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Article

Phase-transfer synthesis of α-$Co(OH)_2$ and its conversion to CoO for efficient electrocatalytic water oxidation

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ABSTRACT

Water splitting is an attractive way to produce recyclable hydrogen energy resource. The oxygen evolution reaction (OER) is the rate-determine step of water electrolysis. The exploring of low-cost, highly efficient and durable electrocatalysts for OER is thus extremely important. In this work, we developed a facile two-phase protocol to fabricate an α-$Co(OH)_2$ using sodium oleate as the phase-transfer surfactant. The crystallinity and structure of the α-$Co(OH)_2$ was regulated by heat treatments toward enhanced electrocatalytic OER activity. With the calcination of the as-prepared α-$Co(OH)_2$ at 200 °C, a networked and well-dispersed CoO nanoparticles were formed. The CoO sample afforded an OER current density of 10 mA cm^{-2} under a low overpotential of 312 mV in a 1 mol L^{-1} KOH aqueous solution. The high activity of the CoO material is believed to be associated with its ultra-small particle size and plentiful open spaces in the material, both of which can provide abundant surface catalytic sites.

1. Introduction

Hydrogen has long been considered as a clean and sustainable energy resource to reduce our dependences on fossil fuels [1]. Water splitting is a reliable way for the large-scale production of hydrogen [2]. However, the main barrier in the process of water splitting is the oxygen evolution reaction (OER), which requires multi steps of proton-coupled electron transfer and needs to overcome the high energy barrier in O–O bond formation [3,4]. In order to accelerate the OER rate, it is of great significance to develop efficient catalysts for water oxidation [5]. To date, RuO_2 and IrO_2 have been regarded as the state-of-the-art OER catalysts [6]. However, the scarcity and high price limited their application prospectives. Thus, it is highly important to develop alternative OER catalysts based on earth-abundant elements [7,8].

Among the many non-noble metal-based electrocatalysts for OER, Co-based materials have been considered as one of the most promising candidates [4,9]. These materials include, but are not limited to, oxides [10], hydroxides [11], phosphides [12], nitrides [13] and chalcogenides [14]. However, the actual active species in many of these Co-based materials were proven to be the in-situ generated surface Co–O(H) sites [15]. Thus, the exposure of more surface sites from cobalt hydroxide would be beneficial for OER catalysis. In literature reports, cobalt hydroxides were typically prepared from electrodepositions or hydrothermal methods [11,16,17]. It is highly desirable to develop other advanced methods for the synthesis of other unique cobalt hydroxides as efficient OER electrocatalysts or catalyst precursors.

Herein, we proposed a fast and facile two-phase protocol to synthesize the α-$Co(OH)_2$ for highly efficient electrocatalytic water oxidation. Generally, the method is based on the translocation of Co^{II} from aqueous phase to organic phase with the assistance of an amphipathic surfactant (sodium oleate, SO). The Co^{II} cations, initially presenting in the aqueous phase, were capped by the oleate anions and subsequently were transferred into the organic phase due to the hydrophobic tails of the formed nuclei. With the addition of ammonia into the two-phase system, Co^{II} was precipitated at the interface of the two phases by the hydroxide anions created from the hydrolysis of ammonia. The obtained solid samples were further annealed by thermal treatment to enhance the OER activity. Specifically, the sample annealed at 200 °C for 3 h (denoted hereafter as Co-200) displayed superior activity, as compared to its counterparts. It requires a low overpotential of 312 mV to drive an OER current density of 10 mA cm^{-2}.

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2. Materials and methods

2.1. Material synthesis

The α-$Co(OH)_2$ was synthesized via a phase-transfer protocol. Typically, cobalt acetate (1 mmol) was first dissolved in deionized water (12.5 mL) at 40 °C under magnetic stirring. Toluene (25 mL) was then added to form a two-phase solution. Subsequently, sodium oleate (1 mmol) was added into the mixture and the stirring was kept for 30 min until the color of the solution became deep purple. Next, ammonia (5 mmol, aqueous solution, 25 wt%) was rapidly added and the stirring was continued for another 30 min until the color of the system changed to olive-green. Finally, the reaction mixture was transferred into a centrifuge tube, and the green product was floated at the interface of the water-toluene system. The resulting product was washed with deionized water and anhydrous ethanol thoroughly, collected by centrifugation, and dried at 60 °C for 12 h. The as-obtained powder sample was further calcined at different temperatures (100–400 °C) for 3 h in a muffle furnace. Sample for control studies was also prepared based on the same procedure without the addition of sodium oleate.

2.2. Physical characterization

The morphologies of the catalysts were observed on a field-emission scanning electron microscope (FESEM, SU8020, Hitachi) with an accelerating voltage of 5 kV. The transmission electron microscope (TEM) images were acquired from a TEM (JEM-2100, JEOL) operating at an accelerating voltage of 200 kV. Energy-dispersive X-ray analysis (EDX) was conducted on an AMETEK Materials Analysis EDX equipped on the TEM. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max2550VB+/PC X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). The X-ray photoelectron spectroscopy (XPS) analyses of the samples were carried out on a Kratos AXIS ULTRA XPS. Monochromatic Al Kα X-ray ($h\nu = 1486.6$ eV) was employed for analysis with photoelectron take-off angle of 90° with respect to the surface plane. Correction of the binding energies was carried out using C 1s peak at 284.6 eV arising from the adventitious hydrocarbon. Infrared (IR) spectra were obtained on a Bruker Tensor 27 spectrometer using a standard KBr-pellet technique.

