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Full Length Article

Facile synthesis and Li-ion storage properties of porous Mn-based oxides microspheres

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ABSTRACT

Porous nanosheets assembled Mn-based oxides (Mn_2O_3, $MnCo_2O_4$ and $CoMn_2O_4$) microspheres of diameters about 3–6 μm and pore size distribution mainly around 10 nm have been synthesized by the same facile solvothermal route without any surfactant followed by a calcination process. In virtue of the porous nanosheets constructed microspheres, the Mn-based oxides microspheres Mn_2O_3 present specific capacities of 650 mAh/g after 100 charge and discharge cycles. Additionally among the three Mn-based oxides the representative specific capacities present an increasing trend as with the increasing percentage of Co element, the plateau of charge and discharge present a lower trend as with the increasing percentage of Mn element which is more suitable as anode materials in high output full batteries. Then the oxides with different components could be applied in different conditions such as the need for high specific capacity or high output lithium-ion batteries. Consequently the easy fabrication of microspheres and excellent electrochemical performances demonstrate Mn-based oxides' great potential in lithium-ion batteries.

1. Introduction

Lithium-ion batteries have been widely used in consumer electronic devices due to their high energy density and long cycle life [1,2]. However as with the fast development of electric vehicles (EVs) and hybrid EVs, the commercial electrode material of graphite can't fulfill the requirement of performance. Transition metal oxides such as Co, Mn and Fe based oxides [3–7] have been widely researched due to their higher theoretical specific capacity. Among the transition metal oxides, Mn based oxides have a relatively lower voltage plateau which can provide higher output when served as anode material in lithium-ion batteries, and are much cheaper than other oxides [8–11]. The fabrication of Mn-based oxides often consists of two-step, one is the fabrication of precursor such as Mn-EG [12,13] or $MnCO_3$ [14–17], which almost need introduce surfactant to construct complex nano/microstructure, the other is the annealing step. Among the recent research about Mn-based oxides, triple-shelled hollow spheres present a specific capacity of 150 mAh/g after 50 cycles [18], the capacity of microspheres can only remain 450 mAh/g after 100 cycles at a current density of 0.1C [19], porous microspheres exhibit a specific capacity of 610 mAh/g after 100 cycles at a current density of 100 mA/g [20], Mn_2O_3 microcubes present specific capacities ranging from 370 or 658 mAh/g based on the different exposed facets after 100 cycles at a current density of 100 mA/g [21]. Consequently the fabrication simplicity and superiority of lithium storage properties of Mn oxides are still not in satisfactory.

Up to now, many ternary metal oxides have presented considerable electrochemical performances due to the synergistic effect between the different metal elements consisting of Co, Mn, Ni and so on [22–26]. Consequently introducing Co element into Mn oxides to form $MnCo_2O_4$ and $CoMn_2O_4$ has been an ideal choice to promote the electrochemical performances [3,27,28]. However the further comparison between the single metal oxide and multiple metal oxides have not yet been researched, hence it is necessary to fabricate the different metal oxides with the similar method in order to obtain the similar morphology to accurately compare the differences between single and multiple metal elements.

Herein porous nanosheets assembled Mn_2O_3, $MnCo_2O_4$ and $CoMn_2O_4$ microspheres have been fabricated through the formation of precursor Mn(Co)-EG with reactant $Mn(CH_3COO)_2$, $Co(CH_3COO)_2$ and without any surfactant. The microspheres

