Supplementary Information

Highly Efficient Zinc Catalyst for Selective Electroreduction of Carbon Dioxide in Aqueous NaCl Solution

Fengjiao Quan, Dan Zhong, Hancheng Song, Falong Jia* and Lizhi Zhang

College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China

*Corresponding Author
E-mail: fljia@mail.ccnu.edu.cn
Experimental

A schematic process is illustrated for the synthesis of the n-Zn electrode (Scheme S1). Firstly, a piece of commercial zinc foil (99.999%, Alfa aesar) was anodized at constant current density (0.3 mA cm$^{-2}$) for 90 min in zincate-saturated solution with reference to the work by Wu et al. To fabricate uniform ZnO nanoplates on the surface of Zn foil, we made some modifications: (a) The Zn foil is firstly electro-activated under cathodic condition (5 mA cm$^{-2}$ for 5 min) in 0.2 M Na$_3$PO$_4$ solution; (b) the anodization was carried out under open atmosphere. The as-formed ZnO was then electroreduced at -1.3 V (vs. SCE) for 30 min in Ar-bubbled 0.5 M NaHCO$_3$ solution. After that, n-Zn was fabricated on the Zn foil and used as a working electrode for CO$_2$ reduction in a H-type cell (Figure 1a) adopted from our previous work. The anode compartment was filled with 0.5 M NaHCO$_3$ solution, and the cathodic compartment was filled with aqueous solutions containing various sodium salts (0.5 M). During the electrolysis, CO$_2$ was bubbled into the solution with a flow rate of 20 scm and was vented directly into the gas-sampling loop of a gas chromatograph (GC, Hengxin GC-2020). Gas-phase product of CO was analyzed by a flame ionization detector, and hydrogen was detected by a thermal conductivity detector using a MolSieve 5A column. The liquid product (formate) was analyzed by an ion chromatograph (ICS-900, Dionex Corporation) after electrolysis with total consumed charge of 5 coulomb.

Scheme S1. Schematic process for fabricating n-Zn catalyst to catalyze CO$_2$ reduction.
Considering that the value of \( j_{CO} \) is proportional to the reaction rate for the conversion of \( CO_2 \) to \( CO \), the relationship between the \( j_{CO} \) and the concentration of salts will provide information to determine if the salts participate into the \( CO_2 \) reduction. The partial current density of \( CO \) production was calculated as follows \(^3\):

\[
j_{CO} = \frac{GC \text{ peak area}}{\alpha} \times \text{flow rate} \times \frac{2Fp_0}{RT} \times (\text{electrode area})^{-1}
\]

where \( R \) is the gas constant, \( F \) is the Faradaic constant, \( p_0 = 1.013 \) bar and \( T = 298.15 \) K. \( \alpha \) is a conversion factor for \( CO \) respectively based on the calibration of the GC.

Surface roughness factors for the n-Zn and Zn foil electrodes relative to mirror-polished Zn working electrode were determined by the integration of charge consumed in the reduction of zinc oxide, which was formed during the anodic scan in alkaline 0.1 M NaClO\(_4\) solution (pH=10, adjusted by NaOH). The roughness factors were calculated to be 23 and 1.5 for the n-Zn and Zn foil electrodes, respectively. X-ray diffraction (XRD) patterns were recorded on a Philips MPD 18801 diffractometer (CuK\( \alpha \) radiation, \( \lambda = 1.5418 \) Å, 20 KV, 150 mA). The morphology of the samples was observed using a JEOL-6700F scanning electron microscopy (SEM). Transmission microscopy (TEM) images were analyzed using Tecnai equipment (Tecnai G2 F30) operating at a voltage of 200 kV. Raman spectra were collected by a confocal laser micro-Raman spectrometer (Thermo DXR Microscope, USA) equipped with a laser (532 nm, 5 mW). In situ Raman spectroscopy measurements utilized a similar spectroelectrochemical cell adopted in a published work \(^4\).

To study the effect of catalyst size on \( CO_2 \) reduction, commercial ZnO nanoparticles were purchased from US Research Nanomaterials, Inc. Three types of ZnO products were investigated in this work, and the corresponding sizes were 80 ~ 200 nm (Stock#: US3555), 35 ~ 45 nm (Stock #: US3580) and 10 ~ 30 nm (Stock #: US3590), respectively. ZnO nanoparticles were coated onto a glass carbon electrode by the following procedure. ZnO nanoparticles (10 mg) were ultrasonically dispersed in 0.5 ml Nafion solution (2 wt% in isopropanol). The ZnO slurry was dropped onto a glass carbon (GC) plate (2 cm\(^2\) exposed area) and a compact film of ZnO
nanoparticles was formed under heating at 50 °C. Then, these ZnO nanoparticles were reduced to Zn by the same electrochemical method introduced above and used as an electrode for CO₂ reduction.

**Figure S1.** LSV curves recorded on an anodized Zn foil electrode in Ar-bubbled 0.5 M NaHCO₃ solution.

**Figure S2.** Current density and FE<sub>CO</sub> obtained on a n-Zn electrode during continuous electrolysis at -1.6 V in CO₂ saturated NaCl solution.
Figure S3. SEM image of a n-Zn electrode after continuous electrolysis at -1.6 V in CO$_2$ saturated NaCl solution.

Figure S4. LSV curves recorded on a Zn foil electrode in Ar- or CO$_2$- saturated NaF (a), NaBr (b), and NaI (c) solutions adjusted to a pH of 4.5. (d) Comparison of current differences from the CO$_2$ and Ar saturated solutions. The result in NaCl solution is calculated by the data listed in Figure 3c.
**Figure S5.** LSV curves recorded on Zn foil electrode in Ar or CO\textsubscript{2} saturated NaClO\textsubscript{4} solutions which were adjusted to a pH of 4.5.

**Figure S6.** TEM images of commercial ZnO nanoparticles in size of 10 ~ 30 nm (a), 35 ~ 45 nm (b) and 80 ~ 200 nm (c).
**Figure S7.** FE$_{\text{CO}}$ versus electrolysis time at -1.6 V on various zinc catalysts in NaCl solution.

**Figure S8.** LSV scans (from -1.7 to -0.9 V) in Ar-saturated 0.1 M NaOH at Zn catalysts with different particle size.
Figure S9. FE\textsubscript{CO} versus electrolysis time at the optimum potential of -1.6 V on Ag nanoparticle catalyst in NaCl or NaHCO\textsubscript{3} solution. Commercial silver nanoparticles (20 ~ 40 nm) were purchased from Alfa aesar without any modification by organic surfactant. The silver nanoparticles were coated onto a glass carbon electrode in the same way as that of ZnO nanoparticles.

Figure S10. Electrocatalytic activity of Zn nanoparticles toward CO\textsubscript{2} reduction in an ionic liquid / H\textsubscript{2}O solution. (a) FE\textsubscript{CO} versus applied potentials. (b) FE\textsubscript{CO} versus electrolysis time at -1.6 V. The ionic liquid / H\textsubscript{2}O was prepared by dissolving 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF\textsubscript{4}) in water at a concentration of 18 mol\% \textsuperscript{5}. The Zn nanoparticles were derived from the reduction of ZnO (35 ~ 45 nm) particles.
References: