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A peapod-inspired MnO@C core-shell design for lithium ion batteries

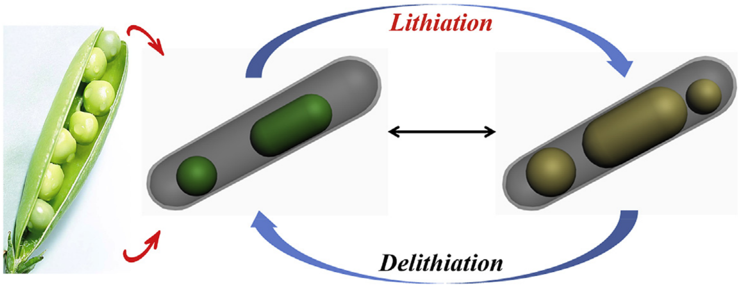
Shengbin Wang [a], Yalan Xing [a], Changlei Xiao [a], Huaizhe Xu [b], Shichao Zhang [a, *]

[a] School of Materials Science and Engineering, Beihang University, Beijing 100191, PR China
[b] Department of Physics, Beihang University, Beijing 100191, PR China

HIGHLIGHTS

- A peapod-inspired MnO@C core-shell anode has been successfully fabricated.
- The peapod structure possesses stable interface and high structural reversibility.
- The MnO@C exhibits superior electrochemical properties for Li ion storages.

GRAPHICAL ABSTRACT



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ABSTRACT

Inspired by the structure of peapod, MnO@C hybrid with internal void space has been prepared. In this bionic structure, the MnO nanoparticles are separated and confined in a conductive carbon sheath that leaves enough room for expansion and contraction during lithiation/delithiation process. Such peapod-like MnO@C can address the issues related to MnO dissolution, pulverization, and aggregation. As a result, the sample demonstrates superior electrochemical performances in terms of high reversible capacity, excellent high-rate capability, and good cyclability.

1. Introduction

Driven by emerging demands for high-performance energy storage system in consumer electronics and electric vehicles, extensive research has been conducted on high-capacity and high-stability electrode materials for lithium ion batteries (LIBs) [1–6]. MnO, with up to 756 mA h g^{-1} theoretical capacity, low conversion potential and voltage hysteresis, has shown a competitive superiority in LIBs as anode material [7–10]. However, successful implementation of MnO has been impeded by inferior electrical conductivity and large volume change during the electrochemical process [11–14]. Specifically, the tremendous repeating volume change during lithiation/delithiation process not only breaks the structural integrity and the interparticle electrical contact, but also destroys the as-formed solid-electrolyte interface (SEI), which will expose much fresh interface for side reactions with electrolyte that results in the limited cycle life and low Coulombic efficiency (Fig. S1) [8–15]. Recently, low-dimensional nanostructured MnO including nanorods, nanoparticles and nanotubes have attracted tremendous attention because of their fascinating mechanical, electrical, and optical properties [16–19]. By the merits of miniscule atomic scale thicknesses and unique structural strength, the

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* Corresponding author.
E-mail address: csc@buaa.edu.cn (S. Zhang).

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nanostructure not only possesses better mechanical stability to alleviate the structure and volume changes, but also can reduce the Li-ion diffusion length to enhance the reaction kinetics efficiently.

Although nanostructure could partly resolve some major problems and immensely extend cycle life, new fundamental challenges have introduced into the nanostructured electrodes. In the nanostructured MnO anode, the exposed large surface area increases side reactions with the electrolyte and lowers the Coulombic efficiency during cycling. Moreover, the reduced size to nanoscale also creates more interparticle space and surface, giving rise to high interparticle resistance to create barrier for the electron transport. These factors altogether hinder the achievement of high-performance electrode for LIBs. To address these problems, constructing internal void space and an advanced carbon layer is proposed and proven to be very powerful [15,20,21]. With the built-in void space and the elastic feature of carbon, the nanostructure electrode not only could effectively relieve the mechanical strain without breaking interparticle connection and structural integrity, but also could greatly enhance the conductivity and maintain chemically and mechanically stable SEI.

Here, inspired by the structure of peapod, we demonstrate a bionic structure for MnO anode (Fig. 1a). In this peapod-like MnO@C hybrid, the MnO nanoparticles are separated and encapsulated by the carbon sheath, with well-defined void space between the MnO and carbon. The overall synthetic procedure of peapod-like MnO@C involves three steps (Fig. 1b): (1) growing α-MnO_2 nanotubes *via* a hydrothermal method (Fig. S2); (2) coating polydopamine on the α-MnO_2 surface; (3) carbonizing and deoxidating in an inert gas to prepare peapod-like MnO@C. With this peapod-like design, several important challenging issues of bulk MnO electrode such as structure fracture, poor electronic conductivity, repeating SEI formation can be totally addressed. As a consequence, this type of MnO-based hybrid exhibits a maximum specific capacity of 934 mA h g^{-1} at rate of 0.3 A g^{-1} with a long cycle life, and an outstanding discharge/charge rate capability (470 mA h g^{-1} at 4 A g^{-1}), demonstrating a great potential as anode materials for LIBs applications.

