

Supporting Information

Functionalized graphene nanomaterials: new insight into direct exfoliation of graphite with supramolecular polymers

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Methods

Materials

UrCy-PPG was synthesized from cytosine, *n*-butyl isocyanate and poly(propylene glycol) diacrylate as described in previously.²¹ Graphite was purchased from Fluka (purum powder, Fluka, Buchs, Switzerland). All other chemicals were purchased from Sigma-Aldrich (Louis, MO, USA) and used without any further purification.

Preparation and processing of graphite/UrCy-PPG composites

Desired amounts of graphite and UrCy-PPG (70:30, 50:50 and 30:70 weight ratios) were dispersed in THF solvent by bath sonication for 3 h. After ultrasonic treatment, the solution was cast into a Teflon dish and dried in an oven at 40 °C for 1 d. The composites were stored in a drybox at room temperature prior to use.

Characterization

Raman spectra. Samples were spin-coated onto the surface of a silicon wafer. All spectra were collected using a confocal Raman microscope (Model CRM 2000, WITec, Inc., Ulm, Germany). Spectral data were recorded between 220-3200 cm⁻¹ at a resolution of 2.0 cm⁻¹ at room temperature. A He-Ne laser (632 nm) with a power density of ca. 3×10^4 W cm⁻² was used as the excitation source.

Wide-Angle X-ray Diffraction (WXAD). WAXD spectra of powders were obtained using a Rigaku D/max-2500 X-ray Diffractometer (Rigaku, Tokyo, Japan). The radiation source was Ni-filtered Cu K α radiation at a wavelength of 0.154 nm. The voltage and current were set at 30 kV and 20 Ma, respectively. The sample was mounted on a circular sample holder; data were scanned over a 2 theta range of 10-50° at a rate of 3° min⁻¹.

X-ray photoelectron spectra (XPS). XPS was performed using a ULVAC-PHI Quantera SXM electron spectrometer from ULVAC-PHI using an Al K α x-ray source (Chanhasen, MN, USA). The base pressure was approximately 5×10^{-10} mmHg.

Scanning Electron Microscopy (SEM). SEM images were obtained using a Hitachi S-4700 field emission SEM microscope (Tokyo, Japan) operated at 15 kV. The samples for SEM investigation were freeze-fractured in liquid nitrogen and subsequently oven-dried for 24 h at 30 °C.

Transmission Electron Microscopy (TEM). TEM images were recorded using an FEI T12 transmission electron microscope with a low-energy electron beam (120 keV; Hillsboro, OR, USA). Test samples were placed on a carbon-coated copper grid.

Atomic Force Microscopy (AFM). Samples were spin coated onto freshly cleaved wafer and then annealed at 30 °C. Tapping mode AFM images were obtained using silicon cantilevers with a NS4/D3100CL/MultiMode Instrument (Digital Instruments, Santa Barbara, CA, USA) in air at 25 °C.

Conductivity Measurements. The frequency-dependent impedance properties (from 10 kHz to 10 Hz) of the thin films were measured using an Autolab apparatus (Eco Chemie, Utrecht, Netherlands). For conductivity measurements, the composite was placed in a conductivity cell between stainless steel blocking electrodes at 30 °C and 100 °C under low humidity conditions (less than 30%). Conductivity was calculated according to the equation:

$$\sigma = \frac{L}{AR_b}$$

where σ is conductivity, L is membranes thickness, A is the section area of the stainless steel electrode, and R_b is bulk resistance.

Differential Scanning Calorimetry (DSC). DSC measurements were carried out using a TA DSC-Q20 controller (New Castle, DE, USA) under a nitrogen atmosphere. Approximately 5 mg of sample was placed in an aluminum pan, and then heated and cooled from -90 to $+150$ °C at a rate of 10 °C min^{-1} .

