Synthesis and Electrochemical Performance of Novel Peanut-Like SbPO4 Aggregates

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Abstract. Hierarchical SbPO4 peanut-like aggregates are successfully prepared through a facile solvothermal route. The X-ray powder diffraction, scanning electronic microscopy, high-resolution transmission electronic microscopy techniques is utilized to characterize the obtained SbPO4 materials. The experimental results indicate that the SbPO4 peanut-like aggregates are composed of numerous nanoplates in an oriented way via a self-assembly process. Additionally, the electrochemical Na-storage property is also preliminarily investigated.

1. Introduction
Hierarchical nanostructures composed of nanoparticles, nanosheets and nanorods as subunits have attracted much attention due to their interesting physical and chemical properties and potential applications in energy-related fields [1-5]. The synthetic strategy towards these novel nanostructures has been intensively pursued and explored in materials science fields. In general, some organic additives such as surfactants, polymers and complexing agents are adopted to act as soft templates to prepare the hierarchical structures [6-9]. However, the facile and large-scale synthesis of these advanced functional nanostructures is still confronted with a big challenge.

To meet the ever-growing energy requirements of the modern society and to lessen resource depletion and environmental pollution, it is imperative to explore high-performance, inexpensive and eco-friendly energy storage and conversion systems [10]. In view of the limited reservation and quite uneven distribution of lithium resources in earth, in recent years, sodium-ion batteries (SIBs) have sprung up to be a promising alternative energy storage device to replace lithium-ion batteries (LIBs) to power electric or hybrid electric vehicles because of low cost and natural abundance of sodium [11]. Graphite is a widespread anode material in LIBs with low theoretical specific capacity and relatively poor rate capability [12]. However, it has been demonstrated that graphite is unable to properly intercalate sodium ions due to the energetic instability of sodium-graphite intercalation compounds [13]. Therefore, developing new type of alternative anode materials for SIBs becomes an urgent task.

Recently, phosphate materials such as transition metal phosphates are now promising electrode materials for energy storage [14, 15]. However, less attention was focused on metalloid-based phosphate as electrode materials. Among the commonly available metalloid phosphates, SbPO4 (antimony phosphate) is a layered phosphate which is composed of layers of tetrahedral PO4 and polyhedral SbO4 concatenated via the corners to form an outstretched framework [16]. Moreover, SbPO4 can serve as an electrode for energy storage which originates from the reversible redox transitions between Sb3+ and Sb metal states [17-21]. Till date, nanosized SbPO4 materials with different morphologies including particles, nanorods and ribbons, hollow spheres have been prepared [20-22]. However, its applications as electrode for SIBs are still seldom. Herein, we report a
solvothermal method to fabricate SbPO$_4$ hierarchical peanut-like aggregates assembled from nanoplates and initially investigate their electrochemical Na-storage performance.

2. Experimental procedure

2.1. Synthesis of SbPO$_4$
In a typical synthesis, 2 mmol of antimony potassium tartrate (APT) was dissolved in 60 mL glycerol under continuous stirring. Then 10 mmol of sodium polyphosphate (SPP) was slowly dropped into the above solution under violent stirring. The resulting colloidal mixture was transferred into a Teflon-lined autoclave and maintained at 180 °C for 2 h. After that, the autoclave was cooled down naturally. The white precipitates were gathered, washed with water and alcohol in sequence and separated by centrifuge, and dried at 60°C for 12 h in a vacuum oven to obtain SbPO$_4$ peanut-like aggregates.

2.2. Characterization
The crystal phase and crystallinity were identified by X-ray diffraction (XRD, D/Max-2550) with monochromatized CuKα radiation. The morphology and microstructure were inspected by scanning electron microscope (SEM, FEI SIRION-100) and high-resolution transmission electron microscope (TEM, JEOL JEM-200CX).

