

Low Temperature Synthesis of CdSiO₃ Nanostructures

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Descreve-se a síntese de nanoestruturas de CdSiO₃ cristalino como fase única a 580 °C; ao que sabemos, esta é a mais baixa temperatura de formação observada até o presente para este composto. A formação da fase desejada ocorre somente a partir de 580 °C, já que a 570 °C os picos de difração estão deslocados para menores ângulos em relação ao padrão JCPDS 85-0310. A fonte de silício influencia diretamente a morfologia do material: Na₂SiO₃ leva à formação de nanopartículas na forma de agulhas, ao passo que sílica mesoestruturada de alta área superficial leva a partículas coralóides. A difratometria de raios X em baixo ângulo mostra que o caráter mesoestruturado da sílica precursora não se mantém no CdSiO₃ resultante. A microscopia eletrônica de varredura sugere que, neste caso, haja uma transição da morfologia esférica do precursor para a morfologia em forma de agulhas do material obtido a partir de Na₂SiO₃. A área superficial do precursor de sílica utilizado tem influência direta na formação de CdSiO₃, pois o uso de sílica comercial de menor área superficial não resulta no produto desejado.

We report the synthesis of single-phase, crystalline CdSiO₃ nanostructures at 580 °C; to the best of our knowledge, this is the lowest temperature at which this material is reported to form. The desired phase does not form below 580 °C, since the diffraction peaks are shifted to lower angles in the material treated at 570 °C when compared to JCPDS Card No. 85-0310. The source of silicon has strong influence on the product morphology: Na₂SiO₃ yields single-phase CdSiO₃ in needle-shaped nanostructures, while high surface area mesostructured SiO₂ yields coralloid-shaped particles. Low angle X-ray diffractometry reveals that the mesostructured nature of the silica precursor is not maintained in the resulting CdSiO₃. Scanning electron microscopy suggests that in this case a transition occurs between the spherical morphology of the precursor and the needle-shape morphology of the material prepared from Na₂SiO₃. The surface area of the silica precursor has a strong influence in the reaction, since the use of commercial silica with a lower surface area does not yield the desired product.

Keywords: cadmium metasilicate, morphology control, molten precursor method

Introduction

In recent years, compounds that exhibit the property of long lasting phosphorescence (LLP) have become of great interest. This phenomenon is observed when a compound is capable of absorbing visible and UV light, storing the energy and releasing it as visible light, resulting in a long lasting afterglow in the dark.¹ These materials have a wide range of applications, such as emergency lighting and road signs, and medicinal applications are possible in principle.^{2,3} The phenomenon has been known since ancient times and a good example is the Stone of Bologna, studied by Galileo himself, which shows a yellow-orange

afterglow when exposed to sunlight due to the presence of BaS impurities.⁴⁻⁶

The silicate family is an attractive class of materials for almost any application due to its interesting properties such as water and chemical resistance, visible light transparency, color variety upon doping and especially ease of preparation.⁷⁻¹⁰ Cadmium metasilicate, CdSiO₃, is a promising material due to its low dimensional structure, which consists of a one-dimensional chain of edge-sharing SiO₄ tetrahedral units with metal cations compensating the negative charge.^{11,12} This type of structure permits easy insertion of ions into the host lattice which can be used to tune the excitation energy storage and subsequent emission at room temperature.¹³ In the last decade, a series of long-lasting phosphors based on CdSiO₃ have

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been prepared, with different colors based on the dopant. Examples include CdSiO₃:Y, La, Gd, Lu (indigo),¹⁴ CdSiO₃:Sm³⁺ (pink),¹⁵ CdSiO₃:Pr³⁺ (reddish-orange),¹⁶ and CdSiO₃:Dy³⁺ (white).¹⁷ Also, different colors have been obtained through the combination of suitable dopants.¹⁸ The so-called conventional solid state route for preparing CdSiO₃ consists of thoroughly mixing the precursors (generally CdCO₃, SiO₂ and the dopant oxide) followed by heating this mixture above 1000 °C for at least 3 h.^{15,18,19} This method has some disadvantages, such as high energy consumption and inhomogeneous mixing, resulting in irregularly shaped and aggregated particles.²⁰ There have been some recent successful attempts at preparing CdSiO₃ at lower temperatures using different precursors. The material has been obtained at 900 °C for 60 min via a sol-gel method²¹ and CdSiO₃:Mn²⁺ has been grown on Si(100) substrates via a vapor-phase deposition process at 700 °C for 60 min.²² In this case, nanowire bundles attached to the substrate are obtained, a morphology different from that normally observed when the conventional high-temperature solid state route is employed.

