Supporting Information

Electrocatalytic carboxylation of halogenated compounds with mesoporous silver electrode materials

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Experimental

1 Synthesis of mesoporous silver materials

KIT-6 was synthesized following methods reported elsewhere [1]. HP-KIT-6 was synthesized by the method reported in one literature [2].

In order to synthesize mesoporous silver, a solution containing 1.48 g of $AgNO_3$ (99% Aldrich), 1.13 g of ethanol and 1.13 g of distilled water was impregnated into 3.0 g of HP-KIT-6. After drying for 24 hours at 353 K, the samples were heated to 573 K in nitrogen flow for 2 hours. After the thermal decomposition process, the silica template was completely removed by treating the composite with 3 M NaOH solution at 273 K for three times. Finally, the mesoporous silver was washed with distilled water and acetone for several times and dried at room temperature. This material named mesoAg-1 was obtained.

The amount of $AgNO_3$, ethanol and distilled water was reduced to 0.9 times, 0.8 times, 0.7 times and 0.6 times of the above amount, while other preparation conditions remained unchanged. The other four mesoporous silver materials were named mesoAg-2, mesoAg-3, mesoAg-4 and mesoAg-5.

2 Preparation of electrode and electrocatalytic reaction

60 mg of mesoporous silver was mixed with 0.1 mL of sodium carboxymethyl cellulose (CMC sodium to water ratio was 1:100) and coated on both sides of carbon paper (2 cm × 2 cm). After drying, the cathode was prepared and its electrocatalytic performance was tested.

A series of galvanostatic electrolysis of five kinds of mesoporous silver modified electrodes was carried out with 15 mL of 0.1 M bromobenzyl-0.1 M TEABr-DMF organic solution in an undivided electrochemical cell. The two-electrode system consisted of a mesoporous silver modified electrode as a cathode and a Mg rod as a sacrificial anode.

