

## In situ introduction of dispersed metallic Ag nanoparticles into the channels of mesoporous carbon CMK-3

Ai Bing Chen, Wei Ping Zhang, Yong Liu, Xiu Wen Han, Xin He Bao\*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Received 27 February 2007

### Abstract

An in situ reduction method has been developed to fabricate metallic Ag nanoparticles inside the channels of mesoporous carbon CMK-3. This approach combines function of the CMK-3 surface by oxidation using  $\text{HNO}_3$  with the subsequent absorption of  $\text{Ag}^+$ . The resultant nanocomposite materials were characterized by nitrogen adsorption, X-ray diffraction, Auger electron spectroscopy and transmission electron microscopy. Compared with the conventional impregnation method, our approach shows that Ag nanoparticles of 2–4 nm can be uniformly incorporated into CMK-3.

© 2007 Xin He Bao. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

**Keywords:** Ag nanoparticles; Mesoporous carbon; CMK-3; In situ synthesis

Nanostructured materials have unique size-dependent properties, which are potential for future applications in catalysis, sensors, and optical devices, etc. [1]. To use porous materials as hosts to limit the growth of nanostructured materials in their pores is a relatively promising scheme. Recently, a new class of mesoporous carbons such as CMK-3 has been reported by Ryoo et al. using ordered mesoporous silica as a hard template [2]. Up to now, a little literature has reported that metal or metal oxide nanoparticles can be synthesized in the ordered mesoporous carbons [3,4]. This may be due to the inert surface of as-made CMK-3 just like the commercial carbon materials. So, activation of its surface is an essential prerequisite for linking the metal nanoparticles into it. In this paper, we report an in situ reduction method to incorporate highly dispersed Ag nanoparticles into the mesochannels of carbon CMK-3. The typical synthesis procedure is as follows: CMK-3 was prepared using calcined AISBA-15 as the hard template [2]. 0.5 g CMK-3 was treated using 50 mL of 6.0 mol/L  $\text{HNO}_3$  solution for 3 h at 80 °C to obtain the surface modified CMK-3. This sample is denoted as m-CMK-3. Then 0.2 gm-CMK-3 was mixed with a required amount of  $\text{AgNO}_3$  solution, stirred for 24 h, filtrated, washed and dried at room temperature to obtain  $x\text{Ag}/\text{CMK-3}$ , where  $x$  stands for the weight percentage of metallic silver obtained by EDX. The metallic silver can be easily obtained from the reduction of silver ions by carbon at ambient temperature [5].

Fig. 1 displays the C1s XPS spectra of CMK-3 and modified CMK-3, respectively. The main peak at 284.6 eV is unambiguously assigned to the C1s of pure graphitic sites in the amorphous CMK-3 carbon matrix. The shoulder of the main peak composed of three peaks, which are assigned to the hydroxyl carbon (285.8 eV), carbonyl carbon (286.8 eV), and carboxyl carbon (289.1 eV), respectively [6]. However, the carbonyl and carboxyl carbon peaks have

\* Corresponding author.

E-mail address: [xhbao@dicp.ac.cn](mailto:xhbao@dicp.ac.cn) (X.H. Bao).

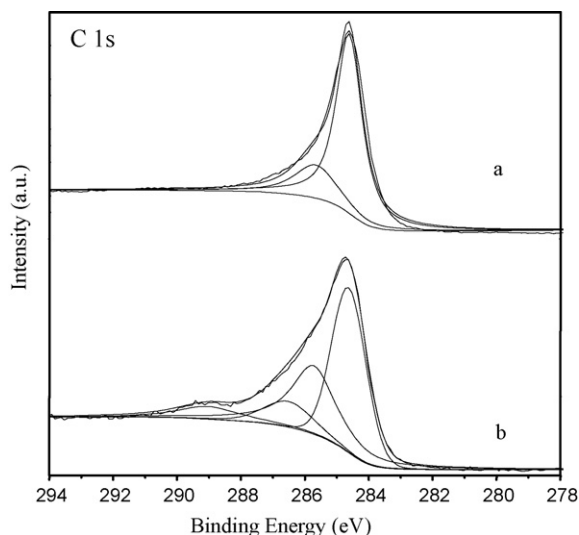


Fig. 1. XPS spectra of mesoporous (a) CMK-3 and (b) m-CMK-3 .

not been observed in the C1s XPS spectrum of pristine CMK-3 (Fig. 1a). The XPS analysis indicates that the surface of m-CMK-3 is bound to the more active groups after oxidation by nitric acid.

The N<sub>2</sub> physisorption isotherms of CMK-3 with different Ag loadings are stepped like type IV (not shown), which is characteristic of mesoporous materials. The BJH pore size of CMK-3 decreases from 3.8 to 3.5 nm after oxidation by HNO<sub>3</sub>. The pore size of m-CMK-3 decreases from 3.5 to 3.2 nm upon introduction of Ag. The BET surface area of m-CMK-3 also decreases from 736 to 673 m<sup>2</sup>/g after addition of Ag which demonstrates that most of the Ag should be remained in CMK-3 hosts. On the hand, the surface area due to micropores increased to 124 m<sup>2</sup>/g (3.2Ag/CMK-3) from 118 m<sup>2</sup>/g (m-CMK-3) due to formation of micropores among the nanoparticles.

