Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

Superfine Ag nanoparticles decorated Zn nanoplates for active and selective electrocatalytic CO_2 reduction to CO

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Experiments

The Ag nanoparticles decorated Zn nanoplates electrodes were prepared by a two-step electrodeposition method on glass carbon (GC) substrate. The electrodeposition was carried out in a glass cell in a three-electrode system in which Pt wire was used as counter electrode and silver/silver chloride reference electrode was used as reference electrode. Before deposition, the GC substrate was polished using commercial Al_2O_3 suspension (particle size 2 μm) for 10 minutes. Then it was cleaned with ultra-pure water before used.

Firstly, Zn electrodes were prepared in a solution with 0.6 mol/L $ZnSO_4$, 0.1 mol/L $(NH4)_2SO_4$ and 1 mM cetyl trimethyl ammonium bromide (CTAB) as previous report.[1] All chemicals were analytical grade and were used without further purification. The cyclic voltammetry curve for this solution was shown in Figure S2a. The peak of Zn^{2+} reduction can be obviously observed at -1.46 V vs. Ag/AgCl. In our experiment, the deposition potential for Zn metal is -1.6 V vs. Ag/AgCl for 60 seconds and the representative current-time curve is shown in Figure S2b.

After Zn deposition on GC substrate, Ag was deposited subsequently on Zn without any treatment in the aqueous electrolyte that consisted of 2.5 mM $AgNO_3$, 10 mM sodium citrate and 0.1 M KNO_3.[2] The cyclic voltammetry curve for the Ag precursor was shown in Figure S3a. The deposition potential for Ag metal is -1.2 V vs. Ag/AgCl in our experiment, and the representative current-time curve is shown in Figure S3b. Pure Ag electrode were prepared by directly electrodeposition in mixed solution of 2.5 mM $AgNO_3$, 10 mM sodium citrate and 0.1 M KNO_3 on glass carbon electrode.

X-ray diffraction (XRD) patterns (SmartLab, Rigaku Corporation, Japan) were used to detect the phase and crystallinity of the samples. Scanning electron microscopy (HITACHI S-4800) was used to show the morphology with an EDS mapping to characterize element composition and distribution. High-resolution TEM (HRTEM, 2100F, JEOL Co., Japan) images were recorded for characterizing the microstructure of samples, with a combined energy dispersive X-ray spectroscopy (EDX) for the determination of element concentration and distribution. X-ray Photoelectron Spectroscopy (ULVAC-PHI, Japan) experiments were tested for the charge value of elements on the surface with C 1s peak at 285.0 eV. ICP-OES

The electrocatalytic reduction of CO_2 was measured on a CHI 660D electrochemical workstation in an H-type cell (Figure S1). Before reaction, Ar was accessed into aqueous 0.1 M $KHCO_3$ solution for 1 hour to exclude the O_2 in the solution. After that, CO_2 was accessed into aqueous 0.1 M $KHCO_3$ solution until saturated with the pH of solution about 6.8. During the CO_2 reduction measurements, Pt and Ag/AgCl reference electrode were used as the counter and reference electrode respectively. Gas products (H_2 and CO) was sampled and measured with a gas chromatograph (GC-14B, Shimadzu). The GC column is 5A molecular sieve.

