

Synthesis and characterization of hyperbranched mesoporous silica SBA-15

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Branched mesoporous silica SBA-15 materials have been prepared in a simple process using non-ionic surfactant in acidic conditions in the presence of metal ions.

Since the discovery of the hexagonal mesoporous materials (M41S family by Beck and coworkers,¹ SBA-15 by Stucky and coworkers,² *etc.*) considerable efforts have been made to understand their structure and control their morphology in terms of pore size (in the range 3–30 nm), wall thickness (in the range 1–4 nm) and texture³ (in micron or even millimeter range of particle size). All these properties are extremely important for the potential application of these materials. In recent years different shapes of these SBA-15 mesoporous materials (films,⁴ spheres,⁵ fibers,⁶ *etc.*) have been synthesized. There have also been several papers that report the controlled growth of small mesoporous particles.^{7,8} Recently, Liu and coworkers⁹ synthesized MCM-41 nanotubes, Zhou and Yuan¹⁰ reported paintbrush-like structures of MCM-41 and its Ti-modified derivative, while Su and coworkers¹¹ investigated the effect of Mn²⁺ ion on the morphology of MCM-41. Zhao *et al.*¹² reported the multiphase assembly of mesoporous–macroporous membranes in ethanol–water systems, in which the inorganic–organic interface plays an important role in the formation of different membrane structures.

In this paper, we report morphology control of SBA-15 ordered hexagonal mesoporous materials using a block copolymer as structure directing agent in acidic aqueous solutions in the presence of metal ions. In each synthesis[†] the chloride salts of the transition metal cations were used at a reaction stoichiometry of Si/Mⁿ⁺ = 50. Our synthesis is based on the acid mediated route, denoted as N⁰(HX⁻)I⁺, where N⁰ is the non-ionic surfactant, an amphiphilic block-copolymer, HX the acid and I⁺ is the inorganic reagent.

Very similar type IV isotherms and large desorption hysteresis were observed for all the samples, which is characteristic of mesoporous materials with 1D cylindrical channels.² A typical nitrogen adsorption isotherm is shown in Fig. 1. The properties of the mesoporous silicas calculated from the nitrogen porosimetry data are summarized in Table 1. It is evident that, compared to the original SBA-15 sample, both the specific surface area, the pore volume and the pore diameter are

higher, thus, using this small amount of metal ion can make the synthesis more efficient.

As shown by the representative XRD pattern in Fig. 1 inset, the samples possess high quality structures—three XRD lines indexed as (100), (110) and (200) reflections corresponding to a two-dimensional hexagonal structure with long-range order can be clearly seen. We note that in the case of metal ion modified samples, the (100) peak is always broader than that of the original SBA-15 sample.

Further evidence for the long-range hexagonal structure was provided by transmission electron micrograph images shown in Fig. 2(a). However, it was observed, that the morphology of the small crystallites of the SBA-15 silica strongly depended on the transition metal ions used in the synthesis mixture. While in case of Co²⁺ and Cd²⁺ ions, the SBA-15 crystallites were about 1 μm in length and 3–400 nm in diameter, Mn²⁺ ions led to smaller, octahedral shape crystallites (Fig. 2(a)). Surprisingly, in the case of Cu²⁺ ions, a branching, network-like mesoporous structure was found (Fig. 2(b)). Careful examination revealed two types of branches, as shown in Fig. 2(c). The mesoporous tubular structure separated neatly at type I branching points without disruption of the pore system, while at type II branching points, the hexagonally ordered mesoporous structure was replaced by a worm-like, disordered morphology. Type I branching points were rare compared to type II. Individually separated silica nanotubes were also observed at type II branching points (Fig. 2(d)).

The effect of different anions was also investigated. Using SO₄²⁻, NO₃⁻, CH₃COO⁻ or ClO₄⁻ anions in the synthesis mixture (with Cu²⁺ as cation), the same micron size crystallite structures were found. However, in contrast to the Cl⁻ containing product, no branched mesoporous structure formation was observed.

All the products synthesized were white and fully washed samples were free of metal ions. On the basis of the morphology as a function of different metal ions used in the synthesis mixture studied by XRD, TEM and nitrogen porosimetry, it can be stated that the polymer–ion interaction plays an important role in the templating effect. In fact, it is well-known, that metal ions form crown-ether-type complexes with polymeric PEO and PPO units,¹³ where the multivalent metal species (Mⁿ⁺) can

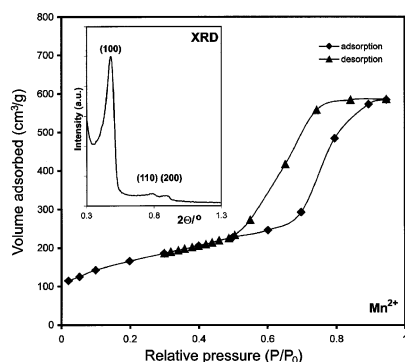


Fig. 1 Nitrogen adsorption–desorption isotherm of the Mn²⁺ modified sample. Inset shows the XRD pattern of the sample.

