Mesostructured Silica with Bush-like Morphology and Its Transformation into Nanometer-sized Mesoporous Silica Particles

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A novel bush-like morphology of mesostructured silica having stems, branches, and leaves has been grown under mild basic conditions via auxiliary solvent evaporation induced self-assembly process.

The design of porous silica materials with complex forms, using surfactant assemblies as supramolecular templates, has ramifications in diverse areas particularly in catalysis, biomolecule separation, drug delivery system, medical implants, semiconductive nanostructures, and optoelectronic devices.[1,2] The great advantage of mesoporous silica is an ease of macroscopic morphological control; numerous morphologies such as nanospheres, films, fibres, threads, monoliths, disc-like, spiral, and toroidal have been obtained.[2,3] Among aforementioned morphologies, mesoporous silica films and fibres are extensively studies, and several studies on their successful applications such as dye lasers, photoluminescent films, and waveguides have been published.[3,4] Earlier, the formation of hairy tube-like mesoporous materials with polymer brushes at the wall was also reported.[5]

In this communication, we describe a simple and rapid procedure for constructing mesostructured silica materials with remarkable bush-like morphology having stems, branches, and leaves. Our strategy combines very mild basic conditions and auxiliary solvent-evaporation-induced self-assembly approach.[3] In that the formation involves short-range forces with energy of self-assembly, including shape fluctuation and interaggregate interactions. Such shorter-range cooperative assembly of silica and surfactant creates unique ordered composite mesostructures wherein balanced energy exerts morphological control during the formation of silica gel or crystals. Silica mesostructured phases prepared in this fashion are shown to have unique structural growth compared to conventional synthetic procedures.[6] With this in mind, we exploited the controls in shape fluctuation between secondary particle and used ethanol as an auxiliary solvent and ammonia solution as a mild base to create interaggregate interactions. Our reaction conditions favour bush-like morphology, and we used scanning electron microscopy (SEM) to catalogue the fundamental bush-like topology and surface patterns, and X-ray diffraction (XRD) analyses for further insights into underlying mesostructures.

Tetraethoxysilane (TEOS) was used as a silica source. A typical procedure was as follows: the surfactant cetyltrimethylammonium bromide (C_{16}TMABr; 0.4 g) was dissolved in 14.6 g of water. Then, 4.9 g of ethanol was added. To this solution, 0.1 g of aqueous ammonia solution (≈25%) was slowly added. Finally 1.25 g of TEOS was introduced with vigorous stirring at room temperature. A white suspension was quickly formed within 10–15 s. Sample aliquots were immediately coated on the smooth glass substrates after 1, 5, 10, 15, 30, 60, and 120 min of reaction with continuous stirring. Mesostructured silica of bush-like morphology were grown on the glass substrates via so-called solvent-evaporation-induced self-assembly process.[3]

Figure 1 shows several representative SEM images of mesostructured silica with bush-like morphology. With this information, we deduce that bush-like morphology can be generated owing to rapid propagation of condensation reaction on solvent evaporation from the gel solution soon after the TEOS was introduced. Figure 1a shows the bush-like morphology after 1 min of the reaction. However, the bushes obtained after 5 min of reaction were with denser branches and leaves (Figure 1b) confirming the further advances in balanced hydrolysis–condenstation reaction within initial silica gel solution. Whereas, the leaf shape and size in the bushes were somewhat affected with prolongation of reaction time. The bushes with highly dense branches and leaves could be observed after 10 min (Figure 1c) and 15 min (Figure 1d) of reaction. This can be simply related to growth exerted shape fluctuation as well as self-assembly forces due to interaggregate interactions. Figure 1d′ shows an enlarged fraction of bushes grown after 15 min of reaction, estimating an average stem and leaf thickness nearly 3 μm and 0.8–1.3 μm, respectively. While Figure 1d″ shows an actual relative density of bush-like morphology, and that estimates an average length of stem and leaf nearly 500 and 20 μm, respectively. In addition, the leaf size was somewhat shortened, having

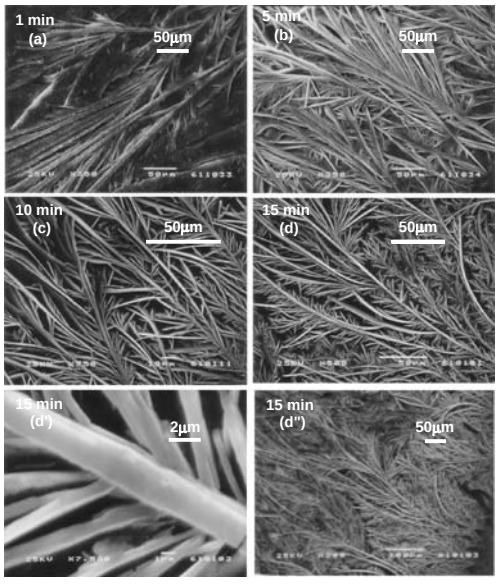

Figure 1. Reaction time dependence of the density of branches and leaves in the bush-like morphology, as seen with SEM.

