

Electronic Supplementary Information

Hybridization of graphene oxide and carbon nanotube at liquid/air interface

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1. Sample preparation

Graphite oxide was prepared by a modified Hummers method.¹ A high-power sonication with an ultrasonic cell disruptor was conducted to prepare graphene oxide (GO) suspension and GO/SWCNT mixture suspension. The typical procedure was as follows: 1) Graphite oxide (160 mg) was added into DI water (80 mL) and sonicated with a high output power of 160 W for 3 h to form GO aqueous suspension with well-dispersed nanosheets; 2) 0.3, 0.5 or 0.8 mg of nanotubes (HiPco SWCNTs, Carbon Nanotechnologies, Inc.) were introduced into the above GO suspensions, respectively, and then sonicated with a low output power of 40 W for 12 h to form homogenous GO-dispersed CNTs suspensions with different fractions of SWCNTs; 3) The suspensions were heated at 353 K for ~30 min in a thermostatted water bath, and smooth and condensed membranes, which were denoted as CNTGO-1 (0.3 mg SWCNT case), CNTGO-2 (0.5 mg case) and CNTGO-3 (0.8 mg case) membranes, were formed at the liquid/air interface. These free-standing membranes were taken out very easily and dried under ambient condition. The thickness of the membranes is controllable and depends on the period of self-assembly process and the concentration of parent suspension. The thickness of the membrane discussed in this study is around 6 μm with self-assembly for 30 min (Fig. S1 shows a cross-sectional image indicating the thickness).

2. Sample characterization

SEM and TEM observations are conducted using Hitachi S-4800 and JEOL 2010F microscopes, respectively. Raman spectra were recorded using a multi-wavelength micro-Raman spectroscopy (JY HR800) and Fourier Transfer Infrared Spectroscopy (FTIR) measurements were conducted by using a FTIR spectroscopy (Bruker-ALPHA).

The electrochemical performance of the uncoated and coated GC electrodes (as working electrode) were measured with an electrochemistry workstation (CHI 660C), where platinum cylinder and Ag/AgCl electrode were used as counter and reference electrodes, respectively. The cyclic voltammetry (CV) measurements were conducted to characterize the electrochemical reactions occurred to the electrodes, and $K_3Fe(CN)_6/KCl$ (0.05 mol/L) aqueous solution of controlled concentrations (0.007 mol/L, 0.014 mol/L, 0.021 mol/L, 0.028 mol/L, 0.035 mol/L, 0.042 mol/L) was employed for the measurements.

The GO-GC and CNTGO-GC electrodes for the electrochemical measurements were prepared with slightly sonicated GO and CNTGO membranes; the slight sonication does not destroy micro-texture of the membranes although these membranes are transformed into small fragments (as shown in Fig. S3). The preparation details of GO-GC and CNTGO-GC electrodes are as follows. First, 0.5 mg of GO or CNTGO membranes were subjected to a slight sonication pretreatment and these membranes were transformed into small fragments that were dispersed in aqueous solution. Then, GO-GC, CNTGO-1-GC and CNTGO-3-GC working electrodes were prepared through dropping GO, CNTGO-1 and CNTGO-3 dispersion (80 μ L) onto the surface of a polished GC electrode, followed by drying the electrode under ambient temperature and clean environment for 12 h. The reference CNT-GC electrode was prepared by the similar process; 0.5 mg of SWCNT was ultrasonicated in water, and then dropped onto the surface of a polished GC electrode, followed by drying the electrode under ambient temperature and clean environment for 12 h.

3. Supplementary figures (Figs.S1-6)

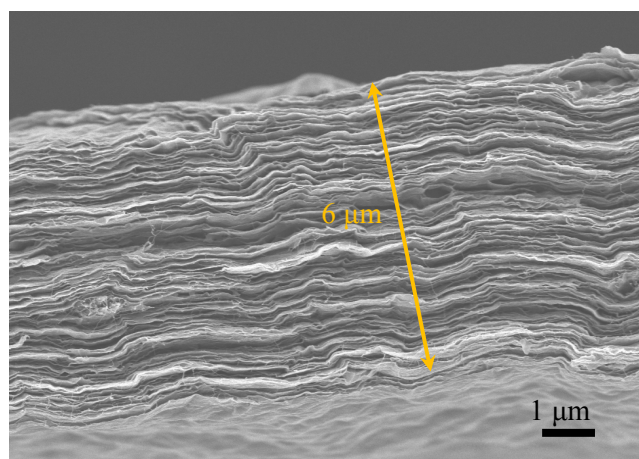


Fig. S1 A cross-sectional SEM image of a CNTGO membrane with self-assembly for 30 min at liquid/air interface. The thickness of the membrane is around 6 μ m.