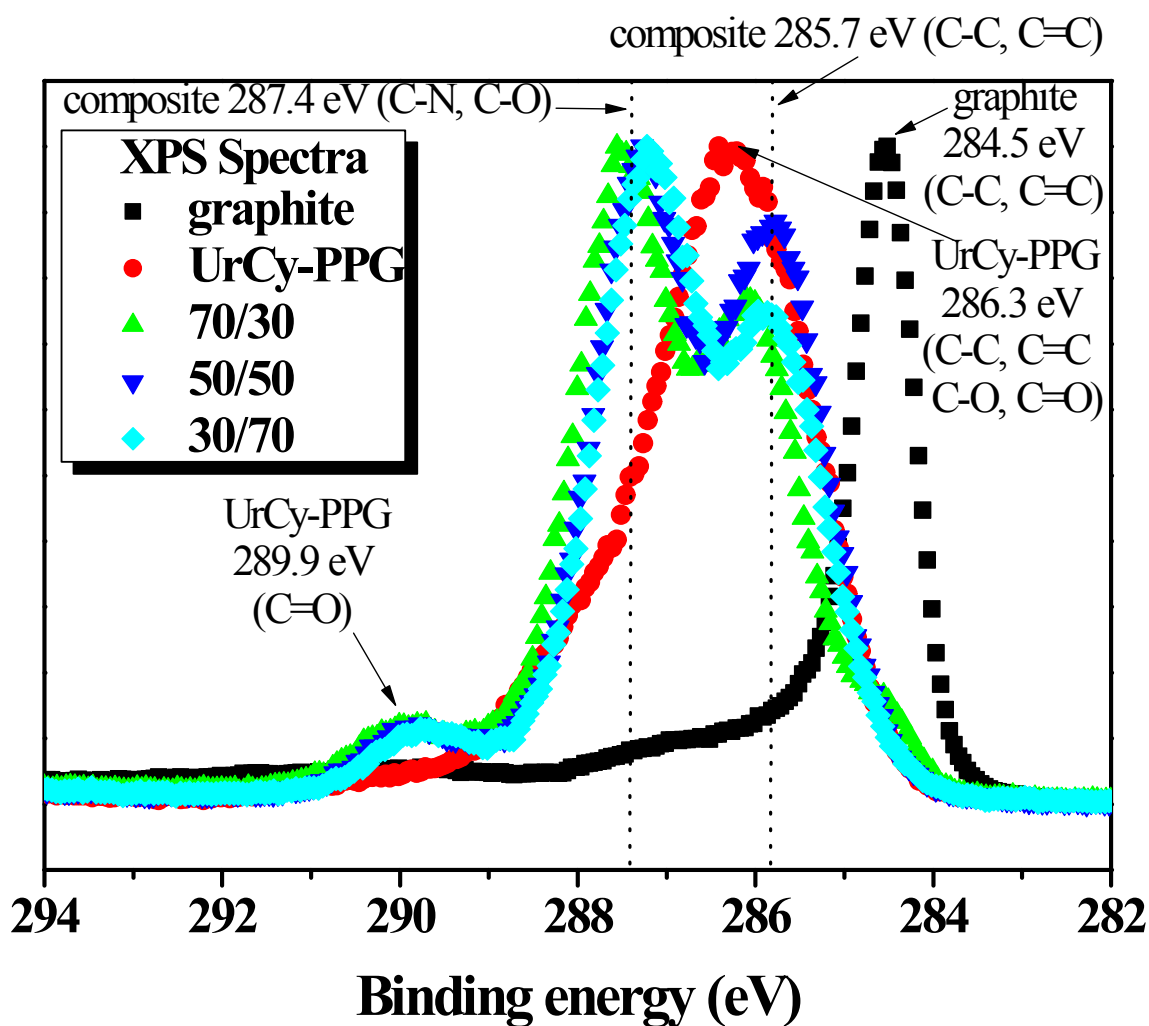


Fig. S1: XPS C1s spectra of graphite, UrCy-PPG, graphite/UrCy-PPG composites.

