Comprehensive study of the role of ethylene glycol when preparing Ag@SBA-15 in supercritical CO₂

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A B S T R A C T
Well-defined Ag nanowires were obtained in SBA-15 at a short deposition time of 5 min in supercritical CO₂ when adding a small amount of ethylene glycol as the co-solvent. Ethylene glycol played a key role in dictating the nanowire morphology. Through detailed investigation of the whole deposition process, including the dissolution of precursor assisted by the co-solvent, the diffusion properties of the precursor into the nano-scale channels of the substrate, and the interaction between the precursor and the substrate, we found that a small amount of precursors were reduced into Ag⁰ by ethylene glycol at the initial stage of the deposition. The resultant Ag⁰ then acted as nuclei leading to a non-equilibrium sorption of the precursor. The rapid adsorption of the precursor onto the substrate resulted in a high loading of Ag in a short deposition time and the formation of nanowire morphology. Furthermore, this method was successfully extended to other porous substrates such as γ-Al₂O₃, SiO₂ and KIT-6, demonstrating its great potentials in the synthesis of nanocomposites.

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1. Introduction
Supercritical carbon dioxide (scCO₂) is an excellent solvent to carry metal precursors into the nanochannels of mesoporous substrates due to its strong solvent power and negligible surface tension. Since Watkins and McCarthy [1] first used scCO₂ to deposit Pt nanoparticles on polymers in 1995, some researchers have employed scCO₂ to support metal nanoparticles on inorganic substrates such as carbon aerogel, carbon black, Al₂O₃, silica aerogel, mesoporous silica, and carbon nanotubes [2–5]. However, in most of the reported work, expensive and even toxic metal-organic compounds were used as the metal precursors [2–5]. Recently, our group and other several groups have made efforts towards the employment of inexpensive inorganic salts as the metal precursors by adding some appropriate co-solvents [6–15] and accomplished effective supercritical fluid deposition (SCFD).

In our previous work [9], we found that when using a mixture of ethanol and ethylene glycol as the co-solvent, Ag@SBA-15 with a high metal loading of 22.1 wt% was obtained at a deposition time of 0.5 h, while a similar metal loading of 20.4 wt% was obtained at a deposition time of 28 h when using only ethanol as the co-solvent. In addition, the morphology of silver nanostructure changed from nanoparticle to well-defined nanowires after the addition of ethylene glycol. In that work, we focused on the optimization of the operating parameters including deposition time, pressure, temperature, as well as the ratio of precursor and substrate, but did not pay much attention to the exact role played by the ethylene glycol. The dramatic difference was tentatively attributed to the solubility enhancement of AgNO₃ in scCO₂ after the addition of ethylene glycol. However, further investigations are required to study the exact role played by ethylene glycol which may be beyond the solubility enhancement. This work will present the subsequent work of depositing AgNO₃ into the nanochannels of SBA-15 by addition of ethylene glycol as the co-solvent in scCO₂. Through detailed investigation of the influence of ethylene glycol on the deposition time and pressure as well as the morphology change of silver nanostructures, we get some insightful understanding of the promotional role of ethylene glycol in SCFD process.

2. Materials, methods and characterizations
AgNO₃ (99.99%) was purchased from Aladdin®. Carbon dioxide (>99%) was obtained from Dalian GuangMing Gas Co. Ltd. Ethanol, ethylene glycol and pyridine were all of analytical grade and supplied by Tianjin FuYu Fine Chemicals Co. Ltd. The
silver nanostructures were characterized by transmission electron microscopy (TEM), X-ray diffractometry (XRD), Inductively coupled plasma (ICP) and X-ray absorption fine structure (XAFS). XRD was used to obtain the phase composition of the composites using a continuous mode from 10° to 90° of 2θ at a scanning speed of 5°/min on a PW3040/60 X’Pert PRO (PANalytical) diffractometer using a Cu Kα radiation source (λ = 1.541874 nm), operated at 40 kV and 30 mA. The morphologies of the silver nanostructures on the substrates were examined by TEM on a JEOL 2000EX electron microscope operating at an accelerating voltage of 120 kV. The metal loading was measured by Optima 2000 DV inductively coupled plasma-atmospheric emission spectroscopy (ICP-AES). XAFS was performed in Shanghai Synchrotron Radiation Facility (SSRF).