Fig. 2 shows the low-angle X-ray diffraction patterns of CMK-3 with different Ag loadings. The parent CMK-3 exhibits three intense diffraction peaks that can be indexed to (1 0 0), (1 1 0) and (2 0 0) diffraction lines using their *d*-spacing values, which is characteristic of the hexagonal structure. After oxidation, the overall pore structure is retained as indicated by the appearance of low-angle diffraction peaks. However, the peak intensity of m-CMK-3 decreases greatly compared to the parent CMK-3. This is probably due to the partial collapse of CMK-3 walls induced by the oxidation process. The parent CMK-3 exhibits a *d*<sub>100</sub> spacing of 7.0 nm and the calculated hexagonal unit cell value

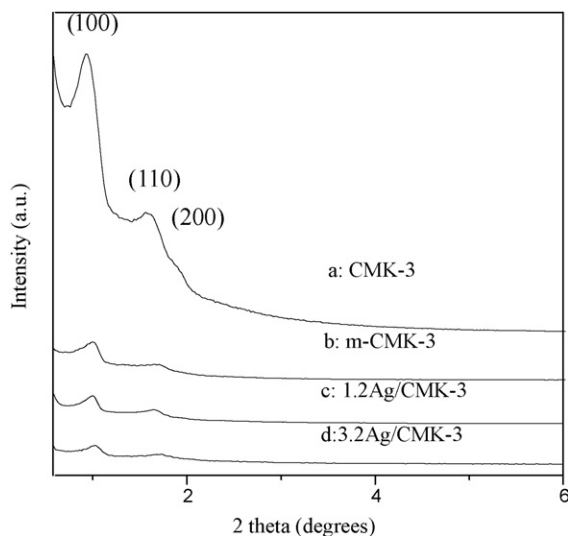


Fig. 2. Small-angle XRD patterns of Ag/CMK-3 samples.

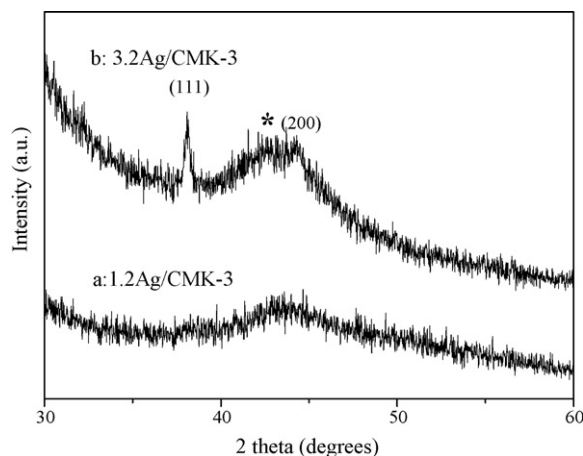


Fig. 3. Wide-angle XRD patterns of Ag/CMK-3.

( $a_0 = 2d_{100}/3^{1/2}$ ) is *ca.* 8.1 nm. However, the  $d_{100}$  spacing of 6.6 nm and calculated hexagonal unit cell value is *ca.* 7.6 nm for m-CMK-3, combined with the data of pore size; the wall thickness of m-CMK-3 was decreased slightly to 4.1 nm with respect to CMK-3 (4.3 nm). That means oxidation itself cannot result in a marked decrease in the wall of CMK-3. If the exorbitant concentration, e.g., 10 mol/L of  $\text{HNO}_3$  is used, the walls of CMK-3 will be collapsed completely. So, it is crucial to choose the moderate concentration of the oxidants. After introducing Ag, the XRD patterns of Ag/CMK-3 samples show further decrease in peak intensity with increasing Ag loadings. This is probably due to the pore filling of the host CMK-3 because pore filling can reduce the scattering contrast between the pores and the walls of the mesoporous material. Fig. 3 shows the wide-angle XRD patterns of the Ag/CMK-3 samples in the  $2\theta$  range of  $30\text{--}60^\circ$ . Besides the broad diffraction peaks from the amorphous CMK-3 carbon, the other two weak peaks can be attributed to (1 1 1) and (2 0 0) lattice planes of the cubic structure of Ag. The average Ag particle size in 3.2Ag/CMK-3 is estimated to be *ca.* 3.2 nm from the XRD peak width of Ag (1 1 1) reflection by using the Scherrer equation [7].

