

Supporting Information

Regulating Work Function of Silver Catalyst via Surface Engineering for Enhanced CO₂ Electroreduction

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1. Figure S1-S10

2. Table S1-S7

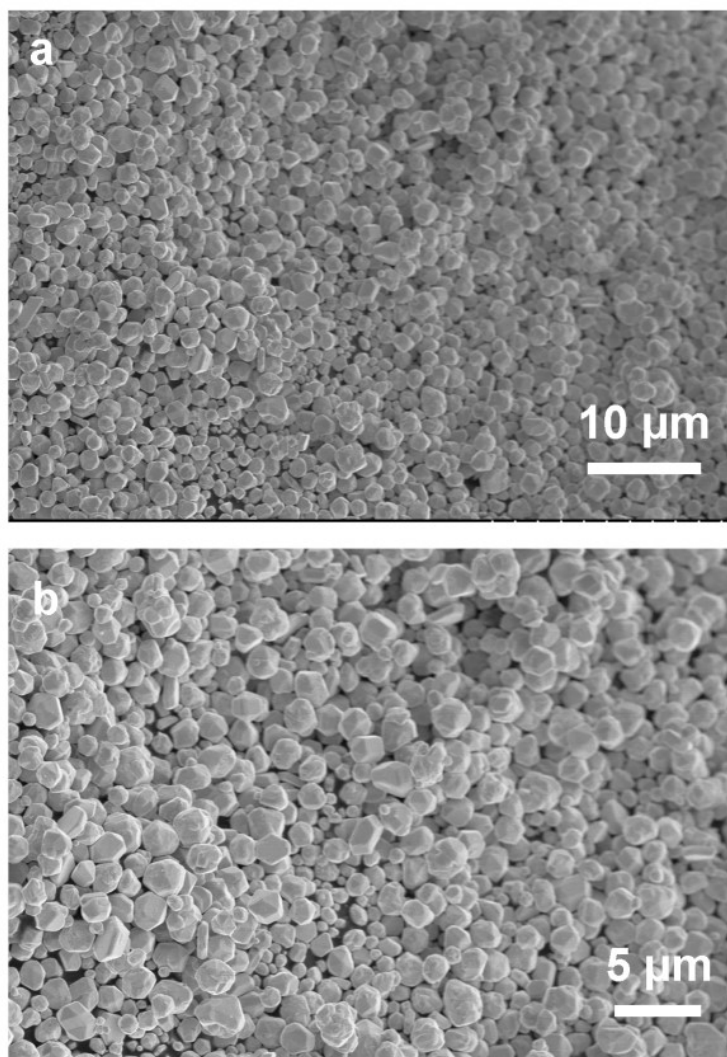


Fig. S1. SEM images of Ag-0 h sample (a, b) under different resolutions.