The deposition process was carried out in a custom-made high-pressure stainless steel reactor with an effective volume of 84 ml. Mesoporous silica SBA-15 was prepared according to the method reported by Zhao et al. [16,17], and it has a BET surface area of 751 m²/g and an average pore diameter of 4–5 nm according to the N₂ adsorption–desorption isotherms. In a typical deposition process, 300 mg AgNO₃ and a certain amount of co-solvent were loaded in the bottom of the reactor. A stainless steel basket containing 300 mg SBA-15 was fixed in the upper part of the reactor to avoid the direct contact of precursor and substrate. Then the reactor was sealed and preheated at 50°C for 1 h. After that, CO₂ was charged into the reactor using a piston pump until the desired pressure was reached. The pressure and temperature were held constant for a certain time for the metal precursor deposition. After the deposition process, the system was slowly depressurized. Finally, the sample in the basket was submitted to calcinations in air at 300°C for 2 h to obtain Ag@SBA-15 composite.

3. Results and discussion

Fig. 1a presents a representative XRD pattern of Ag@SBA-15 prepared in scCO₂ at 50°C, 20 MPa at a deposition time of 60 min using a mixture of ethanol and ethylene glycol as the co-solvent. It clearly shows four strong diffraction peaks at 38.1°, 44.3°, 64.4°, and 77.5°, which correspond to (111), (200), (220), and (311) reflections of crystalline Ag, respectively. The very sharp peaks in Fig. 1a are in accordance with the nanowire structure of silver shown in Fig. 2b. It is worth noting that the intensity ratio of (111) to (200) reflections exhibited a relatively high value of 3.0, while the theoretical ratio of (111) to (200) is only 2.2 according to PDF card (89-3722, 87-0717, 87-0718, 87-0719, 87-0720). This difference suggests that the Ag nanowires grew preferentially along the (111) orientation. To further confirm whether the Ag nanowires were inside the channels of the SBA-15, N₂ adsorption–desorption measurements of SBA-15 and Ag@SBA-15 composite (50°C, 20 MPa, 60 min, 1.5 ml ethylene glycol and 1.5 ml ethanol) were performed. The N₂ adsorption–desorption isotherms (Fig. 1b) showed a typical step in the range of 0.6–0.7 relative pressure (p/p₀) which is characteristic of a highly ordered mesoporous structure. Compared with the mother SBA-15, the BET surface area of Ag@SBA-15 was decreased from 751.3 m²/g to 467.5 m²/g, and the total pore volume which was directly derived from the adsorption isotherm (p/p₀ = 0.995) was decreased from 0.7926 cm³/g to 0.5694 cm³/g. The inset in Fig. 1b shows the pore size distribution of SBA-15 and Ag@SBA-15 which was derived from the BJH adsorption branch. It can be clearly seen that the average pore size of the substrate was decreased from 4.85 nm to 4.46 nm. The decrease of these parameters indicates that Ag nanowires were uniformly dispersed inside the channels of SBA-15.

As reported in our previous work [9,10], compared to the case of only ethanol as the co-solvent, the employment of dual co-solvent of ethylene glycol and ethanol led to the reduction of deposition pressure from more than 20 MPa to 14 MPa and of deposition time from 24 h to 0.5 h. In the present work, we further investigated the deposition process at lower pressures and shorter deposition times. As shown in Fig. 2, well dispersed and continuous nanowires were anchored into the nanochannels of SBA-15 in 5 min (metal loading 5.8 wt%, Fig. 2a) and at a low pressure of 8.5 MPa (metal loading 11.5 wt%, Fig. 2c). As the deposition time was increased from 5 min (Fig. 2a) to 60 min (Fig. 2b), the resultant metal loading increased from 5.8 wt% to 23.1 wt%. Concurrently, the N₂ adsorption–desorption results showed that the BET surface area decreased from 639.2 m²/g to 467.5 m²/g (SBA-15, 751.3 m²/g), the total pore volume decreased from 0.7704 cm³/g to 0.5694 cm³/g (SBA-15, 0.7926 cm³/g) and the average pore size decreased from 4.57 nm to 4.46 nm (SBA-15, 4.85 nm). These results clearly indicated that the loaded Ag nanowires were highly dispersed inside the nanochannels of SBA-15 and the metal loading increased with the increase of deposition time while the morphology was not changed. In remarkable contrast to the above examples in the presence of dual co-solvent, when merely ethanol was used as the co-solvent (Fig. 2d), even though the deposition time was extended to 120 min, non-uniformly dispersed Ag nanoparticles instead of nanowires were formed in the channels of SBA-15 and the metal loading was only 8.7 wt% as determined by ICP analysis. We have performed XRD analysis of the samples 1–4 and their XRD patterns are shown in Supporting Fig. S1. It can be clearly seen that the diffraction peak intensities of the samples prepared with the mixture of ethanol and ethylene glycol (samples 1–3) are much stronger than that with only ethanol as the co-solvent (sample 4).

