

Electronic Supplementary Information

## **‘Bridge’ Effect of CdS Nanoparticles in the Interface of Graphene/Polyaniline Composites**

Yunyun Huang<sup>a</sup>, Yujie Chen<sup>b</sup>, Chenglong Hu<sup>a</sup>, Bin Zhang<sup>a</sup>, Ting Shen<sup>a</sup>, Xudong Chen<sup>a,\*</sup> and  
Ming Qiu Zhang<sup>a,\*</sup>

<sup>a</sup>Key Lab Polym Compos & Funct Mat, Key Lab Designed Synth & Appl Polym Mat, School of  
Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, China

<sup>b</sup>Institute of Photonics, SUPA, University of Strathclyde, Glasgow G4 0NW, UK

### **Experimental**

*Synthesis of graphene/PANI composites:* All the reagents were supplied by Aladdin and used without further purification. The composites were prepared by sonicating 0.1 g graphene in 100 mL hydrochloric acid solution (10%) at 0 °C for 10 min. Then, 1 g aniline monomer was added under nitrogen atmosphere. After 10 min stirring, 100 mL ammonium persulfate (APS, oxidant) was added into the system within 30 min. The composites synthesized for 1, 3 and 6 h are denoted by G-PANI-1, G-PANI-3 and G-PANI-6, respectively. Finally, the products were washed with deionized water and ethanol for several times, and dried.

*Synthesis of CdS nanoparticles:* 100 mL 0.1 M thioacetamide (TAA) solution was added into 100 mL 0.1 M Cd(Ac)<sub>2</sub> aqueous solution at 70 °C with stirring for 10 min. The yellow precipitate was collected by filtration, and then washed with deionized water and ethanol for several times.

*Preparation of CdS/graphene composites:* The composites were prepared by sonicating 0.1 g graphene and 0.05 g CdS nanoparticles in 200 mL water for 1 h.

Then, the mixture was stirred for 6 h. The products were washed with deionized water and ethanol for several times, and dried.

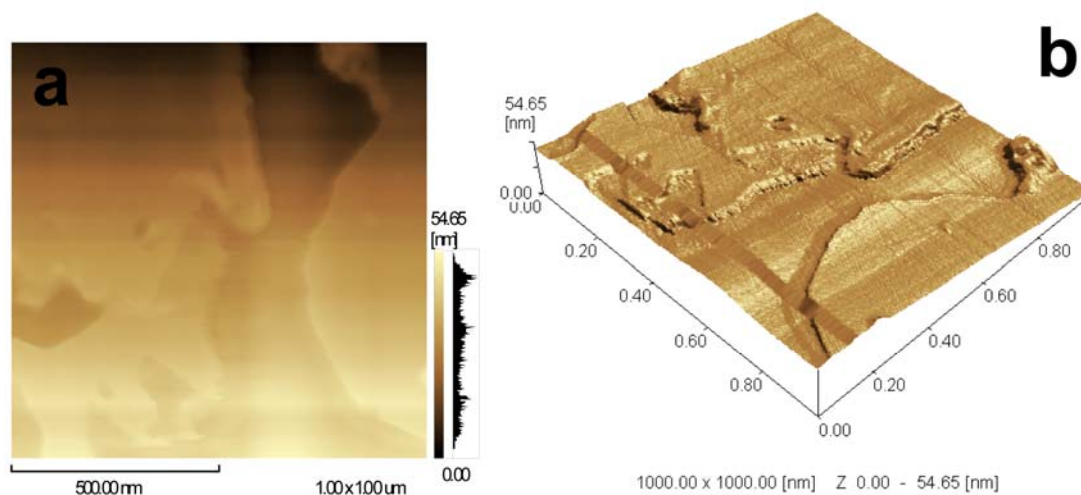
*Preparation of graphene/CdS/PANI composites:* The composites were prepared by sonicating 0.1 g graphene and 0.05 g CdS nanoparticles in 100 mL hydrochloric acid solution (10%) at 0 °C for 10 min. Then, 1 g aniline monomer was added under nitrogen atmosphere. After 10-min stirring, 100 mL APS was added into the system within 30 min. The composites synthesized for 1, 3 and 6 h are denoted by G-CdS-PANI-1, G-CdS-PANI-3 and G-CdS-PANI-6, respectively. The products were washed with deionized water and ethanol for several times, and dried.

