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In situ auto-reduction of silver nanoparticles in mesoporous carbon with multifunctionalized surfaces

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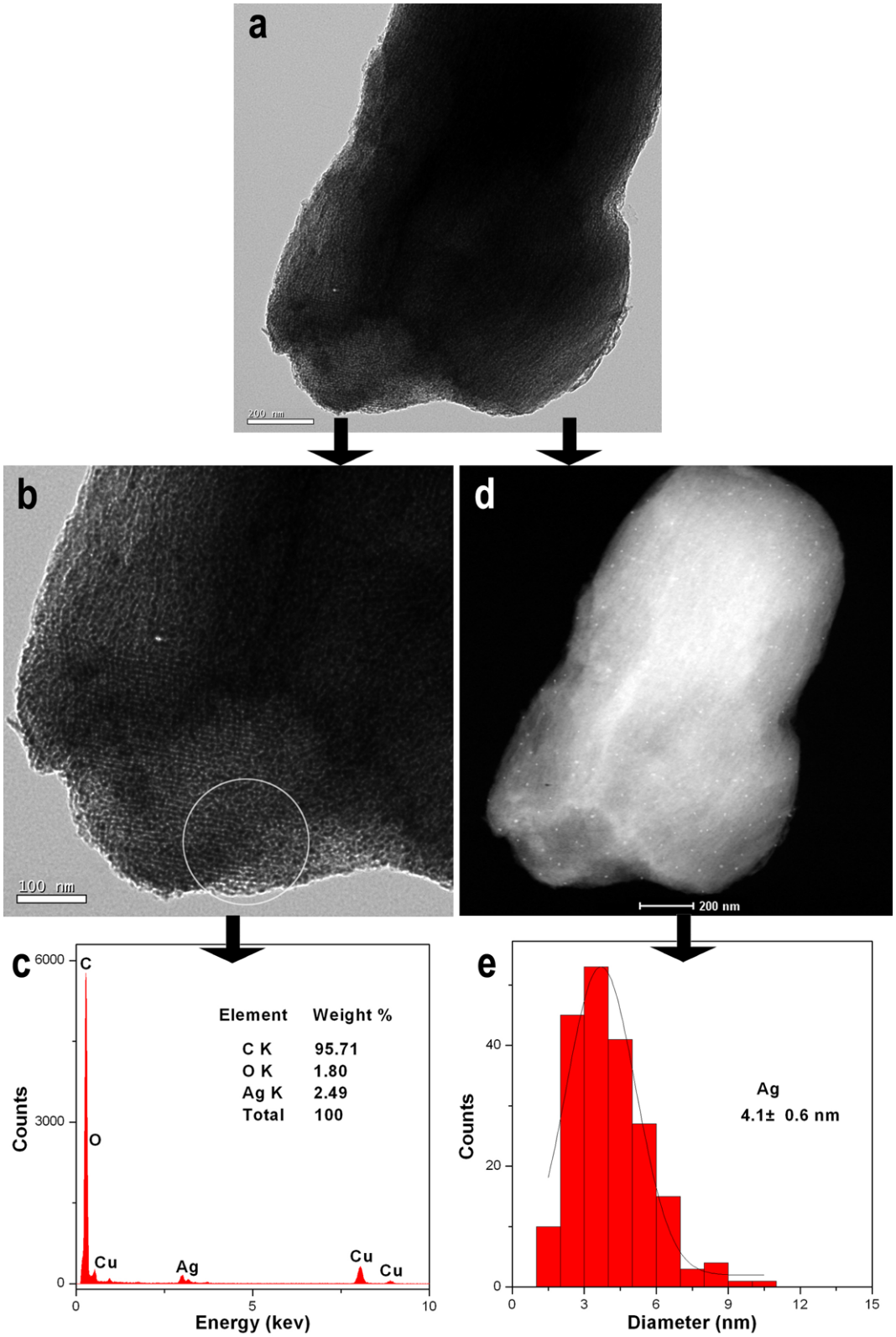

Fig. S1 TEM images of sample Ag-1/CMK-3 viewed at low magnification (a), high magnification (b) and corresponding EDX spectrum (c). STEM images of sample Ag-1/CMK-3 (d) and corresponding size distribution of Ag particles (e). The Ag particles are detected as bright spots in STEM images.