Based on the above results, one can draw a conclusion that the high-quality nanowires are prepared with good reproducibility using the mixture of ethylene glycol and ethanol as the co-solvent.

![Fig. 1](a) XRD pattern and (b) N₂ adsorption–desorption isotherms of mother SBA-15 and Ag@SBA-15 composite (50°C, 20 MPa, 60 min, 1.5 ml ethylene glycol + 1.5 ml ethanol).
Fig. 2. TEM images of Ag@SBA-15 prepared using 300 mg AgNO₃ and 300 mg SBA-15 at 50 °C: (a) 20 MPa, 5 min, 1.5 mL ethylene glycol + 1.5 mL ethanol, sample 1; (b) 20 MPa, 60 min, 1.5 mL ethylene glycol + 1.5 mL ethanol, sample 2; (c) 8.5 MPa, 60 min, 1.5 mL ethylene glycol + 1.5 mL ethanol, sample 3; (d) 20 MPa, 120 min, 13 mL ethanol, sample 4.

and the formation of nanowire morphology is independent of deposition time, pressure and metal loading. In comparison with the deposition with only ethanol as the co-solvent, it is evident that ethylene glycol dictates the formation of nanowire morphology. The deposition process of Ag nanowires in the channels of mesoporous silica can be described as four steps: (i) dissolution of AgNO₃ in scCO₂; (ii) diffusion and impregnation of scCO₂ solution into the pores of the substrates and adsorption of AgNO₃ onto the walls of the channels; (iii) depressurization and phase separation; and (iv) thermal reduction. Taking these four steps into consideration, we propose that ethylene glycol may act in the following aspects.

First, AgNO₃ has a much larger solubility in ethylene glycol, being nine times larger than that in ethanol at room temperature and the standard atmospheric pressure. The enhanced solubility may lead to a large concentration of precursor in scCO₂, which in turn facilitates the deposition of AgNO₃ with a higher loading [18,19] and the more complete filling of the channels, thus leading to the formation of nanowires. To prove this assumption, control experiments with water and pyridine as the co-solvent were performed, respectively. The solubilities of AgNO₃ in the two co-solvents as well as the solubilities of co-solvents in scCO₂ are listed in Table 1. It can be seen that AgNO₃ has a very high solubility in the two co-solvents. The TEM image in Fig. 3a shows that when using ethanol and deionized water as the co-solvent, only several nanoparticles are observed and the metal loading is only 0.15 wt% according to the ICP analysis. No characteristic diffraction peak of crystalline Ag is identified in the XRD pattern of sample 5 (Supporting Fig. S2) because of the low metal loading. When using the mixture of ethanol and pyridine as the co-solvent, uniformly dispersed nanoparticles with a much higher density are formed on the substrate (Fig. 3b) and the metal loading reached as high as 15.9 wt%. Based on the results of the control experiments, it can be concluded that the enhancement of solubility is not the primary reason for the formation of nanowire morphology when using ethylene glycol as the co-solvent. The morphology of the nanostructure when using ethanol and pyridine as the co-solvent is quite different from that of the sample with ethylene glycol as the co-solvent. Only nanowires were obtained even with a small metal loading (sample 1, Fig. 2a) in the case of ethylene glycol. The main reason for the different morphology may be attributed to the different growth mechanism of Ag nanophase when using different co-solvents, as discussed below.

