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Short communication

Direct growth of $FePO_4$/graphene hybrids for Li-ion and Na-ion storage

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ABSTRACT

An environmentally friendly method has been developed for the direct growth of $FePO_4$ nanospheres on graphene nanosheets with uniform morphology and high conductivity of 3.2 S cm^{-1}. The nanoassembled $FePO_4$/graphene hybrids exhibit superior Li-ion and Na-ion storage performance, e.g. high rate capability and good capacity retention upon cycling.

1. Introduction

Rechargeable batteries like Li-ion and Na-ion batteries have become predominant power sources for home electronics and large-scale energy storage devices due to increasing demands of renewable green energy [1–4]. Developing new cathode materials with superior efficiency of energy delivery is important to improve Li-ion and Na-ion batteries [5–9]. Amorphous $FePO_4$ is an environmentally friendly and cost-effective cathode material, and has recently drawn increasing attentions due to its unique physicochemical properties [10–17]. Compared with commercially available crystalline $LiFePO_4$, amorphous $FePO_4$ is easier to synthesize due to its lower processing temperature [13–17]. Furthermore, the isotropic and defect-free nature of amorphous $FePO_4$ provides a large amount of continuous pathways for metal ions (Na^+ or Li^+) [15–18]. However, the low electronic conductivity and poor Li^+ transport of amorphous $FePO_4$ limit its utilization at high charge/discharge rates [13–17]. A common solution is to use carbon nanotubes (CNTs) or graphene as carriers for insulating $FePO_4$ nanoparticles, because both can produce highly conductive networks in the cathode [13,15,16,18–20]. To improve graphene dispersion and the connection between the $FePO_4$ nanoparticles and the carrier, graphene will usually be pre-oxidized during synthesis. But such processing destroys the intact structure of carbon materials and therefore restricts the rate performance of $FePO_4$ [15].

Herein, we report a simple method to directly grow $FePO_4$ nanoparticles on graphene nanosheets without pre-oxidization. Rhodanineacetic acid-pyrene (RAAP) was used to functionalize the graphene nanosheets, and therefore induced the direct growth of $FePO_4$ nanoparticles on the uniform graphene nanosheets. Li-ion and Na-ion batteries with the as-fabricated nanostructure as the cathode exhibited superior performance, i.e. high rate capability and good capacity retention upon cycling.

2. Experimental

A scheme of the sample preparation is shown in Fig. 1. Thermally exfoliated graphene nanosheets with large specific surface area were obtained by the method of thermal treating graphite oxide at 700 °C in N_2 for 2 h [21,22]. The nanosheets (0.4 g) were well dispersed into the dimethylformamide/water (1:1, 500 ml) solution by adding dispersant RAAP (0.08 g). RAAP molecules were expected to be well decorated on the graphene nanosheets due to the strong π–π stacking force between them [23–25]. It was also expected that graphene nanosheets would easily separate from each other and consequently became negatively charged on surface, as a result of their strong hydrophilicity. Then, $FeSO_4 \cdot 7H_2O$ (1.5 M, 25 ml) and $NH_4H_2PO_4$ (1.5 M, 25 ml) solutions were added drop-by-drop sequentially with vigorous stirring. The attraction between Fe^{2+} and the negatively charged nanosheets would finally form the $FePO_4$/graphene hybrids. The as-synthesized sample was annealed at 350 °C for 3 h to remove hydrated water. As a control group, pristine $FePO_4$ was prepared using the same method without graphene nanosheets added.

The morphology of the samples was characterized by transmission electron microscopy (TEM, FEI Tecnai F20 S-Twins) and scanning electron microscope (SEM, Hitachi S-4800). X-ray diffraction (XRD) analysis

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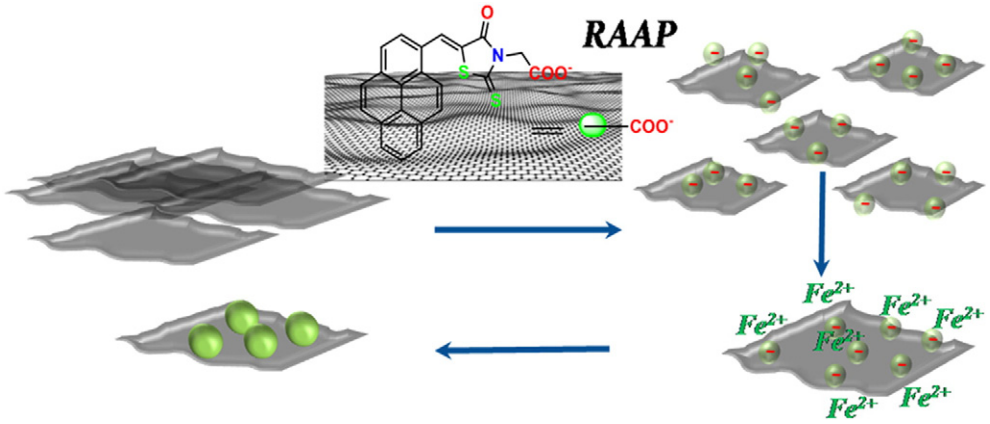

Fig. 1. Scheme for the preparation of $FePO_4$/graphene hybrids.

was performed on a D/Max-RA X-ray diffractometer with Cu Kα irradiation. Raman spectra was recorded by a Renishaw in via spectrometer with excitation at 514.5 nm. Electrical conductivity was measured by 4-probe method with Keithley 2400 Digital Source Meter and the carbon content in as-synthesized hybrids was acquired using a Heraeus CHN-O-Rapid elemental analyser as 6.8 wt.% in the whole sample.

