



Surface engineering induced core-shell Prussian blue@polyaniline nanocubes as a high-rate and long-life sodium-ion battery cathode

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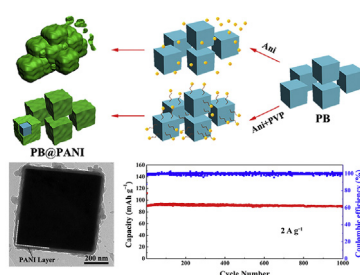
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HIGHLIGHTS

- Prussian blue@polyaniline nanocubes were obtained with the assistance of PVP.
- PANI enhanced the electrical conductivity and the kinetics of Na⁺ transmission.
- Regulated voltage range avoided excessive Na⁺ intercalation and damage of PANI.
- PB@PANI nanocubes exhibited a high reversible capacity and good rate capability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Sodium-ion battery
Prussian blue
Polyaniline
Surface engineering
Rate performance

ABSTRACT

Surface engineering is highly desirable but still challenging for developing high-rate and long-term life energy storage materials. Herein, Prussian blue@polyaniline nanocube is synthesized by an aqueous precipitation method and the following polymerization process of aniline. Benefiting from the coordinating role of polyvinyl pyrrolidone between Prussian blue and polyaniline, Prussian blue@polyaniline nanocube presents a core-shell structure with a diameter of about 600 nm and the uniform polyaniline coating layer is averagely 20 nm in thickness. The incorporation of polyaniline on Prussian blue is efficient to enhance the electrical conductivity and the kinetics of Na⁺ transmission during cycling, leading to the higher specific capacity and better rate performance. The sodium storage properties of the cathode are also investigated in different voltage ranges. Owing to the core-shell structure and the optimized voltage range, Prussian blue@polyaniline electrode delivers a specific capacity of 108.3 mAh g⁻¹ at 100 mA g⁻¹ with a capacity retention of 93.4% after 500 cycles and maintains a considerable specific capacity of 90.3 mAh g⁻¹ even at 2 A g⁻¹ in the voltage range of 2.0–3.6 V. The strategy of polyvinyl pyrrolidone assisted polymerization of polyaniline layer on Prussian blue nanoparticles can be extended to surface modification for other electrode materials.

1. Introduction

Sodium-ion batteries (SIBs) have drawn increasing attention because of their low cost and natural resources in abundance [1].

Although exhibiting lower specific capacity than lithium-ion batteries (LIBs), SIBs can be applied to large-scale electric energy storage (EES) which is much concerned about safety, cost and longevity rather than energy and power density [2]. Many suitable anode materials (e.g.,

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TiO₂ [3–5], SnO₂ [6], and MoS₂ [7]) have been developed, which could exhibit high capability and good cycling stability. On the other hand, the extensively studied cathode materials such as polyanion-type compounds and layered oxides exhibit low specific capacity or poor stability during cycling which can hardly satisfy the requirements of the application [8,9]. Therefore, developing high-energy cathodes is still a big challenge for advanced SIBs.

Recently, Prussian blue (PB) has been regarded as a suitable candidate for SIBs cathode material owing to its high theoretical capacity (~170 mAh g⁻¹ with two Na⁺ intercalation reaction in per formula unit) and 3D open framework for fast Na⁺ diffusion [10,11]. However, there is still an important issue to be solved that the existence of vacancies occupied by coordinated water is the main reason for the poor cycling stability and low Coulombic efficiency [12,13]. The coordinated water is verified to severely inactivate the electrochemical reactions at the higher voltage platform, which is associated with the low-spin Fe^{II}/Fe^{III} (LS–Fe) redox couple bonded to C atoms [14]. Some approaches to slow the nucleation rate have been developed for fewer vacancies and higher crystallinity, such as controlled release method and ligand competition method [10,15,16]. However, these methods cannot entirely remove the coordinated water during precipitation process. Therefore, slightly decreasing the working voltage to eliminate the effect of LS–Fe redox couple can be a compromise method for optimal sodium storage properties [17].

Additionally, owing to the insulating characteristic of PB, its practical capacity is far below the theoretical capacity. The conventional method to improve the electrical conductivity of PB relies on the addition of conductive carbon such as graphene [18,19] and carbon nanotubes [20]. This method can only provide a conductive substrate but cannot form an effective coating layer performing electrical conductivity equally in all directions. Nevertheless, it is impossible to coat the conductive carbon layer on PB because the carbonization generally needs a high-temperature pyrolysis (> 500 °C) and the decomposition of PB occurs at the relatively low temperature (~300 °C) [21,22]. Some conducting materials synthesized at low temperature can be introduced to meet the requirement mentioned above. For example, Tang et al. reported a polypyrrole-promoted Na_xFe [Fe(CN)₆] electrode exhibiting enhanced rate performance (75 mAh g⁻¹ at 3 A g⁻¹) and good cyclability (79% capacity retention after 500 cycles) [23]. However, the growth of conducting polymer was uncontrollable so that it was difficult to generate an intact conducting polymer coating layer on the surface of PB [24]. Note that polyvinyl pyrrolidone (PVP) has surface modification effect on PB nanoparticles and excellent chemical compatibility with PANI [25,26]. It is believed that the uniform PANI layer could be easily anchored on PB if introducing PVP to modify the surface property in advance during the synthesis process.

