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Anatase/rutile-TiO_2 hollow hierarchical architecture modified by SnO_2 toward efficient lithium storage

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ABSTRACT

Hierarchical architecture of anatase/rutile-mixed phases TiO_2 with hollow interior was successfully fabricated via a Topotactic synthetic method, including the synthesis of $CaTiO_3$ precursors and transforming them into TiO_2 through ion-exchange process. The as-synthesized TiO_2 hierarchical architectures as the anode materials were used as lithium-ion batteries (LIBs). Compared with TiO_2 samples, the TiO_2@SnO_2-5% shows the improved lithium storage capacity, cycling performance and rate properties. The impedance of the TiO_2 electrode decreases evidently after adding few amount of SnO_2. The hollow hierarchical structure with different compositions provide much more active sites, and well connect interface among anatase, rutile, and SnO_2, facilitating the electron and ion transport quickly and efficiently. Addition appropriate number of SnO_2 not only well kept the hierarchical architecture but also enhanced the capacity and conductivity of the TiO_2 sample. As a result, TiO_2@SnO_2-5% exhibited excellent lithium storage performance.

Introduction

Lithium-ion batteries (LIBs) have many advantages of high energy density, low cost and long cycle life, which is considered as one of the most promising energy storage devices [1–3]. The three most important performance indicators of LIB are the capacity, cyclic stability and rate capability [4–6]. It is imperative to seek an active electrode material with above excellent performance indicators. TiO_2 materials have been intensively investigated due to their versatile and easy modification of nanostructures, as well as other advantages, such as low-cost, security and environmental friendliness [7–10]. However, the low ionic and electrical conductivity severely limited the storage capacity, inhibiting its practical electrochemical application [11,12]. Thus, the study on TiO_2 as anode material for lithium mass storage to meet the increasing demand still remains a great challenge and has a profound significance.

In order to overcome the above problem of low ionic and electrical conductivity, lots of measures had been undertaken by previous researches [13–15]. Phase composition plays an important role in the physical and chemical properties of TiO_2. Commonly, TiO_2 has four crystalline polymorphs: anatase, rutile, brookite, and TiO_2 (B) [16–19]. TiO_2 nanomaterials with a mixed phase showed superior electrochemical properties in LIBs. Recently, TiO_2 (B) and anatase heterostructures have been reported to exhibit superior electrochemical property,

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which fully shows the advantage of mixed crystals [20]. Fewer researchers have studied on the electrochemical performance of anatase and rutile TiO_2 mixed phase, which have attracted great interest in LIBs. The high anisotropic of Li^+ diffusion in rutile, attracts researchers to create rutile nanorods growth along *c*-axis, which named the channels as a "highway" for Li^+ transport [21–24]. The tetragonal rutile TiO_2 (P42/mnm) consists of TiO_6 octahedral, sharing corners in the *ab* plane and edges in the *c*-direction. The Li^+ diffusion coefficient along the *c*-direction is approximately 10^{-6} cm^2 s^{-1}, much faster than that in the ab-plane (10^{-15} cm^2 s^{-1}). Besides, small size anatase TiO_2 nanoparticles show superior performance in lithium ion batteries [13]. Thus, to construct a structure, constituting of one dimensional rod-like rutile TiO_2 combined with anatase TiO_2, is expected. The special structural characteristics and the low volume expansion (<4%) during Li^+ insertion-desertion process, endows the rutile and anatase TiO_2 heterostructures good structural stability and long cycle life. Additionally, built-in electric field could be formed at the interface between rutile TiO_2 nanorods and small size anatase TiO_2, which induces much lower lithium-ion diffusion resistance and facilitates its transport in both insertion and extraction processes. Unfortunately, the electrical conductivity and capacity of TiO_2 material is limited, which needs to be further improved. SnO_2 has similar crystal structure with rutile TiO_2 and high theoretical capacity than TiO_2 material, however, it has disadvantage of the large specific volume changes through charge and discharge processes [25,26]. Thus, added appropriate number of SnO_2 into the structure is the key to enhance the TiO_2 material conductivity, capacity and well kept the structure.