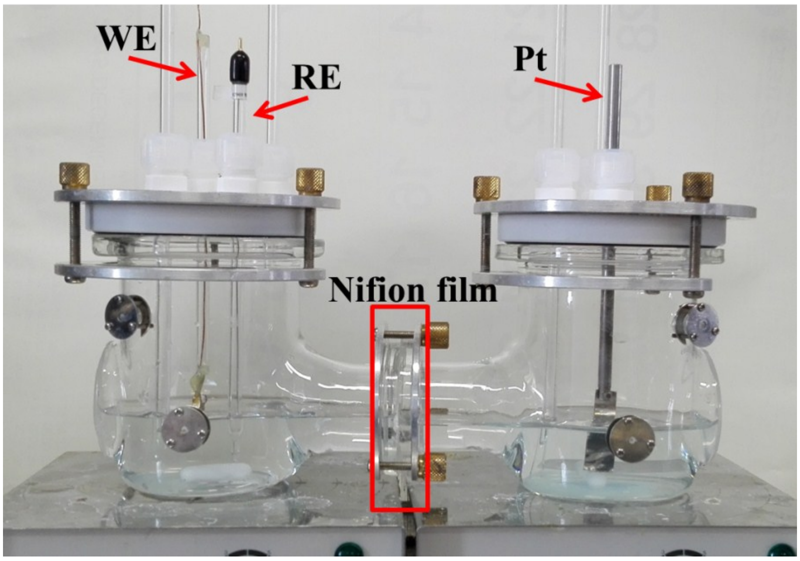

Figure S1. The experimental cell is a gas-tight two compartment H-type cell separated by a Nafion117 film.

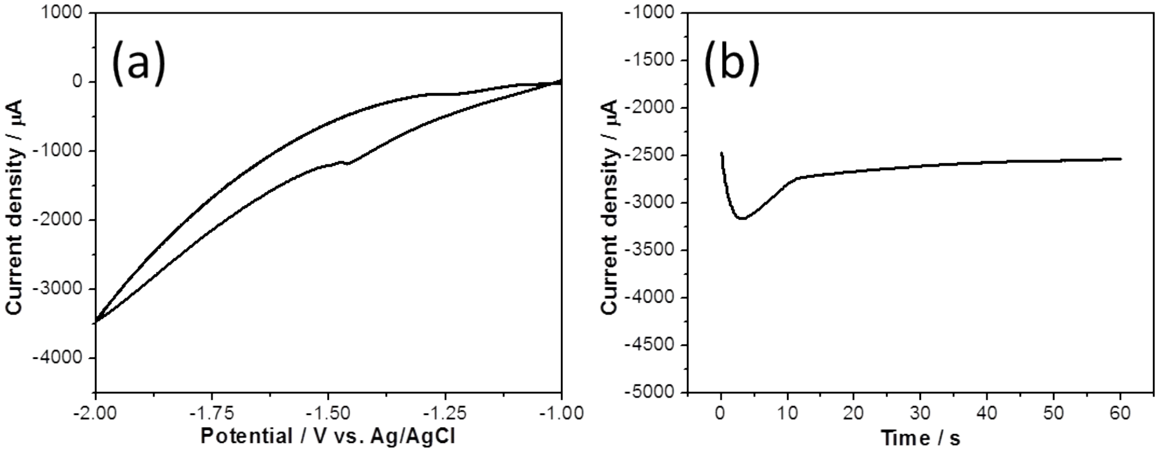

Figure S2. (a) Current-potential curves of Zn precursor on Glass-carbon electrode. (b) Representative current-time curve of Zn deposition at -1.6 V vs. Ag/AgCl.

