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Controllable synthesis of nano-LiFePO₄ on graphene using Fe₂O₃ precursor for high performance lithium ion batteries

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ABSTRACT

LiFePO₄ (LFP) nanocrystals directly grown on graphene sheets (GS) was developed by an in-situ transformation approach using Fe₂O₃ as precursor. This novel strategy ensured intimate contact between LiFePO₄ and graphene sheets, the uniform distribution of both components within the composite. Moreover, the presence of graphene controlled the growth of LiFePO₄ nanocrystals (30–100 nm) and significantly increased electrical conductivity (0.6 S m⁻¹). Consequently, LFP-GS delivered a high specific capacity (165, 160 and 140 mAh g⁻¹ at 0.1 C, 1 C and 5 C, respectively), outstanding cycling stability (160 mAh g⁻¹ at 1 C with no capacity fading after 100 cycles) and rate capability (121 mAh g⁻¹ at 20 C).

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1. Introduction

The rechargeable Li-ion battery (LIB) is widely considered as one of the most probable candidates for electric vehicle power source. Olivine-type LiFePO₄ is an attractive electrode material for LIBs due to its high capacity, thermal stability and low cost [1,2]. However, the low ionic and electrical conductivities seriously limit Li⁺ insertion and extraction [3]. In the past decade, tremendous efforts have been made to solve this problem. One way is to reduce particle size to shorten the diffusion length of electrons and lithium ions [4,5]. Another approach is surface coating of an electronically conductive phase such as carbon to improve the conductivity [1].

Recently, graphene was considered as a new type of carbon coating source because of its high conductivity, high surface area and structure flexibility [6,7]. By compositing LiFePO₄ with graphene, the electrochemical performance can be significantly boosted [8–11]. Ding et al. prepared LiFePO₄/graphene (LFP-GS) by a co-precipitation method using (NH₄)₂Fe(SO₄)₂ as iron source [9], where a long time sintering process (700 °C, 18 h) is needed for the subsequent solid state reaction. LFP-GS composite have also been prepared by simply mixing the two components together [8,10,12]. However, the interfacial interaction between LiFePO₄ and graphene is inferior and graphene was difficult to be uniformly dispersed. The enhancement in electrical conductivity is rather limited. Consequently, it remains necessary to develop an approach to construct effective graphene networks for fully utilizing its potential properties.

Herein, a two-step approach was developed for directly synthesis of LiFePO₄ nanocrystals on graphene sheets. First, Fe₂O₃/graphene oxide (GO) composite was prepared by homogeneous precipitation. The Fe₂O₃ precursor then reacted solvothermally with Li⁺ and PO₄³⁻ and was in-situ transformed into LiFePO₄ on the surface of graphene. Compared with the commonly used Fe²⁺ precursor (such as (NH₄)₂Fe(SO₄)₂), natural abundant and low cost Fe₂O₃ possesses more practical significance for commercial applications. Moreover, this method ensures intimate contact between LiFePO₄ and graphene sheets, the uniform distribution of both components within the composite. As a result, LFP-GS composite showed excellent rate capability and cycle stability.

2. Experimental

Fe₂O₃/GS precursor (the content of Fe₂O₃ and GO was 80 and 100 mg, respectively) was prepared according to reference procedure [13]. To synthesize LFP-GS composite, Fe₂O₃/GS was dispersed in 100 mL DMF, to which 1 mL 1 M LiOH aqueous solution, 1 mL 1 M H₃PO₄ aqueous solution and 0.4405 g ascorbic acid were added under continuous stirring. The mixture was then solvothermally treated at 180 °C for 12 h. Finally, the product was washed with water and centrifuged at 4000 g for 5 min. For comparison, pure LiFePO₄ was synthesized by the same procedure without graphene.

Field-emission scanning electronic microscope (FE-SEM) was performed on JSM-6700F at an acceleration voltage of 10.0 kV. Transmission electron microscopy (TEM) was performed on JEM-2100F Electron Microscope with an accelerating voltage of 200 kV. X-ray diffraction (XRD) was carried out on D/max 2550 V X-ray diffraction-meter with Cu-K α irradiation at $\lambda=1.5406$. Thermal

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gravimetric analysis (TGA) was conducted in air at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. A four-probe resistivity meter (Loresta EP MCP-T360, Mitsubishi Chemical, Japan) was used to measure the conductivity.