In this contribution we report the synthesis of single-phase CdSiO₃ using a molten reactant route in which one of the reactants is in the molten state, since CdCl₂ has a melting point of 564 °C. Molten salt synthesis is a simple, versatile and cost-effective strategy to prepare high-purity, single crystalline phase materials at lower temperatures and shorter reaction times when compared to conventional solid state methods.^{23,24} Above the melting point of the salt, the precursor molecules/units diffuse rapidly through the highly ionic medium, resulting in nucleation and growth of the desired phase. This step is extremely sensitive to reaction conditions such as salt species, amount of salt, reaction temperature and duration.²⁵ Once the reaction is complete, any excess salt can be easily removed by washing with deionized water.

Using this approach, we have obtained CdSiO₃ at 580 °C for 60 min using CdCl₂ and two different Si sources: commercial sodium metasilicate, Na₂SiO₃, and a high surface area mesostructured SiO₂ obtained by a surfactant-template synthesis. Our synthesis conditions, 580 °C for 60 min represent, to the best of our knowledge, the lowest temperature and the shortest time at which pure, single-phase crystalline CdSiO₃ is reported to form.

Experimental

Synthesis of mesostructured silica

Mesostructured silica was prepared as follows: 0.6 g of hexadecyltrimethylammonium bromide (CTAB, Sigma) was added to a mixture of 2.0 mL of 2 mol L⁻¹ NaOH

and 180 mL of water at 80 °C. After 30 min, 3.0 mL of tetraethyl orthosilicate (TEOS, Aldrich) were added dropwise under fast stirring and the resulting suspension was kept at 80 °C for 2 h. The suspension was allowed to cool to room temperature and was filtered and thoroughly washed until the pH of the filtrate was between 6.5 and 7. The material was dried overnight at 80 °C and then heated at 550 °C for 3 h to eliminate excess CTAB. This mesostructured silica shows a narrow pore size distribution with an average pore diameter of 4.6 nm, a pore volume of 0.96 cm³ g⁻¹ and a surface area of 1139 m² g⁻¹.

Synthesis of CdSiO₃ nanoparticles

All reagents were used as received. CdSiO₃ powders were prepared using CdCl₂ (Merck) as the cadmium source and two different sources of silicon: commercial sodium metasilicate, Na₂SiO₃ (Vetec) and a mesostructured silica obtained by the surfactant-templating route described above. The reagents (1:1 Cd:Si molar ratio) were mixed and ground for 10 min in an agate mortar using small amounts of ethanol to aid in mixing. The resulting thick slurry was dried overnight at 60 °C, after which it was ground again. This dry mixture was heated at 580 °C for 60 min using a 5 °C min⁻¹ ramp, and was allowed to cool overnight inside the oven. One experiment using CdCl₂ and Na₂SiO₃ was also done at 570 °C. The resulting CdSiO₃ powders were thoroughly washed in deionized water until no Cd²⁺ could be detected by addition of S²⁻(aq) to the filtrate and no Cl⁻ could be detected by addition of Ag⁺(aq). For clarity, the material prepared using sodium silicate will be called SS-CdSiO₃ and the material prepared using mesostructured silica will be called MS-CdSiO₃.

The CdSiO₃ nanostructures and the mesostructured SiO₂ precursor were characterized by X-ray diffraction (XRD, Shimadzu Maxima XRD-7000, CuK_α, 15.418 nm, 2° per min), scanning electron microscopy (SEM, JEOL JSM-7401 FESEM, operating in SEI mode at 5 kV), transmission electron microscopy (TEM, Zeiss CTEM 902, operating at 80 kV), and focused ion beam microscopy (FIB, FEI Nova 200 Dual Beam SEM/FIB, 5 kV). The BET surface areas given as Supplementary Information (Figure S2) were determined by nitrogen adsorption (Quantachrome Nova 1000e Surface Area Analyzer).

Results and Discussion

Figure 1 shows the XRD patterns of CdSiO₃ (JCPDS Card 35-0810) (a), SS-CdSiO₃ (b) and MS-CdSiO₃ (c).

