Electronic Supplementary Information

Graphene oxide hydrogel at solid/liquid interface

Jiao-Jing Shao, Si-Da Wu, Shao-Bo Zhang, Wei Lv, Fang-Yuan Su and Quan-Hong Yang*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

E-mail: qhyangcn@tju.edu.cn

1. Sample preparation

1.1 Preparation of graphene oxide (GO) hydrogel

Graphite oxide was prepared by a modified Hummers method[1] and the details can be referred to Ref. [2]. A high-power sonication with an ultrasonic cell disruptor was conducted to prepare graphene oxide (GO) dispersion and the AFM observation has confirmed that GO nanosheets in the dispersion are mostly monolayered.[3] The typical procedure was as follows. Graphite oxide (160 mg) was added into DI water (80 mL) and sonicated with a high output power (JY92-2D) of 200 W for 2 hr to form GO aqueous dispersion with well-dispersed nanosheets. The concentration of the as-prepared GO suspension is thus estimated to be 0.2 wt%.

A GO hydrogel was formed at the solid/liquid interface built by a porous anodic aluminum oxide (AAO) membrane and GO aqueous dispersion. The detailed self-assembly process was as follows. An AAO membrane was immersed in the above-prepared GO aqueous dispersion for a period (typical case: 4 hr), and then GO hydrogel was observed to be formed gradually at the AAO/GO dispersion interface. The GO hydrogel became more concentrated with the increase of the immersion period and a GO hydrogel formed at the interface for 7 days could stand an upturned contained test though its water content was up to 99 wt%. The AAO membrane employed in this study was with an average inner pore diameter of ~30 nm and the detailed preparation can be referred to Ref. [4].

1.2 Preparation of SGO and SGN macroform

A lyophilization process with a lyophilizer (FD-1-50) was conducted to prepare SGO starting from GO hydrogel. The typical procedure was as follows. The GO hydrogel was lyophilized for around 20 hr, by which most of the water contained in the hydrogel was removed and the macrotexture was well kept (the volume of the

obtained SGO was almost the same as that of the parent GO hydrogel) to form a sponge-like GO macroform (SGO). SGO was further reduced to SGN by a low temperature annealing process (200 °C for 2 hr, heating rate: 5 °C/min) under vacuum.

1.3 Preparation of the reference samples

A dry GO hydrogel was obtained by heating GO hydrogel at 70 °C in oven under air atmosphere and in this process, the macrotexture of the hydrogel was destroyed and become powdered. A slightly oxidized Al film was obtained by exposing the polished Al sheet to air for 10 min using a spirit lamp and a thin oxidation film was formed on the surface of Al sheet.

2. Sample characterization

The thermogravimetric analysis was conducted by using thermo Rigaku Thermo Plus TG 8120. The SEM observations were conducted using Nova NanoSEM 430, FEI. The XPS measurement was performed by a PHI-1600ESCA system. The powder XRD patterns were collected by a D8 FOCUS (Cu Kα radiation, λ=0.154nm). The rheological measurements were conducted on a RHEOLOGICA Instruments AB using parallel plate geometry with a gap of 1 mm (the frequency sweeps from 0.03 to 10 Hz).

The electrochemical performance of the samples for Lithium-ion battery was measured using a battery tester PCBT-100-32D (Wuhan Lixing, China) at room temperature. The SGN macroform was mixed with 5 wt% conductive additives (SP, Timcal. Ltd, Switzerland) and 5 wt% poly (tetrafluoroethylene) (PTFE) binder. The mixture was suspended in ethanol solution to make slurry, spread uniformly on a nickel foam current collector and dried at 80 °C overnight in a vacuum furnace. The coin cells were assembled in an Ar-filled glovebox and the cells were comprised of the above prepared electrode, lithium foil as the counter electrode, 1 M $LiPF_6$ solution (1:1:1 mixture of ethylene carbonate, dimethyl carbonate and ethylene methyl carbonate as the solvent) as the electrolyte and microporous polyethylene as the separator. The charge/discharged galvanostatic measurement was performed between 0.005~2.5 V vs Li^+/Li. The coin cells were first charge/discharged twice at 20 mA/g for electrochemical activation (see Fig.S5(a)), and then cycled at 40 mA/g (see Fig. S5(b)).

3. Supplementary figures (Figs.S1-5)

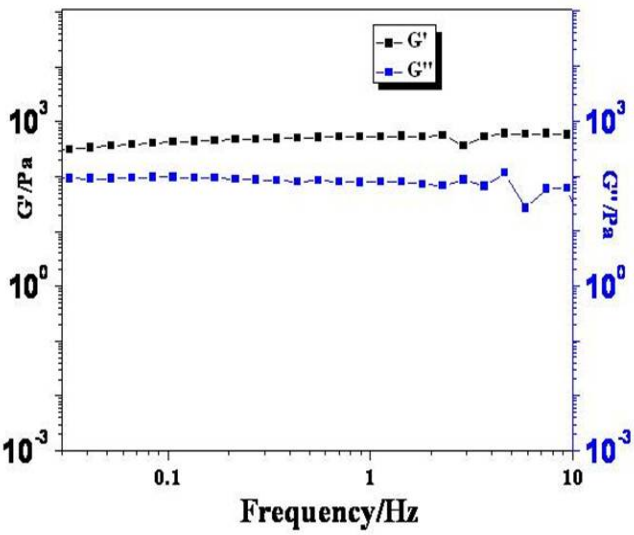

Fig.S1 A dynamic rheological profile of an obtained GO hydrogel.

