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Controlling the Morphology and Optoelectronic Properties of Graphene Hybrid Materials by Porphyrin Interaction

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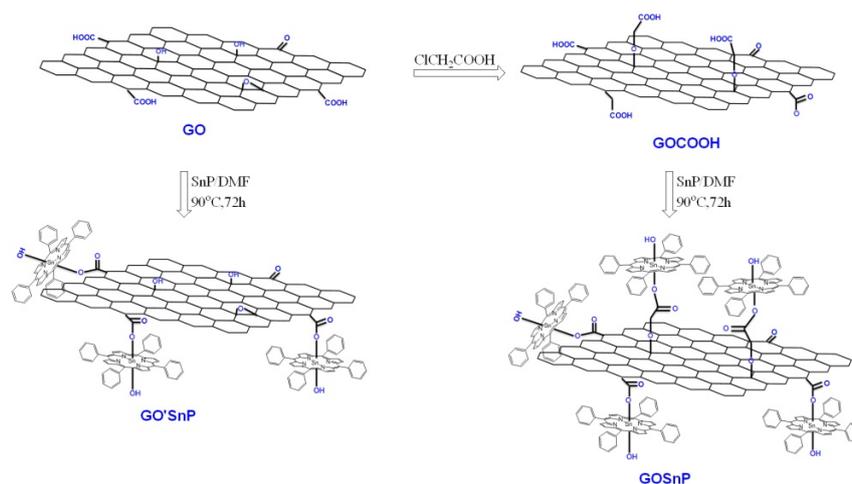
Experimental section

Materials and reagents. All solvents and chemicals were of reagent-grade quality, purchased, and used without further purification. Graphene oxide (GO, purity 99%, single layer ratio 99%) were purchased from Nanjing XFNano Materials Technology Co., Ltd and used as received. Trans-dihydroxo[*meso*-tetraphenyl-porphyrinato] tin(IV) complex (SnP), *meso*-tetraphenyl porphyrin (TPP) and *meso*-tetraphenyl zinc porphyrin (ZnTPP) were synthesized according to the reported procedures (*Macromol. Chem. Phys.*, 211, 2125-2131(2010); *ACS Applied Materials & Interfaces*, 2012, 4(12), 6752-6757); Carboxyl-functionalized graphene oxide (GOCOOH) was prepared according to the literature (*Nano. Res.*, 1, 203 212 (2008)). Ultrapure water obtained from a Millipore water purification system (≥ 18 M Ω , Milli-Q, Millipore) was used.

Instruments. IR spectral measurements were recorded on a Nicolet 5700 FT-IR spectrometer. All infrared (IR) samples were prepared as KBr discs using spectroscopic grade KBr; UV-visible spectra were obtained with a U-4100 UV-visible spectrometer (Hitachi). Steady-state fluorescence spectra were measured on an F-7000 fluorescence spectrophotometer (Hitachi). TGA measurements were run on a SDT Q600 Simultaneous DSC-TGA Instrument under N₂ purge with a heating rate of 10 °C/min. Raman spectra were measured on a Renishaw Invia Raman Microscope with Ar⁺ radiation (excitation at 532 nm); Raman samples were prepared by casting a few drops of the graphene and the functionalized graphene on clean glass substrates and were then dried. Electron micrographs were acquired using a field emission SEM (Ultra Plus, Zeiss) and a TEM (JEM-2100, JEOL, operated at 200 kV). DMF solution of graphene hybrid material were dropped onto the grids and silicon wafer and dried for TEM and SEM image, respectively. The as-prepared samples were also characterized by X-ray energy-dispersive spectroscopy (EDS, INCA) to determine the compositions.

Methods

Preparation of graphene hybrid material covalently modified with porphyrin.



Scheme S1 Synthesis route of two graphene hybrid materials covalently modified with porphyrin in the face-to-face and edge-to-face alignment (GOSnP) and only the edge-to-face alignment (GO'SnP).

To a 20 mL *N, N*-dimethyl formamide (DMF) solution of SnP (20 mg), the solution of GOCOOH (20 mg) in DMF (30 mL) was added. The reaction mixture was stirred 72 h at 90°C , and then the solution was cooled to room temperature. The product was isolated by filtration on a Nylon membrane ($0.22 \mu\text{m}$). The excess SnP and other impurities were removed through five washing cycles, which included sonication, filtration (discarding the filtrate), and re-suspension of the solid in DMF (50 mL). The precipitate was washed with CHCl_3 five times, following the above procedure. UV-Vis spectroscopy was used to check the filtrate to ensure no SnP existed in the final GOSnP material.