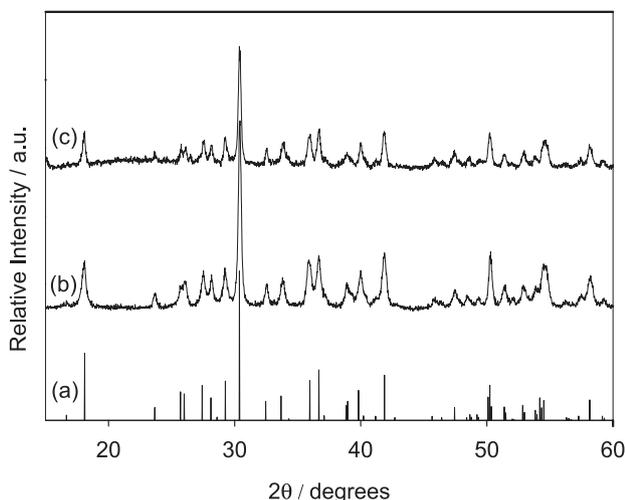


Figure 1. XRD patterns for (a) JCPDS Card No. 35-0810; (b) SS-CdSiO₃; (c) MS-CdSiO₃.

A comparison of the diffractograms with JCPDS Card No. 35-0810 (Figure 1a) confirms that SS-CdSiO₃ consists of pure, single-phase CdSiO₃, whose structure is expected to be similar to that of pseudowollastonite, CaSiO₃.¹⁰ We can also see that MS-CdSiO₃ is slightly less crystalline and exhibits a halo between $2\theta = 20$ and 30° . Sodium metasilicate is sometimes also described as Na₂O·SiO₂, and sodium oxide can react with silica to form the silicate structure which, in the presence of molten CdCl₂, forms the desired product. The attack of SiO₂ by Na₂O prior to CdSiO₃ formation probably leads to higher crystallinity. The XRD patterns of the materials obtained from CdCl₂ and Na₂SiO₃ at 570 °C for 1 and 5 h (Figure S1) are almost identical to that obtained at 580 °C for 1 h, but are shifted by 0.15° to higher values of 2θ (for example, the strongest peak occurs at $2\theta = 30.40^\circ$ and 30.55° for the samples heated at 580 and 570 °C respectively). This indicates that, although the material forms at 570 °C, that is, soon after the melting of CdCl₂, the ordering of the structure is not complete below 580 °C.

The use of a high surface area mesostructured silica also yields CdSiO₃, although with a somewhat lower crystallinity, as evidenced by the broader, less intense XRD peaks. The broad halo between $2\theta = 20$ and 30° indicates that the reaction is not complete, and some amorphous SiO₂ remains. However, low-angle X-ray diffraction (Figure 2) shows that the mesostructure of silica is lost upon the partial conversion to CdSiO₃. At the reaction temperature, we expect SiO₂ to be less reactive than the Na₂O present in the metasilicate precursor. In this case the precursor surface area does play a fundamental role, allowing a more effective contact between the molten CdCl₂ and the Si source. When we used commercial fused silica with a lower surface area (354 m² g⁻¹) as the Si source, no CdSiO₃ was formed at 580 °C for 1 h.

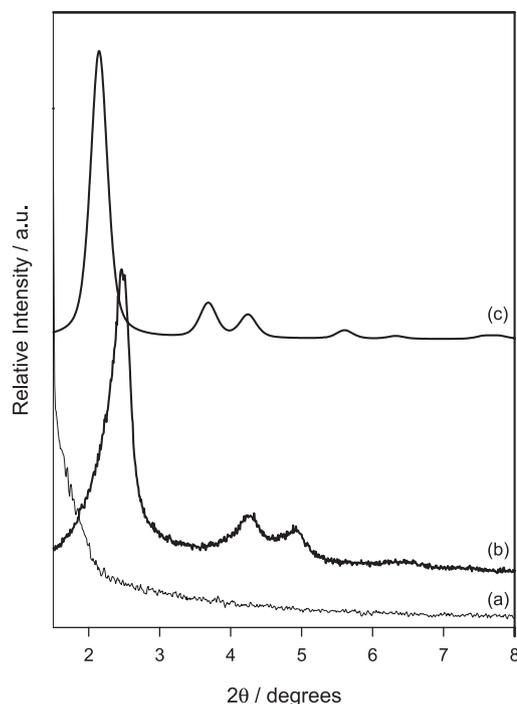


Figure 2. Low angle X-ray diffractograms of MS-CdSiO₃ (a) and of the mesostructured silica used in this work (b). For comparison, the JCPDS card for MCM-41 silica is also shown (c).

