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Unusual one-step formation of Fe₂O₃/MnO₂ core-shell hollow nanorods as a high performance anode material for lithium ion batteries

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Introduction

Recently, the core-shell heterostructured nanomaterials have attracted much attention for their fascinating synergetic properties and multifunctionalities through reinforcement or modification of components^{1,2}. To a great extent, intrinsic properties of heterostructured materials also depends on their interior structure³⁻⁵. However, for the central construction of in-situ tuning, there is still lack of an effective and facile approach. Herein, the Fe₂O₃/MnO₂ core-shell nanorods with different interior structure was built with the inward movement of Mn element under different annealing temperature.

Experimental

First of all, the β-FeOOH nanorods was prepared by the water bath reaction with aqueous solution of FeCl₃·6H₂O and PVP (5,500 MW). Then, the FeOOH/MnO₂ core-shell nanorods was obtained utilizing the chemical deposition reaction between Mn(NO₃)₂·4H₂O and KMnO₄. Finally, the Fe₂O₃/MnO₂ core-shell hollow and Fe₂O₃/(Fe_{0.42}Mn_{0.58})₂O₃/MnO₂ core-shell nanorods were prepared after the precursor was annealed at 500 and 600 °C.

Electrochemical Measurement. The galvanostatic charge-discharge cycling test was conducted with the Neware battery test system (Neware, BTS-5V10mA, China). Cyclic voltammetry (CV) test was performed by using an electrochemical workstation (autolab, PGSTAT302N).

Results and Discussion

In the present paper, the abnormal interior structural change was observed, corresponding to the inward flow of Mn molar under annealing treatment in the air. As shown in Fig. 1a, firstly, the hierarchical MnO₂ shell uniformly grows on the surface of FeOOH nanorods under the assisting of surfactant PVP with chemical deposition reaction. Then, the Fe₂O₃/MnO₂ core-shell porous or hollow nanorods is formed under the annealing condition of low temperature (400 or 500 °C) in the air, which is assigned to the decomposition of the internal FeOOH with the removal of H₂O and organic species. When the calcination temperature increases to 600 °C, the sample undergoes phase transformation: the phase of (Fe_{0.42}Mn_{0.58})₂O₃ is produced in the middle layer, ascribing to the partially solid state reaction between Fe₂O₃ and MnO₂ by the inward movement of Mn element from the shell component (MnO₂). At the same time, the internal cavity turns into the solid structure. Due to their unique intrinsic morphology, the Fe₂O₃/MnO₂ nanorods show exceptional electrochemical performances As anode materials for lithium ion batteries under a high current density (5 C). In the measurement, the capacity retention is measured to be as high as 706 mAh g⁻¹ after 2000 cycles (Fig. 1b). On the one hand, the interior cavity could not only increase the stability of the material's structure but also decrease the diffusion length for Li ion during cycling. On the other hand, the core-shell structure brings out synergistic effects such as lowering the energy barrier for reaction and thus preserves the integrity upon the consecutive Li ion insertion/extraction cycling.

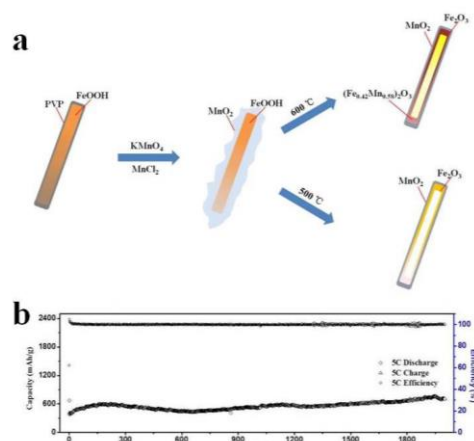


Figure 1. (a) Schematic of the fabrication process of the Fe₂O₃/MnO₂ hollow and Fe₂O₃/(Fe_{0.42}Mn_{0.58})₂O₃/MnO₂ solid core-shell nanorods and (b) cycling performance of the Fe₂O₃/MnO₂ nanorods at a current density of 5C

Conclusions

In summary, the Fe₂O₃/MnO₂ nanorods with different interior structure are constructed. The formation of the interior hollow, porous and solid triple layer structures are results of the decomposition of FeOOH nanorods and the inward flow of the Mn element. It is demonstrated that the core-shell nanorods display superior performance as anode materials for LIBs, attributed by the unique core-shell with complex interior structures.

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