Second, the diffusion process of precursor from the bulk phase of the system to the surface of substrate did not change due to stirring of the precursor and solvent. However, the surface tension and the viscosity of the two systems (binary system of ethanol/scCO₂; ternary system of ethylene glycol/ethanol/scCO₂) may be quite different, thus the diffusion process of precursor into the nanochannels of the substrate probably changes. We studied the phase behavior of binary system of ethanol/scCO₂ (50 °C,
Table 1
Solubility, surface tension, polarity and H-bonding formation ability for different co-solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_{AgNO_3}$ in solvent; (g/100 g solvent) [23]</th>
<th>$\delta_{Solvent}$ in scCO$_2$; (mol fraction)</th>
<th>Surface tension (nN/m) [20]</th>
<th>Polarity; (water as standard) [27]</th>
<th>Relative effectiveness of H-bonding formation [22]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>$0.19^\circ C, 3 g$</td>
<td>$0.333.6^\circ K, 10.2$ MPa; 0.0587 [24]</td>
<td>22.3</td>
<td>65.2</td>
<td>5</td>
</tr>
<tr>
<td>Glycol</td>
<td>$0.20^\circ C, 34 g$</td>
<td>$0.50^\circ K, 19$ MPa; 0.0283 [25]</td>
<td>46.49</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>Water</td>
<td>$0.50^\circ C, 455 g$</td>
<td>$0.323^\circ K, 20.26$ MPa; 0.012 [26]</td>
<td>72.75</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>Pyridine</td>
<td>$0.30^\circ C, 29 g$</td>
<td>–</td>
<td>36.6</td>
<td>30.2</td>
<td>42</td>
</tr>
</tbody>
</table>

20 MPa, 12.94 mol% ethanol, 87.06 mol% CO$_2$; system of sample 4) and ternary system of ethylene glycol/ethanol/scCO$_2$ (50 °C, 20 MPa, 1.62 mol% ethylene glycol, 1.59 mol% ethanol, 96.79 mol% CO$_2$; system of sample 2) and calculated the molar compositions of the gas and liquid phase of the two systems using PR-BM equation of state [20,21] as described in a previous report [10]. For the binary system of ethanol/CO$_2$, only liquid phase was found after calculations; the viscosity was 2.58 mPa s and the surface tension was 0.11 N m$^{-1}$. For the ternary system, the ratio of the vapor volume to the liquid volume was 69:1, so the vapor phase was the bulk phase in the deposition process due to the special design of the reactor [14]. The viscosity of the vapor phase was 0.081 mPa s and the surface tension was 0 N m$^{-1}$ according to the calculations. The details of the SCFD reactor and the gas–liquid interface are shown in Fig. 4. The surface tension and viscosity of ethylene glycol are larger than those of ethanol, but a small amount of ethylene glycol was added to ensure the dissolution of precursor because AgNO$_3$ has a large solubility in it. Therefore, smaller viscosity and surface tension of the bulk phase were obtained when using the mixture of ethylene glycol and ethanol as the co-solvent, which was beneficial for the penetration of precursor into the nanoscale channels. However, the diffusion process can only influence the deposition time to some extent, the adsorption of precursor onto the walls should be paid more attention to.

Third, the interaction among the precursor, the solvent and the substrate will influence the adsorption of AgNO$_3$ (solute) on SBA-15 (adsorbent) from scCO$_2$/co-solvent (solvent) significantly, thus affect the metal loading and the morphology of the nanophase. Inorganic salt is not soluble in scCO$_2$, but is soluble in co-solvent. It is probable that the co-solvent is concentrated at the silanol surface when only a little amount of the co-solvent is present and the salt is held in this thin layer. In other words, the adsorption of inorganic precursor on the substrate mainly depends on the adsorption of co-solvent on the substrate. It was reported that the relative effectiveness of hydrogen-bonding formation between the compounds and the silanol surface reflected the adsorption capacity [22]. If dimethoxytetraethylene glycol is used as standard compound, the relative molar effectiveness for ethanol, pyridine, and ethylene

![Fig. 3. TEM images of Ag@SBA-15 prepared using 300 mg AgNO$_3$ and 300 mg SBA-15 at 50 °C, 20 MPa, 60 min: (a) 2 mL ethanol + 1 mL deionized water, sample 5; (b) 1.5 mL ethanol + 1.5 mL pyridine, sample 6.](image)

![Fig. 4. Reactor and gas–liquid interface (dimensions in mm).](image)
glycol is 5, 42, and 0 (shown in Table 1). The bigger the relative molar effectiveness of hydrogen-bonding, the stronger the adsorption between the solvent and the substrate is. When using the mixture of ethanol and pyridine as the co-solvent, a large amount of Ag nanoparticles were found in the TEM image (Fig. 3b) which might be due to the stronger adsorption between pyridine and SBA-15. However, the zero relative molar effectiveness for ethylene glycol indicated weak adsorption between the co-solvent and silica which could not lead to a large amount of AgNO₃ adsorption onto the silica in a short deposition time of 5 min.