The SEM results are shown in Figure 3. The images show that there is a significant influence of the Si source on the morphology of the resulting product which, in

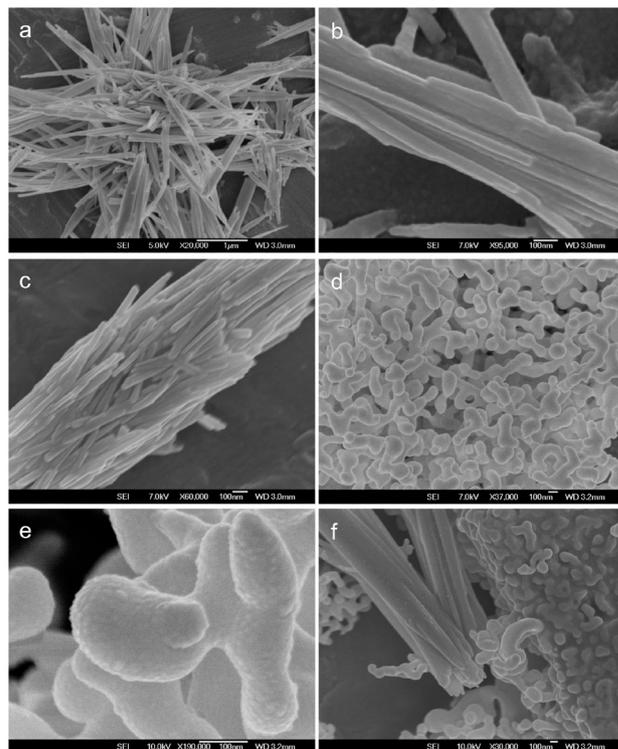


Figure 3. SEM images of SS-CdSiO₃ (a-c) and MS-CdSiO₃ (d-f).

both cases, is very different from the large aggregates seen when the conventional solid state route is used. The material SS-CdSiO₃ (Figure 2 a-c) is composed of needle-shaped nanoparticles which reflect the low dimensionality of the crystal structure. The individual needles are 1-4 μm long by 50-100 nm wide and can be arranged in bundles forming long wires with diameters in the micrometer range, as shown in Figure 2c. This type of morphology cannot be observed in CdSiO₃ prepared by the conventional high-temperature solid state reaction because the high temperatures and long heating times favor particle coalescence into irregular agglomerates. In contrast, the material MS-CdSiO₃ (Figure 3 d-f) shows a coralloid morphology with approximate diameters around 100 nm. The coralloid shape is an indication that CdSiO₃ forms initially in the spherical shape of the precursor silica particles (Figure S3). This means that molten CdCl₂ diffuses into the mesostructures, covering their surface and reacting to form CdSiO₃. The presence of elongated structures in Figure 3f suggests that heating at higher temperatures may lead to the formation of the elongated structures seen in SS-CdSiO₃. This morphology control may have important implications when using these materials as a matrix for long lasting phosphorescence, especially for medical applications, where the shape and size of the particles may determine their path through the human body. To check if these needle-shaped particles are nanotubes, which should be hollow, SS-CdSiO₃ was observed by FIB microscopy and TEM as shown in Figure 4. The FIB images (Figure 4 a-b) show that the individual nanoparticles have an approximately circular cross-section, diameters as small as 25 nm,