The preparation of GO'SnP was the same as GOSnP except GO.

The control sample is a physically mixture of GOCOOH with SnP according to the proportion of the TGA results.

Fabrication of ITO/TiO₂/GOSnP and ITO/TiO₂/GO'SnP Photoelectrode

An optically transparent indium tin oxide electrode (denoted as ITO) was washed by sonication in 2-propanol, cleaned with water and treated with O₂ plasmas in advance. A 15 % TiO₂ colloidal solution (Aldrich) was deposited on the ITO electrode using the “doctor blade” technique and dry at 70°C to yield a 1 mm-thick TiO₂ film. The electrode was denoted as ITO/TiO₂. Then DMF solution of GOSnP and GO'SnP were deposited on ITO/TiO₂ and dried (denoted as ITO/TiO₂/GOSnP and ITO/TiO₂/GO'SnP).

Photoelectrochemistry measurement.

Photoelectrochemical measurements were carried out in a standard three-electrode system by employing a modified indium tin oxide (ITO) as the working electrode, a platinum wire as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. A CHI 660d electrochemical station (Shanghai Chenhua Apparatus Corporation, China) was used for recording I-t characteristics and photocurrent was generated using a 500 W xenon lamp as light source. PBS (0.1 M) aqueous solution was the electrolyte solution. To compare the photoelectrochemical properties of two graphene/porphyrin hybrid material, the Soret-band absorption of GO'SnP and GOSnP on ITO/TiO₂ were adjusted for equal. Photoelectrochemical experiment of two graphene hybrid material (GOSnP, GO'SnP) were performed three times from three separate electrodes under identical experimental and the average value of photocurrent response of three experiment results was provided.

Optical limiting property.

The open-aperture Z-scan experiments are performed with linearly polarized 8 ns pulses at 532 nm generated from a frequency doubled Q-switched Nd:YAG laser. The spatial profiles of the pulses are of nearly Gaussian form after the spatial filter. The pulses are split into two parts: the reflected pulse was used as reference, and we focused the transmitted pulse onto the sample by using a 15-cm focal length lens. The input pulse energy was 16 μ J. The sample was placed at the focus where the spot radius of the pulses was about 20 μ m. The reflected and transmitted pulse energies were measured simultaneously with two energy detectors (Molelectron J3S-10). To compare optical limiting effect, all of the sample concentrations were adjusted to have same linear transmittance of 75 % at 532 nm in 1-mm-thick cells. The open-aperture Z-scan experiments of two graphene hybrid materials (GOSnP, GO'SnP) are performed three times under identical experimental conditions and the average value of transmittance of three experiment results was provided.



Fig. S1 Photographs of GOSnP, GO'SnP, GO'COOH and GO in DMF;

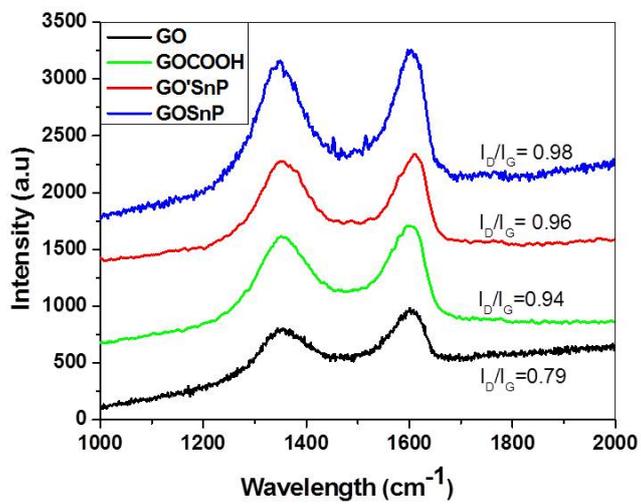


Fig. S2 Raman spectra of GOSnP, GO'SnP, GO'COOH and GO;

