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Ultrafine $Na_3V_2(PO_4)_3$@C nanoparticles embedded in boron-doped graphene as high-rate and long cycle-life cathode material for sodium-ion batteries

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ABSTRACT

Sodium-ion batteries have been regarded as the most attractive alternative to lithium-ion batteries because of their low cost, abundance of sodium resources and promising applications for energy storage systems. In this work, boron-doped graphene decorated $Na_3V_2(PO_4)_3$@C (BG-$Na_3V_2(PO_4)_3$@C) composite is successfully synthesized for the first time by using a simple sol-gel assisted solid-state method. In this composite, the ultrafine $Na_3V_2(PO_4)_3$@C particles are uniformly distributed on the boron-doped graphene sheets. The carbon layer and boron-doped graphene greatly increase the electron/ion transport kinetics of $Na_3V_2(PO_4)_3$ and assure the material structure integrity, leading to excellent electrochemical performances in terms of high-rate capability and long cycle-life. It delivers a high reversible capacity of 94.7 mAh g^{-1} at 10C and keeps 96.4% of the capacity after 100 cycles. These preliminary results reveal that the as-fabricated BG-$Na_3V_2(PO_4)_3$@C composite is a new promising cathode material for sodium energy storage.

1. Introduction

Nowadays, rechargeable sodium-ion batteries are regarded as one of the most widely used energy storage devices in next-generation portable electronics as well as electric vehicles owing to their low cost and abundant sodium resource [1,2]. However, it is still a challenge to find suitable electrode materials for sodium-ion batteries, which is due to the large ionic radius of Na^+-ion. Up to the present, one of the most promising cathode for sodium-ion batteries is the NASICON-type $Na_3V_2(PO_4)_3$ because of its high theoretical capacity (118 mAh g^{-1}), fast Na^+-ion transportable framework and good thermal stability [3,4]. Additionally, $Na_3V_2(PO_4)_3$ has a high voltage plateau of approximately 3.4 V (vs. Na^+/Na) based on the V^{3+}/V^{4+} redox couple. Nevertheless, strongly inhibited by its poor electronic conductivity, the pure $Na_3V_2(PO_4)_3$ shows undesirable high-rate capability and fails to meet the demands for energy conversion and storage [5].

To solve this problem, various approaches have been performed to enhance the sodium storage performance of $Na_3V_2(PO_4)_3$. Nanosized $Na_3V_2(PO_4)_3$ material [6,7] has been studied to greatly increase the battery property by shorting the Na^+-ion diffusion distance. The other approach is to dope an appropriate amount of other metal ions [8–12] to enhance the intrinsic conductivity of $Na_3V_2(PO_4)_3$. What's more, carbon coating [13–16] is regarded as a facile and efficient method to improve the apparent electronic conductivity. Among the various carbon materials, two-dimensional graphene has been proved to be the best coating material for the encapsulation of electrodes due to its large surface, high flexibility, good conductivity and excellent chemical stability [17,18]. For instance, Zhang et al. [19] reported that the graphene scaffolded $Na_3V_2(PO_4)_3$ microsphere was fabricated and the composite exhibited good rate performance and long-cycle stability for sodium-ion batteries. Heteroatom (such as nitrogen, sulfur and boron) doping into graphene sheet is proved to be helpful to further enhance its electronic conductivity [18,20,21]. In 2018, Ramaprabhu's group [18] designed and prepared the boron-doped graphene-decorated tin oxide composite using a novel and one-pot technique and the effect of boron-doped graphene on SnO_2 is studied. However, there has been no report on using boron-doped graphene sheet to enhance the sodium storage property of $Na_3V_2(PO_4)_3$ cathode material.

In this study, we present a novel strategy to attach the $Na_3V_2(PO_4)_3$@C nanocrystals on boron-doped graphene sheets to improve the electrochemical performance of active material in sodium energy storage. The BG-$Na_3V_2(PO_4)_3$@C composite has been prepared

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through a simple sol-gel assisted solid-state method. Due to the conductive network constructed by boron-doped graphene and carbon coating, the designed electrode exhibits an excellent high-rate performance and long cycle-life stability when used as cathode for sodium-ion batteries. The preliminary results show that this new strategy can be applied to fabricate other electrode materials for electrochemical energy storage.

