## **Direct Supramolecular Interacted Graphene Oxide Assembly on**

# **Graphene as an Active and Defect-Free Functional Platform**

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## **Experimental Section**

#### Materials

General chemicals in chemical reagent grade were used as received from Sinopharm Chemical Reagent. Ethanol and deionized water were used as rinsing solvents. N, N-dimethylaminoethylmethacrylate (DMAEMA) was obtained from Alfa Aesar China (Tianjin) Co., Ltd, which was purified by neutral Al<sub>2</sub>O<sub>3</sub> column and dried with a 0.4-nm molecular sieve at room temperature for 3 days. PDMS stamps with line and grid-shaped structures were fabricated from Sylgard 184 (the ratio between component A and B was 1:10) at 70 °C for 2 h on a silicon master.

### Preparation of homogenous dispersion GO aqueous solution

GO sheets were synthesized by a modified Hummers' method and exfoliation of graphite oxide was achieved by a strong ultrasonication method. The obtained brown dispersion was then washed and centrifuged to remove any unexfoliated graphite oxide. After concentration and drying procedures, the obtained GO powders were re-dispersed into the anhydrous ethanol, followed by an ultrasonication procedure for a homogenous suspensions.

### Preparation of 2D patterned GO micropatterns by $\mu CP$ strategy

The PDMS stamp was inked by exposing the stamp features to an ethanol solution of GO for 3 min and drying with nitrogen, before being brought into contact with the receiving target for 1 min to fabricate the patterned SAMs on graphene substrates.

### Preparation of 3D patterned graphene microarchitectures by RAµCP

The PDMS stamp was inked by exposing the stamp features to an ethanol solution of GO until the solvent dried. A roller was employed to roll across the structured PDMS with slow velocity and apt pressure. The operation parameters were systematically adjusted by conducting amounts of experiments. The pressure was measured by a platform balance, which can reach the accuracy of 1g. The velocity was measured by a stopwatch and ruler.

#### Self-initiated photografting and photopolymerization (SIPGP)

The 2D/3D GO micropatterns modified graphene was submerged in ~2 mL of distilled and degassed monomer and irradiated with an UV lamp with a spectral distribution between 300 and 400 nm distribution (intensity maximum at  $\lambda = 365$  nm with a total power of ~ 240 mW/cm<sup>2</sup>) for required time (PS for 1 h and PDMAEMA for 2 h). Following SIPGP (M. Steenackers, A. Kuller, S. Stoycheva, M. Grunze, R. Jordan, *Langmuir* **2009**, *25*, 2225.), the functionalized films were exhaustively rinsed with different solvents (toluene, ethyl acetate, and ethanol for PS and ethanol for PDMAEMA) followed by ultrasonication for several minutes in order to remove any physisorbed polymer.

#### Characterization

The instrument (OCA-20, Dataphysics) used a charge-coupled device (CCD) camera and an image analysis processor. The water (Milli-Q) droplet volume was 3 µL, and the contact angle was measured after the drop was stable on the sample. For each sample, the reported value is the average of the results obtained on three droplets. Optical images were acquired by Polarized Optical Microscopy (Olympus, BX 51TF Instec H601). The Raman scattering measurements were performed at room temperature on a Raman system (inVia-reflex, Renishaw) with confocal microscopy. The solid-state diode laser (532 nm) was used as an excitation source with a frequency range of 3200-1000 cm<sup>-1</sup>. Atomic force microscopy (AFM) images were taken by a multimode AFM (Being Nano-Instruments, Ltd) operating in the contact and/or tapping mode using silicon cantilevers (spring constant: 0.15 Nm<sup>-1</sup>, resonant frequency: 12KHz for cantilever of tapping mode). Static water contact angles were measured at room temperature using the sessile drop method and image analysis of the drop profile. Electrical measurements of devices were performed with a semiconductor parameter analyzer (Keithley 4200). Note that, prior to GO and

polymer modification, the pristine graphene was deposited on two patterned Ag electrodes with a distance of  $\sim$ 5 mm for further electrical measurement.



Fig. S1 Photograph of ethanol dispersed GO solution with a concentration of about 1.5 mg/mL.



Fig. S2 a) Photograph of the single layer graphene on  $Si/SO_2$  target. b) Optical image of the cross-sectional image of the graphene.



Fig. S3 a) Sketch and optical image of the 2D grid-shaped GO micropatterns via μCP method.b) Schematic and optical image of the 3D GO microstructures on GO background by RAμCP strategy.



**Fig. S4** a) Schematic of the 3D GO micropatterns on single layer graphene. b) SEM image of the 3D GO microstructures interacted on graphene surface. c) The enlarged SEM image of b).



Fig. S5 Current-voltage curves of the pristine graphene and GO modified graphene.