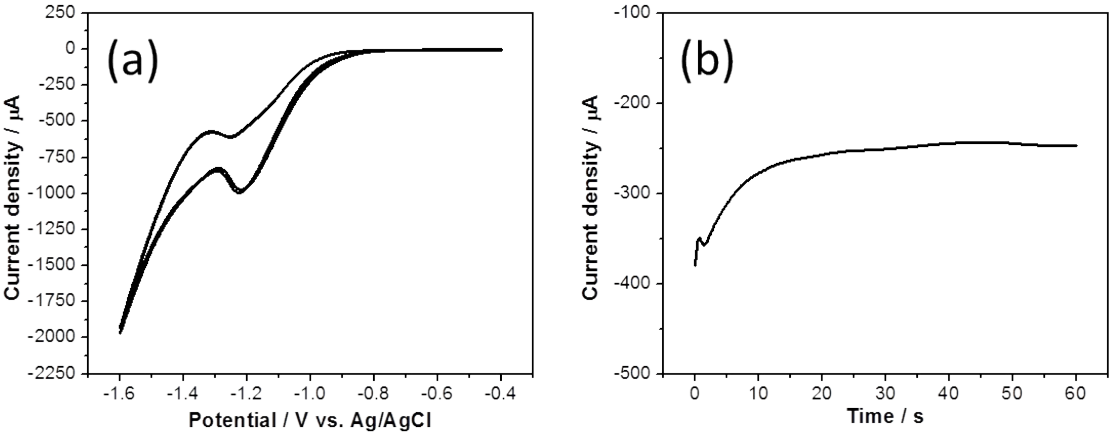

Figure S3. (a) Current-potential curves of Ag precursor on Zn electrode. (b) Representative current-time curve of Ag deposition at -1.2 V vs. Ag/AgCl.

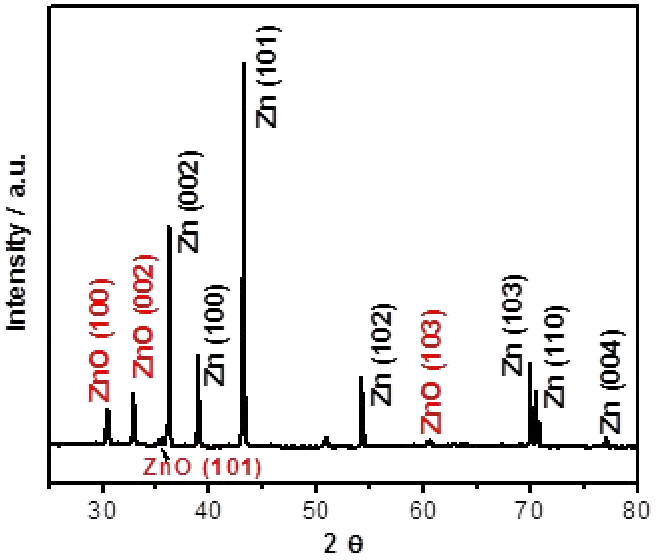

Figure S4. XRD patterns of sample Zn-Ag2.

The composition of the obtained Zn–Ag electrode was first detected by XRD as is shown in Fig. S4. Peaks from Zn metal can be obviously found in the XRD patterns with a preferred direction of (101). A little ZnO was observed during XRD characterization. The small amount of oxidized Zn is due to oxidation of the metals when they come into contact with oxygen in air. No signal for Ag is detected because the amount of Ag is too low to be detected by XRD.

