Electronic Supporting Information

Selective electrochemical CO_2 reduction over highly porous gold film

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Table S1. The bulk pH of aqueous electrolytes before and after CO_2 saturation

Electrolytes	Bulk pH before CO_2 saturation	Bulk pH after CO_2 saturation
0.1 M $KHCO_3$	8.52	6.81
0.2 M $KHCO_3$	8.40	7.10
0.3 M $KHCO_3$	8.39	7.15
0.5 M $KHCO_3$	8.36	7.23
0.05 M $KHCO_3$ + 0.05 M $KClO_4$	8.51	6.62
0.1 M $KClO_4$	6.63	4.71

Table S2. The bycarbonate/carbonate electrolytes with different bulk pH for Au foil electrolysis at -0.5 V versus RHE

Bycarbonate/carbonate electrolytes	Bulk pH
CO_2-saturated 0.5 M $KHCO_3$	7.23
CO_2-saturated 0.94 M $KHCO_3$	7.80
0.94 M $KHCO_3$	8.22
0.94 M $KHCO_3$+0.0094 M K_2CO_3	8.39
0.94 M $KHCO_3$+0.047 M K_2CO_3	8.70
0.94 M $KHCO_3$+0.094 M K_2CO_3	8.93

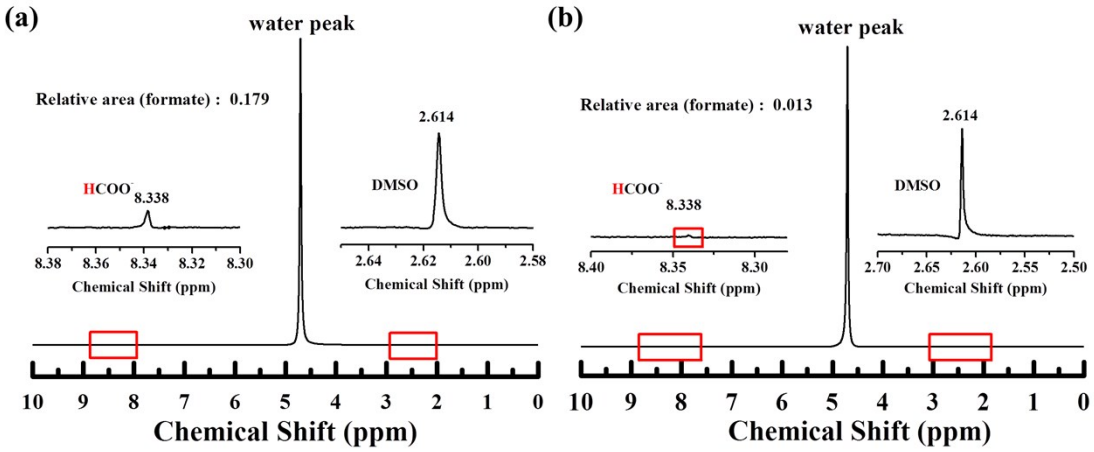

Fig. S1 ^{1}H-NMR spectrum for (a) standard formate sample: 0.5 mL of 0.5 mM formate sodium solution mixed with 0.1 mL D_2O and 0.1 mL 3 mM DMSO solution added as an internal standard, (b) liquid products of PF-Au-75 at -0.6 V：0.5 mL electrolyte mixed with 0.1 mL D_2O and 0.1 mL 3 mM DMSO solution. The relative areas were estimated by following equation:

$$Relative\ area\ (formate) = \frac{peak\ area\ at\ 8.338\ ppm\ (formate)}{peak\ area\ at\ 2.614\ ppm\ (DMSO)}$$

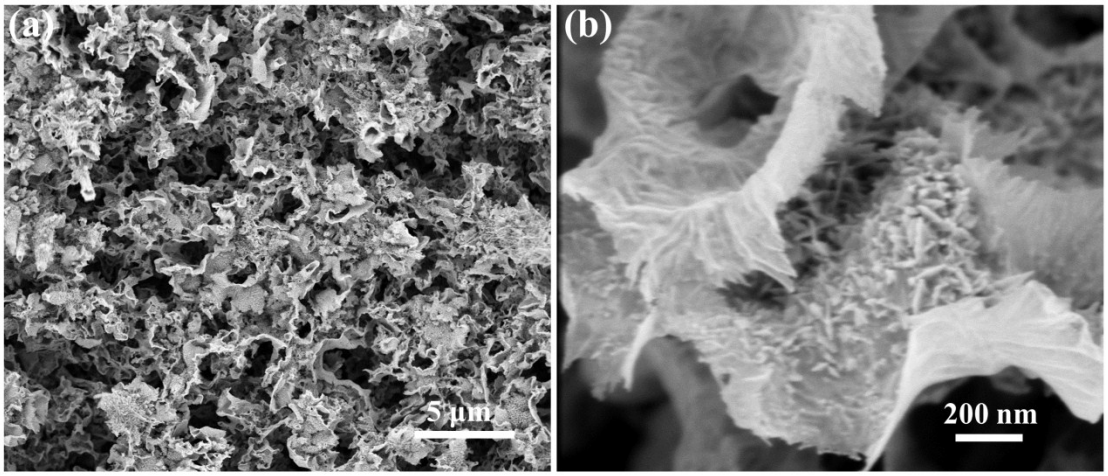

Fig. S2 (a) Low-magnification and (b) high-magnification SEM images of the PF-Au-75 electrodes after 9 h CO_2 reduction.

