### **Supporting Information**

# Confinement of Alkaline Environment for Electrocatalytic CO<sub>2</sub> Reduction in Acidic Electrolyte

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#### **Experimental Section**

#### **Chemicals and Materials**

Tetraethyl orthosilicate (TEOS, 98%) was purchased from Tianjin Luoen Chemical Reagent Co., Ltd. Ethanol (HPLC, 99.8%), resorcinol (AR, 99%), polyvinylpyrrolidone (PVP, MW = 40000, K30), NaOH (AR, 96%), KOH (GR, 95%), K<sub>2</sub>SO<sub>4</sub> (AR, 99%), AgNO<sub>3</sub> (AR, 99.8%) were purchased from Sigma-Aladdin. Formaldehyde solution (38%), H<sub>2</sub>SO<sub>4</sub> (GR), NH<sub>3</sub>·H<sub>2</sub>O (AR) were purchased from Tianjin Yuanli Technology Development Co., Ltd. FAA-3-SOLUT-10 (10 wt%), FAA-3-50 membrane, Nafion 211 membrane were purchased from Fuel Cell Store. Carbon black (VXC72, 99.5%) was supplied by Cabot. All of these reagents were used as received without any purification process. Carbon-based gas diffusion layers (GDLs, AvCarb GDS3250) were purchased from Xima Laya Photo-Electric Technology Co., Ltd., China. 99.999% purity CO<sub>2</sub> and Ar were both purchased from Air Liquide. Ultrapure water (18.25 MΩ·cm) supplied by a UP Water Purification System was used as the solvent throughout the experiments.

#### **Catalyst synthesis**

For the synthesis of Ag@C, monodisperse SiO<sub>2</sub> particles were prepared as templates through the Stöber method and redispersed in absolute ethanol at 2-3 wt% SiO<sub>2</sub> concentration.<sup>1</sup> Then, 16 mL of freshly prepared  $[Ag(NH_3)_2]^+$  ions solution (0.24 mol  $L^{-1}$ ) was quickly added into 18 mL of SiO<sub>2</sub> dispersion with stirring at room temperature for 1 h. The dispersion was added into 80 mL of ethanol containing 1.6 g of PVP and stirred at 70 °C for 7 h. The as-obtained SiO<sub>2</sub>@Ag was added to a solution containing ethanol (30 mL), deionized water (5 mL) and ammonia aqueous solution (3 mL) under stirring after centrifugal washing. Then, 0.2 g of resorcinol and 0.28 mL of formaldehyde solution were added and the solution was kept stirring for 24 h at room temperature. Subsequently, the solution was transferred to an autoclave (40 mL) and hydrothermally treated at 100 °C for 12 h to obtain SiO<sub>2</sub>@Ag@RF. SiO<sub>2</sub>@Ag@C was prepared by annealing SiO<sub>2</sub>@Ag@RF at 800 °C for 3 h in an Ar atmosphere. Ag@C was finally obtained by immersing the sample in NaOH solution (5 mol L<sup>-1</sup>) to etch SiO<sub>2</sub>.<sup>2</sup> C@Ag was prepared through a synthetic process similar to that of Ag@C catalyst. After the obtainment of SiO<sub>2</sub> templates, SiO<sub>2</sub>@RF was synthesized directly through the modified Stöber coating method, in which formaldehyde and resorcinol were used as precursors. Then, SiO<sub>2</sub>@C was prepared through the same annealing procedure in an Ar atmosphere. The as-obtained SiO<sub>2</sub>@C was mixed with freshly prepared [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> ions solution and subsequently reduced to SiO<sub>2</sub>@C@Ag by PVP in ethanol solution. After the removal of SiO<sub>2</sub> in NaOH solution, the C@Ag catalyst was finally synthesized. For the synthesis of Ag/C, 0.2 g of carbon black and 0.22 g of AgNO<sub>3</sub> were added to 60 mL deionized water and kept stirring for 4 h. The composites were dried in a baking oven at 80 °C for 24 h and then annealed at 300°C for 3 h in air to obtain Ag/C.

#### **Electrode preparation**

To prepare gas diffusion electrode, 21 mg of catalyst (Ag@C or Ag/C), 2 mL of deionized water, 2 mL of isopropanol and 32  $\mu$ L of FAA solution (10 wt%) were mixed under sonication for 1 h to obtain a homogeneous catalyst ink. Then, the as-prepared ink was deposited onto a 3×3 cm<sup>2</sup> carbon paper through the airbrushing method with the catalyst loading on GDEs of about 1 mg cm<sup>-2</sup>. The GDEs was dried at room temperature overnight for further electrochemical measurements.