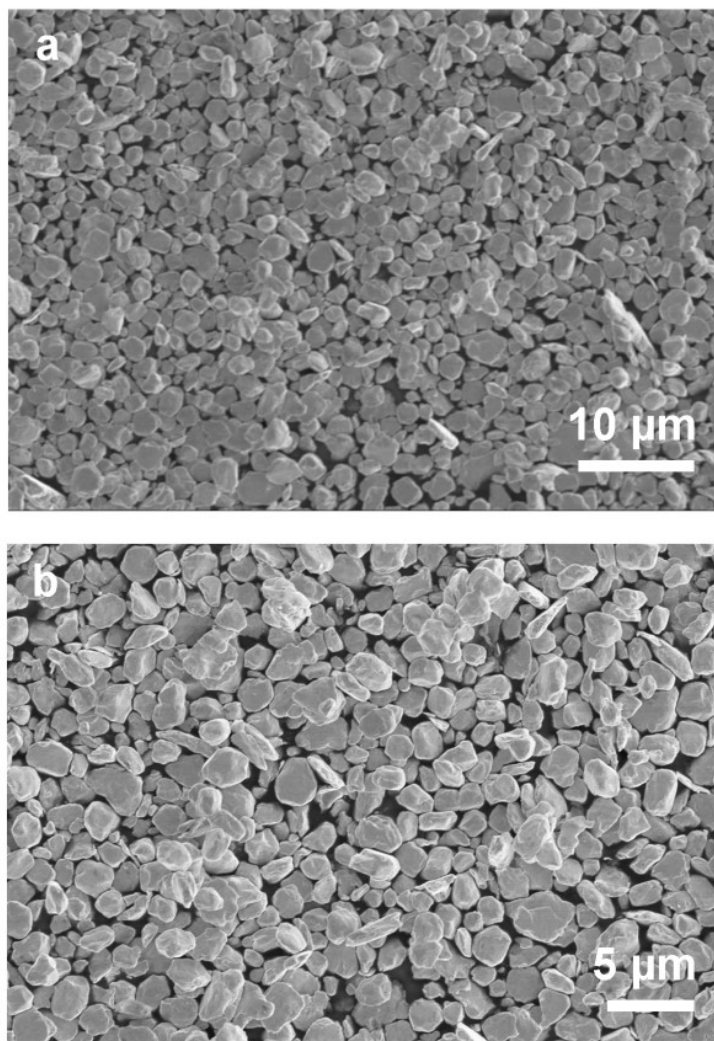


Fig. S2. SEM images of Ag-2h sample (a, b) under different resolutions.

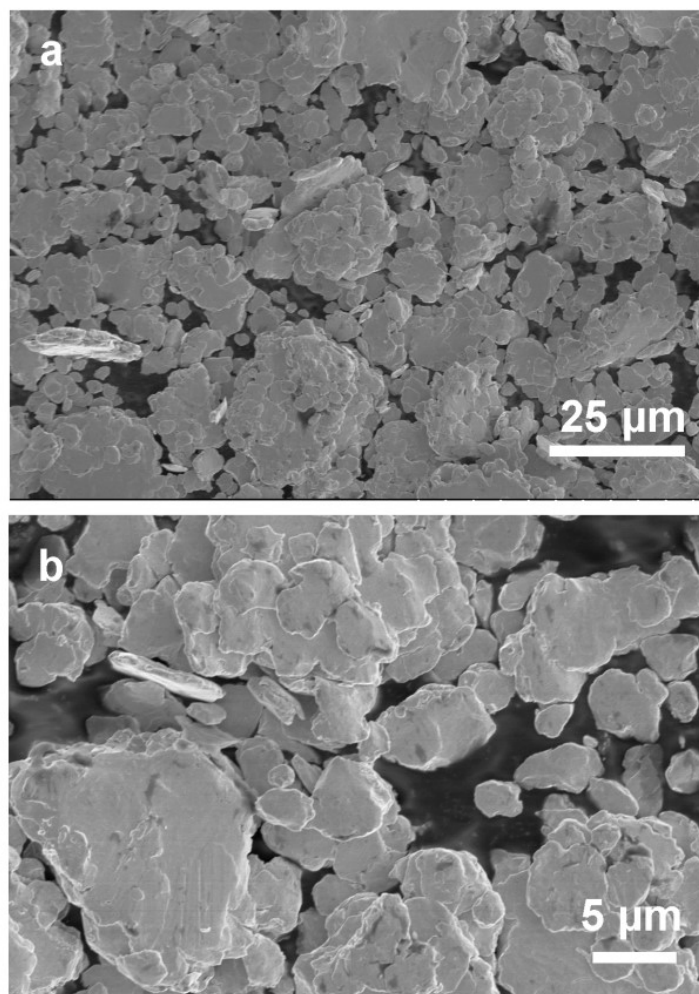


Fig. S3. SEM images of Ag-4h sample (a, b) under different resolutions.

