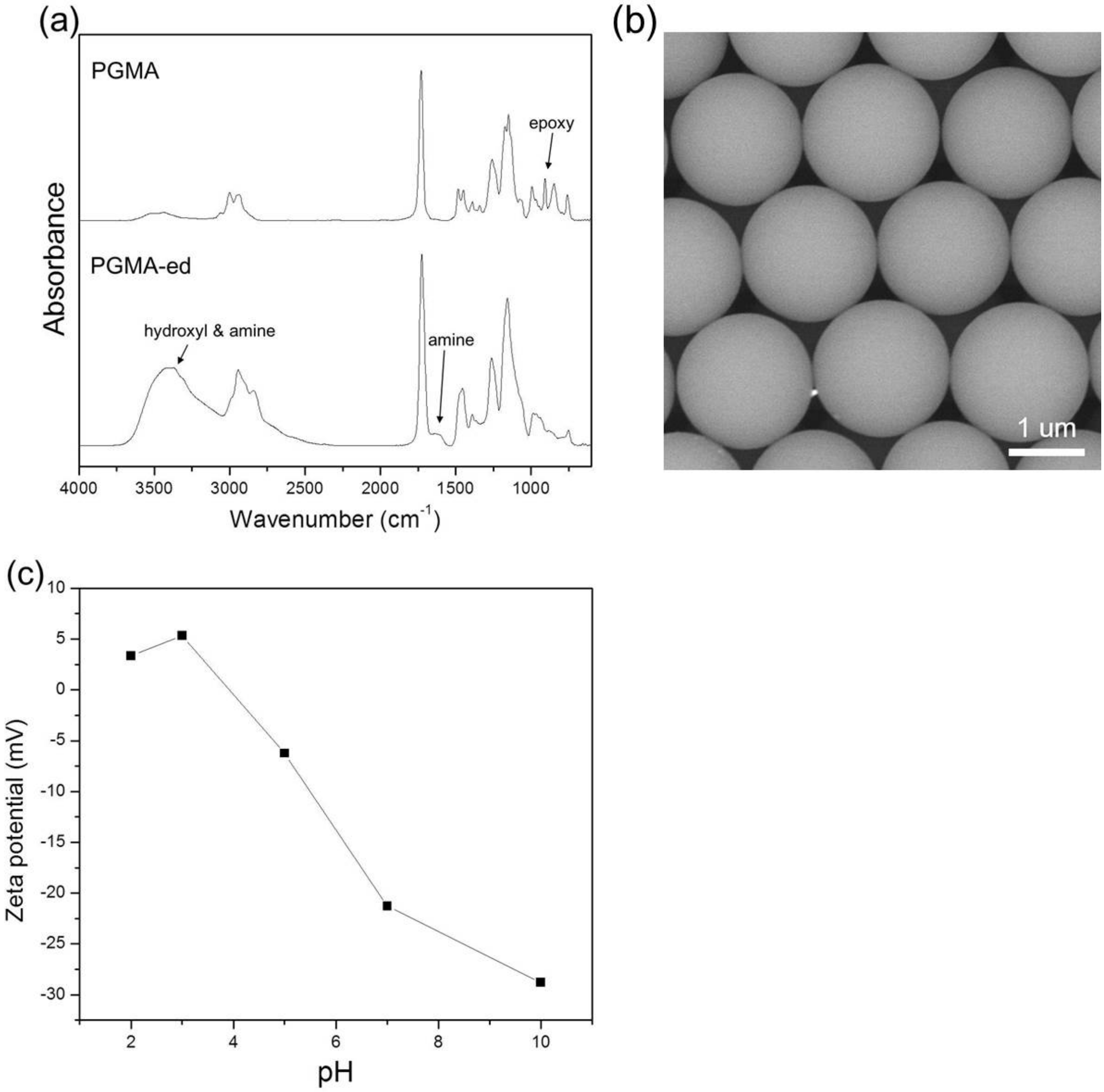

Fig. S1. FT-IR spectra of PGMA and PGMA-ed (a), SEM image (b) and zeta-potential of PGMA-ed (c).

