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Multilayered Zn nanosheets as an electrocatalyst for efficient electrochemical reduction of CO_2

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ABSTRACT

Electrochemical reduction of CO_2 into useful fuels, when powered by renewable energy, is an ideal process for replacing fossil feedstocks and simultaneously decreasing CO_2 emission. Developing inexpensive electrocatalysts for CO_2 reduction to CO with high activity and selectivity is an important part of CO_2 conversion. Zn as a low-cost metal is identified to be a promising electrocatalyst for CO_2 conversion. Here, we report a Zn electrode composed of multilayered Zn nanosheets (MZnNSs) with high density of edge sites. The MZnNSs catalyst exhibited a maximal CO Faradaic efficiency about 86% at −1.13 V vs RHE, which is almost 9 times higher than that of bulk Zn foil. Density functional theory (DFT) calculations suggest that the improvement of the activity and selectivity of MZnNSs for CO_2 reduction is attributed to its high density of edge sites.

1. Introduction

In the past two centuries, human society was taken into an unprecedented era of prosperity by the utilization of fossil fuels, which still account for a predominating proportion of the total energy source for worldwide consumption today [1,2]. However, the combustion of fossil fuels has significantly given rise to the level of carbon dioxide (CO_2) in the atmosphere, which is directly related to global warming and climate changes, making a negative impact on the ecological environment [3]. In view of the inevitable depletion of fossil fuels and undesirable greenhouse gas effect, it is becoming critical to develop a sustainable way to recycle the overly produced CO_2 into reusable carbon forms [4].

Generally, the feasible approaches of CO_2 conversion to usable fuels mainly include chemical methods [5], photocatalytic reduction [6], electrochemical reduction [7] and biological means [8,9]. Among those techniques, electrochemical reduction of CO_2 powered by renewable energy generation or nuclear energy is considered as a promising method. It is also an energy storage strategy for storing intermittent renewable electricity in energy dense carbonaceous fuels [10], such as HCOOH, CH_4, C_2H_4 and CO [11]. The product of CO mixed with byproduct H_2 from CO_2 electrochemical reduction can be utilized for downstream processing of syngas by using Fischer-Tropsch chemistry [12]. However, there are still many obstacles in the reduction of CO_2 to CO. As CO_2 is a thermodynamically stable molecule, the key step of CO_2 reduction to intermediate species $CO_2^{\cdot-}$ requires a high overpotential and suffers from poor reaction selectivity because of competitive proton reduction [13]. Thus, appropriate catalysts that can activate CO_2 need to be developed to simultaneously increase the product selectivity and lower the overpotential [14]. During the past few decades, a number of metal catalysts have been evaluated for electrochemical CO_2 reduction to CO. Typically, precious metals such as Au and Ag are the most active catalyst materials for efficient reduction of CO_2 to CO, but they are too expensive to be commercialized at large scale [11]. Therefore, it is crucial to develop inexpensive metal catalysts that can convert CO_2 to CO with high selectivity, efficiency and high activity [15].

Zn as an affordable and environmentally benign metal has recently attracted much attention for CO_2 conversion applications, because Zn metal can act as an catalyst for chemical [16], photocatalytic [17] and electrochemical [18,19] reduction of CO_2. In the field of electrochemical reduction of CO_2, Zn has been identified to be a promising catalyst with a wide range of CO selectivity in terms of the Faradaic efficiency (3.3–63.3%) [20]. In addition, as

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native surface oxides may be reduced to afford more active surface structures, surface oxidation treatment on the electrocatalysts is effective to improve the performance [21–25]. Therefore, the activity and product selectivity of a catalyst for CO_2 reduction are dramatically influenced by its geometry, morphology and roughness [26]. Density functional theory (DFT) study has predicted that the edge sites of the catalysts are much more active for CO_2 reduction to CO, while the corner sites are much more favorable for H_2 evolution reaction, and this prediction has been validated by experimental results in Au and Ag catalysts [27,28]. Thus, the catalytic performance of Zn catalyst for CO_2 reduction has a great chance to be improved by morphology design or surface modification.

Here, we report a loose and porous structure Zn electrode consisting of multilayered Zn nanosheets (MZnNSs), which is prepared by an oxidation/reduction process, as shown in Scheme 1. During the reduction process of the ordered ZnO nanowires arrays formed by hydrothermal oxidation treatment of Zn foil, a large surface area and more edge sites are formed to offer an improved CO_2 reduction kinetics. The prepared MZnNSs achieved a superior CO Faradaic efficiency about 86% with a CO partial current density above 5.2 mA cm^{-2} at moderately negative potential −1.13 V vs RHE, which is almost 9 times and 14 times higher than that of bulk Zn foil, respectively. Furthermore, the MZnNSs electrode showed a good stability with negligible deterioration during 7 h continuous operation. DFT calculations suggest that the high density of edge sites is benefit for the improvement of the activity and selectivity of MZnNSs for CO_2 reduction.