In this work, we first prepared high-crystallized and well-dispersed Prussian blue nanocubes through a single iron-source aqueous precipitation process and a uniform conducting PANI layer was coated on the surface by the following polymerization reaction of aniline with the assistance of PVP to form a core-shell structure. To find out the optimum voltage range, we also investigated the electrochemical behavior of PB@PANI electrode at different charge cut-off voltage. It is proved that the high-potential LS–Fe redox couple is gradually inactivated during the repeatedly charge-discharge process and the PANI layer could be preserved at the relatively low voltage range. Benefitting from the unique core-shell structure and the controlled charge cut-off voltage, PB@PANI nanocubes here exhibited a competitive sodium storage performance in comparison with the previously reported results and could serve as a high-rate and long-life cathode material for SIBs.

2. Experimental section

2.1. Synthesis of PB nanocubes

PB nanocubes were synthesized according to a previous work with a

slight modification [27]. In a typical synthesis process, Na₄Fe(CN)₆·10H₂O (8 mmol), polyvinyl pyrrolidone (2 g, M_w ~ 40000) and hydrochloric acid (4 mL, 37 wt%) were dissolved in 400 mL deionized water. After stirring for 30 min, the obtained yellow solution was refluxed at 60 °C for 6 h, then aged overnight. The blue precipitate was collected by vacuum filtration, washed with deionized water for several times and dried in vacuum at 100 °C for 24 h.

2.2. Synthesis of PB@PANI nanocubes

PB@PANI nanocubes were synthesized via the following process. PB nanocubes (0.6 g), polyvinyl pyrrolidone (0.5 g, M_w ~ 40000) and aniline monomer (100 μm) were dispersed in a hydrochloric acid solution (100 mL, 1 M) under ultrasonication for 30 min. Subsequently, ammonium persulfate (1.6 mmol) was added into the above solution and stirred for 24 h at room temperature. The green powder was collected by vacuum filtration, washed with deionized water for several times and dried at 100 °C for 24 h under vacuum. For comparison, pure polyaniline (PANI) was synthesized by the same method without adding PB nanocubes in the synthesis process and PB@PANI without adding PVP was also obtained, which was denoted as PB@PANI–NP.

2.3. Characterization

Powder X-ray diffraction was carried out using a Bruker D8 X-ray diffractometer with monochromatized Cu Kα radiation. FT-IR spectra were recorded on a Nicolet iS50 FT-IR Spectrometer (Thermo Scientific) between 400 and 4000 cm⁻¹. The morphology and microstructure were characterized using scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, JEOL JEM-2100F). Elemental mapping images were collected on a Titan G2 60–300 transmission electron microscope with an accelerating voltage of 200 kV. The XPS spectra were tested by a K-Alpha1063 spectrometer with Al Kα radiation at 6 mA and 12 kV. Thermogravimetric analysis (TGA) was carried out on an STA 449C thermoanalyzer from 25 to 800 °C with a ramping rate of 5 °C min⁻¹. DC electrical conductivity analysis was conducted on a four-point probe instrument (ST-2722, Jingge). Before conductivity measurement, the sample (0.3 g) was compressed into a small wafer with a diameter of 0.8 cm under a pressure of 8 MPa.

2.4. Electrochemical measurements

The test electrodes were prepared by mixing the as-prepared cathode material, carboxymethyl cellulose and super P in a weight ratio of 7: 1.5: 1.5 with deionized water as a solvent. The obtained slurry was cast onto an aluminum foil, then dried at 80 °C for 24 h under vacuum. The aluminum foil loaded with electrode materials were cut into round disks with an average mass loading of 1.5 mg cm⁻². Coin-type cells (CR2016) were assembled using home-made sodium metal disk as the counter electrode, glass fiber as the separator, and 1 M NaPF₆ in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1:1:1 vol %) as the electrolyte. Galvanostatic charge/discharge cycling performance was tested using a Neware CT-3008W battery testing system. Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) were measured on a CHI660D electrochemical workstation.

3. Results and discussion

As shown in Fig. 1a and b, the as-prepared PB displays a uniform-sized cubic morphology with a smooth surface, which is about 600 nm in diameter. As can be seen clearly, without adding PVP in the aniline polymerization process, PB nanocubes are severely agglomerated and many disconnected PANI particles growing away from the PB nanocubes are observed (Fig. 1c and d). In contrast, when PVP is introduced, PB nanocubes seem to be independent and are coated by uniform PANI

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