



General synthesis of vanadium-based mixed metal oxides hollow nanofibers for high performance lithium-ion batteries



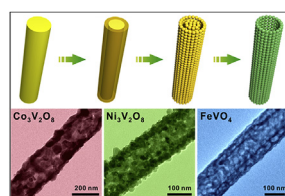
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HIGHLIGHTS

- $M_xV_2O_8$ ($M = \text{Co, Ni, Fe}$) hollow nanofibers were synthesized by a general method.
- An interesting structural evolution process for the hollow nanofibers was observed.
- Superior lithium storage performance was achieved by $\text{Co}_3\text{V}_2\text{O}_8$ hollow nanofibers.

GRAPHICAL ABSTRACT



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ABSTRACT

Hollow nanostructured mixed metal oxides have recently been intensively investigated as electrode materials for energy storage and conversion due to their remarkable electrochemical properties. Although great efforts have been made, the synthesis of hollow nanostructured vanadium-based mixed metal oxides especially those with one dimensional structure is rarely reported. Vanadium-based mixed metal oxides are promising electrode materials for lithium-ion batteries with high capacity and good rate capability. Here, we develop a facile and general method for the synthesis of one dimensional $M_xV_2O_8$ ($M = \text{Co, Ni, Fe}$) tubular structure through a simple single-spinneret electrospinning technique followed by a calcination process. As a demonstration, $\text{Co}_3\text{V}_2\text{O}_8$ hollow nanofibers are evaluated as anode materials for lithium-ion batteries. As expected, benefiting from their unique one dimensional tubular structure, the as-synthesized $\text{Co}_3\text{V}_2\text{O}_8$ exhibits excellent electrochemical properties for lithium storage. To be specific, it can deliver a high specific capacity of 900 mAh g^{-1} at 5 A g^{-1} , and long cycling stability up to 2000 cycles. The present work makes a significant contribution to the design and synthesis of mixed metal oxides with one dimensional tubular structure, as well as their potential applications in electrochemical energy storage.

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1. Introduction

Mixed transition-metal oxides (MTMOs) have attracted great research interest with great potentials as electrode materials for energy storage devices including lithium-ion batteries (LIBs), electrocatalysis and supercapacitors [1–8]. These MTMOs have

demonstrated remarkable electrochemical properties due to their complex chemical compositions and synergetic effects of different metals [6]. Moreover, the presence of multiple valences and relatively low activation energy for electron transfer between cations provide them with good electric conductivities [5,9,10]. For example, Yu and co-workers reported the synthesis of yolk-shelled Ni-Co mixed oxide nanoprisms and investigated their electrochemical properties for both LIBs and hybrid supercapacitors [5]. Recently, vanadium-based MTMOs have received considerable attention in energy storage for both anode and cathode materials of LIBs [11–15]. Han et al. have fabricated moundlily like radial β -

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AgVO₃ nanowire clusters as cathode material for LIBs, demonstrating high discharge capacity and excellent cycling performance due to the reduced self-aggregation [16]. Yang and co-workers reported the synthesis of self-assembled Co₃V₂O₈ multilayered nanosheets, showing outstanding reversible capacity and excellent rate performance [17].

Nanostructured MTMO especially those hollow nanostructures with large surface area, low density and high pore volume have been extensively investigated as electrode materials for energy storage [18–22]. For example, Zhang and co-workers reported a novel penetration–solidification–annealing strategy to synthesize various kinds of multi-shelled mixed metal oxides which exhibit good lithium storage properties [23]. Guo et al. recently developed a general strategy to synthesize hierarchical tubular structures of Mn-based mixed metal oxides. The as-obtained Co-Mn hierarchical nanotubes manifest excellent electrochemical properties for hybrid supercapacitors with remarkable capacity retention [24]. Despite all these achievements, there is still a lack of a general method to synthesize vanadium-based hollow MTMOs, especially those with one dimension (1D) structure which endows merits such as efficient electron transportation, short Li⁺ diffusion length and large Li⁺ flux [25–28]. Moreover, the tubular vanadium-based MTMOs would take over the advantages of both hollow and 1D structure [29]. Hence, it will be of great importance to develop a general and facile strategy to synthesize 1D vanadium-based MTMOs with hollow structure.

Herein, we develop a general strategy to synthesize M_xV₂O₈ (M = Co, Ni, Fe) with 1D tubular structure by electrospinning and subsequent thermal treatment. As an example, the as-synthesized Co₃V₂O₈ hollow nanofibers are evaluated as anode materials for LIBs, exhibiting exceptional electrochemical performance in terms of high capacity, excellent rate capability and long cycling stability.

