Formation of mesoporous Co$_3$O$_4$ replicas of different mesostructures with different pore sizes

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Abstract

Mesoporous metal oxides Co$_3$O$_4$ are prepared via hard templating synthesis method by using various mesoporous silicas with different pore size as templates. The pore size of the mesoporous silicas with the symmetry of two-dimensional (2d)-hexagonal $p6mm$, bicontinuous cubic $Ia3d$ and $Pn3m$ have been controlled in the range of 6.6–10.7, 4.2–7.5 and 5.1–6.7 nm, respectively, by choosing different surfactants and co-surfactants and by adjusting either the aging temperature or the ionization degree of the surfactant. The pore size of the silica template has been considered to be an important factor that determines the mesostructure of the resulting metal oxides. It has been found that for $p6mm$, it is easier to replicate the mesoporous symmetry at large size of mesopores. For $Ia3d$, at large-pore size two sets of bicontinuous meso-channels are replicated into mesoporous Co$_3$O$_4$, while small-pore $Ia3d$ leads to replication of both one set and two sets of meso-channels. Co$_3$O$_4$ can replicate both one set and two sets of bicontinuous $Pn3m$ meso-channels at all pore sizes that can be obtained (5.1–6.7 nm), indicating the existence of ordered complementary micropores within the silica walls.

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composites [10]. The silica template is dissolved away to leave a replica mesoporous structure of the target compound. The hard templating route has opened a way to great varieties of mesoporous transition metal oxides.

The relationship between the pore size of the silica template and that of the obtained metal oxide replicas is an interesting topic. Here, the mesostructures including 2d-hexagonal $q_{60mm}$, cubic $Ia3d$ and $Pn3m$ that possess rod-type pore system have been selected for studying the relationship, because, in the case of cage-type mesoporous silica, it is well known that the small apertures make it difficult for the precursors to completely fill the cages and to form rigid carbon or metal oxide bridges between their nanoparticles prepared in silica cages. Here, we present a report on the study of the effect of pore size and pore symmetry on the formation of mesoporous Co$_3$O$_4$ by preparing the mesoporous cobalt oxide Co$_3$O$_4$ (Fd$ar{3}m$ crystal structure) using mesoporous silicas SBA-15 (2d-hexagonal $q_{60mm}$), KIT-6 (bicontinuous cubic $Ia3d$) and AMS-10 (bicontinuous $Pn3m$) with different pore size as hard templates. The dependence of the structure of replica on pore size and symmetry of the silica template will be discussed in details. Different from earlier literatures, in this study, we will show that solely the pore size of silica template cannot determine the replication extent, and the discussion is valid only when considering the mesopore symmetry. Structural properties of the mesoporous silicas, especially newly developed AMS-10, are also derived from inverse replication.

2. Experimental section

2.1. Synthesis

2.1.1. Synthesis of mesoporous silica

The mesoporous silica templates SBA-15 [23], KIT-6 [24], and AMS-10 [32] were prepared according to the procedure described previously.

2.1.1.1. Synthesis of 2d-hexagonal $q_{60mm}$ structured mesoporous silica (SBA-15) with different pore size. SBA-15 mesoporous silica was synthesized by using the triblock copolymer Pluronics P123 (EO$_30$.PO$_9$_EO$_{29}$, BASF) as surfactant and tetraethoxysilicon (TEOS) as silica source. In a typical synthesis experiment, TEOS (20.8 g) was dissolved in 217 g of distilled water without stirring, and to form rigid carbon or metal oxide bridges between their nanoparticles prepared in silica cages. Here, we present a report on the study of the effect of pore size and pore symmetry on the formation of mesoporous Co$_3$O$_4$ by preparing the mesoporous cobalt oxide Co$_3$O$_4$ (Fd$ar{3}m$ crystal structure) using mesoporous silicas SBA-15 (2d-hexagonal $q_{60mm}$), KIT-6 (bicontinuous cubic $Ia3d$) and AMS-10 (bicontinuous $Pn3m$) with different pore size as hard templates. The dependence of the structure of replica on pore size and symmetry of the silica template will be discussed in details. Different from earlier literatures, in this study, we will show that solely the pore size of silica template cannot determine the replication extent, and the discussion is valid only when considering the mesopore symmetry. Structural properties of the mesoporous silicas, especially newly developed AMS-10, are also derived from inverse replication.