The working electrode was prepared with the mixture of the active materials, carbon black and polyvinylidene fluoride (PVDF) binder in weight ratio of 80:10:10. Li foil was used as the counter electrode. The electrolyte was 1 M LiPF_6 in a 50:50 w/w mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Cell assembly was carried out in glove box with the concentrations of moisture and oxygen below 1 ppm. The batteries were measured using a CT2001 battery tester.

3. Results and discussion

Fig. 1 shows TEM image and XRD pattern of $\text{Fe}_2\text{O}_3/\text{GS}$ precursor. Fe_2O_3 nanoparticles are uniformly decorated on the surface of GO with size about 10 nm. XRD pattern reveals Fe_2O_3 is well crystalline (JCPDS no. 97-002-2505). After the solvothermal reaction, Fe_2O_3 precursor was in situ converted into LiFePO_4 by reacting with LiOH and H_3PO_4 . The reaction can be expressed as:

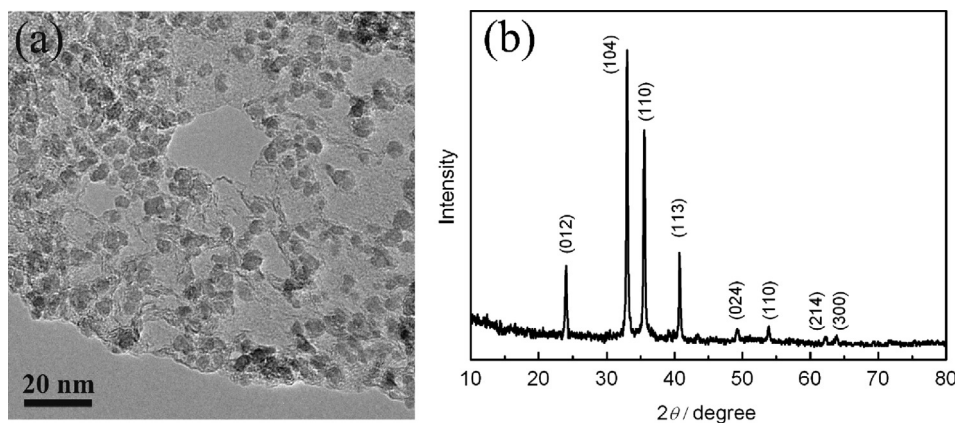
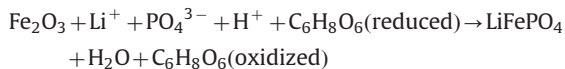


Fig. 1. (a) TEM image and (b) XRD pattern of $\text{Fe}_2\text{O}_3/\text{GS}$ precursor.