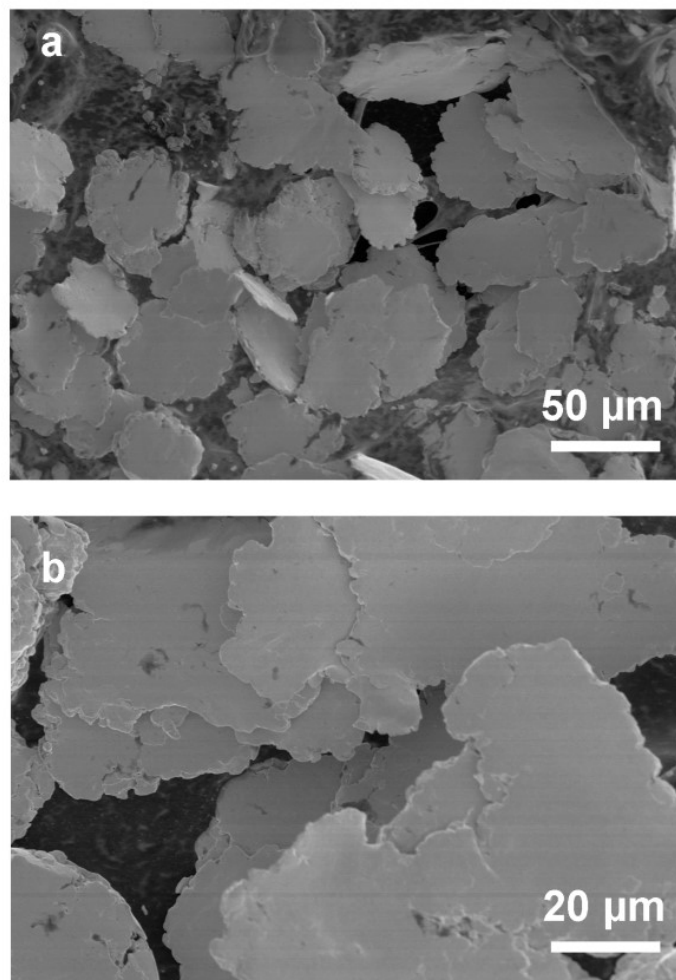


Fig. S4. SEM images of Ag-6h sample (a, b) under different resolutions.

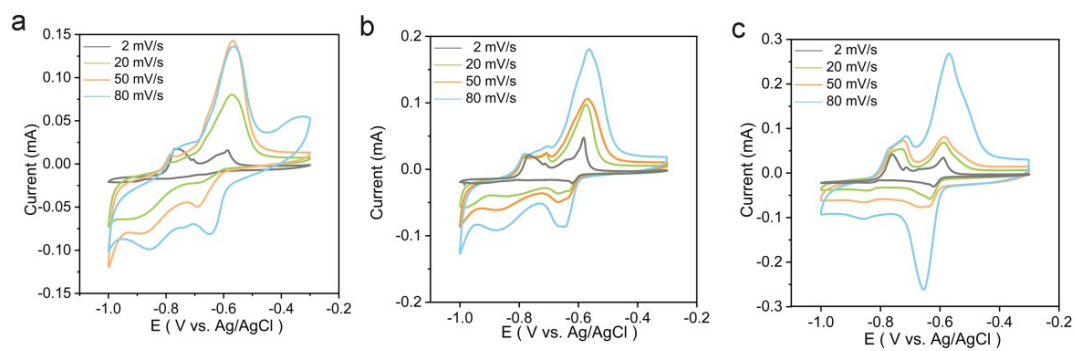


Fig. S5. Pb - UPD cyclic voltammetry curves at different scan rates: (a) Ag-2h, (b) Ag-4h and (c) Ag-6h.

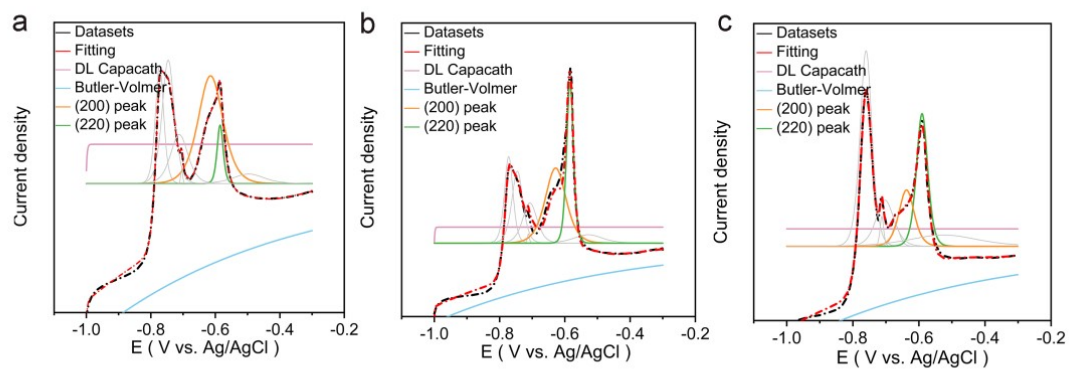


Fig. S6. Results of Pb - UPD curve fitting for different samples at scan rate of 2 mV/s:
 (a) Ag-2h, (b) Ag-4h and (c) Ag-6h.

