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One-pot facile synthesis of hierarchical hollow microspheres constructed with MnO\textsubscript{2} nanotubes and their application in lithium storage and water treatment

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Semiconductor \(\alpha\)-MnO\textsubscript{2} hierarchical hollow microspheres constructed with nanotubes have been facilely synthesized through a bubble template-based self-scrolling solution route. An energy-minimizing-driven self-assembly of \(\alpha\)-MnO\textsubscript{2} nanoparticles on the base of O\textsubscript{2} bubbles is responsible for the formation of hierarchical hollow microsphere structure. The as-obtained \(\alpha\)-MnO\textsubscript{2} products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and UV-vis-NIR spectrophotometry. The Li ion storage and water treatment performances of these \(\alpha\)-MnO\textsubscript{2} hierarchical hollow microspheres constructed with nanotubes were tested. A discharge capacity as high as 983 mA h g\textsuperscript{-1} during the 30\textsuperscript{th} cycle has been delivered at a current density of 300 mA g\textsuperscript{-1}. These as-prepared samples were also used as adsorbents in water treatment, and showed an excellent ability to remove organic pollutants without any other additives.

1. Introduction

The preparation of nanomaterials with defined structures, composition, and tailored properties, has attracted immense scientific and technological interest due to the fact that morphology and structures play a very important role in determining the catalytic, molecular adsorptive, magnetic and electric properties of materials.\textsuperscript{1–2} The hollow and porous structures constructed using nanostructured subunits also show distinctive properties, different from the individual nanoparticles, and have promising applications such as catalysts, delivery vehicles, energy storage, chemical and biological sensors \textit{etc}.\textsuperscript{3–7} Therefore, the creation of a combinatorial structure would be of great significance. Manganese oxides are of considerable importance in technological applications, including ion-exchange, molecular adsorption, catalysis, and electrochemical batteries owing to their structural flexibility combined with novel chemical and physical properties. When the MnO\textsubscript{2} octahedral units are linked in different ways, MnO\textsubscript{2} can exist in several crystallographic forms, such as \(\alpha\), \(\beta\), \(\gamma\), and \(\delta\)-type, \textit{etc}.\textsuperscript{8–9} Among them \(\alpha\)-MnO\textsubscript{2} is used as catalysts, molecular absorbents and electrode materials in Li/MnO\textsubscript{2} batteries.\textsuperscript{10–12} It is well-known that MnO\textsubscript{2} with hollow interiors have attracted significant interest owing to their unique properties, such as high specific surface area, low density, and good permeation.\textsuperscript{13–17} Lately, much research effort has been directed toward synthesis of hollow and core–shell structures \(\alpha\)-MnO\textsubscript{2}. Zhou \textit{et al}. reported that three types of hollow urchin like \(\alpha\)-MnO\textsubscript{2} nanostructures have been synthesized through a facile hydrothermal method.\textsuperscript{18} Fei and co-workers reported a simple controlled preparation of hierarchical hollow microspheres and micropores of MnO\textsubscript{2} nanosheets through self-assembly with an intermediate crystal-templating process.\textsuperscript{19} Wang’s group has reported that a 3D macro-assembly with \(\alpha\)-MnO\textsubscript{2} nanowires as flexible building blocks was obtained by a simple hydrothermal method.\textsuperscript{20} The sample with an interconnected open porous structure shows excellent mechanical strength, selective adsorption of cationic dyes and some certain types of toxic heavy metal ions. Li’s group demonstrate a facile exfoliation and scrolling approach to fabricate \(\alpha\)-MnO\textsubscript{2} nanotubes.\textsuperscript{21} Manganese oxides with hierarchical hollow microspheres constructed with some unique subunits such as one-dimensional (1D) hollow nanotubes might be good candidates for molecular absorbents and Li ion storage electrode materials, yet few studies have been carried out on these research areas due to the distinct difficulties in synthesis of such microstructured MnO\textsubscript{2}. Moreover, morphology-controlled synthesis of manganese oxide nanostructures might offer an avenue to understanding the role that morphology plays in affecting the corresponding molecular absorption and ion storage performances.

