

Electronic Supplementary Information

Experimental section

Materials: $\text{Fe}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KI, PVP and KHCO_3 were purchased from Aladdin Ltd. (Shanghai, China). Commercially pure Ag foil (99.99%, 0.25 mm in thickness) was purchased from Jia Yun Metal Materials Co., Ltd (Hebei, China). All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Synthesis of AgI: Ag foil was cleaned by sonication sequentially in concentrated HCl, ethanol and water for several times to remove the surface impurities. In a typical synthesis process, $\text{Fe}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.5 M), KI (0.5 M), and PVP (150 mM) were dissolved in deionized water. After continuously stirring for 30 min, the resulting mixture was maintained at RT until it became pale brown. The silver foil (2 × 3 cm) was placed in the obtained solution and maintained for 6 h. After that the sample was taken out and thoroughly washed with deionized water and ethanol several times alternatively, followed by drying overnight at 60 °C. In order to further confirm the influence of surface I^- on the CO_2 reduction activity, the Ag nano-coral sample was annealed in a H_2 atmosphere at 400 °C for 2 h, to remove the adsorbed I^- from the Ag surface while retaining the porous structure.

Characterizations: XRD measurements were performed using a LabX XRD-6100 X-ray diffractometer with Cu $\text{K}\alpha$ radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM images were collected on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV.

Electrochemical measurements: Electrochemical measurements were performed with a CHI660E potentiostat (CH Instruments, China) in a standard three-electrode setup, using AgI as working electrode, a graphite rod as counter electrode and Ag/AgCl as reference electrode. The potentials reported in this work were calibrated to RHE, using the following equation: $E(\text{RHE}) = E(\text{Ag/AgCl}) + (0.197 + 0.059 \text{ pH})$

V. Polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s^{-1} . The temperature of the solution was maintained at around $25 \text{ }^\circ\text{C}$ during the whole measurements process. The as-generated gas was carried into a gas chromatograph (SC-3000B online system) every 10 min during CO_2 electrolysis for detection of products.

Determination of Faradaic efficiencies of gaseous using Gas Chromatography

(GC) Data: A representative set of GC data obtained during CO_2 electroreduction on ID-Ag is presented in Table S1.

Table S1. Data obtained from the GC analysis of CO_2 reduction products using ID-Ag. The volume of the sampling loops are 1 cm^3 (for CO and H_2)

Sample	Time of sample injection (s)	Current (mA)	Amount of gaseous products (ppm)	
			CO	H_2
1	200	4.165	748.47	43.56
2	870	4.152	746.14	43.42
3	1540	4.08	736.85	38.01
4	2210	4.02	722.18	41.28
5	2880	4.0	716.30	43.36
6	3550	3.97	708.67	45.30
Average (3-6)		4.01	721.00	41.99

Calculation of Faradaic efficiencies (%) of gaseous products:¹ To ensure that the reported data is from a system under equilibrium condition, only the 3rd - 6th GC measurements were used for calculating the Faradaic efficiencies.

$$\text{Recorded amount of product} = y \text{ (mol)} = Vj \times \frac{PV \times 10^{-3}}{RT}$$

Where V_j : is volume percentage obtained from the GC analysis of CO_2 reduction products, $P = 101.325 \text{ KPa}$, $R = 8.314 \text{ KPa L K}^{-1} \text{ mol}^{-1}$, Volume of sampling loop = $V \text{ cm}^3$, $T = 298.15 \text{ K}$

Recorded current = $I \text{ (A)}$

$$\text{Recorded flow rate} = r \text{ (sccm)} = \frac{r}{60} \text{ cm}^3 \text{ s}^{-1}$$

Number of moles of electrons required for reducing CO_2 to a particular product:

$$e_{\text{output}} = y \times \text{Number of electrons required to obtain 1 molecule of product}$$

The number of electrons required to form a molecule of CO (from CO_2) and H_2 (from H^+) are both 2 electrons.

Total number of moles of electrons measured during the sampling period:

$$e_{\text{input}} = \frac{Q}{F}$$

where $F = \text{Faraday constant, } 96485 \text{ C mol}^{-1}$ and $Q = \text{measured charge}$

The measured charged can be determined using Faraday's laws of electrolysis:

$$Q = I \times t$$

The time required to fill the sampling loop (t):

$$t = \frac{V}{\frac{r}{60}} \text{ seconds}$$

$$\text{Faradaic efficiency of the product} = \frac{e_{\text{output}}}{e_{\text{input}}} \times 100\%$$