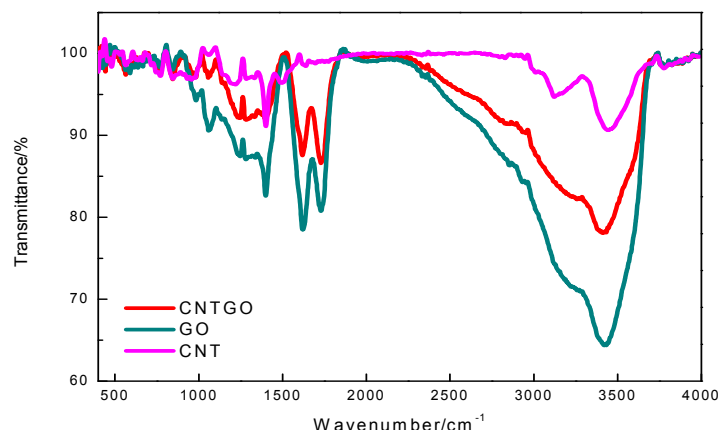


Fig. S2 FTIR spectra of CNTGO membrane, GO membrane and SWCNT powder, which mainly demonstrate the information of edge groups bonded to basal carbon planes. It is likely that, compared with the GO membrane, no peak shifts occur for the major peaks of the hybrid membrane after the introduction of SWCNT. Apparently, CNTGO shows a combined FTIR feature from both CNT and GO. No interaction occurs between the edge groups of nanotubes and GO. Combined with the Raman results, it is confirmed that GO interacts with CNT through π - π stacking of carbon planes and no strong interaction occurs between the edge groups.

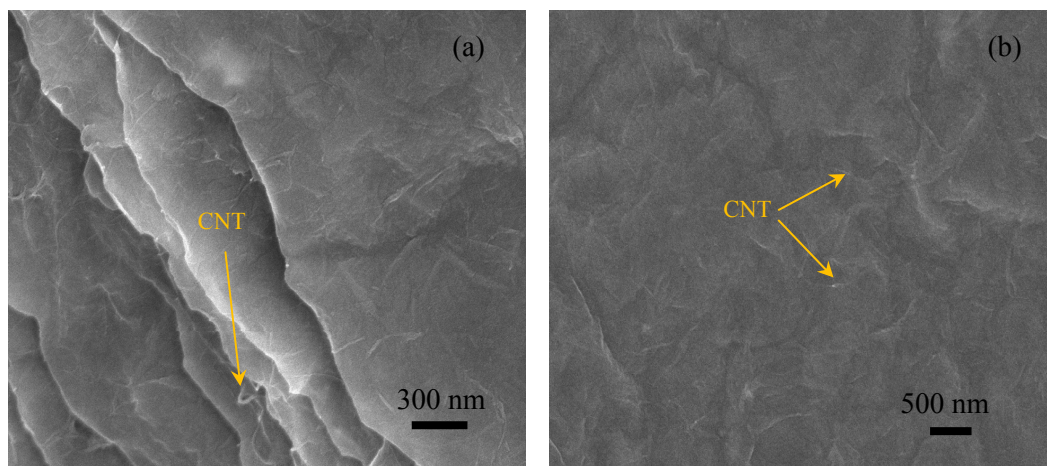


Fig. S3 SEM images of CNTGO hybrid membrane subjected to a slight ultrasonication pretreatment for electrochemical measurements, which demonstrate that the layered microstructure of the membrane is preserved under a slight sonication. However, subjected to a relatively strong sonication for TEM specimen preparation, the layered structure is totally destroyed and SEM image is hard to demonstrate details for nanotube interacting with a single GO plane as TEM image does in Fig. 3d.