#### **Electrochemical measurements**

All electrochemical CO<sub>2</sub> reduction measurements were performed in a typical threeelectrode flow cell reactor connected to an electrochemical workstation (Autolab PGSTAT204). The effective electrode geometric area is 1 cm<sup>2</sup> for both cathode and anode. For the CO<sub>2</sub>RR in alkaline conditions, 1.0 M KOH was used as the electrolyte. Anolyte and catholyte chambers were separated by an anion exchange membrane (FAA-3-50). Hg/HgO was used as reference electrode and the potentials were converted to the RHE reference scale using the relation: E (vs RHE) = E (vs Hg/HgO) + 0.098 V + 0.0591 × pH. For acidic CO<sub>2</sub>RR, 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M K<sub>2</sub>SO<sub>4</sub> (pH 1.1) were employed as the electrolyte. The anolyte and catholyte chambers were separated by Nafion 211 membrane. The potentials were measured *versus* the Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode and converted to the RHE scale using the relation: E (vs RHE) = E (vs Hg/Hg<sub>2</sub>SO<sub>4</sub>) + 0.656 V + 0.0591 × pH. For both systems, IrO<sub>x</sub>/Ti was used as the counter electrode and the flow rate of the electrolytes were set to ~15 mL min<sup>-1</sup> by Peristaltic pumps (EC200-01, Gaossunion Co., Ltd.). A mass flow controller (MC-Series, Alicat Scientific) was used to set the CO<sub>2</sub> gas flow rate at 20 sccm.

#### **Product analysis**

The gas products were analyzed by online gas chromatography (GC7890B, Agilent Technologies, Inc.) equipped with a thermal conductivity detector (TCD) connected to a MolSieve 5A packed column for the detection of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and a back flame ionization detector (FID) connected to a Porapak Q packed column for the detection of CO. Ar was employed as the carrier gas. The Faradic efficiency (FE) of each product was calculated as follows:

$$FE = V \times C \times N \times F / (I \times V_m) \times 100\%$$
<sup>(1)</sup>

Where V is the gas flow rate, C is the concentration of single product in ppm, N is the electron transfer for every detected product molecule, F is the Faradic constant (F = 96485 C mol<sup>-1</sup>), I is the total current and V<sub>m</sub> is the unit molar volume of the outlet gas.

The single pass carbon efficiency (SPCE) of  $CO_2$  towards CO was calculated based on the following equation at 25 °C, 1 atm:

$$SPCE = j \times 24.05 / (N \times F \times V) \times 100\%$$
(2)

Where j is the partial current density of CO, N is the electron transfer for the generation of one CO molecule, V is the inlet flow rate of  $CO_2$ .

#### **Mass transport simulations**

The concentration of local species ( $H^+$ ,  $OH^-$ ,  $CO_2$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ) were tracked by finite-element method (FEM) simulations based on a reaction-diffusion model. A sector domain was selected as the model for the calculation. The ring with a thickness of 40

nm represented the carbon layer and a liquid diffusion layer was assumed to be 50  $\mu$ m as suggested by previous publications.<sup>3-5</sup>

In simulations, the following electrochemical reactions (CO<sub>2</sub>RR and HER) on the inner surface of catalysts and homogenous equilibrium reactions in the entire domain were considered.

$$CO_2 + H_2O + 2e^- \to CO + 2OH^-$$
 (3)

$$2H_2O + 2e^- \to H_2 + 2OH^-$$
 (4)

$$CO_2 + H_2 O \rightleftharpoons H^+ + HCO_3^- \tag{5}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \tag{6}$$

$$H_2 0 \rightleftharpoons H^+ + 0H^- \tag{7}$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$
 (8)

$$HCO_3^- + OH^- \rightleftharpoons H_2O + CO_3^{2-} \tag{9}$$

The transport of relevant species is based on the following equations:

$$\frac{\partial c_i}{\partial t} + \nabla j_i = R_i \tag{10}$$

$$j_i = -D_{e,i} \frac{\partial C_i}{\partial x} \tag{11}$$

Where  $j_i$  is the molar flux,  $R_i$  is the rate of each species which can be broken into electrochemical reactions and carbonate equilibria reactions.  $D_{e.i}$  is the effective diffusivity in the carbon layer, which is corrected with porosity,  $\varepsilon_m$ , and tortuosity,  $\tau_m$ , of the medium using the Bruggeman relationship according to related work.<sup>6</sup> The species diffusion coefficients are listed in Table S3.

$$D_{e.i} = \frac{\varepsilon_m}{\tau_m} D_i = \varepsilon_m^{3/2} D_i \tag{12}$$

