

Supplementary information

One-step Synthesis of Superior Dispersion of Chemically Converted Graphene in Organic Solvents†

Viet Hung Pham, Tran Viet Cuong, Thuy-Duong Nguyen-Phan, Hai Dinh Pham, Eui Jung Kim, Seung Hyun Hur, Eun Woo Shin, Sunwook Kim, Jin Suk Chung*

School of Chemical Engineering and Bioengineering, University of Ulsan, Ulsan 680-749, Republic of Korea

Descriptions of chemicals, GO synthesis, CCG-P characterizations, elemental analysis, XPS and XRD data.

1. Chemicals

Expandable graphite (Grade 1721) was supplied by Asbury Carbon. Concentrated sulfuric acid (H₂SO₄), potassium permanganate (KMnO₄), hydrochloric acid (HCl), hydrogen peroxide (H₂O₂), phenylhydrazine (C₆H₅NHNH₂), *N,N'*-dimethylacetamide (DMAc), *N,N'*-dimethylformamide (DMF), propylene carbonate (PC), and 1-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich. All chemicals were used as received without further purification.

2. Synthesis of GO

A small amount of expandable graphite was charged into a 1-L beaker and heated for 10 s in a microwave oven (Panasonic, NN-5653A). The graphite expanded to about 150 times its original volume. Graphene oxide (GO) was synthesized from expanded graphite according to a modified Hummer method [1]. Typically, 500 mL of concentrated H₂SO₄ was charged into a 3-L, three-necked flask equipped with a mechanical stirrer (Teflon impeller). The flask was put into an ice bath to chill to 0°C. Five grams of expanded graphite were gradually added under stirring to make a suspension. Then, 30 g of KMnO₄ was slowly added so that the temperature did not exceed 20°C. The temperature was then elevated to 35°C, and the suspension was stirred for 2 h. The flask was then chilled again in the ice bath, and 1 L of deionized water was slowly added to maintain a temperature below 70°C. The mixture was stirred for 1 h and subsequently diluted with 5 L of deionized water. Fifty milliliters of H₂O₂ (30 wt%) was slowly added, and vigorous bubbles appeared as the color of the suspension changed from dark brown to yellow. The suspension was centrifuged and washed with 10% HCl solution four times, followed by centrifuging at 10,000 rpm and washings with deionized water to completely remove the acid until the pH of the GO dispersion reached 6. The as-synthesized GO dispersion was a paste. The concentration of GO was 1.0 wt%, which was determined after drying the GO dispersion at 80 °C under vacuum for 24 h.

3. Characterization

The UV-vis absorbance of GO and CCG-P in ethanol as functions of reduction time were measured by a microplate spectrophotometer (Spectra Max® Plus 384). The elemental compositions of GO and CCG-P were analyzed by an element analyzer (Flash 2000, Thermo Scientific). X-ray photoelectron spectroscopy (XPS) spectra were recorded on a K-alpha (Thermo Fisher). Raman spectra were measured using a confocal Raman microscope

(Alpha300S, WITec) with a 633 nm wavelength incident laser light. The thermogravimetric analysis (TGA) of GO and CCG-P was characterized under nitrogen atmosphere at a heating rate of 10 °C min⁻¹ (Q50, TA Instrument). X-ray diffraction (XRD) was recorded by a Rigaku RAD-3C diffractometer (35 kV, 20 mA, Japan) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate of 2° (2 θ) min⁻¹. The atomic force microscope (AFM) image was taken using a Veeco dimension 3100 SPM with a silicon cantilever operated in the tapping mode. The electrical resistance of CCG-P paper was measured by the four-point probe method using Advanced Instrument Technology (AIT) CMT-100 MP with a Jandel Engineering probe. The thickness of CCG-P paper was determined by a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6500FE) image of the cross-section.

