



Electrocatalytic reduction of carbon dioxide over reduced nanoporous zinc oxide



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ABSTRACT

Nanoporous zinc oxide (ZnO) is prepared by a hydrothermal method followed by thermal decomposition for electrocatalytic reduction of CO₂. In situ X-ray absorption spectroscopy results indicate that ZnO is reduced to Zn under the electrolysis conditions for catalyzing CO₂ electroreduction. The reduced nanoporous ZnO exhibits obviously higher CO Faradaic efficiency and current density than commercial Zn foil with a maximum CO Faradaic efficiency of 92.0%, suggesting that the nanoporous structure facilitates electrocatalytic reduction of CO₂ over reduced nanoporous ZnO, probably due to increased surface area and more coordination unsaturated surface atoms.

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1. Introduction

Electrocatalytic reduction of CO₂ to chemical feedstock and liquid fuel is an important approach for renewable energy storage and carbon cycle utilization. So far, developing selective and efficient catalysts is one of the most challenging issues toward CO₂ electroreduction [1]. Noble metals such as Au [2,3], Ag [4] and Pd [5,6], have shown high Faradaic efficiencies for CO production, however, the high cost and terrestrial scarcity of noble metals hinder extensive use for CO₂ electroreduction. Therefore, one major challenge is to replace the noble metal catalysts with earth-abundant materials for efficiently catalyzing CO₂ electroreduction [7–9].

Zinc is abundant and inexpensive, and bulk Zn has shown promising applications in electrocatalytic reduction of CO₂ to CO with Faradaic efficiency ranging from 16.8% to 53.4% [10,11]. Recently, dendrite-like Zn was electrodeposited on Zn substrate to catalyze CO₂ electroreduction with a maximum CO Faradaic efficiency of 79.0%, suggesting that the morphology of Zn has a critical effect on CO₂ electroreduction [12]. Due to their high surface area and high density of coordination unsaturated surface atoms, nanoporous metals have attracted increasing attention in electrocatalysis [13–15]. Nanoporous Ag has been applied

to catalyze CO₂ electroreduction, showing higher CO Faradaic efficiency and lower overpotential compared with polycrystalline Ag [4,15]. Inspired by the merits of nanoporous structures, nanoporous ZnO was constructed for electrocatalytic reduction of CO₂ in this work. A maximum CO Faradaic efficiency of 92.0% and CO current density of 15.1 mA cm⁻² was achieved at -1.66 V (vs. Ag/AgCl), which are much higher than those over commercial Zn foil (55.5%, 3.3 mA cm⁻²). In situ X-ray absorption spectroscopy (XAS) results indicate that nanoporous ZnO was reduced to Zn during the electrolysis.

2. Experiment section

2.1. Catalyst preparation

Zinc acetate dehydrate (Zn(Ac)₂·2H₂O), urea, sodium dodecyl sulfate (SDS), and n-butanol were purchased from Sinopharm Chemical Reagent Co. Ltd. Commercial Zn foil was purchased from Alfa Aesar (99.994%, 0.25 mm). Nanoporous ZnO was synthesized as follows: 1.09 g of Zn(Ac)₂·2H₂O and 2.42 g of urea were dissolved in 50 mL of distilled water under vigorous stirring for 30 min. Meanwhile, 0.25 g of SDS was dissolved in a mixture of H₂O and n-butanol under vigorous stirring to form a clear solution [16]. Then the SDS was added into the Zn(Ac)₂·2H₂O solution dropwise under magnetic stirring. After 3 h, the mixture was transferred into Teflon-lined stainless autoclave with a capacity of 100 mL and was kept at 100 °C for 12 h. The obtained white precipitate was filtered, and then washed with distilled water and ethanol thoroughly, followed with drying at 60 °C. Finally the

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white powder was annealed in a furnace at 500 °C for 2 h in air to form nanoporous ZnO.

2.2. Physicochemical characterization

X-ray diffraction (XRD) was measured on a PANalytical X'pert PPR diffractometer equipped with CuK α radiation source ($\lambda = 1.5418 \text{ \AA}$), operated at 40 mA and 40 kV. The samples were pretreated at 200 °C for 10 h in Ar atmosphere, and then nitrogen adsorption/desorption was investigated by a Quantachrome Autosorb iQ2 system at 77 K. The specific surface areas of different samples were determined by the Brunauer–Emmett–Teller (BET) equation. The morphologies of the samples were investigated by a QUANTA 200 FEG scanning electron microscope (SEM) at 20 kV and a HITACHI S-5500 ultra-high resolution SEM. High resolution transmission electron microscopy (HRTEM) was carried out on a JEM-2100 microscope operated at 200 kV.

2.3. Electrochemical measurements

The electrochemical measurements were carried out in an H-cell (separated by Nafion 115). Toray carbon fiber paper coated with catalyst layer, prepared according to our previous work, acted as the working electrode with a geometric size of $1 \text{ cm} \times 2 \text{ cm}$ [5]. The loading of ZnO in the electrode is 2 mg cm^{-2} . The Pt wire and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. Electrocatalytic reduction of CO₂ was performed in CO₂-saturated 0.25 M K₂SO₄ solution (pH 4.2) at room temperature. Potentiostatic electrolysis was performed using an Autolab potentiostat (PGSTAT 302N) at each potential for 30 min. Prior to electrolysis, the K₂SO₄ solution was purged with CO₂/N₂ gas (volume ratio of 95:5, N₂ acts as the internal standard gas) for at least 30 min. Quantification of gas products of CO₂ electroreduction was performed using an on line gas chromatograph (GC) (Agilent 490) with a Molsieve 5A column and a TCD detector every three minutes. The K₂SO₄ solution after electrolysis was collected and analyzed on a Bruker AVANCE III 400 MHz nuclear magnetic resonance (NMR) spectrometer to determine the liquid products. For comparison, commercial Zn foil with a geometric size of $1 \text{ cm} \times 2 \text{ cm}$ was used as the working electrode for CO₂ electroreduction, and the current density in this manuscript is the current divided by the geometric area

of the working electrode (2 cm^2). In situ XAS experiments were conducted in a home-made Teflon cell filled with CO₂-saturated 0.25 M K₂SO₄ solution at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF).

