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N-doped hollow urchin-like anatase TiO_2@C composite as a novel anode for Li-ion batteries

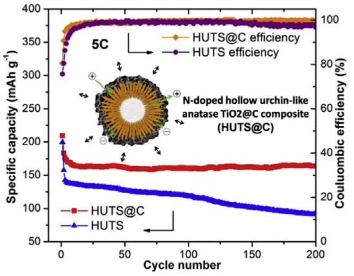
Yalan Xing[a], Shengbin Wang[a], Baizeng Fang[b], Ge Song[a], David P. Wilkinson[b,*], Shichao Zhang[a,**]

[a] School of Materials Science and Engineering, Beihang University, 37 Xueyuan Road, Beijing, 100191, China
[b] Department of Chemical & Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, BC, V6T 1Z3, Canada

HIGHLIGHTS

- Hollow urchin-like anatase TiO_2 microsphere coated with N-doped carbon is prepared.
- The HUTS@C possesses an enhanced percentage of exposed {001} facets.
- The HUTS@C shows outstanding Li-storage performance.
- The electron transfer and lithium ion diffusion are greatly improved in the HUTS@C.

GRAPHICAL ABSTRACT



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ABSTRACT

N-doped hollow urchin-like anatase TiO_2 spheres (HUTSs) with carbon coating (HUTS@C) are prepared through a facile and scalable hydrothermal reaction followed by coating of polypyrrole and carbonization. The HUTS is composed of radially grown anatase nanorods and possesses an enhanced percentage of exposed {001} facets compared with P25 TiO_2 nanoparticles. After the carbon coating, the HUTS@C retains the hollow nanostructure although covered with an N-doped carbon layer. As an anode for Li-ion batteries, the HUTS@C delivers a higher capacity of 165.1 mAh g^{-1} at 1C after 200 cycles and better rate capability (111.7 mAh g^{-1} at 10C) than the HUTS. Further electrochemical studies reveal that the HUTS@C has a better electrochemical reversibility, lower charge-transfer resistance, and higher Li-ion diffusion coefficient due to its unique nanosctructure including the hollow core, anatase phase of TiO_2 microspheres with high exposed {001} facets and the N-doped carbon layer, which facilitates mass transport and enhances electrical conductivity.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have played an important role in the revolution of consumer electronic devices in the last decade by making them more portable and wearable [1,2]. But meanwhile, the demands for higher capacity, better cycling stability and rate capability are increasing dramatically, especially for electric vehicle applications [3,4]. The commonly used graphite as an anode material is limited by its poor rate capability and security issues [5]. Therefore, new non-carbon anode materials are widely studied to replace carbonaceous materials, e.g., Si and transition metal oxides. TiO_2 is regarded as a promising candidate due to its excellent structural stability based on intercalation/extraction mechanisms and safe working potential (~1.7 V vs. Li^+/Li) to avoid excessive formation of the solid electrolyte interphase (SEI) and lithium plating on the anode [6,7]. Moreover, the intrinsic features such as low cost and environmental benignity make

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: dwilkinson@chbe.ubc.ca (D.P. Wilkinson), csc@buaa.edu.cn (S. Zhang).

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TiO_2 attractive from an industry consideration. Among the various polymorphs of TiO_2, anatase TiO_2 is more favorable as a lithium-ion intercalation host [8]. However, the poor electrical conductivity and lithium-ion diffusivity have hindered the application of TiO_2.

In order to improve its electrochemical performance, various nanostructures of TiO_2, including nanosphere, nanosheet, nanotube and nanocable, or mesoporous structure have been developed to reduce the Li-ion diffusion length in the solid phase [9–13]. But the agglomeration and insufficient structural stability of nanomaterials are still a challenge for preparation of TiO_2 nanostructured materials with high quality and a potential risk of electrochemical performance degradation when used as an anode electrode material in LIBs. Assembling the nanomaterials into three-dimensional (3D) structures has proven to be an effective strategy to yield high packing density and good performance [14–17]. Coating with conductive materials like carbon is also a powerful approach to improve the rate performance [16]. There have been reports of TiO_2—C solid sphere [15,17] or TiO_2 hollow spheres [18,19] prepared through the template method for improved lithium-storage performance. However, constructing hollow 3D nanostructures of anatase TiO_2 with carbon coating through a template-free method remains a challenge.

Furthermore, a hierarchical nanostructure composed of mesopores in combination with macropores or larger mesopores favors fast mass transport and improves electrochemical performances in LIBs [20,21], electrochemical capacitors [22,23], electrochemical hydrogen storage [24,25], and fuel cells [26]. In particular, a hollow macroporous core-mesoporous shell nanostructure has been proven to be advantageous because it can serve as an electrolyte reservoir, greatly shortening the diffusion length for electrolyte ions, and resulting in considerably reduced resistance to mass transport [27–30].

Recently it was reported that the exposed facets of TiO_2 nanocrystals also have an important influence on their electrochemical/photoelectrochemical performance. Anatase TiO_2 crystals with a large percentage of active facets {001} show higher photocatalytic activity [31]. It is found that the TiO_2 nanosheets with exposed {001} facets possess fast lithium insertion/extraction kinetics since the Li-ion diffusion is more efficient along the [001] direction [32–35]. However, {101} facets are dominant in anatase TiO_2 due to its lower surface energy. Therefore, producing TiO_2 nanostructures with a high percentage of {001} facets could improve the rate capability in LIBs.