In the present study, we report on the facile synthesis of a novel hierarchical structure of hollow microsphere \(\alpha\)-MnO\textsubscript{2} with...
spherically aligned nanotubes on a large scale. At the same time, the formation mechanism of hollow microsphere-structured α-MnO₂ and the Li ion storage and molecular absorption performances of these synthesized hierarchical products are presented and discussed. A discharge capacity as high as 983 mA h g⁻¹ during the 30th cycle has been delivered at a current density of 300 mA g⁻¹. Water treatment trials confirmed that these hierarchical hollow microspheres constructed with MnO₂ nanotubes exhibited high rates and removal capacity of anionic dye, Congo red from aqueous solutions without adjusting the pH value. These excellent capabilities of Li-ion storage and Congo red absorption ability are related to several structural features including the hollow interior for enhancement of the electrolyte/electrode interaction, the small diameter of nanotube subunits, and hierarchical microstructure with high Brunauer–Emmett–Teller (BET) specific surface area.

2. Experiment section

Preparation of MnO₂ hierarchical hollow microspheres constructed with nanotubes

All chemical reagents used in this experiment were of analytical grade. A typical synthesis process is as follows: 2–4 mmol of KMnO₄ and 5–10 mmol concentrated HCl were dissolved in 30–60 mL of distilled water to form a homogeneous solution. After the addition of 4–8 mL of 30% H₂O₂, the reaction mixture was loaded into a Teflon-lined, stainless steel autoclave. The autoclave was sealed and heated in an oven at 140 °C for 20 h. When cooled to room temperature, a resulting brown-black precipitate was collected by centrifugation; washed with distilled water; and finally, dried at 100 °C overnight.

Characterizations

The as-synthesized samples were examined by X-ray diffractometry (XRD) measurement on a Rigaku-DMax 2400 diffractometer equipped with graphite monochromatized CuKα (λ = 1.5406 Å). The morphology of the samples was investigated by using a scanning electron microscope (SEM, Hitachi S-3500N). The transmission electron microscopy (TEM) and high resolution transmission electron microscope (HRTEM) images were recorded on a Philips CM200/FEG transmission electron microscope using an accelerating voltage of 200 kV. The N₂ adsorption/desorption isotherm was obtained at 77 K using Beishide Instrument-ST, 3H-2000PS2.

Electrochemical measurement

The electrochemical performances of the as-prepared products were measured by using CR2025 coin cells at 0.01–3.0 V with NEWARE-BTS battery test system. For the preparation of the working electrode, a mixture of MnO₂ hollow microspheres, carbon black, and polyvinylidene fluoride (PVDF) in the weight ratio of 80 : 15 : 5 was ground in a mortar with N-methyl-2-pyrrolidone (NMP) as solvent to make slurry. A Li foil was used as the counter electrode and a solution of 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1 : 1 in volume) was used as electrolyte. The charge/discharge curves and cycling capacity were evaluated by NEWARE-BTS battery tester in the cut-off voltages of 0.01 and 3.0 V.

Water treatment experiment

Commercial γ-Fe₂O₃ nanoparticle powder (20–30 nm) was purchased from Alfa Aesar Chemicals Co. Commercial MnO₂ (20–30 μm) used was obtained from Beijing Chemicals Co. (Beijing, China). A taper flask (capacity 50 mL) was used as the reactor vessel. 20 mg of the adsorbent sample was added to the system containing 20 mL Congo red (C₃₂H₄₂N₆O₆S₂Na₂, Amresco Inc.) solution (100 mg L⁻¹) under stirring. A Hitachi U-3010 spectrophotometer was used to record the UV/Vis spectra of various samples and different intervals.