Table 1 Texture properties of the samples[‡]

Sample	Ion ^a	d_{100}^b /nm	SA ^c /m ² g ⁻¹	PD ^d /nm	PV ^e /cm ³ g ⁻¹
1	—	8.70	567	5.32	0.765
2	Co ²⁺	8.83	577	6.18	0.902
3	Mn ²⁺	8.70	571	6.23	0.899
4	Cu ²⁺	8.65	582	6.20	0.912
5	Cd ²⁺	8.48	636	5.07	0.816
6	Mg ²⁺	8.76	626	6.09	0.963
7	Al ³⁺	8.66	604	5.89	0.900
8	Fe ³⁺	8.23	590	5.69	0.853

^a The modifying ion used in the synthesis mixture. ^b d_{100} spacing of the characteristic reflection. ^c Specific surface area. ^d Mean pore diameter (from N₂ porosimetry). ^e Pore volume.

associate preferentially with the hydrophilic PEO moieties, because of their different binding affinities for PEO and PPO. If the synthesis mixture contains metal ions, the modified pathway can be now denoted as $N^0[(M^{n+} + H^+)X^-]I^+$, where M^{n+} is the modifying ion. Thus, the proposed assembly mechanism for these diverse mesoporous metal oxides includes PEO-metal chelating interactions in conjunction with electrostatics, van der Waals forces, etc., to direct mesostructure formation.¹⁴ Furthermore, since the structure directing effect is irrespective of the anions used in the synthesis, and only the Cl^- anion resulted in a branched, network-like structure, presumably the complex symmetry (Scheme 1) may also play an important role in the synthesis by modification of the electrostatic interaction or the local curvature energy at the interface of the inorganic silica and the surfactant. However, based on this scheme, the reason why only Cu^{2+} causes morphology changes is not clear and is a current topic of research. It may result from the peculiar preference of Cu^{2+} ions to form square planar complexes in contrast to the other metal ions investigated.

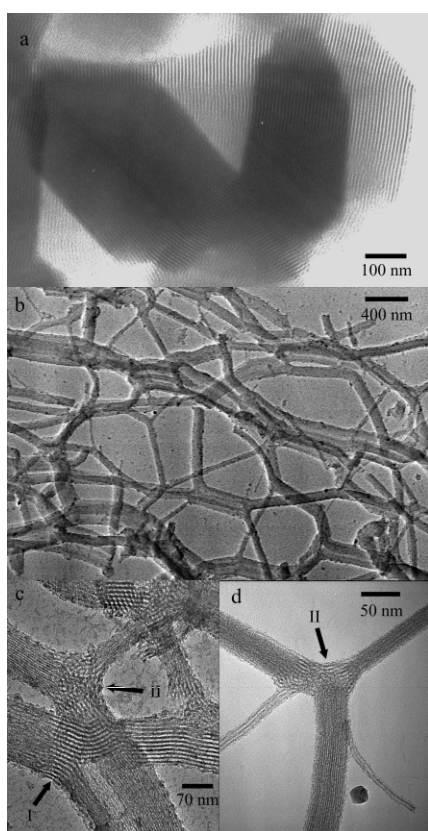
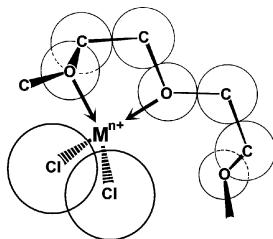


Fig. 2 TEM images of (a) Mn^{2+} modified SBA-15: (b)–(d) Cu^{2+} modified hyperbranched SBA-15. Two types of branches are seen in (c), separated individual silica nanotubes are seen in (d).



Scheme 1 Molecular model of the transition metal–PEO interaction.

In conclusion, we have shown that using a small amount of metal ion ($M^{n+}:Si = 1:50$) in the synthesis of mesoporous silica SBA-15 the microscopic structure can be modified and in the case of Cu^{2+} ions a branched, network-like structure was formed. Further studies are needed to investigate this interesting structure, including optimization of the synthesis, clear explanation of the formation mechanism, and stability considerations.

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Notes and references

† *Experimental*: mesoporous silica SBA-15 was synthesized according to the procedure developed by Stucky and coworkers.² Briefly, materials were prepared by dissolving Pluronic P-123 amphiphilic block-copolymer (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) PEO₂₀PPO₇₀PEO₂₀ (BASF)) and the corresponding transition metal salt in diluted hydrochloric acid (2 mol dm⁻³). After 1 h stirring tetraethylorthosilicate (TEOS) was added to the solution to obtain a PEO₂₀PPO₇₀PEO₂₀:cc.HCl:TEOS:H₂O = 2:15:3.6:60 mass ratio. Subsequently, the mixture was stirred for 24 h at 35 °C and then aged for 24 h at 80 °C. The solid product was filtered off and washed with deionized water. The organic structure-directing block copolymer was removed by calcination at 923 K for 24 h.

‡ *Characterization*: the SBA-15 mesoporous silica samples were characterized by a combination of physical techniques. Low-angle XRD spectra were recorded on a Philips X'Pert diffractometer, equipped with a graphite monochromator, using Mo-K α (50 kV, 30 mA) radiation. The scanning range was from 0.2–3° 2 θ with 0.01° stepsize and 5 s counting time. Transmission electron microscopy (TEM) images were obtained using a JEOL 200 kV microscope. BET specific surface areas and the porosities were calculated from the nitrogen adsorption experiments measured at 77 K. Nitrogen porosimetry data were collected using a Quantachrome Autosorb 1 surface area analyzer with 60-point analyses at a temperature of 77 K. Surface areas were calculated using the BET adsorption–desorption method and pore size distributions were analyzed by the BJH method.¹⁵

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