4. Elemental analysis

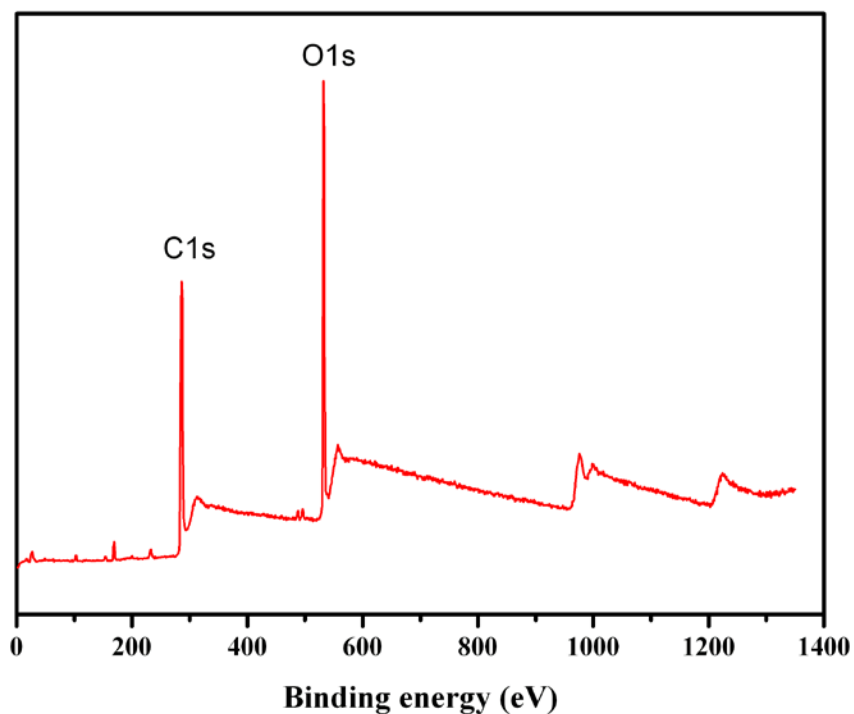
To prepare the samples for elemental analysis, as-synthesized CCG-P obtained by reduction of GO with phenylhydrazine was filtered and washed repeatedly with methanol to remove any unreacted phenylhydrazine, and subsequently dried in a vacuum oven at 80 °C for 24 h. The as-synthesized GO was also dried in a vacuum oven at 80°C for 24 h. The elemental analysis results showed that the C/O atomic ratio increased from 1.68 for GO to 9.51 for CCG-P (Table S1). The nitrogen content was about 3 wt%, which could be attributed to N bonded to CCG-P by phenylhydrazine reduction.

Table S1. Elemental composition of GO and CCG-P

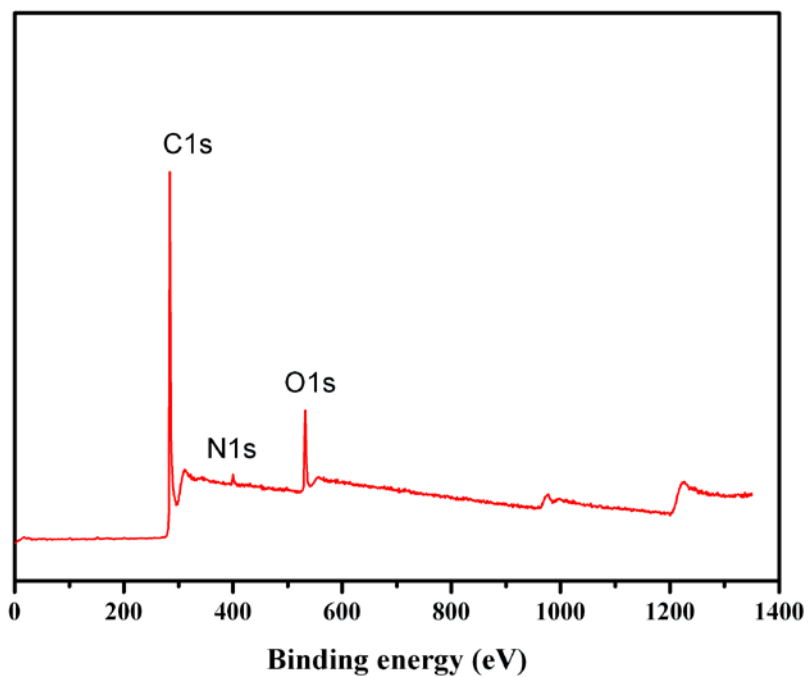
Sample	C (wt%)	O (wt%)	H (wt%)	N (wt%)	C/O	C/N
GO	54.53	43.29	2.18	0	1.68	n/a
CCG-P	83.75	11.72	1.54	2.99	9.51	32.67

