Fine control over the morphology and structure of mesoporous silica nanomaterials by a dual-templating approach†

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Mesoporous silica nanomaterials with varied morphologies and pore structures, including nanospheres, nanoellipsoids, helical nanorods and multi-lamellar nanovesicles, were synthesized by using cetyltrimethylammonium bromide (CTAB) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as co-templates.

Nanostructured silica materials have attracted much attention as they process practical applications in the fields of catalysis,[1] sensing,[2] adsorption,[3] drug delivery and controlled release.[4] Despite successes of the surfactant-assisted assembly synthesis of ordered mesoporous silicas, it is difficult to fabricate sophisticated mesoporous silicas using only one template. Therefore, a so-called co-template route has become the focus of controlled synthesis of mesoporous silicas. It is known from the chemistry of surfactants, various shapes and morphologies of surfactants, *e.g.*, micelles, vesicles and liquid crystal phases, can be found in mixed surfactant solutions.[5] Yu's group prepared periodic mesoporous silica hollow spheres and nanopods using fluorocarbon compounds and surfactants as co-templates.[6,7] Chiral mesoporous silica fibres, tubes and bundles were also prepared using chiral molecules and achiral surfactants as co-templates by the groups of Che[8–10] and Yang and Hanabusa,[11] respectively.

The internal structure and the external morphology of silica nanomaterials have a significant influence on their practical applications. Therefore, it is important to develop facile methods to regulate both their pore structure and surface morphology. We report here facile and finely-controlled synthesis of mesoporous silica nanomaterials (nanospheres, nanoellipsoids, nanorods with chiral channels, and multi-lamellar nanovesicles) with high yields simply by adjusting the weight ratio of co-templates of CTAB and AOT. To our best knowledge, there have been, so far, few reports both on the finely controlled synthesis of silica nanomaterials with different morphology and pore structure by adjusting a single parameter in an identical approach, and on formation of helical structures using a combination of chiral and achiral surfactants as co-templates.[12] Such a synthetic route is reported for the first time for synthesis of mesoporous silica with different morphologies.

The mesoporous silica nanomaterials were prepared in basic solution using CTAB and AOT as co-templates and tetraethoxysilane (TEOS) as silica source (for experimental details see ESI†). The calcined mesoporous silicas using weight ratios (*R*) of AOT/CTAB of 0, 0.1, 0.2 and 0.5, were named as S0, S1, S2 and S3, respectively. All the samples were characterized by small-angle X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen absorption–desorption measurements.

Fig. 1 shows the XRD patterns of calcined silicas S0–S3. S0 had a strong (10) peak (Fig. 1(a)), showing that it had a weakly ordered structure.[6] When *R* was increased, the order of the silica obtained also increased. As shown in Fig. 1(b) and (c), three characteristic diffraction peaks were recorded for S1 ($R = 0.1$) and S2 ($R = 0.2$), respectively. They could be indexed to (10), (11) and (20) diffractions, based on the two-dimensional *p*6 *mm* unit cell, indicating that these samples had highly ordered hexagonal mesoscopic structures.[4,8,13] When *R* was increased further to 0.5 (S3), no diffractions peaks were found (Fig. 1(d)), showing that a non-ordered porous material was obtained.

The morphologies of the silica samples were observed by TEM. Fig. 2 shows typical TEM images of S0–S3. Spherical particles (S0, Fig. 2(a)) of 30–60 nm in size were obtained without adding AOT. The spherical particles changed in one direction with increase of *R*, and gradually developed into

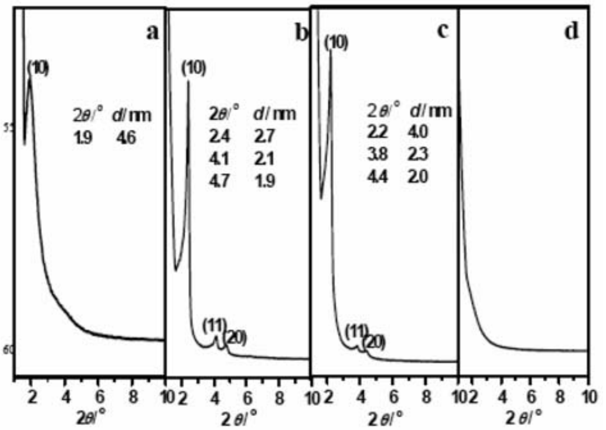

Fig. 1 Small-angle XRD patterns of calcined samples prepared at different weight ratios (*R*) of AOT/CTAB: (a) ($R = 0$, S0), (b) ($R = 0.1$, S1), (c) ($R = 0.2$, S2) and (d) ($R = 0.5$, S3), respectively.

