Urchin-like α-Fe$_2$O$_3$/MnO$_2$ hierarchical hollow composite microspheres as lithium-ion battery anodes

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HIGHLIGHTS

- Composite has been synthesized by using carbon as sacrificial templates.
- Hollow composite spheres are built from MnO$_2$ nanorods and Fe$_2$O$_3$ nanoparticles.
- Combining the advantages of Fe$_2$O$_3$ nanoparticles and MnO$_2$ nanorods.
- The composites exhibit high capacity and superior cyclic capability.
- Superior cyclic capability is relative to reinforced structural stability.

GRAPHICAL ABSTRACT
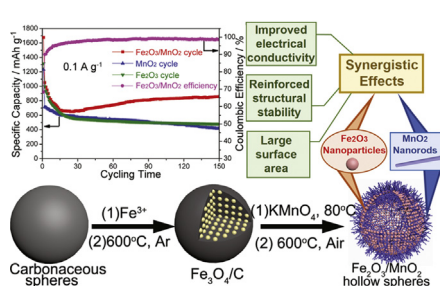
ARTICLE INFO

ABSTRACT

Urchin-like α-Fe$_2$O$_3$/MnO$_2$ hierarchical hollow composite microspheres have been synthesized by using carbon as sacrificial templates. By combining the advantages of Fe$_2$O$_3$ with high electrical conductivity and MnO$_2$ with high theoretical capacity, the urchin-like α-Fe$_2$O$_3$/MnO$_2$ composites present better electrochemical performances as a lithium ion battery anode compared with α-Fe$_2$O$_3$ hollow spheres and MnO$_2$ hollow spheres. The α-Fe$_2$O$_3$/MnO$_2$ composites exhibit high initial discharge capacity of 1531 mAhg^{-1} and excellent reversible capacity of 860 mAhg^{-1} after 150 cycles at 0.1Ag^{-1}. Furthermore, the composites retain a discharge capacity of 494 mAhg^{-1} after 500 cycles at 0.5 Ag^{-1}. The excellent performances may originate from reinforced structural stability, large surface area and good electrical conductivity. The urchin-like α-Fe$_2$O$_3$/MnO$_2$ composite material may serve as a potential anode material for lithium-ion battery.

1. Introduction

As we all know, lithium-ion batteries (LIBs) have been wildly applied to electrical automotive vehicles and other household appliances due to their excellent advantages [1,2]. However, the relatively low theoretical capacity of graphite anode materials (372 mAhg^{-1}) in LIBs limits their further applications in large-scale energy storage. For the sake of excellent performances, numerous kinds of anode materials have been explored. Among many materials, nanometer-sized transition metal oxides (TMOs) have been attracting research attention because of their wide availability, low cost, and especially higher special

theoretical capacities [3–5].

Manganese dioxide (MnO$_2$), as one of TMOs, is known as a quite promising material because of its low toxicity and natural abundance. However, for MnO$_2$ nanomaterials using as LIBs anode, there are some obvious drawbacks, for instance drastic volume variation during lithiation/delithiation, low electrical conductivity, and subsequent deterioration of electrochemical performances [6–9]. To overcome the above issues, two different strategies have generally been employed.

The first one is the controlled synthesis of TMOs hollow nanostructures. TMOs hollow nanostructures can offer more active sites for Li$^+$ storage due to their high surface area, and buffer cyclic variations

in volume due to their large hollow interiors, resulting in the outstanding electrochemical performances [10–12]. In particular, hierarchical hollow structures assembled from nanosized building units, such as nanoparticles and nanorods, are highly desirable because their electrochemical performances are more outstanding than those of both bulk particles and discrete nanoparticles [13–15]. Xie's group has reported that urchin-like MnO_2 hierarchical hollow structures assembled from nanorods exhibit better Li storage properties than discrete nanorods and solid urchins [16].

Another available route is to introduce another TMO into MnO_2. Recently, the hybridization of TMOs has aroused much attention because of the enhanced electrochemical performances of the composite compared with the individual component [17,18]. For instance, Wang et al. have reported that α-MoO_3@MnO_2 nanorods prepared by a facile two-step method exhibit outstanding electrochemical performances [19]. Qiu et al. have reported that $ZnCo_2O_4$/MnO_2 nanocone forests with a mesoporous, hierarchical core-shell structure by hydrothermally growing on 3D nickel foam possess excellent electrochemical performances in both supercapacitors and Li-ion batteries [20]. Liao et al. have reported that multifunctional TiO_2-C/MnO_2 nanowires with prominent Li^+ storage properties have been achieved by combining the advantages of TiO_2 with outstanding cyclic stability and MnO_2 with high theoretical capacity (1232 mAhg^{-1}) [21]. Zhong et al. have reported that NiO@MnO_2 microtube arrays with preeminent electrochemical performances have been synthesized by the anodic electrodeposition [3]. The aforementioned reports have indicated the composite nanomaterials can reinforce or modify the synergetic properties, and thereby enhance electrochemical performances. Among TMOs, iron oxide (Fe_2O_3) has been considered as a potential LIB anode material due to its natural abundance, low cost and relatively high theoretical capacity (1007 mAhg^{-1}) [22,23]. Specifically, owing to its relatively higher electrical conductivity compared with MnO_2, Fe_2O_3 nanoparticles can be used as an inserted matrix for MnO_2 to improve electrical conductivity, thus leading to the improved Li^+ storage properties.

