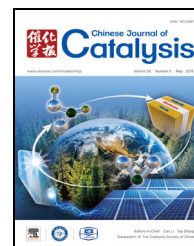


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Article

A highly efficient flower-like cobalt catalyst for electroreduction of carbon dioxide



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ABSTRACT

Electrochemical conversion of CO₂ into fuel has been regarded as a promising approach to achieve the global carbon cycle. Herein, we report an efficient cobalt catalyst with a unique flower-like morphology synthesized by a green and facile hydrothermal method, in which *n*-butylamine is used as the capping agent. The resultant catalyst shows superior electrocatalytic activity toward CO₂ electroreduction, which is highly selective for generating formate with a Faraday efficiency of 63.4%. Electrochemical analysis reveals that the oxide on the surface is essential for the electrocatalysis of the CO₂ reduction reaction. Cyclic voltammograms further suggest that this catalyst is highly active for the oxidation of reduced product, and can thus be seen as a bifunctional catalyst.

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1. Introduction

Due to fossil fuel combustion, the concentration of CO₂ in the atmosphere has recently reached 400 ppm and is expected to rise continuously, which can lead to numerous environmental problems such as global warming, rising sea levels, and more erratic weather patterns [1,2]. Therefore, CO₂ reduction reaction (CORR) has become a research focus to control the atmospheric concentration of CO₂. Various CO₂ reduction approaches, including electrochemical [3], biochemical [4], photochemical [5,6], and thermochemical [7] methods, have been proposed and explored in the past decades. Among them, electrocatalysis is a very promising method as it can be operated under ambient conditions.

During the past decades, heterogeneous electrochemical CO₂ reduction has been explicitly investigated, and various catalysts have been investigated to generate products such as carbon monoxide, formic acid, methane, and methanol [8–10]. Recently, Kanan et al. [11,12] suggested that the activity of metal catalysts obtained by the reduction of metal oxides is usually higher than that in other methods. Xie et al. [13] investigated cobalt, associated with loosely bonded *d* electrons and high electrical conductivity, as a promising catalyst for the CORR. They synthesized two-dimensional cobalt/cobalt oxide hybrid by using a solvothermal method with high electrocatalytic activity for the CORR, and the main product was formate. It was proposed that the metal/metal oxide interface plays a key role in catalyzing the CORR.

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In this work, we develop a green and facile synthetic strategy for unique nanostructured cobalt by using nontoxic capping and reductant agents. The electrochemistry of the CORR on the resultant Co is then explicitly investigated. The flower-like Co, which favors the exposure of the active sites and the accessibility of the species, is found to show superior electrocatalytic activity than the bulk Co. Nuclear magnetic resonance (NMR) results indicate that the main product is formate, and the yield is highly dependent on the applied potential.

2. Experimental

2.1. Synthesis of flower-like Co, bulk Co, and Co(OH)₂

Flower-like Co: First, CoCl₂·6H₂O powder was dissolved in a liquid mixture of 21 mL deionized water and 9.0 mL *n*-butylamine to yield a concentration of 50 mmol/L. Second, NaH₂PO₂·H₂O was added as a reductant with a concentration of 0.40 mol/L. After vigorous stirring, the mixture was transferred to a Teflon cup in a stainless steel-lined autoclave for conditioning at 140 °C for 24 h. Then, the system was allowed to naturally cool down to room temperature, and the black fluffy solid product was collected by centrifuging the mixture. The product was rinsed with deionized water and ethanol in sequence, and then dried in a vacuum oven at 60 °C for 4 h.

Bulk Co and Co(OH)₂: The preparation of bulk Co and Co(OH)₂ followed the abovementioned procedure, except that *n*-butylamine was not used for bulk Co and the hydrothermal treatment time was shortened to 3 h for Co(OH)₂.

2.2. Physicochemical characterization

X-ray diffraction (XRD) measurements were carried out on a TD-3500 X (Tongda Technology) diffractometer with a Cu K_α radiation source operated at 40 keV. The patterns were collected at a scan rate of 0.05°/s in the 2θ range 10° to 80°. Scanning electron microscopy (SEM) observations were carried out on a Nova NanoSEM 430 scanning electron microscope.

