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Soft-templating synthesis and adsorption properties of mesoporous carbons with embedded silver nanoparticles

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Abstract Mesoporous carbons containing silver nanoparticles have been successfully synthesized under acidic conditions by employing resorcinol and formaldehyde as carbon precursors and triblock copolymer $EO_{101}PO_{56}EO_{101}$ (Lutrol F127) as a soft template. Silver nanoparticles of ~90 nm were added to the synthesis mixture to achieve 10 wt% and 20 wt% of Ag loading in the carbon. Also, tetraethyl orthosilicate (TEOS) was introduced to the system in order to improve adsorption properties of the silver-carbon composites and to reinforce its structure. The resulting carbons with incorporated silver nanoparticles featured high surface areas, large total pore volumes and primary mesopores in the range between ~6–7 nm.

Keywords Soft-template method · Mesoporous carbons · Silver nanoparticles · Adsorption properties

1 Introduction

Nanoporous materials containing metal nanoparticles attract a lot of attention due to unique features arising from nanometer scale of both active metal centers and hosting scaffolds (Sun and Bao 2008). This class of materials holds great promise for applications ranging from adsorption and catalysis to advanced sensors and optical devices (Hu et al. 1999). Among nanoporous materials, mesoporous carbons (mesopore range spans from 2 to 50 nm) are of particular interest because they possess high surface area, uniform and easily accessible pores of desired size and geometry (Choma et al. 2007, 2009; Liang et al. 2008; Jaroniec et al. 2009). Therefore, mesoporous carbons are materials of choice for applications in chromatography and separation of large molecules (Choma et al. 2008b). Since 1999, when the nanocasting synthesis of ordered mesoporous carbons has been reported for the first time (Ryoo et al. 1999), there is a growing interest in this area of research. A few years later this synthesis route was extended to the preparation of mesoporous carbon composites containing metal or metal oxide nanoparticles (Zhu et al. 2005; Cao et al. 2005; Górka and Jaroniec 2008).

Silver due to its antibacterial properties is commonly used additive for a variety of carbon materials prepared for water treatment and purification-type applications. For example, Ryu et al. (1999a, 1999b) added silver to steam-activated carbon nanofibers obtained from soot. The as-prepared composite materials showed good adsorption of iodine and methylene blue from solutions. Moreover, both the carbon nanofibers with and without silver nanoparticles exhibited comparable nitrogen uptake proving that the presence of silver did not affect adsorption properties of the final material. Similar observations obtained in another set of experiments by Ryu et al. (1999a) confirmed the aforementioned finding for pure carbon nanofibers and active carbon nanofibers loaded with 1000–10000 ppm of silver. Park and Jang (2002) studied the antibacterial properties of a carbon-silver composite prepared by impregnation of carbon fibers with $AgNO_3$ solution. It was found that the fiber impregnation with just 1 wt% of $AgNO_3$ shows strong antibacterial activity towards Staphylococcus aureus and Escherichia coli. It is suspected that the distribution of silver nanoparticles in carbon materials is an important factor affecting the

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overall properties of the final composites. In the case of the aforementioned composites, the TEM and XRD analysis revealed that silver nanoparticles are non-uniformly dispersed in the carbon matrix (Ryu et al. 2003).

Another interesting synthesis route towards preparation of mesoporous carbons with silver nanoparticles was reported by Jaroniec et al. (2008) and Choma et al. (2008a), utilizing colloidal silica as the hard template. This synthesis procedure involved the pressing silica and silver nanoparticles together to form a monolith, which then was impregnated with phenolic resin used as a carbon precursor. The as-prepared composite material was carbonized and treated with hydrofluoric acid in order to dissolve silica template. The final mesoporous carbons with silver nanoparticles exhibited large and uniform mesopores resembling the size of the silica nanoparticles used (27 nm), high surface area (~830 m^2/g) and large pore volume (~2.32 cm^3/g).

