Electronic Supplementary Information (ESI)

Photoelectrocatalytic reduction of CO_2 to syngas over Ag nanoparticle modified p-Si nanowire arrays

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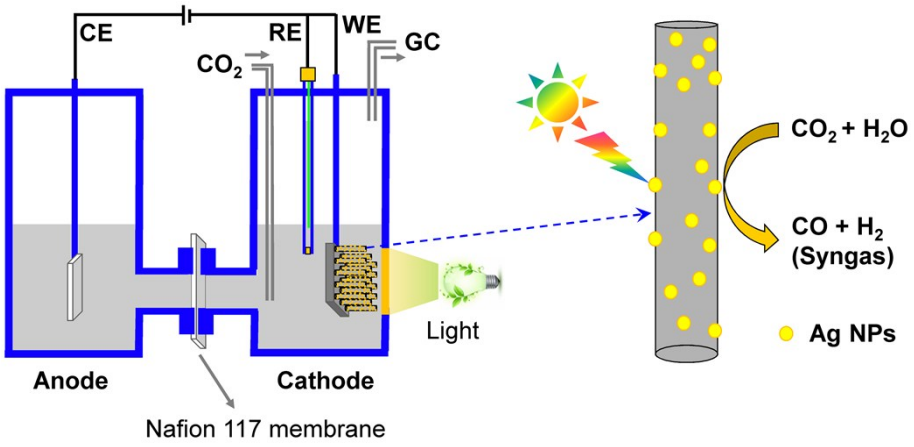

CE: counter electrode; RE: reference electrode; WE: working electrode

Fig. S1 Schematic illustration of the H-cell photoelectrocatalytic reaction system.

Table S1 The photoelectrocatalytic behaviours of SiNWs and metal/SiNWs in CO_2-saturated 0.1 M $KHCO_3$ solution at −1.0 V vs. RHE[a]

Photocathode	Faradic efficiency (%)				Current density (mA cm^{-2})	H_2/CO molar ratio
	H_2	CO	HCOOH	CH_3OH		
planar Si	95	3.5	0	0	0.23	27
SiNWs	91	7.4	2.4	0	1.6	12
Pt/SiNWs	93	5.5	0.16	0	6.8	17
Pd/SiNWs	73	22	3.5	0	2.4	3.3
Au/SiNWs	30	59	1.9	3.6	3.2	0.51
Ag/SiNWs	55	37	2.1	1.6	2.7	1.5

[a] Reaction conditions: Pt plate counter electrode; Ag/AgCl (saturated KCl) reference electrode; light source, Xe lamp equipped with AM 1.5G at 100 mW cm^{-2}; reaction time, 4 h.

Table S2 The electrocatalytic behaviours of Ag-*x* catalysts with different Ag NPs sizes for CO_2 reduction in CO_2-saturated 0.1 M $KHCO_3$ solution at −1.0 V vs. RHE[a]

Cathode	Formation rate (μmol cm^{-2} h^{-1})		Faradic efficiency (%)		Current density (mA cm^{-2})
	H_2	CO	H_2	CO	
Ag-4.2	3.0	5.6	32	60	0.50
Ag-6.3	2.9	10	26	66	0.81
Ag-8.2	4.0	14	21	75	1.0
Ag-11	5.2	9.4	33	59	0.85
Ag-14	5.5	7.8	38	54	0.77
Ag-16	3.4	3.7	46	49	0.40

[a] Reaction conditions: Pt plate counter electrode; Ag/AgCl (saturated KCl) reference electrode; reaction time, 2 h.

Table S3 The electrocatalytic behaviours of Ag-8.2 catalyst for CO_2 reduction in CO_2-saturated 0.1 M $KHCO_3$ solution at different applied potentials[a]

Potential (V vs. RHE)	Formation rate (μmol cm^{-2} h^{-1})		Faradic efficiency (%)		Current density (mA cm^{-2})
	H_2	CO	H_2	CO	
−0.8	2.7	2.0	56	41	0.26
−1.0	4.0	14	21	75	1.0
−1.2	5.0	27	15	81	1.8
−1.4	26	31	42	51	3.3
−1.6	57	37	57	37	5.4

[a] Reaction conditions: Pt plate counter electrode; Ag/AgCl (saturated KCl) reference electrode; reaction time, 2 h.

