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General Synthesis and Lithium Storage Properties of Metal Oxides/MnO_2 Hierarchical Hollow Hybrid Spheres

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Metal oxides/MnO_2 hierarchical hollow hybrid nanostructures have attracted significant attention because of their wide potential applications. However, the exploration of a general synthetic approach for fabricating hierarchical hollow hybrid nanostructures is still a great challenge. Herein, a "penetration-carbonization and reduction-coating–annealing" route is presented for the generalized synthesis of metal oxides/MnO_2 hierarchical hollow hybrid spheres, including NiO/MnO_2, Co_3O_4/MnO_2, and CuO/MnO_2. Because of the unique hierarchical hollow hybrid nanostructures, NiO/MnO_2 nanomaterials possess a desirable capacity (1520 mA h g^{-1}) and outstanding cyclic stability (909 mA h g^{-1} at the 200th cycle) as Li-ion battery anode materials. The work reported herein can not only pave the way for the generalized synthetic strategy of metal oxides/MnO_2 hierarchical hollow hybrid nanostructures, but also provide a promising application of NiO/MnO_2 nanomaterials for Li-ion battery anode.

1. Introduction

Lithium-ion batteries (LIBs) have been receiving worldwide interests because of the increasing demands of reliable energy sources for consumer electronics and electric vehicles.[1,2] Nanostructured metal oxides (MOs) are widely considered to be one of the promising anode candidates for LIBs due to their 2–4 times higher theoretical capacity (800–1250 mA h g^{-1}) than that of traditional carbon/graphite anodes.[3–6] Nonetheless, nanostructured MOs with the single component as the LIBs anode have limitations, including large volume changes during extended cycling, resulting in poor cyclability.[2,3] To overcome the limitations, some novel nanostructures with advanced architectures are introduced into MOs nanomaterials. Hollow micro- and nanostructures of MOs possess volume-buffering effects, leading to the improved cycle life.[4–6] Recently, hierarchical nanostructures assembled from nanoscale building blocks have been increasingly reported due to their improved properties compared with traditional bulk materials and nanoparticles.[7,8] Moreover, it is generally believed that hybridization of multiple metal oxide nanocomponents can efficiently improve their performances owing to the synergistic effects of multiple nanocomponents.[9,10] Therefore, the development of a general synthetic approach for the hierarchical hollow hybrid nanomaterials with the aforementioned three structural features combined is of great significance.

More recently, significant efforts have been focused on the fabrication of MnO_2-based hierarchical hybrid nanostructures.[11–19] MnO_2 nanomaterials can be used as the nanocomponents of the advanced materials owing to their merits, such as low cost, earth abundance, outstanding performances, and environmental friendliness.[20–25] Many researches have also demonstrated that MOs/MnO_2 hierarchical hybrid nanostructures have better properties for applications, such as catalysis,[12] supercapacitors,[13–15] sensors,[16] batteries,[14,17,18] and microwave absorbers.[19] For example, Co_3O_4@PPy@MnO_2 hierarchical nanowires with the prominent electrochemical performance have been synthesized by a "hydrothermal-electrodeposition-soaking" route.[13] Cheng and co-workers have reported the synthesis of Co_3O_4@MnO_2 hierarchical porous nanoneedle array by a hydrothermal method, which exhibits excellent electrochemical performances in both Li-ion batteries and supercapacitors.[14] Yang and co-workers have reported the excellent lithium storage capacity of the hierarchical branched nanorods built from MnO_2/Fe_2O_3 synthesized by oriented self-assembly.[17] Chen and co-workers have reported the fabrication of TiO_2-C/MnO_2 nanowire arrays with enhanced lithium storage performances through a layer-by-layer deposition technique.[18] However, these synthetic methods are always restricted to some specific MOs/MnO_2 hierarchical hybrid nanomaterial and cannot be universally employed to fabricate various MOs/MnO_2 nanomaterials. Thus, the exploration of a general synthetic approach for fabricating metal oxides/MnO_2 hierarchical hollow hybrid nanostructures is still a great challenge.