2.1.1.2. Synthesis of bicontinuous $Ia3d$ structured mesoporous silica (KIT-6) with different pore size. The large-pore cubic $Ia3d$ mesoporous silica KIT-6 was synthesized by using $N$-myristoyl-$\gamma$-glutamic acid sodium salt (C$_{14}$GluAS, one of the carboxylic acid groups of the glutamic acid was neutralized by sodium hydroxide) as surfactant, $N$-trimethoxysilylpropyl-$N$-$N$-$N$-trimethylammonium chloride (TMAPS) as co-structure-directing agent (CSDA) and TEOS as silica source. In a typical synthesis experiment, HCl (0.417 g of 1 mol L$^{-1}$ solution) was added to a solution of C$_{14}$GluAS (0.379 g, 1 mmol) in deionized water (36 g) under stirring at 80°C. After the solution became homogeneous, a mixture of TMAPS (0.773 g, 50 wt.% in methanol, 1.5 mmol) and TEOS (3.12 g, 15 mmol) was added, and the mixture was stirred at 80°C for 10 min. The molar composition of the final gel was C$_{14}$GluAS/TMAPS/TEOS/H$_2$O/HCl = 1:1.5:15:2000:0.42. The precipitation was then aged at 80°C for 2 days, filtered, and calcined at 550°C for 6 h to remove the surfactants. The pore size of AMS-10 was controlled by adjusting the HCl/C$_{14}$GluAS molar ratio in the range of 0.42–0.48. The samples with four pore sizes were synthesized with different HCl/C$_{14}$GluAS molar ratios of 0.42, 0.44, 0.45, and 0.48. They were denoted as AMS-10-0.42, AMS-10-0.44, AMS-10-0.45 and AMS-10-0.48, respectively.

2.1.2. Synthesis of mesoporous Co$_3$O$_4$ replica

In a typical synthesis of mesoporous Co$_3$O$_4$, 0.75 g of Co(NO$_3$)$_2$.6H$_2$O (98% Aldrich) was dissolved in 16 mL of ethanol followed by addition of 0.5 g of mesoporous silica templates. The mixture was stirred at room temperature until nearly dry powder had been obtained; the sample was then heated slowly to 300°C and calcined at the same temperature for 3 h to pyrolyze the nitrate. The impregnation procedure was repeated twice with 0.4 g of Co(NO$_3$)$_2$.6H$_2$O and 0.25 g of Co(NO$_3$)$_2$.6H$_2$O dissolved in 16 mL ethanol, followed by calcination at 550°C for 5 h with a ramp of 1°C min$^{-1}$ for metal oxide to crystallize. The resulting samples were treated with 10% HF to remove the silica template, centrifuged, washed with water and ethanol, and then dried at 60°C in air. The samples were denoted as Co$_3$O$_4$:SBA-15-X, Co$_3$O$_4$:KIT-6-X and Co$_3$O$_4$:AMS-10-Y (X: aging temperature of silica template in °C; Y: molar ratio of HCl/C$_{14}$GluAS in the synthesis of AMS-10).

2.2. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2000/PC Multiplex instrument using Cu Kα radiation ($\lambda = 0.15406$ nm), operated at 40 kV and 20 mA (0.8 kW) at the rate of 1.0° min$^{-1}$ over the range of 0.8–60° (2θ).

$N_2$ adsorption–desorption isotherms were measured at −196°C on a Quantachrome Nova 2400e volumetric adsorption analyzer. Before the adsorption measurements, all samples were outgassed at 200°C in the port of the adsorption analyzer for 4 h. Specific surface areas were calculated via the Brunauer–Emmett–Teller (BET) model in regions applicable to the derivation of the model between $P/P_0$ values of 0.05–0.3. The total pore volume was determined from the uptake of nitrogen at a relative pressure of $P/P_0 \approx 0.99$. Pore size distribution curves were obtained from the adsorption branch by using the Barrett–Joyner–Halenda (BJH) method.

Scanning electron microscopy (SEM) features of all the samples were observed by SEM (JEOL JSM-7401F). The samples were observed without any metal coating. High-resolution transmission electron microscopy (HRTEM) images were taken from thin edges of particles supported on a porous carbon grid, using JEOL JEM-3010 electron microscope (point resolution 1.7 Å, Cs = 0.6 mm).
operated at 300 kV. Samples were crushed in an agate mortar, suspended in ethanol using ultrasonics and then dropped onto the carbon grid.