3. Results and discussion

The phase and purity of the products were examined by XRD technology. The XRD pattern of the MnO₂ nanotubes with hollow microsphere shape is shown in Fig. 1. All the diffraction peaks can be indexed as the tetragonal phase (space group: I4/m) of α-MnO₂ with lattice constants of a = 9.782 Å and c = 2.681 Å, which are in accordance with the standard data [JCPDS no. 44-0141]. No other phase was detected in Fig. 1 indicating the high purity of the final products. The small crystallite size of the MnO₂ nanotube units are evidenced by the broadening intensity of the diffraction peaks.

The morphology and microstructure of the as-prepared α-MnO₂ products were studied by SEM images as shown in Fig 2. Fig. 2a shows a panoramic SEM image of the product, which is composed of uniform microspheres and is present in high quantity. A magnified SEM image of the sample in Fig. 2b indicates that these α-MnO₂ microspheres look like some natural urchins, with diameters of 2–4 μm and numerous 1D nanostructures compactly growing around their surfaces. Further SEM observation indicates that the obtained α-MnO₂ microspheres have hollow interiors. The magnified SEM images (Fig. 2c and d) show that some broken MnO₂ hierarchical hollow microspheres exist in the product. The broken microspheres presented in high-magnification SEM image (Fig. 2d) indicate that the as-presented α-MnO₂ hierarchical microspheres are hollow.

![Fig. 1 XRD patterns of α-MnO₂ hierarchical hollow microspheres constructed with 1D nanotubes.](image-url)
To determine the microstructure of the $\alpha$-MnO$_2$ hollow microspheres constructed by nanotubes, some samples were examined in detail by TEM. Fig. 3a shows the TEM image of the spheres with diameter of about 3 µm. A relatively dark contrast between the surface and center of the sphere is observed. It indicates a hollow structure with the shell consisting of the nanotubes array. The nanotubes are knitted loosely with each other, exhibiting the integrality and consistency of these spherical architectures generated by mechanical interaction between nanotubes. This is in agreement with the SEM observation for the broken spherical shell. The detailed construction of the nanotubes on the spherical shell was shown in Fig. 3b. The outer diameter of the nanotubes ranges between 30 and 80 nm and is very uniform along the individual nanotubes. The wall thickness at the nanotube end is typically between 10 and 20 nm. However, the diameter of the inner cavity is not uniform along the nanotube (Fig. 3c), and it gradually reduces from one end to the other. In fact, the inner cavities (Fig. 3c) rarely extend through the entire nanotube. Clearly observation indicates that these small MnO$_2$ nanotube subunits were formed by self-scrolling nanosheets during the hydrothermal crystallization route, which is the typical formation mechanism of nanotubes with layered crystallographic structures.$^{21}$ The selected area electron diffraction pattern (inset Fig. 3d) taken from the red rectangular area (Fig 3c) shows the nanotubes are single-crystal. The pattern (inset Fig. 3d) can be indexed as the $\alpha$-MnO$_2$ recorded from the [001] zone axis with the same crystalline parameter as calculated results from XRD measurement. Fig. 3d is a HRTEM image of this $\alpha$-MnO$_2$ single-crystalline and nanoporous nanotube. The fringes with lattice spacing of about 0.49 nm correspond to the (200) plane of tetragonal $\alpha$-MnO$_2$ structure. Combining HRTEM and

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**Fig. 2** SEM images of $\alpha$-MnO$_2$ hierarchical hollow microspheres constructed with 1D nanotubes: (a and b) panoramic SEM images; (c and d) magnified SEM images with typical open hollow urchin of product.

**Fig. 3** (a) Low-magnification TEM image of $\alpha$-MnO$_2$ hierarchical hollow microspheres constructed with 1D nanotubes; (b) high-magnification TEM image which clearly shows that MnO$_2$ hollow microspheres are constructed by nanotubes; (c) TEM image of several MnO$_2$ nanotube subunit; (d) HRTEM image with clearly resolved fringes of (200) planes. The inset of d shows the ED pattern taken from the red rectangular area.

