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# A general gelatin-assisted strategy to hierarchical porous transition metal oxides with excellent lithium-ion storage

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## ABSTRACT

Transition metal oxides are widely researched as anode materials for lithium-ion batteries due to their high theoretical capacity. However, the application of this material is always restricted by the low electroconductivity and huge volume change. In this work, we develop a general strategy, the gelatin-assisted hydrothermal-calcination process, to prepare hierarchical porous transition metal oxides and their composites, including $Fe_2O_3$, $Mn_2O_3$, $Co_3O_4$, $ZnCo_2O_4$, $MnCo_2O_4$ and $(Co,Mn)_3O_4$. Depending on the unique molecular structure of gelatin, metal ions in the solution can be located in amino and carboxyl existing in natural polymer, which lead to the formation of hierarchical precursor. Typically, step-like hierarchical porous $Fe_2O_3$ and $ZnCo_2O_4$ exhibit the outstanding performance of 1301.7 mAh $g^{-1}$ after 600 cycles and 1005.8 mAh $g^{-1}$ after 180 cycles at 500 mA $g^{-1}$ for lithium-ion storage. In addition, $Na_{0.7}MnO_2$ cathode material prepared from $MnCO_3$ also delivers the 140.9 mAh $g^{-1}$ over 50 cycles at 40 mA $g^{-1}$ for sodium-ion storage. The stable structure, abundant materials, low toxicity and excellent performance promote the development of anode materials. Moreover, this easily-extended method also provides a strategy to obtain hierarchical materials, which expands the application of transition metal oxides in other fields.

## 1. Introduction

The rapid development of electronic technology urges the new requirements of energy conversion device, which cause the continually increasing research interests and actual demand of lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) [1,2]. Low solution, portability, high rated voltage and good capacity [3–6] are the typical features of these types of batteries. Importantly, it is still a breakthrough to prepare high-performance, low-cost and safe electrode materials through a realizable process. According to conversion reaction presented by Poizot et al. [7], transition metal oxides (TMOs) as potential substitutions for commercial graphite arouse great attention due to their ultra-high theoretical capacity [8]. Unfortunately, most of TMOs are semiconductive material possessing relatively low electroconductivity [9] that leads to the aggravating polarization and poor ability in high current density. Moreover, multi-electron conversion reaction brings the high specific capacity and huge volume change of electrode materials causing to the capacity decline, simultaneously, which also hinder the practical application of TMOs anode materials [10].

Compared with nanoparticles, micro/nano-structured materials exhibit the enhanced performance by means of their unique morphology. On the one hand, TMOs with the micro-sized frame have the lower surface free energy than nanoparticles, which allows for restraining the agglomeration of materials and the loss of active sites [11,12]. In addition, the suitable specific surface area is also beneficial for the formation of a thin solid electrolyte interface (SEI) film [13] leading to the improved electron transport and electrochemical performance. On the other hand, porous materials based on micro-frame, especially in mesoporous materials, offer the potential opportunity in the high-performance anode materials because of the particular advantages such as controllable pore size, relatively high surface area, which also deliver the nanostructure effect [14–16]. It is noticed that three dimensional (3D) hierarchical porous structure based on nanosheets has some unique advantages when used as electrode materials. The porous nanosheets greatly facilitate lithiation/delithiation due to the short diffusion [17]. Meanwhile, the hierarchical structure assembled from nanosheets

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not only improves the contact area between the active material and electrolyte, but also enhances the stability of materials because of the interspace between different layers, which promote many high-performance materials with this special architecture [18].

It is investigated that the functional materials based on template method with various porous structures have an essential effect on the modification of performance [19–22]. The appropriate pore sizes and tunable morphologies make a large contribution to the superior lithium storage. Hard-template process is effective to obtain the highly ordered pore structures, which ask for the strict requirement and elaborate design of template. Mesoporous $Co_3O_4$@carbon nanotube arrays have been prepared through SBA-15-assisted method [23], which exhibit the specific capacity of ~400 mA h $g^{-1}$ at the current density of 5 A $g^{-1}$. In addition, an easily processable way to achieve porous materials or their precursors is soft-template method involved in assembly, which highly depend on the choice reaction conditions to develop a universal approach [24]. The submicrometer-sized monodisperse Fe-soc-MOF cube may be the possible anode material synthesized from the solvothermal approach because of the outstanding morphology and composites [25]. Some self-template strategies with diffusion and etching can also prepare a series of porous materials with unique shape [26,27]. However, the exact control of etching depth and degree of reaction is necessary, which directly influence the porosity and strength of electrode.

In virtue of the synergy effects between the different materials, many composites have been synthesized to improve the performance such as the coated composites and the doped composites [28,29]. As mentioned before, the extreme volume effect and poor conductivity are the main two thorny issues, which indicate that the complementation of reaction activity and mechanical property is necessary. For example, carbon-based TMOs and ternary metal oxides exhibit the increasing stability than single-component TMOs during the repeated charge/discharge [30]. Moreover, in the field of TMOs electrodes, a stable shell or a proper amount of doping could increase the stability of materials due to the formation of buffer structures [31]. The chestnut-like core-shell $TiO_2$@α-$Fe_2O_3$ [13] and the hollow nanobarrel-like $ZnCo_2O_4$ [30] have been obtained, which show the good stability of 820 mAh $g^{-1}$ over 1000 cycles and 1350 mAh $g^{-1}$ over 300 cycles at 500 mA $g^{-1}$, respectively. In conclusion, finding a realizable and easily-extended preparation to the structurally stable and high-performance TMOs is urgent for the possible application of these materials.