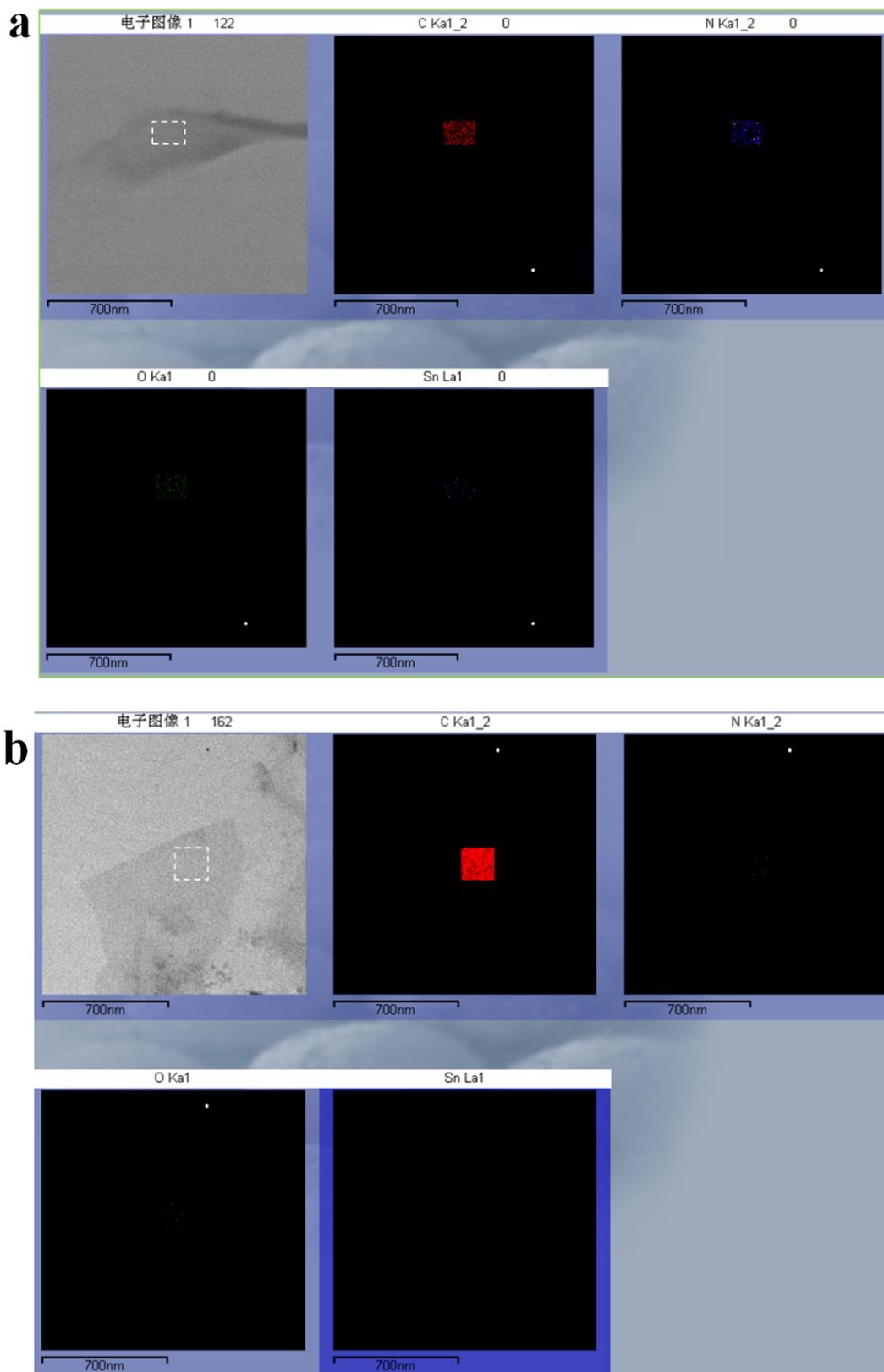


Fig. S3 TEM image and the corresponding EDS element mapping images. (a) GOSnP; (b) GO'SnP.

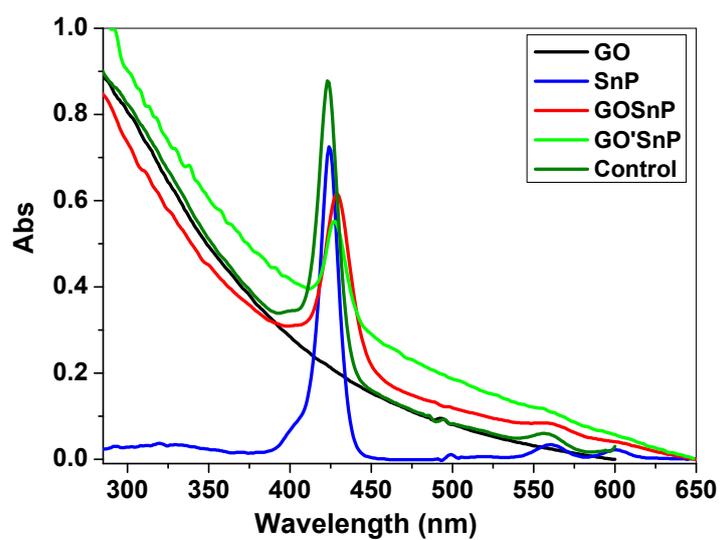


Fig. S4 UV-Vis absorption spectra of GO, SnP, GO'SnP, GOSnP and the control sample.

