

## Supplementary information

### Poly (N-isopropylacrylamide) on Two-dimensional Graphene Oxide Surfaces

Junjie Qi, Weipeng Lv, Guoliang Zhang, Fengbao Zhang and Xiaobin Fan\*

\*Address: School of Chemical Engineering & Technology, Tianjin University, Tianjin, PR China.  
Fax: +86-22-27408778; Tel: +86-22-27408778  
E-mail: [xiaobinfan@tju.edu.cn](mailto:xiaobinfan@tju.edu.cn)

#### 1. Experimental Section

##### 1.1. Materials

Graphite, potassium persulfate (KPS) and N, N, N, N-tetramethylethylenediamine (TEMED) were purchased from Tianjin Guangfu Ltd.. N-isopropylacrylamide (NIPAM) (Sigma-Aldrich) was purified by recrystallization from hexane. All other reagents were purchased from commercial sources and used as received.

##### 1.2. Preparation of the nanocomposites

Graphite oxide was prepared by Hummer method<sup>1</sup> and exfoliated into GO by sonication in water.<sup>2</sup> According to the previous reports of attaching PNIPAM on exfoliated inorganic clay nanoparticle surfaces,<sup>3-5</sup> the PNIPAM–GO hybrids were prepared via in-suit free-radical polymerization (using KPS and TEMED as catalyst). 0.1 g NIPAM was dissolved in 20 mL water and then mixed with the GO suspension by stirring under N<sub>2</sub> atmosphere. Next, TEMED (10 μL) and KPS (0.01 g) in H<sub>2</sub>O (1 mL) were added to the solution at ~ 0 °C while stirring. Then, free-radical polymerization was allowed to proceed at 30 °C for 24 h. The obtained PNIPAM–GO hybrids were purified by repeated washing, dialysis and centrifugation to remove free PNIPAM. The successful attachment of PNIPAM on GO surfaces was attested by FTIR and XPS.

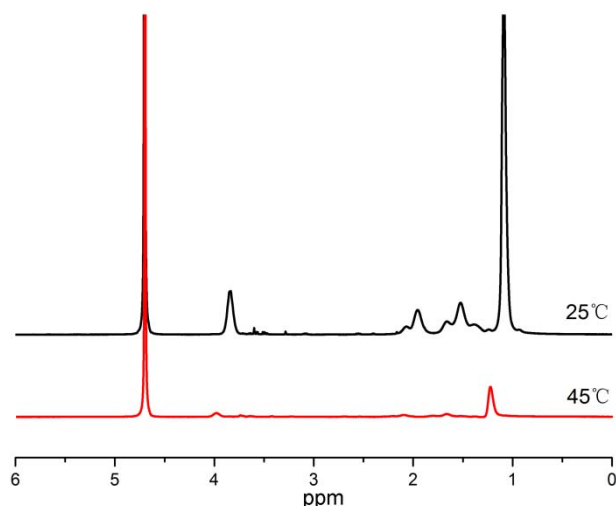
The samples for AFM measurements were prepared by depositing a drop of GO–PNIPAM hybrids / GO solution on a mica substrate and drying at different conditions: (a) drying under vacuum at 25 °C for 12 h; (b) drying at 25 °C for 2 h and then heating at 50 °C; (c) heating the suspension at 50 °C and drying it under vacuum at 50 °C. The thin film of PNIPAM–GO hybrids / GO was prepared by microfiltration at 25 °C.

### **1.3. Characterization**

FTIR spectra were recorded on Nicolet Nexus FTIR. XPS spectra were obtained by PHI 1600 spectrometer. Atomic force microscopy (AFM) images were taken by CSPM 5000 scanning probe microscope in contacting mode. <sup>1</sup>H NMR measurement was performed on Bruker DRX-500 spectrometer operating at 500 MHz at different temperatures in D<sub>2</sub>O. SEM images were collected by the S4800 scanning electron microscope. Transmission electron microscope (TEM) images were obtained by a Tecnai G2 F20 instrument. The static contact angels were measured by a Dataphysics OCA15EC meter at different temperatures by using 808 nm NIR laser irradiation (power density=1.5 W·cm<sup>2</sup>). Raman scatterings were recorded performed on NTEGRA Spectra at room temperature. Thermogravimetric analysis (TGA) measurements were run on a METTLER-TOLEDO TGA/DSC 1 system under N<sub>2</sub> purge with a heating rate of 10 °C min<sup>-1</sup>. The thin film of PNIPAM–graphene oxide hybrids for CAs measure and SEM is prepared by microfiltration at 25 °C.