On the other hand, it is well known that the properties of materials are strongly dependent on their morphology [27–30]. Severe aggregation would happened due to the high surface energy of nanoparticles. To establish a high-order multi-dimensional structure composed by low-dimensional nanoparticles may offer opportunities to "tune-in" properties that is desirable for the intended application [31,32]. Researches have been reported to synthesize TiO_2 hollow shells, aiming at enlarging the specific surface area for increasing the reaction active site. Other than increasing the electrolyte/electrode contact area, the nanostructure also provides a shorter path for Li^+ transport to reduce ionic conductivity. Hollow structured nanomaterials as electrode materials exhibit an excellent electrochemical performance, owing to the enhanced diffusion kinetics and structural stability [33,34].

Up to now, various approaches have been developed to controllably synthesize different hollow structured metal oxides [35–37]. To achieve uniform and well-defined hollow structured metal oxides, the hard-templating method has been considered as one of the most effective and straight forward strategies [38]. However, simple template method can hardly achieve the requirement to construct a special structure which not only creates hollow structure, but also makes one dimensional rod-like rutile TiO_2 combined with anatase TiO_2.

Previous researches reported that one dimensional anatase/rutile TiO_2 hierarchical nanorods were acted as anode electrode materials, and the lithium storage capacity need to be improved [14,39]. Herein, we used Topotactic synthetic method to obtain the waxberry-like TiO_2 hierarchical architecture. The method makes anatase and rutile phase of TiO_2 connect closely with each other. Meanwhile, the special hollow hierarchical structure provides much more active sites, which is in favour of the improvement the electrochemical performance. When Sn source added in the initial solution, the hierarchical structure of TiO_2@SnO_2 samples were fabricated. TiO_2@SnO_2-5% with well connect interface among anatase, rutile, and SnO_2 as well as *c*-channel formed inside stacked (001) planes in rutile TiO_2 nanorods, which facilitates the electron and ion transport quickly and efficiently, showing an excellent performance in LIBs.

Experimental section

Synthesis of $CaTiO_3$ and $CaTiO_3$-Sn precursor microcubes

In a typical synthesis, 0.11 g of Calcium chloride dihydrate ($CaCl_2$ $2H_2O$) and a certain amount of $SnCl_4$ $5H_2O$ (0, 0.0169 and 0.0338 g, respectively) were dissolved in mixed solution of 15 mL of ethanol and 5 mL of poly(ethylene glycol) (PEG-200, AR). After stirring for a while, 0.33 mL of Titanium n-butoxide (TBT, AR) was injected in the above mixture. Then 0.24 g of NaOH was added into the mixture. After mixing well, the feedstock was poured into a 50 mL Teflon-lined stainless-steel autoclave, and heated at 180 °C for 15 h in an oven. The obtained samples were washed with deionized (DI, resistivity 18 MW cm^{-1}) water for 3 times, and then dried at 60 °C for further characterization and application. The addition amounts of $SnCl_4 \cdot 5H_2O$ were 0, 0.0169 and 0.0338 g, which corresponds to the obtained samples named as $CaTiO_3$, $CaTiO_3$-Sn-5%, $CaTiO_3$-Sn-10%, respectively. ($CaTiO_3$-Sn sample indicates the composite structure of $CaTiO_3$ and $CaSnO_3$).

Synthesis of hollow waxberry-like TiO_2 and TiO_2@SnO_2 samples

75 mg of as-synthesized $CaTiO_3$ or $CaTiO_3$-Sn samples and 0.34 g of EDTA-2Na were dispersed in a mixed solution of ethylene glycol (EG, 10 mL) and DI water (30 mL). After mixing, the final mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 12 h. The products were washed with water and dried at 60 °C. The obtained powders were calcined at 400 °C for 2 h with a temperature rising rate of 5 °C min^{-1}. The as-obtained samples were denoted as TiO_2, TiO_2@SnO_2-5%, and TiO_2@SnO_2-10%, respectively.

Characterization

X-ray diffractometer (XRD, Germany Bruker D8-Advance) was used to characterize the crystal structure and phase composition of samples. High-resolution Raman spectrometer (LabRAM HR Evolution, HORIBA JOBIN YVON SAS) was carried out to analyse Raman spectra. Field-emission scanning electron microscope (SEM, QUANTA 250 FEG, FEI, USA) and the high-resolution transmission electron microscopy (HRTEM, FEI

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