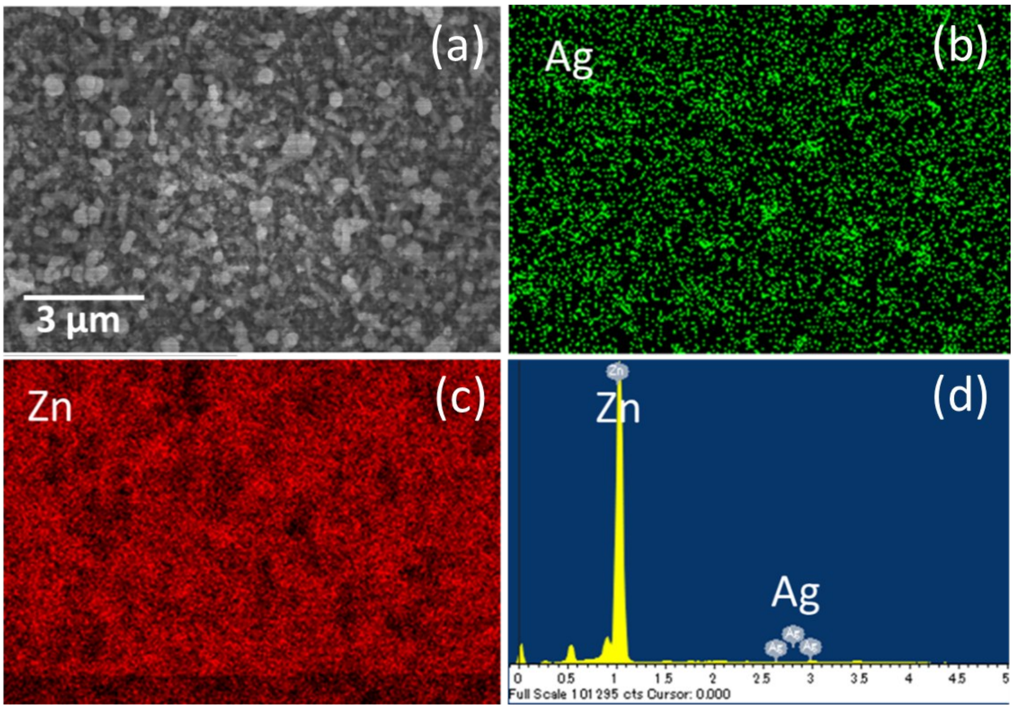

Figure S5. EDS mapping of sample Zn-Ag2 with the corresponding SEM image as reference. (a) the SEM image; (b) element mapping for Ag; (c) element mapping for Zn and (d) element concentration for Zn and Ag by EDS.

Sample ID	**Zn / µg**	**Ag / µg**	**Ag atomic ratio / %**
Zn-Ag1	220	0.05	0.014
Zn-Ag2	220	0.06	0.016
Zn-Ag3	260	0.11	0.025
Zn-Ag4	240	0.13	0.033

Table S1. ICP-OES experiments for Zn and Ag elements for Zn-Ag2 respectively.

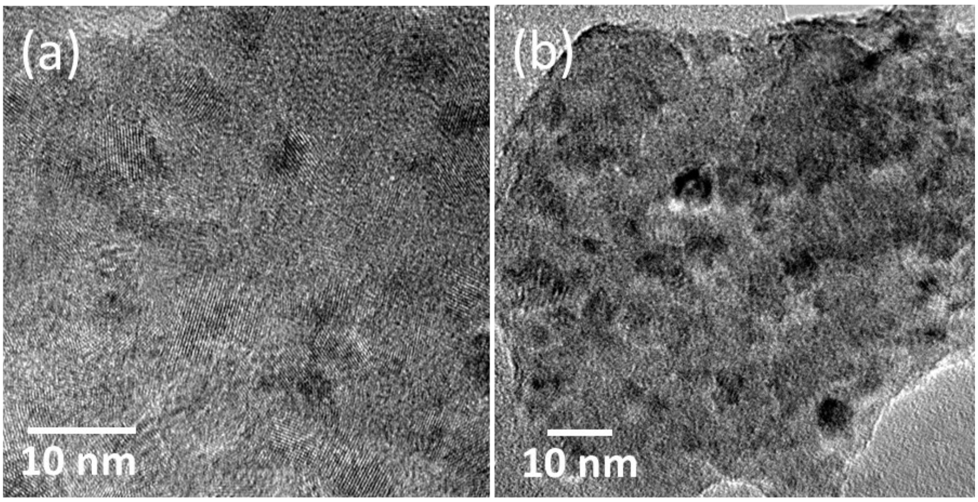

Figure S6. TEM images of sample Zn-Ag3 (a) and Zn-Ag4 (b) respectively.