*Preparation of graphene/PANI composites via galvanizing method:* The electrochemical preparation was carried out in a conventional two-electrode cell via electrodeposition at constant voltage of 30 V for 30 min. The indium-tin oxide-coated glass (ITO) was ultrasonically cleaned in distilled water, ethanol and acetone, respectively, and then rinsed in distilled water again prior to electrodeposition. The electrolytic solution contained 5 mL graphene dispersion (0.025 g graphene dispersed in 25 mL dimethylformamide (DMF)) and 5 mL aniline solution (0.25 g aniline dissolved in 25 mL DMF).

*Preparation of graphene/CdS/polyaniline composites via galvanizing method:* The preparation is the same as that for making graphene/PANI composites mentioned above. The electrolytic solution contained 5 mL graphene and CdS dispersion (0.03 g graphene dispersed in 25 mL dimethylformamide (DMF)), 5 mL Cd(Ac)<sub>2</sub> aqueous solution (Cd(Ac)<sub>2</sub> (0.01 M) and TAA (0.01 M) in DMF) and 5 mL aniline solution (0.3 g aniline dissolved in 25 mL DMF).

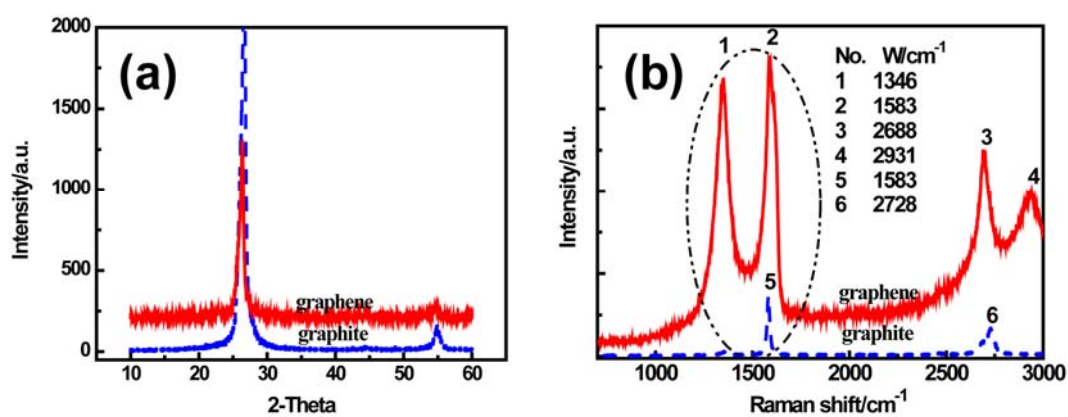
*Characterization:* Surface morphology and inner structure of G-PANI, CdS-graphene and G-CdS-PANI composites were observed by field emission scanning electron microscope (JSM-6330F and Hitachi S-4800, Japan) and transmission electron microscope (JEM-2010HR, Japan). The chemical compositions of the as-prepared films were investigated using X-ray photoelectron spectroscopy (XPS), which was

conducted on a ESCALAB 250 electron spectrometer using Al K $\alpha$  line excitation source with the reference of C 1s at 284.8 eV. Raman spectroscopy was applied using a Renishaw inVia Raman system with 514.5 nm excitation. The water contact angle were measured with a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature. The fluorescence spectra were recorded using a RF-5301PC spectrofluorophotometer and the absorption spectra were collected using a UV-3150 UV-Vis-NIR spectrophotometer. Photoelectric properties were measured on an electrochemical station (CH Instruments 660C, Shanghai Chenhua Inc., China) using conventional three-electrode configuration with a platinum sheet as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte containing 0.1 M KCl dissolved in aqueous solution was deoxygenated under N<sub>2</sub> flow for 20 min. A 50 W Xe lamp and a Spex minimate monochromator were employed. The light was focused on a diaphragm to create a light spot (10 × 3 mm<sup>2</sup>).

