Supporting Information

Synthesis of Ag Nanoparticles/Ordered Mesoporous Carbons as Highly Efficient Catalyst for the Electroreduction of Benzyl Bromide

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1 Chemicals and instruments

All reagents were commercially available (Aldrich) and were directly used without further purification.

The X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu-Kα radiation ($\lambda = 1.5418$ Å) at 35 kV and 25 mA.

The FT-IR spectra were recorded on a Nicolet NEXUS 670 infrared spectrometer.

Thermogravimetric analysis (TGA) was carried out using a Metzsch TGA-STA449F3 analyzer from 25 to 800ºC in an air flow of 80 mL min^{-1} at a heating rate of 10 ºC·min^{-1}.

The amounts of Ag in OMC were quantified by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer after dissolving the samples in HNO_3 solution and filtered.

Nitrogen adsorption–desorption isotherms were measured on a Quancachrome Autosorb-3B instrument after evacuating the samples at 573 K for 6 h. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method and the pore distribution was calculated by the Barrett-Joyner-Halenda (BJH) method from adsorption branches of isotherms.

The Scanning Electron Microscope (SEM) images and Energy Dispersive X-Ray Spectroscopy (EDX) were obtained on a Hitachi S-4800 field-emission scanning microscope.

The Transmission Electron Microscope (TEM) images were recorded using a JEOL-JEM-2010 microscope after the specimens were dispersed in ethanol and placed on holey copper grids.

All electrochemical experiments were performed on a CHI 600C electrochemical work station (Chenhua, Shanghai, China) in an undivided cell

The conversion and selectivity of products were quantified on a Shimadzu GC-2014 GC equipped with a flame ionization detector and a Rtx®-5 column (30 m × 0.25 mm × 0.25 μm) using biphenyl as an internal standard.

2 Electrochemical process

Cyclic voltammograms were carried out using a traditional three-electrode system with a GC (d = 2 mm), Ag (d = 2 mm), OMC/GC (d = 2 mm) or Ag/OMC/GC (d = 2 mm) as working electrode, a Pt net as counter electrode and a Ag/AgI/I$^-$ as reference electrode, in 10 mL MeCN-0.1 M TEABF$_4$-5 mM PhCH$_2$Br at a scan rate of 0.1 V·s^{-1}.

The potentiostatic electrolysis was carried out in a mixture of substrate PhCH$_2$Br (0.05 M) and TEABF$_4$ (0.1 M) in 20 mL solvent (MeCN) under a slow stream of N$_2$ in an undivided glass cell equipped with a magnesium rod as sacrificial anode, a Ag/AgI/I$^-$ as reference electrode and a Ag, OMC or Ag/OMC as working electrode until 1-1.5 F/mol of charge was passed. The reaction mixture was hydrolyzed and extracted with Et$_2$O, and the organic layers was washed with H$_2$O, dried over MgSO$_4$, and filtered. The products were analyzed by gas chromatography to obtain the yields based on the starting materials.

The electrochemically active surface area of working electrodes was determined by measuring the charge associated with the stripping of an underpotential deposited (UPD) Pb monolayer. The electrodes were immersed in an aqueous HClO$_4$ (0.1 M) solution containing

Pb(ClO$_4$)$_2$ (1 mM) purged with N$_2$ in an electrochemical cell with a Pt counter electrode and an Ag/AgCl (1 M KCl) reference electrode. Cyclic voltammagrams from 0.0~−0.45 V with a scan rate of 50 mV·s^{-1} were acquired until traces converged. The charge corresponding to full coverage of lead on silver is 400 µC·cm^{-2}.[1]

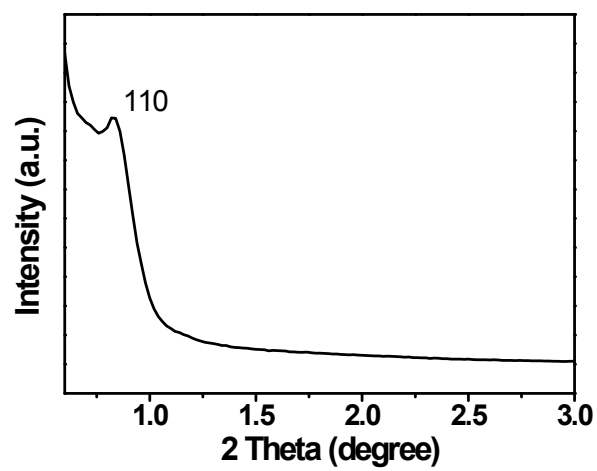**3 Small-angle XRD pattern of the Ag-free mesoporous carbon sample (OMC)**

Fig. S1 Small-angle XRD pattern of the Ag-free mesoporous carbon sample.

