Synthesis and lithium-storage properties of MnO/reduced graphene oxide composites derived from graphene oxide plus the transformation of Mn(VI) to Mn(II) by the reducing power of graphene oxide

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1. Materials Synthesis

Graphene oxide was synthesized according to the modified Hummers' method as described in our previous work [1]. 0.5g graphene oxide was dissolved in 250 mL H_2O (three copies), then different amounts of $KMnO_4$ (0.5 g, 1.0 g and 2.0 g, respectively) were added into the three GO suspensions. All the mixed suspensions were put into a water bath and kept at 60 ^oC for 24 h. The resulted products were collected and separated by centrifugation at a speed of 8000 rpm and the alternant redispersion was carried in water for several times. After dried at 60 ^oC overnight, the

precursors named P-MNP, P-MGC1 and P-MGC2 were obtained. Further calcination of these precursors at 500^{o}C under Ar condition for 90 min resulted in the final products, i.e., MNP, MGC1 and MGC2, respectively.

2. Material Characterization

Specimens were characterized by XRD on a D/max2500 with a Cu Kα source (λ = 1.541 Å). SEM-EDX images were obtained with a XL-30 ESEM. TEM images were performed on a JEM-2010. Raman spectra were measured using a LabRam HR by a regular model laser at 514.5 nm. TGA measurements were carried out by a Shimadzu TGA-50 thermogravimetric analyzer from room temperature to 700 ^{o}C with the heating rate of 10 ^{o}C/min and air flow rate of 25 mL/min. XPS was tested by an ESCALAB 250.

3. Electrochemical Measurements

The working electrodes were made by manually coating a slurry which was composed of 80 wt% active material, 10 wt% poly(vinylidene fluoride) and 10 wt% Super P. The slurry was uniformly plastered on a copper foil current collector and then dried at 80 ^{o}C under vacuum overnight. The mass loading of electrode is in the range of 1.0 mg-1.2 mg. Then the electrodes were assembled into half cells in an Ar-filled glove box using Li foil as the counter electrodes and the polypropylene microporous films (Celgard 2300) as the separators. The electrolyte was 1 mol/L $LiPF_6$ dissolved in ethylene carbonate(EC)-dimethyl carbonate (DMC) with volume ratio of 1:1. The galvanostatic discharge/charge cycling was measured from 0.05 to 3.5V(*vs.* Li/Li^{+})

with different constant current densities. The potentialstatic discharge/charge cycling was measured by a step of 25 mV/h from 0.05 to 3.0 V. The cell for electrochemical impedance spectroscopy (EIS) test was prepared in the same process as that for the galvanostatic and potentialstatic discharge/charge cycling test. EIS were recorded on a PARSTAT 2273 advanced electrochemical system over the frequency range of 0.1 Hz to 100 kHz using the fresh cell.