The wall thickness \( w \) of mesoporous silicas was calculated combining the unit cell parameter \( a \) derived from XRD pattern and pore diameter \( d \) derived from \( N_2 \) adsorption–desorption. For 2d-hexagonal \( p6mm \) symmetry, \( w \) was calculated as \( a/d \). For bicontinuous cubic \( la\)-3d symmetry, \( w \) was calculated as \( a/2.30919-d/2 \) [33,34]. For bicontinuous cubic \( Pn-3m \) symmetry, \( w \) was determined as \( d_{110}-d \), i.e., \( w = a/1.4142-d \) (structure model, Ref. [32]).

3. Results and discussion

3.1. Mesoporous \( \text{Co}_3\text{O}_4 \) synthesized by SBA-15 with \( p6mm \) structure as hard template

Trilblock copolymer Pluronic P123 was used as a template to synthesize SBA-15. It was reported that the pore size can be modulated by aging temperature [23]. PEO moieties are hydrophobic while PPO moieties are hydrophilic. PEO moieties are expected to interact with the inorganic species more strongly and closely associated with the inorganic wall than the hydrophobic PPO. As temperature rises, the PEO moieties become more hydrophobic, resulting in increased hydrophobic domain volume and shorter length of the PEO segments associated with the inorganic wall, thus the pore size increases.

All the SBA-15-X (X: aging temperature in °C) samples show three well-resolved XRD peaks in the region of 2\( \theta \) = 0.5–2.5°, which correspond to \( 10 \), \( 11 \) and \( 20 \) reflections based on the 2d-hexagonal system (Fig. S1). In addition, the higher hydrothermal aging temperature gives rise to 2d-hexagonal \( p6mm \) silica with larger pores and improved structural integrity. The resultant products show the increasing \( d \)-spacing indicated from the fact that the \( 10 \) reflection peak shifts to a smaller angle with increasing hydrothermal aging temperature from 40 to 100 °C.

\( N_2 \) adsorption and desorption isotherms for SBA-15-X (Fig. S2) are of type IV according to the IUPAC classification [35]. Significant H1 type hysteresis loop is observed for all isotherms, and the capillary condensation occurs at increasing relative pressure with increasing aging temperature, indicating increasing size of cylindrical mesopores. In addition, the capillary condensation step becomes narrowed with increasing synthesis aging temperature, which indicates the degree of pore uniformity is increased. Interestingly, the pore size distribution curves, BJH plots of derivative of the pore volume per unit weight with respect to the pore diameter \( (dV/dD) \) versus the pore diameter \( (D) \), show a clear shift of pore diameter from 6.6 to 10.7 nm as the aging temperature is increased from 40 to 100 °C (Fig. S2).

Table 1 summarizes the structural properties of the SBA-15-X mesoporous silicas. All the SBA-15-X samples have BET surface area larger than 700 m² g⁻¹, and the pore volume increases from 0.70 to 1.18 cm³ g⁻¹ with higher aging temperatures. The wall thickness has also been determined on the basis of unit cell parameter and pore diameter, and it can be seen that the wall thickness decreases from 2.4 to 0.7 nm when the aging temperature increases from 40 to 100 °C in the synthesis.

Fig. 1 shows the XRD patterns of mesoporous \( \text{Co}_3\text{O}_4 \) after removal of silica, using SBA-15 with different pore sizes as hard templates. After cobalt oxide is embedded within the mesopores of SBA-15, the intensities of the \( 10 \), \( 11 \) and \( 20 \) reflections are dramatically reduced. The obtained mesoporous cobalt oxides synthesized by large-pore samples SBA-15-80 and 100, show well-resolved \( 10 \) reflection while lose the \( 20 \) reflection peak. It indicates that the mesostructures are well retained but the structural order decreases during replication process. Sample \( \text{Co}_3\text{O}_4\text{-SBA-15-40} \) templated by mesoporous silica with the smallest pore size gives no significant X-ray reflection peak in the range of 2\( \theta \) = 0.5–4°. It suggests that after the removal of silica template, the hexagonal arrangements of nano-wires collapse, which is confirmed by later TEM characterization. From the large-angle XRD pattern, it can be concluded that the \( \text{Co}_3\text{O}_4 \) products are well crystallized and the crystal structure is cubic \( Fd\text{3m} \) (not shown).

As is seen in the SEM images (Fig. S3), the morphology of the \( \text{Co}_3\text{O}_4 \) replica is close to that of the mesoporous silica template (SBA-15-100). Cobalt nitrate was deposited in the straight channels of templates. Nuclei were formed simultaneously in the channels with the temperature increase, followed by the growth of the cobalt oxide. The confinement of the straight channels of the SBA-15 allowed the cobalt oxide to grow in one direction and completely fill the pores, keeping the morphology.

