Electronic Supplementary Information for

Superior radical polymer cathode material with a two–electron process redox reaction promoted by graphene

Wei Guo,[a,b] Ya-Xia Yin,[a] Sen Xin,[a,b] Yu-Guo Guo*[a] and Li-Jun Wan[a]

[a] *Beijing National Laboratory for Molecular Sciences (BNLMS), Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing, 100190, P.R. China;*

[b] *Also at the Graduate School of CAS, Beijing 100064, P. R. China.*

* *To whom correspondence should be addressed. E-mail: ygguo@iccas.ac.cn*

Experimental Details

Preparation of PTMA

PTMA was prepared according to the reported method with minor modifications. To a mixture of 2,2,6,6-tetramethylpiperidine methacrylate (MTMP) monomer (TCI) (2.25g, 10 mmol) and 2,2'-azobisisobutyronitrile (AIBN) (TCI) (0.04 g, 0.24 mmol) in 6 mL of acetic acid. The mixture was stirred at 70 ^{o}C for 12 h under N_2 atmosphere. The reaction mixture was added to 50 mL of ethyl ether and stirred for 5 min. The product (PMTMP) (1.8 g, 80% yield) was obtained by filtration. To a solution of PMTMP (1.0 g 8.3mmol) in 20 mL methanol, $Na_2WO_4 \cdot 2H_2O$ (0.3 g, 0.9 mmol), ethylenediaminetetraacetic acid (EDTA) (0.2 g, 0.68 mmol), 30% H_2O_2 (2 mL) and H_2O (10 mL) were added and stirred at 60 ^{o}C for 40 h. The mixture was filtrated and washed with H_2O and ethyl ether to afford PTMA as a pale red solid (1.0 g, 95% yield).

Characterization

Infrared (IR) absorption spectrum measurements were performed using a Tensor–27 spectrometer. The electron spin resonance (ESR) spectra were recorded on ESP–300 spectrometer. Solid–state ^{13}C NMR was performed with Avance III 400 spectrometer. The TGA measurement was carried out under a stream of N_2 at a heating rate of 10 min^{-1} using a TG/DTA6300 instrument. X–ray diffraction (XRD) analysis was performed with a Rigaku D/max-2500 using filtered Cu Kα□radiation. The microscopic features of the products were characterized by scanning electron microscopy (SEM, JEOL–6701F) and transmission electron microscopy (TEM, JEM-2100).

Electrochemical characterization

Electrochemical measurements were performed using two–electrode Swagelok–type cells assembled in an argon-filled glove box. The PTMA/graphene composite electrodes were prepared through a dispersing–depositing process: 10 % PTMA was first dissolved in the *N*-methylpyrollidinone (NMP) solvent, 20 % carbon black was added into the solution and stirred 30 min. 60 % graphene and 10 % Poly (vinyl difluoride) (PVDF) NMP solution was added into the above solution under stirring. The slurry was pressed on an aluminum current collector (99.6 %, Goodfellow). The electrodes were dried in a vacuum oven at 80 °C for 12 h to remove the solvent completely before test. The pristine PTMA electrode was prepared by the mixture of 10 % PTMA, 80 % carbon black and 10 % PVDF binder. The control group electrode was prepared by the mixture of 60 % graphene, 20 % carbon black and 10 % PVDF binder. Lithium foil was used as counter electrodes. A glass fiber (GF/D) from whatman was used as separator. The electrolyte consisted of a solution of 1 M $LiPF_6$ in ethylene carbonate (EC) / dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in wt %) obtained from Tianjin Jinniu Power Sources Materials Co., Ltd. Cyclic voltammograms (CVs) were measured on a Parstat 2273 advanced electrochemical system at a scan rate of 0.1mv s^{-1} in the voltage range of 2.0–4.0 V (vs. Li^+/Li). Galvanostatic cycling tests of the assembled cells were carried out on an Arbin BT2000 system in the voltage range of 2.0–4.0 (vs. Li^+/Li) under different current densities.

