



Additive-free macroscopic-scale synthesis of coral-like nickel cobalt oxides with hierarchical pores and their electrocatalytic properties for methanol oxidation



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ABSTRACT

Coral-like nickel cobalt oxides with hierarchical pores were massively synthesized via a one-pot additive-free solvent thermal decomposition route coupled with a post calcination treatment. The physicochemical properties of nickel cobalt oxides were characterized via X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS) and nitrogen sorption measurements. The unique 3D hierarchical porous NiCo₂O₄ coral structures exhibit enhanced electrocatalytic properties for methanol oxidation with a desirable stability. The large-scale and facile additive-free synthetic technique can be applied to the construction of other metal oxide with complex hierarchical structures.

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1. Introduction

The energy always plays an essential role in human being's life. Over the past decades, fuel cell has become an arresting device that can best meet our energy demands and abate pollution of the environment. Among them, direct methanol fuel cells (DMFCs), due to their merits of high energy density, easy operation, low emission high theoretical energy conversion efficiency and convenient storage and transport of liquid fuel [1–3], have reemerged as a promising power source for portable electronic devices and electric vehicles. One effective way to enhance the performance of DMFCs is to explore electrocatalysts with high activity and stability. The noble metals, such as platinum (Pt), palladium (Pd), ruthenium (Ru) and those based alloys [4,5], are considerably powerful electrocatalyst for methanol oxidation. However, the high cost of noble metals hinders DMFCs commercialization [6], which greatly limits the industrial application.

Non-noble metallic oxides such as CeO₂, TiO₂, SnO₂ and WO₃ are used as an electrocatalyst of DMFCs owing to their superiorities of abundance, cheapness and stable capability [7–10]. As

a rising star of metal oxide, spinel-type (AB₂O₄, B = Fe, Co, Mn) binary metal oxides are a family of promising functional materials which exhibit a widespread prospect in applications of energy storage and electrocatalysis [11–15]. Among them, nickel cobaltite (NiCo₂O₄) is typical and representative, which has been widely utilized in the fields of electrochemical capacitors (ECs) [16–21], Li-ion batteries (LIBs) [22–24], Li–O₂ batteries [25,26], chemical sensors [27], optoelectronic devices [28] and magnetic apparatus, etc [29]. In addition, NiCo₂O₄ materials have also shown excellent electrocatalytic activities towards various electrode reactions, for instance, Cl₂ evolution reaction (CER) [30], O₂ evolution reaction (OER) [31,32], O₂ reduction reaction (ORR) [33,34], H₂O₂ reduction reaction [35,36] and CH₃OH [35–37] oxidation reaction [15]. On the other hand, three-dimensional (3D) hierarchical nanostructures have been proved to be one of the most significant factors directly influencing the electrocatalytic activity of Au, which displays superior electrocatalytic activity compared with zero-dimensional structures [38,39].

Among the reported work, NiCo₂O₄ was mainly synthesized via hydrothermal methods using aqueous alkali or other additives and the final yield is low [40–43]. Due to the widespread use of NiCo₂O₄, it is necessary to find some low-cost ways to obtain massive nickel cobalt oxides. For this reason, Ding *et al.* have synthesized porous NiCo₂O₄ at gram-scale using two additive (Na₂CO₃ and PEG) with less satisfactory uniformity and structure [44,45].

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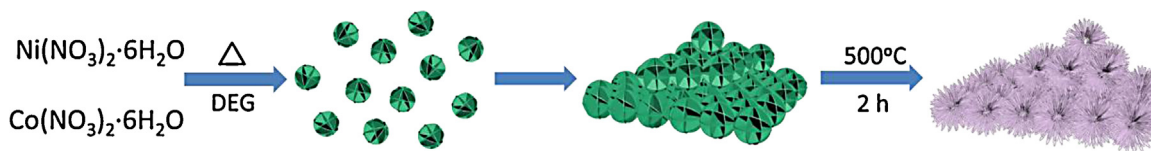


Fig. 1. The growth mechanism of the hierarchical nickel cobalt oxides.

Herein, we develop a high yield (13 gram at a time) and simple strategy to fabricate multiple hierarchical nickel cobalt oxides coral structure. The growth process is illustrated in Fig. 1. The 3D nickel cobalt oxides structures were synthesized via a one-pot thermal decomposition route of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in cheap and nontoxic di(ethylene glycol) (DEG) coupled with a post calcination treatment. The electrocatalytic behavior of the nickel cobalt oxides for methanol oxidation was investigated, which displays a desirable catalytic activity and stability.

2. Experimental

2.1. Reagent

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, di-ethylene glycol (DEG) and N,N-dimethyl formamide (DMF) were obtained from Shanghai Chemical Reagent Manufacturing Co. All other reagents were of analytical grade and used as received without further purification. Ultrapure fresh water was obtained from a Millipore water purification system (MilliQ, specific resistivity > 18 M Ω cm, S.A., Molsheim, France) and used in all runs.