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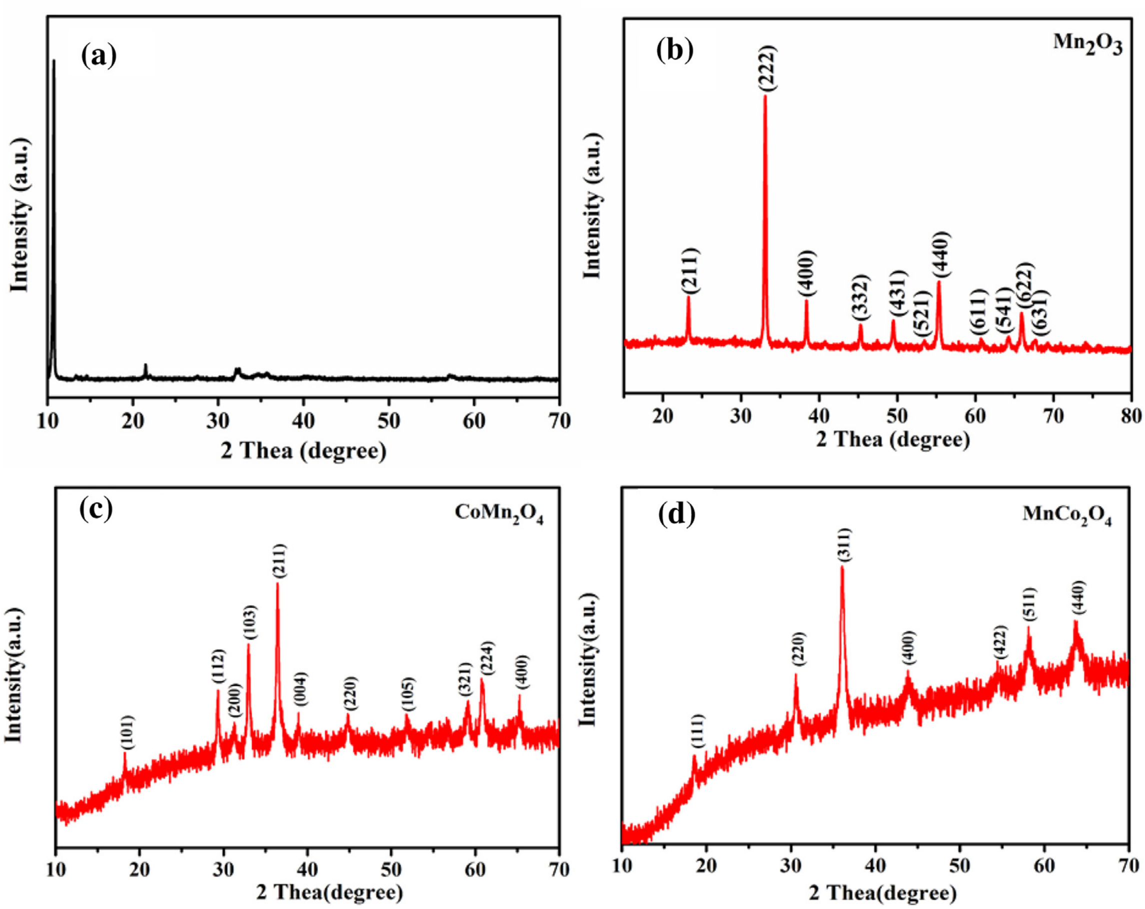

Fig. 1. XRD patterns of (a) the as prepared precursor, porous (b) Mn_2O_3, (c) $CoMn_2O_4$ and (d) $MnCo_2O_4$ hierarchical microspheres.

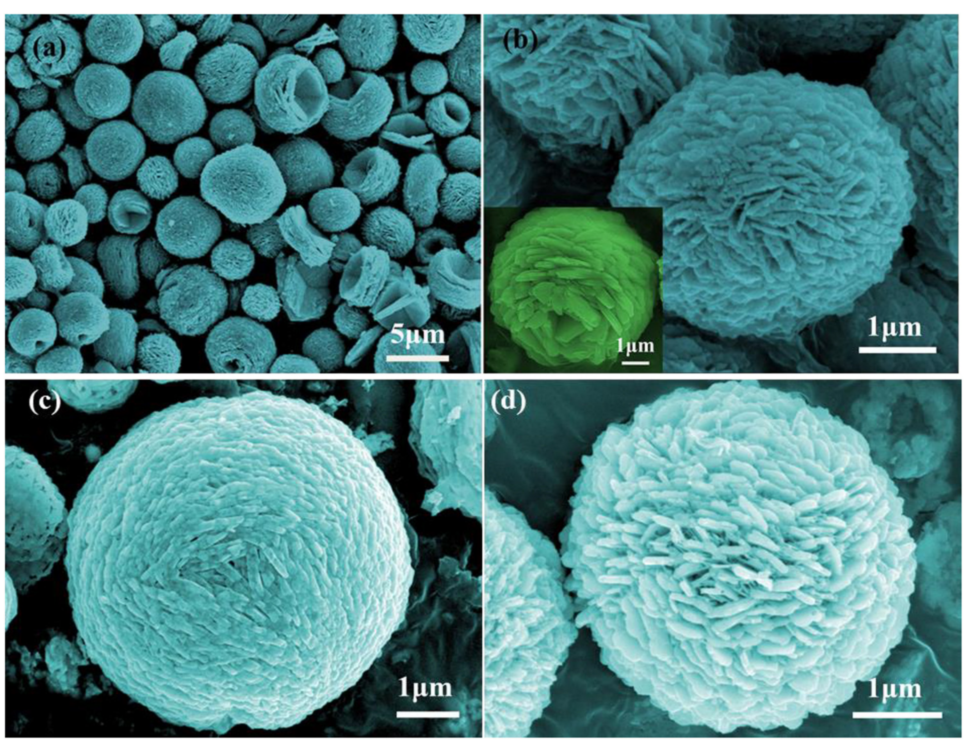

Fig. 2. SEM images of the porous (a, b) Mn_2O_3, (c) $CoMn_2O_4$ and (d) $MnCo_2O_4$ hierarchical Microspheres. Inset shows the SEM image of the as prepared precursor.