

## Electronic Supporting Information

# **Boosting CO<sub>2</sub> electroreduction over silver nanowires modified by mild sulfidation and subsequent electrochemical de-sulfidation**

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## **Experimental methods**

### **Materials.**

Potassium bicarbonate ( $\text{KHCO}_3$ , 99.95% trace metal basis), NaCl (99.99% trace metal basis), KBr (99% ACS reagent), sulfur powder, Nafion solution (5 wt%), ethylene glycol (EG, 99.8%),  $\text{AgNO}_3$  and poly(vinylpyrrolidone) (PVP,  $M_w = 55,000$ ) were purchased from Sigma-Aldrich. The chemicals were used without purification. All electrolytes were prepared using deionized water. Ag foil (99.998%) was purchased from Alfa Aesar.

### **Synthesis of Ag nanowires (Ag NWs)**

Ag nanowires were prepared by a modified salt-mediated polyol reaction with NaCl and KBr.<sup>1, 2</sup> In a typical synthesis, 0.385 g PVP was dissolved in 25 ml ethylene glycol (EG) under continuous stirring and mild heating. Then, 0.3 ml 10 mM NaCl and 10 mM KBr in EG solution was injected to the PVP solution. After 30 min, 10 ml  $\text{AgNO}_3$  solution (0.15 M solution in EG) was added to the mixture by drop-wise over a period of 10 min. The obtained mixture was heated to 150 °C and kept for 240 min with stirring. After temperature was finally dropped down to room temperature, the suspension was diluted with acetone and centrifuged at 2000 rpm for 10 min, and Ag nanowires were collected and washed by water and ethanol for several times.

### **Synthesis of core-shell Ag@Ag<sub>2</sub>S nanowires (Ag@Ag<sub>2</sub>S NWs).**

In a typical process, 4 ml as-prepared Ag NWs suspension (10 mg/ml) was added to 16 ml ethanol and stirred for at least 30 min. Subsequently, 2.36 mg sulfur powder

was added under continuously stirring. After 12 h, the suspension became reddish brown from light-yellow, and then was centrifuged at 3000 rpm for 10 min. The as-synthesized products were collected and washed with absolute ethanol for three times. The resulted material can be simply denoted as Ag@Ag<sub>2</sub>S NWs.

### **Synthesis of DS-Ag NWs.**

In a typical process, 10 mg as-prepared Ag@Ag<sub>2</sub>S NWs was dispersed in a mixture of 650 ul ethanol and 200 ul deionized water by sonicating for 15 min to form a homogeneous ink. Next, 6 ul of the catalyst ink was dropped onto a clean glassy carbon (GC) electrode with 5 mm diameter and dried in ambient conditions overnight. The DS-Ag NWs were prepared by electrochemical reduction for 1 h at an applied potential of  $-0.75$  V vs. RHE in CO<sub>2</sub> saturated 0.5 M KHCO<sub>3</sub> solution. The resulted catalyst can be simply denoted as DS-Ag NWs, where DS is short for de-sulfidation.

Similarly, DS-Ag NWs( $-0.55$ V) was prepared by de-sulfating Ag@Ag<sub>2</sub>S NWs at  $-0.55$  V vs. RHE in CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> solution.

### **Characterizations.**

The crystalline structures were determined by powder X-ray diffraction (XRD, Rigaku MiniFlex). The morphology and high-resolution structure of catalysts were observed by a scanning electron microscope (SEM, SU-8010, Hitachi) and a transmission electron microscope (TEM, FEI, Tecnai F20). XPS (Kratos AXIS Ultra) was utilized to investigate the surface elemental chemistry of catalysts with the adventitious carbon (C 1s) at the binding energy (BE) of 284.6 eV as the reference.

