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Supplementary Information

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

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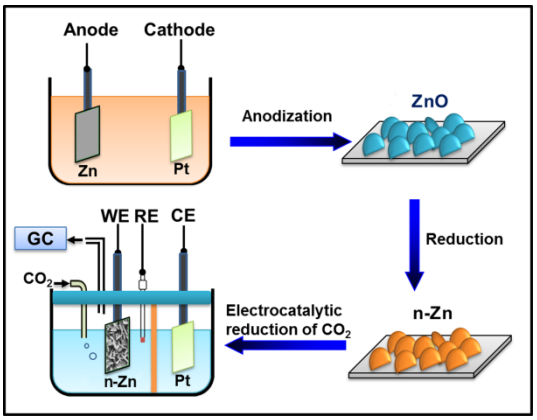
Experimental

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 [1]. 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_3PO_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 [2]. 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 sccm and was vented directly into the gas-sampling loop of a gas chromatograph (GC, Hengxin GC-2020) [2]. 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 concentraion 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]:

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

where R is the gas constant, F is the Faradaic constant, p_0 = 1.013 bar and T = 298.15 K. α 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 diffraction-meter (CuKα radiation, λ = 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 CO_2 reduction.

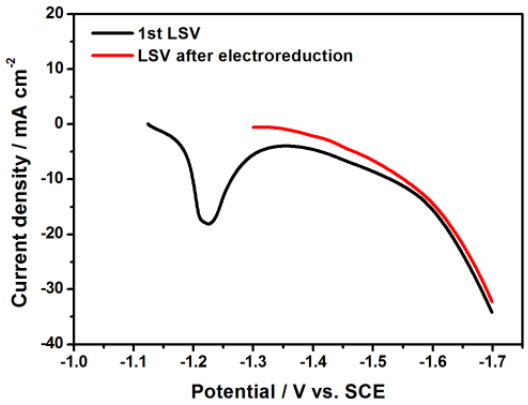


Figure S1. LSV curves recorded on an anodized Zn foil electrode in Ar-bubbled 0.5 M $NaHCO_3$ solution.

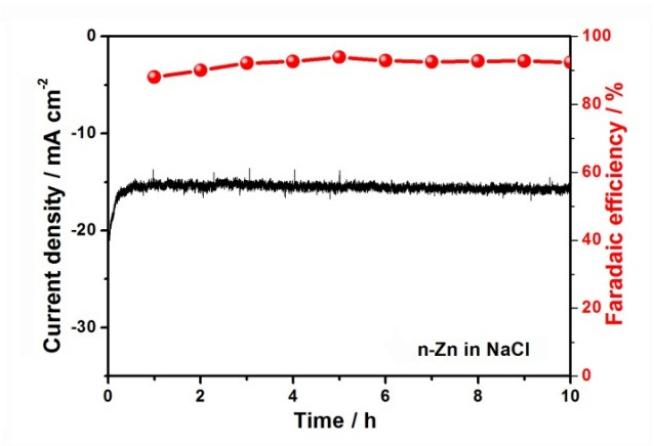


Figure S2. Current density and FE_{CO} obtained on a n-Zn electrode during continuous electrolysis at -1.6 V in CO_2 saturated NaCl solution.

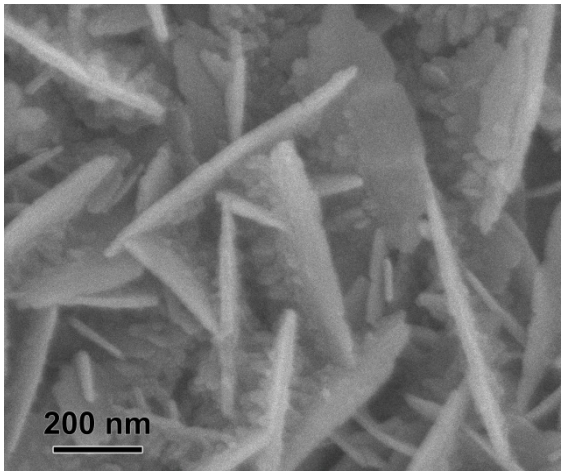


Figure S3. SEM image of a n-Zn electrode after continuous electrolysis at -1.6 V in CO_2 saturated NaCl solution.