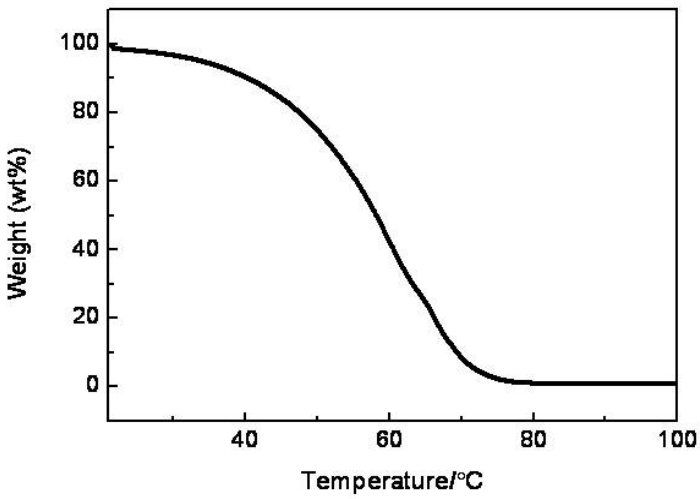

Fig.S2 TGA profile of a GO hydrogel with a heating rate of 1 °C/min (air atmosphere). Such a hydrogel was prepared with an immersion period of 7 days.

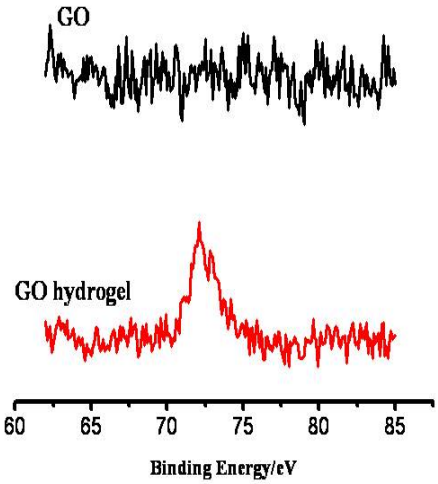

Fig.S3 Al_{2p} XPS profiles of an as-prepared GO (dried at 70 °C, without AAO immersion) and a formed GO hydrogel (dried at 70 °C). No Al is detectable in GO while ~1.8 atom% Al (C/Al≈38) is in a GO hydrogel.

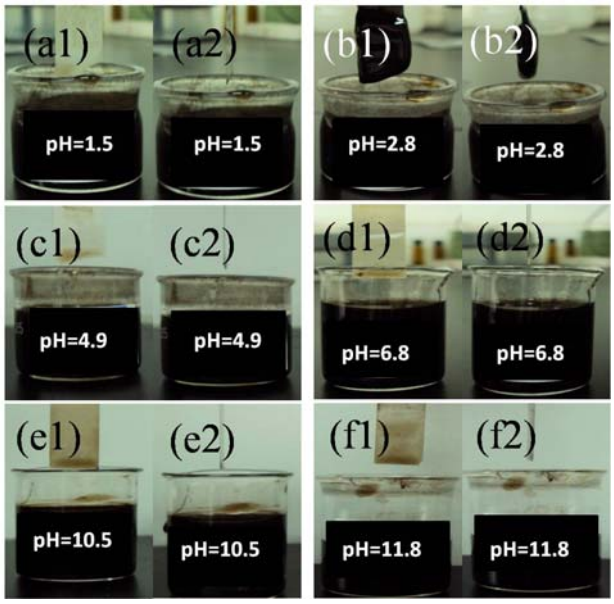

Fig.S4 Front and side photos of AAO membranes immersed in GO dispersions of different pH values for 12 h. (a1, a2) pH = 1.5 (adjusted by HCl solution). (b1, b2) pH=2.8. (c1, c2) pH=4.9. (d1, d2) pH=6.8. (e1, e2) pH=10.5. (f1, f2) pH=11.8. (c-f): adjusted by NaOH solution.
* Here, pH value of the as-prepared GO dispersion is 2.8.

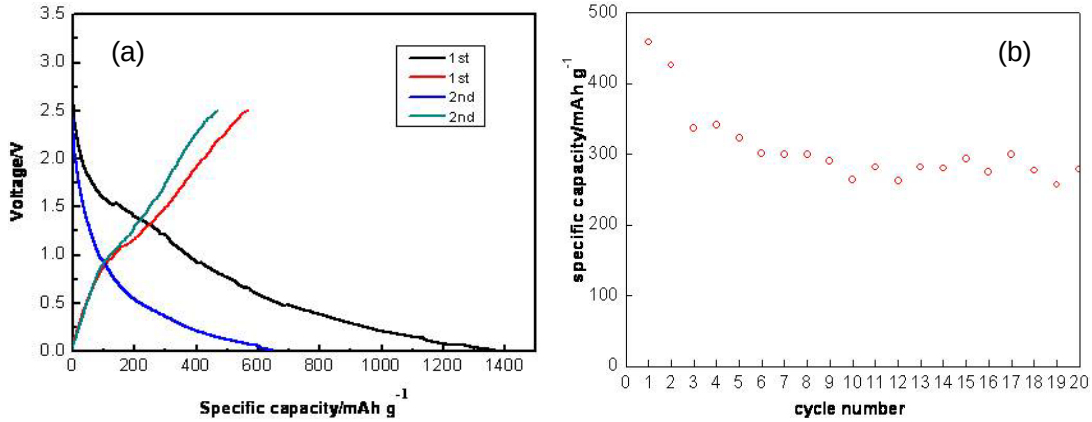

Fig.S5 Electrochemical performance (Li-ion battery) of a SGN macroform. (a) First and second cycle charge/discharge profiles for electrochemical activation (20 mA /g) and (b) cycling performance profile (40 mA /g) .

References

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