### **Electrochemical experiments**

Electrochemical experiments were performed in H-type cell with two compartments (Fig. S1) at ambient temperature and pressure. The cathodic and anodic compartment were separated by a proton-exchange membrane (Nafion 117, Dupont, USA). The electrolyte used for all CO<sub>2</sub> reduction experiment was 0.5 M KHCO<sub>3</sub> saturated with CO<sub>2</sub> (pH = 7.2). A saturated Ag/AgCl electrode and a Pt mesh served as the reference and counter electrode, respectively. Catalyst-modified GC was used as work electrode. 10 mg catalyst (Ag NWs) was dispersed in a mixture of 650 ul of ethanol and 200 ul deionized water by sonicating for 15 min to form a homogeneous ink. 6 ul of the catalyst ink was dropped onto the glassy carbon (GC) and dried in ambient conditions overnight, obtaining Ag NWs modified GC. Besides, DS-Ag NWs modified GC and Ag foil are also used as the work electrodes. The linear sweep voltammetry (LSV) of catalyst (Ag NWs or DS-Ag NWs)-modified GC electrode or Ag foil was conducted in 0.5 M KHCO<sub>3</sub> electrolyte saturated with Ar or CO<sub>2</sub> by purging for at least 30 min before the measurements. During the electrolysis, the electrolyte was stirred with a magnetic stirrer, and LSV was performed with the scan rate of 5 mV/s. The electrocatalytic CO<sub>2</sub> reduction reaction for catalyst (Ag NWs or DS-Ag NWs)-modified GC electrode or Ag foil was carried out in the CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> electrolyte at room temperature. All the potentials were *iR* corrected, and converted to the Reversible Hydrogen Electrode (RHE) scale using  $E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197 \text{ V} + 0.0592 \times \text{pH}$ .

#### **Detection and quantification of products.**

In order to evaluate the selectivity of CO<sub>2</sub> electroreduction, we used the online

electrochemical gas chromatography technique to detect gas products and estimated their Faradaic efficiencies (FEs). The gas product composition was analyzed by gas chromatography (GC 9790, FULI) until the current kept stable. H<sub>2</sub> concentration was determined by a thermal conductivity detector (TCD), and CO were determined using a flame ionization detector (FID).

Liquid products in the working compartment were collected and analyzed on a 600 MHz spectrometer. The samples were prepared by mixing 0.2 ml electrolyte, 0.1 ml D<sub>2</sub>O and 0.05 ul dimethyl sulfoxide (DMSO, Sigma, 99.99%) acted as an internal standard. The <sup>1</sup>H spectrum was measured with water suppression using a pre-saturation method. Faradaic Efficiency (FE) was calculated through the following equation:

$$FE = x n F / Q$$

Where: x = number of electrons exchanged (for CO and H<sub>2</sub>, x = 2)

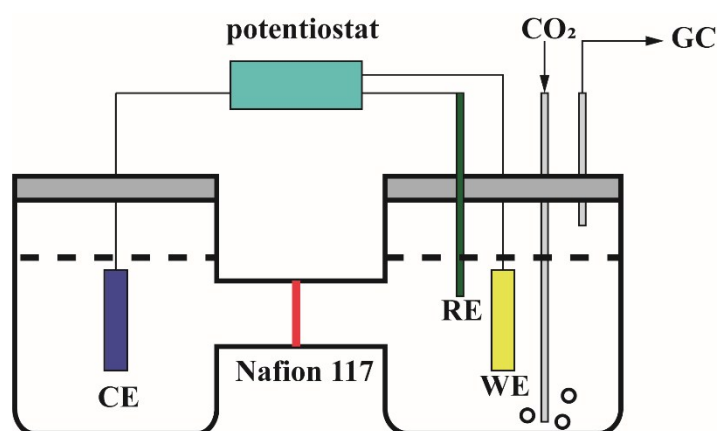
n = the number of moles for specific product

F = Faraday's constant (F = 96485 C/mol)

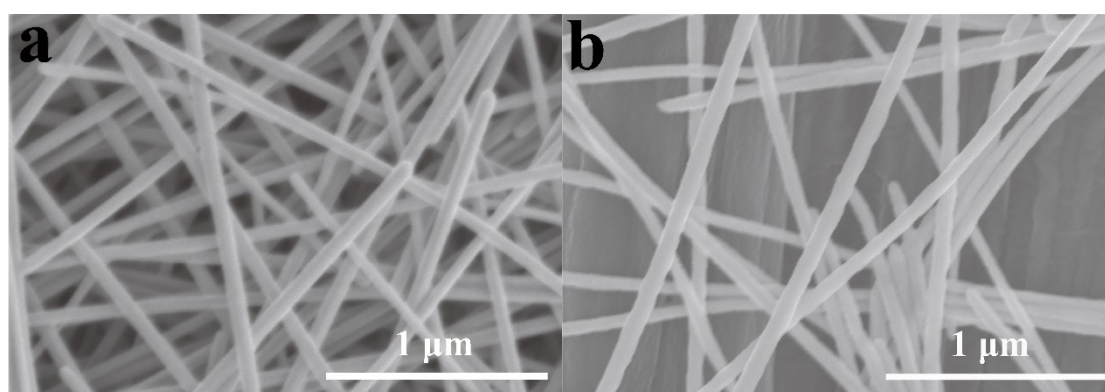
Q = the charge passed (C)

The partial current density for a specific product was calculated by multiplying total current density by Faradaic efficiency for this product.