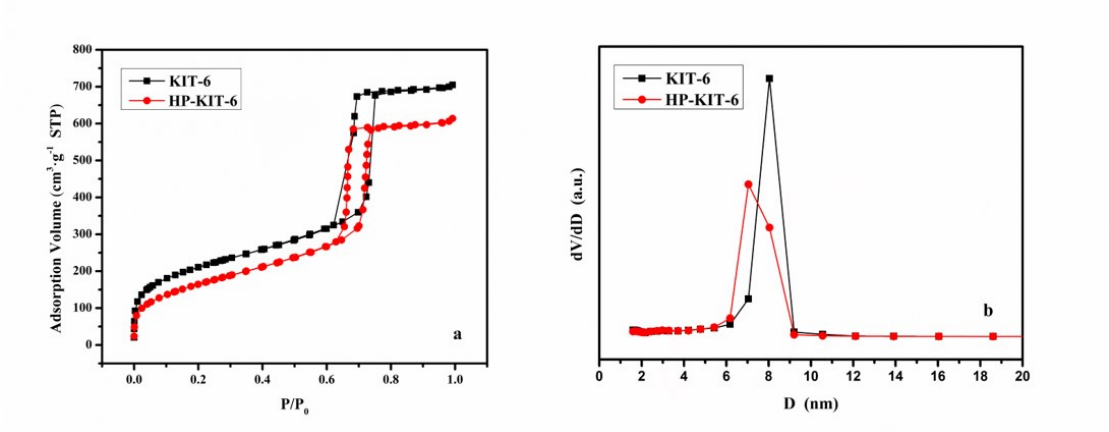
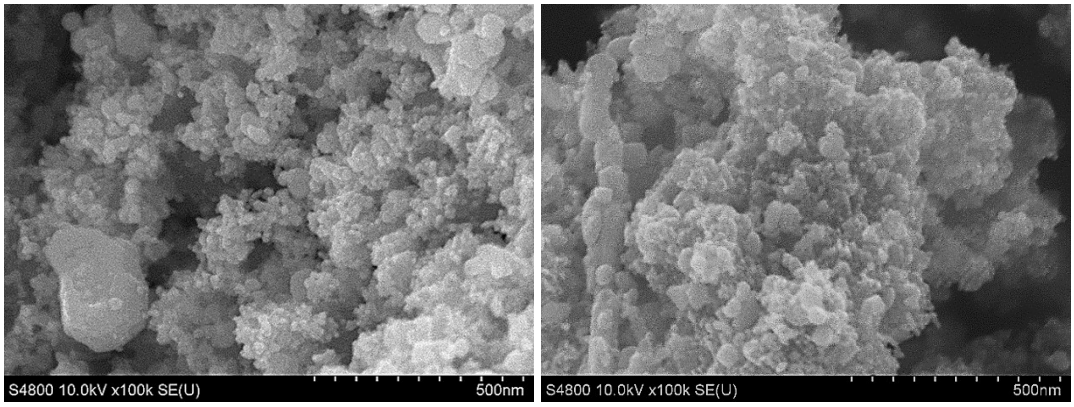
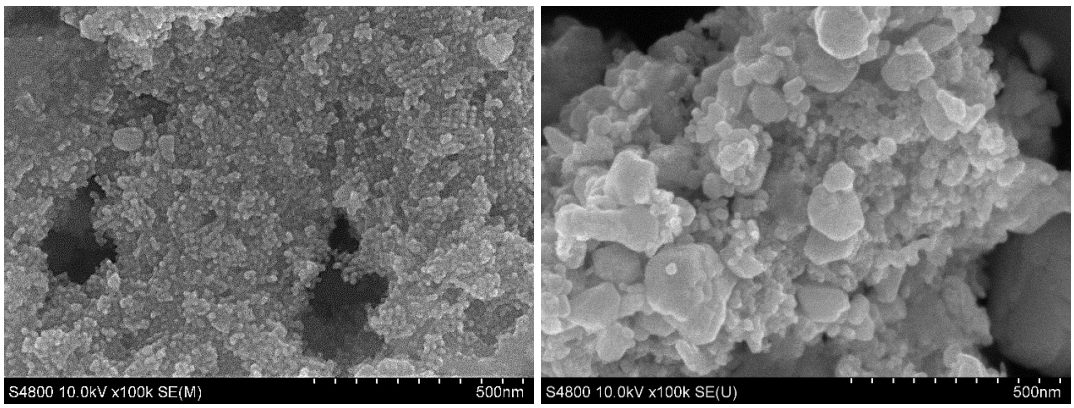