**Fig. 4** TEM images of the process of $\alpha$-MnO$_2$ spheres formation at different hydrothermal time: (a) and (b) 2 h; (c) and (d) 6 h, HRTEM image shows that the platelet trends to be exfoliate into thinner and scrolled platelet; (e) and (f) 12 h.
ED techniques, the axis direction of the \(\alpha\)-MnO\(_2\) nanotubes could be determined as [001] growth.

In order to understand the effect of reaction time on the microstructure and morphology of samples, time-dependent experiments were carried out and the resultant products were analyzed by TEM. The morphology of samples obtained by hydrothermal reaction for 2 h is shown in Fig. 4a and b, which reveals that the sample has a flower-like morphology with 300 to 400 nm diameter. The TEM image (Fig. 4b) demonstrates that the products are built up nanosheets with 10–20 nm thick. Meanwhile, from the TEM and HRTEM images (Fig. 4c and d) of MnO\(_2\) nanoflowers treated for 6 h, it was found that the platelets tended to be exfoliated into thinner platelets. Further increasing the reaction time to 12 h, scrolling nanotubes (Fig. 4e and f) began to form. It can be revealed that not all of the samples (Fig. 4e and f) have been transformed into nanotubes, for part of nanotubes not being completely scrolled. When increasing the hydrothermal reaction time (Fig. 3), the ratio of nanotubes has been further improved.

On the basis of the above observation, the formation of \(\alpha\)-MnO\(_2\) hierarchical hollow microspheres constructed with nanotubes can be explained by a bubble template-based self-scrolling solution route. The bubble template mechanism has been considered as effective interpretation for the formation of hollow inorganic materials.\(^{23–27}\) As illustrated in Fig. 5, after initial nucleation, the MnO\(_2\) nuclei will grow into nanoparticles (step a). These nanocrystals have a tendency to aggregate due to their high surface energies, and grow by the effect of Ostwald ripening, transformed irreversibly into larger MnO\(_2\) nanoparticles. At the same time, lots of bubbles of O\(_2\) generated in situ (produced by the decomposition of H\(_2\)O\(_2\) in the hydrothermal environment) in the reaction provide the aggregation center (step b). Driven by the minimization of interfacial energy, small MnO\(_2\) nanocrystals may aggregate and grow by the effect of Ostwald ripening, firstly transformed irreversibly into layered MnO\(_2\) nanosheets, and then self-scrolled into 1D nanotubes (driven by the intrinsically layered crystallographic structure of layered manganese dioxide precursors\(^{21,28}\)) around the gas-liquid interface between bubble and solvent (the top-inset of Fig. 5). Therefore, finally \(\alpha\)-MnO\(_2\) hollow microspheres constructed by nanotubes were finally achieved (step c). The presence of H\(_2\)O\(_2\) in a reaction mixture plays a crucial role for the nanotubes formation. When the reaction was carried out under the same conditions but without H\(_2\)O\(_2\) in the reaction mixture, unassembled individual MnO\(_2\) nanotubes were grown instead of hierarchical hollow microspheres constructed with nanotubes (Fig. 6), which is mainly caused by the lack of plenty gas O\(_2\) bubble centers.

The surface area of these \(\alpha\)-MnO\(_2\) hierarchical hollow microspheres constructed with nanotubes was measured using the Brunauer–Emmett–Teller (BET) method. Fig. 7 shows the N\(_2\) adsorption/desorption isotherms at 77 K and the pore size distribution by the Barrett–Joyner–Halenda (BJH) method. The adsorption/desorption isotherms (Fig. 7a) can be classified as a typical IV isotherm with a hysteresis loop, which suggests the presence of a mesoporous structure. BET specific surface area of 174.7 m\(^2\) g\(^{-1}\). The shape of the pore distribution curve indicates that these hollow \(\alpha\)-MnO\(_2\) spheres constructed by nanotubes are mesoporous materials, and display a wide pore size distribution in the range 2–20 nm (Fig. 7b). The high specific surface area of 174.7 m\(^2\) g\(^{-1}\) would be very beneficial for Li ion storage and adsorbing and removing organic contaminants in waste water. Such hierarchical microstructures are attractive for energy storage application due to their hollow interior and the small diameter of the nanotube subunits.

