# **Supporting information**

# Carbon quantum dots-covered porous Ag with enhanced activity for selective electroreduction CO<sub>2</sub> to CO

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### **Preparation of p-Ag**

To form the porous structure, the as-prepared  $Ag_2O$  (0.25 g) was dispersed in 0.5 M NaOH (30 ml) solution and sonicated for 3 h. Then the obtained porous  $Ag_2O$  was reduced with D-glucose (0.3 g). Finally, the suspension was collected by centrifugation at 4000 rpm for 5 min and washed with water for several times.

#### **Preparation of CQDs**

The CQDs were fabricated with a chemical method reported in prior work.<sup>1</sup> The Glucose was dissolved in deionized water (50 ml) to form a clear solution (1 mol/L). NaOH (50 ml, 1 mol/L) solution was added into the solution of glucose, then the mixture was treated ultrasonically for 3 h. The color of the solution changed to brown. The CQDs were purified by dialysis (MWCO of the dialysis membrane: 1000).

## Preparation of the physical mixture of p-Ag and CQDs

The physical mixture of p-Ag and CQDs was prepared by adding 0.2 g p-Ag and 30 ml CQDs solution into a glass beaker with magnetic stirring for 3 h. The obtained product was collected by centrifugation at 4000 rpm and washed with water for three times.



Fig. S1. (a) SEM image and (b) partial enlarged view of Ag<sub>2</sub>O precursor.



Fig. S2. N<sub>2</sub> adsorption-desorption isotherms and pore size distribution (inset) of p-

Ag/CQDs.



**Fig. S3.** (a) TEM image and HRTEM image (inset) of CQDs. (b) The size distribution of CQDs.



**Fig. S4.** SEM image of p-Ag/CQDs after 4 h electrolysis and (b) XRD patterns of p-Ag/CQDs before and after the electrolysis.



**Fig. S5.** SEM images of (a) Ag foil, (b) p-Ag and the partial enlarged view (inset) and (c) the physical mixture of p-Ag and CQDs.



**Fig. S6.** XRD patterns of Ag foil, p-Ag, the mixture of p-Ag and CQDs and p-Ag/CQDs.



**Fig. S7.** (a) H<sub>2</sub> Faradaic efficiency and (b) H<sub>2</sub> current density for Ag foil, p-Ag and p-Ag/CQDs versus applied potential.



**Fig. S8.** LSVs of CQDs under Ar and CO<sub>2</sub> atmosphere in 0.5 M KHCO<sub>3</sub> electrolyte; (b) Faradaic efficiency of the electrolysis product under different potentials.



**Fig. S9.** Lead underpotential deposition experiments to determine the electrochemically active surface area (ECSA) of (a) Ag foil, (b) p-Ag and (c) comparison of Ag foil (black trace), p-Ag (green trace) and p-Ag/CQDs composite (red trace).

The ECSA of the Ag-based catalysts were measured based the underpotential deposition (UPD) method. The desorption peak of Pb UPD was integrated to calculate the electrochemical surface area assuming 420  $\mu$ C cm<sub>ec</sub><sup>-2</sup> for Ag-based samples.

[HCO <sub>3</sub> -]	[HClO <sub>4</sub> -]	рН
0.1	0.9	6.07
0.2	0.8	6.30
0.5	0.5	6.86
0.7	0.3	7.11
1.0	0	7.45
0.5	0	7.2

 Table S1. pH values of electrolytes used for bicarbonate dependent studies and

 comparison to electrolyte used for electrocatalyst testing.

#### **Reference:**

- Y.-C. Hsieh, S.D. Senanayake, Y. Zhang, W. Xu, D.E. Polyansky, Effect of Chloride Anions on the Synthesis and Enhanced Catalytic Activity of Silver Nanocoral Electrodes for CO<sub>2</sub> Electroreduction, ACS Catal. 5 (2015) 5349–5356.
- [2] S. Guo, S. Zhao, J. Gao, C. Zhu, X. Wu, Y. Fu, H. Huang, Y. Liu, Z. Kang, Cu-CDots nanocorals as electrocatalyst for highly efficient CO<sub>2</sub> reduction to formate, Nanoscale. 9 (2017) 298–304.