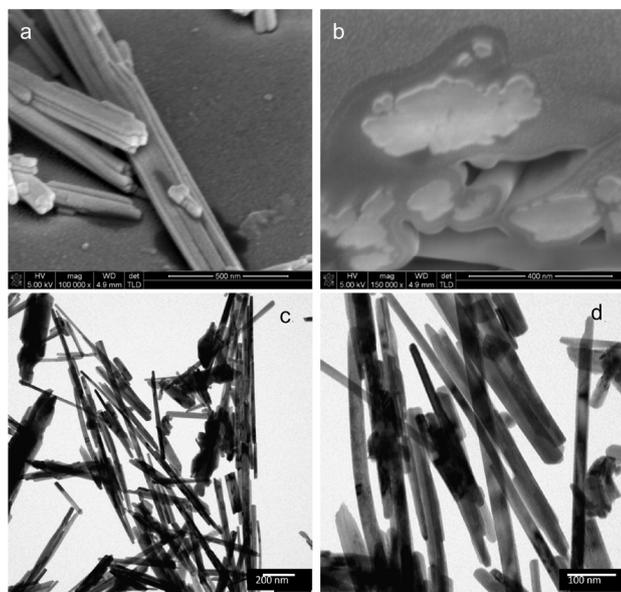


Figure 4. FIB (a, b) and TEM images (c, d) of SS-CdSiO₃.

and are not hollow, which means that they are best described as nanorods. Transmission electron microscopy (Figure 4 c-d) shows that the primary nanoparticles are 500-700 nm long by 20-50 nm wide, with high aspect ratios, varying from 10:1 to 35:1.

Conclusions

CdSiO₃ nanostructures have been prepared at the lowest temperature and shortest reaction times known to us, using two very simple synthetic routes. The use of molten CdCl₂ as a reagent in a molten salt-type approach yields pure, single-phase nanorods when Na₂SiO₃ is used as the Si source, while a coralloid morphology, representing a transition from spherical to needle-like form, is observed when the Si source is high surface area mesostructured SiO₂. In this case, the conversion is not complete and amorphous silica is still present. This is a very promising method because it is simple, straightforward and cost-effective. The choice of an adequate precursor allows a morphology control of the resulting particles, with possible implications in medical applications.

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

Acknowledgments

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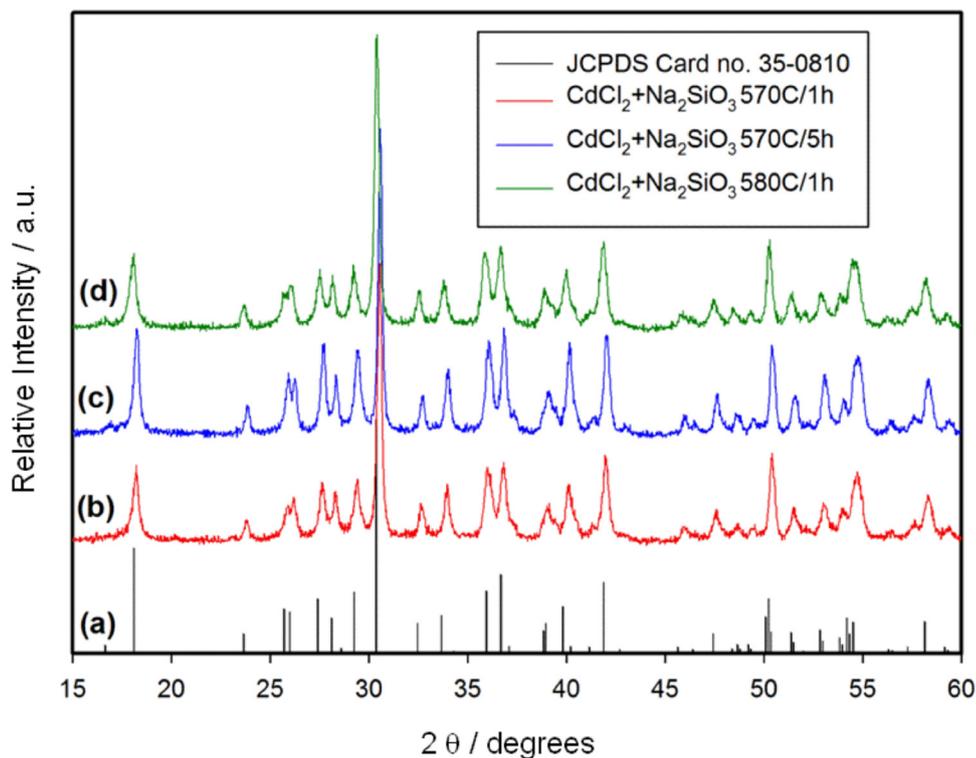


Figure S1. X-ray diffractograms. (a) JCPDS Card 35-0810 (CdSiO₃); (b) material resulting from heating stoichiometric amounts of CdCl₂ and Na₂SiO₃ at 570 °C for 1 h; (c) material resulting from heating stoichiometric amounts of CdCl₂ and Na₂SiO₃ at 570 °C for 5 h; (d) material resulting from heating stoichiometric amounts of CdCl₂ and Na₂SiO₃ at 580 °C for 1 h. All heat treatments were followed by cooling overnight.