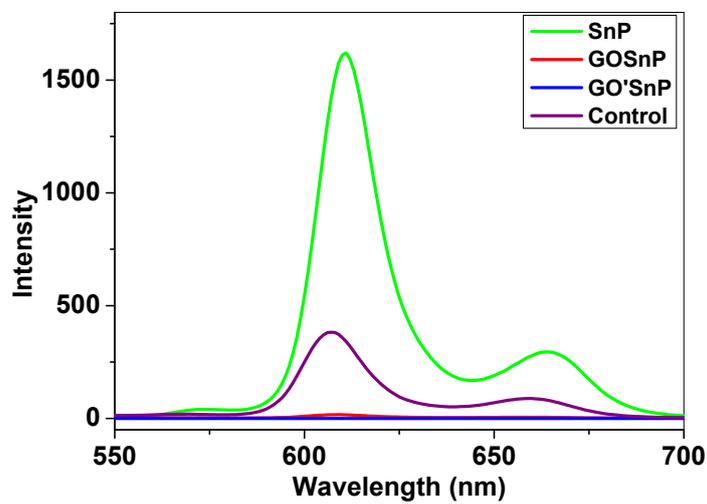


Fig. S5 Fluorescence spectra of SnP, GO'SnP, GOSnP and the control sample with the matching absorbencies at the excitation wavelength.

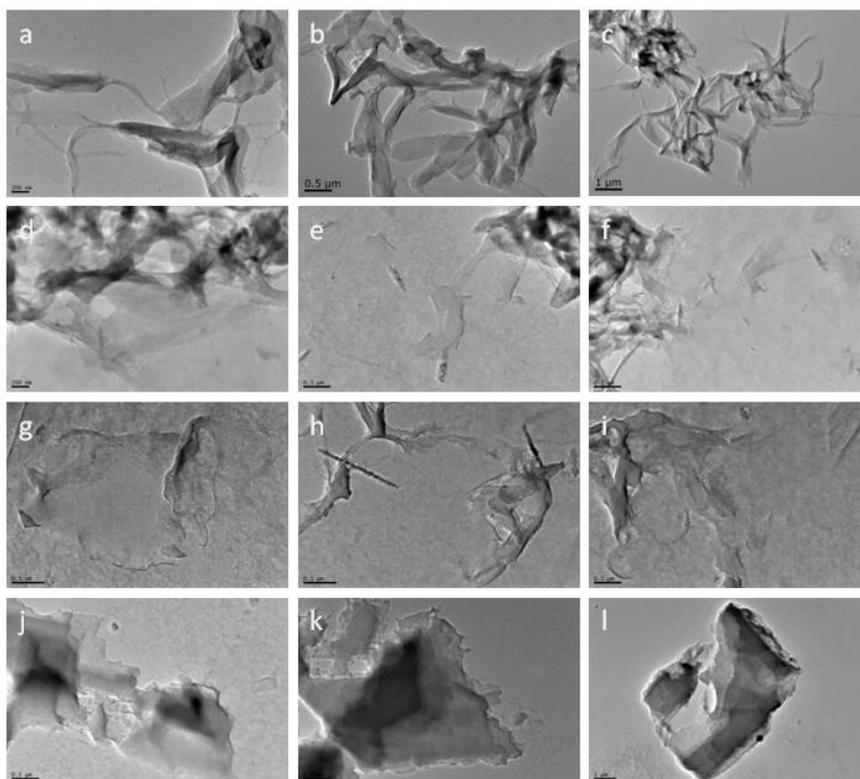


Fig. S6 TEM images of (a-c) GOSnP, (d-f) GOSnP with 0.5-fold free SnP, (g-i) GOSnP with 1-fold free SnP, (j-l) GOSnP with 3-fold free SnP;