Fig. 2 shows the \( N_2 \) adsorption–desorption isotherms of the silica-free \( \text{Co}_3\text{O}_4 \) mesoporous replicas synthesized by using SBA-15-80 and 100. The structural properties are summarized in Table 2. The isotherms are of type IV classification, which have typical hysteresis loops of mesoporous materials. With SBA-15-100 mesoporous silica as template, the silica-free mesoporous \( \text{Co}_3\text{O}_4 \) sample has a surface area of 86 m² g⁻¹ and a pore volume of 0.17 cm³ g⁻¹. It is noticeable that its isotherm is different from that of SBA-15-100, giving a pore size distribution centered at 2.3 nm, indicating the expected pore dimension, which is larger but is still in scale with the wall thickness of SBA-15 as shown in Table 1. Similarly, the pore size of mesoporous \( \text{Co}_3\text{O}_4 \) templated by SBA-15-80 is also close to the wall thickness of silica template. It suggests that the SBA-15-100 and 80 are successfully replicated.

Fig. 3a and b are TEM images of the \( \text{Co}_3\text{O}_4 \) mesoporous replicas synthesized with small-pore SBA-15-40 (6.6 nm) and large-pore SBA-15-100 (10.7 nm), respectively, as hard templates. The length of \( \text{Co}_3\text{O}_4 \) nano-wires ranged from several tens to several hundreds of nanometers, and the average diameters of \( \text{Co}_3\text{O}_4 \) nano-wires are about 6.3 and 9.8 nm, respectively, which match the pore sizes of the corresponding SBA-15 templates very well. It can be clearly seen from Fig. 3b that mesoporous \( \text{Co}_3\text{O}_4 \) replica well retains the ordered 2d-hexagonal \( p6mm \) structure of the large-pore silica template SBA-15-100. However, the mesoporous \( \text{Co}_3\text{O}_4 \) replicas templated by small-pore SBA-15-40 (Fig. 3a) are isolated nano-wires without interconnections to retain the symmetry of silica template.

Notably, the corresponding HRTEM of Fig. 3a and b marked by arrows are given on the right. From the HRTEM images it can be seen that the mesoporous \( \text{Co}_3\text{O}_4 \) replicas are crystalline, and each

Table 1
Structure properties of the mesoporous silica SBA-15-X (X: aging temperature in °C) with 2d-hexagonal \( p6mm \) symmetry.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit cell parameter (nm)</th>
<th>( S ) (m² g⁻¹)</th>
<th>( V ) (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
<th>Wall thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-40</td>
<td>9.0</td>
<td>794</td>
<td>0.70</td>
<td>6.6</td>
<td>2.4</td>
</tr>
<tr>
<td>SBA-15-80</td>
<td>10.0</td>
<td>711</td>
<td>0.96</td>
<td>8.9</td>
<td>1.1</td>
</tr>
<tr>
<td>SBA-15-100</td>
<td>11.3</td>
<td>714</td>
<td>1.18</td>
<td>10.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>
of them can be regarded as a single crystal although the crystal orientations of the two adjacent Co$_3$O$_4$ nano-wires are different.

In summary, SBA-15 with large-pores (larger than 8.9 nm) can be fully replicated by Co$_3$O$_4$, retaining the mesostructure of silica template, while replication of small-pore SBA-15 (6.6 nm) results in separated nano-wires. It is probably due to the microporous defects in the walls of SBA-15. If the pore dimension gets larger, the pore wall becomes thinner, and the pore-forming P123 in adjacent micelles would share hydrated PEO and therefore forms micropores that connect mesopores, which plays a vital role in retaining the template symmetry during the inverse replication [36].