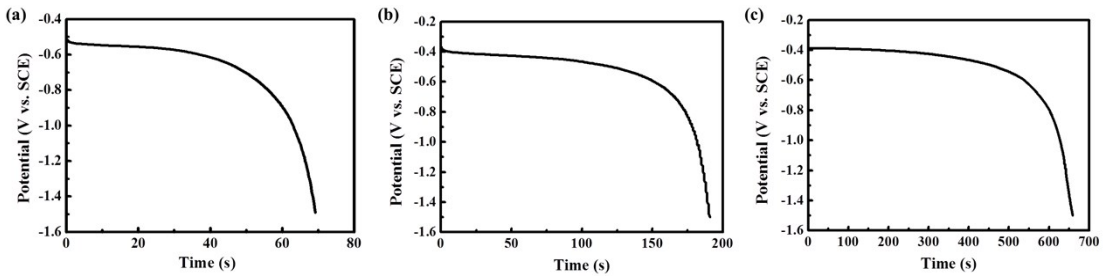

Fig. S3 Potential curves for the reduction of AgCl at a constant current density of 10 mA cm^{-2} to prepare (a) PF-AuAg-6, (b) PF-AuAg-18, (c) PF-AuAg-75 electrodes in CO_2-saturated 0.1 M $KHCO_3$ electrolyte.

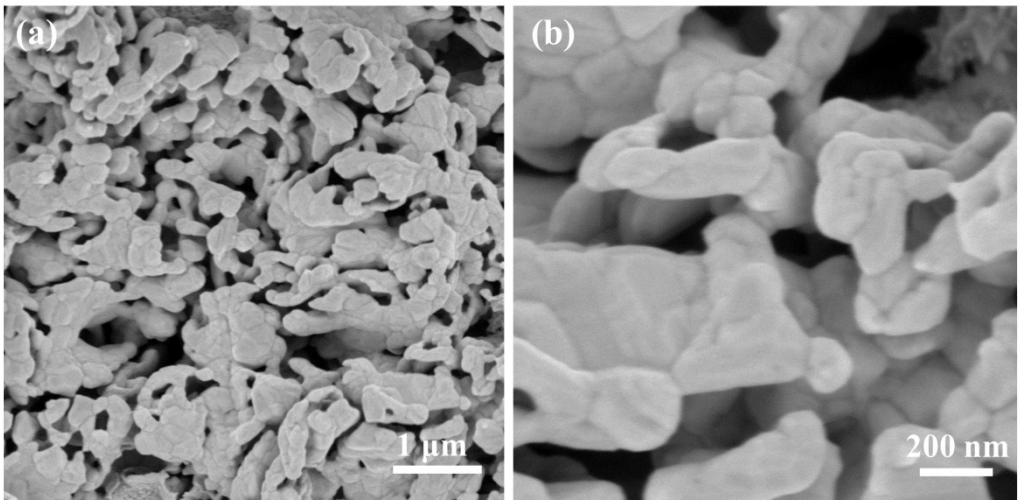

Fig. S4 (a) Low-magnification and (b) high-magnification SEM images of PF-AuAg-75 electrodes reduced from PF-Au/AgCl-75 precursor at 10 mA cm^{-2} in CO_2-saturated 0.1 M $KHCO_3$ electrolyte.

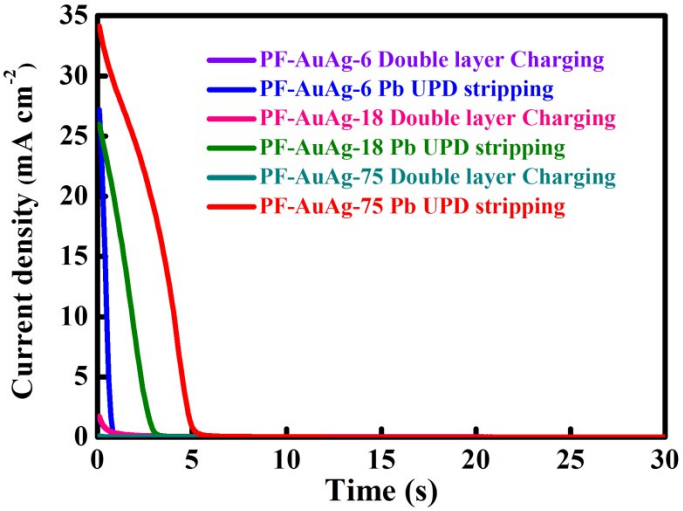

Fig. S5 Current density curves of Pb UPD stripping on PF-AuAg samples at the potential of 0.650 V (vs. Pb/Pb^{2+}).