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Short communication

Direct growth of $FePO_4$/graphene and $LiFePO_4$/graphene hybrids for high rate Li-ion batteries

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HIGHLIGHTS

- $FePO_4$/graphene and $LiFePO_4$/graphene hybrids were synthesized by a simple method.
- A simple and environmentally friendly RAAP-induced growth method was used.
- $FePO_4$ and $LiFePO_4$ were direct grown on the graphene-assembled scaffolds.
- $FePO_4$/graphene hybrids present superior electrochemical properties.
- $LiFePO_4$/graphene hybrids present superior electrochemical properties.

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ABSTRACT

$FePO_4$/graphene and $LiFePO_4$/graphene hybrids have been synthesized by an eco-friendly RAAP-directed growth method. With this strategy, $FePO_4$ and $LiFePO_4$ particles have been grown on the exfoliated graphene-assembled scaffolds. Both of the hybrids present superior electrochemical properties, i.e., high rate capability combined with good capacity retention upon cycling, indicating the great potential as the cathode materials for Li-ion batteries.

1. Introduction

Due to the significant requirements of renewable green energy technology, Li-ion battery(LIB)becomes the predominant power source for home electronics and large-scale energy storage devices [1,2]. Developing new cathode materials which deliver more energy density is important for us to achieve better LIBs [3–8]. Among various cathode materials, phosphate ion-based materials ($LiFePO_4$ and $FePO_4$) come into prominence with regard to their relatively high theoretical capacity, excellent cycling performance, low cost, nontoxicity, environmental friendliness and safe nature, leading to strong focus on polyanionic chemistries [4,9–17]. However, both of the two cathode materials suffer from poor electronic conductivity and poor transport, resulting in reduced utilization at high charge/discharge rates. A common solution is to use carbon nanotubes (CNTs) and graphene as carriers for insulating $LiFePO_4$ or $FePO_4$ nanoparticles, because both can produce highly conductive networks in the cathodes [12,18–22]. In order to improve the dispersity of the carbon material and modify the connection between the active materials and the carriers, CNTs and graphene were usually pre-oxidized in the synthesize process. However, such processing destroys the intact structures of carbon materials, leading to the relatively low utilization of the active materials.

Herein, a facile synthesize method was developed to grow the $FePO_4$ and $LiFePO_4$ particles on the thermally exfoliated graphene-

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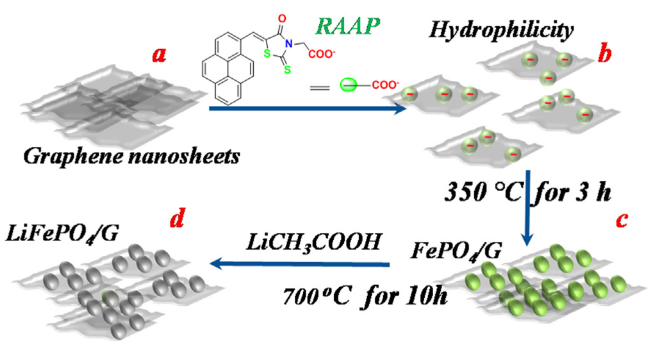
sheets (TGs). Rhodanineacetic acid-pyrene (RAAP) was used to functionalize the graphene nanosheets to induce the growth of $FePO_4$ particles on the graphene nanosheets, and then thermal reduction method was used to transform the $FePO_4$/graphene to $LiFePO_4$/graphene hybrids. Both of the fabricated composites were used as the cathodes in Li-ion batteries which exhibit superior performance, i.e., high rate capability combined with good capacity retention upon cycling.

2. Experimental

In a typical synthesis, Thermally exfoliated graphene nanosheets (TGs) with large specific surface area were obtained by the method of thermal treating graphite oxide at 700 °C in N_2 for 2 h. As-synthesized TGs were selected to prepare $FePO_4$/graphene and $LiFePO_4$/graphene hybrids (Scheme 1) [23]. They (0.4 g TGs) were well dispersed into the dimethylformamide (DMF)/water solution (1:1, 500 ml) with the dispersant RAAP (0.08 g). As the strong $\pi-\pi$ stacking force between the RAAP and TGs, RAAP molecules were well decorated on the TGs. Due to their strong hydrophilicity, TGs can be easily separated from each other and the surface of them became negative charged (Scheme 1b). Then, $FeSO_4 \cdot 7H_2O$ (1.5 M, 25 ml) and $(NH_4)H_2PO_4$ (1.5 M, 25 ml) solution were added drop-by-drop sequentially with vigorous stirring. Since the effect as heterogeneous charges attraction, Fe^{2+} ions were attracted onto the surface of TGs and finally formed the $FePO_4$/graphene hybrids which were then annealed at 350 °C for 3 h to remove the hydrated water (Scheme 1c).

As-synthesized $FePO_4$/graphene hybrids were used to fabricate $LiFePO_4$/graphene hybrids. Such composites were well mixed with the $LiCH_3COOH$ using vacuum pressure infiltration. The obtained mixtures were subsequently fired in an argon atmosphere at 700 °C for 10 h and finally acquired the $LiFePO_4$/graphene hybrids (Scheme 1d). As a control group, pristine $FePO_4$ and $LiFePO_4$ were prepared using the same method without graphene nanosheets and RAAP added.

