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Metal organic frameworks route to prepare two-dimensional porous zinc-cobalt oxide plates as anode materials for lithium-ion batteries

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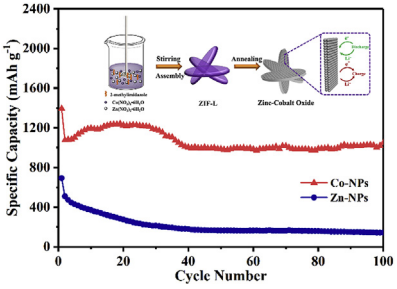
HIGHLIGHTS

- A series of porous two-dimensional zinc-cobalt oxide plates are derived from metal organic frameworks.
- The ratio of metal in the zinc-cobalt oxide plates is continuously adjusted.
- The zinc-cobalt oxide plates show excellent cycling stability and rate capability.
- The preparation method can motivate the preparation of other bimetallic transition metal oxides.

GRAPHICAL ABSTRACT

A series of two-dimensional porous zinc-cobalt oxide plates are synthesized with the help of a morphology-maintained annealing treatment of metal organic frameworks. The ratio of metal in zinc-cobalt oxide is continuously adjusted. When evaluated as electrode materials for lithium-ion batteries, the nanocomposite exhibits large reversible capacity, excellent cycling stability and superior rate capability.



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ABSTRACT

Two-dimensional morphological (2DM) metal oxides are highly desirable for the improvement of electrochemical performance of lithium-ion batteries (LIBs). Herein, a facile and scalable strategy to fabricate porous 2DM zinc-cobalt oxide (ZCO) plates is reported, with the help of a morphology-maintained annealing treatment of metal organic frameworks (MOFs). Through change the proportion of metal nitrates in the precursors, a series of porous ZCO plates are synthesized. Thanks to the porous structure, 2DM morphological features and nano-sized building block of Co_3O_4 plates, the Co_3O_4 plates electrode as anode materials for LIBs display the high reversible capacity (1027 mA h g^{-1} at 100 mA g^{-1} after 100 cycles), remarkable rate capability (541 mA h g^{-1} even at 1000 mA g^{-1}). Furthermore, this strategy of synthesizing the ZCO plates with MOFs provides a new approach to design bimetallic transition metal oxides that the ratio of transition metal is continuously adjusted and has great lithium storage properties.

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1. Introduction

In recent years, metal-organic frameworks (MOFs) and coordination polymers with porous structures have received considerable attention for their unique physical and chemical properties and many potential applications [1–3]. The morphology of MOFs can be designed by careful selection of metal centers, different functional linkers and synthetic conditions. For example, blue nanocubes [4], ZIF-67 rhombic dodecahedron [5] and MIL-88-Fe nanorods [6] have been synthesized. Because the unique dimension-related properties, such as larger specific surface area and more accessible active sites, two-dimensional morphological (2DM) MOFs [7,8] is the immediate areas of recent research focus.

Because of their tunable porosities, various morphologies and versatile functionalities, MOFs hold dramatic applications in catalysis [9], gas adsorption [10], separation [11,12], drug delivery [13] and energy storage [14–16]. Especially, MOFs feature exceptional specific surface areas and pore volume and show great promise in using them as precursors/templates to derived metal oxides [17,18], metal sulfides [19] and phosphides [20,21] nanocomposites for electrode materials for energy storage and conversion. For example, spindle-like [22] and cube-like porous [23] Fe_2O_3 derived from MIL-88-Fe and Prussian blue nanocubes have exhibited excellent lithium storage performances, owing to their robust porous structure. By using core-shell Fe_2Ni MIL-88/Fe MIL-88 nanorods as precursors, Huang et al. have fabricated $NiFe_2O_4/Fe_2O_3$ nanotubes, exhibiting good cycling stability and rate capability [24]. Recently, ZIF-67 have been introduced to obtain CoS_2 nanoparticles within thin N-doped porous carbon shell electrodes, displaying an improved cycling performance with a reversible capacity of 560 mA h g^{-1} after 50 cycles under a current density of 100 mA g^{-1} [25].