2.2. Synthesis of NiCo_2O_4

Briefly, 0.5 mol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 mol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 500 mL DEG in a 1 L flask. Then the mixed reactants were rapidly heated at 190 °C for 4 h and then cooled to room temperature. After collection by centrifugation, the obtained products were washed with distilled water and ethanol three times, which were further dried at 60 °C for 12 h. Finally, the resulting sample was heated to 500 °C at a rate of 1 °C min⁻¹ and kept at this temperature for 2 h. The final products cooled to room temperature and the yield of the NiCo_2O_4 is about 13 g.

2.3. Apparatus

All electrochemical measurements were performed on a CHI 660C electrochemical workstation (Chenhua Instrument Co. Shanghai, China). A conventional three-electrode electrochemical cell was used, a modified glass carbon electrode (GCE, diameter 3.0 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. X-ray diffraction (XRD) analysis was performed with a Rigaku Dmax-2000 diffractometer using Cu K α radiation. The morphologies of the samples were characterized by scanning electron microscopy (SEM) measurements from a JSM-6390LV microscope (JEOL). Transmission electron microscopy (TEM) was conducted at 200 kV with a JEM-2100F field emission TEM. The pore characteristic of the sample was determined by nitrogen adsorption at -196 °C using NOVA 4000e Surface Area & Pore Size analyzers. The sample was degassed at 200 °C under vacuum at 1×10^{-3} Torr for a period of at least 2 h. The surface area was calculated using the multipoint Brunauer-Emmett-Teller (BET) method. The further evidence for the composition of the product was inferred from X-ray photoelectron spectroscopy (XPS), using a ESCALAB 250Xi spectrometer (Thermo Scientific, U.S.) with Al K α X-ray as the excitation source.

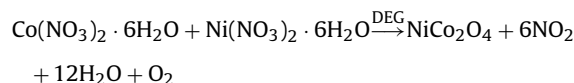
2.4. Preparation of the modified electrode

Before each modification, the bare GCE was sequentially polished with 0.3 and 0.05 μm alumina power slurries to a mirror-shiny surface and sonicated in ethanol and ultrapure water. NiCo_2O_4 /Nafion/GCE was performed in the following manner: 5.0 μL of NiCo_2O_4 DMF (2 mg/ml) solution was dripped onto the surface of a freshly polished glassy carbon electrode. The electrode was allowed to dry, and then 2.0 μL of 0.05%w/w nafion solution was pipetted into it. The electrode was then allowed to air-dry at room temperature.

3. Results and discussion

3.1. The characterization of the NiCo_2O_4

This solvent thermal decomposition process can be described by the following formula:



Meaningfully, the output of these multiple nickel cobalt oxides with hierarchical structures made via the direct thermal decomposition coupled with a post calcination treatment can be easily amplified. To demonstrate this, we prepared about 13.2 g of nickel cobalt oxides hierarchical structures by amplifying the feeding chemicals in proportion during the synthesis. Thus, it is believed that the yield can be further scaled up if an enough large reactor is adopted, which is very important for the practical applications of such materials.

As noted earlier, the growth of NiCo_2O_4 was not additive assisted (Fig. 1). Instead, the successful synthesis of NiCo_2O_4 is explained by a kinetically controlled dissolution–recrystallization mechanism, where the most important factor is the solubility of the salt and crystal coarsening via Ostwald ripening in which larger crystals grow at the expense of smaller [46–48]. The samples were treated at reaction times to investigate the structural evolution of the coral structures via SEM shows in Fig. 2. In the initial stage, dispersed nanosheet-based assembly structures observing (about 500 nm in diameter) were collected after a reaction time of 2 h (Fig. 2a). When the reaction duration was prolonged to 4 h (Fig. 2b and 2c), assembly structures further grew and connected to each other to form moss-like structures (the thickness of nanosheet is about 1.67 nm). After calcination treatment, coral structures were finally created and samples remained the frame of precursor on the whole (Fig. 2d and 2e). The nanosheets of sample split into porous nanobelts. Further morphology characterization of the microspheres was performed on TEM, as shown in Fig. 2f, which is in good agreement with the results of SEM. The high resolution TEM (HRTEM) (insert in Fig. 2f) reveals a distinct set of visible lattice fringes with an inter-planar spacing of 0.47 nm, corresponding to the (111) plane of spinel NiCo_2O_4 [26].

The powder XRD patterns of the prepared nickel cobalt oxides were displayed in Fig. 3a. Moss-like NiCo_2O_4 structures have no apparent diffraction peaks, which prove sample to be

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