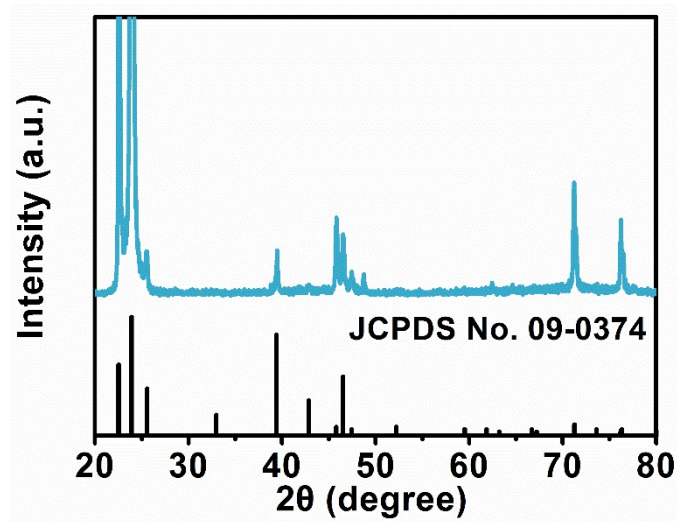


Fig. S1 XRD pattern of of Ag foil.

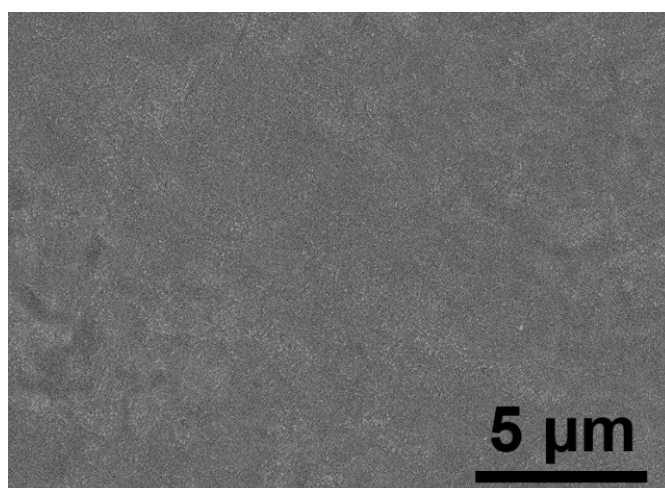


Fig. S2 SEM image for Ag foil.

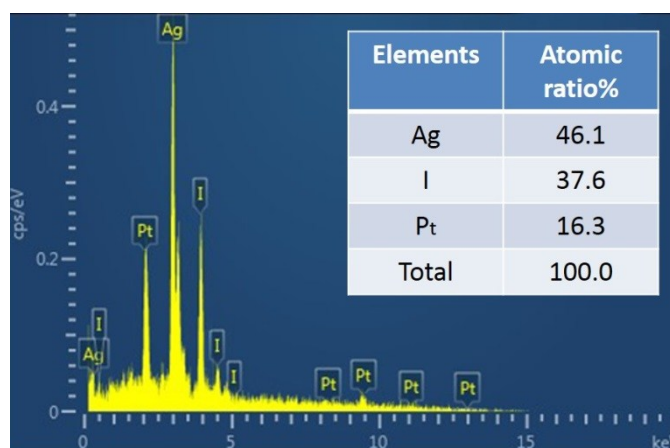


Fig. S3 EDX spectrum of AgI.

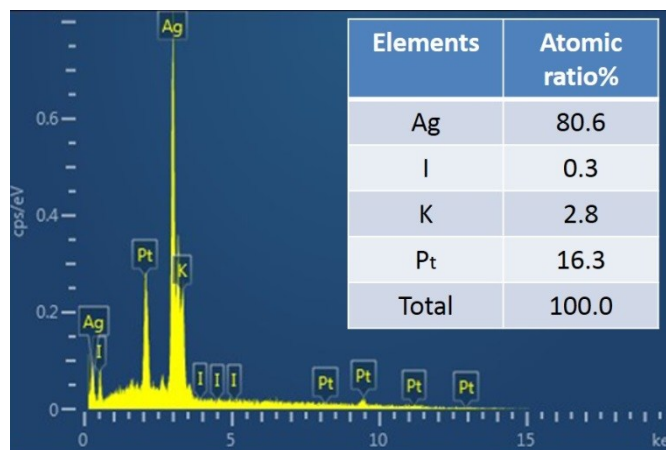


Fig. S4 EDX spectrum of ID-Ag.

