



Letter

Facile synthesis of well dispersed spinel cobalt manganese oxides microsphere as efficient bi-functional electrocatalysts for oxygen reduction reaction and oxygen evolution reaction



A B S T R A C T

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Developing catalysts with high bi-functional electrocatalytic activity for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is essential for the fuel cells and metal-air batteries because of the sluggish kinetics of oxygen electrochemical reaction. Herein, we prepared a porous and well dispersed spinel MnCo_2O_4 (MCO) catalyst through a facile solvothermal method followed by a calcination process. $\text{CH}_3\text{COONH}_4$ used in solvothermal process played an important role in control of the size and morphology of MCO. The as-prepared MCO submicrospheres feature a porous structure and a high specific surface area. Tested by the rotating ring disk electrode (RRDE) technique, the sample MCO-10 and MCO-5 shows best catalytic towards ORR and OER, respectively. In particular, MCO-10 exhibits a high diffusion limiting current density (5 mA cm^{-2}) and a better stability comparable to commercial Pt/C (20 wt% Pt on carbon) catalyst.

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1. Introduction

There is an emergency to develop electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) because of their importance in oxygen electrochemical process, like fuel cells and metal-air batteries [1]. Over the past decades, precious metals based electrocatalysts such as Pt and Ru have shown the excellent catalytic activity for ORR and OER. Their high cost and poor stability, however, limit their future development and application [2,3]. Therefore, diminishing the catalyst cost and developing new type catalysts with comparable activity attracted great interests. In the former case, many efforts aimed to reduce the amount of noble metals by alloying Pt with low cost transition metal, preparing the defined crystal surface of Pt on special structure metal skeleton, and so on [4–8]. In the latter case, binary transition metal oxides, for example, spinel transition metal oxides, have attracted much attentions and exhibited excellent bifunctional catalytic activity [9–11], because of their high abundance, low cost, relative stability and considerable activity compared with commercial Pt/C catalyst [12–15].

Moni Prabu et al., reported a simple procedure to obtain 1D- NiCo_2O_4 with porous tubular and rod-like structures, and they found the electrospinning parameters are key points for the formation of uniquely structure [9]. Si et al., prepared hexagonal Mn_2AlO_4 nanosheets showing via a facile dealloying-annealing strategy [10]. Yang et al. adopted a facile precursor pyrolysis method to obtain controllable morphologies and crystalline structures of spinel-

type $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$. It was believed that the capping agent play a key role for the formation of various morphologies and structures [11]. All the spinel catalysts mentioned above exhibited brilliant ORR performance with higher stability than commercial Pt/C catalyst.

As we all know, the electrochemical reaction of oxygen occurs on the interface or surface of the catalysts [16]. Therefore, improving electro-active surface area and enhancing the kinetics of ions on the electrode and electrode/electrolyte interface is important to obtain high activity [17]. Porous nanostructured materials with reducing size and uniform dispersion can provide high surface area and rapid mass transport. Up to now, porous nanostructured materials can be fabricated by a general solvothermal method with carbonates as precursors. The final product usually inherits the morphology of its carbonate precursor and gets porous after calcination in air with the emission of carbon dioxide [18]. These nanostructured materials usually favor the ORR and OER. However, because of the Ostwald ripening, this method usually produces relatively large particles about 1–2 μm , with uneven size distribution [19,20]. The smaller particle size of catalyst may provide more efficient activity sites. Therefore, finding an effective way to decrease the particle size was very essential. The more efficient activity sites in catalyst, the better catalytic activities.

Aiming to develop highly active bi-functional electrocatalysts based on earth-abundant elements, we prepared a series of porous MnCo_2O_4 microspheres through a facile solvothermal method followed by a calcination process. $\text{CH}_3\text{COONH}_4$, as an effective

additive, plays an important role in control of morphology and size during the solvothermal procedure. The as-prepared catalyst sub-microspheres with very uniform distribution possess improved surface area and pore size, thus exhibited considerable ORR and OER performance in alkaline electrolytes.

2. Experimental

2.1. Synthesis of spinel $MnCo_2O_4$

All the chemicals were of analytical grade and used without any further purification. The formation processes of spinel $MnCo_2O_4$ catalysts were based on a solvothermal method, followed by the thermal decomposition process in air. In a typical procedure, 1 mmol $Mn(CH_3COO)_2 \cdot 4H_2O$, 2 mmol $Co(CH_3COO)_2 \cdot 4H_2O$ and 10 mmol of CH_3COONH_4 were added to a solvent of 40 mL ethylene glycol with vigorous stirring. Then, 30 mmol NH_4HCO_3 was added to the above solvent. Finally, the dark red mixtures were transferred into a Teflon-lined autoclave, which was heated gradually to 200 °C and maintained at the same temperature for 20 h. The pink precursor was collected by centrifugation and washed with deionized water and ethanol for five times, before drying at 80 °C for 5 h in an oven. The final black product (marked as MCO-10) was prepared in the following steps: heating the corresponding pink products in a muffle furnace in laboratory air at a ramping rate of 1 °C min^{-1} to 700 °C, then keeping at 700 °C for 10 h, followed by a natural cooling to room temperature. To investigate the effect of CH_3COONH_4 , we also synthesized three other samples of MCO-0, MCO-5, MCO-15, at different dosage of CH_3COONH_4 with 0 mmol, 5 mmol and 15 mmol, respectively.

