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Highly ordered lamellar V_2O_3-based hybrid nanorods towards superior aqueous lithium-ion battery performance

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ABSTRACT

Lithium-ion batteries with green and inexpensive aqueous electrolytes solve the safety problem associated with conventional lithium-ion batteries that use highly toxic and flammable organic solvents, which usually cause fires and explosions. However, the relatively low capacities (usually < 65 mAh g^{-1}) and less than 50% capacity retention over 50 cycles unfortunately limit their promising applicability. Herein, a novel model of ordered lamellar organic–inorganic hybrid nanorods is first put forward as an excellent platform to circumvent the above issues. Taking the synthetic highly ordered lamellar V_2O_3-based hybrid nanorods as an example, they deliver a capacity up to 131 mAh g^{-1}, nearly 1.5 and 2 times higher than that of 10-nm V_2O_3 nanocrystals (90 mAh g^{-1}) and 2-μm bulk V_2O_3 (73.9 mAh g^{-1}). Also, their excellent cyclability of 88% after 50 cycles is remarkably better than that of 10-nm V_2O_3 nanocrystals (64%) and 2-μm bulk V_2O_3 (41%). This work provides a facile route for gram-scale synthesizing highly ordered lamellar hybrid materials and proves that these unique structures are excellent platforms for significantly improving aqueous lithium-ion battery performances especially at high discharge rates, giving tantalizing perspectives in future design and synthesis of high-performance active materials for aqueous lithium-ion batteries.

1. Introduction

Since the early 1990s, rechargeable lithium-ion batteries with non-aqueous electrolytes have been widely used in portable equipments [1]. Although the performances of non-aqueous lithium-ion batteries are often satisfactory, their practical applications are still handicapped by the high cost and severe safety problems arising from the use of highly toxic and flammable solvents, which might cause fires and explosion [2]. In exploring new types of alternative battery systems with high safety and low cost, aqueous lithium-ion batteries have attracted much attention [3–6]. Since this new type of lithium-ion batteries utilizes aqueous electrolytes, they fundamentally resolve the safety problem resulting from organic electrolytes and avoid rigorous assembly conditions [4]. In addition to possessing high safety, low cost and environmental friendliness, the fascination also comes from their electrolytes affording two orders of magnitude higher ion conductivity than those of non-aqueous systems [7,8]. Despite these excellent advantages, the relatively low capacities (usually < 65 mAh g^{-1}) associated with less than 50% capacity retention over 50 cycles unfortunately hinder their promising applicability [3,5,9,10]. Thus, further breakthroughs in the design and synthesis of novel electrode materials, with high specific capacities and stable cycling life, hold the key to the development of aqueous lithium-ion batteries.

Herein, we first put forward a novel and ideal model system of ordered lamellar organic–inorganic hybrid nanorods as an excellent platform to circumvent the above issues. This designed geometry has several tantalizing advantages in enhancing the capacity and cycling life of aqueous lithium-ion batteries, as illustrated in Scheme 1a. Within these hybrids, the organic component can be used to tailor the electronic properties of inorganic framework by defining its reduced dimensionality and mediating the electronic coupling between inorganic unites [11]. In this case, the use of dimensionally confined ultrathin inorganic layers as lithium hosts helps to shorten the lithium ion diffusion length and enhance the surface area contact with electrolyte, thus contributing to achieve faster kinetics and higher capacity [12,13]. Also, the ultrathin inorganic components allow for facile strain relaxation without fracture and shedding that occur in bulk or micron-sized materials (Scheme 1c) so that much more stable cycling life can be achieved [14]. Moreover, the rod-like configuration has direct one-dimensional (1D) electrical pathways facilitating efficient charge transport [15], whereas the electronic charge carriers

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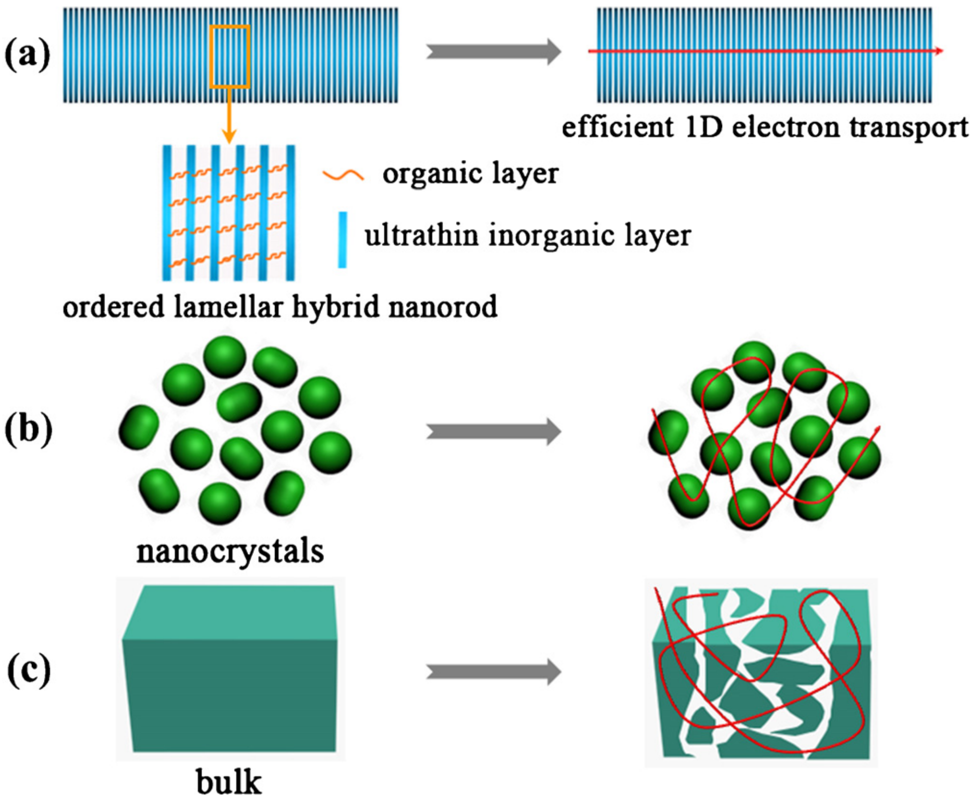