Fig. S1. (a) N_2 adsorption-desorption isotherms; (b) pore size distributions



（a） mesoAg-1　　（b） mesoAg-2



（c） mesoAg-4　　（d） mesoAg-5

Fig. S2. SEM images for mesoporous silver materials

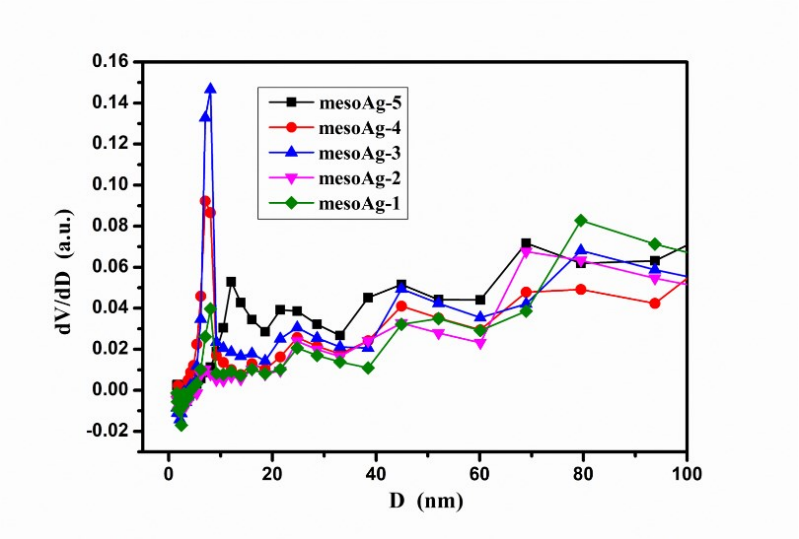


Fig. S3. BJH pore size distribution curve for the mesoporous silver materials

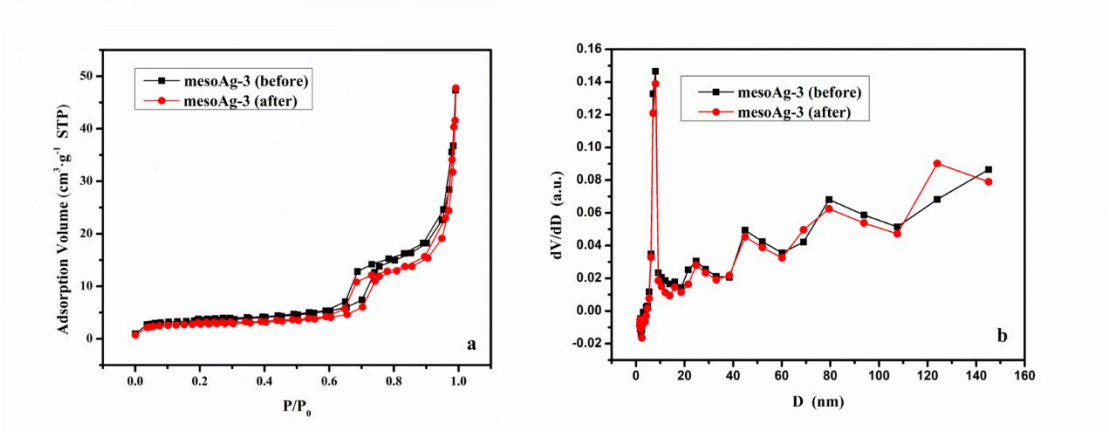


Fig. S4. (a) N_2 adsorption-desorption isotherms; (b)pore size distributions of mesoAg-3 before and after use.

Table S1 Physicochemical properties of mesoporous materials

Materials[a]	Organic content[b] (wt%)	BET surface area[c] ($m^2 \cdot g^{-1}$)	Total pore volume[d] ($cm^3 \cdot g^{-1}$)	Average pore size[e] (nm)
KIT-6		762	1.09	8.0
HP-KIT-6	3.7	605	0.95	7.1

[a] HP-KIT-6 denote hydrophobic KIT-6.

[b] Organic contents obtained by TGA analysis (weight loss between 473K and 873K).

[c] BET surface areas calculated from the N2 adsorption branches in the range of relative pressure ($p/p0$) = 0.05 – 0.20.

[d] Total pore volumes measured at $p/p0$ = 0.99.

[e] Pore diameters obtained from N2 adsorption branches by BJH method.

Table S2 Structure parameters for Ag

Material	BET surface are[a] ($m^2 \cdot g^{-1}$)
silver nanopartiles	1.94
foam silver	1.50

[a] BET surface areas calculated from the N_2 adsorption branches in the range of relative pressure (p/p_0) = 0.05 – 0.20.

Table S3 Structure parameters for mesoporous Ag before and after use

Material	BET surface are[a] ($m^2 \cdot g^{-1}$)	Total pore volume [b] ($cm^3 \cdot g^{-1}$)	Average pore size[c] (nm)
mesoAg-3 (before)	12	0.07	8.0
mesoAg-3 (after)	10	0.07	8.0

[a] BET surface areas calculated from the N_2 adsorption branches in the range of relative pressure (p/p_0) = 0.05 – 0.20. [b] Total pore volumes measured at p/p_0 = 0.99.

[c] Pore diameters obtained from N_2 adsorption branches by BJH method.

References:

[1] Kim, T.-W. , Kleitz, F., Paul, B., Ryoo, R. MCM-48-like large mesoporous silicas with tailored pore structure: facile synthesis domain in a ternary triblock copolymerbutanolwater system. J. Am. Chem. Soc., 2005, 127(20), 7601-7610.

[2] Shon, J. K. , Kong, S. S. , Kim, J. M. , Ko, C. H. , Jin, M. , Lee, Y. Y. , et al. Facile synthesis of highly ordered mesoporous silver using cubic mesoporous silica template with controlled surface hydrophobicity. Chem. Commun., 2009, 45(6), 650-652.