2. Experimental section

2.1. Preparation of electrodes

A piece of Zn foil (1.5 × 4.0 cm^2, thickness 0.1 mm, 99.99%) was first mechanically polished to remove the native oxide layer. After rising with water/ethanol and drying under Ar, the Zn foil was put into a 100 mL Teflon-lined stainless-steel autoclave, which contained 25 mL 0.6 mM malic acid solutions. The autoclave was placed in an oven at 190 °C for 8 h and then cooled to room temperature. The Zn foil was taken out from the solution, rinsed with deionized water and then dried in an oven at 120 °C for 4 h to obtain the ordered ZnO nanowires array, which is denoted as O-ZnO. As control sample, the disordered oxidized Zn nanowires were prepared by the similar process with exception of that malic acid solution was replaced by deionized water, which is denoted as D-ZnO. The multilayered Zn nanosheets (MZnNSs) and RD-ZnO were obtained by reducing the O-ZnO and D-ZnO respectively at −0.63 V (vs RHE) for 30 min in CO_2-bubbled 0.5 M $NaHCO_3$ solution.

2.2. Materials characterizations

The scanning electron microscopy (SEM) images were obtained on a JSM-7800F microscope. X-ray diffraction (XRD) patterns were collected from 30° to 90° in 2θ at a scanning rate of 1° min^{-1} on a DX-2700 X-ray diffractometer (Dandong Haoyuan Instrument Co.,) using the a Cu Ka radiation source at 40 kV and 30 mA (λ = 0.154 nm). Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images were recorded on a JEOL JEM-2000EX (120 kV). X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALAB 250Xi spectrometer equipped with a nonmonochromatized Al Kα X-ray source.

2.3. Electrochemical measurements

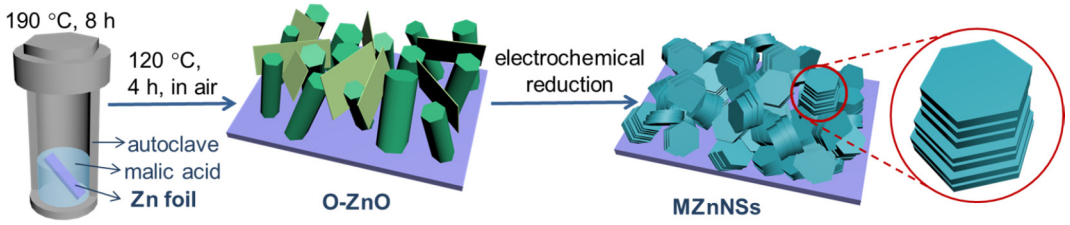
The electrochemical CO_2 reduction measurements of the catalysts were conducted with a 2273 potentiostat (EG&G Instrument) through a three-electrode system. The working electrode was the as-prepared electrode (exposed area: 3 cm^2). The counter electrode was a Pt sheet and the reference electrode was a Hg_2Cl_2/Hg/saturated KCl electrode (SCE), respectively. All the applied potentials are reported as reversible hydrogen electrode (RHE) potentials scale using E (vs. RHE) = E (vs. SCE) + 0.242 V + 0.0591 V × 7.2. The electrochemical measurements were conducted in a gas-tight two-compartment electrochemical cell with a piece of proton exchange membrane Nafion 115 (Dupont, USA) as a separator. 0.5 M $NaHCO_3$ saturated with CO_2 and 0.1 M H_2SO_4 aqueous solution were adopted as cathode and anode electrolyte, respectively. During the CO_2 reduction experiments, the cathodic electrolyte was stirred at the rate of 500 rpm and continuously saturated with CO_2 gas at the flow rate of 60 ml min^{-1}. The output gas was vented directly into the gas-sampling loop of a gas chromatograph (GC, Shimadzu GC-2014). Argon and nitrogen were used as the carrier gases. The hydrogen was quantified through a thermal conductivity detector (TCD) and CO was quantified by a flame ionization detector (FID). The liquid product was quantified by ion chromatography (ICS-1100, Dionex Corporation). The current densities are calculated based on geometric area (3 cm^{-2}).

The electrochemical active surface areas (EASC) were determined by measuring electrochemical double-layer capacitance [29]. ECSA = R_fS, in which S stands for the geometric area (3 cm^{-2}). The roughness factor R_f was estimated from the ratio of double-layer capacitance. The roughness measurement of the electrodes were conducted in N_2 purged 0.5 M Na_2SO_4 aqueous solution at various scan rates. The scanning potential ranges from −1.33 to −1.23 V vs SCE. The current densities were obtained from the double layer charge/discharge curves at −1.28 V vs SCE.

3. Results and discussion

3.1. Characterizations of the prepared electrodes

Zn foil (Fig. S1) was firstly treated under hydrothermal condition with the presence of malic acid to fabricate ZnO with morphology of relatively ordered nanowires. SEM images in Fig. 1a and b show that the hexagonal O-ZnO nanowires are generated and grown at some angle to the surface of Zn foil. Typical diameters of the obtained nanowires are in the range of 50–500



Scheme 1. Preparation process of the MZnNSs.