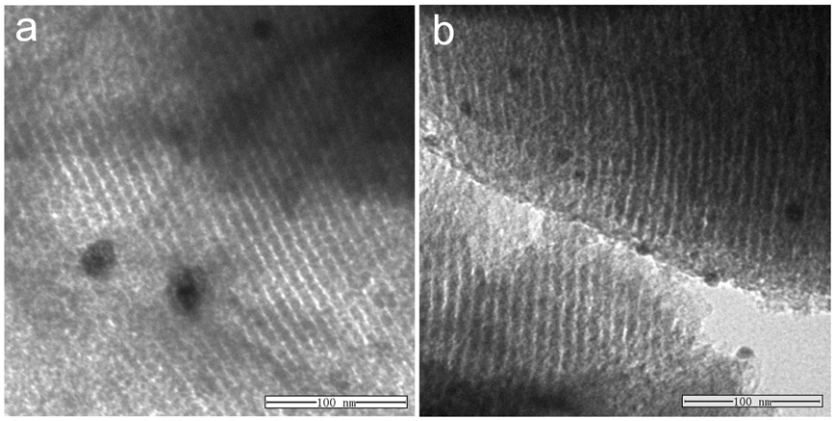

Fig. S2 TEM images of the samples in the control experiment: Ag-2/CMK-3 (a), Ag-3/CMK-3 (b).

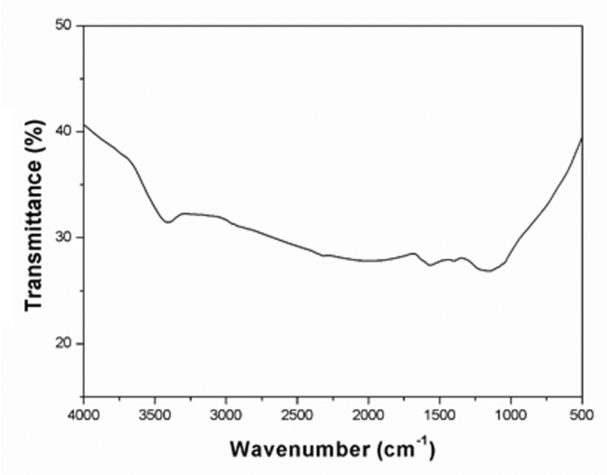

Fig. S3 FTIR spectrum of pure CMK-3.

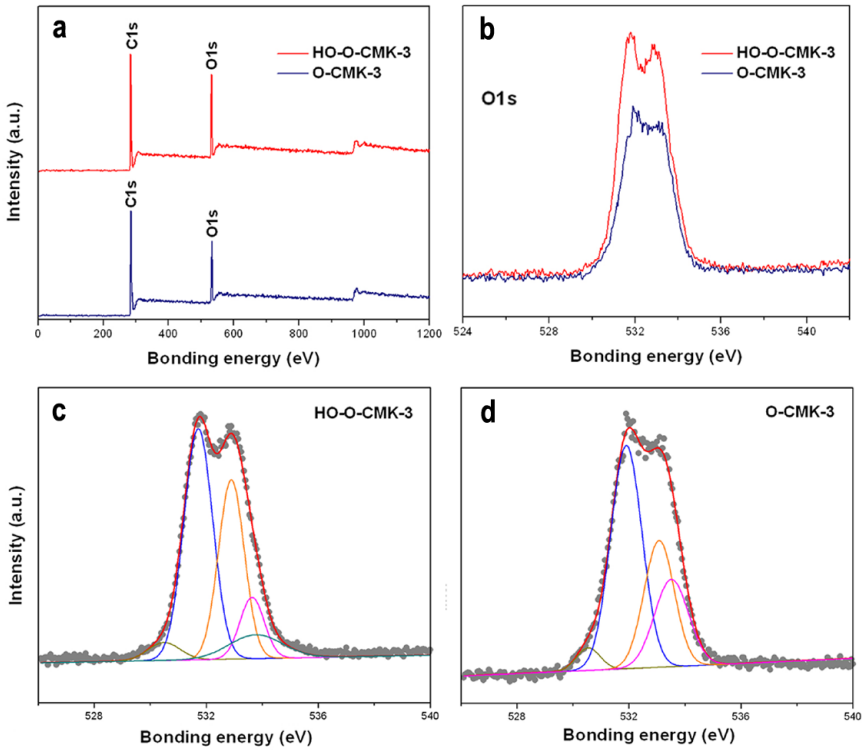

Fig. S4 XPS fully scanned spectra of HO-O-CMK-3 and O-CMK-3 (a), XPS spectra of O1s for HO-O-CMK-3 and O-CMK-3 (b), XPS spectrum of O1s for HO-O-CMK-3 (c), XPS spectrum of O1s for O-CMK-3 (d).

