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One-step solution-based catalytic route to fabricate novel α-MnO_2 hierarchical structures on a large scale†

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A new type of hierarchical structure, a core-shell structure with spherically aligned nanorods, was prepared *via* a simple room-temperature solution-based catalytic route in the case of α-MnO_2.

In recent years, microscale inorganic materials with one-dimensional (1D), hollow and core-shell structures have attracted considerable attention, for their structural characteristics endow them with a wide range of potential applications. The 1D nanostructures exhibit superior electrical, optical, mechanical and thermal properties, and can be used as fundamental building blocks for nano-scale science and technology.[1–4] The core-shell particles and hollow spheres constructed using nanostructured materials also show distinctive properties, different from the individual nanoparticles, and have promising applications such as catalysts, delivery vehicles, photonic materials, chemical and biological sensors *etc.*[5–9] Therefore, the creation of a combinatorial structure including the above three kinds of structure would be of great significance. And such a kind of hierarchical structure is expected to be used as a versatile material in a broader field. Recently, a lot of effort has been focused on the integration of nanorods/nanowire as building blocks into three-dimensional (3D) complex superstructures. For example, hierarchical ZnO nanostructures, penniform $BaWO_4$ nanostructures, a trigonal Se nanowire network and dandelion-like CuO nanostructures have been successfully prepared.[10–13] These results not only provide feasible ways to assemble 1D nanostructures for future microscale functional devices but also offer opportunities to explore their novel collective properties. However, it is still a challenging task to integrate a hierarchical structure including both core-shell structure and spherically aligned 1D nanostructures.

Manganese dioxide has many kinds of polymorphs, such as α-, β-, δ- and ε-type, offering attractive chemical and physical properties, when the basic unit $[MnO_6]$ octahedron links in different ways. Among them, α-MnO_2 is widely used as catalysts, ion or molecular sieves and electrode materials in Li/MnO_2 batteries.[14–16] In this communication, we provide a simple room-temperature solution-based catalytic route to fabricate a novel hierarchical structure of α-MnO_2, core-shell spheres with spherically aligned nanorods on a large scale. To the best of our knowledge, this kind of hierarchical structure has never been observed before.

Analytical grade $MnSO_4{\cdot}H_2O$ (0.3380 g, 2 mmol), $(NH_4)_2S_2O_8$ (0.4564 g, 2 mmol) and 2 mL concentrated sulfuric acid were mixed in 50 mL distilled water at room temperature. Then 1 mL of 10 mL $AgNO_3$ (0.1052 g, 0.059 mmol) solution was added. After the homogeneous solution was allowed to stand for 1–2 days, the products were filtered off, washed with absolute ethanol and distilled water respectively for several times, and then dried in vacuum.

The X-ray powder diffraction (XRD) analysis was performed on a Japan Rigaku D/max-γA X-ray diffractometer equipped with graphite monochromatized high-intensity Cu-Kα radiation (λ = 1.54178 Å), using an operation voltage and current of 50 kV and 100 mA, respectively. All the peaks of the XRD pattern in Fig. 1 could be clearly indexed to the pure tetragonal phase of α-MnO_2 (JCPDS 44-0141) with lattice constants a = 9.784 Å, c = 2.863 Å. No peaks for other type or amorphous MnO_2 were observed in the XRD patterns, indicating high purity and crystallinity of the final sample.

The morphologies of the products were then studied by the field emission scanning electron microscope (FESEM, JEOL JSM-6700F SEM). Fig. 2a indicated that the sample consisted of microscopic spheres with diameters of 2–3 μm and presented in high quantity. The magnified FESEM image (Fig. 2b) showed that nanorods with uniform diameters around 30–40 nm were fixed on the surfaces of the spheres, and they were densely parked and spherically aligned. After 10 minutes' ultrasonic treatment of the products, many spheres were broken, as shown in Fig. 2c, revealing the core-shell nature of these spheres. The diameters of these cores were around 1.4–2.2 μm, and each core occupied 60–90% volume in a sphere. Careful observations on a typical "opened" core-shell structure with a large core are shown in Fig. 2d, indicating that the core was constructed from tightly aggregated nanoparticles. The inset of Fig. 2d is the typical morphology of the shell. From it one can see that the nanorods

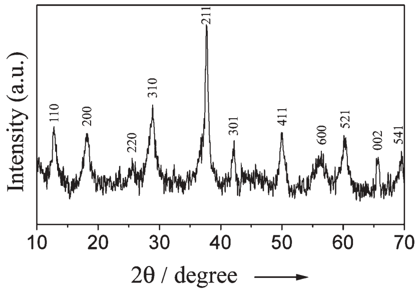

Fig. 1 XRD pattern of the prepared α-MnO_2 sample.