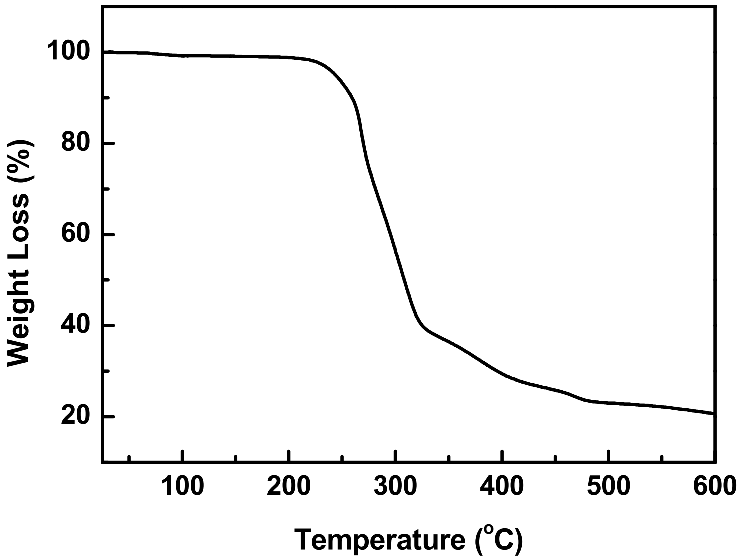

Figure S1. TGA curve of PTMA.

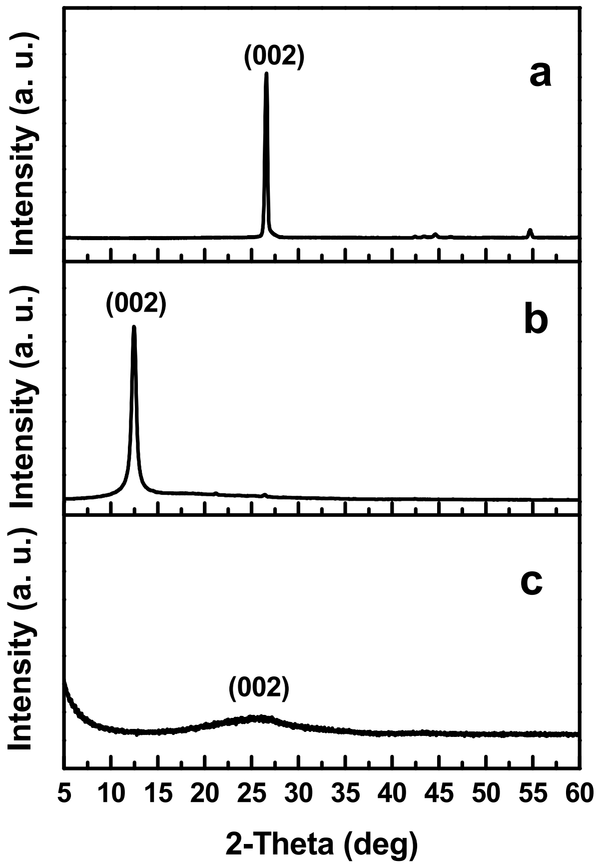

Figure S2. XRD patterns of (a) pristine graphite, (b) as-synthesized GO, and (c) graphene.

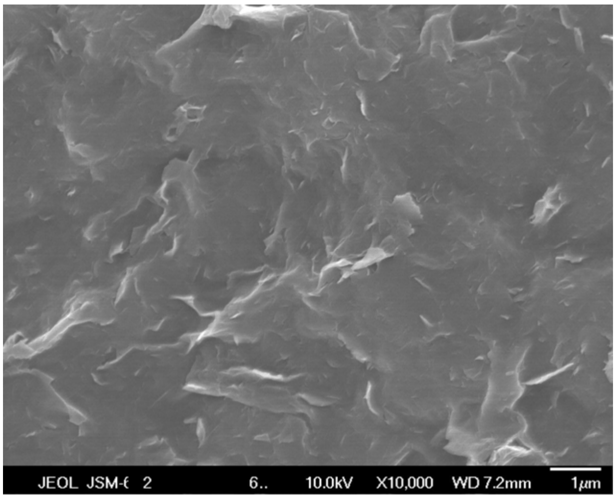

Figure S3. SEM image of PTMA/graphene composite.