Table S1 XPS analysis results of HO-O-CMK-3 and O-CMK-3

HO-O-CMK-3				O-CMK-3			
Peak number	Binding energy	Area %	Assignment	Peak number	Binding energy	Area %	Assignment
O1	530.5	3.87	Surface hydroxyl groups O-H	O1	530.5	3.85	Surface hydroxyl groups O-H
O2	531.9	45.52	C=O, O-C=O	O2	531.9	48.93	C=O, O-C=O
O3	532.9	32.05	C-O-H, C-O-C	O3	533	26.72	C-O-C
O4	533.5	10.35	The second oxygen present in COOH O-C=O	O4	533.5	20.5	The second oxygen present in COOH O-C=O
O5	533.7	8.21	Ester C-O-C=O				

Estimation of the extent of glycol functionalization

The component peaks and attributions of XPS spectra are shown in Fig. S4 and Table S1. In our experiment, glycol treatment can introduce the groups $COOCH_2CH_2OH$. As seen in Fig. S4, there is noticeable change in the main peak of the O1s spectrum for HO-O-CMK-3 and O-CMK-3. Before glycol treatment, four peaks were required to fit the spectra of the O1s spectrum for O-CMK-3 (Table S1). However, after the glycol treatment, a new O1s peak (peak O5) appeared at 533.7 eV for HO-O-CMK-3, which can be assigned to the C-O-C=O present in $COOCH_2CH_2OH$ species. In addition, the increase in peak O4, which increases from 26.72% to 32.05%, is also attributed to C-O-H introduced by $COOCH_2CH_2OH$ species.

In the O1s spectrum of HO-O-CMK-3, peak O4 is assigned to the residual -COOH groups and peak O5 is assigned the C-O-C=O present in $COOCH_2CH_2OH$ species. The extent of glycol functionalization can be estimated by the proportion of the C-O-C=O present in $COOCH_2CH_2OH$ and the residual -COOH in HO-O-CMK-3, which is equal to the area ratio of peak O5 and peak O4 in HO-O-CMK-3.

∴ The extent of glycol functionalization = 8.21/(8.21+10.35) = 44.2%

∴We can estimate that ca. 44 percent of the -COOH groups in O-CMK-3 can covalent link with glycol by the esterification reaction in our experiment.

The -COOH density estimated by titration was found to be ca. 3.1 mmol g^{-1} for O-CMK-3.

∴ The $COOCH_2CH_2OH$ density is ca. 1.36 mmol g^{-1} in HO-O-CMK-3.

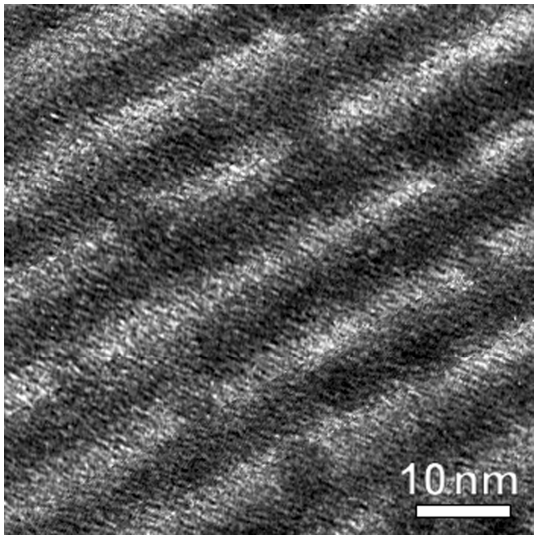

Fig. S5 TEM image of Ag/FDU-15.