4. XRD Patterns of the Precursors

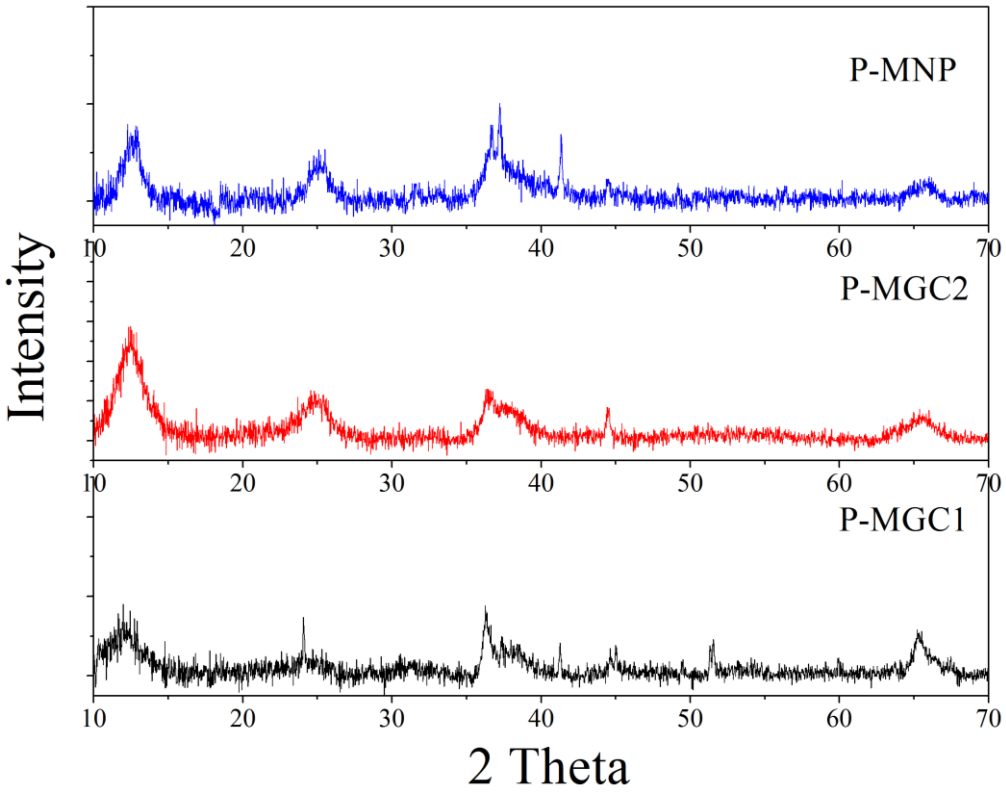

Figure SI 1. XRD patterns of the precursors

5. Component Analysis of Precursors and Final Products by TGA

In the air flow, for the precursors, the weight loss between room temperature and 250

^{o}C is due to the adsorbed water on the surface and in the interlayers of δ-MnO_2. The weight loss between 250 ^{o}C and 340 ^{o}C is considered due to the thermolysis of graphene oxide to generateCO or CO_2. For the MGC1 and MGC2, the weight loss from the adsorbed water is very small as compared with their precursors. In the higher temperature area, it undergoestwo ambivalent reactions. One is the thermolysis of graphene oxide, and the other is the oxidation of MnO to form MnO_2 by the oxygen in the air, which makes it impossible to know the graphene oxide content from the apparent weight loss between 250 ^{o}C and 340 ^{o}C. The only way to measure the MnO content in the composites is to calculate from the remaining MnO_2 at 700 ^{o}C, and the graphene oxide content can be calculated by deducting the MnO content from the composites.