Inspired by the above, we prepared N-doped carbon-coated hollow urchin-like anatase TiO_2 spheres (HUTS@C) with a high percentage of {001} facets through a facile and scalable hydrothermal reaction followed by the coating of polypyrrole (Ppy) and carbonization. Hollow urchin-like TiO_2 spheres (HUTS) were developed from TiO_2 solid spheres based on a dissolution-recrystallization mechanism induced by an etching agent [36]. Ppy was used as the carbon source since it is a redox active conducting polymer, and could yield N-doped carbon [11,37], which can generate more defects in the resultant material [38]. The prepared HUTS with carbon coating (HUTS@C) possesses a nanorod assembled spherical structure with a hollow macroporous core which can serve as the electrolyte reservoir, offer fast diffusion paths for the electrolyte, and provide good accommodation of the strain produced during cycling. Highly exposed {001} facets also facilitate the fast intercalation/deintercalation of Li ions. The N-doped carbon coating can improve the electronic and ionic conductivity effectively. As expected, the tailored unique nanostructure demonstrates excellent electrochemical performance as an anode material for LIBs.

2. Experimental

2.1. Synthesis of HUTS

The HUTS was prepared based on the article by Pan et al. [36]. Solid TiO_2 spheres were firstly prepared by controlling the hydrolysis of titanium isopropoxide (TTIP) under room temperature. For a typical synthesis, 5 ml of TTIP was added to a mixed solution of ethanol (180 ml), acetonitrile (120 ml), ammonia (0.5 ml) and H_2O (1 ml) under vigorous stirring, followed by magnetic stirring for 6 h. The precipitate was collected by centrifuge and washed several times with ethanol and deionized water in sequence and then dried at 80 °C overnight. 1.5 g of solid TiO_2 spheres were dispersed in 50 ml of deionized water, and 0.1 g of NaF was introduced as an etching agent, followed by the addition of 0.45 g of polyvinyl pyrrolidone (PVP, $M_w = 30{,}000\ g\ mol^{-1}$). After 1 h of stirring, the suspension was transferred into a Teflon-lined stainless steel autoclave (100 ml), and maintained at 110 °C for 5 h in an oven. After the hydrothermal reaction, the autoclave was cooled naturally to room temperature. The white product was collected by centrifuge and washed with ethanol and water. After drying in air at 80 °C, HUTS was obtained.

2.2. Synthesis of HUTS@C

0.1 g of HUTS was dispersed into a solution of 200 ml of deionized water and 0.02 g of sodium dodecyl sulphate with ultrasonic application for 5 min, and then kept under vigorous stirring for 2 h. The solution was cooled in a refrigerator for 10 min, and then 0.1 ml of pyrrole was introduced. A solution containing 0.39 g of $FeCl_3{\cdot}6H_2O$ and 5 ml of H_2O was added as an oxidizing agent. Immediately, the mixture was covered and put under ultrasonic conditioning for 10 min and then stirred for another 2 h. The resulting HUTS@Ppy precipitate was centrifuged and washed with water. After drying in the oven at 50 °C overnight, HUST@C was obtained by the calcination of HUTS@Ppy at 700 °C for 3 h under N_2 flow with a ramping rate of $5\ °C\ min^{-1}$.

2.3. Materials characterization

Surface and structural characterizations were performed by various techniques, such as X-ray diffraction (XRD, Rigaku D/Max-2400) with Cu Kα radiation, scanning electron microscopy (FESEM, Hitachi S-4800) with an energy dispersive X-ray analyzer (EDS), and transmission electron microscopy (TEM, FEI Tecnai G^2 F30). N_2 adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP-2020 Gas Adsorption Analyzer. X-ray photoelectron spectroscopy (XPS) measurements were conducted in a Thermo VG ESCALAB250 spectrometer. Raman spectroscopy was recorded by Lab Ram HR800 with 1.96 eV (632.8 nm) excitation laser.

2.4. Cell preparation and electrochemical characterization

The HUTS@C composite powder (active material, 80 wt%) was ground with poly(vinylidene fluoride) (binder, 10 wt%) and acetylene black (conductive agent, 10 wt%), and mixed with small amount of N-methyl-pyrrolidone to make a homogenous slurry, which was then coated onto a piece of copper foil and dried under vacuum at 60 °C for 12 h. A coin-type cell was constructed with a metallic Li sheet as the counter and reference electrodes, and the as-prepared HUTS@C as the working electrode. 1 M $LiPF_6$/EC-DEC (1:1 by volume ratio) was used as the electrolyte. The cells were assembled in an argon-filled glove box (MB-10-G with TP170b/mono, MBRAU) and were aged for 12 h at room temperature prior to electrochemical tests.

The galvanostatic charge-discharge measurements were carried out by a battery test system (NEWARE BTS-610, Neware Technology Co., Ltd., China) at room temperature. The cut-off voltage window was 1.0 and 3.0 V (*vs.* Li/Li^+). Cyclic voltammetry (CV) testing was carried out on a CHI 660d electrochemical workstation at a scan rate of $0.1\ mV\ s^{-1}$. The electrochemical impedance spectrum (EIS) measurements were carried out in a frequency range from 0.01 Hz to 100 kHz with an amplitude of 5.0 mV.