Except carbons, silver nanoparticles have been often added to mesoporous silicas. One of the examples includes mesoporous silica aerogels with 1, 5, 10 and 25 wt% of silver used for selective oxidation of benzene (Balkis Ameen et al. 2007). It was shown that silica aerogels containing 1 wt% of silver were most effective catalysts for benzene oxidation due to high percentage of conversion and good selectivity. Armelao et al. (2007) prepared mesoporous silica from TEOS and Brij 76, where Ag^+ was grafted on the pore walls during post-synthesis impregnation with aqueous solution of silver acetate. Based on the number of characterization techniques (X-ray photoelectron spectroscopy (XPS), X-ray excited Auger electron spectroscopy (XE-AES), X-ray diffraction (XRD) and transmission electron microscopy (TEM)) it was found that the monodispersed spherical silver nanoparticles with crystallite size between 3 nm and 20 nm were formed.

Here we report the fabrication of silver-carbon nanocomposites obtained by soft-templating. A schematic illustration of this synthesis strategy is presented in Fig. 1. Silver nanoparticles were directly introduced to the synthesis mixture. The main goal of this work was to obtain mesoporous carbons with silver nanoparticles embedded in the carbon matrix. Moreover, the synthesis was performed in the presence of tetraethyl orthosilicate (TEOS) to introduce silica species, which after their dissolution with HF generated an additional microporosity, resulting in an enlargement of the surface area. All studied materials were characterized by nitrogen adsorption at −196 °C, X-ray diffraction and thermogravimetric analysis.

2 Experimental

2.1 Chemicals

Resorcinol, Ag nanopowder (90 nm) and TEOS were purchased from Sigma-Aldrich, Germany. Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer, Lutrol F127 ($EO_{101}PO_{56}EO_{101}$, MW = 12600) was acquired from BASF, Germany, while ethanol (96%), HCl (35–38%) and formaldehyde from Chempur, Poland.

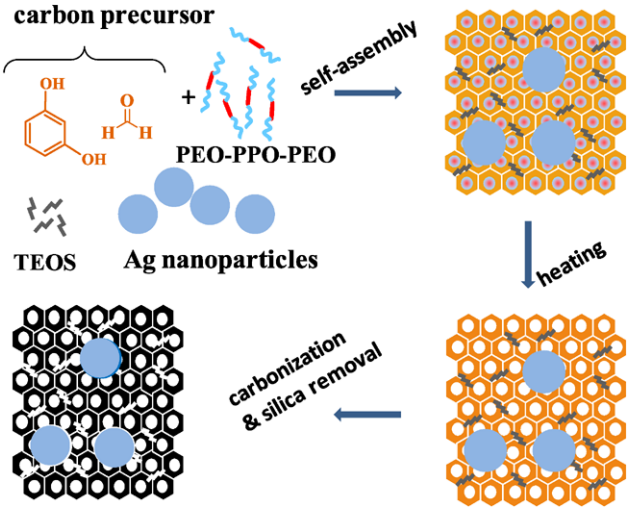

Fig. 1 Illustration of the soft-templating synthesis of mesoporous carbons with embedded silver nanoparticles

2.2 Synthesis procedure

Mesoporous carbons were prepared according to a slightly modified recipe of Wang et al. (2008). In a typical synthesis, 2.5 g of resorcinol and 2.5 g of Lutrol F127 triblock copolymer were dissolved in 11.9 mL of ethanol and 6.6 mL of water. After complete dissolution the reaction mixture was supplied with 0.1 g or 0.2 g of silver nanoparticles and stirred vigorously for 30 min. Then 2.2 mL of 37% HCl was added to the solution as a catalyst and stirred for additional 30 min. Next, the synthesis mixture was supplied with 2.5 mL of 37% formaldehyde and 3.75 mL of TEOS, stirred until turned cloudy and allowed to separate into two layers. The polymer-rich bottom layer was spread onto Petri dish and transferred to an oven at 100 °C for 24 h. Thermal treatment and carbonization of the resulting film were performed in the tube furnace under nitrogen flow using a heating rate of 1 °C/min up to 400 °C and with 5 °C/min up to 850 °C, and finally keeping the sample at 850 °C for 2 h. The samples were labeled according to the formula ST-A-Agx%-TEOS-y, where x stands for a weight percentage of silver nanoparticles (10 or 20%) and y refers to a molar ratio of TEOS used (0.35 or 0.70).

