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One-pot synthesis of ordered mesoporous silver nanoparticle/carbon composites for catalytic reduction of 4-nitrophenol

Yue Chi[a], Jinchun Tu[b], Minggang Wang[a], Xiaotian Li[c,*], Zhankui Zhao[a,*]

[a] College of Material Science and Engineering, Key Laboratory of Advanced Structural Materials, Ministry of Education, Changchun University of Technology, Changchun 130012, China
[b] College of Material and Chemical Engineering, Ministry of Education Key Laboratory of Application Technology of Hainan Superior Resources Chemical Materials, Hainan University, Haikou 570228, China
[c] School of Material Science and Engineering, Key Laboratory of Automobile Materials of Ministry of Education, Jilin University, Changchun 130012, China

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ABSTRACT

Ordered mesoporous silver nanoparticle/carbon composites have been produced by a “one-pot” synthesis method. They have open mesopores (4.2–5.0 nm), large specific surface areas (465–584 $m^2\ g^{-1}$) and high pore volumes (0.29–0.50 $cm^3\ g^{-1}$) and contain stable, confined but accessible Ag nanoparticles. As a result, they show high performance in catalytic reduction of 4-nitrophenol (4-NP). The mesostructure and particle size as a function of Ag content were studied and correlated with the catalytic activity. The ordered mesoporous carbon framework and highly dispersed Ag nanoparticles make the material a novel system for effective contacting with the reactants and catalysis of the reaction.

1. Introduction

Porous carbon materials are of great interest because of their high specific surface area, large pore volume, electrical conductivity, thermal stability, and chemical inertness. These features have been contributing to many areas of modern science and technology [1–4]. Recently, one main development in this field is directed to the porous nanocrystalline/carbon composites, in which “foreign” nanocrystalline materials are assembled into the matrix of mesoporous carbons. Compared with single phase mesoporous carbon materials, the mesoporous nanocrystalline/carbon composites possess greatly extended applications [5–8].

Metal nanoparticles have shown remarkable potential for numerous applications in electronic, chemical, biological, and catalytic fields due to their distinctive properties [9–11], when compared to their bulk counterparts. In the field of catalysis, dispersion and size of active metals play an important role in overall performance. However, metal nanoparticles are active and tend to coalesce during preparation and catalytic process. Therefore, when working with them, metal nanoparticles are often stabilized in inert matrix hosts to prevent aggregation. Besides, catalytic activities of metal are not only dependent on their particle size but also on their porosity, total surface area, structural uniformity and stability. Confining metal nanoparticles inside mesoporous compounds is not only the high dispersion of metal itself but also an increased resistance against aggregation of nanoparticles and, as a consequence, a longer working lifetime without a decrease in catalytic activity [12,13]. As a relatively inexpensive noble metal, silver nanoparticles have been applied in a variety of catalytic reactions, such as selective butadiene epoxidation, ethanol oxidation, and selective NO_x reduction [14–18]. Owing to the excellent features of mesoporous carbon, synthesis of a mesoporous silver nanoparticle/carbon composite could deliver the enhanced performance. Traditionally, silver nanoparticles incorporated into mesoporous compounds is achieved by wet impregnation of porous materials with silver precursors in solution phase and subsequent reduction to metallic silver, which is a multi-step and time-consuming process [19–21]. Therefore, there is still a critical need to develop a more facile and feasible method to prepare mesoporous silver nanoparticle/carbon composites.

In this contribution, we demonstrate a “one-pot” route for the synthesis of mesoporous silver nanoparticle/carbon composites. In this simple route, resol and silver nitrate were used as precursors, and Pluronic F127 as a template. After co-assembly of the precursors with F127 template, ordered mesoporous silver nanoparticle/carbon composites with high specific surface area, large pore volume and tunable silver content could be easily obtained. We also demonstrate the high catalytic efficiency of mesoporous silver nanoparticle/carbon composite toward 4-NP by sodium

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* Corresponding authors. Fax: +86 431 85168444 (X. Li). Fax: +86 431 85716644 (Z. Zhao).

E-mail addresses: xiaotianli@jlu.edu.cn (X. Li), zhaozk@mail.ccut.edu.cn (Z. Zhao).

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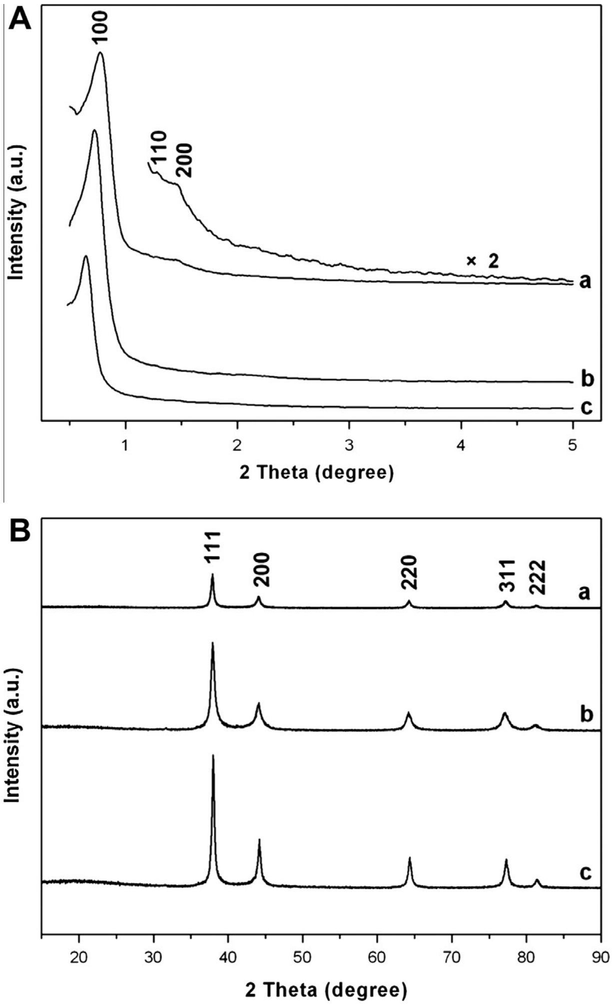