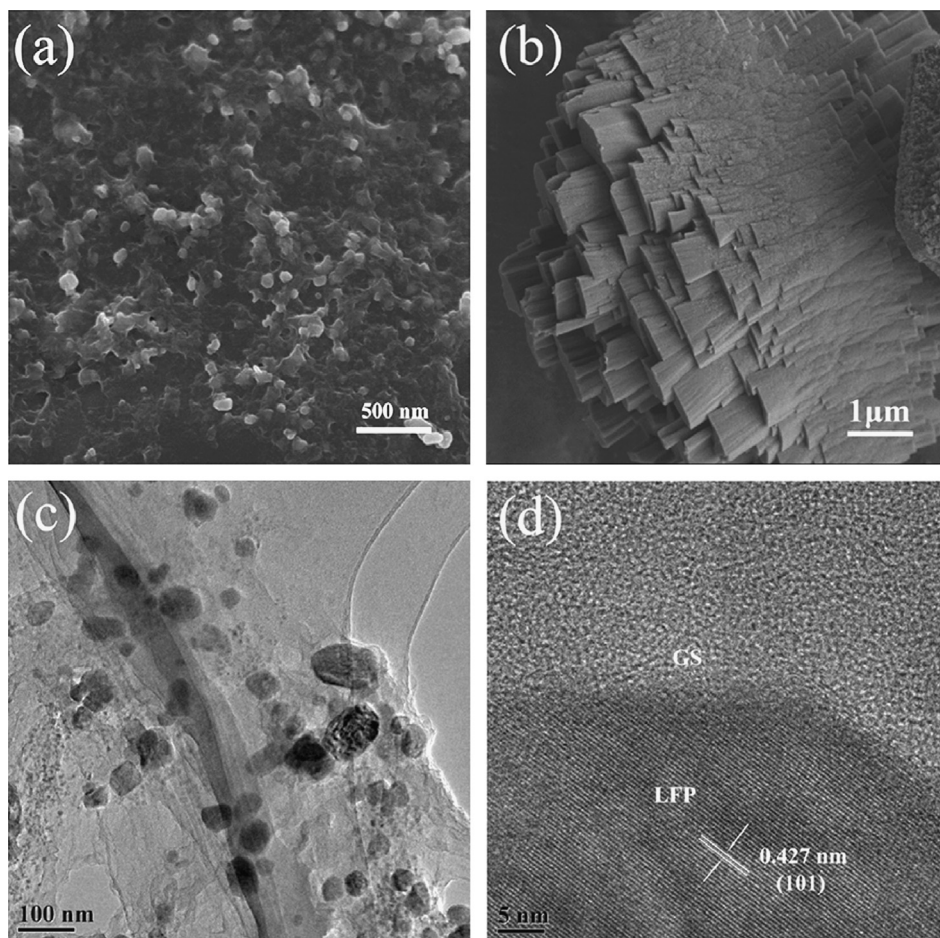


Fig. 2. (a and b) SEM images of LFP-GS and pure LiFePO_4 ; (c and d) TEM and HRTEM images of LFP-GS.

As shown in Fig. 2a, LiFePO_4 nanocrystals maintain the uniform distribution on graphene, and some of the nanocrystals are tightly encapsulated within graphene (Fig. 2a). Unlike those simply mixing process, the covalent bonding affords a fast transportation channel for electron and charge [14]. The grain size of LiFePO_4 in LFP-GS was 30–100 nm, which can shorten the lithium ion diffusion length [15] (Fig. 2c). In a control experiment, the grains grew up seriously if GO was not added (Fig. 2b). Obviously, introduction of GO is quite effective in restricting the grain growth of LiFePO_4 .

HRTEM (Fig. 2d) shows LiFePO_4 was single crystalline. The lattice fringe has an interlayer distance of 0.427 nm, agrees well with the spacing between the (1 0 1) planes of LiFePO_4 crystals. An XRD diffraction pattern (Fig. 3a) matches well with standard orthorhombic LiFePO_4 (JCPDS no. 83-2092), suggesting a perfect crystallinity without impurities. The graphene content was 15% determined by TG analysis [6] (Fig. 3b). The electrical conductivity of LFP-GS reached 0.6 S m^{-1} , which is 10^8 times higher than that of pure LiFePO_4 .

Electrochemical performance of LFP-GS was investigated with Li foils as the counter electrodes. Charge and discharge profiles with increasing current rates from 0.1 C to 15 C between 2.0 and 4.2 V are presented in Fig. 4a. The curve exhibits typical voltage plateau along 3.5 and 3.4 V due to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple reaction, corresponding to lithium extraction and insertion in LiFePO_4 nanocrystals [7]. The discharge capacity of LFP-GS is 165 mAh g^{-1} at 0.1 C with a narrow voltage gap of 50 mV. The capacity can still reach 120 mAh g^{-1} at 15 C. In the control experiment, pure LiFePO_4 showed much lower specific capacity even at low rates ($\sim 5 \text{ mAh g}^{-1}$ at 0.1 C, Fig. 4b).

The cell was also measured at different rates ranging from 1 C to 20 C (Fig. 4c). Discharge specific capacity of the LFP-GS decreases to 148, 133, 130, 126 and 121 mAh g^{-1} when current rate increases to 2, 5, 10, 15 and 20 C, respectively. Noteworthy, full capacity recovery to 160 mAh g^{-1} was observed at 1 C cycle even after continuous 20 C rate cycles, indicating the integrity of the electrode has been preserved even after high rate charge and

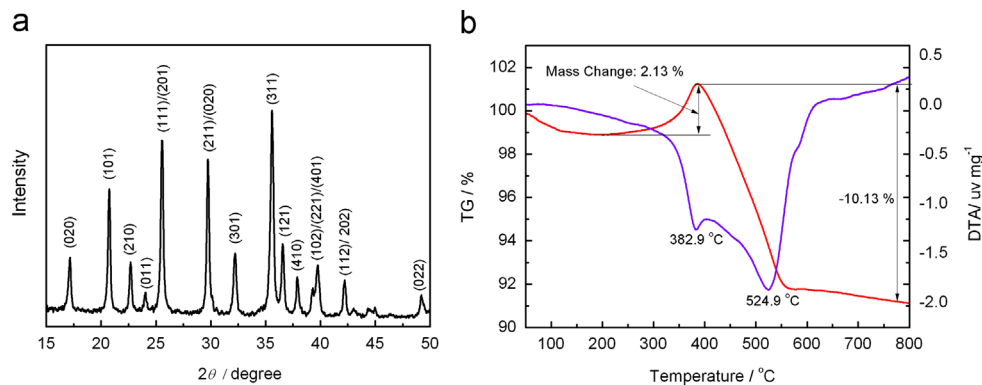


Fig. 3. XRD pattern (a) and TG-DTA curves (b) of LFP-GS.