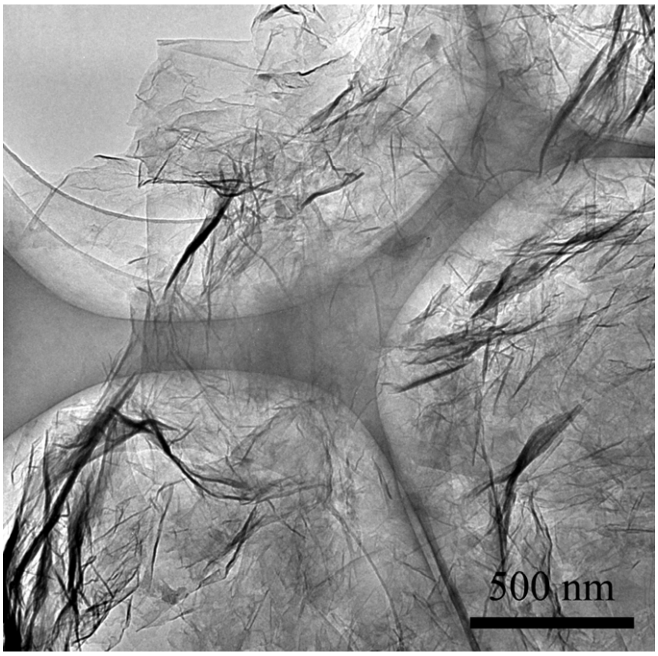

Figure S4. TEM image of PTMA/graphene composite

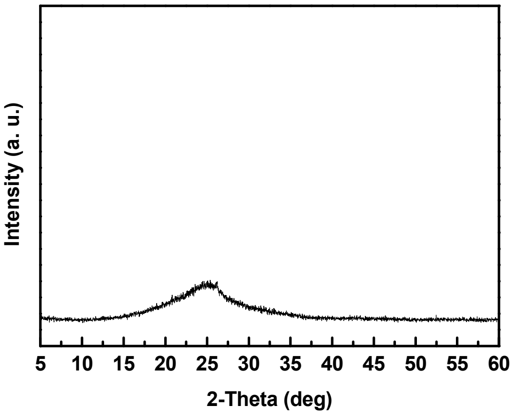

Figure S5. XRD pattern of the PTMA/graphene composite.

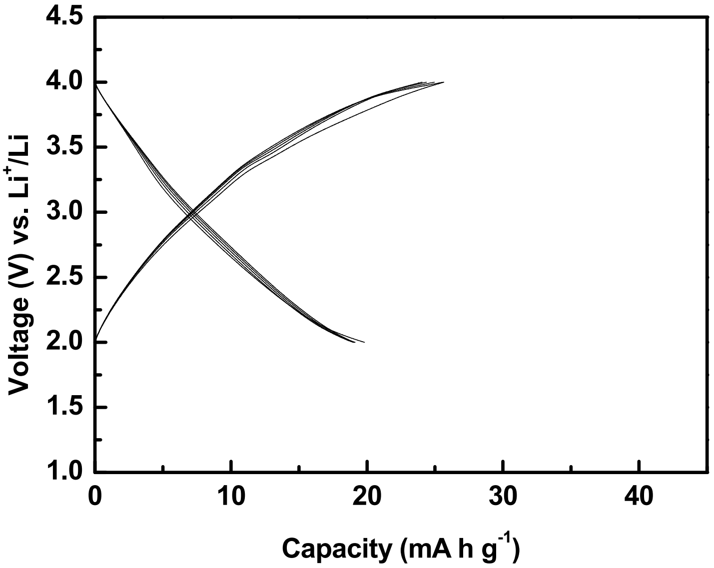

Figure S6. The charge-discharge voltage profiles of graphene and carbon black cycled between 2.0 and 4.0 V at a rate of 1 C.