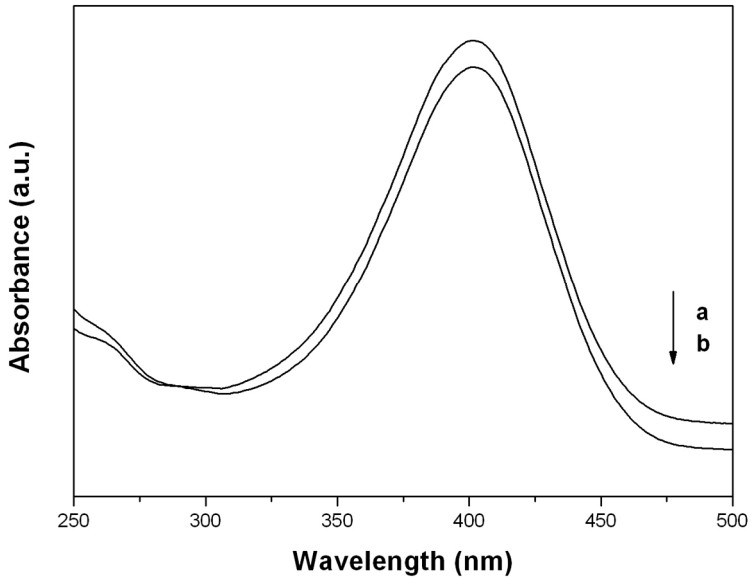

Fig. S6 UV-vis spectra of (a) a mixture solution of 4-NP and $NaBH_4$, (b) a mixture solution of 4-NP and $NaBH_4$ recorded after adding aqueous dispersed HO-O-CMK-3 (recorded after 1 h).

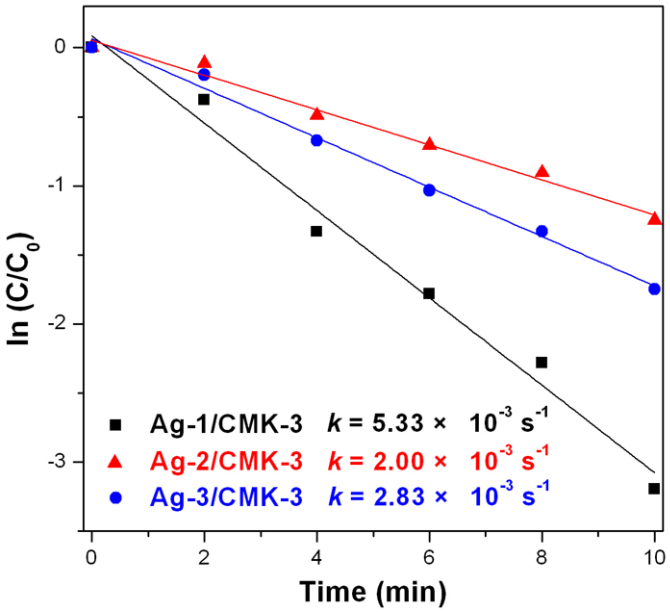

Fig. S7 The relationship between $\ln(C/C_0)$ and reaction time.

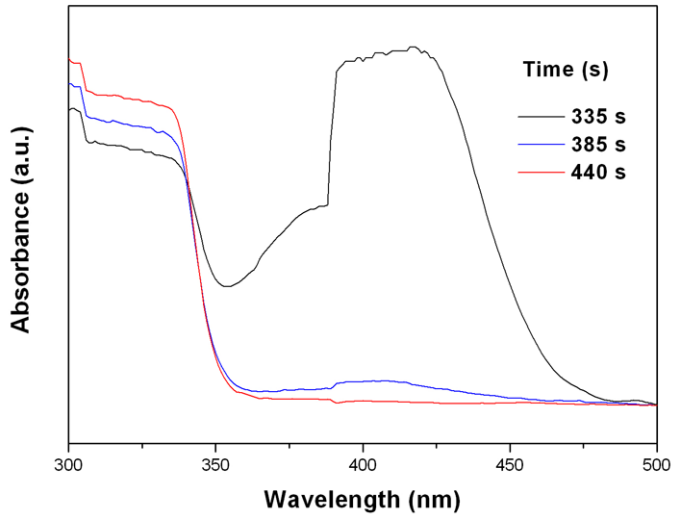

Fig. S8 UV-vis spectra of the reaction mixture consisting of 4NP (1 mL, 75 mM), $NaBH_4$ (1.5 mL, 5 M) and aqueous dispersed Ag-1/CMK-3 composite (2g, 0.05 wt %), recorded as a function of time. The optical density of spectrum recorded at 335 s beyond the measurable values, while the optical density of spectra recording at 385 s and 440 s has reached measurable values. The absorption peak at 400 nm disappeared after 440 s.