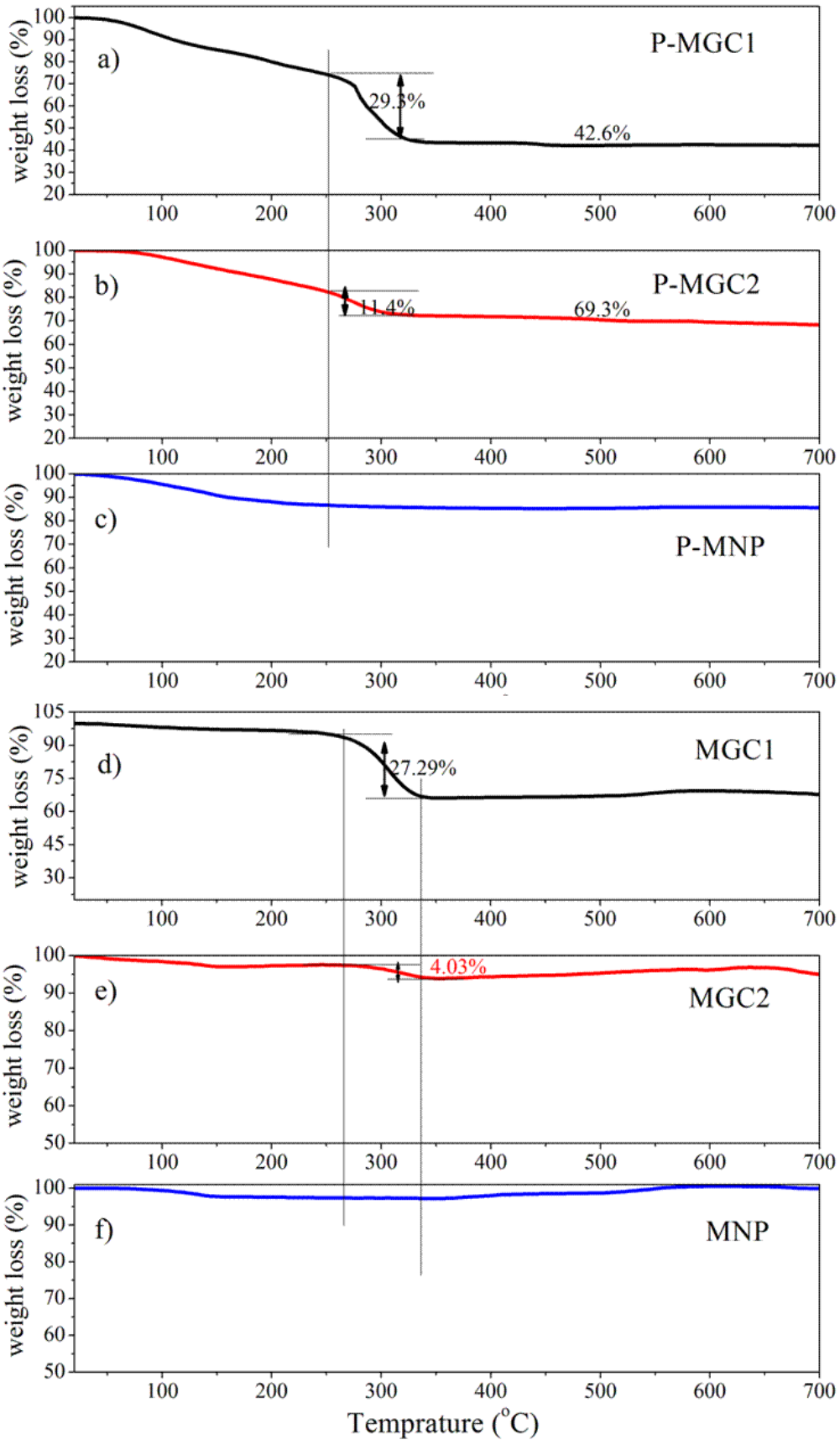

Figure SI 2. TGA of the precursors (a-c) and the final products(d-f).

6. N_2 adsorption-desorption Isotherms of MGC1 and MGC2

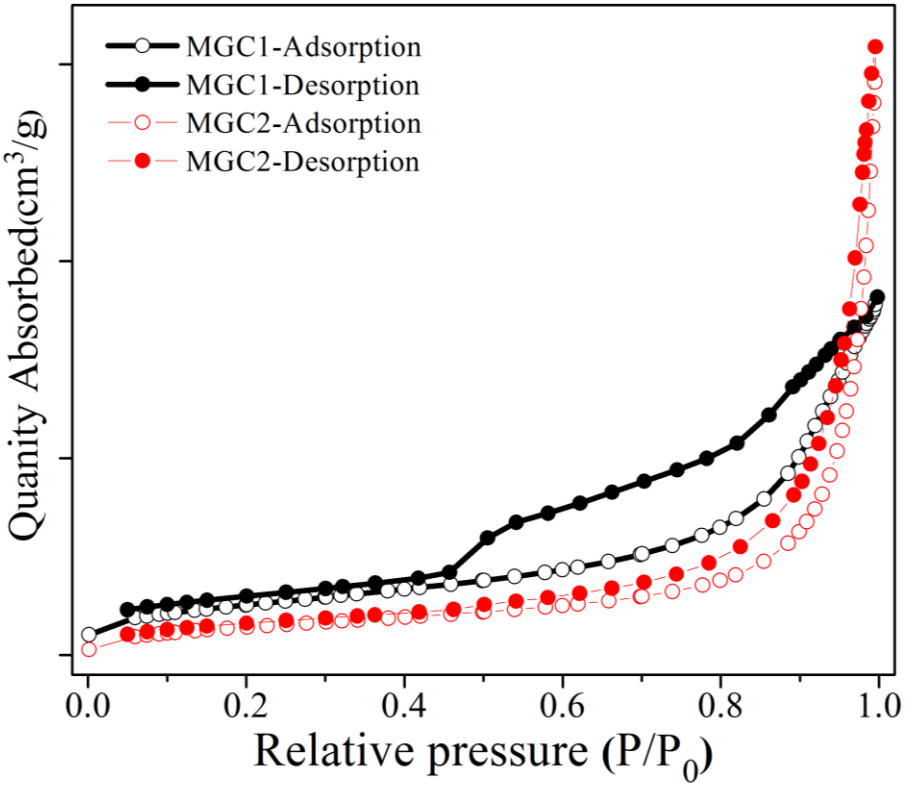

Figure SI 3. N_2 adsorption-desorption isotherms of MGC1 and MGC2

Reference

[1] G. Zhao, J. Li, X. Ren, C. Chen and X. Wang, *Environ. Sci. Technol.*, 2011, **45**, 10454-10462.