Herein, we present a "penetration–carbonization and reduction–coating–annealing" route for the novel generalized synthesis of MOs/MnO_2 hierarchical hollow hybrid spheres (MOs/MnO_2 HHHSs) using carbonaceous spheres (CSs) as sacrificial templates (**Scheme 1**). Different MOs/MnO_2 HHHSs, such as NiO/MnO_2, Co_3O_4/MnO_2 and CuO/MnO_2, can be adjusted by soaking CSs in the corresponding metal salt solution for the first step (penetration step). Because of the unique hierarchical hollow hybrid nanostructures, NiO/MnO_2 nanomaterials possess a desirable capacity and outstanding cyclic stability as Li-ion battery anode materials. The hybridization of MnO_2 and NiO can effectively improve the electrical conductivity and remarkably enhance the effective utilization of MnO_2 with high

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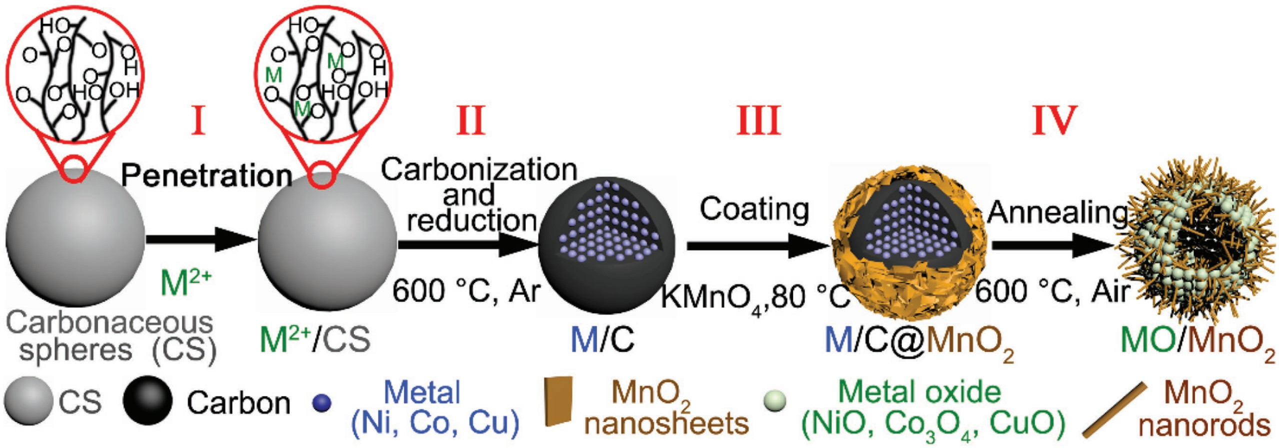

Scheme 1. The formation process used for fabricating MO/MnO_2 hierarchical hollow hybrid spheres.

theoretical capacity (1233 mA h g^{-1}), resulting in the improved electrochemical performance of the NiO/MnO_2 HHHSs electrode.[14,17,24,26–28] The hierarchical hollow structures and void space within NiO and MnO_2 nanoscale building units can effectively accommodate the huge mechanical stress during repetitive cycling, therefore maintaining the structural stability and improving the cyclic stability.[1,3,4,6]