2.3. Electrochemical studies

All electrochemical experiments were carried out using a CH Instruments Electrochemical Analyzer (CHI 660E) at 20 °C. Cyclic voltammograms (CVs), at a scan rate of 50 mV s^{-1}, were conducted in 15 mL of 1 mol L^{-1} KOH aqueous solution using a conventional three-electrode configuration with catalyst-loaded glassy carbon electrode (GC, 0.07 cm^2) as the working electrode, saturated Ag/AgCl as the reference electrode, and Pt wire as the auxiliary electrode. The loading of catalysts on the GC was prepared through a drop casting method. Typically, 2 mg of sample and 30 μL of Nafion solution (5 wt%, DuPont) were dispersed in 1 mL of water–ethanol solution at volume ratio of 2:1 by ultrasonicating for 1 h to form a homogeneous suspension. Then 5 μL (optimized amount) of the mixture was loaded onto the GC electrode working area. The mass loading for all samples on the GC electrodes was 0.143 mg cm^{-2}. All potentials were reported versus the reversible hydrogen electrode (RHE) based on the equation: $E_{RHE} = E_{Ag/AgCl} + (0.197 + 0.0591 \times pH)$ V. Cell resistance was compensated through the CV experiments. Chronopotentiometry and chronoamperometry were recorded at the same experimental conditions without compensating iR drop. Tafel plots were acquired from stable electrolysis currents at different potentials. The electrochemical impedance spectroscopy (EIS) was recorded at 1.65 V in a 1 mol L^{-1} KOH solution on GC electrode over a frequency range from 0.1 Hz to 1 MHz at the amplitude of the sinusoidal voltage of 5 mV. The explicit Nyquist plots were thus obtained based on the EIS data. Electrochemical surface area (ECSA) was obtained by measuring the electrochemical double layer capacitance from CVs within the non-faradaic potential window at different scan rates.

3. Results and discussion

The XRD patterns of the samples from thermal treatment at different temperatures are displayed in Fig. 1a. The sample obtained at room temperature has an α-$Co(OH)_2$ structure with four characteristic peaks, which are consistent with the (003), (006), (100), (110) facets [18]. By increasing the annealing temperature to 200 °C, the $Co(OH)_2$ structure transforms gradually to an CoO phase. Under further elevated temperatures, a pristine Co_3O_4 structure is formed with sharp diffraction peaks [19]. The corresponding SEM images of the samples are displayed in Fig. 1b–f. Aggregated morphology with macropores is observed in all the samples. Specially, the aggregation sizes are reduced from samples prepared at temperatures higher than 200 °C. We used IR spectra to study the residence of the SO surfactants in the samples (Fig. 2a). The peaks at 2850 and 2930 cm^{-1} can be assigned to the C–H stretching vibrations [7], which are presumably from the SO anions intercalated in the Co-based samples. There are still visible IR peaks from $-CH_3$ groups from samples after thermal treatment at 200 °C. These peaks can barely be observed in the samples prepared at higher temperatures, and instead, the emerged peaks between 500 and 700 cm^{-1} are from the Co-O vibration modes [20]. In a short summary, the as-synthesized α-$Co(OH)_2$ sample contains SO molecules. By thermal treatment, the residue SO was gradually removed and the crystal structure of the sample evolved from $Co(OH)_2$ to CoO and finally to Co_3O_4. The morphologies of the samples remained almost unchanged upon heat treatment.

We studied the electrocatalytic water oxidation activity of the samples by CV method in a 1 mol L^{-1} aqueous KOH solution (Fig. 3). The Co-200 sample outperformed its counterparts dominantly. The OER onset potential is only 290 mV. The overpotentials required to drive OER current densities of 10 and 100 mA cm^{-2} are, respectively, 312 and 390 mV, which are among those lowest values reported in literature for electrocatalytic OER from catalysts based on earth abundant elements [21–27]. We selected two recent reports here to compare the OER activity. One is a Co-based OER material, and another one is a well-documented NiFe system. For example, the recently reported NiFe LDH@graphene [28] and the Co–P foam [29] materials require overpotentials of 337 and 300 mV, respectively, to reach a current density of 10 mA cm^{-2}. It should also be noted that we did not adopt any conductive material to facilitate the charge transfer. In contrast, the Co-RT, Co-300 and Co-400 samples exhibit lower OER activity with an overpotential of ~390 mV to achieve a current density of 10 mA cm^{-2}, and the Co-100 sample needs an overpotential of 360 mV to get the same current. The enhanced water oxidation activity of the Co-200 sample may be attributed to the active CoO phase and the removal of the blocking SO molecules in the sample. The different synthesis conditions (different moles of ammonia and sodium oleate) were systematically studied to examine the effects on the electrocatalytic activity and morphology of the $Co(OH)_2$. The CVs of the $Co(OH)_2$ synthesized under different conditions showed that the highest performance was from the $Co(OH)_2$ synthesized with the addition of 5 eq. of ammonia and 1 eq. of sodium oleate (Fig. S1 online). The morphologies of aforementioned $Co(OH)_2$ under different conditions are displayed in

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