

Supporting Information

Title: Dynamic configuration of reduced graphene oxide in aqueous dispersion and its effects on thin film properties

Authors: Yufei Wang, Xuehua Zhang* and Dan Li*

Experimental section

The reduced graphene oxide (rGO) dispersions were prepared by chemical reduction of graphene oxide (GO), following the procedure we have previously reported.¹ A drop of rGO dispersion was deposited on poly(diallyldimethylammonium chloride (PDDA) coated mica surface, and the sample was placed in a fluid cell. To exam the configuration of rGO sheets in aqueous solution, tapping mode Atomic Force Microscopy (Multimode IV, Veeco) was carried out in the fluid cell, with the cantilever (NP with the nominal spring constant of 0.32 N/m, Veeco) pre-treated by UV light before use. By comparison, dried samples were also prepared by drop-casting of rGO on a piece of freshly prepared mica surface, followed by drying in air. AFM images of the dried samples were obtained by a Molecular Imaging Picoscan II instrument in tapping mode with oxide-sharpened, silicon nitride tips with integrated cantilevers with a nominal spring constant of 0.38 N/m were used.

The rGO hydrogel films for water permeation experiment were prepared by vacuum filtration of 3 ml of rGO dispersions (0.05 mg/ml) through a nitrocellulose mixed ester filter membrane (47 mm in diameter, 0.2 μm pore size, Millipore). Once the water has drained, certain amount of water was immediately poured on top of the as-formed rGO hydrogel membrane for the measurement of water flux. Alternatively, dried rGO thin films for water permeation experiment were formed by vacuum drying of the as-formed hydrogel films, followed by water flux measurement. Note that it is difficult to directly measure the thickness of the above rGO hydrogel and dry films. Alternatively, we have prepared thick and free-standing rGO hydrogel and dry films using 30 ml of rGO dispersions (0.5 mg/ml) at different stages, and measured their thickness. It is found that the thickness of the rGO hydrogel films (with different stages) are almost the same, and so do the dry films. Moreover, the film thickness is proportional to the amount of rGO used for film formation. Therefore, the thickness of rGO hydrogel films and dry

films used for water permeation experiments is estimated to be about 1.8 μm and 60 nm, respectively. In addition, the water contents of the rGO hydrogel films prepared at different stages are all around 90 wt%. On the other hand, the dried rGO thin films for electrochemical test were prepared by vacuum filtration of 15 ml of rGO dispersions (0.5 mg/ml) at different stages, and their thickness are found to be all around 3 μm (Fig. S7). The electrochemical test was carried out using a Versastat-4 potentiostat by assembling rGO films into supercapacitor with a symmetrical two-electrode configuration (1M H_2SO_4 as electrolyte). In addition, the UV–Vis spectra were collected using a Varian Cary 300 UV/Visible spectrometer, and zeta-potential was obtained by Zetasizer Nano Z (Malvern).

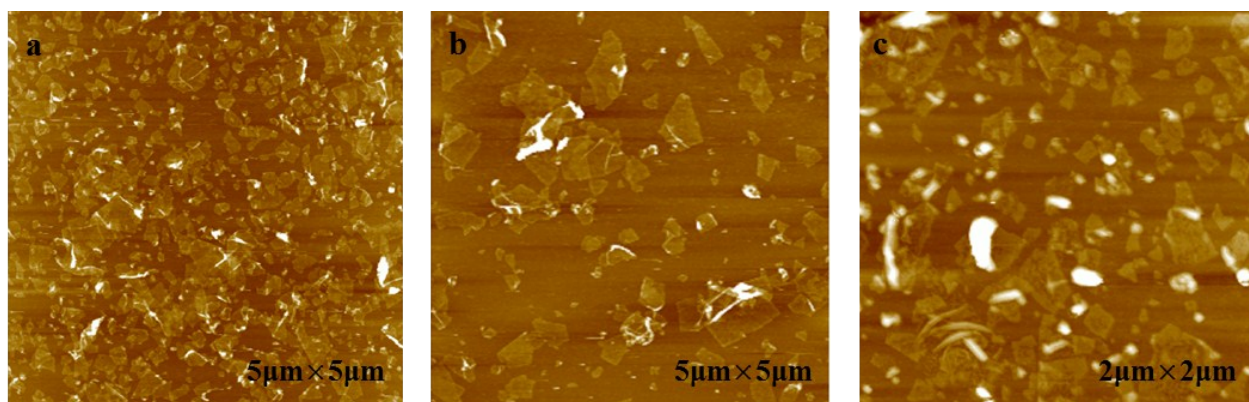


Figure S1 AFM images of rGO sheets on poly-(diallyldimethylammonium chloride) (PDDA) coated mica surface obtained in liquid state in stage 1