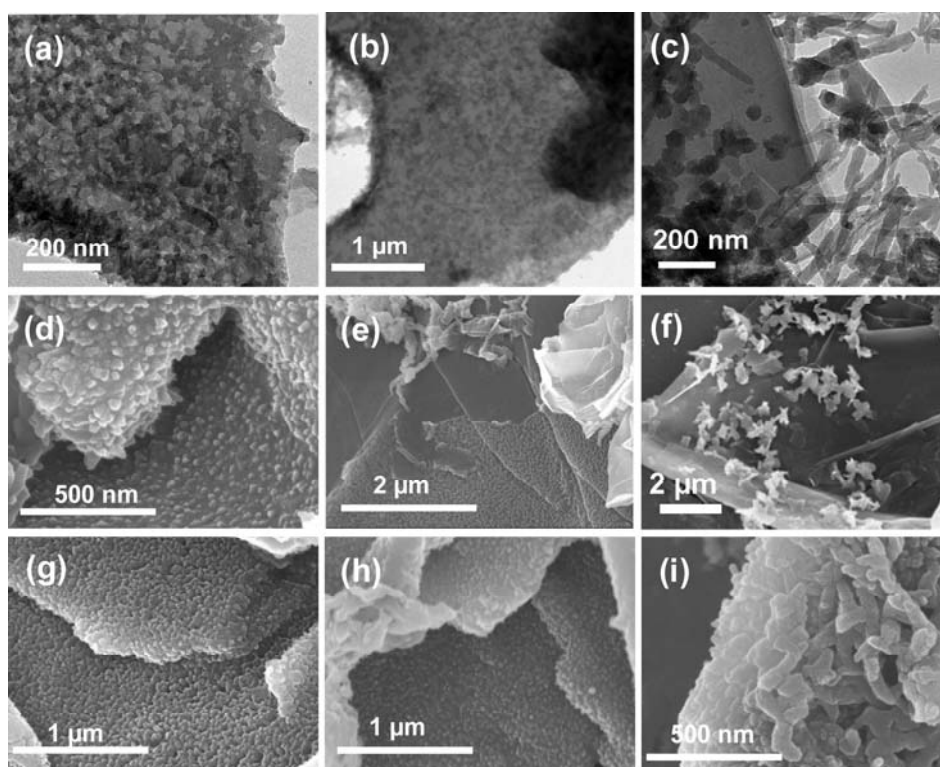


**Figure S1.** AFM images of graphene. (a) Height trace; (b) 3D picture of height trace.

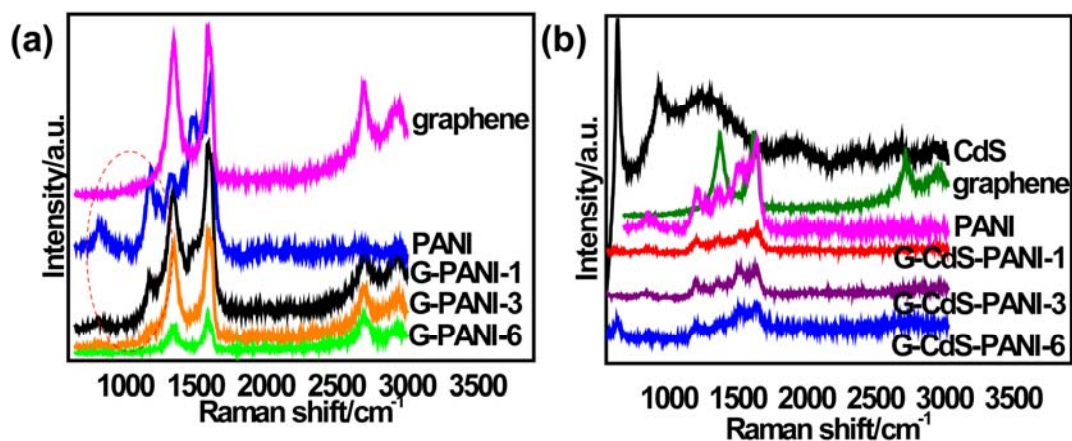
The AFM images in Figure S1 show that thickness of the as-prepared graphene is about 0.642 nm. The joint results of XRD and Raman spectroscopy in Figure S2 indicate that the obtained graphene is about a few layers thick.