Xia and co-workers [28–31] have demonstrated the synthesis of silver nanocrystals with different morphologies based on the reduction of silver nitrate by ethylene glycol in the presence of poly(vinyl pyrrolidone). In their work, most experiments were carried out at a temperature higher than 100 °C. Chih and Cheng [32,33] reported that uniform silver nano-particles could be formed at 50 °C by using ethylene glycol to reduce AgNO₃ assisted by scCO₂ in the presence of polyvinyl pyrrolidone. In those papers, ethylene glycol was used to reduce silver nitrate while poly(vinyl pyrrolidone) played a role of capping agent which provided steric protection of as-synthesized nanoparticles from agglomeration. In our present work, all the experiments were conducted at 50 °C, therefore we speculate that a small amount of AgNO₃ was reduced into Ag⁰ during the deposition process. Fig. 5a shows the TEM image of sample 2 (50 °C, 20 MPa, 60 min, 1.5 mL ethylene glycol + 1.5 mL ethanol) after the process of deposition without calcinations treatment. This sample was defined as as-prepared sample 2. A few Ag nanorods have already formed in the channels of SBA-15, indicating that AgNO₃ can be reduced to Ag at 50 °C with the assistant of CO₂. To further confirm the reduction of precursor during the deposition process, X-ray absorption fine structure (XAFS) was performed in Shanghai Synchrotron Radiation Facility (SSRF) to analyze the valence of silver in the as-prepared sample 2. Fig. 6a showed that the pattern of the as-prepared sample 2 was in accordance with the standard pattern of AgNO₃, and the near edge data (Fig. 6b) showed that the valence of Ag in the as-prepared sample 2 was slightly lower than that of AgNO₃. This result clearly demonstrated that a small amount of precursors were reduced into Ag⁰ during the deposition process.

Based on the above experiments, characterization and analysis, an insightful understanding of the ethylene glycol function was achieved. As shown in Fig. 7, for the synthesis of Ag@SBA-15 in scCO₂ using the mixture of ethylene glycol and ethanol as the co-solvent, AgNO₃ was first dissolved in scCO₂ with the assistance of the co-solvent and then it diffused easily into the nanochannels of SBA-15 due to the negligible surface tension and low viscosity of scCO₂. In the nanopores of SBA-15, a small amount of AgNO₃ was reduced to Ag⁰ by ethylene glycol, then the reduced Ag⁰ served as nuclei to attract a large amount of AgNO₃, leading to a significant decrease of the local precursor concentration inside the pores. Because of a large difference in the AgNO₃ concentration inside and outside the pores, AgNO₃ diffused rapidly from the bulk phase into the nano-scale channels and thus a rapid non-equilibrium sorption occurred. That was the reason for a high metal loading obtained in such a short deposition time. This deposition process with the addition of ethylene glycol is quite different from that using other co-solvents. When using ethanol, water or pyridine as the co-solvent, the deposition process could be attributed to the adsorption of precursor on SBA-15 which was determined by the interaction of co-solvent with the silanol groups.
It was further found that this ethylene glycol-assisted deposition process could be extended to the synthesis of silver nanostructures on other substrates such as commercial γ-Al₂O₃, SiO₂, and the mesoporous three-dimensional KIT-6. As shown in Fig. 5b-d, small and uniformly dispersed Ag nanoparticles were formed on different supports by using the mixture of ethylene glycol and ethanol as the co-solvent.

4. Conclusions

In summary, well-defined Ag nanostructures were successfully prepared by using AgNO₃ as the precursor, scCO₂ as the solvent and a mixture of ethylene glycol and ethanol as the co-solvent. The success of this method could be attributed to the near-zero surface tension of scCO₂ and the rapid adsorption of precursors due to the reduction of a small amount AgNO₃ by ethylene glycol at the first stage. This work for the first time provided an insightful understanding of the role of ethylene glycol in the whole deposition process. Moreover, this method was successfully extended to other substrates such as γ-Al₂O₃, SiO₂ and KIT-6, offering its great opportunities for applications in the controllable synthesis of nanomaterials.

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Fig. 6. XAFS results of as-prepared sample 2 (20 MPa, 60 min, 1.5 mL ethylene glycol + 1.5 mL ethanol).

Fig. 7. The mechanism of Ag growth in SBA-15 using the mixture of ethanol and ethylene glycol as co-solvent in scCO₂.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.supflu.2014.05.007.

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