Supporting information (SI)

LiFePO$_4$/graphene as a Superior Cathode Material for Rechargeable Lithium Batteries: Impact of Stacked Graphene and Unfolded Graphene

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Experimental

Synthesis of stacked graphene and unfolded graphene

Stacked graphene used in this study was prepared through the thermal expansion of graphite oxide (GO). And unfolded graphene was obtained by hydrazine reduction of GO. [1-3] In detail, we first use concentrated sulfuric acid and potassium permanganate to oxidize the graphite powder to GO, followed by ultrasonication of GO in 2 L batches bath ultrasound (VWR B2500A-MT) with 3 h. Then, use different way to reduction graphite oxide. One way is thermal reduction, by using 30 s thermal treatment around 1050 °C in the furnace, GO was reduced into expanded stacked graphene. The other way is to use hydrazine reduce GO in the suspension. After centrifuge, the centrifugate was collected. And single- and few-layer graphene sheets

were readily prepared, homogeneously and stably suspended in the good solvent medium.

Synthesis of LFP/SG and LFP/UG

The following describes a typical synthesis for LFP/SG composites. First: 22.5 mg of stacked graphene was dissolved in 30 mL of water via strong ultrasonic agitation for 30 min. Next, 1.039 g lithium dihydrogen phosphate (LiH_2PO_4, Sigma) was dissolved in 100 mL of water and stirred at 80 °C for 1 h. Separately, 1.739 g iron (II) acetate ($Fe(AC)_2$, Sigma) was dissolved in 70 mL of water by stirring at 70 °C for 1 h. The two solutions and the stacked graphene suspension were mixed together and dried at 70 °C for 24 h. For the LFP/UG composites, the procedure was similar, except that the stacked graphene solution was replaced with the unfolded graphene suspension (0.2 g L^{-1}). After thorough grinding of the xerogel followed by annealing in a furnace filled with an argon atmosphere at 700 °C and a heating rate of 10 °C min^{-1}, the composites were obtained.

Characterization

The synthesized material was then characterized by various methods. Powder X-ray diffraction (XRD, Rigaku, Japan) using a Co Ka radiation source was used to identify the crystalline phase. FESEM (S-4800, Hitachi) with an operating voltage of 5 kV, TEM (H-7000, Hitachi) and HRTEM (JEOL 2010F) was used to determine the morphology and microstructure of the samples. A Raman scattering spectroscopy apparatus (HORIBA) equipped with a 532.4 nm laser was performed to study the phonon modes of Fe, P, O and C. The Fe K-edge XANES spectra were obtained on

the Soft X-ray Microcharacterization Beamline (SXRMB, $\Delta E/E$: 10^{-4}), and C K-edge

were conducted on the undulator Spherical Grating Monochromator (SGM) beamline

at the Canadian Light Source (CLS) located at the University of Saskatchewan in

Saskatoon.

Electrochemical Measurement

The electrochemical cell used in our study was a CR2032 coin cell. The electrolyte

used in our experiment was 1 M LiPF6 in a mixture of ethylene carbonate/dimethyl

carbonate (1: 1 v/v) solvents. All electrochemical tests were performed in an Arbin

BT-2000 Battery Test Station within a voltage range of 2.5-4.2 V (versus Li^+/Li). The

composites were mixed with acetylene black and poly-(vinylidene fluoride) (PVDF)

binder with a weight ratio of 75:15:10, using N-methyl-2-pyrolidene (NMP) as the

solvent, and then the mixture was ground in a mortar and pestle and pasted onto pure

Al foils. The coin cells were assembled in a high-purity argon filled glove box, and all

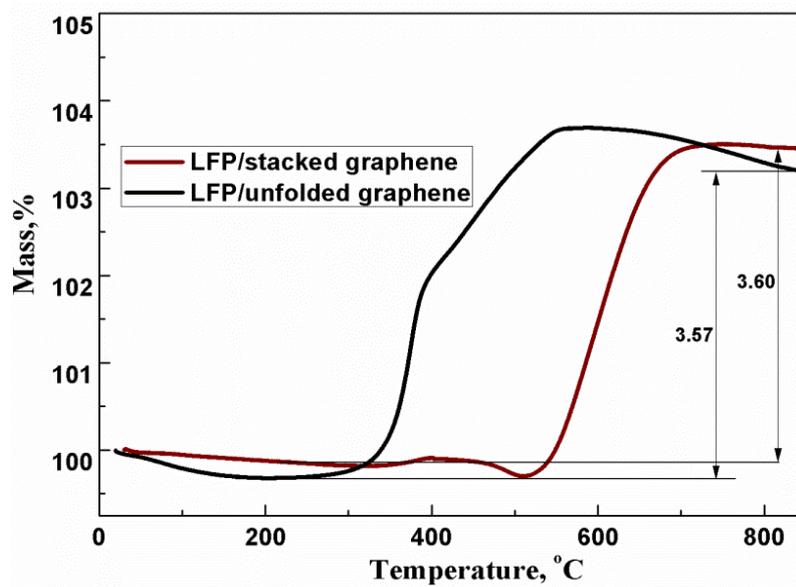of the electrochemical measurements were conducted at room temperature.