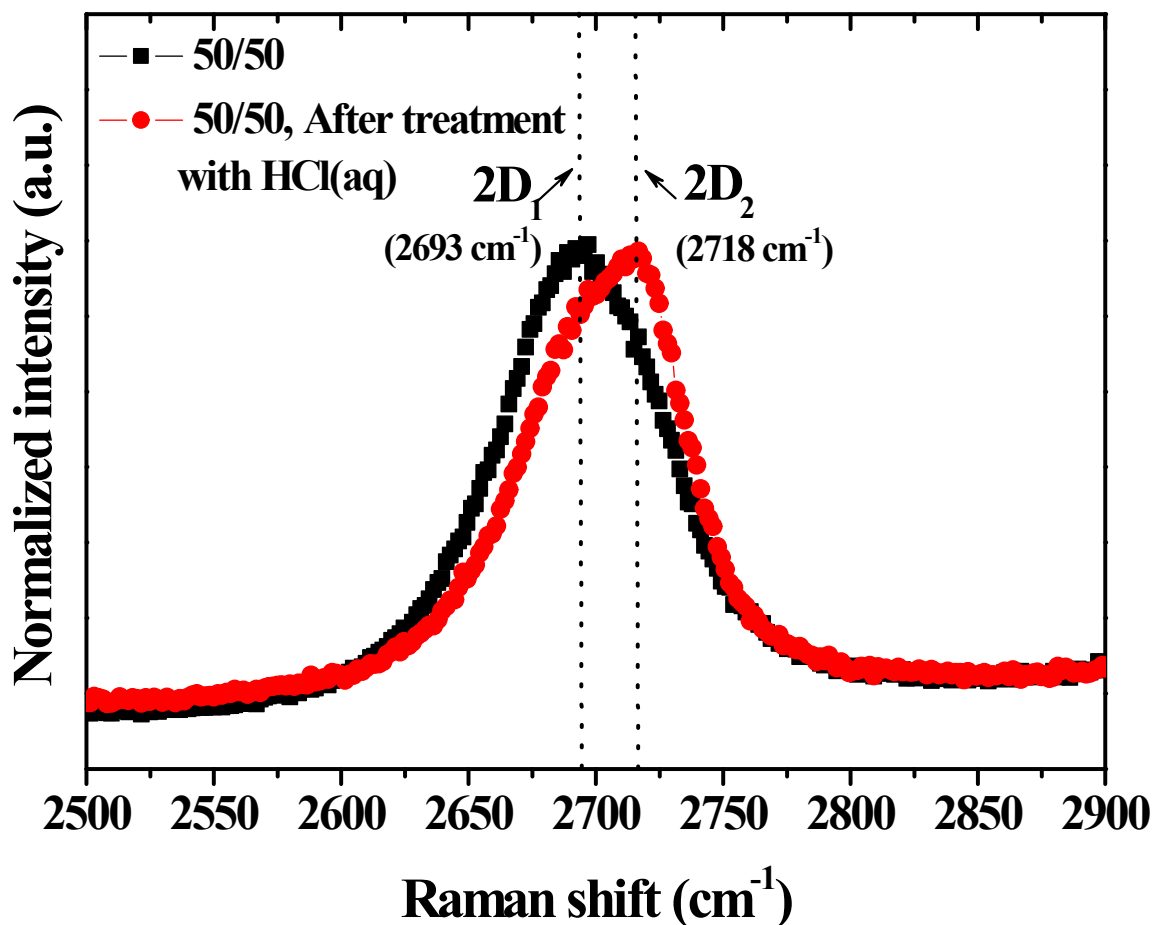


Fig. S2: Raman spectra of 50/50 graphite/UrCy-PPG composite before and after HCl treatment.

After HCl treatment, the peak at 2693 cm^{-1} corresponding to $2D_1$ band shifted to lower wavenumber and the $2D_2$ band at 2718 cm^{-1} appears significantly for the 50/50 composite in Figure S2, indicating that the hydrogen bonds of UrCy-PPG are destroyed completely and then results in a transition of the entire few-layer graphene composite from a graphene-like to a graphite-like structure.

Table S1. Electrical conductivity of pristine UrCy-PPG.