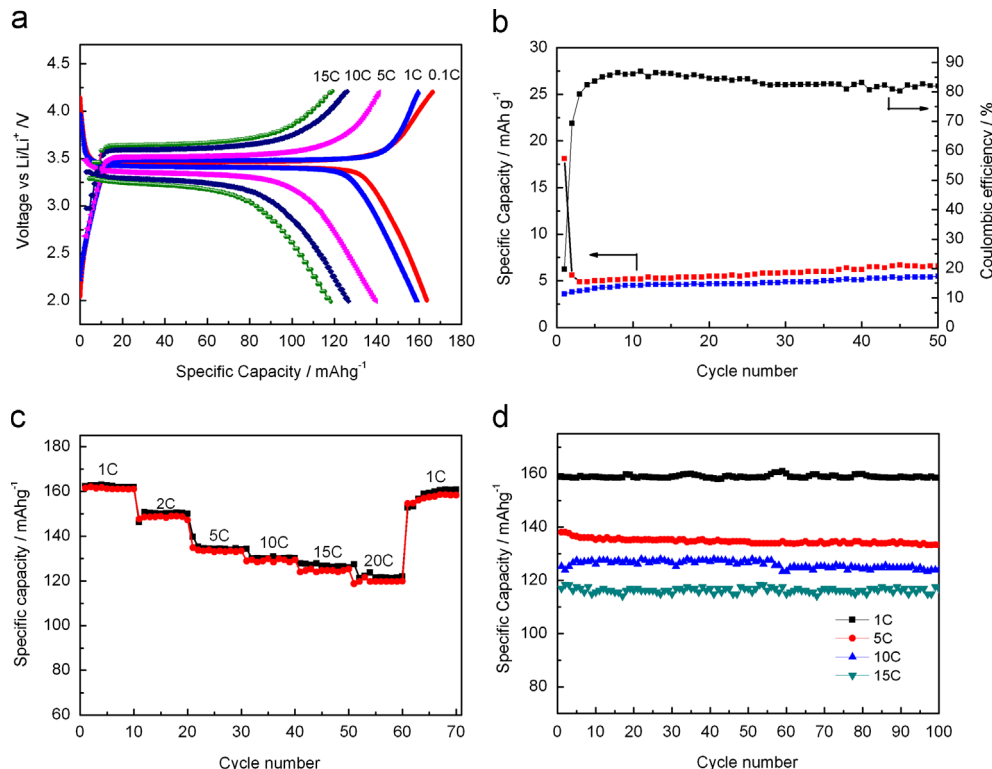


Fig. 4. (a) Charge-discharge curves of LFP-GS at various current rates; (b) Charge/discharge capacity and the coulombic efficiency of pure LiFePO_4 at 0.1 C and (c and d) rate capability and cycle performance of LFP-GS.

discharge. Additionally, LFP-GS also exhibits good cycling performance. It was found that the capacity fading was invisible after 100 cycles at 1 C (Fig. 4d). Even at high current density of 5 C, 10 C and 15 C, the capacities still maintained at 133, 124 and 117 mAh g⁻¹ without noticeable decrease.

The above results effectively prove that LFP-GS composite has desirable specific capacity, rate capability and cycle performance, which could be attributed to the following factors: First, the highly conductive graphene can provide a 3D electronic network, facilitating ion and electron transport. Second, the small size of the LiFePO₄ nanocrystals shortens the diffusion length for both lithium-ions and electrons within the crystals. Furthermore, the intimate interaction by covalent bonds between LFP and underlying graphene could also greatly facilitate the charge transfer.

4. Conclusions

LiFePO₄ nanocrystals (30–100 nm) have been in situ grown on graphene by a solvothermal process. Low-cost Fe₂O₃ was used as the starting precursor. The intimate contact between graphene network and LiFePO₄ greatly facilitate charge transfer. Accordingly, LFP-GS delivered high specific capacity (160 mAh g⁻¹ at 1 C), high rate capability (121 mAh g⁻¹ at 20 C) and excellent stability.

Acknowledgments

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