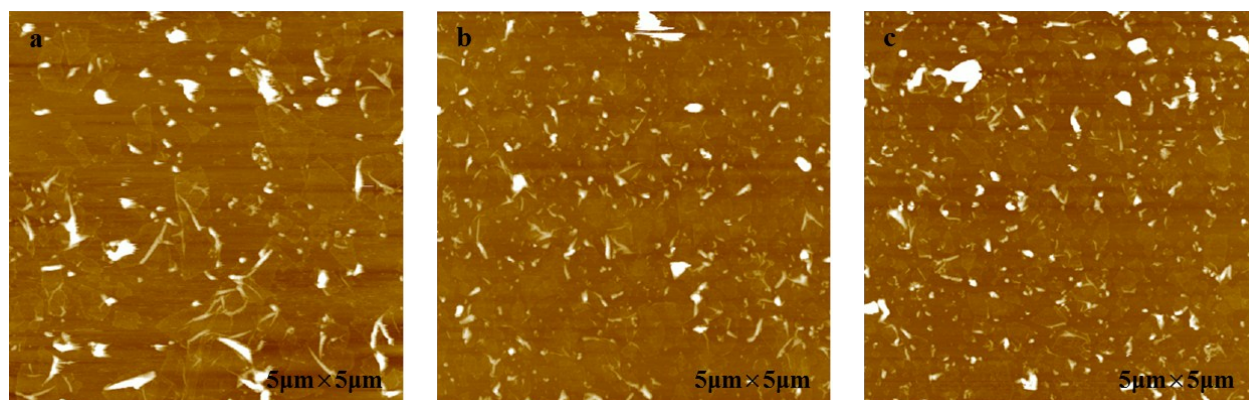


Figure S2 AFM images of rGO sheets on poly-(diallyldimethylammonium chloride) (PDDA) coated mica surface obtained in liquid state in stage 2

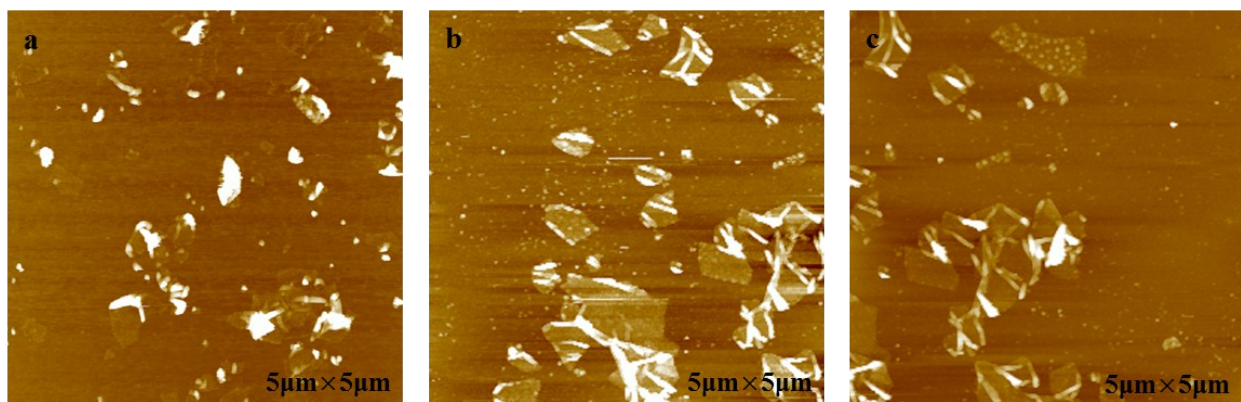


Figure S3 AFM images of rGO sheets on poly-(diallyldimethylammonium chloride) (PDDA) coated mica surface obtained in liquid state in stage 3

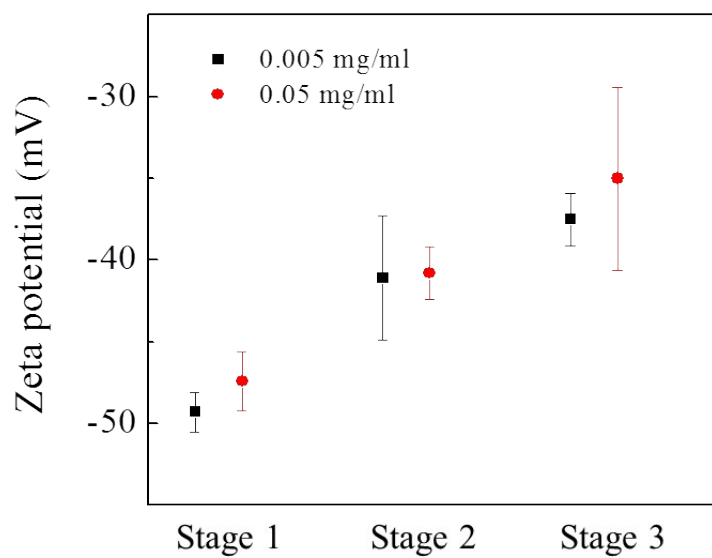


Figure S4 Zeta potential of rGO dispersion with different concentrations at different time scales

