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## ARTICLE

# A porosity difference based selective dissolution strategy to prepare shape-tailored hollow mesoporous silica nanoparticles

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Adem Yildirim<sup>a,b\*</sup> and Mehmet Bayindir<sup>a,b,c\*</sup>Received 00th January 2014,  
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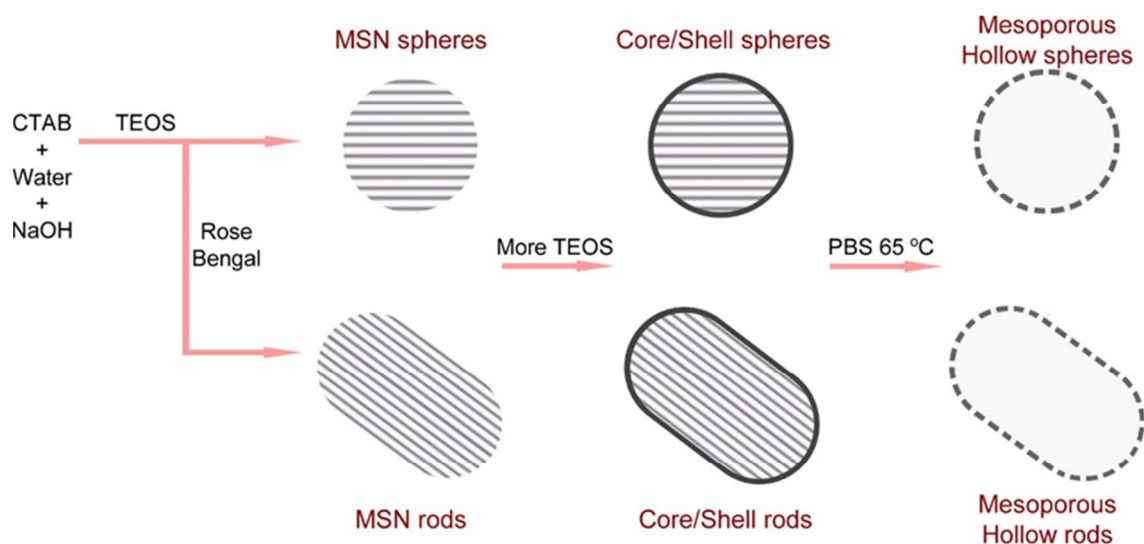
This article reports a general method to prepare hollow mesoporous silica nanoparticles with tailored morphology. The method is based on selective dissolution of porous cores of solid silica shell/porous silica core nanoparticles in mild conditions without the need of corrosive or toxic etchants. First, core/shell nanospheres or nanorods are prepared in a one-pot reaction. Then, mesoporous cores of the nanoparticles are selectively dissolved by incubating them in phosphate buffered saline (PBS) at 65 °C for one day. Surprisingly, shells of resulting hollow particles contains both small and large mesopores which makes the particles very suitable for adsorption and desorption of wide range of molecules. In addition, we proposed a mechanism for selective dissolution of porous cores of the core/shell nanoparticles.

## Introduction

Hollow silica nanostructures are attracting a great deal of interest in many research areas including catalysis, controlled drug delivery, bioimaging, optical coatings and absorbents due to their unique properties such as high surface area and pore volume, ease of surface functionalization, chemical stability and low toxicity.<sup>1-3</sup> They are often prepared using template based methods in which a variety of hard<sup>4-11</sup> (polymer or inorganic micro/nano-particles) or soft<sup>12-19</sup> templates (droplets, bubbles, micelles etc.) can be applied. However, template based methods have some drawbacks which prevent their widespread applications. For instance, hard templating methods have tedious multistep and time-consuming procedures including core synthesis, surface functionalization of core, silica deposition and core etching. Soft template based methods, on the other hand, involves less synthesis steps; however products of these methods are often have ill-defined shapes and polydisperse in size due to deformability of soft-templates.<sup>1</sup> Recently, templateless or homogenous templating methods such as surface protected etching<sup>20-22</sup> and selective etching<sup>23-28</sup> have emerged to fulfil the need for simple, effective and scalable synthesis of hollow silica nanostructures. However, these methods usually require corrosive and toxic etching agents (strong alkaline or HF solutions) to selectively etch cores of solid silica particles. A few recent works reported that under the mild conditions (water or slightly acidic solutions) silica nano/microparticles can go spontaneous structural change from solid spheres into hollow particles.<sup>29-33</sup> Unfortunately, in these methods a special care must be taken to control the shell thickness and particles morphology since they are very dependent to the reaction conditions such as pH, temperature, and etch time. Also, the shells of resulting hollow particles usually do not have accessible mesopores which restricts their

applications in many fields such as controlled drug release, catalysis and pollutant adsorption. In addition, the shape of the hollow particles prepared through spontaneous structural change process is generally limited with spheres since their synthesis often started with spherical Stöber silica nanoparticles.<sup>34</sup> Other than spheres, rods or tubes can be more desired for some applications. For example, rod shaped particles are proved to be more effective in biological applications than their spherical counterparts due to their higher cellular uptake.<sup>35</sup> Overall, facile and scalable preparation of hollow silica nanostructures with tailored shape and porosity is still a great challenge.