In virtue of the above two strategies, the hierarchical hollow nanostructures can be introduced into Fe_2O_3/MnO_2 composite nanomaterials, which can improve cyclic stability and rate capability for LIBs, thus making the best use of the synergistic effect between MnO_2 and Fe_2O_3 nanosized building units. However, there is no report on the use of Fe_2O_3/MnO_2 hierarchical hollow composite microspheres (Fe_2O_3/MnO_2 HHCMs) as anode materials of LIBs.

Herein, we have synthesized α-Fe_2O_3/MnO_2 HHCMs by using carbonaceous spheres (CSs) as sacrificial templates. α-Fe_2O_3/MnO_2 HHCMs predominantly consist of uniform hollow spheres built from MnO_2 nanorods and Fe_2O_3 nanoparticles which support each other and thus reinforce the hollow structures [17,18]. Compared with the reported procedures on TMOs/MnO_2 composites [3,19–21], the present route has two main features: (1) No surfactants and organic solvents are used in the procedure; (2) the introduced Fe_2O_3 and MnO_2 materials, as the two nanocomponents of the composite, have two advantages, such as low cost and natural abundance, which are in favor of the practical application. By combining the advantages of Fe_2O_3 and MnO_2, Fe_2O_3/MnO_2 HHCMs exhibit better electrochemical properties compared with Fe_2O_3 hollow spheres and MnO_2 hollow spheres. It is noted that the hollow structure possesses outstanding stability without any collapse phenomenon after 150 cycles [17,24,25].

2. Experimental section

2.1. Preparation of Fe_3O_4@C spheres

Fe_3O_4@C spheres were achieved as described in the previously reported references [26–28]. CSs were firstly prepared through a reported sucrose-hydrothermal method [29,30]. Then, CSs (0.4 g) were saturated with iron (III) ion solution (30 mL, 2 M), and aged for 6 h. After that, the specimen was repetitively collected and washed with ultrapure water. The sample was subsequently annealed at 600 °C for 3 h with a slow heating rate of 1 °Cmin^{-1} under Ar atmosphere.

2.2. Synthesis of α-Fe_2O_3/MnO_2 HHCMs

The obtained powder of Fe_3O_4@C spheres (0.108 g) was first dispersed in $KMnO_4$ solution (30 mL, 0.03 g $KMnO_4$). Then, the suspension was stirred in a hot water bath at 80 °C for 4 h, and the specimen was centrifuged and repetitively washed with ultrapure water before drying in air. Finally, the product was obtained by thermally treating at 600 °C in air for 3 h with a slow heating rate of 1 °Cmin^{-1}.

2.3. Materials characterization

The samples were thoroughly characterized by transmission electron microscopy (TEM, FEI Tecnai F20) with energy-dispersive X-ray (EDX) spectroscopy, field emission scanning electron microscopy (FESEM, Hitachi S-4800), X-ray powder diffraction (XRD, Bruker D8 ADVANCE), X-ray photoelectron spectroscopy (XPS, ESCALAB 250, ThermoFisher Scientific USA), and thermogravimetrics (TG, DTG-60AH).

2.4. Electrochemical tests

The testing anodes were composed of the as-prepared hollow composites, acetylene black and poly (vinylidene fluoride) (PVDF) (w/w/w = 80:10:10). The loading mass of electrodes is ~1.1 mg cm^{-2}. Li foil and Cu foil were selected as counter electrode and current collector, respectively. The electrolyte was $LiPF_6$ (1 M) in a mixed solution of dimethyl carbonate, ethylene methyl carbonate and ethylene carbonate (v/v/v = 1:1:1). In an Ar-filled glove box, all of the above components were cautiously assembled into coin cells. The galvanostatic charging/discharging tests were performed on a LAND CT2001A battery tester.

3. Results and discussion

The synthesized process of α-Fe_2O_3/MnO_2 HHCMs is shown in Scheme 1. First of all, CSs are prepared by a conventional sucrose-hydrothermal method. The CSs have a mass of −OH, −CO = radicals, which can effectively absorb metal ions [29]. Fig. S1a presents TEM images of CSs with the size of around 1.3 μm. Subsequently, the CSs are penetrated by a portion of iron (III) ions and then heated at 600 °C under Ar atmosphere, resulting in the formation of Fe_3O_4/C spheres. As seen from Fig. S1b, XRD pattern of the sample can be assigned to Fe_3O_4 (JCPDS file No. 03-65-3107) [31,32], indicating the formation of Fe_3O_4/C spheres. Then, MnO_2 nanosheets constantly gather on the surface of the Fe_3O_4/C spheres through the redox reaction between $KMnO_4$ and the carbon of Fe_3O_4/C spheres (eq. (1)) [18,25,33]. It is noted that the generation of carbon after the calcination treatment in Ar is very important for the coating of MnO_2 due to the redox reaction between $KMnO_4$ and carbon. Finally, when Fe_3O_4/C@MnO_2 spheres are annealed in air (Figs. S1c–d), Fe_3O_4 in the Fe_3O_4/C@MnO_2 spheres is thoroughly oxidized to Fe_2O_3 (eq. (2)), the carbon in the Fe_3O_4/C@MnO_2 spheres turns to CO_2 and MnO_2 nanosheets convert to MnO_2 nanorods, resulting in the formation of α-Fe_2O_3/MnO_2 HHCMs (Fig. 1).
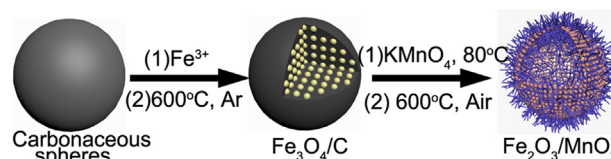
Scheme 1. The synthesized process of α-Fe_2O_3/MnO_2 HHCMs.