### 3.2. Mesoporous Co$_3$O$_4$ synthesized by KIT-6 with bicontinuous Ia$\overline{3}$d structure as hard template

Similar to the case of SBA-15, the pore size of bicontinuous cubic Ia$\overline{3}$d mesoporous silica KIT-6 can also be modulated by changing the aging temperature. All the KIT-6-X (X: aging temperature in °C) materials show three well-resolved XRD peaks in the region of $2\theta = 0.8–2.8^\circ$ (Fig. S4), which correspond to (2 1 1), (2 2 0) and (3 2 1) reflections, based on a cubic system. The bicontinuous cubic Ia$\overline{3}$d symmetry is confirmed by combining the XRD pattern and HRTEM images (not shown). For KIT-6-X, higher hydrothermal aging temperature gives mesoporous silicas with larger pores and improved structural integrity. The resultant products show increasing d-spacing with the (2 1 1) reflection peak shifting to a smaller angle, when the hydrothermal treatment temperature gets higher. The N$_2$ adsorption–desorption isotherms of the materials (Fig. S5) are type IV with a sharp capillary condensation step at high relative pressures and a H1 type hysteresis loop, indicative of large channel-like pores in a narrow range of size. The pore size distributions (Fig. S5) illustrate the pore size changes from 4.2 to 7.5 nm when the aging temperature rises from 40 to 100 °C.

Table 3 summarizes the structural properties of KIT-6-X. From this table it can be seen that all the materials have good mesoporosity. As the aging temperature gets higher, the pore diameter increases, while the wall thickness decreases from 4.2 to 3.4 nm.

![Fig. 1. XRD patterns of the mesoporous Co$_3$O$_4$ templated by SBA-15-X.](image)

![Fig. 2. N$_2$ adsorption–desorption isotherms and pore size distributions of mesoporous Co$_3$O$_4$ replicas templated by SBA-15-X. The isotherm of Co$_3$O$_4$-SBA-15-100 was moved vertically by 20 cm$^3$ g$^{-1}$.](image)
Fig. 6 shows the N2 adsorption–desorption isotherms of silica-free mesoporous Co3O4 replicas (Co3O4-KIT-6-X). The structural properties are summarized in Table 4. The isotherms are of type IV classification, which have typical hysteresis loops of mesoporous materials. With KIT-6-100 as template, the silica-free mesoporous Co3O4 sample has a surface area of 64 m² g⁻¹ and a pore volume of 0.14 cm³ g⁻¹. It is noticeable that its isotherm is different from that of template KIT-6-100, giving pore size distribution centered at 3.5 nm, reflecting exactly the wall thickness of KIT-6-100 (3.4 nm). This value is in good agreement with the pore diameters anticipated for a replica structure of KIT-6, indicating that the two sets of mesopores are successfully fabricated. As for the mesoporous Co3O4 templated by KIT-6-40 and 80, the pore sizes are not equal to the wall thickness of silica template. The pore size distribution curves centered at 10.7 and 7.5 nm for Co3O4-KIT-6-40 and Co3O4-KIT-6-80, respectively, much larger than the wall thickness of the corresponding silica template, 4.2 nm for KIT-6-40 and 3.6 nm for KIT-6-80. This might come from partial replication of only one set of the bicontinuous meso-channels. And this conclusion is further proved by TEM observations.

Fig. 7a–c shows TEM images of mesoporous Co3O4 replicas synthesized using KIT-6 with different pore sizes (4.2, 6.6 and 7.5 nm, respectively) as the hard template, taken along the [1 0 0], [1 1 0] and [1 1 1] directions. It is clear from TEM images that all the Co3O4 replicas maintain a 3d structure and the channels are arranged in a well-ordered bicontinuous cubic structure.
indicates that when the cobalt nitrate was introduced into KIT-6 and reduced, the Co₃O₄ replica was formed inside the channels of KIT-6 without destroying the channel geometry. It is well known that KIT-6 has $Ia\overline{3}d$ space group symmetry and possesses two non-intersecting channel networks separated by the silica wall which follows Gyroid minimal surface. From Fig. 7a (Co₃O₄-KIT-6-40) and 7b (Co₃O₄-KIT-6-80), it can be clearly seen that only one set of the nonintersecting channel network is replicated at the edge of the Co₃O₄ replica crystal, however, in the thick areas both non-intersecting channel networks are replicated and the symmetry is slightly destroyed due to the shift of the two networks. It also explains the difference of pore size distributions between replicas and the corresponding silica templates. Fig. 7c (Co₃O₄-KIT-6-100) clearly shows that two nonintersecting channel networks are completely replicated and the Co₃O₄ replica keeps the same space group symmetry as KIT-6. From Fig. 7a to c, it can be concluded that the pore size of KIT-6 template determines the extent of the replication, and two sets of channel networks can be completely replicated when the pore size is above or equal to 7.5 nm. Furthermore, when the pore size of KIT-6 template is small ($<6.6$ nm), Co₃O₄ can only replicate one set of pores at the edge of the particles and the area of one set replication is larger when the template pore size is smaller. Results of TEM observations are consistent with and strongly support the N₂ adsorption data.