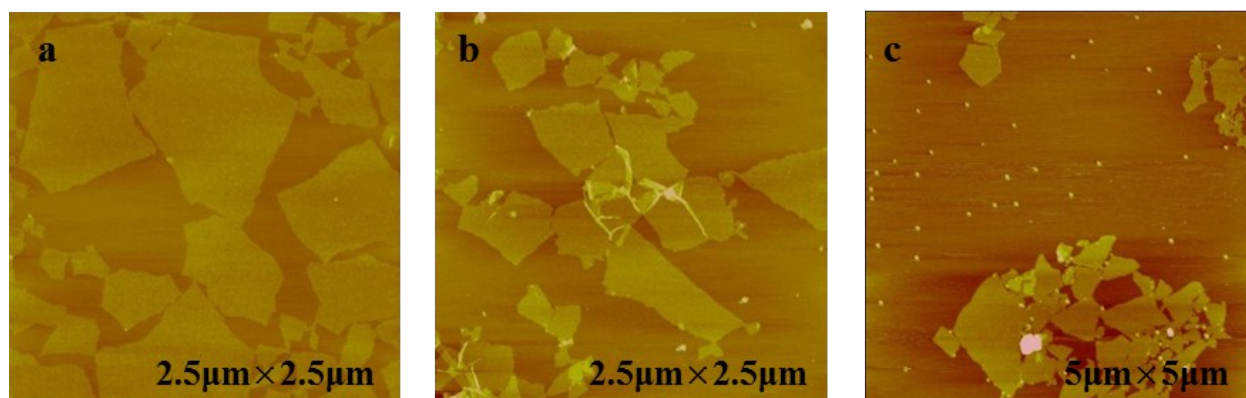


Figure S5 AFM images of rGO sheets on mica surface obtained in dried state in (a) stage 1, (b) stage 2 and (c) stage 3, respectively. All the freshly prepared rGO sheets show flattened morphology on mica surface due to the drying effect² (Fig. S5a), and similar morphology is also shown in Stage 2 (Fig. S5b). However, many crumpled rGO are observed in Fig. S5c, indicating that rGO sheets undergo configuration transition in dispersion, followed by direct deposition on mica surface. These AFM images follow the similar trend as those shown in liquid state.

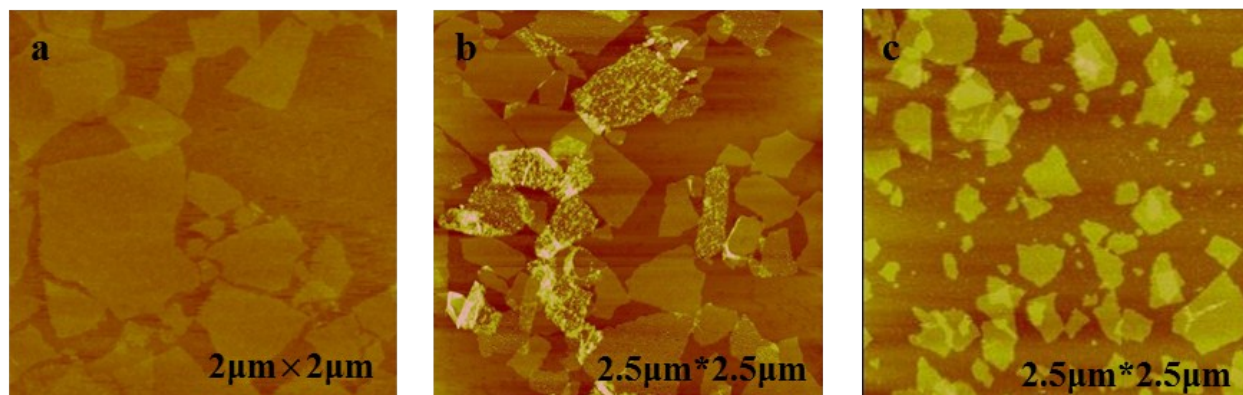


Figure S6 AFM images of rGO with the concentration of (a) 0.005 mg/ml and (b) 0.05 mg/ml in stage 3, respectively; and (c) AFM image of GO sheets prepared by holding GO dispersion (0.5 mg/ml) for 2 months before imaging. The diluted rGO dispersions present much less corrugated configuration of rGO in stage 3, and this is probably due to reduced collision between rGO sheets in solution. On the other hand, all the GO sheets seem very flat, and we surmise that the abundant oxygen-containing functional groups in GO sheets are able to inhibit the bending of its aromatic domains, preventing from configuration transition of suspended GO sheets.