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† Electronic supplementary information (ESI) available: additional TEM and FESEM studies of the core-shell structure; XPS data of prepared product; and XRD patterns of intermediate products. See http://www.rsc.org/suppdata/cc/b4/b414204g/

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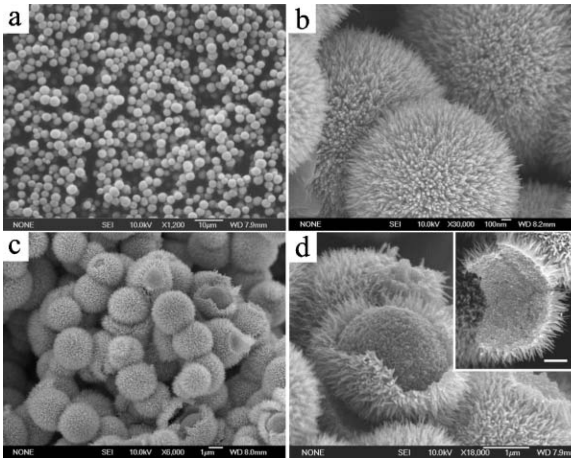

Fig. 2 a) Low magnification and b) high magnification FESEM image of the prepared product; c) low magnification and d) high magnification FESEM image of the prepared product after 10 min ultrasonic treatment. The inset in d) is the FESEM image of a typical shell separated from the core-shell structures. The scale bar is 400 nm.

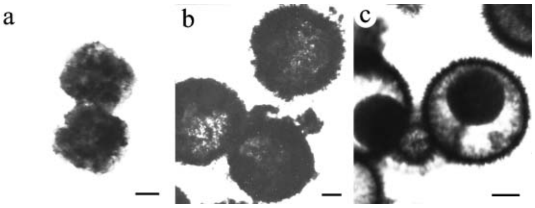

Fig. 3 Typical TEM images of the products prepared with different experimental time. (a) 6 h; (b) 12 h; (c) 24 h (final product). All the scale bars are 500 nm.

were grown from a thin shell (*ca.* 30–50 nm), and the lengths of these nanorods were *ca.* 200–300 nm (more information in ESI†).

The chemical reaction in the process to obtain α-MnO_2 core-shell structures could be formulated as follows:

$$\mathrm{MnSO_4 + (NH_4)_2S_2O_8 + 2H_2O \xrightarrow{Ag^+}}$$
$$\mathrm{\alpha - MnO_2 + (NH_4)_2SO_4 + 2H_2SO_4}$$

The Ag^+ was used as catalyst to help the reaction proceed at room temperature, while it generally needed higher temperature (above 100 °C) without catalyst Ag^+.[17] Herein, it was found that the existence of Ag^+ was essential for the formation of α-MnO_2 core-shell structures in our experiments. Only with catalyst Ag^+ could the core-shell structures be obtained. Variations in other experimental parameters such as replacing $(NH_4)_2S_2O_8$ by $K_2S_2O_8$, or changing the reactants proportions and amounts, had little effect on the final product. On the other hand, the concentration of catalyst Ag^+ had a great effect on the reaction rate. For example, the formation of α-MnO_2 core-shell structures needed about 100 h if the amount of Ag^+ decreased to 10% of that used in the described experiment.

Considering no additional templates were added in the formation process, the α-MnO_2 nanorods were thought to be epitaxially grown from the shell due to the growth habit of this crystal.[18,19] In order to investigate the formation process of the core-shell structure, samples which had reacted for 8 h, 16 h and 24 h (final product) were respectively studied by transmission electron microscopy (TEM, Hitachi Model H-800) and XRD. Three obvious evolution stages could be clearly observed and are shown in Fig. 3. In the initial stage, many colloids loosely adhered with a spherical shape, shown in Fig. 3a. Fig. 3b shows many nanorods have epitaxially grown from the surface of these spheres. Meanwhile the XRD analysis of these two samples showed that they both contained many amorphous components (see ESI†). Fig. 3c is the TEM image of the final products shown as the final stage. From it one can see the colloids in the sphere tightly aggregate together to form a core, separating from the shell. Correspondingly, the amorphous components disappeared in the XRD patterns (Fig. 1). From the observed morphologies and XRD patterns of products in different stages of evolution, it was possible to interpret the formation mechanism of the hierarchical structures as follows: (1) MnO_2 colloids are initially formed under the synthetic condition with catalyst Ag^+. And the initially formed colloids are loosely adsorbed together with a spherical appearance; (2) As the reaction proceeded, the reaction rate slowed down with the decrease of the reactants' concentration. As a result, the whole system was inclined to provide a thermodynamically stable environment. The newly formed MnO_2 colloids tended to nucleate and grow larger. Therefore, α-MnO_2 nanorods were epitaxially grown on the surface based on its one-dimensional growth habit. This process was very similar to recent work reported by Xia *et al.* on the catalytic growth of Pt nanowires.[20] (3) The loosely adhered colloids with many amorphous components in the spheres had a tendency to be gradually crystallized. As the crystallization proceeded, the spheres were inclined to shrink. Since the surface has been well-fixed by the nanorods, the shrinkage was apt to separate the sphere into two parts, the core and the shell. It was thought that the interstice between the core and shell resulted from both the shrinkage and rearrangement induced by the crystallization of colloids.

In summary, a one-step solution-based catalytic route was successfully promoted to synthesize a novel hierarchical structure of an α-MnO_2, core-shell structure with spherically aligned nanorods at room temperature on a large scale. The characterization, evolution process and possible formation mechanism of the hierarchical structure have also been investigated. This simple catalytic method casts new light on the development of new superstructures.

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