The presence of metallic Ag nanoparticles in the channels of CMK-3 has also been detected for the Ag/CMK-3 samples by XPS (not shown). However, the photoelectron chemical shift of Ag is small, and chemical state identification based on photoelectron energy alone becomes difficult [8]. More detailed chemical information can be extracted from the corresponding Ag MNN Auger electron spectra (Fig. 4). The Auger spectra show two distinctive kinetic energy peaks at 357.2 and 351.1 eV, respectively, which are characteristic of metallic Ag [8]. No obvious peaks

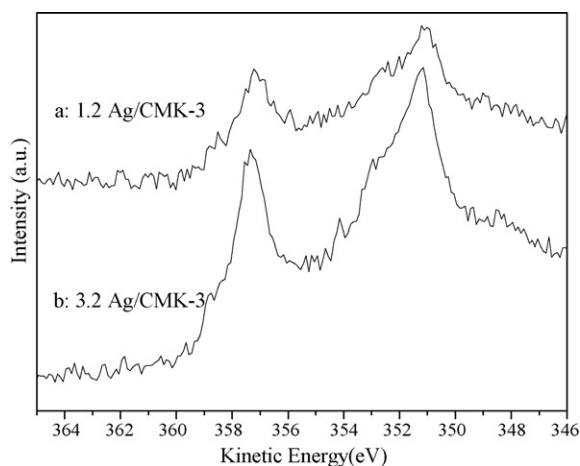


Fig. 4. MNN Auger spectra of Ag/CMK-3 samples.

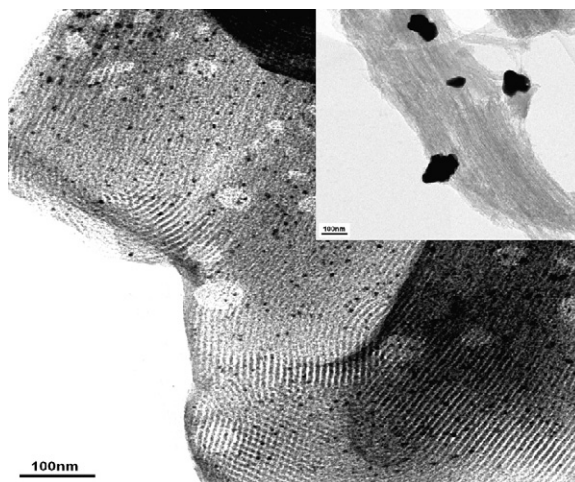


Fig. 5. TEM images of 3.2Ag/CMK-3 samples (inset: impregnated Ag/CMK-3).

of  $\text{Ag}^+$  are observed at 355.1 and 349.1 eV. This further confirmed that most of the  $\text{Ag}^+$  ions have been in situ reduced into metallic Ag in the CMK-3 host.

Transmission electron microscope investigation provides direct observation of the morphology and distribution of Ag nanoparticles in the CMK-3 host. As shown in Fig. 5, highly dispersed Ag nanoparticles have been incorporated in CMK-3 at the Ag loading of 3.2 wt.%. The average Ag particle size is about 2–4 nm. But further increasing Ag loadings, more large aggregates can be found outside the mesochannels. Our results shows that the functional groups on the surface of CMK-3 are very crucial for the formation of dispersed Ag nanoparticles. Only the Ag ions adsorbed inside the CMK-3 channels by the oxygen-containing groups can be reduced into the well-dispersed Ag nanoparticles. This may be due to the confinement effect of the CMK-3 mesochannels, which can restrict the further growth of Ag nanoparticles. Those exist on the external surface will easily grow up to exceed the pore size of the CMK-3 host. As a comparison to the conventional impregnation method, our approach can introduce uniformly Ag nanoparticles into the mesochannels of CMK-3.

In conclusion, Ag nanoparticles have been synthesized within the channels of modified mesoporous carbon CMK-3 by a new in situ reduction process. The CMK-3 was oxidized by  $\text{HNO}_3$  to obtain a functional sample. Ag ions adsorbed on the oxygen-containing groups can be reduced into metallic Ag nanoparticles by the CMK-3 host. The Ag nanoparticles are very uniform and well dispersed in CMK-3 with the particle size of 2–4 nm, which retains the mesostructure of CMK-3. But larger aggregates may be formed outside the mesochannels of CMK-3 at higher Ag loadings.

## Acknowledgments

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (no. 20573106) and the Ministry of Science and Technology of China through the National Key Project of Fundamental Research.

## References

- [1] J. Hu, T.W. Odom, C.M. Lieber, *Acc. Chem. Res.* 32 (1999) 435.
- [2] W. Kim, I.S. Park, R. Ryoo, *Angew. Chem.* 115 (2003) 4511.
- [3] S. Zhu, H. Zhao, M. Hibino, et al. *Adv. Funct. Mater.* 15 (2005) 381.
- [4] J.M. Cao, Y.L. Cao, X. Chang, et al. *Stud. Surf. Sci. Catal.* 156 (2005) 423.
- [5] S. Chen, H. Zeng, *Carbon*. 41 (2003) 1265.
- [6] H. Hiura, T.W. Ebbesen, K. Tanigaki, *Adv. Mater.* 7 (1995) 275.
- [7] R. Jenkins, R.L. Snyder, *Chem. Analys.* 138 (1996) 90.
- [8] X. Wen, S. Wang, Y. Xie, et al. *J. Phys. Chem. B.* 109 (2005) 10100.