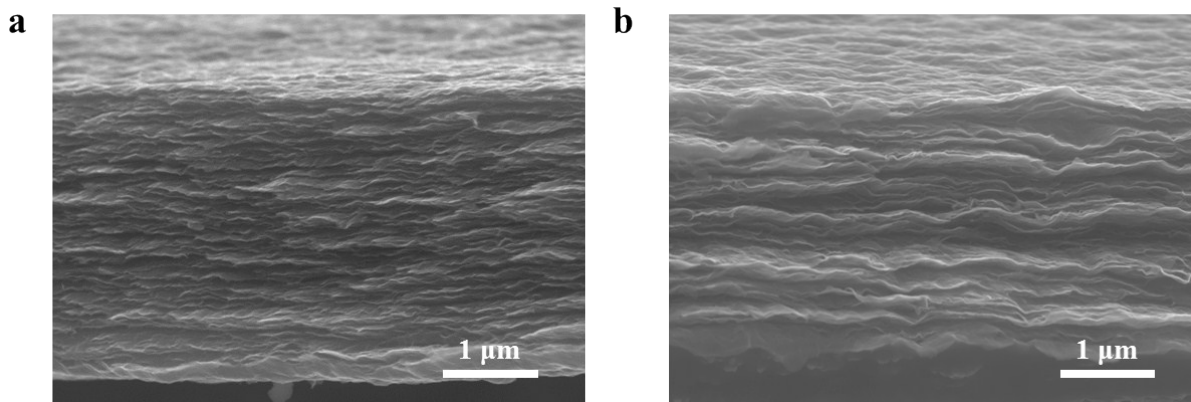


Fig. S7 SEM images of the cross-section of rGO films prepared by rGO dispersion at (a) stage 1 and (b) stage 3.

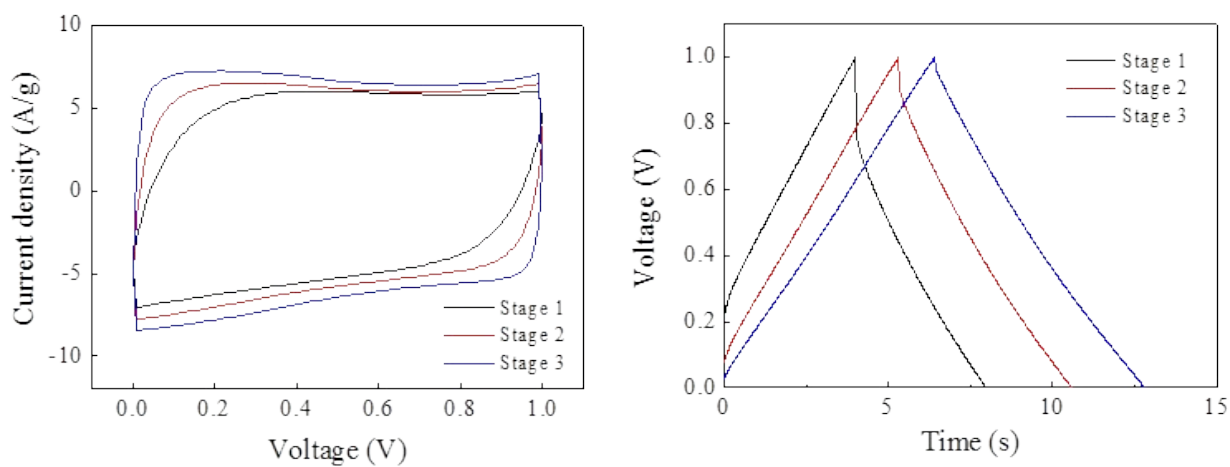


Figure S8 Electrochemical characterizations of rGO thin films prepared at different time scales (a) CV curves at 100 mV/s and (b) charge-discharge curves at 10 A/g

References

- 1 D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nature Nanotech.*, 2008, **3**, 101-105.
- 2 X. Zhang, Y. Wang, S. Watanabe, M. H. Uddin and D. Li, *Soft Matter*, 2011.