## Supplementary Figures



**Fig. S1** Schematic diagram of two-compartment three-electrode H-type cell used in eCO<sub>2</sub>RR experiments.



**Fig. S2** Low magnification SEM images of (a) Ag NWs and (b) Ag@Ag<sub>2</sub>S NWs

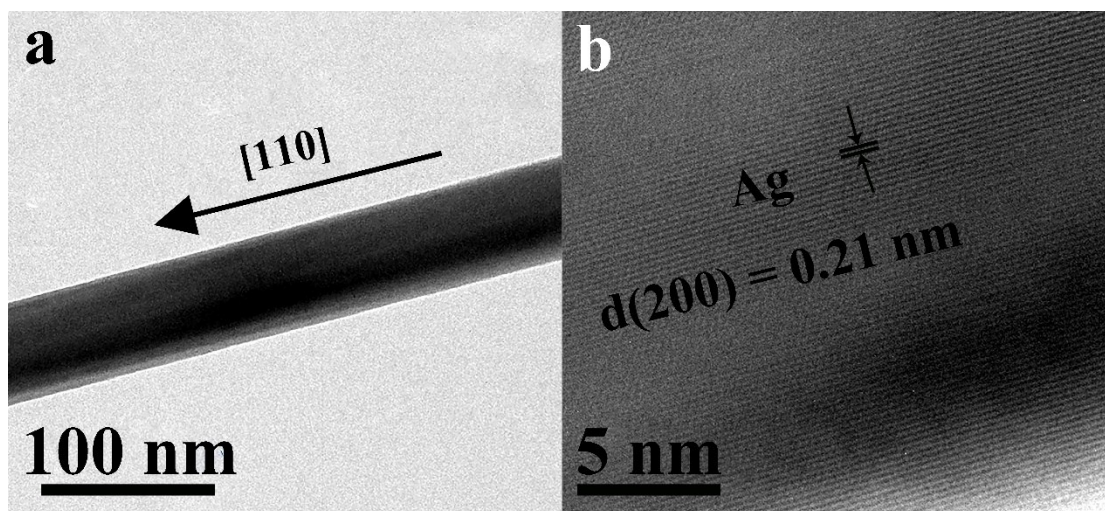


Fig. S3 (a) TEM and (b) HRTEM images of Ag NWs

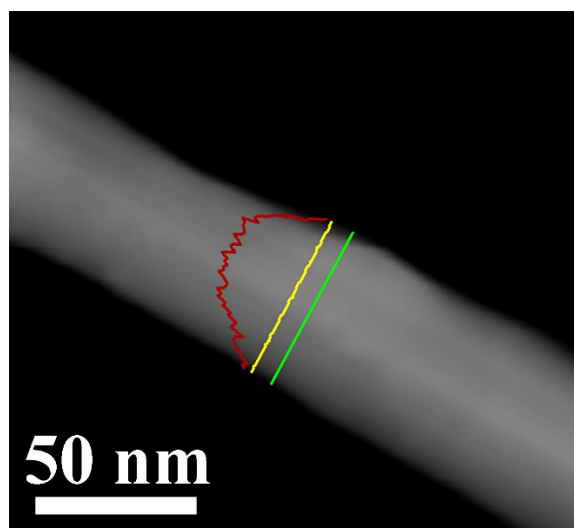
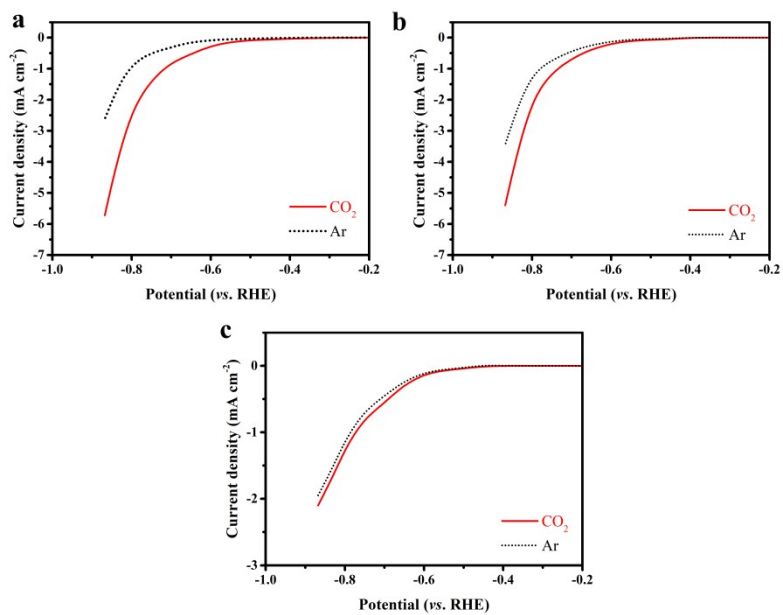
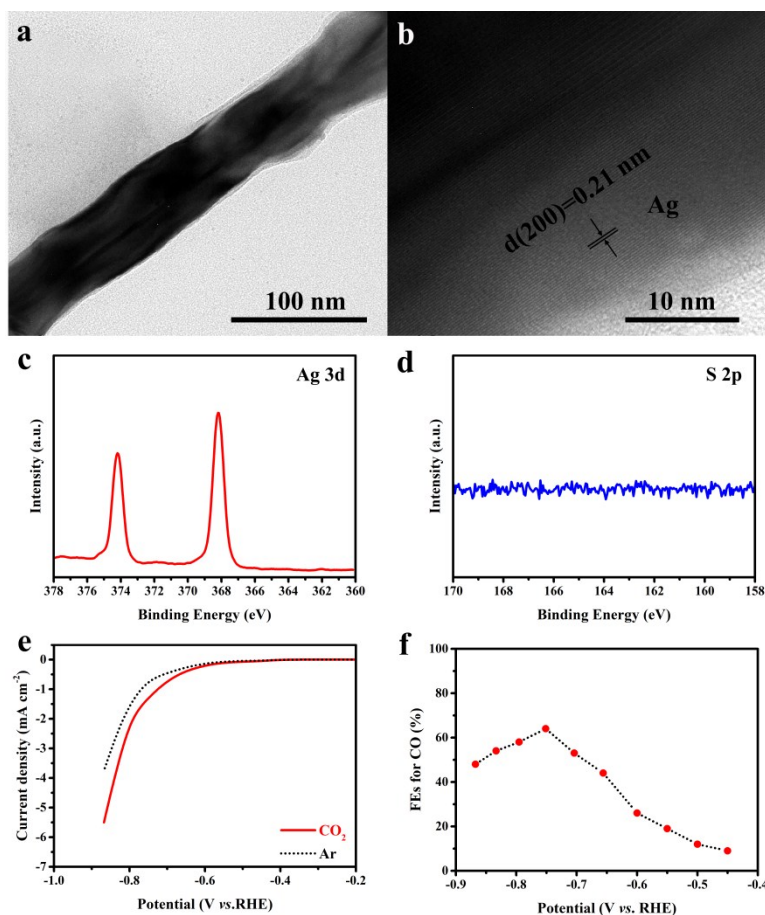


Fig. S4 STEM image and line-scan profile of Ag L (dark-red curve) and S K (yellow curve) for DS-Ag NWs.



**Fig. S5** LSV scans of (a) DS-Ag NWs, (b) Ag NWs, and (c) Ag foil at 5 mV/s in (solid line) CO<sub>2</sub>- and (short dot line) Ar-saturated 0.5 M KHCO<sub>3</sub>.





**Fig. S6** (a) TEM and (b) HRTEM images of DS-Ag NWs ( $-0.55$  V). XPS spectrum of DS-Ag NWs ( $-0.55$  V): (c) Ag 3d and (d) S 2p. (e) LSV scans of DS-Ag NWs ( $-0.55$  V) at  $5$  mV/s in (solid line)  $\text{CO}_2$ -saturated and (short dot line) Ar-saturated  $0.5$  M  $\text{KHCO}_3$ , (f) CO FEs of DS-Ag NWs ( $-0.55$  V) in  $\text{CO}_2$ -saturated  $0.5$  M  $\text{KHCO}_3$ .

## References:

- 1 C. Yang, H. Gu, W. Lin, M. M. Yuen, C. P. Wong, M. Xiong and B. Gao, *Advanced Materials*, 2011, **23**, 3052-3056.
- 2 C. Jia, P. Yang and A. Zhang, *Materials Chemistry and Physics*, 2014, **143**, 794-800.