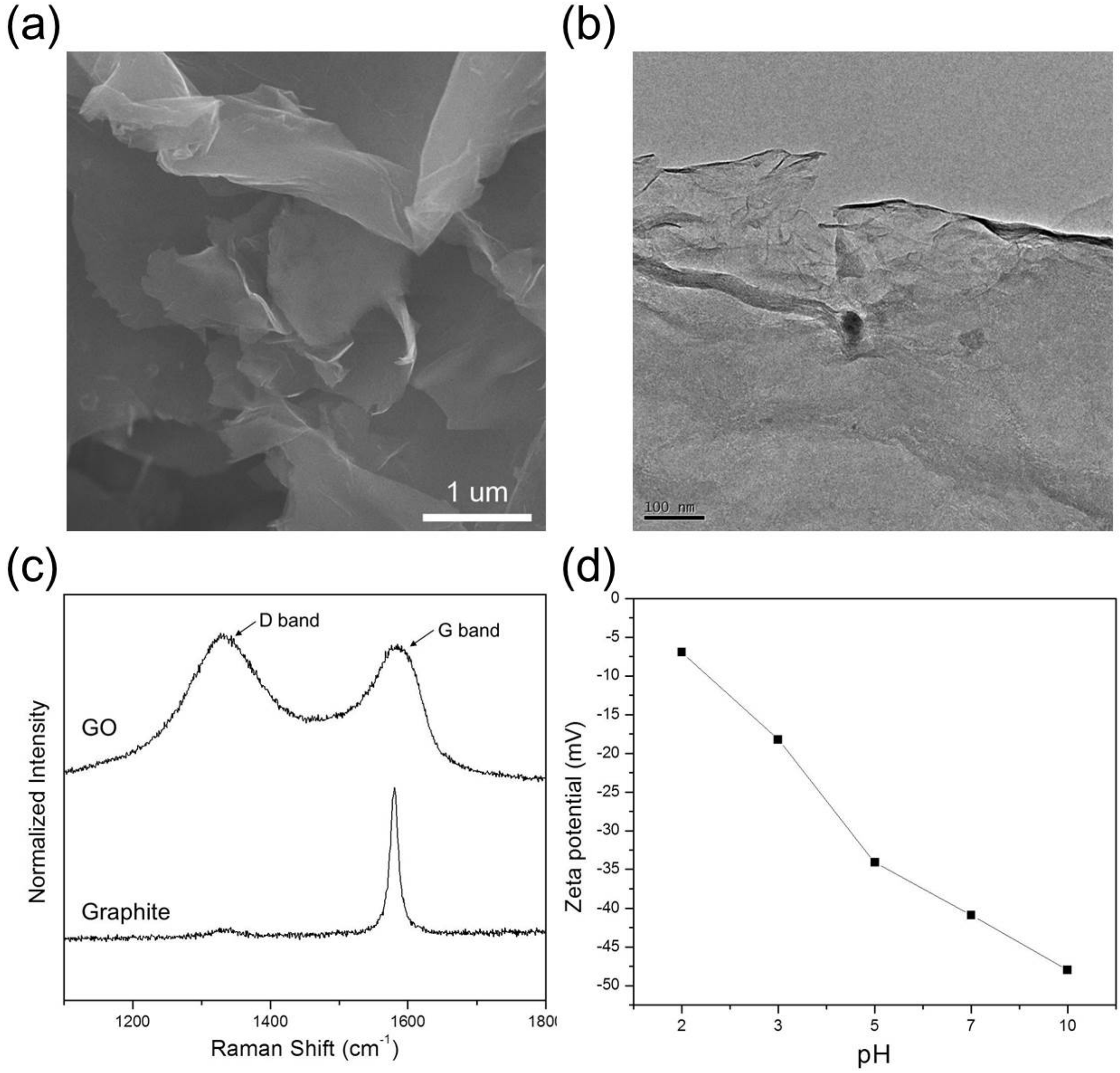

Fig. S2. SEM (a) and TEM (b) images of GO, Raman spectra of GO and graphite (c), and zeta-potential of GO (d).