2.3 Measurements

Nitrogen adsorption isotherms were measured at −196 °C on ASAP 2020 volumetric analyzer manufactured by Micromeritics, Inc. (Norcross, GA, USA). All samples were

outgassed at 200 °C for 2 h prior to adsorption measurements.

Wide angle X-ray diffraction analysis was performed on PAN-alytical X'Pert PRO MPD X-ray diffraction system using Cu Kα radiation (40 kV, 40 mA). All patterns were recorded using 0.02° step size and 4 s per step in the range of $20° \leq 2\theta \leq 80°$.

High resolution thermogravimetric analysis was made using a TA Instrument TGA 2950 thermogravimetric analyzer from 30 to 800 °C under air flow with a heating rate of 10 °C/min.

2.4 Calculations

The BET (Brunauer-Emmett-Teller) specific surface area S_{BET} was calculated from nitrogen adsorption isotherms in the range of relative pressures from 0.05 to 0.2 using the cross-sectional area of 0.162 nm^2 per nitrogen molecule (Brunauer et al. 1938). The single-point pore volume (Gregg and Sing 1982) was estimated from the volume adsorbed at a relative pressure of ~0.99.

The pore size distributions (PSDs) were calculated from the adsorption branch of nitrogen adsorption-desorption isotherms using the Barrett-Joyner-Halenda (BJH) method (Barrett et al. 1951) improved by Kruk-Jaroniec-Sayari (KJS) (Kruk et al. 1997b; Jaroniec and Solovyov 2006; Choma et al. 2002; Kruk et al. 1996). The BJH method is based on the Kelvin equation, which correlates the capillary condensation pressure with the pore diameter. The pore width at the maximum of the KJS pore size distribution was used for characterization of the samples studied. The volume of micropores and small mesopores (up to 3 nm) was obtained by integration of the PSD curve (Kruk et al. 1998).

3 Results and discussion

As can be seen from the schematic illustration (Fig. 1), a typical soft-templated synthesis of phenolic resin-based carbons is well suited for the addition of nanoparticles such as silver and TEOS to the reaction mixture. Carbonization of the resulting composite and silica dissolution led to the mesoporous carbon material, the structural parameters of which were tuned by varying the amounts of TEOS and silver nanoparticles added during the synthesis.

Nitrogen adsorption isotherms measured at −196 °C are presented in Figs. 2–4. According to IUPAC classification of adsorption isotherms (Sing et al. 1985) all experimental isotherms for the materials studied are type IV, which is characteristic for mesoporous solids. The H1 hysteresis loops confirm the presence of accessible mesopores. Structural parameters calculated from adsorption isotherms are listed in Table 1.

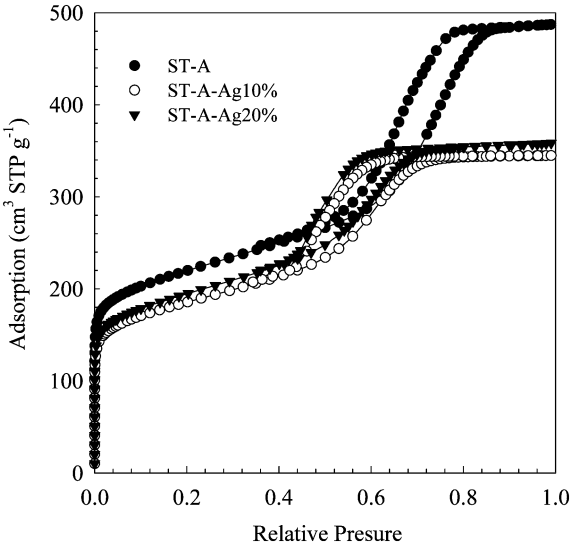

Fig. 2 Nitrogen adsorption isotherms for mesoporous carbons without silver nanoparticles (ST-A) and with silver nanoparticles (ST-A-Ag10% and ST-A-Ag20%)