Figure S1. TGA curves of the LiFePO$_4$/stacked graphene and LiFePO$_4$/unfolded graphene composites.
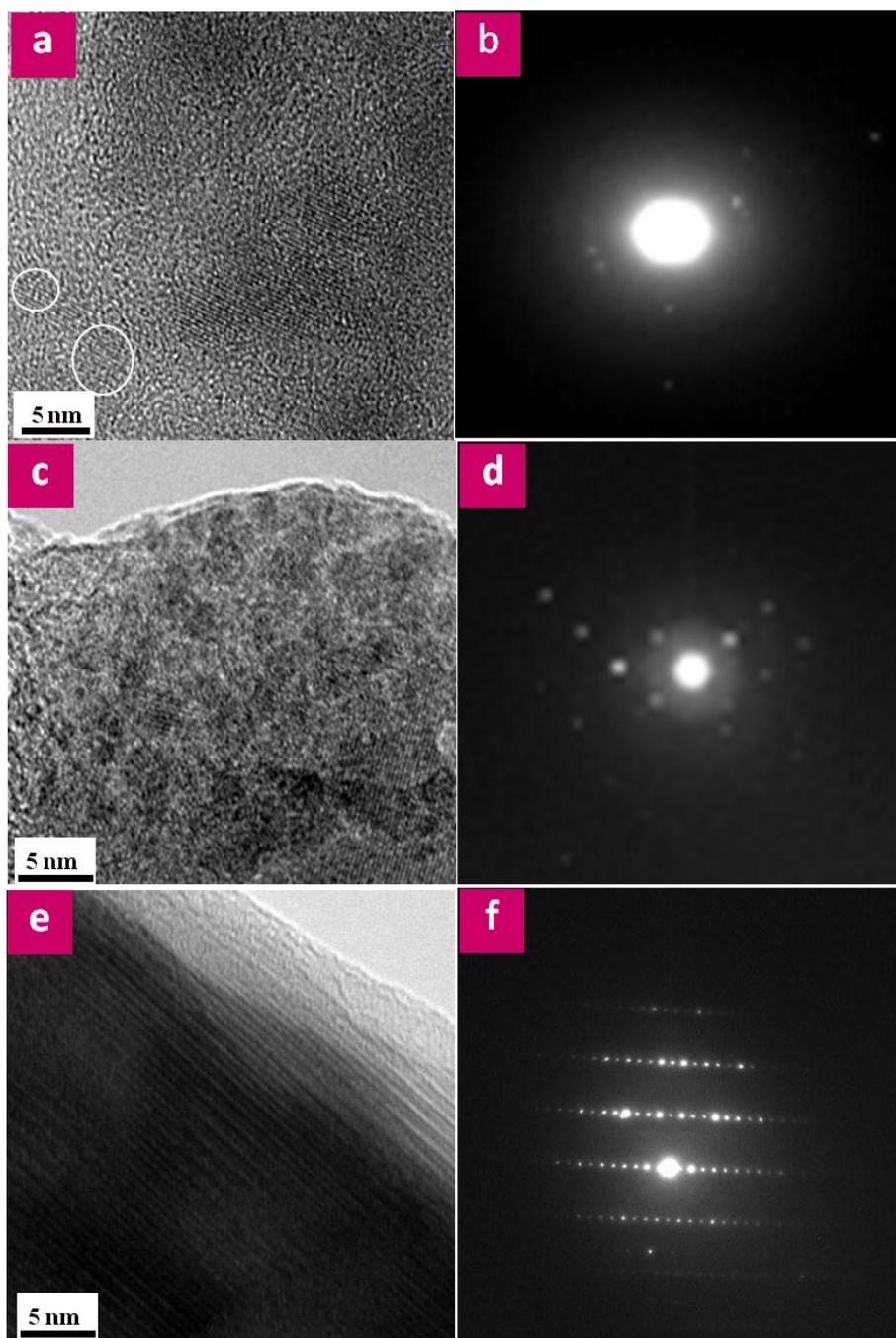
Figure S2. HRTEM and SAED of LiFePO$_4$/unfolded graphene composites annealed at different time. (a) and (b) 2h; (c) and (d) 6h; (e) and (f) 24h.

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3 D. Geng, Y. Chen, Y. Chen, Y. Li, R. Li, X. Sun, S. Ye and S. Knights, *Energy Environ. Sci.*, 2011, **4**, 760-764.