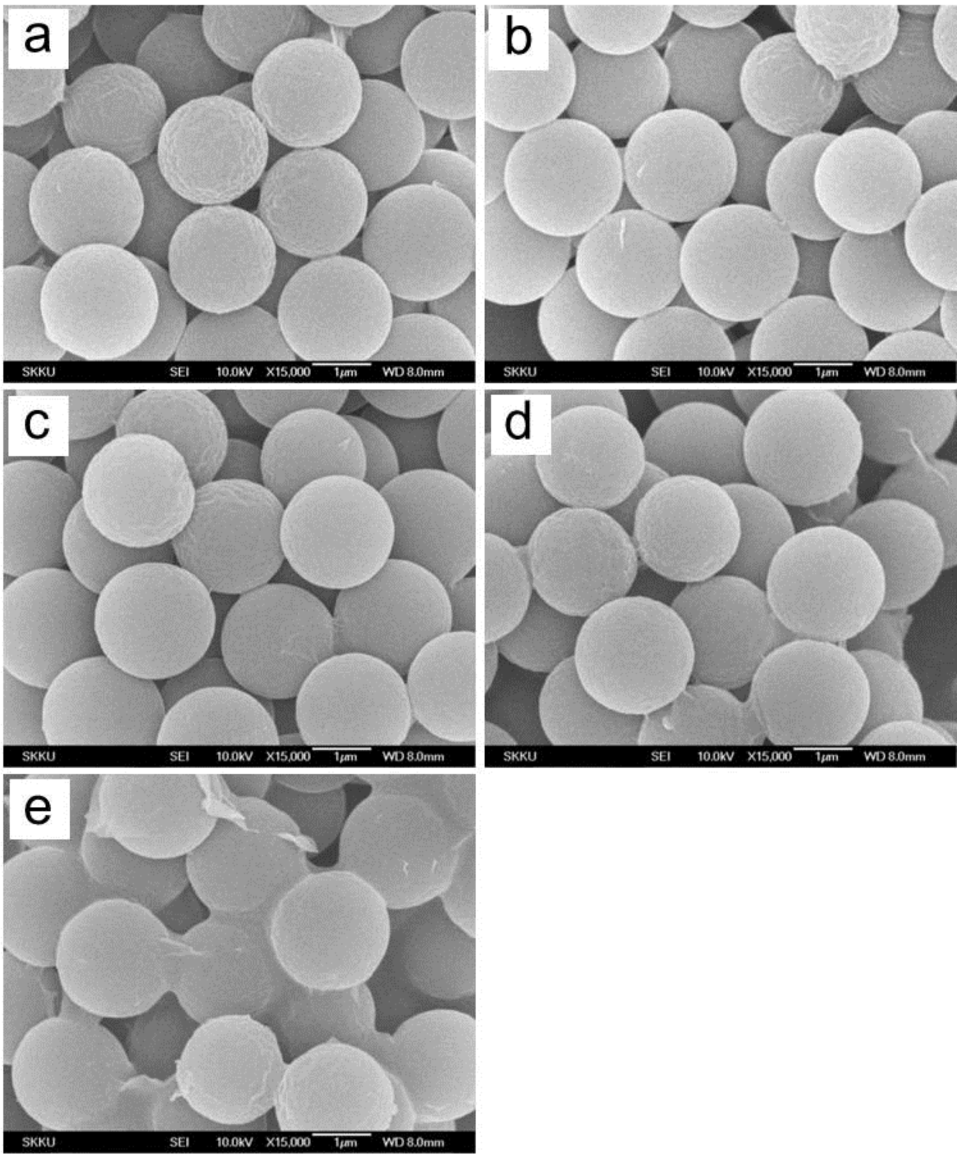

Fig. S3. SEM images of GO/PGMA-ed core-shell microspheres produced at pH 10 (a), 7 (b), 5 (c), 3 (d), and 2 (e).

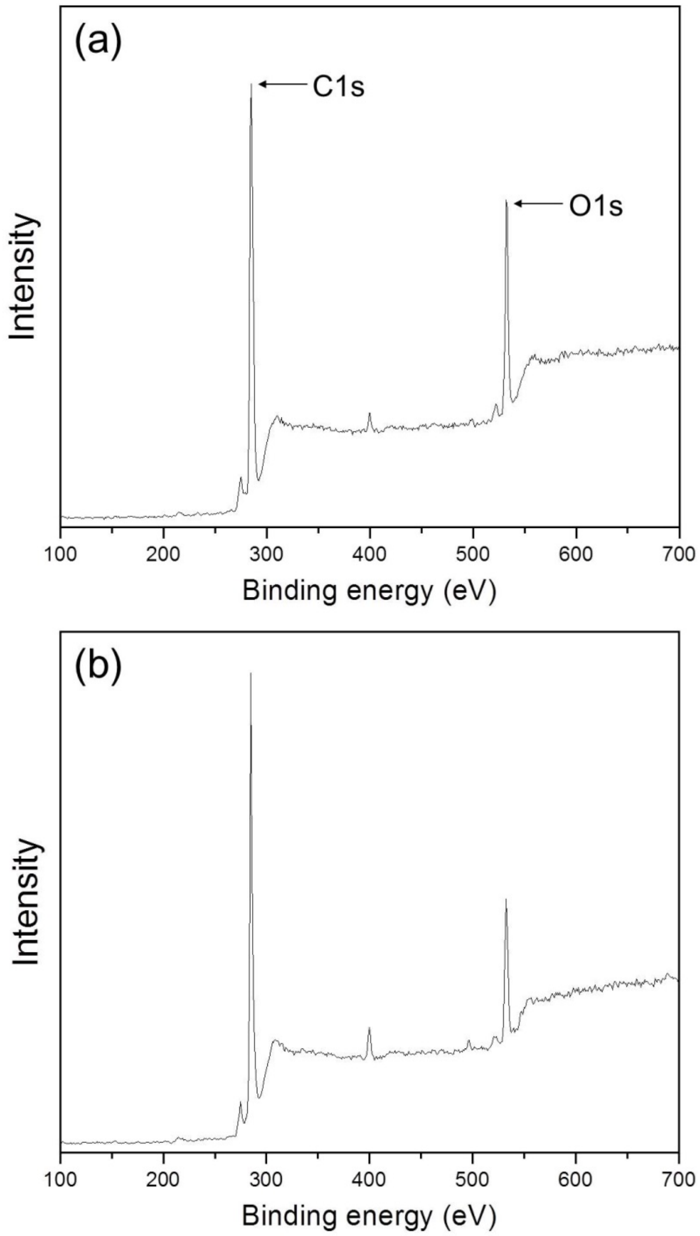

Fig. S4. XPS spectra of GO/PGMA-ed (a) and RGO/PGMA-ed (b).