As compared with other metal-oxide electrode materials for Li-ion batteries, MnO\(_2\) has attracted much more attention because of its low cost, low toxicity, environmental friendliness, and nature abundance.\(^{29–35}\) The finally hierarchical \(\alpha\)-MnO\(_2\)
hollow microspheres composed of small nanotubes were tested as the anode materials for Li-ion batteries in half cells. Though the diameter of these \(\alpha\)-MnO\(_2\) hollow microspheres is approximate several micrometers, these porous hollow microspheres consist of distinct small nanometer-sized nanotubes, which shorten distances for Li ion and electron transport. Fig. 8a shows the first 30th discharge/charge curves (i.e., voltage vs. capacity) at a current density of 300 mA g\(^{-1}\) and a temperature of 25 °C. A distinct voltage plateau at 0.4 V is the typical characteristic of MnO\(_2\)\(^{21,36}\). These hierarchical \(\alpha\)-MnO\(_2\) hollow microspheres exhibit a large initial discharge capacity of 983 mA h g\(^{-1}\) and show a very high reversible capacity of 720 mA h g\(^{-1}\) at a current density of 300 mA g\(^{-1}\) (Fig. 8a). The irreversible capacity in the first few cycles could be mainly due to the partially irreversible MnO\(_2\) conversion reaction with Li and the formation of the solid electrolyte interface (SEI) in the first few lithiation and delithiation cycles.\(^{21,36}\) Fig. 8b shows the discharge and charge capacity versus cycle number for the electrode fabricated by these hierarchical \(\alpha\)-MnO\(_2\) hollow microspheres composed of nanotubes at a current density of 300 mA g\(^{-1}\), which exhibits that the reversible capacity was stable after 30 cycles. Except the first cycle (about 983 mA h g\(^{-1}\)), the other twenty-nine cycles almost maintained constant at approximate 700 mA h g\(^{-1}\), which shows small irreversible capacity, high reversible capacity and good cycle life. The Li ion storage performance of these hierarchical \(\alpha\)-MnO\(_2\) hollow microspheres composed of small nanotubes are superior to \(\alpha\)-MnO\(_2\) hollow urchins constructed with nanorods\(^{12}\) and \(\gamma\)-MnO\(_2\) hollow microspheres constructed with nanoparticles.\(^{33}\) The superior electrochemical performances of the \(\alpha\)-MnO\(_2\) product can be attributed to its large surface area, 3D hierarchical hollow microsphere morphology, 1D nanotube subunit shape, and its 2 × 2 tunnel structure, which decreased the effective diffusion path and increased the effective space for insertion and extraction of Li ions.\(^{37–39}\)

Types of transition metal oxides have been found to effectively remove organic waste from water by adsorption and subsequent catalytic combustion at room temperature.\(^{40,41}\) Water treatment experiments were generally carried out in the neutral system, which is beneficial to future practical application. As an example of potential applications, the prepared \(\alpha\)-MnO\(_2\) hollow spheres constructed by nanotubes were used as an adsorbent in wastewater treatment. Congo red is an example of an anionic secondary diazo dye and has been considered as a primary toxic pollutant in water resources. Fig. 9a illustrates the time-dependent absorption spectra of the Congo red solution absorbed by the hollow \(\alpha\)-MnO\(_2\) microspheres, and the
characteristic absorption of Congo red approximately 500 nm was used to monitor the process of adsorption. When the initial concentration of Congo red in water solution is 100 mg L\(^{-1}\), the as-obtained \(\alpha\)-MnO\(_2\) spheres could remove about 96% of the Congo red without any additives at room temperature, as shown by the photo and UV/Vis adsorption curves at different times in Fig. 9a.