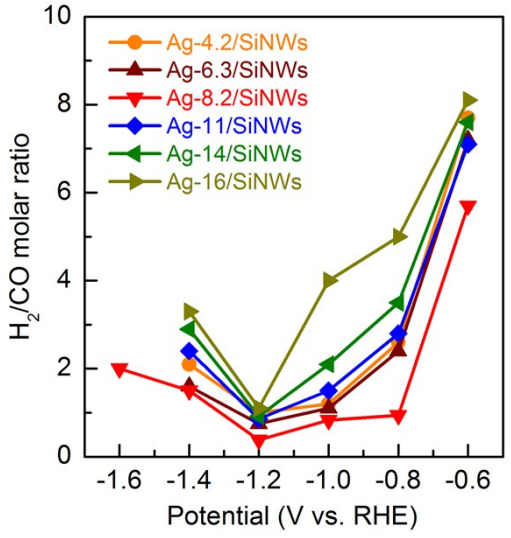

Fig. S2 The H_2/CO molar ratio of Ag-*x*/SiNWs catalysts at different applied potentials.

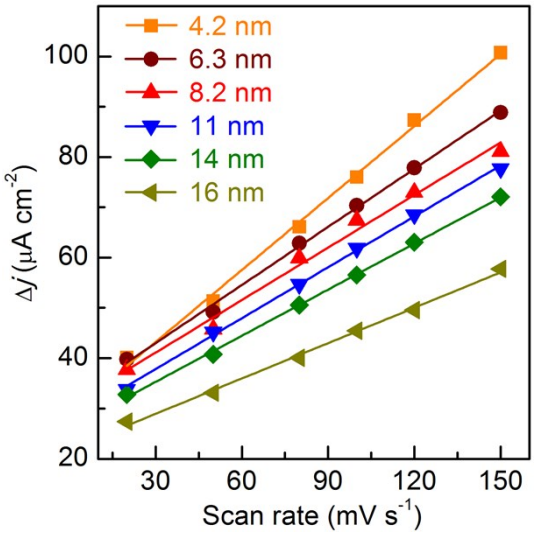

Fig. S3 Charging current density differences (Δj) of Ag NPs with different sizes plotted against scan rates.

Table S4 The electrochemical surface area (ECSA) of Ag NPs with different sizes.

Ag NPs (nm)	Slop (μF cm^{-2})	C_{dl} (μF cm^{-2})	R_f	ECSA (cm^2)
4.2	477	239	12	12
6.3	385	193	9.6	9.6
8.2	348	174	8.7	8.7
11	337	169	8.4	8.4
14	305	153	7.6	7.6
16	234	117	5.9	5.9

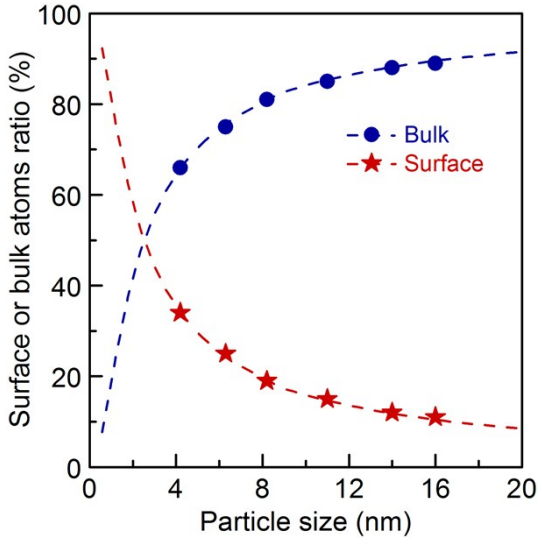

Fig. S4 The surface and bulk atoms ratio of Ag NPs with different sizes calculated from the theoretical Ag NPs model.