The  $\varepsilon_m$  is calculated according to the definition:

$$\varepsilon_m = \frac{V_p}{V_0} \tag{13}$$

Where  $V_P$  is the volume of pores,  $V_0$  is the volume of the catalyst carbon layer. According to BET analysis (Figure S4),  $V_P$  is set to be 0.18m cm<sup>3</sup>, where m is the mass of catalyst.  $V_0$  is calculated as follows:

$$V_0 = \frac{m}{\rho} \times \frac{\frac{4}{3}\pi (R^3 - r^3)}{\frac{4}{3}\pi R^3}$$
(14)

Where  $\rho$  is the density of the catalyst, R is the radius of the spherical catalyst,

r is the radius of the cavity. The density of Ag@C catalyst was estimated by the drainage method. Both R and r can be obtained from TEM images. Based on this method, the porosity of the catalyst carbon layer is calculated to be 0.3.

The rate of electrochemical reactions is calculated as follows:

$$r_{CO_2} = -\frac{i}{F} \frac{FE_{CO}}{2} \tag{15}$$

$$r_{OH^-} = -\frac{i}{F} \tag{16}$$

In the model, a constant supply of  $CO_2$  was set at the outer surface of the carbon layer and the maximum concentration of  $CO_2$  is calculated based on Henry's Law.

$$C^{0}_{co2,aq} = K^{0}_{H} C^{0}_{co2,gas} \tag{17}$$

$$\ln(K_H^0) = 93.4517 \left(\frac{100}{T}\right) - 60.2409 + 23.3585 \ln \frac{T}{100}$$
(18)

Where  $K_H^0$  is the Henry's constant, T is the temperature and T=293.15 K. The saturated concentration of CO<sub>2</sub> is further corrected due to the high concentration of ions in the electrolyte by using Sechenov equation.

$$\log\left(\frac{C_{co_2,aq}^0}{C_{co_2,aq}}\right) = K_s C_s \tag{19}$$

$$K_s = \sum (h_{ion} + h_G) \tag{20}$$

$$h_G = h_{G,0} + h_T (T - 298.15) \tag{21}$$

Where  $C_s$  is the molar concentration,  $K_s$  is the Sechenov's constant which is calculated based on previous publications.<sup>7,8</sup>

## **Supplementary Figures**



Figure S1. SEM images of (a)  $SiO_2$  and (b)  $SiO_2@Ag$ .



Figure S2.  $N_2$  adsorption-desorption isotherm of Ag@C catalyst.



Figure S3. Pore size distribution of Ag@C catalyst.



Figure S4. Cumulative pore volume of Ag@C catalyst.



**Figure S5.** (a, b) TEM, (c) HRTEM and (d) EDS elemental mapping images of the Ag/C catalyst. The inset in (a) is the size distribution of metal particles.



Figure S6. XRD patterns of the Ag@C and Ag/C catalysts.



Figure S7. XPS spectra of the Ag@C and Ag/C catalysts.



Figure S8. Raman spectra of the Ag@C and Ag/C catalysts. The ratios of peak intensity  $(I_D/I_G)$  are similar.



Figure S9. (a) SEM and (b) TEM images of C@Ag catalyst.



Figure S10. Schematic of carbonate formation and crossover in alkaline media.



Figure S11.  $CO_2$  electroreduction performance of Ag@C in 0.5 M K<sub>2</sub>SO<sub>4</sub> electrolyte with different pH obtained by the adjustment with H<sub>2</sub>SO<sub>4</sub>.



Figure S12. Cathodic potentials in  $0.5 \text{ M} \text{ K}_2 \text{SO}_4$  and  $0.05 \text{ M} \text{ K}_2 \text{SO}_4$  (pH 4.0).



**Figure S13.** FE<sub>CO</sub> of Ag@C and C@Ag catalysts at different current densities in 0.5 M K<sub>2</sub>SO<sub>4</sub> (pH 1.1).



**Figure S14.** SEM images of Ag@C after CO<sub>2</sub>RR stability test in 0.5 M K<sub>2</sub>SO<sub>4</sub> (pH 1.1).



**Figure S15.** TEM images of Ag@C after CO<sub>2</sub>RR stability test in 0.5 M K<sub>2</sub>SO<sub>4</sub> (pH 1.1).



**Figure S16.** EDS elemental mapping images of Ag@C after CO<sub>2</sub>RR stability test in 0.5 M K<sub>2</sub>SO<sub>4</sub> (pH 1.1).



**Figure S17.** XPS spectra of Ag@C catalyst before and after CO<sub>2</sub>RR stability test in 0.5 M K<sub>2</sub>SO<sub>4</sub> (pH 1.1).