Fig. 1. Small-angle (A) and wide angle (B) XRD patterns of mesoporous Ag/C composites with different Ag contents: Ag/C-0.05 (a), Ag/C-0.1 (b), and Ag/C-0.2 (c).

borohydride. High reusability was demonstrated without significant decrease in the catalytic performance after running 10 times.

2. Experimental section

2.1. Preparation of resol precursors

Soluble resols were prepared from phenol and formaldehyde according to the reported method with some modification [22]. For a typical preparation, 6.1 g of phenol was melted at 40–42 °C in a flask and mixed with 1.3 g of 20 wt% sodium hydroxide (NaOH) aqueous solution under stirring. After 10 min, 1.05 g of 37 wt% formaldehyde solution was added dropwise. Upon further stirring for 1 h at 70 °C, the mixture was cooled to room temperature. The pH was adjusted with 0.6 M HNO_3 solution until it reached a value of ~7.0, and water was removed by vacuum evaporation below 50 °C. The final product was dissolved in ethanol (25 wt% ethanolic solution) for further use.

2.2. Preparation of mesoporous silver nanoparticle/carbon composites

Using the as-prepared resol precursor as carbon source, mesoporous silver nanoparticle/carbon composites were prepared by a procedure based on solvent evaporation-induced self-assembly (EISA) method with polymeric surfactant F127 (M_w = 12,600, $PEO_{106}PPO_{70}PEO_{106}$) as a template in an ethanol solution. The compositions were in the range of F127:resol:$AgNO_3$:EtOH (mass ratio) = 1:1:(0.05–0.2):20. In a typical experiment, 1.0 g of F127 was dissolved in 20.0 g of ethanol at 40 °C. Then 4.0 g of 25 wt% ethanolic solution of resol was added and stirred for 5 min. A certain amount (0.1–0.4 g) of 50 wt% $AgNO_3$ aqueous solution together with 0.035–0.14 g of nitric acid were dropped into the above mixture. After further stirring for 2 h, the mixture was cast onto glass dishes, and kept at room temperature for 5–8 h to remove ethanol. After ethanol was evaporated, the dishes were put into an oven of 100 °C for thermopolymerization for 24 h. After cooling, the films were scrapped off and grounded into powders, followed by pyrolyzing in a tube furnace at 650 °C for 3 h under N_2 atmosphere to decompose the triblock copolymer template, carbonize the resol precursor and in situ generate silver nanoparticles. The ramping rate of the temperature was 1 and 5 °C min^{-1} before and after 600 °C, respectively. The final composites were denoted as Ag/C-*x*, where Ag/C stands for silver nanoparticles supported carbon (silver nanoparticles/carbon), and *x* for the weight ratio of $AgNO_3$ to resol.

2.3. Catalyzed reduction of 4-NP

To study the catalytic activity, 30 mL of 4-NP aqueous solution (0.12 mM) was mixed with 29 mL of fresh $NaBH_4$ solution (12 mM). 1 g of aqueous dispersed Ag/C composite (0.2 wt%) was then added. The reaction was carried out at 298 K with continuous stirring. At various time intervals, parts of the mixture were taken and centrifuged for the determination with UV–vis absorption spectra at the wavelength of absorbance maximum in the range of 250–500 nm. To study the reusability of Ag/C composites, the used sample was separated from the solution after monitoring the whole reduction process. The recycled sample was washed with ethanol and water several times for the next cycling. Similar to the above reduction process, the obtained composite was redispersed in 1.0 g of deionized water, then mixed with 30 mL of aqueous 4-NP solution (0.12 mM) and 29 mL of $NaBH_4$ (12 mM) solution. With a stiff limit of 12 min kept for completion of the

Table 1
Textural properties of ordered mesoporous Ag/C composites with different Ag contents and Ag free mesoporous carbon.

Sample	a_0[a]/nm	S_{BET}[b]/$m^2 g^{-1}$	Vt[c]/$cm^3 g^{-1}$	D[d]/nm	Wall thickness[e]/nm	Particle size/nm	Ag[f]/wt%
Ag/C-0	9.8	580	0.38	3.2	6.6	–	0
Ag/C-0.05	13.2	584	0.44	4.2	9.0	13.2	4.4
Ag/C-0.1	14.0	566	0.50	4.9	9.4	15.9	8.6
Ag/C-0.2	15.7	465	0.29	5	10.7	19.1	16.4

[a] The cell parameters calculated from small-angle XRD patterns.
[b] The BET specific surface areas evaluated in P/P_0 from 0.05 to 0.25.
[c] The total pore volumes estimated based on the volume adsorbed at P/P_0 ~0.995.
[d] The pore sizes derived from the adsorption branches of the isotherms by using the BJH method.
[e] The pore wall thicknesses were calculated from the formula of $h = a - D$, wherein *a* and *D* represent the unit cell parameter and pore size, respectively.
[f] The Ag weight percentage obtained by combusting the carbon components.