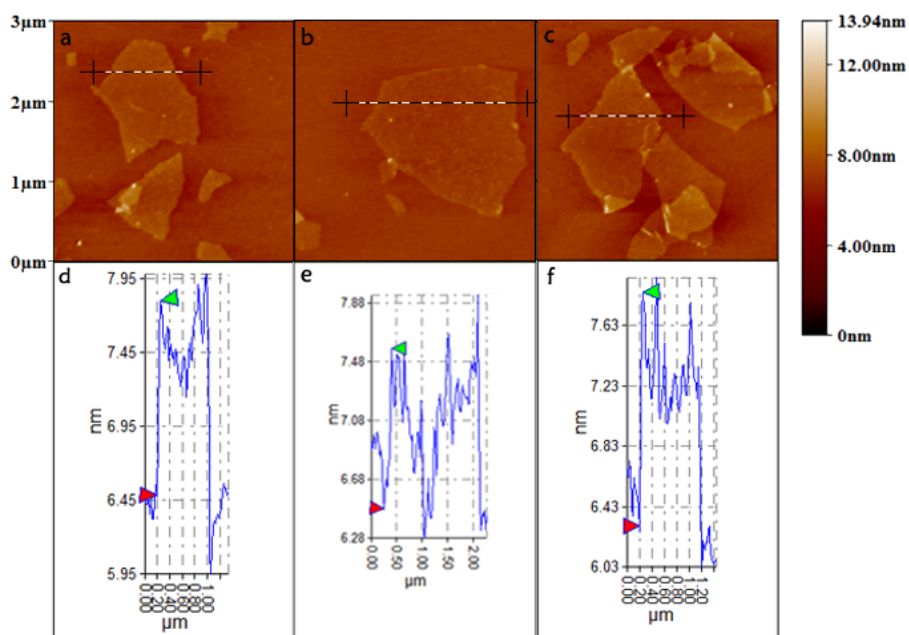
## **2. Supplementary Results**

### **2.1 <sup>1</sup>H NMR spectra of PNIPAM–GO**



**Fig. S1** <sup>1</sup>H NMR spectra of PNIPAM–GO at different temperatures (concentration = 10 mg·mL<sup>-1</sup> in D<sub>2</sub>O). At 25 °C, the proton signals at 1.3–2.2 ppm attributed to the resonance of PNIPAM chains can be clearly detected. The increase of temperature to 45 °C led to a drastically decrease in the signal intensity of PNIPAM chains. This is attributed to the dehydration of the PNIPAAm chains, indicating the formation of heat-induced interactions between PNIPAAm chains.

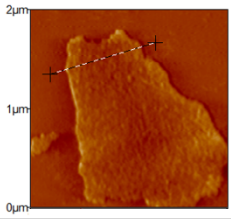
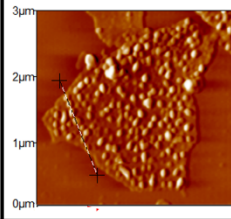
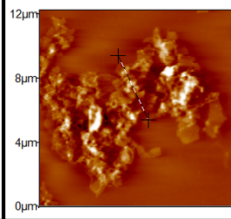
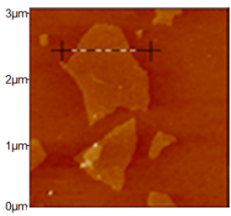
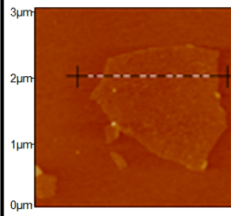
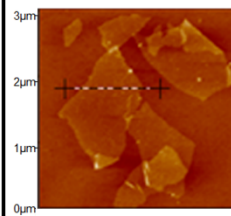
## 2.2 The AFM images of raw grapheme oxide