Herein, we report a general approach to build the hierarchical porous TMOs and their composites by the gelatin-assisted hydrothermal-calcination process, including $Fe_2O_3$, $Mn_2O_3$, $Co_3O_4$, $ZnCo_2O_4$, $MnCo_2O_4$ and $(Co,Mn)_3O_4$ (Co:Mn = 1:2). Gelatin is a natural polymer derived from partial hydrolysis of collagen with abundant $-NH_2$ and $-COOH$ that coordinating with metal ions [32]. In addition, the interaction between molecular chains of gelatin also offers an opportunity to self-assembly [33]. These two factors provide a great possibility for gelatin acted as a soft template to obtain hierarchical precursors. As we except, the precursors of the whole mentioned materials display the hierarchical structure assembled from many nanosheets. Typically, $Fe_2O_3$ with step-like hierarchical porous structure has been selected as research object because of the rich raw materials and environmentally-friendly features, which demonstrates the superior lithium-ion storage of 1301.7 mAh $g^{-1}$ after 600 cycles at 500 mA $g^{-1}$ and 888.8 mAh $g^{-1}$ after 500 cycles at 1000 mA $g^{-1}$. In addition, $ZnCo_2O_4$ electrode also has the good capacity of 1005.8 mAh $g^{-1}$ over 180 cycles at 500 mA $g^{-1}$. Remarkably, $Na_{0.7}MnO_2$, prepared from hierarchical $MnCO_3$ precursor, also exhibits the good sodium-ion storage of 140.9 mAh $g^{-1}$ after 50 cycles at 40 mA $g^{-1}$. This general hydrothermal-calcination process combines well the advantages of materials and the stability of structure, which provide a certain value to synthesize hierarchical porous materials with satisfactory performance applied in LIBs and other fields.

## 2. Experimental section

### 2.1. Preparation of the hierarchical precursors of binary oxides

Typically, 2.5 g of gelatin was dissolved in 20 mL deionized water named solution A. Next, 0.556 g (2 mmol) $FeSO_4 \cdot 7H_2O$ and 1.5 g (25 mmol) $CO(NH_2)_2$ were dissolved in 20 mL deionized water to form solution B. Then, the solution B was mixed with solution A at 30 °C to obtain the beige solution C. After stirring for 30 min, solution C was transferred into a 50 mL Teflon-lined stainless steel autoclave with 140 °C for 12 h. When the autoclave was cooled naturally, the powders were collected and washed with deionized water and ethanol for three times, respectively. The as-prepared product was dried in vacuum at 50 °C for 12 h, named Fe-Precursor. The Co-Precursor and Mn-precursor were obtained by the same process with 0.562 g $CoSO_4 \cdot 7H_2O$ and 0.338 g $MnSO_4 \cdot H_2O$ to replace $FeSO_4 \cdot 7H_2O$, respectively.

### 2.2. Preparation of the hierarchical precursors of ternary oxides

The precursor of $ZnCo_2O_4$ was prepared as the similar process. The difference is that solution B consisted of 0.562 g (2 mmol) $CoSO_4 \cdot 7H_2O$ and 0.288 g (1 mmol) $ZnSO_4 \cdot 7H_2O$ according to the mole ratio of 2:1. In addition, solution C was placed in a water bath with 60 °C for 1 h and the hydrothermal temperature is 160 °C. The precursors of $MnCo_2O_4$ and $(Co,Mn)_3O_4$ (Co:Mn = 1:2) could be obtained by changing the metal sulfates according to chemical formulas.

### 2.3. Preparation of hierarchical porous TMOs

The Fe-Precursor was annealed at 500 °C, 600 °C, 700 °C and 800 °C with a heating rate of 2 °C $min^{-1}$ for 2 h in air. The final red powers were collected and stored in 60 °C, named Fe-500, Fe-600, Fe-700 and Fe-800, respectively. Other TMOs and composites were annealed at 600 °C with a heating rate of 2 °C $min^{-1}$ for 2 h in air. In addition, $Na_{0.7}MnO_2$ microsphere was prepared from a solid phase method[2].

### 2.4. Material characterization

The crystalline phases of precursors and oxides were measured by X-ray powder diffraction (XRD) (Bruker AXS, D8 Advance) with Cu Kα radiation. The surface environment of sample was tested with X-ray photoelectron spectroscopy (XPS) (Thermo Fisher, ESCALAB 250XI) with Al Kα radiation. The morphologies of products were performed by field emission scanning electron microscopy (FESEM) (Hitachi, S-4800), transmission electron microscopy (TEM) (Hitachi, HT-7700). The high resolution transmission electron microscopy (HRTEM) (FEI, Tecnai G2 F30) was used for the images of crystal lattice and the energy dispersive spectroscopy (EDS) mappings of composites. The Brunauer-Emmett-Teller (BET) surface areas and the Barrett-Joyner-Halenda (BJH) pore sizes were characterized using automated gas sorption analyzer (Quantachrome, Autosorb-IQ).

### 2.5. Electrochemical characterization

The electrochemical performances were performed by CR2032-type coin cells assembled in a glove box that was full of Ar with lithium metal as the counter electrode. The working electrodes