All carbons studied exhibit relatively small microporosity, which is typical for soft-templated phenolic resin-based carbons. The specific surface area was found to be in the range from 769 m^2/g for pure soft-templated carbon (ST-A) to 517 m^2/g for ST-A-Ag10%-TEOS-0.35 sample. As can be seen from Fig. 2, the carbons containing silver nanoparticles possess lower surface area and pore volume than pure carbon, which is due to the addition of non-porous high-density silver nanoparticles. The situation is more complex for the carbon samples with silver nanoparticles and TEOS. For a fixed amount of Ag in the carbon samples, the lower amount of TEOS caused a small decrease in the surface area and pore volume due to possible accumulation of TEOS on Ag nanoparticles, but higher TEOS loadings overcome this effect and resulted in an enlargement of the aforementioned quantities due to the additional porosity created by the dissolution of excessive silica incorporated into the carbon matrix.

As mentioned before, the small microporosity of soft-templated phenolic resin-based carbons justify the addition of a small organosilane such as TEOS in order to increase the amount of micropores and to enlarge the BET surface area. It was shown that TEOS can easily accommodate in organic-organic mesostructure leading to mesoporous carbons with uniformly distributed silica species in the framework, which after their dissolution create micropores that cause an enlargement of the surface area (Górka and Jaroniec 2010). Shown in Figs. 3 and 4 are carbons prepared with 10 wt% and 20 wt% of silver, respectively, and two different loadings of TEOS. In both cases it was either 0.35 or 0.70 moles of TEOS added with respect to carbon precursor. As expected, much better results in terms of the specific sur-

Table 1 Structural parameters of the carbons and carbon-based composites studied

Sample	S_{BET} m^2/g	V_t cm^3/g	V_{me} cm^3/g	V_{mi} cm^3/g	w_{mi} nm	w_{me} nm	Mesoporosity %
ST-A	769	0.75	0.56	0.19	2.04	6.29	75
ST-A-Ag10%	644	0.53	0.39	0.14	2.04	6.06	74
ST-A-Ag10%-TEOS-0.35	517	0.50	0.40	0.10	2.31	5.82	80
ST-A-Ag10%-TEOS-0.70	725	0.63	0.45	0.18	2.05	6.70	71
ST-A-Ag20%	676	0.55	0.39	0.16	2.05	5.97	71
ST-A-Ag20%-TEOS-0.35	547	0.52	0.41	0.11	2.06	6.24	79
ST-A-Ag20%-TEOS-0.70	736	0.65	0.47	0.18	2.30	6.39	72

S_{BET}—specific surface area; V_t—single-point total pore volume calculated at $p/p_o = 0.99$; V_{mi}—volume of micropores and small mesopores calculated by integration of the PSD curve up to 3 nm; V_{me}—mesopore volume calculated by subtracting V_{mi} from V_t; w_{mi}—diameter of small pores (up to 3 nm) at the maximum of the PSD curve obtained by the KJS method; w_{me}—mesopore width at the maximum of the PSD curve obtained by the KJS method; Mesoporosity—the percentage of the volume of mesopores to the total pore volume

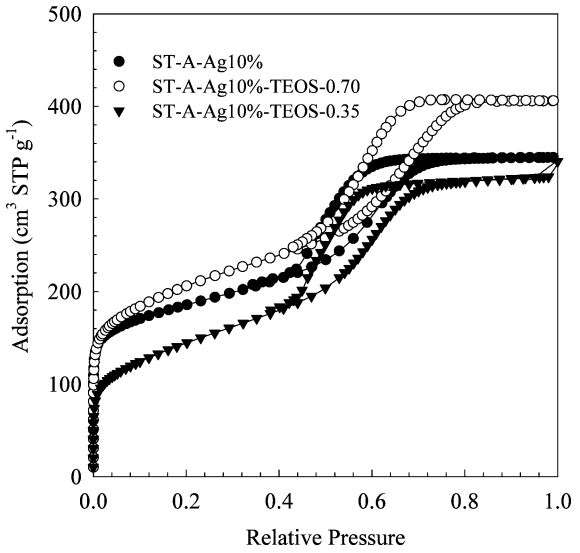

Fig. 3 Nitrogen adsorption isotherms for mesoporous carbons with silver nanoparticles (about 10 wt%) and TEOS (0.70 or 0.35 moles)