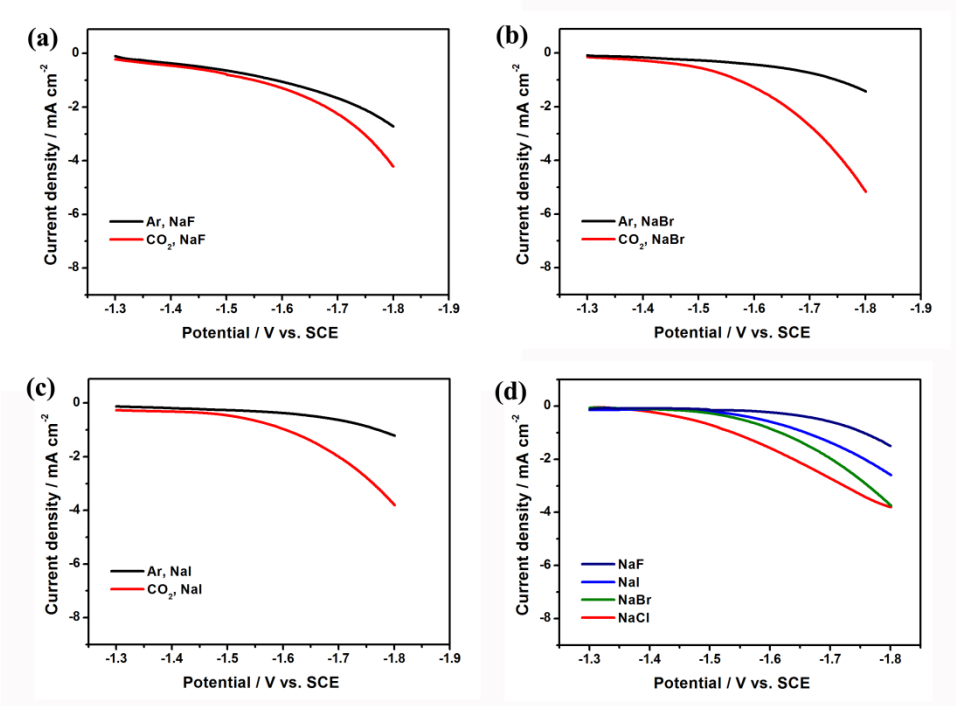


Figure S4. LSV curves recorded on a Zn foil electrode in Ar- or CO_2- saturated NaF (a), NaBr (b), and NaI (c) solutions adjusted to a pH of 4.5. (d) Comparison of current differences from the CO_2 and Ar saturated solutions. The result in NaCl solution is calculated by the data listed in Figure 3c.

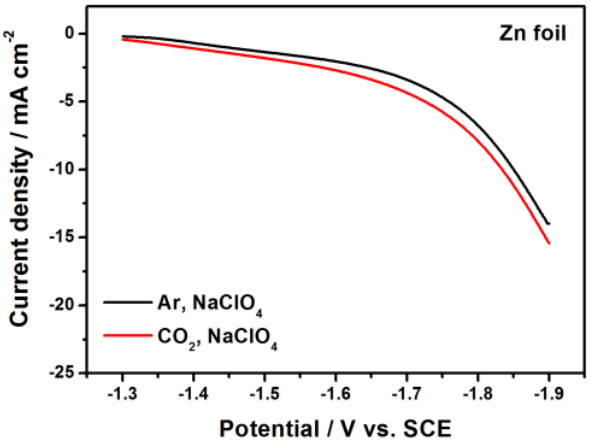


Figure S5. LSV curves recorded on Zn foil electrode in Ar or CO_2 saturated $NaClO_4$ solutions which were adjusted to a pH of 4.5.

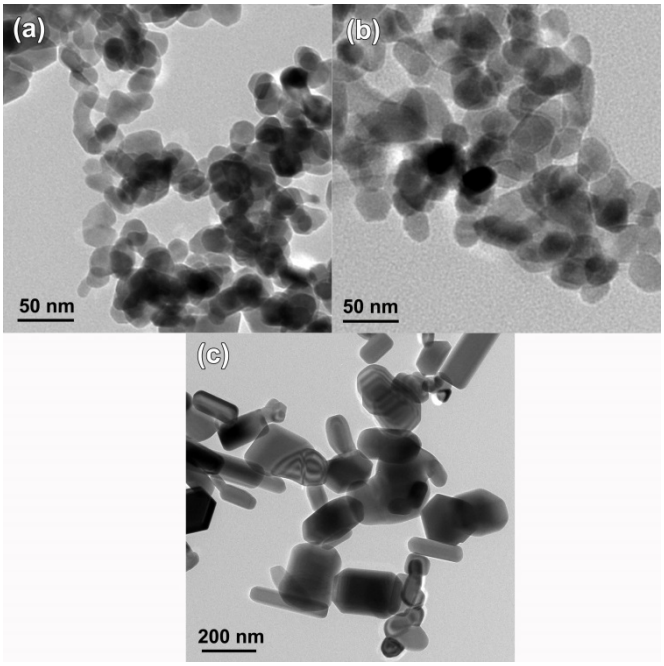


Figure S6. TEM images of commercial ZnO nanoparticles in size of 10 ~ 30 nm (a), 35 ~ 45 nm (b) and 80 ~ 200 nm (c).