At the same time, the intensity of the peak became too weak to be observed, suggesting the high efficiency for removing Congo red after only 4 min. The color of the suspension (the inset of Fig. 9a) changes gradually, demonstrating that the Congo red is adsorbed. The enhancement of the adsorption rate originates from the \(\alpha\)-MnO\(_2\) hollow spherical supports, which provide a high concentration environment of organic molecules around the adsorbents. This means that more effective adsorption sites are obtained and an increase in the surface complexation rate of hydrogen bonding and hydroxyl groups present on the surface of the as-prepared \(\alpha\)-MnO\(_2\) and the amine groups of Congo red molecules in the solution occurs.\(^{42}\) As comparison experiments, we selected the commercial MnO\(_2\) and \(\gamma\)-Fe\(_2\)O\(_3\) nanoparticles to detect the removal capacity of Congo red species, respectively.\(^{43,44}\) We took 30 mg of each of the above samples and the same amount of \(\alpha\)-MnO\(_2\) hierarchical hollow microsphere sample to remove the 20 mL.

Congo red water solution (100 mg L\(^{-1}\)) at pH 7.6. UV-vis absorption spectroscopy was used to record the adsorption behavior of the solution. It is shown in Fig. 9b that the as-prepared \(\alpha\)-MnO\(_2\) hierarchical hollow microsphere product has obviously better removal ability than the commercial MnO\(_2\) or commercial \(\gamma\)-Fe\(_2\)O\(_3\). Specially, our prepared MnO\(_2\) hierarchical hollow microspheres constructed with nanotubes have faster dye removing ability than that of previous MnO\(_2\) hierarchical hollow microspheres and microcubes constructed with nanosheets.\(^{41}\) This might be ascribed to the unique hierarchical hollow microstructure, high specific surface area, and subunit nanotube shape of as-obtained MnO\(_2\) products, which provide a new and more efficient material for the application in organic water treatment. The stability of the sample during the adsorption process is crucial to its application. Herein, the \(\alpha\)-MnO\(_2\) hollow microspheres containing Congo red could be regenerated by combustion at 300 °C in air for 4 h. As shown in Fig. 9b, the regenerated materials could retain almost the same adsorption performance in the second, third and fourth regenerations. The electrostatic attraction between the \(\alpha\)-MnO\(_2\) surface and the Congo red species in solution at pH 7.6 was responsible for the dye removal.\(^{45}\) Therefore, the enhanced performance should be attributed to the distinct morphology construction with hollow sphere and tube structures.

4. Conclusions

In summary, hierarchical hollow microspheres of \(\alpha\)-MnO\(_2\) self-organized from small nanotubes have been synthesized under facile hydrothermal conditions via bubble template-based self-scrolling route. Such well-defined microstructures can effectively accommodate the volume change and shorten the diffusion path of Li ion and electrons when used as anode electrode material, leading to superior Li ion storage performance, e.g. a discharge capacity as high as 983 mA h g\(^{-1}\) is delivered during the 30\(^{th}\) cycle at a current density of 300 A g\(^{-1}\). The as-synthesized \(\alpha\)-MnO\(_2\) hollow microspheres constructed by nanotubes also exhibit a high and stable performance to remove an organic pollutant in waster water. This kind of material will probably have potential applications in catalysis, sensors, and other nanodevices.

Acknowledgements

The authors gratefully acknowledge the financial support of Special Foundation of University of Science and Technology Liaoning (2011ZX14), Foundation of Anshan Administration of Science & Technology (no. 2013MS27), the Scientific Research Foundation of Educational Department of Liaoning Province and National Natural Science Foundation of China (L2013122, 51202207).
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