**Fig. S2** AFM images of a droplet of GO suspension dried at different conditions: (a) dried under

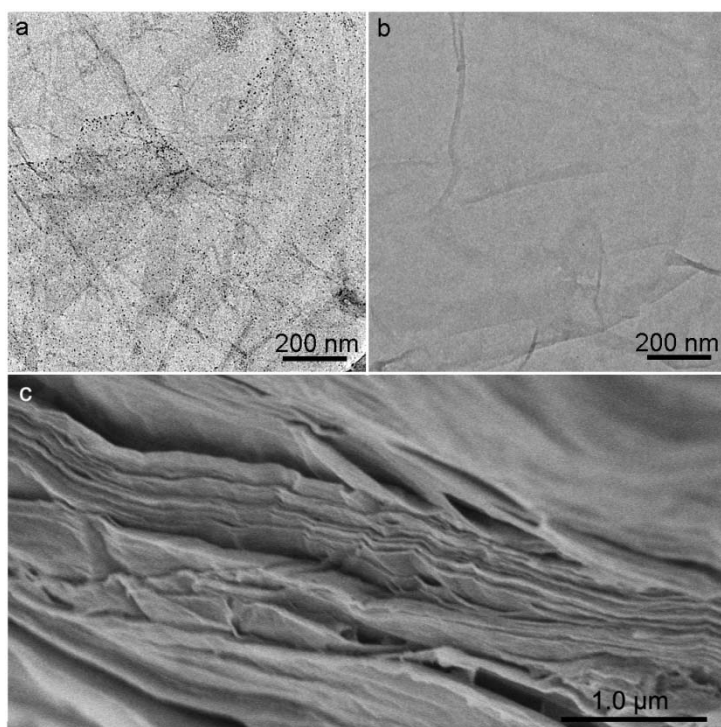
vacuum at 25 °C; (b) partially dried at 25 °C and heated at 50 °C; and (c) heated and dried under vacuum at 50°C. The surfaces of GO films are very smooth with a thickness of  $\sim 1$  nm. The morphology and thickness of GO drying at different conditions are unchanged. No change in its morphology and can be observed.

### 2.3 The table comparing the preparation conditions and results

Sample	Drying condition		
	drying under vacuum at 25 °C for 12 h	drying at 25 °C for 2 h and then heating at 50 °C for 2h	heating the suspension at 50 °C and drying it under vacuum at 50 °C
GO-PNIPAM			
GO			

**Table. S1** The table of AFM images of GO–PNIPAM and GO drying under different condition

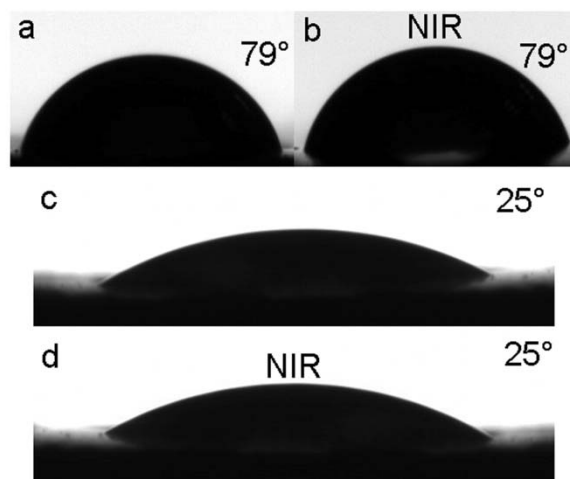
### 2.4 TEM and SEM images



**Fig. S3** TEM images of (a) GO–PNIPAM hybrids and (b) GO; (c) SEM image of GO.

Abundant spherical “dark spots” can be readily observed on the surfaces of the GO–PNIPAM hybrids (Fig. S3a). As comparison, in Fig. S3b the GO sample shows clear surfaces as previous studies. From Fig. S3c, it shows layer structure with very small spacing. This result is in line with previous studies on GO,<sup>6</sup> but obvious different from the GO–PNIPAM hybrids film.