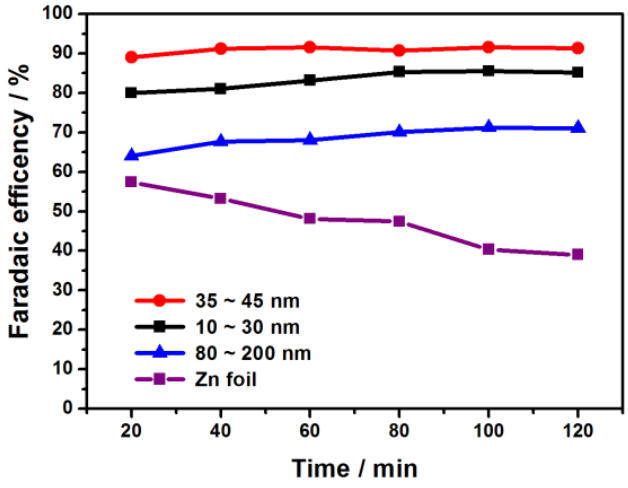


Figure S7. FE_{CO} versus electrolysis time at -1.6 V on various zinc catalysts in NaCl solution.

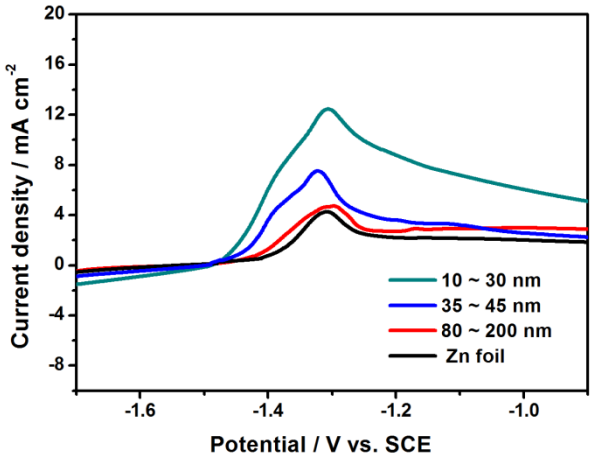


Figure S8. LSV scans (from -1.7 to -0.9 V) in Ar-saturated 0.1 M NaOH at Zn catalysts with different particle size.

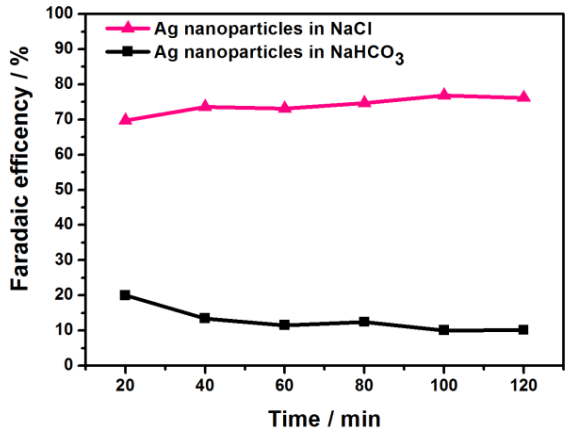


Figure S9. FE_{CO} versus electrolysis time at the optimum potential of -1.6 V on Ag nanoparticle catalyst in NaCl or $NaHCO_3$ solution. Commercial silver nanoparticles (20 ~ 40 nm) were purchased from Alfa aesar without any modification by organic surfactant. The silver nanoparticles were coated onto a glass carbon electrode in the same way as that of ZnO nanoparticles.

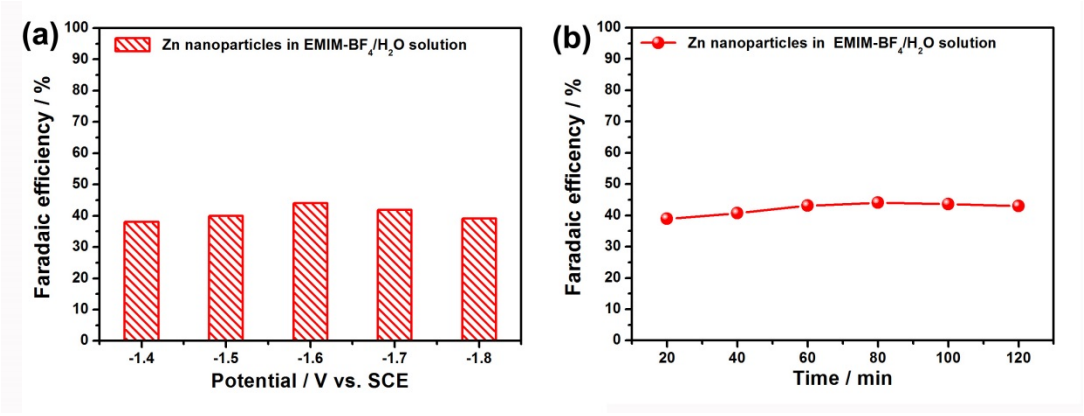


Figure S10. Electrocatalytic activity of Zn nanoparticles toward CO_2 reduction in an ionic liquid / H_2O solution. (a) FE_{CO} versus applied potentials. (b) FE_{CO} versus electrolysis time at -1.6 V. The ionic liquid / H_2O was prepared by dissolving 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF_4) in water at a concentration of 18 mol% [5]. The Zn nanoparticles were derived from the reduction of ZnO (35 ~ 45 nm) particles.

References:

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2. H. Zhang, Y. Ma, F. Quan, J. Huang, F. Jia and L. Zhang, *Electrochem. Commun.*, 2014, **46**, 63-66.
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