Scheme 1. Electron transport pathway (indicated by red line) and morphological change that occur in different structured electrode materials during electrochemical cycling: (a) ordered lamellar hybrid nanorod consists of ultrathin inorganic layers, regularly separated from each other by intercalated organic molecules. Advantages of this novel electrode include efficient 1D electron transport, facile strain relaxation, short lithium insertion distance, large contact area with electrolyte, extra lithium storage space and easy electrolyte infiltration. (b) Nanocrystals do not pulverize into smaller particles after cycling thanks to their facile strain relaxation, but the disconnected particles increase transport distance of electrons and lithium ions. (c) Large volume expansion in bulk materials leads to their pulverization and shedding during cycling. The cracked particles increase transport distance of electrons and lithium ions, while the loss of active materials decreases specific capacity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

must move through the interparticle contact area in the disconnected nanocrystals or cracked bulk materials (Scheme 1b and c). Furthermore, the large interlayer distance between inorganic layers not only provides easy electrolyte infiltration and extra storage space for lithium ions but also acts as an elastic zone to buffer volume change during lithium uptake-release [16,17], thereby maintaining good electronic contact and guaranteeing excellent powder performance.

As is well-known, good conductivity is a prerequisite for an excellent electrode material. In this regard, atomic structural analysis gives us inspiration that rhombohedral V_2O_3 seems to be an appealing candidate for the desirable electrode material. As shown in Fig. 1a, the rhombohedral V_2O_3 possesses a 3-dimensional V–V framework where the V3d electrons could itinerate along the V–V chains [18], thus rendering it to take on an intrinsic metallic behavior which is further verified by the simulation on its band structure and density-of-states (Fig. S1). More strikingly, the presence of tunneled structures in rhombohedral V_2O_3 (Fig. 1b–d) facilitates the intercalation/deintercalation of lithium ions and endows it with a theoretical capacity as high as 356 mAh g^{-1} [19,20], which makes it particularly suitable as an active material for aqueous lithium-ion batteries where the capacity is a big concern. Inspired by the aforementioned concepts, highly ordered lamellar hybrid nanorods consisting of ultrathin V_2O_3 layers with thickness of 0.65 nm, regularly separated from each other by organic phenylacetate layers, are first successfully synthesized on a gram-scale via a novel and facile pathway and then introduced as the aqueous lithium-ion battery electrode, in efforts to achieve greatly enhanced capacity and cyclability.

2. Experimental

2.1. Synthesis of highly ordered lamellar V_2O_3-based hybrid nanorods

1.0 mL $VOCl_3$ was added into 80 mL phenethyl alcohol. After vigorous stirring for 30 min, the mixture was transferred into a 100 mL Teflon-lined autoclave, sealed and heated at 220 °C for 48 h. After cooling to room temperature naturally, the final product was collected by centrifuging the mixture, washed with dichloromethane and absolute ethanol for several times, and then dried in vacuum overnight for further characterization.

2.2. Characterization

XRD patterns were recorded by using a Rigaku TTR-III diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The FE-SEM images were performed by using a FEI Sirion-200 SEM. The TEM images were performed by using a JEOL-2010 TEM with an acceleration voltage of 200 kV. X-ray photoelectron spectra (XPS) were acquired on an ESCALAB MKII with Mg Kα ($h\upsilon = 1253.6$ eV) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.5 eV. The IR spectra were measured on a NICOLET FT-IR spectrometer, using pressed KBr tablets. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on an Atomscan Advantage (Thermo Jarrell Ash Corporation (USA)). Elemental analysis was carried out on a Vario EL III (Elementar Analysensysteme, Germany). Thermal gravimetric analysis (TGA) of the as-synthesized sample was carried out on a NETZSCH TG 209