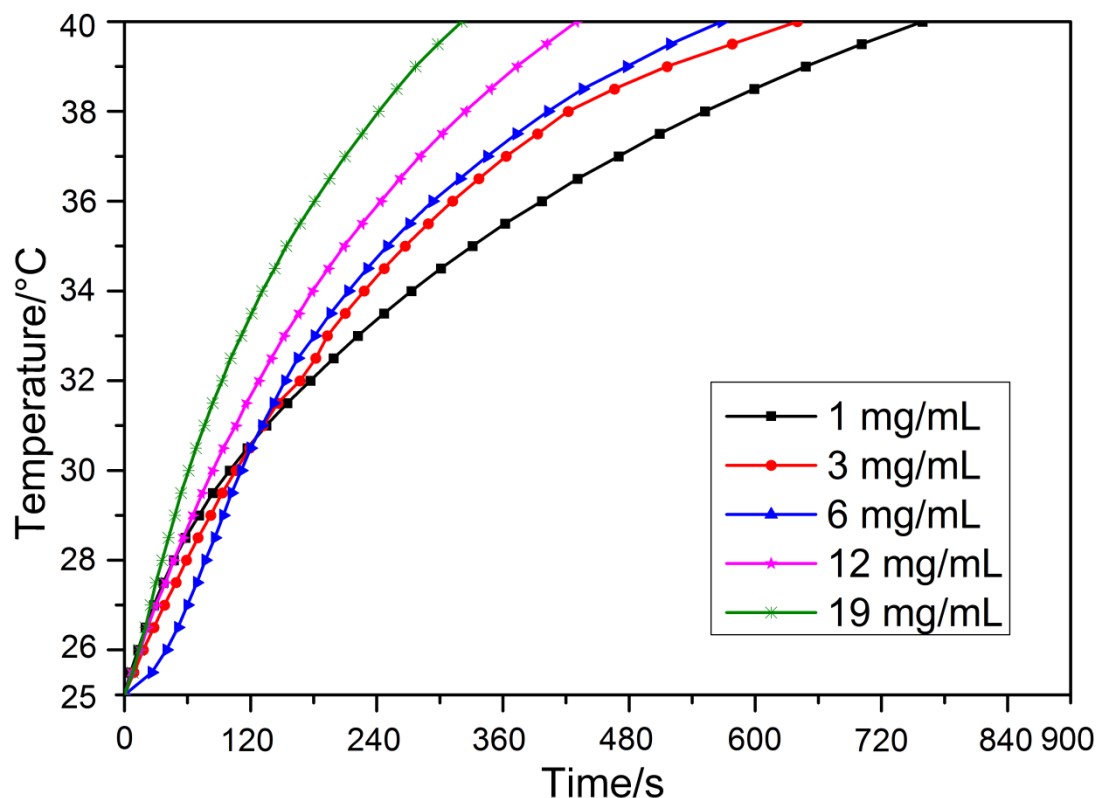
## ***2.5 Connect angle of GO and PNIPAM***



**Fig. S4** Contact angle of (a) GO and (b) after NIR irradiation, contact angle of (c) PNIPAM and (d) after NIR irradiation.

As Shown in Fig. S4, neither the GO film nor the PNIPAM sample shows switching of wettability on exposed to NIR light (10 min). The contact angle of GO film is  $79^\circ$ , and the contact angle of PNIPAM film is  $25^\circ$  in room temperature (because PNIPAM has no near-infrared absorption).

## ***2.6 The relationship between the time of NIR irradiation GO suspension and the temperature of GO suspension***



**Fig. S5** The curves of the relationship between the time of NIR irradiation GO suspension and the temperature of GO suspension

To evaluate the temperature variation on the surfaces of the GO film during the contact angle test, we also prepared a series of GO suspension for irradiation. As shown in Fig. S5, the temperatures of all the suspension samples can increase to over 38 °C within 10 min. Therefore, during the contact angle test of GO film, we expect that the temperature on the surfaces of GO film should be over 38 °C (over LCST of PNIPAM) after exposure to NIR for 10 min.

### Reference

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