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Controllable synthesis of nano-$LiFePO_4$ on graphene using Fe_2O_3 precursor for high performance lithium ion batteries

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ABSTRACT

$LiFePO_4$ (LFP) nanocrystals directly grown on graphene sheets (GS) was developed by an in-situ transformation approach using Fe_2O_3 as precursor. This novel strategy ensured intimate contact between $LiFePO_4$ and graphene sheets, the uniform distribution of both components within the composite. Moreover, the presence of graphene controlled the growth of $LiFePO_4$ 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).

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 $LiFePO_4$ 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 $LiFePO_4$ with graphene, the electrochemical performance can be significantly boosted [8–11]. Ding et al. prepared $LiFePO_4$/graphene (LFP-GS) by a co-precipitation method using $(NH_4)_2Fe(SO_4)_2$ 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 $LiFePO_4$ 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 $LiFePO_4$ nanocrystals on graphene sheets. First, Fe_2O_3/graphene oxide (GO) composite was prepared by homogeneous precipitation. The Fe_2O_3 precursor then reacted solvothermally with Li^+ and $PO_4{}^{3-}$ and was in-situ transformed into $LiFePO_4$ on the surface of graphene. Compared with the commonly used Fe^{2+} precursor (such as $(NH_4)_2Fe(SO_4)_2$), natural abundant and low cost Fe_2O_3 possesses more practical significance for commercial applications. Moreover, this method ensures intimate contact between $LiFePO_4$ 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

Fe_2O_3/GS precursor (the content of Fe_2O_3 and GO was 80 and 100 mg, respectively) was prepared according to reference procedure [13]. To synthesize LFP-GS composite, Fe_2O_3/GS was dispersed in 100 mL DMF, to which 1 mL 1 M LiOH aqueous solution, 1 mL 1 M H_3PO_4 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 $LiFePO_4$ 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-Kα irradiation at $\lambda = 1.5406$. Thermal

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gravimetic analysis (TGA) was conducted in air at a heating rate of 10 °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 Fe_2O_3/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:

$$Fe_2O_3 + Li^+ + PO_4{}^{3-} + H^+ + C_6H_8O_6(\text{reduced}) \rightarrow LiFePO_4 + H_2O + C_6H_8O_6(\text{oxidized})$$

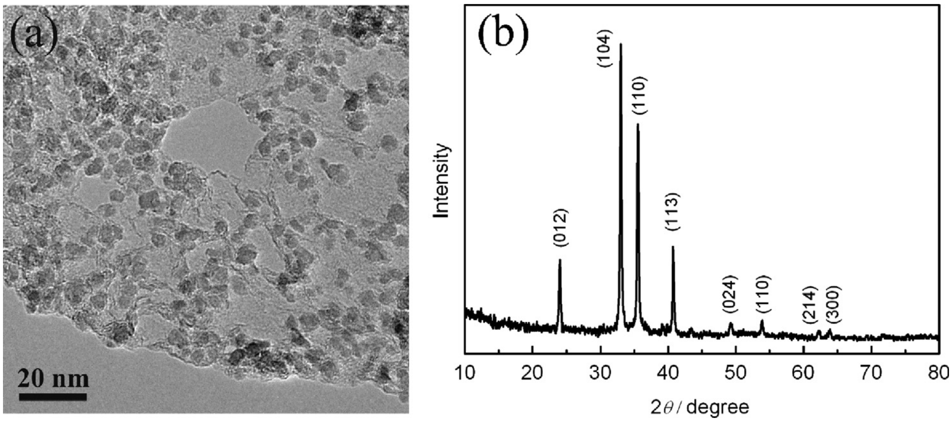

Fig. 1. (a) TEM image and (b) XRD pattern of Fe_2O_3/GS precursor.

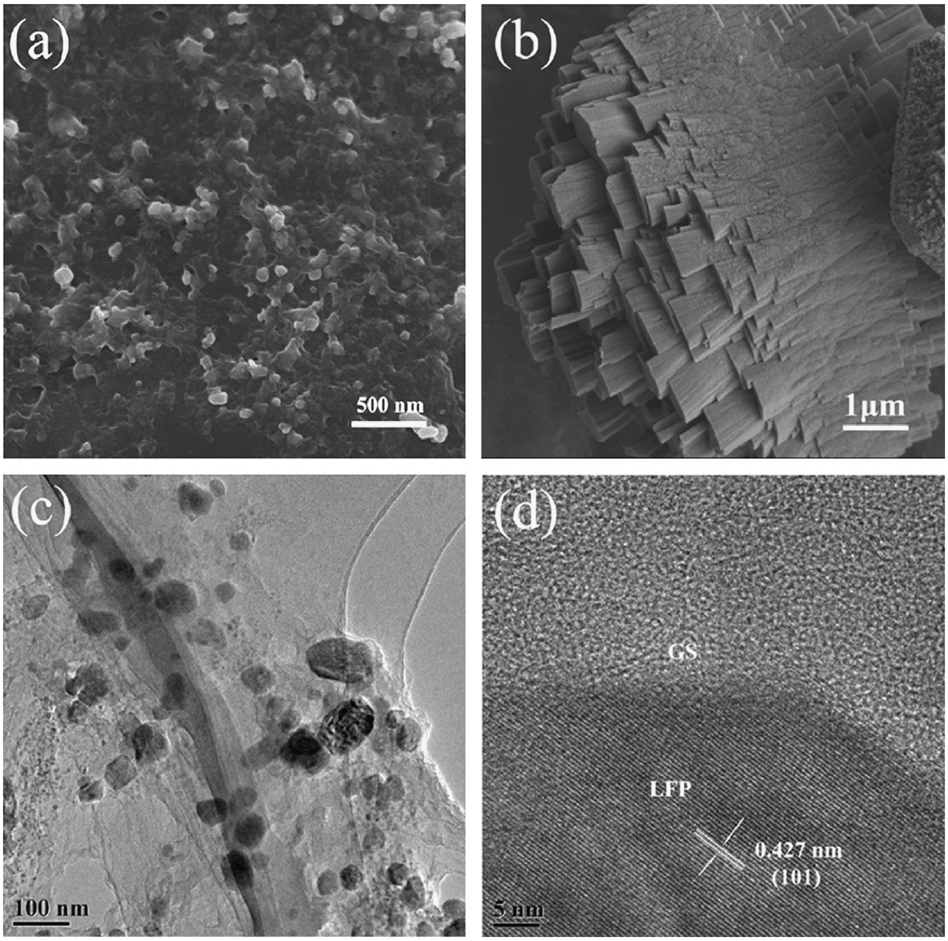

Fig. 2. (a and b) SEM images of LFP-GS and pure $LiFePO_4$; (c and d) TEM and HRTEM images of LFP-GS.