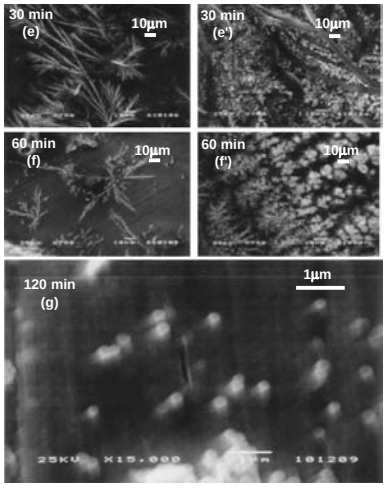

Figure 2. Reaction time dependence of the density of branches and leaves in bush-like morphology.

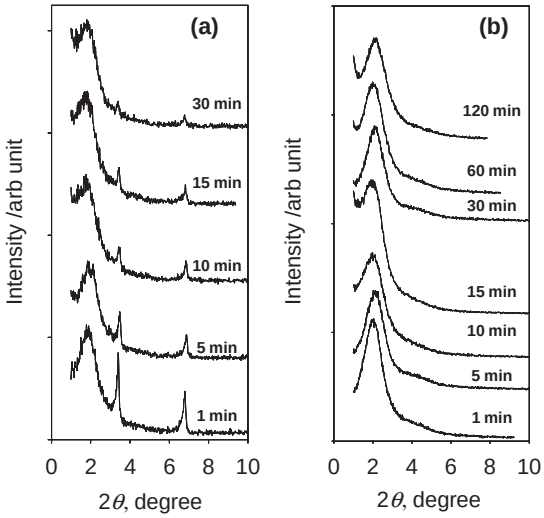

Figure 3. X-ray diffraction patterns of (a) as-grown mesostructured bushes with varied reaction time and (b) after calcinations confirming the mesoporous nature of the materials.

sharp edges compared to bushes grown until 5 min of reaction time.

Further, we found that after prolonged reaction time (≈30 min) the silica gel mixture was unable to grow the bushes with high density of branches and leaves (Figure 2e). Wherein, the solvent-evaporation-induced self-assembly of bushes begins to disintegrate into nanometer-sized silica particles (Figure 2e′). In event of prolongation of reaction, such disintegration of bush-like morphology was further accelerated, and surprisingly, after 60 min of reaction the most of the stems, branches, and leaves of bushes were disintegrated into nanometer-sized silica cluster or particles (see Figures 2f and 2f′). Finally, after the 120 min of reaction a well-defined morphology of nanometer-sized mesostructured particles could be discreetly observed (Figure 2g). Also, after calcinations only nanometer-sized particles morphology was observed.

As-grown bushes were scratched from the glass substrate and subsequently subjected to X-ray diffraction (XRD) analysis for further insights into the mesostructured nature and the surface shape of the bush-like morphology. Figure 3 depicts the X-ray diffraction patterns of the grown bushes before and after calcinations at 550 °C for 6 h in air-flow. Depending on the reaction time, as-grown bushes showed a low angle diffraction [d_{10}] reflection peak with d spacing between 4.7–4.9 nm, which was found increasing with reaction time (Figure 3a). In addition, two reflections [100] and [200] with constant spacings of 2.6 and 1.3 nm, respectively, also were observed in the XRD pattern, corresponding to lamellar nature of surfactant molecules, which later disappeared upon calcinations. Figure 3b displays only one reflection peak [d_{10} spacing between 4.2 and 4.5 nm] confirming the mesophase of silica with bush-like morphology. Nitrogen adsorption isotherm of the representative mesoporous bushes grown after 15 min of reaction time exhibits clearly type IV isotherm with small H_2 type adsorption–desorption hysteresis at relative pressure above ≈0.4. The pore diameter calculated from the adsorption branch by the BJH (Barrett–Joyner–Halenda) method was 2.4 nm, while BET (Brunauer–Emmett–Teller) surface area and the primary mesopore volume were 652 $m^2\ g^{-1}$ and 0.76 $cm^3\ g^{-1}$, respectively.

As seen with SEM (Figure 2g), an average particle size of resulted mesoporous nanometer-sized particles after complete disintegration of mesostructured bush-like morphology was nearly 200 nm. Additional insights into the growth of mesoporous bushes can rely on the choice of reaction parameters and hydrolysis–condensation reaction controls which usually govern by diffusion or free energy of self-assembly functions. Therefore, we have evidently demonstrated that auxiliary solvent-evaporation-induced self-assembly process under very mild basic conditions is able to create remarkable bush-like mesostructured silica having stems, branches, and leaves. Such bush-like morphology could be particularly important for functionalized mesoporous silica materials in diverse applications wherein the dendrimer materials have been currently in use.

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