In summary, large-pore KIT-6 with $Ia\overline{3}d$ structure facilitates the replication of both sets of the bicontinuous networks, and partial replication of one set network occurs when using small-pore KIT-6 as the hard template. The disordered micropores connecting adjacent mesopores is among the reasons, similar to the case of replication of SBA-15. In addition, another possibility also answers for this fact. It is known that when the mesopore of $Ia\overline{3}d$ structure gets larger, ordered complementary micropores are present on the thinnest part of the pore walls, which connect the two independent mesopore networks [36]. Through the disordered micropores and ordered complementary micropores, the cobalt precursor diffuses between the two disconnected bicontinuous networks and therefore replication of both sets of $Ia\overline{3}d$ networks is achieved.

3.3. Mesoporous Co₃O₄ synthesized by AMS-10 with bicontinuous $Pn\overline{3}m$ structure as hard template

In our previous work, we have found that both the mesostructure and pore size strongly depend on the ionization degree of the two-headed anionic surfactant [38]. The mesoporous materials synthesized with the surfactant neutralized with low HCl amount having larger effective head group areas often show smaller pore sizes, regardless of the type of CSDA. It has been proposed that the hydrophobic “tail” of the surfactant with larger effective head group area would “coil” to fill the space and thus maximize their van der Waals interactions, leading to lowering of the overall
energy. Lower surfactant packing density leads to more tightly coiled surfactant hydrocarbon tails and smaller pore size. It has been found that the unit cell parameter and pore size are significantly different even between the same mesostructures.

Mesoporous silicas AMS-10 with different pore sizes are synthesized by adding different amount of HCl into the C14GluAS solution. The synthesis molar composition is: C14GluAS/TMAPS/TEOS/H2O/HCl = 1:1.5:15:2000:Y. Two X-ray reflection peaks of each samples can be distinguished with a reciprocal spacing ratio of about 1:1.225 and can be indexed to (1 1 0) and (1 1 1) reflections of bicontinuous cubic PnC223m mesophase (Fig. S6). The HRTEM images (not shown) confirm that all of the space groups of these mesoporous materials are bicontinuous cubic Pn3m. The resultant products show increasing d-spacing with the reflection peak [1 1 0] shifting to the smaller angle from 1.39° to 1.14° with increasing HCl/C14GluAS molar ratio from 0.42 to 0.48.

The N2 adsorption–desorption isotherms of the samples AMS-10-Y (Y = HCl/C14GluAS) (Fig. S7) show type IV features, typical for mesoporous materials, and three well-distinguished regions of the adsorption isotherm are observed including monolayer-multilayer adsorption, capillary condensation, and multilayer adsorption on the outer surface. All the samples clearly show the hysteresis loop of H1 type and the capillary condensation occurs at increasing relative pressure with increasing HCl/C14GluAS molar ratio, indicating increasing size of cylindrical mesopores. Interestingly, the pore size distribution curves, BJH plots of derivative of the pore volume per unit weight with respect to the pore diameter (dV/dD) versus the pore diameter (D), show a clear shift of pore diameter from 5.1 to 6.7 nm, as the molar ratio of HCl/C14GluAS changes from 0.42 to 0.48 (Fig. S7).

The porous properties of AMS-10-Y are summarized in Table 5. All the samples show large surface areas (larger than 600 m2 g⁻¹) and pore volumes (larger than 0.8 cm³ g⁻¹), indicating high mesoporosity of the samples. As the HCl/C14GluAS molar ratio increases, the pore size increases significantly. However, the wall thickness is almost the same around 1.2 nm for all the samples.

Fig. 8 shows the XRD patterns of Co3O4 mesoporous replicas synthesized with AMS-10-Y as the template. After Co3O4 is embedded in the mesopores and silica is removed, the XRD patterns show no significant peaks within the range of 0.8–6.0° (2θ). Only one reflection peak with low intensity is observed from each pattern, which can be reasonably assigned to the (1 1 0) reflection, showing the d-spacing close to that of the silica template. These peaks can be explained as the X-ray reflections from the mesoporous Co3O4 that is obtained by replication of two sets of the bicontinuous mesopore networks, which shows the same unit cell dimensions as the silica template. The low intensity of the X-ray reflection indicates that replication of two sets of bicontinuous mesopore network by Co3O4 occurs partially. Replication of only one set of the meso-channels may also occur, which doubles the unit cell dimensions (structural model of Pn3m, Ref. [32]) and therefore the X-ray reflections shift to a much smaller angle (2θ).