4 FT-IR of Ag/OMC
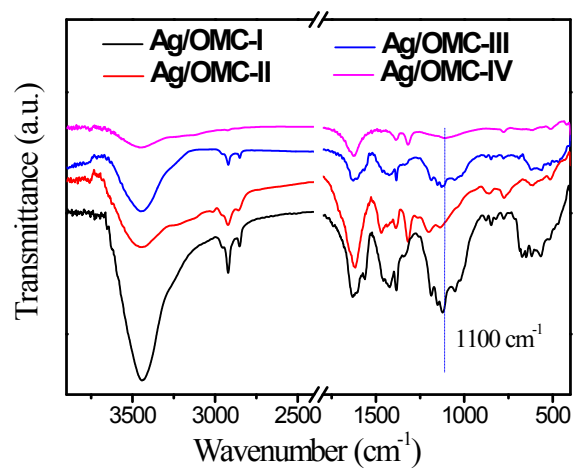
Fig. S2 FT-IR spectra of the ordered mesoporous carbon/nanoparticle Ag composites with different Ag contents.

5 TGA of Ag/OMC
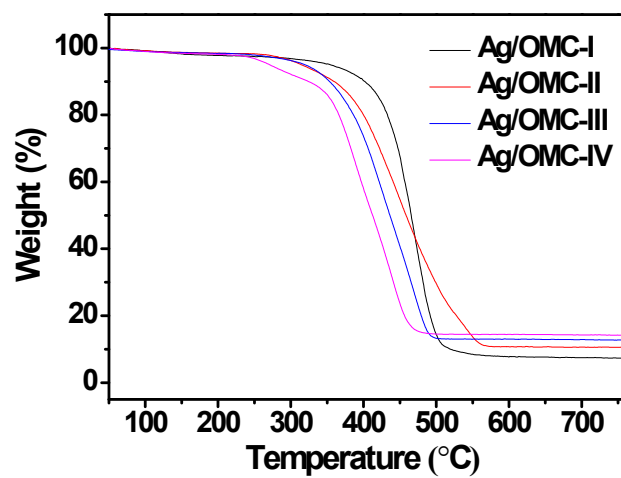
Fig. S3 TGA curves recorded in air of the ordered mesoporous carbon/nanoparticle Ag
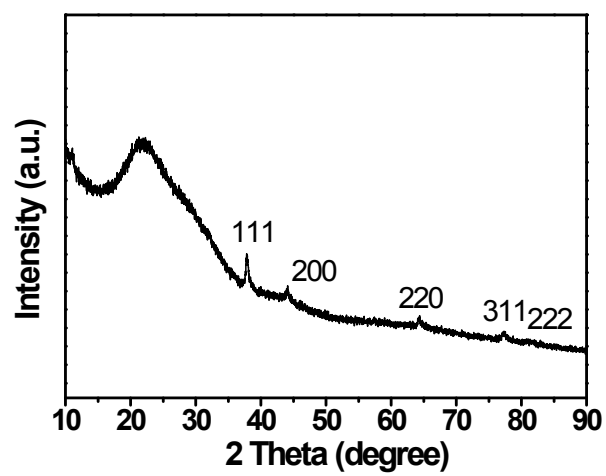
composites with different Ag contents.

6 XRD of as-made-Ag/OMC

Fig. S4 Wide-angle XRD pattern of the as-made-Ag/OMC-III sample.