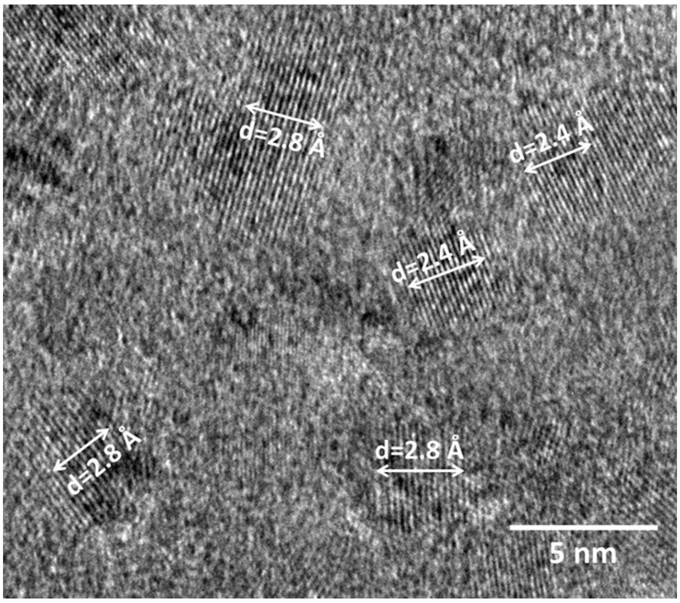

Figure S7. HRTEM image for the sample Zn-Ag3.

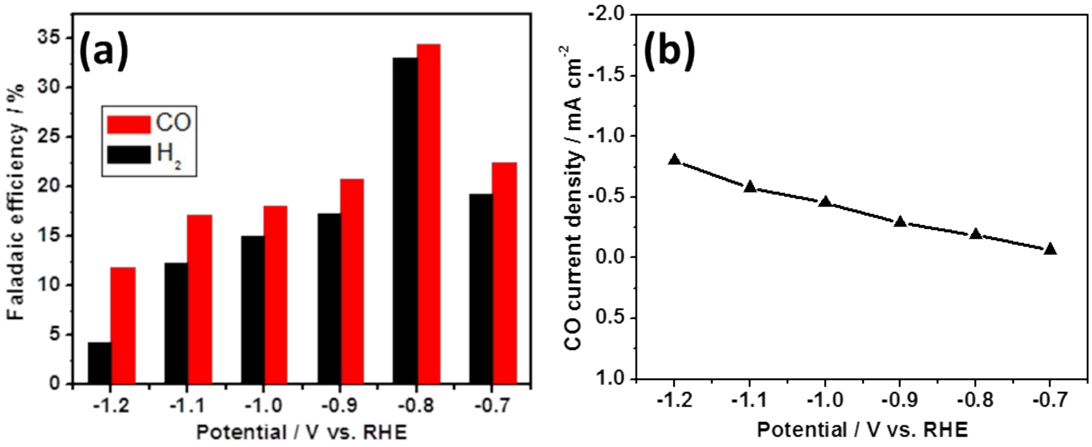

Figure S8. (a) Faradaic efficiencies for both H_2 and CO and (b) CO current density of pure Ag electrodes.

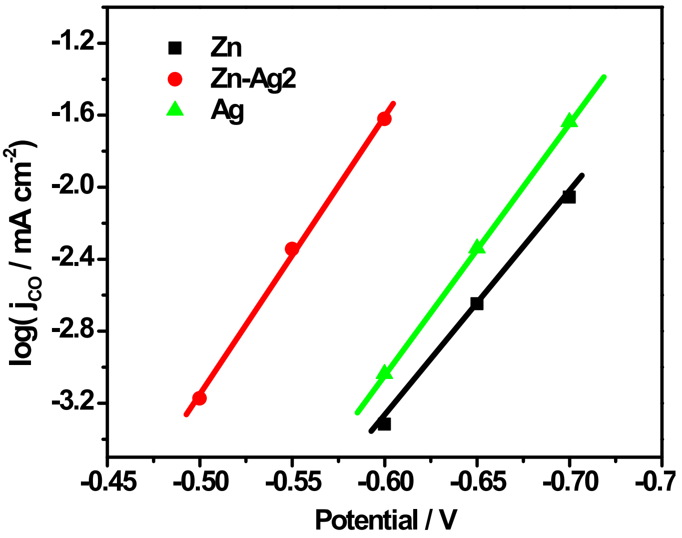

Figure S9. Tafel plots for pure Zn, pure Ag and Zn-Ag2.

References:

[1] A. Gomes and M. I. da Silva Pereira, *Electrochim. Acta*, 2006, **51**, 1342.

[2] J. Bian, Z. Li, Z. Chen, H. He, X. Zhang, X. Li and G. Han, *Appl. Surf. Sci.*, 2011, **258**, 1831.