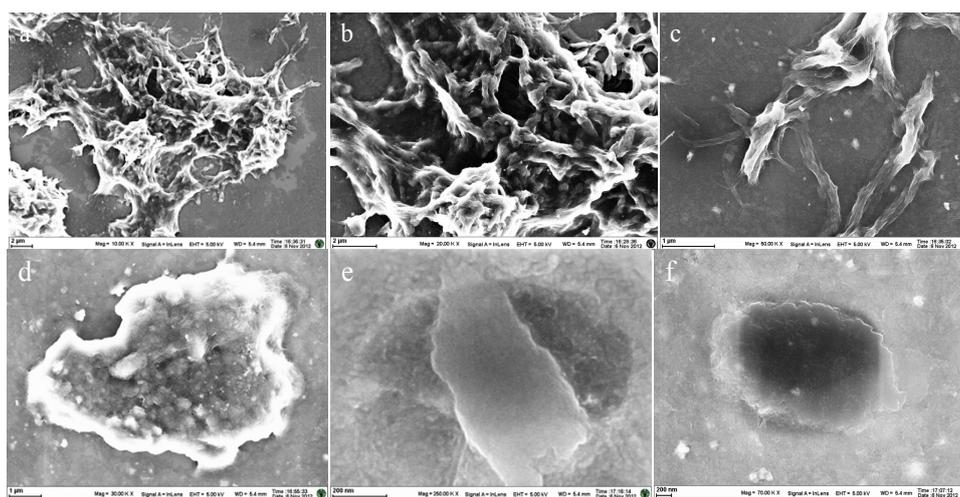


Fig. S7 SEM TEM images of (a-c) GOSnP and (d-e) GOSnP with 3-fold SnP on the SiO_2/Si substrate;

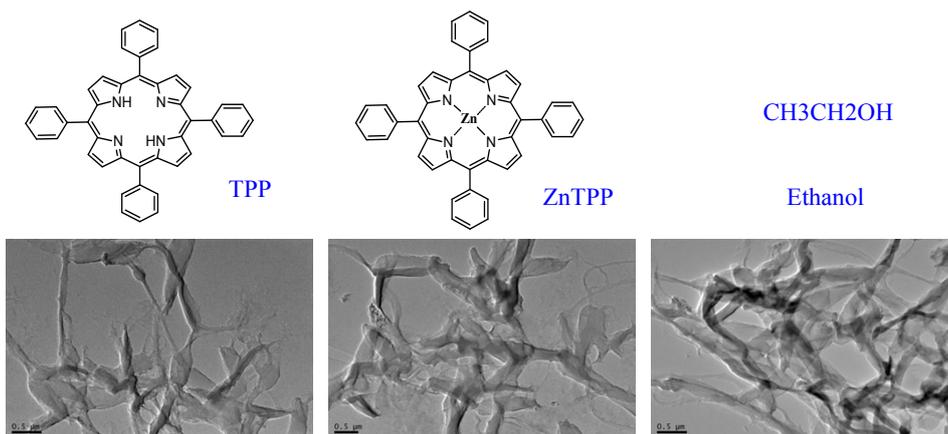


Fig. S8 TEM images of GOSnP after adding TPP, ZnPP and ethanol, respectively.

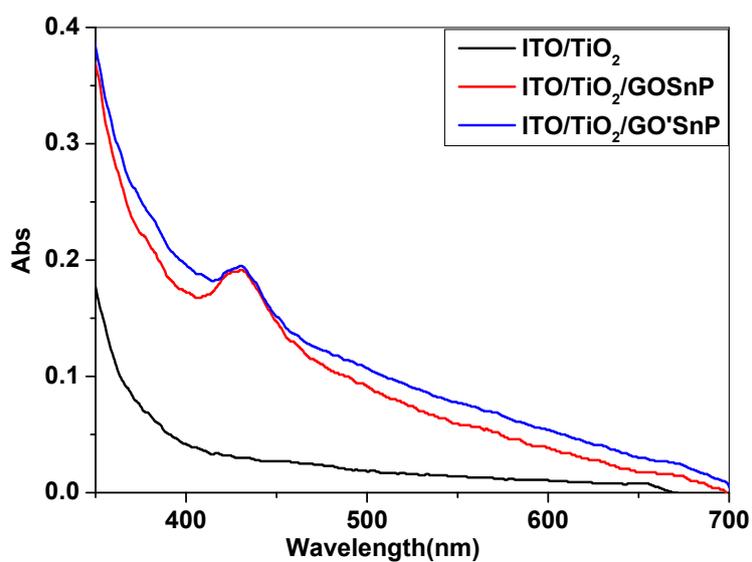


Fig. S9 UV-Vis absorption spectra of three photoelectrode for photoelectrochemistry study.