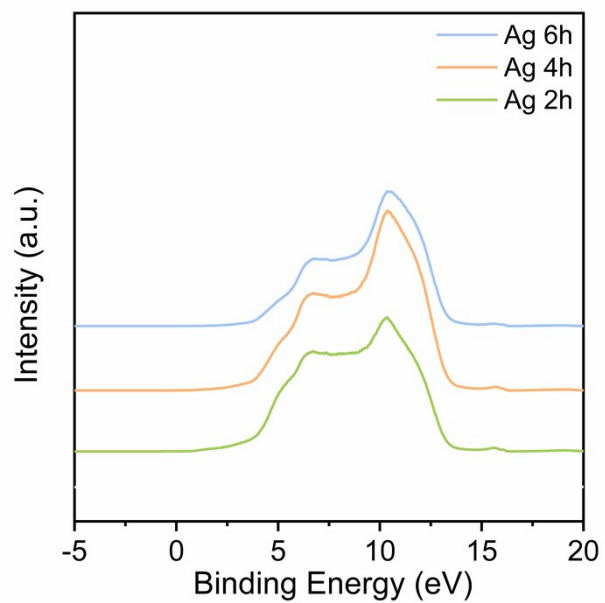


Fig. S7. work function of ball-milling Ag powders subjected to different milling times obtained by ultraviolet photoelectron spectroscopy.

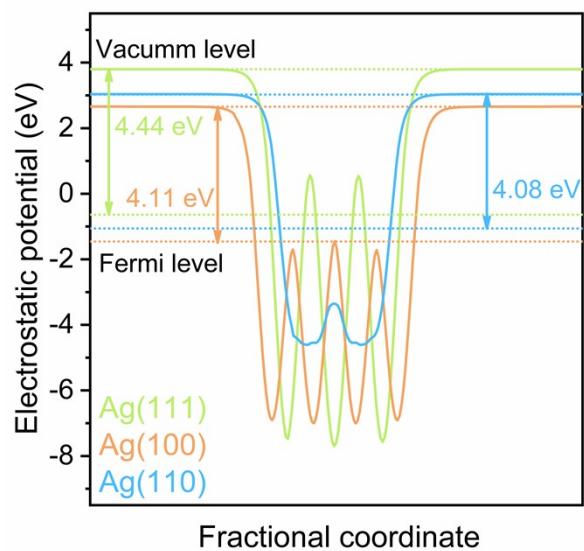


Fig. S8. Calculated work functions of various Ag surfaces- Ag(111), Ag(100) and Ag(110).

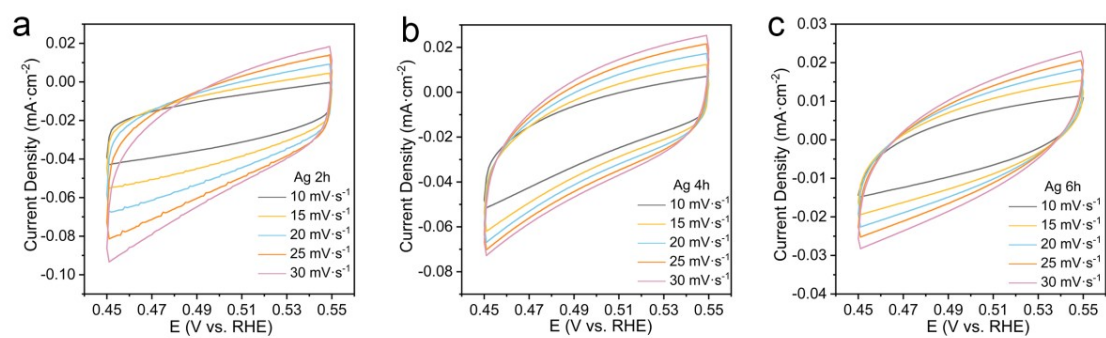


Fig. S9. Cyclic voltammograms under different scan rates for (a) Ag-2 h, (b) Ag-4 h and (c) Ag-6 h.