2. Experimental section

2.1. Synthesis of 1D M_xV₂O₈ (M = Co, Ni, Fe) tubular structure

All the chemicals were directly used after purchase without further purification and the synthesis of M_xV₂O₈ (M = Co, Ni, Fe) hollow nanofibers involves two steps: electrospinning and subsequent calcination. For the synthesis of Co₃V₂O₈ precursor nanofibers (donated as CoV-PVP), 0.309 g cobalt acetylacetonate and 0.212 g vanadium acetylacetonate were dissolved in 2.5 g N, N-dimethylformamide (DMF). After stirring for 10 min, 0.5 g polyvinylpyrrolidone (PVP, Mw = 1300, 000) was added and the mixture was vigorously stirred for 12 h at 50 °C. The solution was then transferred into a plastic syringe with a stainless steel nozzle. Electric fields of 17, 18 and 19 kV were applied between the orifice and the ground with a distance of 15 cm and the electrospinning rate of 1, 2 and 3 mL h⁻¹ was applied. The precursor solution was directly electrospun on Al₂O₃ substrates. Finally, the as-electrospun nanofibers were thermally treated in air at 500 °C for 3 h at a ramping rate of 1 °C min⁻¹. The synthesis of Ni₃V₂O₈ and FeVO₄ precursor nanofibers is similar to that of Co₃V₂O₈. For the synthesis of Ni₃V₂O₈ precursor nanofibers (donated as NiV-PVP), 0.3083 g nickel acetylacetonate, 0.212 g vanadium acetylacetonate and 0.5 g PVP were dissolved in 2.5 g DMF. An electric field of 19 kV was applied between the orifice and the ground with a distance of 15 cm and the electrospinning rate was tuned from 1 to 4 mL h⁻¹. The NiV-PVP nanofibers were calcinated at 500 °C for 3 h at a ramping rate of 2 °C min⁻¹. For the synthesis of FeVO₄ precursor nanofibers (donated as FeV-PVP), 0.3532 g iron acetylacetonate, 0.2652 g vanadium acetylacetonate and 0.5 g PVP were dissolved in 2.5 g DMF. An electric field of 19 kV was applied and the distance between orifice and the ground is 15 cm. The electrospinning rate

was tuned from 1 to 4 mL h⁻¹. Afterwards, the FeV-PVP nanofibers were calcinated at 400 °C for 3 h at a ramping rate of 1 °C min⁻¹. To study the structural evolution process of the Co₃V₂O₈ hollow nanofibers, the as-electrospun CoV-PVP nanofibers were heated to 300 and 500 °C at a ramping rate of 1 °C min⁻¹ without any stay.

2.2. Materials characterization

The morphology of the M_xV₂O₈ (M = Co, Ni, Fe) tubular structure was characterized by field emission scanning electron microscopy (FESEM, JEOL-6700) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). The composition and elemental mapping of the product was analyzed by energy-dispersive X-ray spectroscope (EDS) attached to the TEM instrument. X-ray diffraction (XRD, Rigaku D/MAX RINT-2000) measurement was performed to investigate the structural properties with Cu-Kα as the radiation source. Thermogravimetric analysis (TGA) was performed using a SDT Q600 Auto-DSCQ20 system within a temperature range of 10–600 °C and at a heating rate of 10 °C min⁻¹ under static air atmosphere.

2.3. Electrochemical measurements

The electrodes were prepared by mixing electroactive materials (Co₃V₂O₈ hollow nanofibers), conductive carbon and polyvinylidene fluoride (PVDF) with a mass ratio of 80: 10: 10 to obtain slurry. The slurry was then casted on the copper foil as the working electrode for LIBs. The working electrodes were dried at 80 °C in vacuum oven overnight. 1 M LiPF₆ in a 1: 1 (V: V) mixture of ethylene carbonate–ethyl methyl carbonate was used as the electrolyte. Cells were assembled in an argon filled glove box by stacking a Li metal as counter electrode and a polypropylene as separator. The electrochemical performances of the cells were evaluated using a galvanostat/potentiostat (TOSCAT 3000, Toyo Systems, Tokyo, Japan). Cyclic voltammetry measurements were conducted on an Autolab potentiostat/galvanostat (Model PGSTAT-72637) electrochemical workstation.

3. Results and discussion

The Co₃V₂O₈ hollow nanofibers are first synthesized through the electrospinning and subsequent thermal treatment method. As illustrated in Fig. 1a, the FESEM image shows that the as-obtained CoV-PVP nanofibers are uniform in size of about 450 nm with a smooth surface (the inset in Fig. 1a). The rate and applied voltage of electrospinning is optimized to be 2 mL h⁻¹ and 19 kV, respectively, to get well-defined CoV-PVP nanofibers with uniform size distribution (Fig. S1). After thermal treatment, the crystallographic structure of the as-synthesized samples is examined by XRD (Fig. S2). All of the diffraction peaks can be well indexed to orthorhombic Co₃V₂O₈ (Co₃V₂O₈, JCPDS: 74-1486), with no peaks of other impurities. A large scale FESEM image of as-prepared Co₃V₂O₈ reveals that the structure of the Co₃V₂O₈ nanofibers is perfectly maintained after thermal decomposition with length over 10 μm (Fig. 1b). At the same time, the diameter of the Co₃V₂O₈ hollow nanofibers decreases to around 250 nm (Fig. 1c). Furthermore, the 1D hollow architecture of Co₃V₂O₈ is investigated by TEM, as shown in Fig. 1d–f. The hollow interior of the tubular structure can be clearly observed from a low magnification TEM image (Fig. 1d) with a sharp contrast between the center and edge. In addition, it is found that the Co₃V₂O₈ hollow nanofibers are highly porous (Fig. 1e), constructed by nanoparticles with size ranging from 20 to 50 nm (Fig. 1f). The lattice fringes in a typical high-resolution TEM images (Fig. S3) are separated by 0.575 nm, in good agreement with the (020) plane of Co₃V₂O₈. The elemental

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