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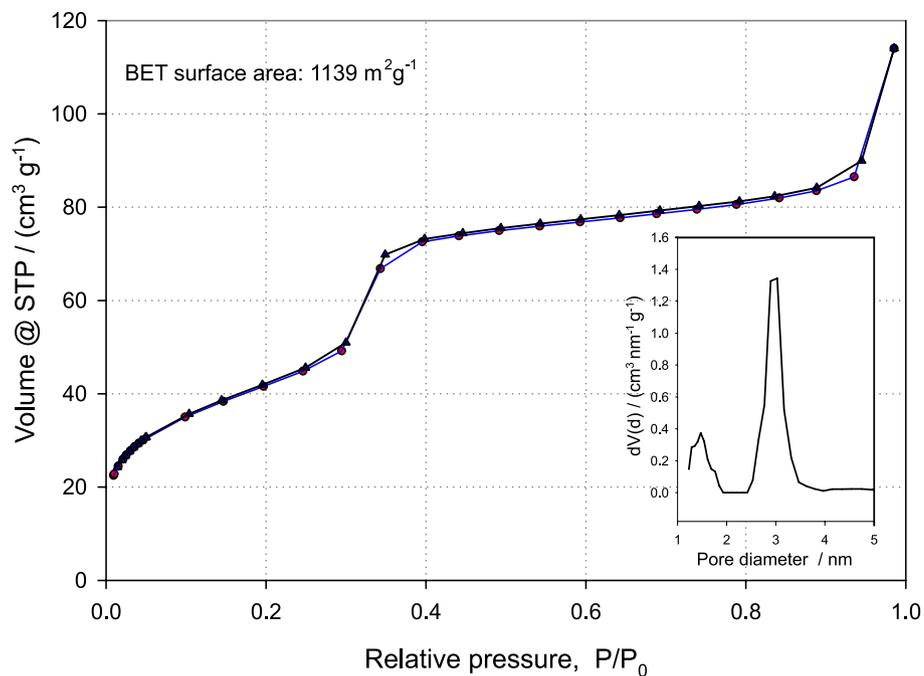


Figure S2. Nitrogen adsorption / desorption isotherm and BJH pore size distribution (inset) for the mesostructured silica used in this work.

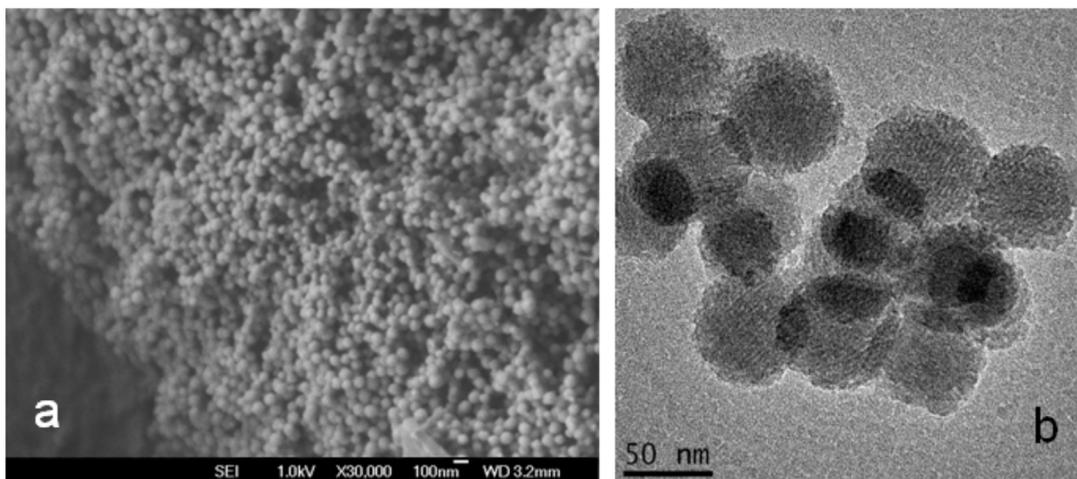


Figure S3. Scanning (a) and transmission (b) electron micrographs of the mesostructured silica used in this work.