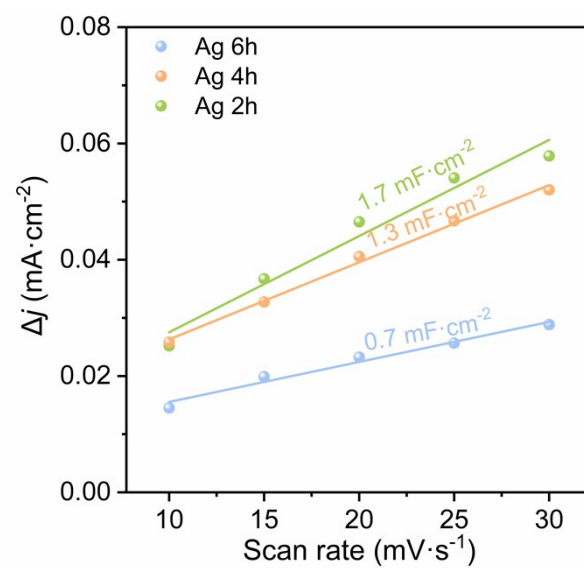


Fig. S10. ECSA obtained from the change of charging current density related to scan rate

Table S1 Geometric mean particle size versus ball milling time.

Time	Geometric mean particle size(μm)
0 h	2
2 h	3
4 h	20
6 h	50

Table S2 Crystal plane peak height (I_{hkl}) versus ball milling time.

Time	$I_{(111)}$	$I_{(200)}$	$I_{(220)}$	$I_{(311)}$
PDF#99-0094	100	48	29.1	33
2 h	883	304	188	158
4 h	1107	361	259	225
6 h	736	238	381	205

Table S3 Crystal plane texture coefficient (TC_{hkl}) versus ball milling time.

Time	$TC_{(111)}$	$TC_{(200)}$	$TC_{(220)}$	$TC_{(311)}$
PDF#99-0094				
2 h	1.337	0.959	0.978	0.725
4 h	1.291	0.877	1.038	0.795
6 h	0.931	0.627	1.656	0.786

Table S4. The results of Pb - UPD curve fitting for different samples at scan rate of 2 mV/s:

Time	peak position of (110)(V)	peak area of (110)($\text{F} \times 10^{-6}$ mol)	peak position of (100)(V)	peak area of (100)($\text{F} \times 10^{-6}$ mol)	ratio of Ag(110) to Ag(100)
2 h	-0.585	1.1737	-0.614	8.8882	0.13
4 h	-0.584	6.3085	-0.628	8.9919	0.70
6 h	-0.590	8.3691	-0.637	4.7634	1.75

Table S5 PZC and work function versus ball milling time

Time	PZC(v.s. Ag/AgCl)	Work function in vacuum (eV)
2 h	0.33	4.41
4 h	0.30	4.27
6 h	0.26	4.18

Table S6 The calculated work function, electrostatic potential and Fermi energy level of Ag (111), Ag (100) and Ag (110).

	Work function (eV)	Electrostatic potential (eV)	Fermi energy level (eV)
Ag (111)	4.4354	3.799	-0.6364
Ag (100)	4.1116	2.656	-1.4556
Ag (110)	4.0847	3.027	-1.0577

Table S7 Work function and coordination number $\bar{CN}^d$ of (110), (100) and (111) plane of FCC structure.

	$\bar{CN}^d$	Work function
Ag (110)	6.83	4.06
Ag (100)	7.64	4.21
Ag (111)	8.94	4.34
Cu (110)	7.11	4.20
Cu (100)	7.93	4.47
Cu (111)	8.92	4.71
Au (110)	7.37	4.93
Au (100)	8.14	5.00
Au (111)	9.18	5.16