2.3. Electrochemical measurements
The as-prepared samples were molded into a coin-type half-cell (CR2032) to investigate electrochemical performance. The half-cell was composed of sodium foil as counter and reference electrode, glass fiber (Whatman) as separator, NaPF$_6$ solution (1 M) in EC/DMC (1:1 in volume) as electrolyte and the sample-based electrode as the working electrode. The working electrode was made as follows. The sample (active material), acetylene black (conductive reagent) and the polyvinylidene fluoride (binder) were mixed with N-methyl pyrrolidone according to a mass ratio of 75: 10: 15 to form a slurry. Then the slurry was uniformly smeared on a copper foil and was dried at 120 °C in a vacuum drying oven for 12 h and pressed. The assembly of half-cells was completed in an argon-filled glove box. Cyclic voltammetry tests were proceeded on an electrochemical workstation (CHI660E) in the range of 0.01~3.00 V vs. Na/Na$^+$ at a sweep rate of 0.5 mV/s. Galvanostatic charge/discharge tests were conducted on a Land battery tester (CT2001A) in the cut-off voltage range of 0.005-3.00 V.

3. Results and discussion

![Figure 1. XRD patterns of SbPO$_4$ sample](image)

The crystal structure and the phase purity of the products were determined by XRD. Figure 1 depicts that the major diffraction peaks can be readily indexed to the monoclinic phase of SbPO$_4$ consistent with the standard powder diffraction file (JCPDS 35-0829). No other diffraction peaks from impurities can be observed, meaning the high purity of SbPO$_4$. 


It can be seen from Figure 2a that SbPO₄ samples display uniform well-defined peanut-like morphologies with an average length of 1.4 μm and width of 450 nm. In addition, it seems that these peanut-like aggregates have quite rough surfaces. Careful examination in Figure 2b reveals that many nanoplates are orderly arranged on the surface of peanut-like particles, which testifies that the hierarchical SbPO₄ peanut-like aggregates are comprised of nanoplates as building blocks. Figure 2c clearly reveals that numerous nanoplates stretch out towards the edges of the aggregates. The lattice fringes of (101) plane with a d-spacing of 0.332 nm can also be discerned in Figure 2d.

Figure 2. (a, b) SEM images and (c, d) TEM images of the SbPO₄ samples

Control experiments were conducted to investigate the formation mechanism of the SbPO₄ products as shown in Figure 3. When the reaction proceeded for 5 min, tiny SbPO₄ nanoparticles appeared. As the reaction time rose up to 15 min, these nanoparticles became flatted nanoplates. With the reaction time arrived at 30 min, these nanoplates gradually arranged and aggregated in an oriented way. The above morphological evolution confirms that the SbPO₄ peanut-like aggregates are assembled by nanoplates.

Figure 3. SEM images of the morphology evolution of SbPO₄ sample after different reaction time, (a) 5 min; (b) 15 min and (c) 30 min
Figure 4. Cycle performance at a current density of 0.1 A g⁻¹ of the as-prepared SbPO₄ sample

Figure 4 shows that the SbPO₄ electrode for SIBs delivers an initial high discharge capacity of 555 mAh g⁻¹ and a charge capacity (reversible capacity) of 256 mAh g⁻¹, with a coulombic efficiency of 46%. The irreversible capacity loss might arise from the irreversible reactions during the discharge/charge processes, such as the formation of solid electrolyte interphase (SEI) film and a small amount of some sodium trapping inside the defects and disorder structures [23, 24]. From 2nd cycle, the coulombic efficiency rises up to more than 90%. Additionally, the reversible capacity of the SbPO₄ electrode descends to a certain extent after repeated discharge/charge. After 50 cycles, the capacity arrived at 135 mAh g⁻¹. The capacity decay is attributed to the pulverization of electroactive materials arising from the large volume expansion during discharge/charge processes [25].

4. Conclusions
In conclusion, a facile solvothermal method has been developed to prepare hierarchical SbPO₄ peanut-like aggregates with nanoplates as building blocks. A possible self-assembly process was presented to account for the formation of the as-prepared SbPO₄ aggregates. Furthermore, the electrochemical performance of SbPO₄-based electrode as an anode for SIBs is also investigated.

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