2.3. Electrochemical characterization

The electrochemical behavior was characterized by cyclic voltammetry and linear sweep voltammetry using a three-electrode cell on an electrochemical workstation (CHI660E), at room temperature (25 °C). A gold wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The working electrode was a glassy carbon disk (5.0 mm in diameter, PINE) covered with a thin layer of Nafion-impregnated catalyst. Typically, the thin-film electrode was prepared as follows: 10 mg of the catalyst was dispersed in 1.0 mL Nafion/ethanol (0.84 wt% Nafion) by sonication for 120 min. Then, 10 μL of the dispersion was transferred onto the glassy carbon disk by using a pipette, yielding a loading of 0.50 mg/cm².

The electrolyte solution, 0.10 mol/L of KHCO₃, was bubbled with either Ar (99.999%) or CO₂ (99.999%) for 30 min before the test. The cyclic voltammograms (CVs) were collected at 20

mV/s in the potential range between −1.25 and −0.4 V (vs. SCE) in Ar- and CO₂-saturated electrolyte solution. The linear sweep voltammograms (LSV) were collected by scanning the potential from −0.6 down to −1.2 V in Ar- or CO₂-saturated electrolyte solution. All the potentials are referenced to SCE in this study.

For controlled-potential electrolysis, 50 μL of the dispersion was loaded onto a gas-diffusion carbon paper with an area of 1 cm² to form a working electrode. The counter and reference electrodes were gold wire and SCE, respectively. The electrolysis was performed in an H-type cell with a piece of Nafion®117 cation-exchange membrane (H⁺ form) as a separator. 20 mL of KHCO₃ solution (0.10 mol/L) was introduced into the cathode chamber, and CO₂ was continuously bubbled throughout the experiment to ensure saturation. The electroreduction of CO₂ was performed at a constant potential of −0.75, −0.85, −0.95, −1.05, and −1.15 V. The electrolysis was prolonged for 10 h to enrich the reduction product.

The liquid products were quantified by ¹H NMR (Bruker AVANCE III 400) spectroscopy, for which 0.25 mL electrolyte was mixed with 0.50 mL dimethyl sulfoxide-D₆ and 5.0 mg methylbenzene was added as an internal standard. The faradaic efficiency of formate (η_{formate}) was calculated from the total amount of charge Q (C) passed through the material and the total amount of formate produced n_{formate} (mol).

$$\eta_{\text{formate}} = 2Fn_{\text{formate}}/Q = 2Fn_{\text{formate}}/\int Idt$$

where I (A) is the reduction current at a specific applied potential and t (s) is the time.

3. Results and discussion

3.1. Physical characterization

Fig. 1(a) reveals that cobalt hydroxide has a hexagonal sheet structure. After reduction, serious aggregation of Co, namely bulk Co, is observed in the absence of *n*-butylamine (see Fig. 1(b)); in comparison, a flower-like Co covered with curved nanosheets, which inherits the morphology features of Co(OH)₂, is synthesized by adding *n*-butylamine (see Fig. 1(c)). The difference in the morphology can be attributed to the chemical adsorption of *n*-butylamine on the facets of Co(OH)₂, thus preventing the aggregation of Co. The unique flower-like morphology of Co favors both the exposure of the active sites and the accessibility of the active species, thus facilitating the electrocatalysis (*vide infra*). The corresponding XRD patterns are shown in Fig. 2. As seen in Fig. 2(1), Co(OH)₂ shows the characteristic peaks of β-Co(OH)₂ (No. 45-0031). Both bulk Co and flower-like Co basically show the same patterns with the diffraction peaks at 41.68°, 44.76°, 47.57°, 62.73°, and 75.94° (see Fig. 2(2, 3)), indicating that they are bulk metal of the hexagonal close-packed (hcp) phase (No. 05-0727).

3.2. Electrochemical measurements

The CO₂ reduction activity of flower-like Co, bulk Co, and Co(OH)₂ is evaluated by collecting the LSVs. As seen in Fig. 3(a), for the three catalysts, a broad cathodic reduction wave is observed between −1.2 and −0.6 V, which is then followed by a

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