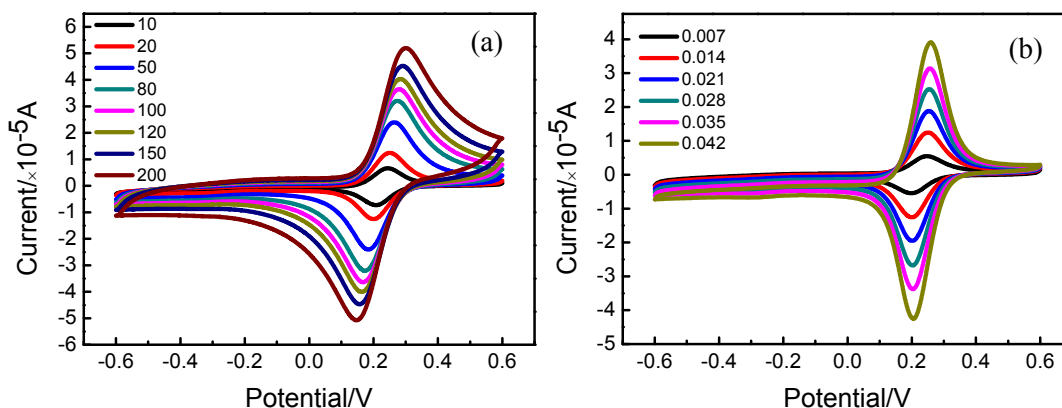


Fig. S4 CV profiles of the CNTGO-1-GC electrode in ferricyanide solution. (a) CV profiles of CNTGO-1-GC electrode in 0.014 mol/L ferricyanide solution at different scan rates (mV/s). (b) CV profiles of CNTGO-1-GC electrode in ferricyanide solution of different concentration (mol/L) at a scan rate of 20 mV/s.

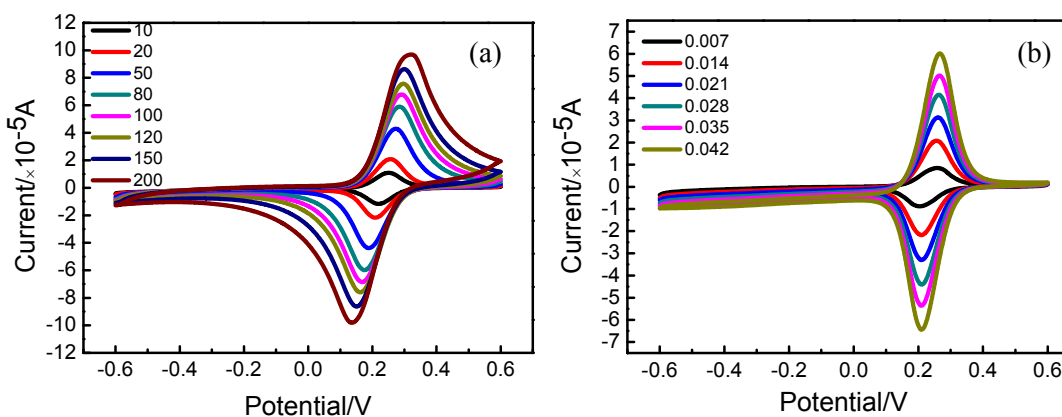


Fig. S5 CV profiles of the GNTGO-3-GC electrode in ferricyanide solution. (a) CV profiles of CNTGO-3-GC electrode in 0.014 mol/L ferricyanide solution at different scan rates (mV/s). (b) CV profiles of CNTGO-3-GC electrode in ferricyanide solution of different concentration (mol/L) at a scan rate of 20 mV/s.

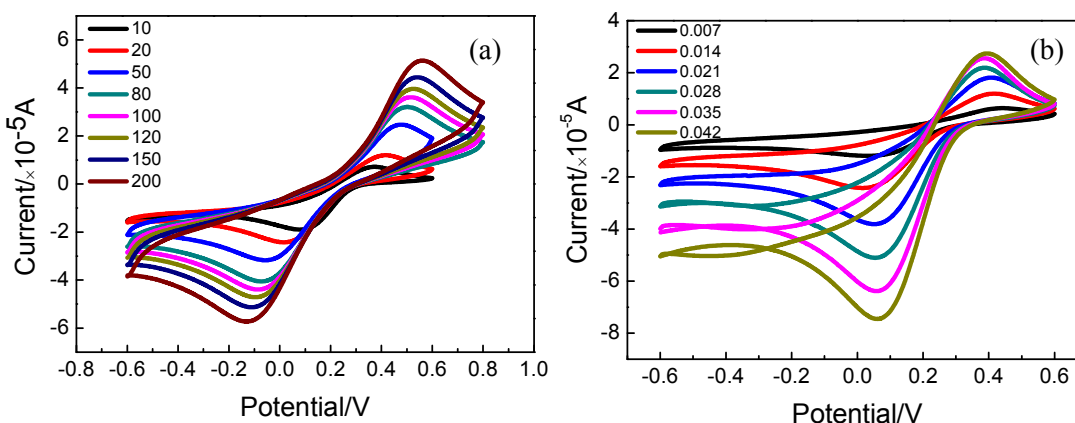


Fig. S6 CV profiles of the UGC electrode in ferricyanide solution. (a) CV profiles of UGC electrode in 0.014 mol/L ferricyanide solution at different scan rates (mV/s). (b) CV profiles of UGC electrode in ferricyanide solution of different concentration (mol/L) at a scan rate of 20 mV/s.

References

- (1) W. S. Jr. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.