For the cathode preparation, flexible hybrids were admixed with polyvinylidene fluoride (PVDF) in a weight ratio of 10:1, the mixture was spread and pressed onto a porous Al-mesh, followed by overnight drying at 100 °C; As for the control group, the pristine $FePO_4$ cathode was prepared by mixing 80% of pristine $FePO_4$, 5% carbon black, 5% graphene nanosheets and 10% PVDF dispersed in N-methylpyrrolidinone. The homogenous slurries were then coated on an Al-foil and dried at 100 °C for 10 h.

Li-ion battery was assembled in a 2032-type coin cell with lithium metal as anode, a porous polypropylene as separator (Celgard 3501), and 1 M $LiPF_6$ in 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC) as electrolyte. Na-ion battery was assembled with sodium as counter electrode, Celgard 3501 as separator, and 1 M $NaClO_4$ in a mixture of ethylene carbonate/dimethyl carbonate (1:1 by volume) as electrolyte [18]. Electrochemical performance was tested using Landte CT2001-A battery test.

3. Results and discussion

After thermal treatment, graphene nanosheets reveal an "accordion-like" structure as Fig. 2a which consists of numerous exfoliated graphene sheets loosely stacked together. Fig. 2b shows the SEM image of the high-dispersed RAAP decorated graphene nanosheets.

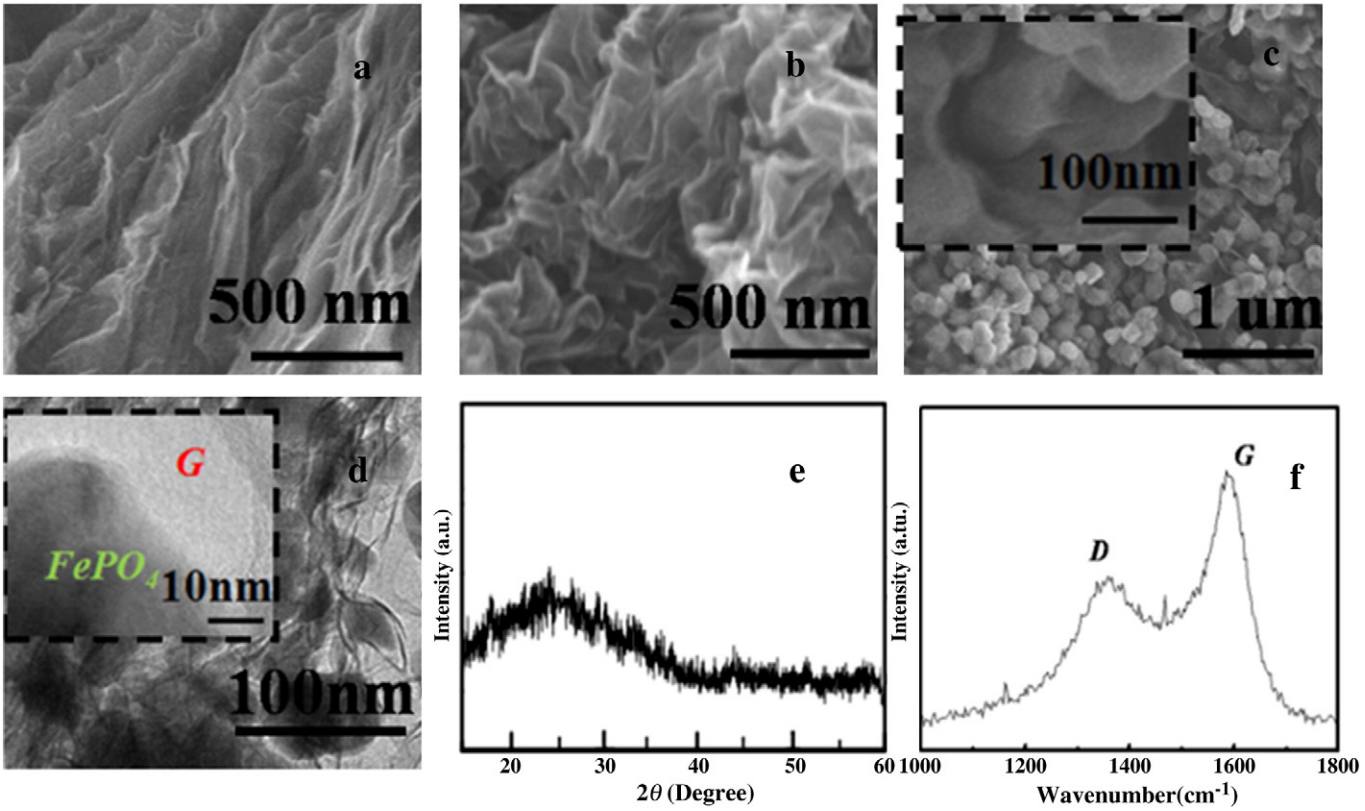

Fig. 2. SEM image of the thermally exfoliated graphene nanosheets (a) and RAAP decorated graphene nanosheets (b); SEM image (c) and TEM image (d) of $FePO_4$/graphene hybrids; XRD pattern (e) and Raman spectra (f) of $FePO_4$/graphene hybrids.