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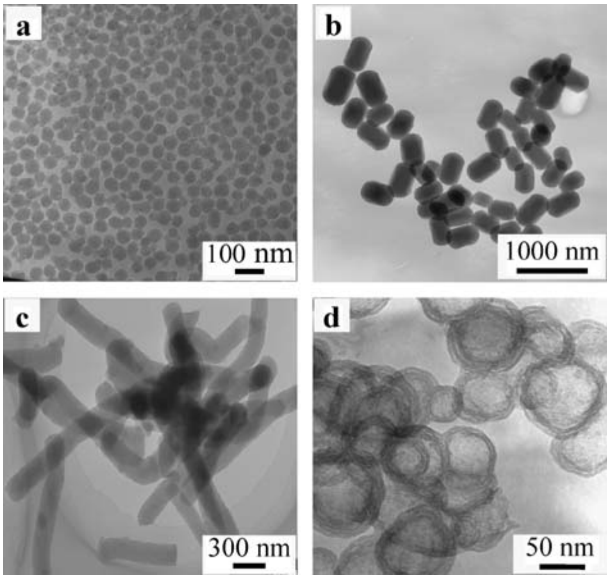

Fig. 2 TEM images of calcined samples prepared at different weight ratios (R) of AOT/CTAB: (a) ($R = 0$, S0), (b) ($R = 0.1$, S1), (c) ($R = 0.2$, S2) and (d) ($R = 0.5$, S3), respectively.

ellipsoid-like (Fig. 2(b), $R = 0.1$) and long rod-like particles (Fig. 2(c), $R = 0.2$).[7] Ellipsoid-like silica ($R = 0.1$) was 210–250 nm in outer diameter, and 330–540 nm in length, respectively. The width and the length of the long rod-like silica were in the ranges of 170–230 nm and >1 μm, respectively. When the R value was further increased to 0.5, multilamellar silica nanovesicles were obtained (Fig. 2(d)).

To shed light on the detailed internal structures of the silica samples, high-magnification TEM observations of S0–S2 were carried out (Fig. 3). Channel-like pores were clearly seen for S0 (Fig. 3(a) and (b)), which were MCM-41 type pores.[13] The streaks in Fig. 3(b) are those of ordered domains whose *c* axis is perpendicular to the line of vision.[4,8] The *d* spacing of (10) planes of S0 was estimated be *ca.* 4.7 nm, in good agreement with the XRD result (*ca.* 4.6 nm). A highly ordered hexagonal structure was observed for S1 (Fig. 3(c)), which was also evidenced by its XRD pattern with an intense (10) peak along with well-resolved (11) and (20) peaks. The streaks are those of ordered domains (10) whose *c* axis is perpendicular to the line of vision.[4,8] When R was increased to 0.2 (S2), a special internal structure was noticed, as shown in Fig. 3(d) and (e), in that a *chiral* mesoporous silica was obtained![7–11] Each visible fringe repeats the (10) interplanar spacing, and the distance between two fringes is one-sixth of a pitch, which means a 60° rotation through the center of the long axis (Fig. 3(d)).[4a,8] It was noted that there were two types of fringes that are highlighted by white and black arrows in Fig. 3(d) and (e). They correspond to the interplanar spacings (10) and (11), respectively.[4,8,10] When the electron beam was parallel to the ⟨10⟩ directions (*i.e.*, perpendicular to the page), the interplanar spacing fringes of (10) appeared.[4,8] Because the silica nanorods were not precisely perpendicular to the electron beam, the appearance of some longer (10) fringes in some places was not surprising. It is important to note that all the fringes distinctly curve in the same direction within one rod (Fig. 3(c)). Therefore, when R was 0.2, hexagonally shaped nanorods with two-dimensional chiral channels running inside were obtained.[8]