2. Experimental section

2.1. Preparation of α-MnO_2 nanotubes

α-MnO_2 nanotubes are prepared by a facile hydrothermal synthesis method according to previous report [22]. $KMnO_4$ in deionized water (0.1 M, 75 mL) is prepared with ultrasonic agitation, and then 3 mL of HCl (37 wt.%) is added to the solution. The mixture is transferred into a Teflon-lined stainless steel autoclave, heated at 140 °C for 12 h. The α-MnO_2 nanotubes are then collected from the autoclave, washed thoroughly with distilled water and dried in air.

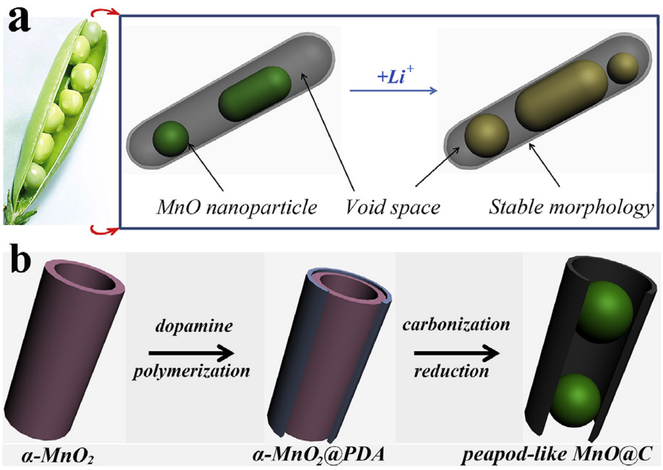

Fig. 1. (a) Three dimensional view of peapod-like MnO@C before and after electrochemical cycling, (b) Schematic illustration on the preparation of the peapod-like MnO@C.

2.2. Preparation of peapod-like MnO@C

Firstly, The as-prepared α-MnO_2 nanotubes precursor (0.2 g) are mixed with dopamine (0.1 g) in Tris-buffer solution (100 mL, pH 8.5) under stirring at room temperature for 24 h, generating a polydopamine coating. Afterwards, the precipitates, *i.e.* α-MnO_2@-polydopamine, are collected by suction filtration, washed by deionized water, and dried in air. Finally, the peapod-like MnO@C hybird are obtained by heating the α-MnO_2@polydopamine at 700 °C for 2 h with flowing N_2 atmosphere.

2.3. Characterization

2.3.1. Material characterization

The obtained samples were characterized by X-ray diffraction (XRD, Rigaku D/Max-2400, Cu Kα), scanning electron microscope (SEM, Hitachi S-4800), transmission electron microscopes (TEM, JEOL JEM-2010), Thermogravimetric analysis (TGA, NETZSCH STA 449C), Raman spectra (labRAM ARAMIS, $\lambda = 532$ nm) and X-ray photoelectron spectra (XPS, Thermo VG ESCALAB250). The specific surface area determination, pore size analysis are determined by nitrogen adsorption–desorption at 77 K using a Quantachrome Autosorb-1C-VP analyzer. The carbon and nitrogen contents are measured by a Vario EL cube organic element analyzer.

2.3.2. Electrochemical characterization

The electrochemical performance is examined by the use of Coin-type cells (CR 2032). The working electrode is fabricated by 80% peapod-like MnO@C, 10% acetylene black and 10% PVDF binder with the mass loading for around 2.5 mg cm^{-2}. Cells are assembled by the use of lithium foil as the anode, Celgard 2400 as the separator, 1 mol L^{-1} $LiPF_6$ in ethylene carbonate/diethyl carbonate/dimethyl carbonate (volume ratio of 1:1:1) as the electrolyte. Electrochemical data are collected by the use of LAND CT2001A test system (Galvanostatic discharge/charge, 0.01–3.0 V *vs.* Li^+/Li), CHI 660E electrochemical workstation (cyclic voltammograms, CV, 0.1 mV s^{-1} between 0.01 and 3.0 V), and Zahner IM6e electrochemical workstation (Electrochemical impedance spectra, EIS, 1 MHz–10 mHz).

3. Results and discussion

Fig. S3 shows the XRD pattern of the as-prepared hybrid. The sample shows strong diffraction peaks located at 34.9, 40.7 and 58.9°, which can be assigned to the face-centered cubic (*fcc*) MnO (JCPDS, 78-0424). No other characteristic peaks from impurities are observed, indicating the effective transformation from α-MnO_2 to MnO. The morphology and structure of the as-prepared hybrid are first investigated by SEM and TEM. As is shown in SEM image of Fig. 2a, the MnO-based material retained nanorod-like structure with several micrometers in length. Interestingly, from the TEM images (Fig. 2b and c), the MnO nanoparticles are encapsulated and well-confined in the carbon sheath, forming a peapod-like morphology. Such a structure can provide a large void space between the two adjacent nanoparticles. The carbon sheath, although only a few nanometres thick, firmly supports the peapod-like structure (Fig. 2d). To further understand the formation of