The morphology and structure of the samples were characterized by transmission electron microscopy (TEM, FEI Tecnai F20 S-Twins) and scanning electron microscope (SEM, Hitachi S-4800) with energy-dispersive X-ray spectroscopy (EDS, Phoenix). X-ray diffraction (XRD) analysis was performed on a D/Max-RA X-ray diffractometer and Raman spectra was recorded by a Renishaw in via spectrometer with excitation at 514.5 nm provided by Ar^+ laser. XPS measurements were acquired with a monochromatic Al Kα X-ray source on a PHI 5000 Versa Probe XPS spectrometer. The carbon content in the $FePO_4$/graphene composites was measured using a Heraeus CHN–O–Rapid elemental analyser as 6.8 wt% in the whole sample and the carbon content in the $LiFePO_4$/graphene was measured with the same method as 6.2 wt%.



Scheme 1. Illustration of the procedures for preparation of $FePO_4$/graphene and $LiFePO_4$/graphene hybrids.

For the cathode preparation, $FePO_4$/graphene and $LiFePO_4$/graphene hybrids were admixed with poly vinylidene 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 in vacuum; As for the control group, the pristine $FePO_4$ cathode and $LiFePO_4$ cathode were prepared by mixing 80% of active material (pristine $FePO_4$ or $LiFePO_4$), 5% carbon black, 5% graphene nanosheets and 10% PVDF dispersed in N-methylpyrrolidinone (NMP). The homogenous slurries were coated on an Al-foil and then dried at 100 °C for 10 h. All of the charge–discharge tests were performed in a land battery cycler with voltage of 2.0–4.2 V and the electrochemical impedance spectroscopy (EIS) measurements were carried out on a CHI660-C potentiostat/galvanostat (Shanghai Chenhua Technology Inc., China).

3. Results and discussion

The thermal reduced TGs reveal an “accordion-like” structure which consists of many highly-wrinkled graphene sheets as shown in Fig. 1a. Such composites are well decorated with the dispersant RAAP in the DMF/water solution, Fig. 1b shows the SEM image of the highly dispersed RAAP decorated TGs. From the pattern, the exfoliated graphene sheets are well separated from each other because of the strong hydrophilicity. The morphology of as-prepared $FePO_4$/graphene hybrids is shown in Fig. 1c. It can be seen that a large quantity of $FePO_4$ particles are attached into the TGs. Fig. 1d shows more details about the hybrids. The amorphous $FePO_4$ particles are uniform distributed on the high dispersed exfoliated graphene sheets; most of the graphene wrapped particles show sphere-like morphology. The elemental analysis of the composite carried out by EDS is shown in Fig. 1e, proving that components of $FePO_4$ as the ratio of Fe: P is near 1:1. Fig. 1f and Fig. S1 (shown in the Supplementary material) shows the morphology of the $LiFePO_4$/graphene hybrids transformed from as-prepared $FePO_4$/graphene composites. After the thermal reduction process, the morphology and particle size of thus obtained $LiFePO_4$/graphene composites were in general similar to those of the $FePO_4$/graphene precursor. This result clearly indicated that the thermal reduction process did not significantly change the hybrid structure of the precursors and thus retained the well connection between the $LiFePO_4$ nanospheres and flexible conductivity graphene sheets.

The crystallographic structures of the as-prepared $FePO_4$/graphene and $LiFePO_4$/graphene hybrids were further examined by X-ray diffraction (XRD). As shown in XRD pattern of $FePO_4$/graphene hybrids in Fig. 2a, no diffraction peaks of $FePO_4$ but only a broad peak between 20 and 40° is observed, corresponding to the graphene nanosheets [18]. This amorphous feature of $FePO_4$ is anticipated because of the low synthesis temperature (350 °C) [4]. Fig. 2b shows the XRD plot of as-synthesized $LiFePO_4$/graphene hybrids. All the diffraction peaks can be well indexed to the orthorhombic $LiFePO_4$ phase with the space group of Pnma, indicating thermal reduction strategy can acquire pure olive phase $LiFePO_4$ [18]. The Raman spectrums of $FePO_4$/graphene and $LiFePO_4$/graphene hybrids are shown in Fig. 2c and d. From the patterns, $FePO_4$/graphene and $LiFePO_4$/graphene hybrids show similar Raman spectra as two broad peaks at ~1351 and ~1600 cm^{-1} which can be assigned to the D and G peaks of graphene [14,24,25]. Both hybrids show stronger G band compared to D band indicating such hybrids show highly ordered graphene structure. The intensity of I_D/I_G of $FePO_4$/graphene and $LiFePO_4$/graphene hybrids are 0.76 and 0.72, indicating the thermal reduction process can improve graphitization degree of the hybrids. It should be pointed out that the width at half-maximum of both the D band and G band for the $LiFePO_4$/graphene is apparently smaller than that of $FePO_4$/graphene, suggesting that the graphene sheets of the $LiFePO_4$/graphene hybrids