Vertical silver@silver chloride core-shell nanowire array for carbon dioxide electroreduction

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Figure S1. Schematic illustration of Ag@AgCl_x CSNWs fabrication process. (a) Hot pressing process with AAO mold on Ag foil. (b) Ag NWs were directly pressed in the Ag foil substrate. (c) After removing the AAO. (d) Ag NWs were chlorinated on 0.5 M NaCl solution.

Figure S2. Characterizations of Ag foil and Ag@AgCl_x foil. SEM images of (a) Ag foil and (b) Ag@AgCl_x foil. Scale bars of (a) and (b) are 1 μm .

Figure S3. TEM characterization of Ag NWs. (a) Low-magnification and (b) High-resolution TEM images of Ag NWs. Scale bar are 200 nm and 5 nm respectively.

Figure S4. XRD spectra of Ag foil, Ag@AgCl_x foil, Ag NWs and Ag@AgCl_x CSNWs. Black clubs refer to Ag peaks and black diamonds refer to AgCl peaks.

Figure S5. XPS spectra for Ag@AgCl_x CSNWs. (a) Ag 3d for the Ag@AgCl_x CSNWs before and after CO₂ reduction reaction. (b) Cl 2p for the Ag@AgCl_x CSNWs before and after CO₂ reduction reaction.

Figure S6. Electrocatalytic CO₂ reduction performance. Total electrode activities including (a) Faradaic efficiencies for H₂ evolution. (b) H₂ partial current densities j_{H_2} . Specific activity including ECSA-normalized (c) H₂ partial current densities $j_{H_2\_ECSA}$.

Figure S7. Measurement of double-layer capacitance. (a, c, e, g) CVs of Ag, Ag@AgCl_x foil, Ag NWs, and Ag@AgCl_x CSNWs. (b, d, f, g) Linear fitting results of the double layer charging currents vs. RHE at different scan rates for different samples.

Figure S8. Adsorption of CO on Ag100(a) and Ag111(b). Blue and green atoms represent Ag and Cl.

Figure S9. The relaxed structures of Ag111_Cl by substituting a surface (b) or subsurface (c) Ag atom by Cl, and inserting a Cl atom into the Ag atom layers on fcc (d), hcp I and top I site. G_{ad_CO} is labeled on the top of structures. Blue and green atoms represent Ag and Cl. For b, e and f, Cl atom is squeezed out the Ag bulk after relaxation, demonstrating those modifications are unstable and can't be the active structures, hence CO adsorption is not tested.

Figure S10. The relaxed structures of Ag₂₁₁-Cl by substituting a surface (b) or subsurface (c) Ag atom by Cl, and inserting a Cl atom into the Ag atom layers on bridge (d), top I and hollow I site. G_{ad_CO} is labeled on the top of structures. Besides, a similar structure with I-fcc of Ag₁₁₁ was established (g). For b, e and f, Cl atom is squeezed out the Ag bulk after relaxation, demonstrating those modifications are unstable and can't be the active structures.

Table S1. Summary of performances for CO₂ reduction including Ag@AgCl_x CSNWs in this work and other Ag catalysts with *iR* corrected.

Electrode	Electrolyte	Applied potential vs. RHE (V)	j_{CO} (mA/cm ²)	FE (%)	j_{CO_ECSA} (μA/cm ²)	Ref.
Ag foil	0.5M KHCO ₃	-0.6	0.036	4	36	This work
Ag@AgCl _x NWs	0.5M KHCO ₃	-0.46	1.93	90	151	This work
Ag@AgCl _x NWs	0.5M KHCO ₃	-0.6	6.54	75	511	This work
Planar Ag film	0.1M KHCO ₃	-0.8	~0.017	~4.3	~4.25	1
Ag nanocoral	0.1M KHCO ₃	-0.6	6.62	95	162	2
Ag nanoparticles	0.1M KHCO ₃	-0.856	~0.56	64.9	N/A	3
Plasma-activated Ag	0.5M KHCO ₃	-0.6	~2.1	90	N/A	4
Nanostructured Ag	0.5M KHCO ₃	-0.89	~10	70	N/A	5
AE-Ag	0.1M KHCO ₃	-0.55	~0.9	~90	~80	6
Ultrathin Ag NWs	0.5M KHCO ₃	-0.9	~5.5	78	N/A	7

Table S2. Summary of performances for CO₂ reduction including Ag@AgCl_x CSNWs in this work and other Ag catalysts without *iR* corrected.