**Figure S18.** (a) Stability performance of Ag/C catalyst at 100 mA cm<sup>-2</sup> in 0.5 M K<sub>2</sub>SO<sub>4</sub> (pH 1.1). Inset shows the photograph of the backside of GDE after stability test. (b) TEM image of Ag/C after CO<sub>2</sub>RR stability test. Inset is the particle size distribution of Ag.



Figure S19. Graphical illustration of the model.



**Figure S20.** Computed concentration distribution of species at 50 mA cm<sup>-2</sup> (pH 1.1). (a) OH<sup>-</sup>. (b) CO<sub>2</sub>. (c) HCO<sub>3</sub><sup>-</sup>. (d) CO<sub>3</sub><sup>2-</sup>.



**Figure S21.** Computed concentration distribution of species at 100 mA cm<sup>-2</sup> (pH 1.1). (a) OH<sup>-</sup>. (b) CO<sub>2</sub>. (c) HCO<sub>3</sub><sup>-</sup>. (d) CO<sub>3</sub><sup>2-</sup>.



**Figure S22.** Computed concentration distribution of species at 150 mA cm<sup>-2</sup> (pH 1.1). (a) OH<sup>-</sup>. (b) CO<sub>2</sub>. (c) HCO<sub>3</sub><sup>-</sup>. (d) CO<sub>3</sub><sup>2-</sup>.



**Figure S23.** Computed concentration distribution of species at 200 mA cm<sup>-2</sup> (pH 1.1). (a) OH<sup>-</sup>. (b) CO<sub>2</sub>. (c) HCO<sub>3</sub><sup>-</sup>. (d) CO<sub>3</sub><sup>2-</sup>.



**Figure S24.** Computed concentration distribution of species at 250 mA cm<sup>-2</sup> (pH 1.1). (a) OH<sup>-</sup>. (b) CO<sub>2</sub>. (c) HCO<sub>3</sub><sup>-</sup>. (d) CO<sub>3</sub><sup>2-</sup>.



**Figure S25.** Computed concentration distribution of species at 300 mA cm<sup>-2</sup> (pH 1.1). (a) OH<sup>-</sup>. (b) CO<sub>2</sub>. (c) HCO<sub>3</sub><sup>-</sup>. (d) CO<sub>3</sub><sup>2-</sup>.

Sample	Ag content	C content
	(wt%)	(wt%)
Ag@C	38.8	61.2
Ag/C	42.4	57.6

Table S1. Composition of Ag@C and Ag/C catalysts measured by ICP-OES  $% \mathcal{A}$ 

Dissolved Ag
No detected
No detected

**Table S2.** The amount of dissolved Ag in the electrolyte quantified by ICP-OES

Diffusion coefficient	Value $(10^{-9} \text{ m}^2 \text{ s}^{-1})$
$D_{H^+}$	9.310
D <sub>OH</sub> -	5.273
$D_{CO_2}$	1.910
$D_{HCO_3^-}$	1.185
D <sub>CO3</sub> <sup>2-</sup>	0.923

Table S3. Diffusion coefficients

#### References

- 1. Z. W. Deng, M. Chen and L. M. Wu, J. Phys. Chem. C, 2007, 111, 11692-11698.
- S. Feng, W. Li, Q. Shi, Y. Li, J. Chen, Y. Ling, A. M. Asiri and D. Zhao, *Chem. Commun.*, 2014, **50**, 329-331.
- N. Gupta, M. Gattrell and B. MacDougall, J. Appl. Electrochem., 2005, 36, 161-172.
- 4. Y. C. Tan, K. B. Lee, H. Song and J. Oh, *Joule*, 2020, **4**, 1104-1120.
- J. E. Huang, F. W. Li, A. Ozden, A. S. Rasouli, F. P. G. de Arquer, S. J. Liu, S. Z. Zhang, M. C. Luo, X. Wang, Y. W. Lum, Y. Xu, K. Bertens, R. K. Miao, C. T. Dinh, D. Sinton and E. H. Sargent, *Science*, 2021, **372**, 1074-1078.
- L. C. Weng, A. T. Bell and A. Z. Weber, Phys. Chem. Chem. Phys., 2018, 20, 16973-16984.
- Y. Xie, P. Ou, X. Wang, Z. Xu, Y. C. Li, Z. Wang, J. E. Huang, J. Wicks, C. McCallum, N. Wang, Y. Wang, T. Chen, B. T. W. Lo, D. Sinton, J. C. Yu, Y. Wang and E. H. Sargent, *Nat. Catal.*, 2022, 5, 564-570.
- Y. Qiao, W. Lai, K. Huang, T. Yu, Q. Wang, L. Gao, Z. Yang, Z. Ma, T. Sun, M. Liu, C. Lian and H. Huang, ACS Catal., 2022, 12, 2357-2364.