Sample	Conductivity (S m^{-1}) ^a
UrCy-PPG	7.5×10^{-11} (at $100\text{ }^\circ\text{C}$) 3.2×10^{-11} (at $30\text{ }^\circ\text{C}$)

a. Electrical conductivity was measured at 30% relative humidity.

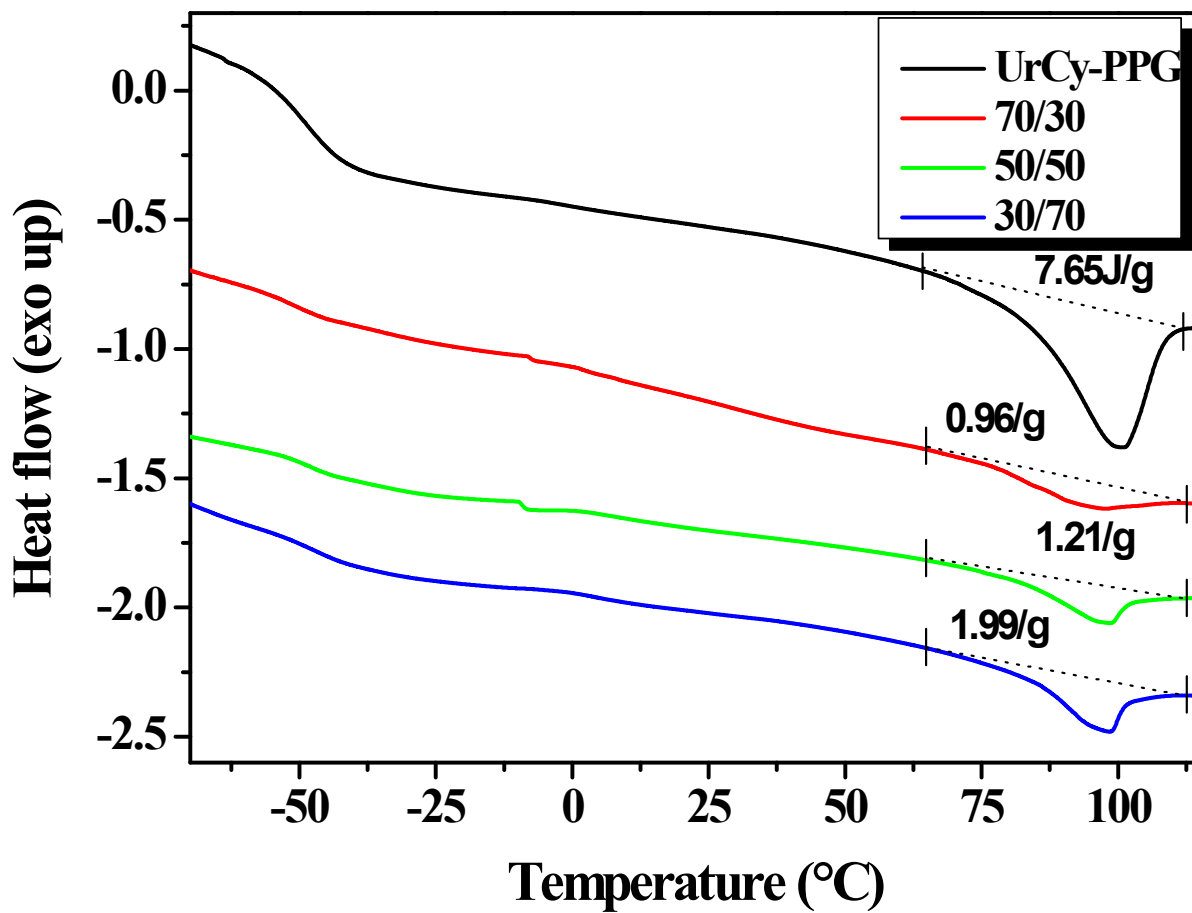


Fig. S3: DSC curves for graphite, UrCy-PPG, graphite/UrCy-PPG composites.