2. Experimental

2.1. Material synthesis

The graphene oxide sheets were firstly fabricated from the graphite flakes by a modified Hummers' method [22]. The boron-doped graphene was prepared by thermally treating graphene oxide with boric acid (H_3BO_3) at 2450 °C using a graphite furnace in an argon atmosphere as previously reported [23]. For the preparation of BG-$Na_3V_2(PO_4)_3$@C sample, the NH_4VO_3 and citric acid used as chelating agent and carbon source were added to the distilled water under vigorous stirring. Afterwards, the solution was heated to 80 °C and the boron-doped graphene was put into the mixture under sonication for 30 min to get a homogeneous solution. Then, stoichiometric amounts of Na_2CO_3 and $NH_4H_2PO_4$ were dispersed into the solution under stirring and heating at 80 °C to evaporate the excess distilled water until a gel was formed. Finally, the resulting precursor was preheated at 350 °C for 4 h and calcined at 750 °C for 10 h in flowing argon/hydrogen (95:5 in volume) atmosphere to obtain the BG-$Na_3V_2(PO_4)_3$@C composite. Furthermore, the $Na_3V_2(PO_4)_3$@C sample was also prepared in a similar approach except that the boron-doped graphene was not added.

2.2. Material characterization

The phase analysis of the as-fabricated samples was conducted via an X-ray diffraction (XRD, Bruker D8 Advance) using Cu-Kα radiation (λ = 1.5418 Å) over an angular range of 10°-90°. The morphology and microstructure of $Na_3V_2(PO_4)_3$@C and BG-$Na_3V_2(PO_4)_3$@C composites were characterized using the transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Raman spectrum was performed on a Raman microscope under a laser operating at 532 nm. The surface chemical composition of BG-$Na_3V_2(PO_4)_3$@C sample was identified by X-ray photoelectron spectroscopy (XPS, Kratos Model XSAM800) equipped with an Mg-Kα achromatic X-ray source. The amounts of carbon materials for $Na_3V_2(PO_4)_3$@C and BG-$Na_3V_2(PO_4)_3$@C were measured using an elemental analyzer.

2.3. Electrochemical measurements

The sodium storage properties of $Na_3V_2(PO_4)_3$@C and BG-$Na_3V_2(PO_4)_3$@C electrodes were performed using the CR2032 coin-type cells. The working electrodes were fabricated by spreading the slurry containing active material (80 wt%), carbon black (10 wt%) and polyvinylidene difluoride (PVDF, 10 wt%) on the aluminum foil. Afterwards, the electrodes were dried at 120 °C overnight in vacuum to evaporate the *N*-methyl-2-pyrrolidone (NMP). Note that the mass loading of the active material was about 2.6 mg cm^{-2}. Finally, the electrode was assembled into coin-cells in an Ar-filled glove box using sodium metal as the counter electrode and glass microfiber filter as the separator. The 1 M $NaClO_4$ in the propylene carbonate (PC) was used as the electrolyte. The galvanostatic charge/discharge measurements were performed on a CT2001A instrument in the potential range of 2.5 and 3.8 V (vs. Na^+/Na) based on the theoretical capacity of 118 mAh g^{-1}. The charge and discharge capacities of the cathodes were calculated based on the weight of $Na_3V_2(PO_4)_3$ material. The electrochemical impedance spectra (EIS) tests were conducted using a CHI600A electrochemical workstation with an amplitude of 5 mV over the frequency range from 100 kHz to 10 mHz.