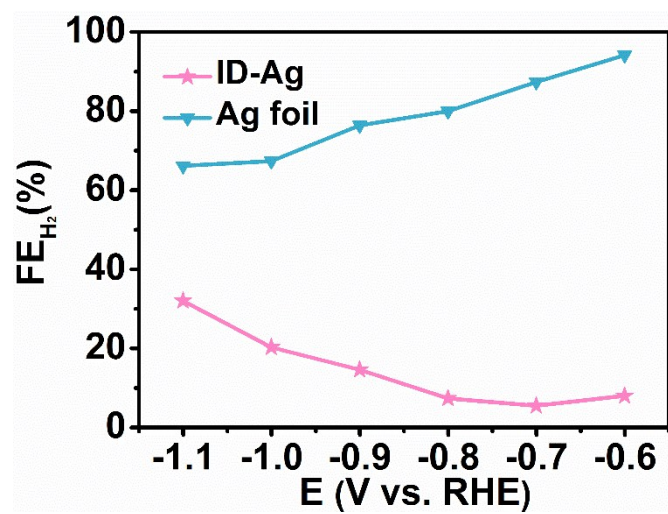


Fig. S5 Faradaic efficiency for H₂ on Ag foil and ID-Ag at various potentials in CO₂-saturated in 0.5 M KHCO₃.

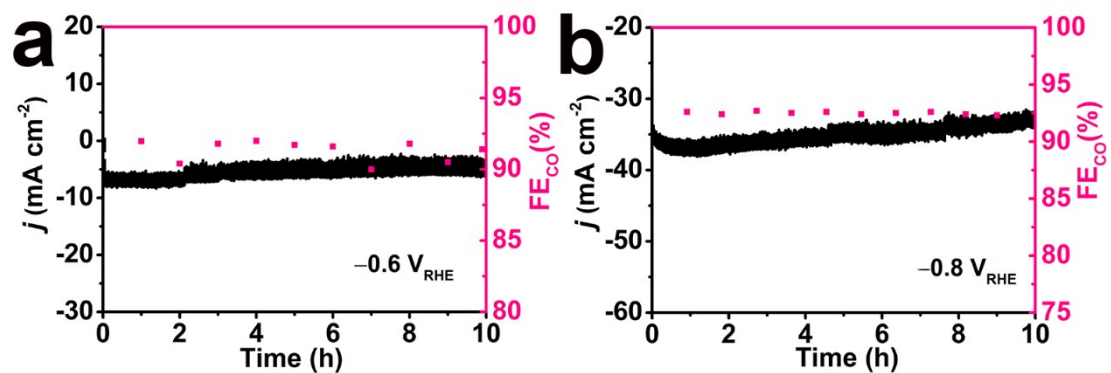


Fig. S6 The total current density (left axis) and the CO faradaic efficiency (right axis) on ID-Ag at -0.7 V (a) and -0.8 V (b) versus RHE in CO_2 -saturated 0.5 M KHCO_3 electrolytes.

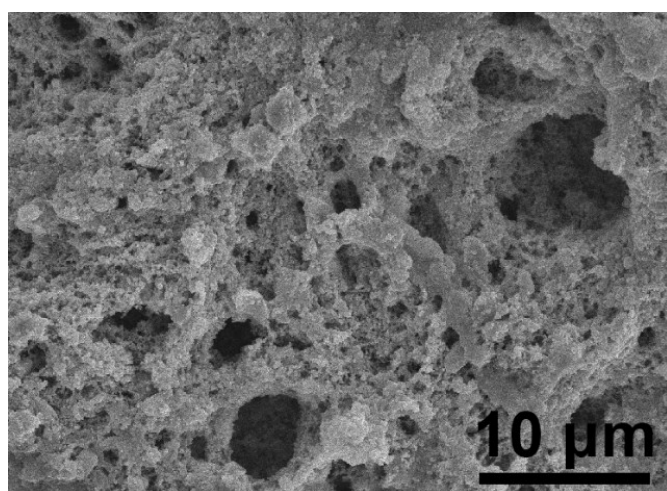


Fig. S7 SEM image for ID-Ag after H₂ annealing.

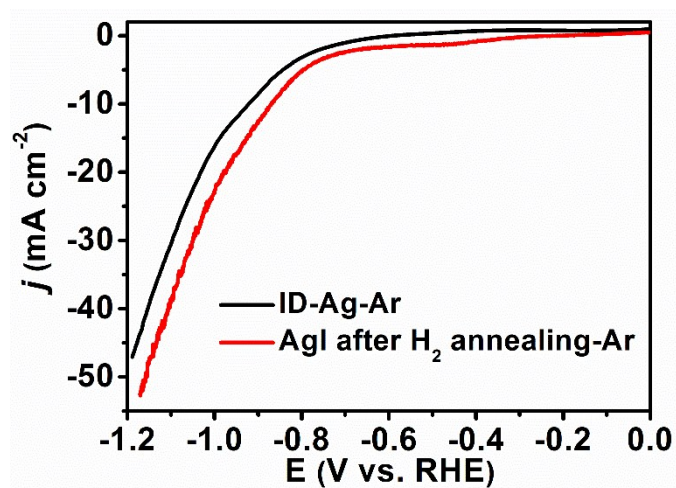


Fig. S8 Linear sweep voltammetric curves for ID-Ag before (black) and after (red) H₂ annealing measured in Ar-saturated 0.5 M KHCO₃.