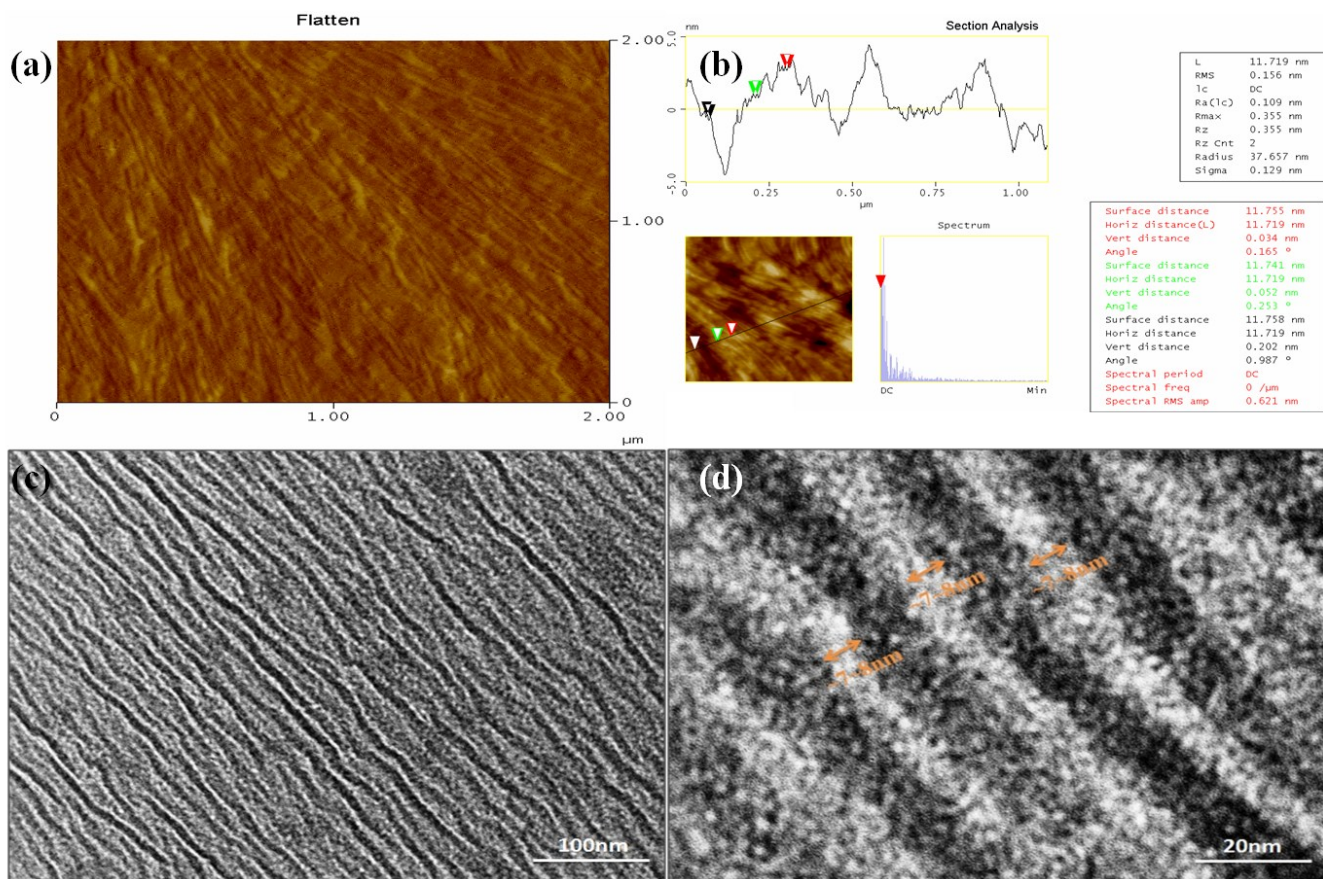


Fig. S4: AFM (a, b) and TEM (c, d) images showing the lamellar structures of annealed UrCy-PPG; the width of the lamellar structures is indicated by arrows in (d).