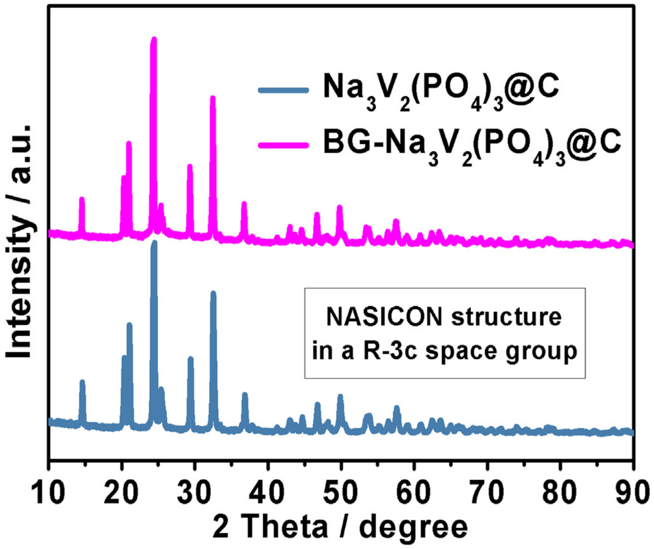

Fig. 1. XRD patterns of $Na_3V_2(PO_4)_3$@C and BG-$Na_3V_2(PO_4)_3$@C powders.

3. Results and discussion

The XRD patterns of $Na_3V_2(PO_4)_3$@C and BG-$Na_3V_2(PO_4)_3$@C powders are illustrated in Fig. 1. It can be noted that the peak positions, peak sharpness and intensity ratios of the as-prepared composites are similar. All reflections of both samples can be indexed to the $Na_3V_2(PO_4)_3$ phase (R-3c space group) without noticeable impurities [5]. Furthermore, no peaks related to the decomposed carbon and boron-doped graphene can be observed in the XRD curves, revealing that the residual carbon decomposed from citric acid and boron-doped graphene are present in an amorphous state or in a very small amount. The XRD results are in good agreement with the previously reported literatures [16,19,20].

Fig. 2 shows the TEM and HRTEM images of the as-fabricated BG-$Na_3V_2(PO_4)_3$@C and $Na_3V_2(PO_4)_3$@C particles. According to Fig. 2a,b, it is found that the boron-doped graphene sheets in the BG-$Na_3V_2(PO_4)_3$@C composite are visible. The $Na_3V_2(PO_4)_3$@C nanocrystals with particle size of about 80 nm are distributed uniformly on the boron-doped graphene. The inset in Fig. 2b illustrates the HRTEM image of BG-$Na_3V_2(PO_4)_3$@C sample. The highly crystalline $Na_3V_2(PO_4)_3$ particles are dispersed in the conductive network constructed by the carbon layer and boron-doped graphene, which can significantly enhance the transport of electron [5,19]. Fig. 2c gives the TEM image of $Na_3V_2(PO_4)_3$@C, which presents a uniform distribution of the particles. The average particle size of $Na_3V_2(PO_4)_3$@C is about 100 nm, which is larger than that of BG-$Na_3V_2(PO_4)_3$@C. This demonstrates that the graphene sheets can hinder the particles from growing bigger [24]. As illustrated in Fig. 2d, the HRTEM image of $Na_3V_2(PO_4)_3$@C reveals that an amorphous carbon layer with the thickness of several nanometers is coated on the surface of $Na_3V_2(PO_4)_3$. It should be noted that the carbon contents of $Na_3V_2(PO_4)_3$@C and BG-$Na_3V_2(PO_4)_3$@C composites obtained by elemental analysis are about 3.7 wt% and 7.5 wt% respectively.

The Raman spectra for the $Na_3V_2(PO_4)_3$@C and BG-$Na_3V_2(PO_4)_3$@C samples are also recorded as shown in Fig. 3. Obviously, two bands related to the typical Raman features of carbon [25] can be observed for both samples. The bands located at 1360 cm^{-1} and 1600 cm^{-1} are corresponded to the D-band and G-band, respectively. D-band is attributed to the disorders or defects in graphite structure, whereas G-band stands for the presence of graphite carbon [26]. The intensity ratio of D-band and G-band (I_D/I_G) can be used to estimate the amount of