Fig. 9 shows the N2 adsorption–desorption isotherms and pore size distributions of silica-free Co3O4 mesoporous replicas templated by AMS-10-Y. The porous properties are shown in Table 6. The isotherms are of type IV classification, which have typical
hysteresis loops of mesoporous materials. The pore size distributions show similar feature that the materials have bimodal porous structure, with two maxima of $\frac{dV}{dD}$ within the pore size regions of 2–5 nm and 5–15 nm. Considering that the pore size and wall thickness of silica template are 5.1–6.7 nm and 1.2 nm, respectively, it is reasonable that the pore size distribution of mesoporous Co$_3$O$_4$ within 2–5 nm is attributed to the replication of two sets of the bicontinuous mesopores of AMS-10. One the other hand, the pore size of mesoporous Co$_3$O$_4$ within 5–12 nm is much larger than the wall thickness of silica template, which might be due to the replication of only one set of the bicontinuous meso-channels. The large mesopore of Co$_3$O$_4$ is close to the expected value, twice of the wall thickness plus pore diameter of silica template, on condition that only one set of meso-channels is replicated. Therefore, it can be concluded that, within the full range of pore size of AMS-10, Co$_3$O$_4$ replicates both one set and two sets of the bicontinuous meso-channels. It could be further proved by TEM observations.

Fig. 10a and b shows TEM images of mesoporous Co$_3$O$_4$ replicas synthesized from AMS-10 with different pore sizes (5.1 and 6.7 nm, respectively) taken along [1 1 0] and [1 1 1] directions. It can be clearly seen that all the Co$_3$O$_4$ replicas have a 3d structure and the channels show a well-ordered bicontinuous cubic structure. This implies that the Co$_3$O$_4$ replica is formed inside the channels of AMS-10 like in the channel of KIT-6 described above. Similar to KIT-6, AMS-10 has two nonintersecting channel networks as well. However, those two channel networks are separated by the silica wall which follows Diamond minimal surface and AMS-10 possesses Pn$\overline{3}$m space group symmetry. From Fig. 10a (Co$_3$O$_4$-AMS-10-0.42) and 10b (Co$_3$O$_4$-AMS-10-0.48), it is clear that only one set of the nonintersecting channel network was replicated in the edge of the Co$_3$O$_4$ replica crystal, but in the thick areas both nonintersecting channel networks were replicated and further the contrast between two channel networks is different from each other which results in the break of the symmetry. The presence of the replication of one set of channel network illustrates the difference of pore size distributions between both replicas and the corresponding templates.

Therefore, it can be summarized that mesoporous Co$_3$O$_4$ prepared by using AMS-10 with pore size of 5.1–6.7 nm is obtained by replication of both one set and two sets of bicontinuous meso-channel networks. AMS-10 is synthesized by using anionic surfactant as the template, and therefore no micropore is present.

Table 5

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<thead>
<tr>
<th>Sample</th>
<th>Unit cell parameter (nm)</th>
<th>$S$ ($m^2 g^{-1}$)</th>
<th>$V$ ($cm^3 g^{-1}$)</th>
<th>Pore diameter (nm)</th>
<th>Wall thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS-10-0.42</td>
<td>9.0</td>
<td>649</td>
<td>0.87</td>
<td>5.1</td>
<td>1.3</td>
</tr>
<tr>
<td>AMS-10-0.44</td>
<td>9.5</td>
<td>624</td>
<td>0.90</td>
<td>5.5</td>
<td>1.2</td>
</tr>
<tr>
<td>AMS-10-0.45</td>
<td>9.8</td>
<td>640</td>
<td>0.94</td>
<td>5.8</td>
<td>1.1</td>
</tr>
<tr>
<td>AMS-10-0.48</td>
<td>11.0</td>
<td>640</td>
<td>1.04</td>
<td>6.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Fig. 8. XRD patterns of mesoporous Co$_3$O$_4$ templated by AMS-10-Y.

Fig. 9. $N_2$ adsorption–desorption isotherms and pore size distributions of the mesoporous Co$_3$O$_4$ replicas templated by AMS-10-Y. The isotherms of Co$_3$O$_4$-AMS-10-0.44, 0.45 and 0.48 were moved vertically by 100, 200 and 300 cm$^3 g^{-1}$, respectively.
in the silica wall growing following the Diamond minimal surface. A reasonable explanation is the existence of ordered complementary micropores at the thinnest part of the silica wall, similar to the case of KIT-6 [37]. These ordered micropores in the silica wall facilitate the diffusion of cobalt precursor between two sets of bicontinuous meso-channels. As a result, in the thick part of the particles, a complete replication of two sets of meso-channels is achieved.