7 SEM of Ag/OMC and OMC
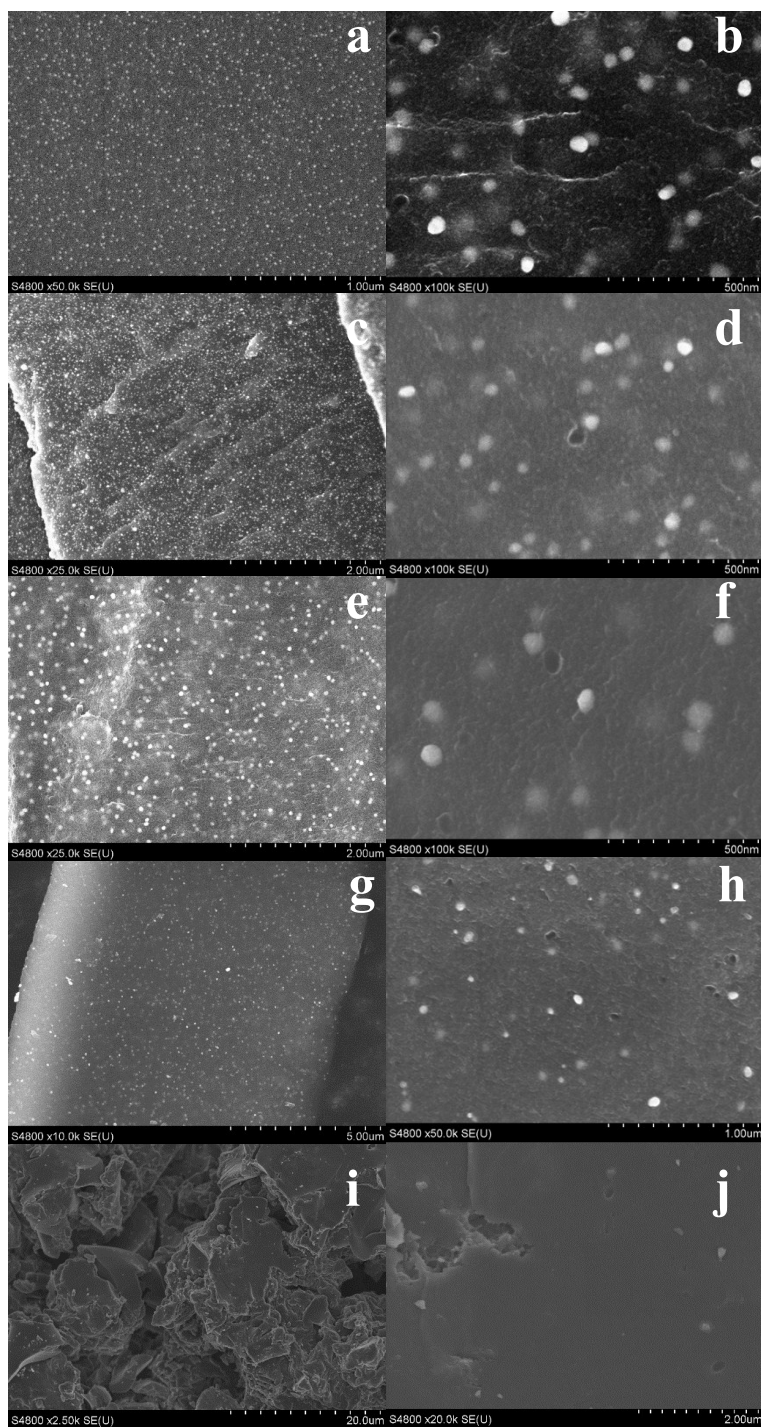
Fig. S5 SEM images of the Ag/OMC and OMC: (a, b) Ag/OMC-I, (c, d) Ag/OMC-II,

(e, f) Ag/OMC-III, (g, h) Ag/OMC-IV, (i, j) OMC.
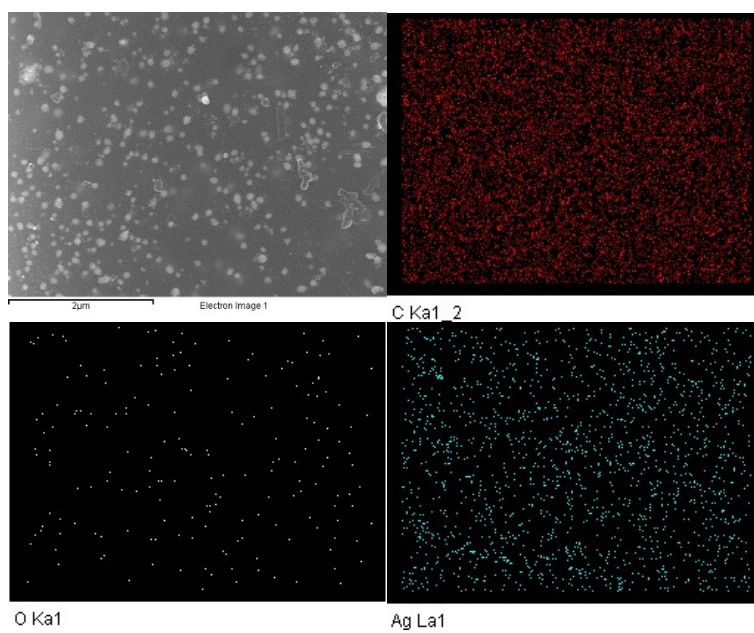
8 EDX-Mapping of Ag/OMC