Electrode	Electrolyte	Applied potential vs. RHE (V)	j_{CO} (mA/cm ²)	FE (%)	$j_{\text{CO.ECSA}}$ (μA/cm ²)	Ref.
Ag foil	0.5M KHCO ₃	-0.6	0.034	4	34	This work
Ag@AgCl _x NWs	0.5M KHCO ₃	-0.46	1.79	90	140	This work
Ag@AgCl _x NWs	0.5M KHCO ₃	-0.6	5.27	75	413	This work
Nanoporous Ag	0.5M KHCO ₃	-0.6	16.3	92	6	8
Three dimensional porous Ag	0.1M KHCO ₃	-0.99	10.8	94.7	N/A	9
Ag NWA	0.5M KHCO ₃	-0.6	4.47	91	18.78	10
Triangular Ag nanoplates	0.1M KHCO ₃	-0.856	~1.25	96.8	N/A	11
Oxide-derived nanostructured Ag	0.1M KHCO ₃	-0.8	1.15	89	N/A	12
an-Ag	0.1M KHCO ₃	-0.5	~4	92.8	N/A	13

1. Yoon, Y.; Hall, A. S.; Surendranath, Y., Tuning of silver catalyst mesostructure promotes selective carbon dioxide conversion into fuels. *Angew. Chem. Int. Ed.* **2016**, *55* (49), 15282-15286.
2. Hsieh, Y.-C.; Senanayake, S. D.; Zhang, Y.; Xu, W.; Polyansky, D. E., Effect of Chloride Anions on the Synthesis and Enhanced Catalytic Activity of Silver Nanocoral Electrodes for CO₂ Electroreduction. *ACS Catal.* **2015**, *5* (9), 5349-5356.
3. Kim, C.; Jeon, H. S.; Eom, T.; Jee, M. S.; Kim, H.; Friend, C. M.; Min, B. K.; Hwang, Y. J., Achieving Selective and Efficient Electrocatalytic Activity for CO₂ Reduction Using Immobilized Silver Nanoparticles. *J. Am. Chem. Soc.* **2015**, *137* (43), 13844-50.
4. Mistry, H.; Choi, Y. W.; Bagger, A.; Scholten, F.; Bonifacio, C. S.; Sinev, I.; Divins, N. J.; Zegkinoglou, I.; Jeon, H. S.; Kisslinger, K.; Stach, E. A.; Yang, J. C.; Rossmeisl, J.; Roldan Cuenya, B., Enhanced Carbon Dioxide Electroreduction to Carbon Monoxide over Defect-Rich Plasma-Activated Silver Catalysts. *Angew. Chem. Int. Ed. Engl.* **2017**, *56* (38), 11394-11398.
5. Jee, M. S.; Jeon, H. S.; Kim, C.; Lee, H.; Koh, J. H.; Cho, J.; Min, B. K.; Hwang, Y. J., Enhancement in carbon dioxide activity and stability on nanostructured silver electrode and the role of oxygen. *Appl. Catal., B* **2016**, *180*, 372-378.
6. Ma, M.; Liu, K.; Shen, J.; Kas, R.; Smith, W. A., In Situ Fabrication and Reactivation of Highly Selective and Stable Ag Catalysts for Electrochemical CO₂ Conversion. *ACS Energy Lett.* **2018**, *3* (6), 1301-1306.
7. Xi, W.; Ma, R.; Wang, H.; Gao, Z.; Zhang, W.; Zhao, Y., Ultrathin Ag Nanowires Electrode for Electrochemical Syngas Production from Carbon Dioxide. *ACS Sustain. Chem. Eng.* **2018**, *6* (6), 7687-7694.

8. Lu, Q.; Rosen, J.; Zhou, Y.; Hutchings, G. S.; Kimmel, Y. C.; Chen, J. G.; Jiao, F., A selective and efficient electrocatalyst for carbon dioxide reduction. *Nat. Commun.* **2014**, *5*, 3242.
9. Daiyan, R.; Lu, X.; Ng, Y. H.; Amal, R., Highly Selective Conversion of CO₂ to CO Achieved by a Three-Dimensional Porous Silver Electrocatalyst. *ChemistrySelect* **2017**, *2* (3), 879-884.
10. Luan, C.; Shao, Y.; Lu, Q.; Gao, S.; Huang, K.; Wu, H.; Yao, K., High-Performance Carbon Dioxide Electrocatalytic Reduction by Easily Fabricated Large-Scale Silver Nanowire Arrays. *ACS Appl. Mater. Interfaces* **2018**, *10* (21), 17950-17956.
11. Liu, S.; Tao, H.; Zeng, L.; Liu, Q.; Xu, Z.; Liu, Q.; Luo, J. L., Shape-Dependent Electrocatalytic Reduction of CO₂ to CO on Triangular Silver Nanoplates. *J. Am. Chem. Soc.* **2017**, *139* (6), 2160-2163.
12. Ma, M.; Trzesniewski, B. J.; Xie, J.; Smith, W. A., Selective and Efficient Reduction of Carbon Dioxide to Carbon Monoxide on Oxide-Derived Nanostructured Silver Electrocatalysts. *Angew. Chem. Int. Ed. Engl.* **2016**, *55* (33), 9748-52.
13. Zhou, L. Q.; Ling, C.; Jones, M.; Jia, H., Selective CO₂ reduction on a polycrystalline Ag electrode enhanced by anodization treatment. *Chem. Commun.* **2015**, *51* (100), 17704-7.