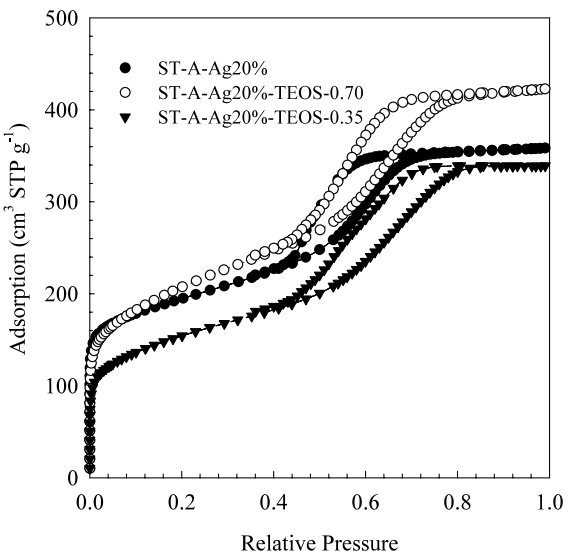

Fig. 4 Nitrogen adsorption isotherms for mesoporous carbons with silver nanoparticles (about 20 wt%) and TEOS (0.70 or 0.35 moles)

face area were obtained for higher loading of TEOS. For example, ST-A-Ag10% has the BET surface area of 644 m^2/g, which after TEOS addition increased up to 725 m^2/g for ST-A-Ag10%-TEOS-0.70. Analogous changes were observed for a series of samples containing 20% of silver nanoparticles. Interestingly, the TEOS addition also improved mesoporosity as well as the micropore volume, what suggests that in this particular system TEOS also altered mesoporosity. The pore size distribution curves were calculated from adsorption branch of isotherms using Kruk-Jaroniec-Sayari (KJS) method (Kruk et al. 1997a, 1997b) for the carbons prepared with silver or silver and TEOS; these curves are shown in Figs. 5 and 6. Each of these plots consists of two peaks, one corresponding to micropores with maxima ~2.04–2.31 nm and the second one assigned to mesopores with diameters in the range of 5.82–6.70 nm. In addition to the change in microporosity, the peaks corresponding to mesopores became taller as more silver and TEOS was introduced to the reaction system. This is also reflected in higher percentage of mesoporosity contributing to the total pore volume, which can reach even up to 80% (Table 1).

Wide angle X-ray diffraction patterns (Fig. 7) were recorded in order to prove the presence of silver nanoparticles in carbon matrix. All peaks were assigned to silver with cubic *Fm3m* symmetry (card number: 087-0597). Also, the fact that the crystallite sizes calculated by using Scherrer equation were found to be not bigger than 90 nm, which is in a good agreement with manufacturer's specification for the Ag nanopowder used, suggests that the recrystallization of Ag nanoparticles did not occur.

The decomposition profiles recorded in flowing air were used to estimate the loading of silver nanoparticles. Residue obtained for carbons with expected loading of nanoparticles

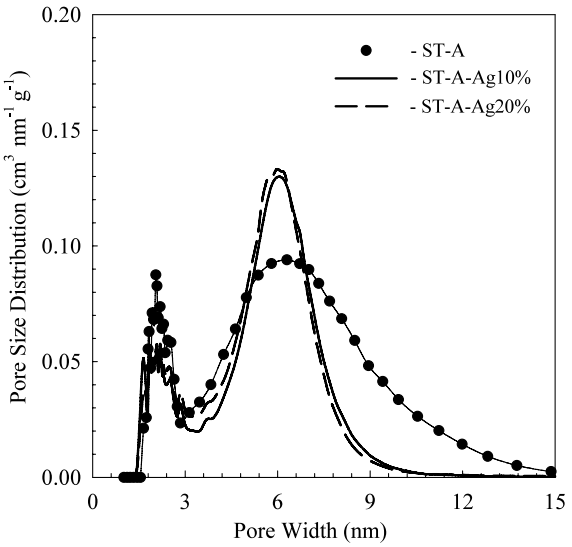

Fig. 5 Pore size distributions for the ST-A carbon without Ag nanoparticles and the ST-A-Ag10% and ST-A-Ag20% carbons containing silver nanoparticles