**Figure S2.** (a) XRD and (b) Raman spectra of graphite and graphene.



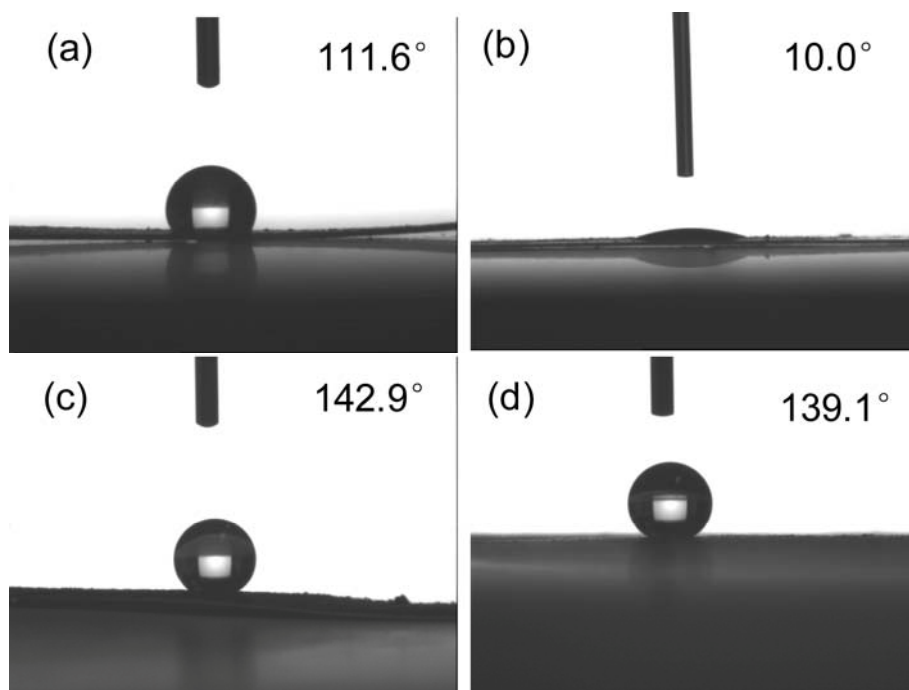
**Figure S3.** TEM images of (a) G-PANI-1, (b) G-PANI-3, (c) G-PANI-6; and SEM images of (d) G-PANI-1, (e) G-PANI-3, (f) G-PANI-6, (g) G-CdS-PANI-1, (h) G-CdS-PANI-3, and (i) G-CdS-PANI-6.



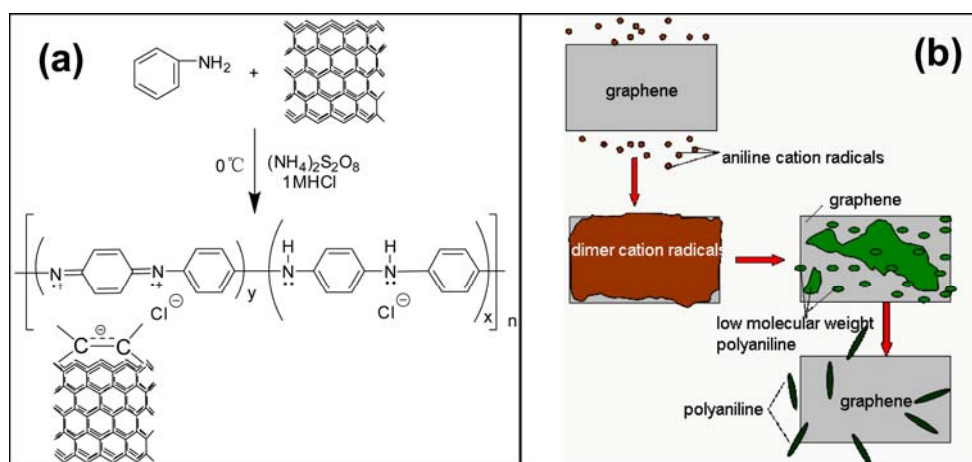
**Figure S4.** Raman spectra of (a) G-PANI-1, G-PANI-3, G-PANI-6, PANI and graphene; and (b) G-CdS-PANI (G-CdS-PANI-1, G-CdS-PANI-3 and G-CdS-PANI-6) and CdS ( $\lambda = 514\text{nm}$ ).

In Figure S4a, all the composites (G-PANI-1, G-PANI-3, G-PANI-6) show peaks at about  $1352$ ,  $1600$ ,  $2692$  and  $2834\text{ cm}^{-1}$ , corresponding to D-band and G-band of graphene, C-C stretching of PANI, and 2D band of graphene, respectively.<sup>12</sup> In addition, there are peaks at around  $1185\text{ cm}^{-1}$  for G-PANI-1 and G-PANI-3 (i.e.  $1175\text{ cm}^{-1}$  on the spectrum of G-PANI-1 and  $1195\text{ cm}^{-1}$  on the spectrum of G-PANI-3, and the former is more remarkable than the latter), while these peaks disappear in the spectrum of G-PANI-6. The peak near  $1200\text{ cm}^{-1}$  in PANI is attributed to C-H bending vibration of quinone/benzene ring. Interaction between PANI and graphene causes it to shift to lower wavenumber regime. Since the peak at  $1175\text{ cm}^{-1}$  on the spectrum of G-PANI-1 is the most obvious as compared to those on the spectra of G-PANI-3 and G-PANI-6, it is known that the interaction between benzene (in graphene) and quinone (in PANI) is the strongest in G-PANI-1 and negligible in G-PANI-6. Moreover, the ratio of peak intensity at  $2692\text{ cm}^{-1}$  to that at  $2834\text{ cm}^{-1}$  on the spectrum of G-PANI-1 is about 1, and it becomes higher in the case of G-PANI-3 and G-PANI-6. For G-PANI-6, the value approaches to that of graphene, suggesting that PANI gradually falls off graphene from G-PANI-1 to G-PANI-6.