Fig. S6 EDX-Mapping images of Ag/OMC-III.
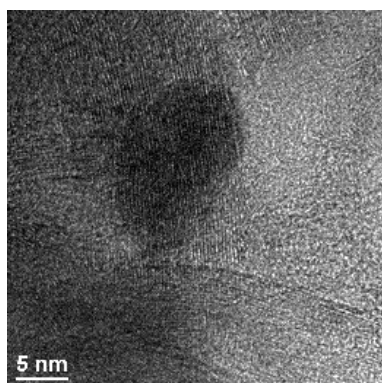
9 Magnified TEM image

Fig. S7 Magnified TEM image of Ag/OMC-III.
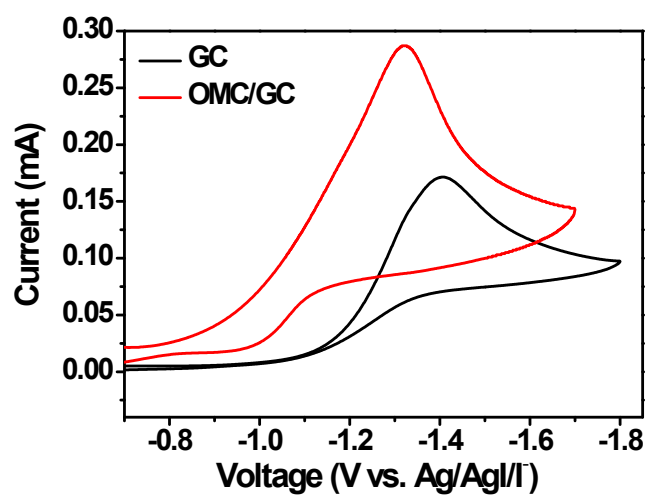
10 Cyclic voltammograms of OMC

Fig. S8 Cyclic voltammograms recorded at a scan rate of $0.1 V \cdot s^{-1}$ using different electrode in MeCN–0.1 M TEABF$_4$–5 mM PhCH$_2$Br.

11 Pb-UPD
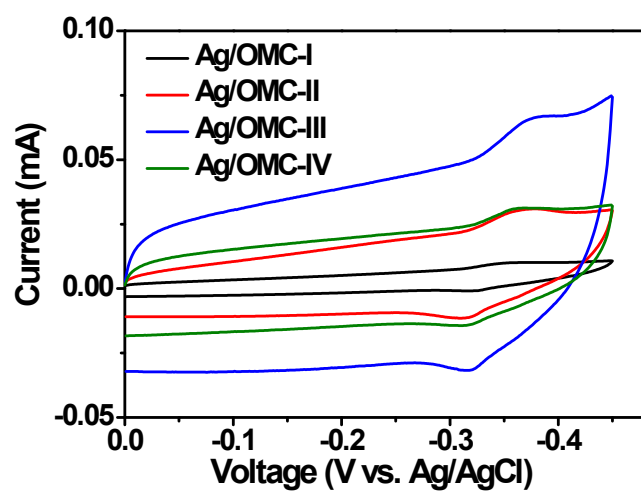

Fig. S9 Cyclic voltammograms recorded at a scan rate of 50 mV·s^{-1} using different

electrode in H_2O–0.1 M $HClO_4$–1 mM $Pb(ClO_4)_2$.

12 Characterization of Ag/OMC- III after using 8 times
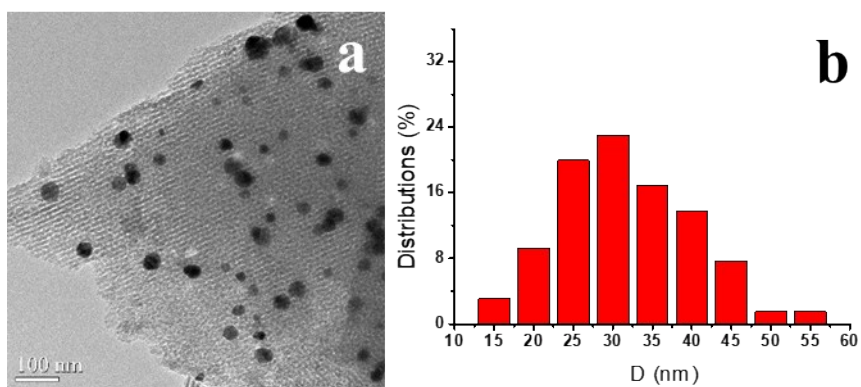

Fig. S10 TEM images (a) and grain diameter distribution maps (b) of Ag/OMC- III after

using 8 times.

References

1.   E. Kirowa-Eisner, D. Tzur and E. Gileadi, *Journal of Electroanalytical Chemistry*, 2008, **621**, 146-158.