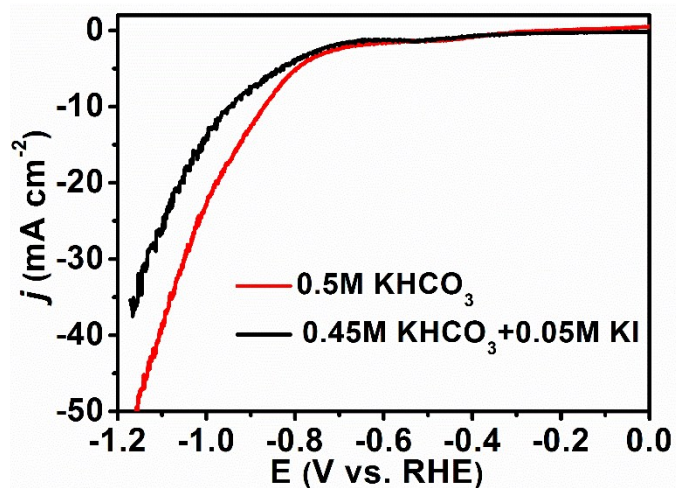


Fig. S9 Linear sweep voltammetric curves for the ID-Ag after H₂ annealing, as a function of I⁻ ion in the electrolyte, measured in Ar-saturated 0.5 M KHCO₃ (black) and measured in Ar-saturated 0.45 M KHCO₃ + 0.05 M KI.

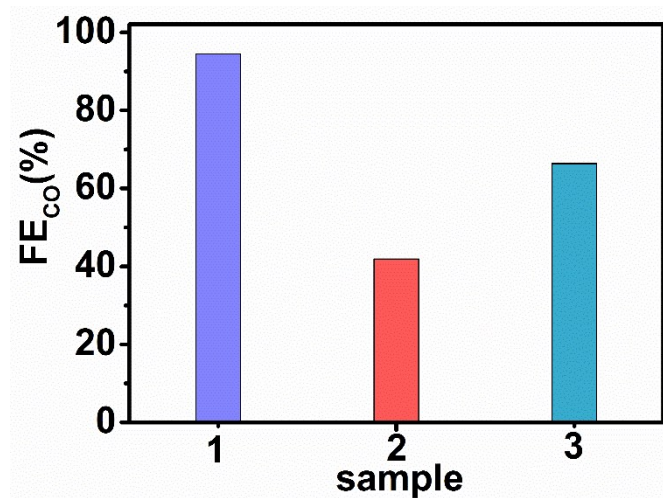


Fig. S10 Faradaic efficiency for CO on ID-Ag before (sample 1) and after (sample 2) H₂ annealing in CO₂-saturated 0.5 M KHCO₃, ID-Ag after H₂ annealing in CO₂-saturated 0.45 M KHCO₃ + 0.05 M KI (sample 3) at -0.7 V.

Table S2. Comparison of CO₂RR performance for ID-Ag with other Ag-based electrocatalysts.

Catalyst	Potential	Electrolyte	FE(%)	Ref.
ID-Ag	-0.7 V	0.5 M KHCO ₃	94.5	This work
coral-like Ag	-0.47 V	0.1 M KHCO ₃	95	2
triangular silver nanoplates	-0.855 V	0.1 M KHCO ₃	96.8	3
Ag foil	-1.72 V vs. Pt wire	1-butyl-3-methyl-imidazolium trifluoromethanesulfonates in propylene carbonate	63.3	4
plasma-treated Ag foils	-0.6 V	0.1 M KHCO ₃	90	5
Ag nanoparticles 3 nm 5nm 10nm	-0.75 V	0.5 M KHCO ₃	76.8 88.4 70.5	6
Bulk Ag	-1.5 V	EMIM-BF ₄ in water	96	7
oxide-derived nanostructured Ag	-0.59 V	0.1 M KHCO ₃	80	8
nanoporous silver Ag	-0.5 V	0.5 M KHCO ₃	90	9
Ag-IO	-0.7 V	0.1 M KHCO ₃	80	10

Ag/TiO ₂	-1.7V	1 M KOH	90	11
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References

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