2. Results and Discussion

MOs/MnO_2 HHHSs, including NiO/MnO_2, Co_3O_4/MnO_2, and CuO/MnO_2, were fabricated by a "penetration–carbonization and reduction–coating–annealing" route (Scheme 1). To explore the formation process of MOs/MnO_2 HHHSs, we select NiO/MnO_2 HHHSs as an example. In the first step (penetration), CSs are first prepared through a reported sucrose-hydrothermal method[5,29,30] and then saturated with nickel (II) ion solution. The key to the first step is that CSs with sufficient surface functional groups are used to adsorb nickel (II) ions, which has been reported in the previous literatures.[5,30] **Figure 1**a displays the field emission scanning electron microscopy (FESEM) image of monodisperse CSs with the size of about 2 µm as sacrificial templates. In the second step (carbonization and reduction), when heated at 600 °C under Ar atmosphere, the CSs are carbonized,[29] whereas some nickel (II) ions adsorbed on the CSs are gradually reduced to Ni by the above-produced amorphous carbon, which leads to the formation of Ni/carbon (Ni/C) precursor. As seen from Figure 1b, the X-ray powder diffraction (XRD) pattern of the precursors in the second step can be indexed to Ni (JCPDS file No. 87–0712), indicating the formation of nickel. It is noted that no clear phase of crystalline carbon can be detected because the carbon is amorphous.[29,31] In the third step (coating), $KMnO_4$ is mainly reduced by the carbon of Ni/C precursor via a redox process (Equation (1)),[14,15,18,32] and the reduced MnO_2 nanosheets are gradually deposited on the surface of Ni/C spheres. As shown in Figure 1c,d, nanosheets are deposited on the surface of the sphere in the third step, which confirms the formation of the Ni/C@MnO_2 hierarchical spheres. In the final step (annealing), when annealed in air, Ni in Ni/C@MnO_2 hierarchical spheres is completely oxidized to NiO, the carbon in Ni/C@MnO_2 is combusted and MnO_2 nanosheets gradually turn to MnO_2 nanorods, which results in the formation of NiO/MnO_2 HHHSs (**Figure 2**). Thermogravimetric analysis results indicate that the carbon in Ni/C@MnO_2 can be completely combusted at 600 °C in air (Figure S1, Supporting Information).

$$4MnO_4^- + 3C + H_2O \rightarrow 4MnO_2 + CO_3^{2-} + 2HCO_3^- \quad (1)$$

The hollow, hierarchical, and hybrid structures of the obtained NiO/MnO_2 HHHSs were revealed by FESEM and transmission electron microscopy (TEM). As seen from Figure 2a–f, NiO/MnO_2 HHHSs with diameters of 1.0–1.5 µm

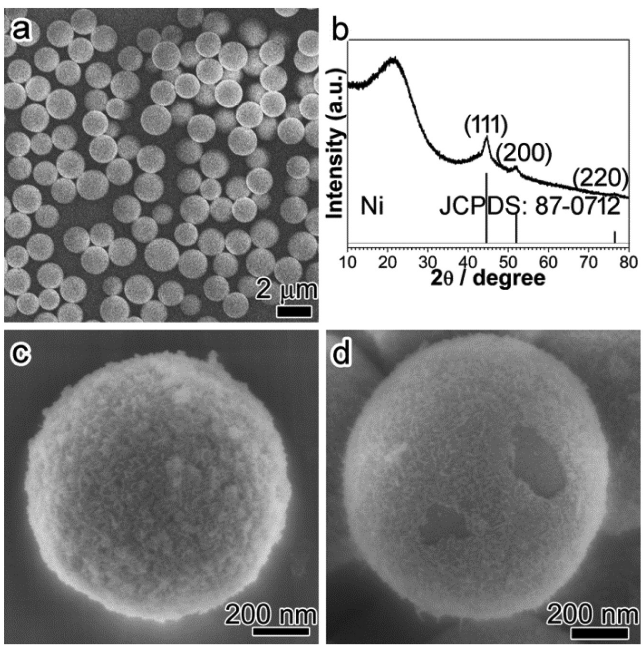

Figure 1. a) FESEM images of monodisperse CSs used as the templates in the first step of the formation process; b) XRD pattern of Ni/C precursor (Ni, JCPDS file No. 87–0712) obtained in the second step; FESEM images of c) a single Ni/C@MnO_2 sphere and d) a broken Ni/C@MnO_2 sphere obtained in the third step.