2.2. Physical characterizations

The crystal structure of as-prepared MCO catalysts were characterized on a Bruker D8 Advanced diffractometer using Ni filtered Cu-K α radiation taking $\lambda = 1.54184 \text{ \AA}$. The morphology and microstructure of the as-prepared MCO catalysts were confirmed by field-emission scanning electronic microscopy (FESEM, Hitachi SU8010) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100). Energy Dispersive Spectrometer (EDS, Oxford instruments X-Max) analysis was utilized to determine the composition of as-prepared MCO catalysts. N_2 adsorption isotherms were recorded at 77 K using a TriStar 3020 (Micromeritics)

apparatus. Before the measurement, the as-prepared MCO catalysts were degassed at 300 °C for 12 h under vacuum. The specific surface area and pore size were calculated by using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively. The elements binding environment of the samples were studied with X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific Escalab 250Xi with a monochromatic Al K α radiation ($h\nu = 1486.6 \text{ eV}$).

2.3. Electrochemical measurements

The electrocatalytic activity for the ORR and OER of the as-prepared MCO catalysts were evaluated in a rotating ring-disk electrode (RRDE) using a Pine instrument (AFMSRCE rotator) interfaced with AfterMath v1.3.6972 software. The Ag/AgCl (3 M KCl) electrode and Pt-wire were used as the reference and counter electrodes, respectively. The RRDE electrode consisted of a GC disk and surrounded by a Pt ring, the geometric surface area of them were 0.2475 cm^2 and 0.1866 cm^2 , respectively. The electrolyte was 0.1 M KOH solution and it was prepared fresh at the time of use. Commercial Pt/C catalyst (20 wt%, JohnsonMatthey) was used for comparison at the same condition.

In order to obtain a catalyst film-coated GC disk, 5 mg catalysts and 5 mg acetylene black were dispersed in 350 μL isopropanol solution which contains 95 μL Nafion solution (5 wt%) by sonication for 0.5 h to form a homogeneous ink finally. After that, 7 μL of ink was dropped onto the surface of GC electrode and drying in air for 0.5 h, yielding a catalyst level of 0.32 $mg\ cm^{-2}$.

For the ORR test, the electrolyte was bubbled with O_2 at a flow rate of 25 sccm over 0.5 h to ensure O_2 saturation. The CV measurement was performed by sweeping the potential from -1 to 0.2 V at a scan rate of 50 $mV\ s^{-1}$. The RRDE test were carried out by sweeping the potential from -1 to 0.2 V at a scan rate of 10 $mV\ s^{-1}$, with the electrode rotating at 400, 900, 1600 and 2500 rpm, respectively. Prior to each measurement, the CV measurement was performed in N_2 saturated electrolyte to subtracted background capacitive current.

For the OER test, the electrolyte was bubbled with O_2 at a flow rate of 25 sccm over 0.5 h to ensure O_2 saturation. In addition, the electrode rotating was hold at 1600 rpm. The CV measurement was performed in by sweeping the potential from 0 to 1 V at a scan rate of 10 $mV\ s^{-1}$.

For the stability test, a Chronoamperometric (CA) method was

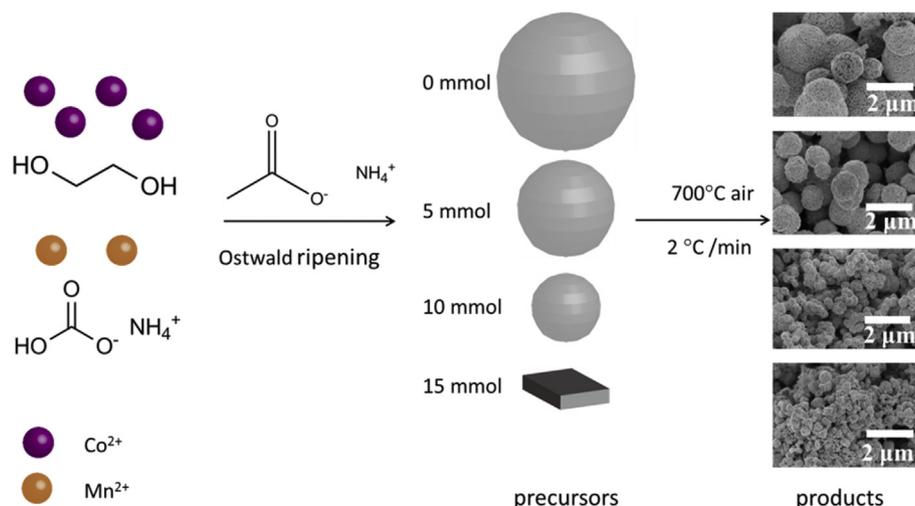


Fig. 1. The synthesis route of spinel MCO with different morphology and particle size.

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