Metal oxide inverse replication provides additional structural information of the silica template AMS-10. The bicontinuous networks are visualized by this means. And as discussed above, the materials have thin silica wall (∼1.2 nm) and at the thinnest parts there are ordered complementary micropores which connect the two independent bicontinuous meso-channels.

3.4. Comparison of pore size effect in the inverse replication

As has been discussed in details above, it is clear that the pore size of template silica will greatly influence the structure of inverse Co₃O₄ replica. However, this discussion of the effect of pore size is valid when taking the pore symmetry into consideration.

SBA-15 (p6mm) normally have large-pore size and small wall thickness. When the pore size is 6.6 nm or smaller, separated nano-wires of Co₃O₄ replicas are obtained, due to a lack of micropore connections between adjacent mesopores. In the case of KIT-6 (Ia3d), when the pore size is 6.6 nm or smaller, both replication of one set and two sets of bicontinuous mesopores are replicated, indicating mesopore connections by micropores in the wall. It is worth noting that the wall thickness of KIT-6 with Ia3d symmetry (>3.6 nm) is much larger than that of SBA-15 with p6mm symmetry (2.4 nm), which may have less micropore connections without considering the pore symmetry. However, because the Ia3d structure has an inhomogeneous wall thickness, some part of the silica wall is fairly thin though the mean wall thickness is high, which may have micropore connections. Besides, ordered complementary micropore connections might also exist in Ia3d structure. Therefore, different pore symmetry differs much in inverse replication.

AMS-10 (Pn3m) materials have similar pore size to KIT-6 (Ia3d), but they have a large porosity. The change of pore size does not change the wall thickness significantly, and all of materials possess ordered micropore connections between mesopores. Therefore, the effect of pore size is ignoring, and all the replication process includes replication of one set and two sets of the bicontinuous mesopore networks.

4. Conclusion

Mesoporous silica with different pore size of p6mm, Ia3d, Pn3m symmetries are employed as hard templates to synthesize mesoporous Co₃O₄ replica. It is found that for p6mm, large-pores facilitate the replication and that for Ia3d and Pn3m, the pore size determines the extent of the replication. For p6mm, at small-pore sizes, the structure of Co₃O₄ replica collapses and isolated nanowires have been obtained; At large-pore sizes, complete replication can be achieved, retaining the original symmetry of silica template.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S (m² g⁻¹)</th>
<th>V (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₃O₄-AMS-10-0.42</td>
<td>134</td>
<td>0.23</td>
<td>1.9, 7.6</td>
</tr>
<tr>
<td>Co₃O₄-AMS-10-0.44</td>
<td>119</td>
<td>0.27</td>
<td>3.1, 8.8</td>
</tr>
<tr>
<td>Co₃O₄-AMS-10-0.45</td>
<td>151</td>
<td>0.34</td>
<td>3.6, 10.6</td>
</tr>
<tr>
<td>Co₃O₄-AMS-10-0.48</td>
<td>141</td>
<td>0.26</td>
<td>2.0, 6.6</td>
</tr>
</tbody>
</table>

Fig. 10. TEM images of mesoporous Co₃O₄ replicas prepared by (a) small-pore AMS-10-0.42 (pore size: 5.1 nm) and (b) large-pore AMS-10-0.48 (pore size: 6.7 nm) taken along [1 1 0] and [1 1 1] directions.
For \( Ia3d \) structure, at large-pore sizes two sets of the mesopores are replicated, and at small-pore sizes, both two sets and one set of the bicontinuous mesopore networks are replicated by \( \text{Co}_3\text{O}_4 \). For \( Pn3m \) structure, unlike \( Ia3d \), within the pore size range of 5.1–6.7 nm, both one set and two sets of the bicontinuous meso-channel networks are replicated. The discussion of pore size effect on replication is valid only when pore symmetry of silica template is specified.

In the inverse replication, disordered micropores in the walls of SBA-15 and KIT-6 play an important role, and ordered complementary micropores in the walls of KIT-6 and AMS-10 are the vital factors in determining the extent of replication. Inverse replication also provides structural information of silica template. It is proposed that for AMS-10, there are ordered complementary micropores at the thinnest parts of the wall, which connect the two independent bicontinuous meso-channels.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2009.04.017.

References