Relative to metal sulfides and phosphides, transition metal oxides, such as MnO_2, Co_3O_4, ZnO, NiO and Fe_2O_3, have been widely studied owing to their high theoretical capacities (> 600 mA h g^{-1}), low charge-discharge potentials and abundant sources. Among the reported transition metal oxide, Co_3O_4 materials with the great cycle performance and rate capacities have attracted research interest as anode materials for LIBs [5,26–28]. While, the low electrical conductivity, the huge volume change during charge/discharge process of the Co_3O_4 as well as the high cost and toxic nature of cobalt impede its commercialization. There are different ways to moderate these problems: first, downsize the Co_3O_4 to nano-size. Such as pompon-like Co_3O_4 porous spheres [29], the nano-sized structure can increase electrode-electrolyte contact area and decrease solid-state diffusion path for electron and Li^+ ion. Second, synthesize nanomaterials with porous structure. A porous nanostructure and suitable volume-occupying rate of the electrode material can ensure fast electrolyte diffusion and accommodate the volume change during cycling, thereby improving cycling stability and rate capability. For instance, ZIF-67 derived porous Co_3O_4 hollow dodecahedra showed excellent cycling life and rate performance when used as LIBs anode [30]. Third solution is to fabricate 2DM nanostructures. As is well-known, the structural and morphology of electrode have a great influence of its lithium storage properties. The 2DM nanostructure has large specific surface area [31,32]. This character of 2DM nanostructure makes it can buffer the volume change during charge/discharge process [33]. Moreover, this structure could expose more active surface and reduce the diffusion path of Li^+ ion and electrons. For example, Wen's group have reported the synthesis of Co_3O_4 nanoplates [27] using lamellar structured cobalt-based coordination polymers as template. As an anode for LIBs, Co_3O_4 nanoplates exhibit excellent electrochemical performances. Finally, replace the Co in spinel structured Co_3O_4 by cheaper and environmentally friendly metals, such as Zn, Ni, and Cu, which are also capable of reversible electrochemical reaction with Li^+. Among them, ZCO is an attractive material for evaluation as anode for LIBs because it is low-cost, environmentally benign relative to the pure cobalt oxide compound, and has a high theoretical capacity. For example, Liu's group have reported the $ZnCo_2O_4$ microspheres, it exhibited high specific capacity and good cycling stability [34]. Therefore, it is necessary to develop a new method to synthesize bimetallic transition metal oxides with 2DM and pores nanostructure.

Herein, 2DM bimetallic Zn-Co MOFs with tunable ratio of metal ions have been fabricated by a facile room-temperature stirring method. The obtained 2DM MOFs are further annealed to form porous 2DM ZCO plates. The 2DM ZCO is composed of small nanoparticle building blocks. The 2DM ZCO manifests great cycling and rate capability when used as anode material for LIBs.

2. Experimental

2.1. Synthesis of ZIF-L plates

To prepare ZIF-L plates, 15.83 mmol of 2-methylimidazole and 2 mmol of metal nitrate were added into 45 mL of deionized water respectively. Then, the solution of metal nitrate was dissolved into the solution of 2-methylimidazole under stirring. The mixture was stirred at room temperature for another 4 h. The product was collected by repeated centrifugation and washed by water for several times. Finally, the sample was dried in an oven at 60 °C overnight. When the molar ratios of Zn and Co were 1:0, 1:1, 1:2 and 0:1, the products were denominated Zn-ZIF-L, ZnCo-ZIF-L, $ZnCo_2$-ZIF-L and Co-ZIF-L respectively.

2.2. Synthesis of ZCO plates

Typically, the powder of ZIF-L was loaded into a porcelain boat placed in a muffle furnace. Then it was heated to 400 °C with a ramp rate of 1 °C·min^{-1} and maintained for 2 h in air. The product was collected after cooled to ambient temperature naturally. When used the Zn-ZIF-L, ZnCo-ZIF-L, $ZnCo_2$-ZIL-L and Co-ZIL-L as precursors, the obtained products were named as Zn-NPs, ZnCo-NPs, $ZnCo_2$-NPs and Co-NPs, respectively.

2.3. Materials characterization

X-ray diffraction (XRD) patterns were performed on a Bruker D8 Focus Powder X-ray diffractometer. The Hitachi S-4800 field emission scanning electron microscope (FESEM) was used to determine the morphology and microstructure of product. The thermogravimetric (TG) analysis was test with STA 449 Jupiter (NETZSCH) thermogravimetry analyzer with a heating rate of 10 °C min^{-1} from 25 to 800 °C under flowing air.

2.4. Electrochemical measurements

The electrochemical performance of the ZCO plates were measured using CR 2025 coin-type cells at room temperature. The working electrode was prepared by mixture of sample, acetylene black and PVDF in NMP solvent with mass ratio of 70:20:10. Then the slurry was coated on Cu foil and dried at 60 °C for 24 h in a vacuum oven. The loading mass of the active materials of electrode is about 1 mg. The counter electrode was pure lithium foil and the separator is Celgard 2400 membrane, and 1 M $LiPF_6$ dissolved in EC and DEC (1:1 in volume) is the electrolyte. The CR 2025 coin-type cells were fabricated in an argon-filled glovebox. The LAND CT2001A multichannel battery testing system was used to test the cycle and rate performance of electrode material. And the BioLogic VMP3 electrochemical workstation was used to measurement the cyclic voltammogram and electrochemical impedance spectral measurements.

3. Results and discussion

The overall synthetic process for the ZCO plates is schematized in Fig. 1. ZIF-L is synthesized by coordination reaction between metal