5. X-ray photoelectron spectroscopy

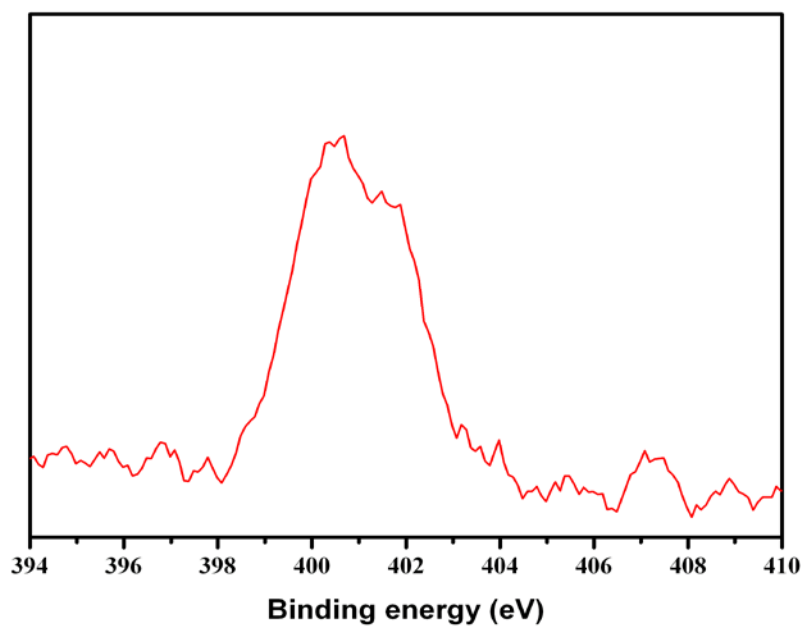
As-synthesized CCG-P obtained by reduction of GO with phenylhydrazine was filtered and washed repeatedly with methanol to remove any unreacted phenylhydrazine. CCG-P and as-synthesized GO were dispersed in methanol. The CCG-P suspension and GO suspension were dropped on the silicon substrates and subsequently dried in a vacuum oven at 80 °C for 24 hours. XPS spectra recorded on a K-alpha (Thermo Fisher) are shown in Figs. S1(a) – (c).



(a)



(b)



(c)

Figure S1. (a) Survey spectrum of GO, (b) Survey spectrum of CCG-P, (c) N1s spectrum of CCG-P

The C1s XPS spectrum of GO showed that there are three kinds of peaks assigned to oxygenated functional groups such as hydroxyl, epoxide, and carbonyl. After reduction, the C1s XPS spectrum of CCG-P also exhibited these peaks, but their intensities were much lower than those in GO, indicating that most of the oxygenated groups were removed. The deconvolution of the C1s spectrum of CCG-P showed a new peak at 285.8 eV corresponding to C=N bonding.

6. X-ray diffraction

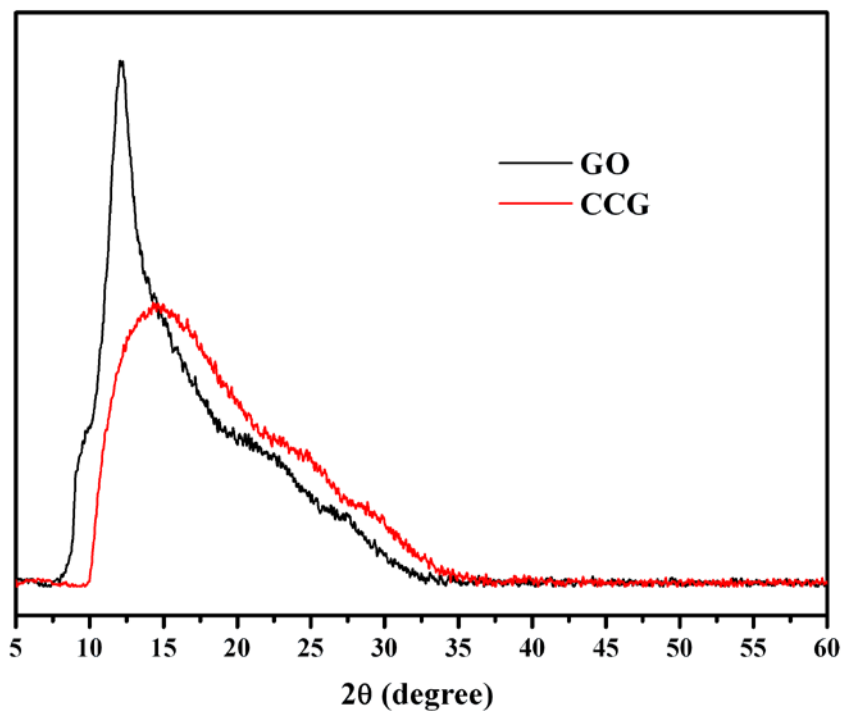


Figure S2. XRD of GO and CCG-P