3. Results and discussion

The XRD pattern of nanoporous ZnO is shown in Fig. 1a, which indicates a typical wurtzite ZnO structure (JCPDS: 36-1451). There are no other peaks for impurities detected, confirming that hydrothermally-synthesized Zn₅(CO₃)₂(OH)₆ was completely decomposed to ZnO. The SEM image of nanoporous ZnO in Fig. 1b shows that uniform ZnO microspheres were composed of many nanosheets. HRSEM images in Fig. 1c and d show the presence of nanoporous structure in ZnO. Similarly, the HRTEM image in Fig. 1e also confirms the nanoporous structure of ZnO, and typical ZnO (002) planes with the characteristic lattice spacing of about 0.26 nm are observed in the inset image of Fig. 1e.

Electrocatalytic reduction of CO₂ over nanoporous ZnO and commercial Zn foil was evaluated in CO₂-saturated 0.25 M K₂SO₄ by controlled potential electrolysis ranging from -1.66 V to -1.26 V (vs. Ag/AgCl) over the same electrode. CO and H₂ are detected as the major products, and only a small amount of formate with Faradaic efficiency of about 5% on Zn foil is detected by NMR, while there is no formate produced over nanoporous ZnO. As shown in Fig. 2a, the current density over nanoporous ZnO at -1.66 V (vs. Ag/AgCl) decreases gradually in the initial 600 s and the current becomes stable after 600 s. The calculated quantity of electric charge before 600 s at -1.66 V (vs. Ag/AgCl) is 22.6 C, which is much higher than the required quantity of electric charge for ZnO electroreduction to Zn (9.5 C), suggesting that the ZnO and CO₂ electroreduction occurred simultaneously at -1.66 V (vs. Ag/AgCl) before 600 s. Fig. 2b shows that the maximum CO Faradaic efficiency is 92.0% at -1.66 V (vs. Ag/AgCl) on reduced nanoporous ZnO, which is much higher than that on Zn foil (55.5%) at the same potential. Current densities for CO production increase with the applied potential (Fig. 2c). Due to the high total current density and CO Faradaic efficiency, CO partial current density on reduced nanoporous ZnO is an order of magnitude higher than that on Zn foil at -1.36 V (vs. Ag/AgCl). Tafel analysis was then performed to gain insights into the kinetics of CO₂ electroreduction to

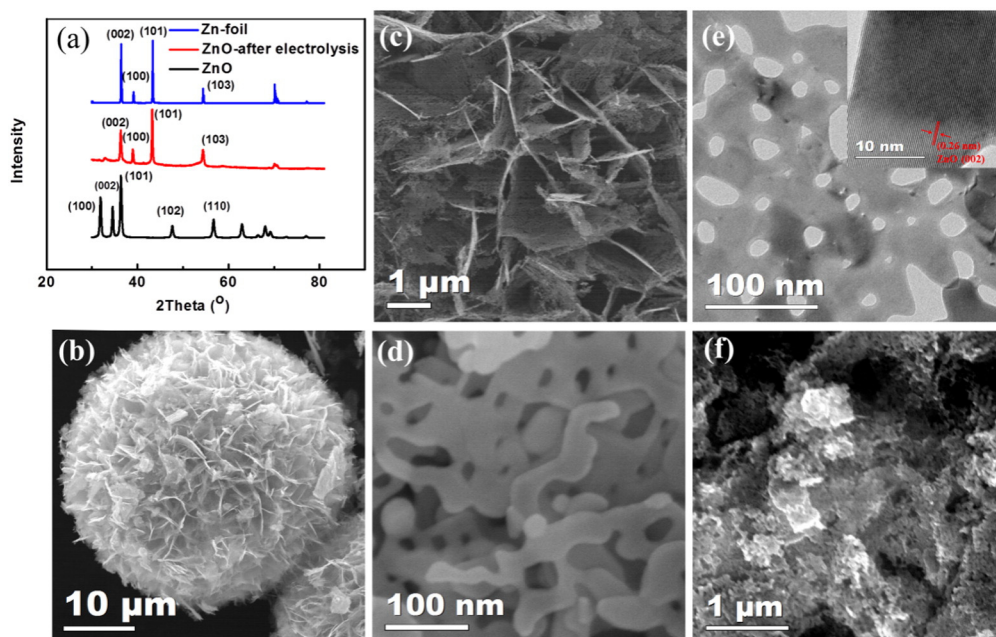


Fig. 1. XRD patterns of nanoporous ZnO, Zn foil and reduced nanoporous ZnO after electrolysis (a). SEM (b, c) and HRSEM (d) images of nanoporous ZnO. HRTEM (e) images of nanoporous ZnO. SEM (f) image of reduced nanoporous ZnO after electrolysis. Inset of (e) corresponding HRTEM image of nanoporous ZnO.

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