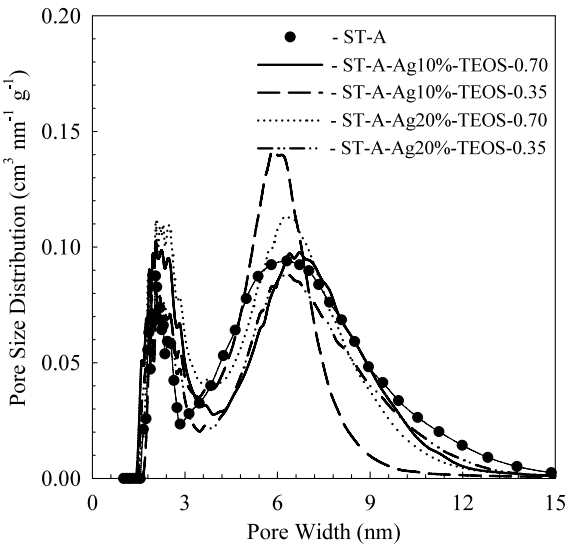

Fig. 6 Pore size distributions for the ST-A carbon prepared without Ag nanoparticles and carbons with different loadings of silver and TEOS

of 10% changes in the range of 7.3–14.9% and for carbons with 20% of silver stays around 15%. This suggests that a portion of nanoparticles was not incorporated during synthesis or the nanoparticle distribution in the carbon framework was somewhat non-uniform due to small amount of the sample used in TG analysis. Since the results were inconclusive, larger amounts of the carbons were analyzed than those used in TG analysis; this analysis revealed that ST-A-Ag10% and ST-A-Ag20% samples possess 7 wt% and 14 wt% of silver, respectively. Based on that result, it seems that the distribution of Ag nanoparticles in the carbon matrix was non-uniform as it was deducted on the basis of TG analysis.

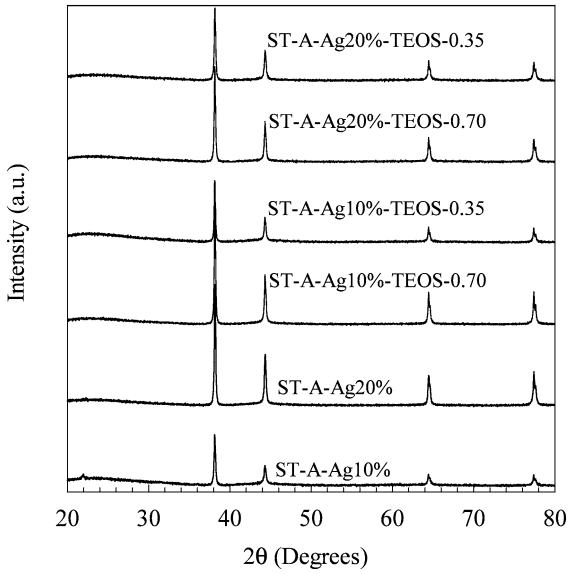

Fig. 7 Wide-angle XRD patterns of the carbons studied

4 Conclusions

The soft-templated mesoporous carbons with silver nanoparticles were successfully synthesized using resorcinol and formaldehyde as carbon precursors and triblock copolymer Lutrol F127 as a soft template. The reaction mixture was additionally supplied with TEOS to reinforce the mesophase formation during the synthesis and to improve the overall structural properties of the final materials. The obtained results suggest that the addition of silver nanoparticles slightly lowers the BET surface area. On the other hand, the TEOS addition affects also mesoporosity, which contribution to the total pore volume may be as high as 80%. The TGA data show that small fraction of silver nanoparticles was not introduced to the carbon matrix. Since the final materials feature a well-developed porosity, even lower silver loadings than expected should be sufficient for successful applications of these composite materials in adsorption and catalysis.

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