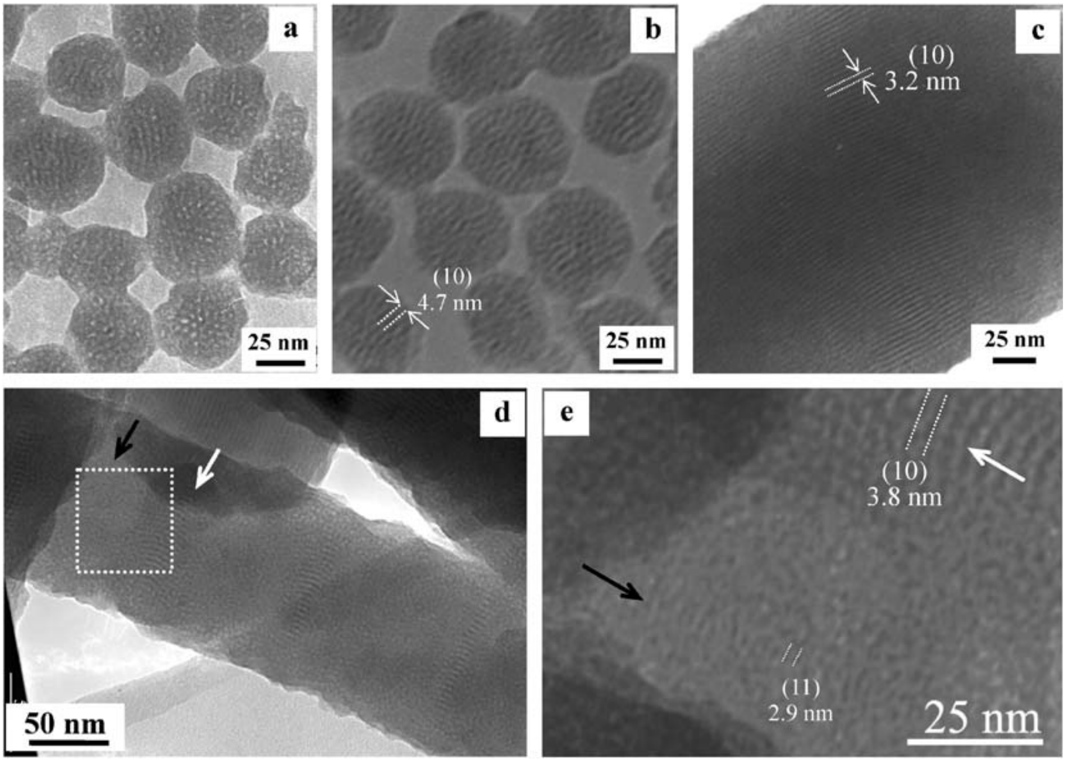

Fig. 3 High-magnification TEM images of S0–S2 showing the details of their mesostructures: (a) and (b) (S0), (c) (S1), and (d) and (e) (S2), respectively.

Nitrogen sorption isotherms obtained (Fig. S2a, ESI†) all showed type IV features. For S0, a steep increase in nitrogen uptake occurred at P/P_0 of 0.9–1.0, indicating the presence of textural (disordered) porosity.[13] S1 and S2 had similar nitrogen sorption isotherms, indicating that they had similar pore structures, in agreement with the XRD patterns. The smaller hysteresis loops of S1 and S2 featured nearly horizontal adsorption and desorption branches. This feature is normally attributed to narrow pore-size distributions. The nitrogen sorption isotherm of S3 differed from those of the other samples. S3 had a larger hysteresis loop in a relative pressure (P/P_0) range of 0.4–1.0, which should be normally attributed to narrow slit-like pores.[14] However, the larger hysteresis loop might also arise from large pores embedded in a matrix with much smaller pores.[14b] The isotherms for S0, S1 and S2 exhibited a condensation step between 0.2 and 0.35. The more pronounced condensation step for S1 and S2 indicated narrow pore-size distributions. In the case of S3, the condensation step at low pressures was poorly resolved and very broad; however, this sample had a very broad hysteresis loop closing suddenly at about 0.4 relative pressure due to pore constrictions. The results are consistent with the pore structures of multilayer hollow spheres as reported previously.[6a,14] All the samples were confirmed to have uniform mesopores with Barrett–Joyner–Halenda (BJH) pore diameters of 2.5–3 nm (Fig. S2b, ESI†). S3 had a broader pore-size distribution than S0–S2. These physicochemical parameters are summarized in Table S1 for comparison (see ESI†).

From the above results, it is clear that with an increase of R (from 0 to 0.5), the silica nanomaterials prepared using CTAB and AOT as co-templates underwent a structural transformation.[7,15] The cationic CTA^+ surfactant had a strong electrostatic interaction with the functional groups (sulfate and ester) of AOT.[9] At low R values (*e.g.*, $R = 0.1$), the AOT molecule might insert into the hydrophobic part of the CTAB micelle to form a straight hexagonal array.[16] The hexagonal array transferred from a Moire-like hexagonal array ($R = 0$) to a straight hexagonal array ($R = 0.1$), which was in good accordance with the XRD patterns (Fig. 1(a) and (b)) and TEM images (Fig. 3(a)–(c)) of S0 and S1. When the R value increased to 0.2, AOT might counteract more cationic charges of CTA^+, but might not have a significant enough influence to change the hexagonal array of the micelles.[7,15,17] The AOT molecules mainly played a role in reducing the surface energy and promoting the formation of helical morphology, as also revealed previously in other systems.[7,8] When increasing the R value further to 0.5, a bilayer structure was formed, and coalescence of the bilayer structure led to multi-lamellar silica nanovesicles.[7,16–18]

In summary, we have discovered a facile approach to finely-controlled synthesis of mesoporous silica nanomaterials of different structures, including nanospheres, nanoellipsoids, helical nanorods and multi-lamellar nanovesicles, simply by tailoring the weight ratio of two common surfactants (AOT and CTAB). The current approach may also be applicable to the synthesis of ordered mesoporous nanomaterials of other compositions. The results not only help us better understand chirally self-assembled supramolecules in nature, but also provide a flexible route to the design and construction of new functional nanoarchitectures, which may be useful for shape-selective separation, adsorption, and catalysis, *etc*.

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