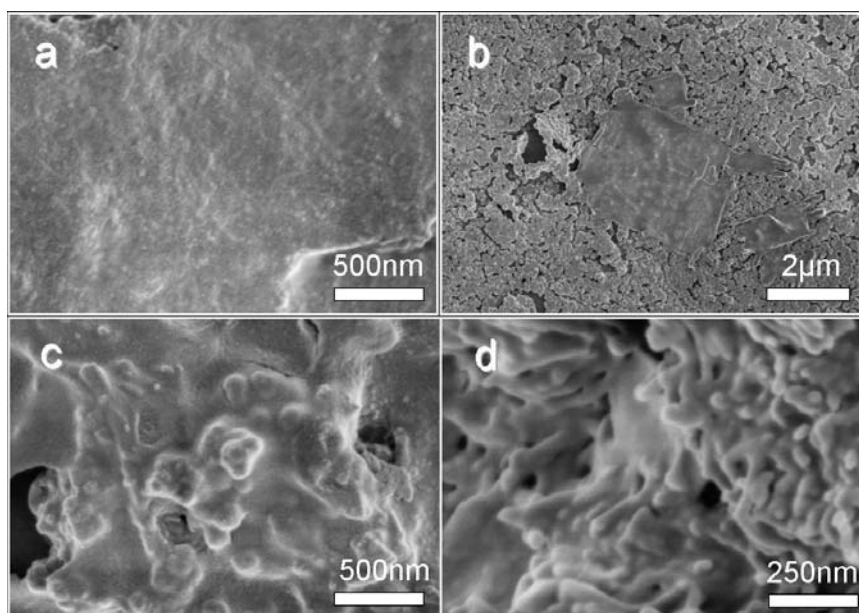
Figure S4b shows that all the composites have a PANI-like Raman shift, suggesting that the composites must be covered by PANI during the polymerization. Moreover, as there is no typical peak of either CdS or graphene, CdS must be covered by PANI and connect graphene with PANI.



**Figure S5.** Contact angles of (a) graphene, (b) PANI, (c) G-PANI-6, and (d) G-CdS-PANI-6. Accordingly, the surface tensions  $\gamma_G$ ,  $\gamma_{\text{PANI}}$ ,  $\gamma_{\text{G-PANI-6}}$  and  $\gamma_{\text{G-CdS-PANI-6}}$  were estimated to be 16.16, 71.71, 3.70 and 3.57 N/m, respectively.

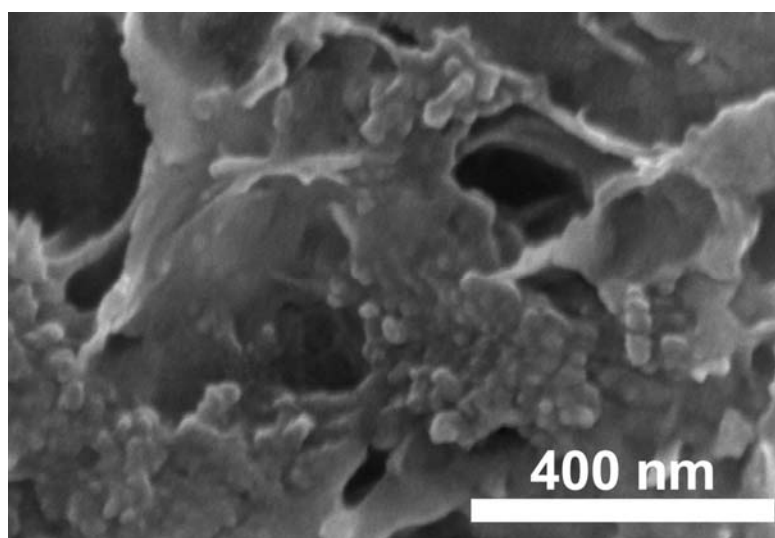


**Figure S6.** (a) Schematic of aniline adsorption on graphene in the first step of polymerization; (b) growth mechanism of PANI on graphene.



**Figure S7.** SEM photos of control composites (synthesized by galvanizing method). (a) CdS-graphene; (b) G-PANI; (c) and (d) G-CdS-PANI.

The composites synthesized by galvanizing method have the same appearances as those synthesized by in-situ polymerization. That is, graphene and PANI are separated from each other in the absence of CdS nanoparticles, while PANI can grow on the surface of graphene in the presence of CdS nanoparticles.



**Figure S8.** SEM photos of G-ZnO-PANI nanocomposite.