In this article, we report a porosity difference based selective dissolution strategy to prepare hollow silica nanospheres and nanorods with mesopores on their shells using a mild etching agent; phosphate buffered saline (PBS) (Fig. 1). The method is based on the selective dissolution of mesoporous silica cores of solid silica shell/mesoporous silica core nanoparticles, which gives a good control over particle size, shell thickness, porosity and particle shape (sphere or rod). The method involves two steps; (i) synthesis of core/shell nanospheres or nanorods in a one pot reaction and (ii) selective etching of mesoporous cores in PBS. The particle morphology can be controlled using rose Bengal (RB) dye. Rod-shaped mesoporous silica nanoparticles (MSNs) with controllable aspect ratio can be prepared in the presence of RB; in the absence of RB particles are spherical. Solid silica shells can be coated over these particles by simply addition of excess silica precursor during the synthesis. To our surprise, during the hollowing process, mesopores developed on the solid silica shells which provides accessibility to the hollow interior of the particles.



**Fig. 1** Schematic representation of synthesis of hollow nanospheres and nanorods. In the presence of RB dye rod-shaped particles are formed. Addition of excess TEOS during the reaction produces uniform silica shell around particles. PBS selectively dissolves the cores and creates mesopores on the shells of the particles.

## Experimental Section

**Materials.** Cetyltrimmoniumbromide (CTAB), F127 pluronic polymer, and Rose Bengal were purchased from Sigma Aldrich (USA). Tetraethyl orthosilicate (TEOS) was purchased from Merck (Germany). All chemicals were used as purchased.

**Preparation of mesoporous silica nanospheres and nanorods.** Nanospheres were prepared by modifying previous reports.<sup>36–38</sup> Briefly, 200 mg CTAB was dissolved in 95 mL of water and 1 mL of F127 solution (5 mg/mL in water) and 0.7 mL of 2 M NaOH were added onto this solution. Then the reaction mixture was heated to 80 °C while stirring vigorously (600 rpm). After temperature was fixed at 80 °C, 1.2 mL of TEOS was rapidly added and reaction mixture was further stirred for 2 h. Finally, reaction solution was cooled down to the room temperature and particles were collected by centrifugation at 9000 rpm for 20 min and washed with water twice. To synthesize nanorods, we added appropriate amount of RB (for example 10 mg for the particles with the aspect ratio of 1.9) which is dissolved in 2 mL of water, to the reaction mixture after addition of TEOS. Other parameters were same with the nanosphere synthesis.

**Preparation of core/shell nanoparticles.** To prepare core/shell particles we added appropriate amount of additional TEOS (0.5 to 3 mL) after 1 h of first TEOS addition and reaction mixture was further stirred for 1 h. For example, to prepare the nanoparticles with 8 nm shell thickness we added 1 mL of TEOS in the second step. Other parameters were same with the nanosphere or nanorod synthesis.

**Preparation of hollow nanoparticles.** Cores of the core/shell particles were dissolved by incubating the particles in PBS (10 mM, pH 7.4) at 65 °C for 1 d under gentle stirring. Particle concentration in PBS solution was 0.5 mg/mL for nanospheres and 1 mg/mL for nanorods. Particles were collected by

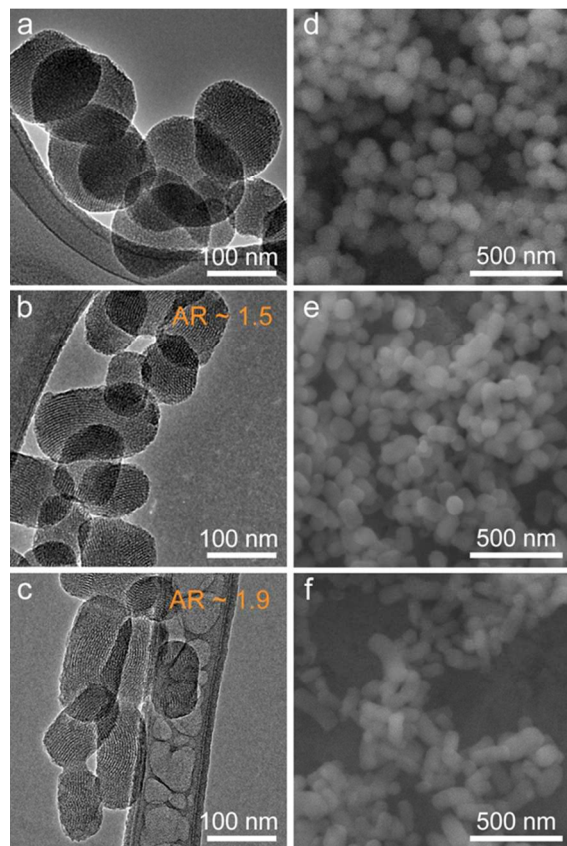
centrifugation at 9000 rpm for 20 min and washed with water twice.

**Surfactant removal.** In the final step, nanoparticles, (nanospheres, nanorods, core/shell particles of hollow particles) were calcinated at 550 °C for 5 hours (ramp rate was 5 °C/min) to remove the CTAB surfactant and RB molecules.

**Characterization.** Transmission electron microscopy (TEM) images were obtained using a Tecnai G2 F30 (FEI) microscope. The scanning electron microscopy (SEM) images of particles were obtained using an E-SEM; Quanta 200F (FEI). FTIR spectra of nanospheres were obtained by using a Fourier transform infrared spectrometer (FTIR, Vertex 70, Bruker). Surface area, pore volume and pore size distribution of the particles were determined using an iQ-C (Quantachrome). X-ray powder diffraction (XRD) spectra of the particles were taken using an X'Pert Pro (Panalytical).

## Results and Discussion

**Effect of RB on Morphology of MSNs.** Fig. 2 shows the effect of RB on the morphology of MSNs. In the absence of RB, particles are almost spherical (Fig. 2 a,d) which is typical for MCM-41 type MSNs.<sup>36</sup> Average particle size of spherical MSNs was calculated to be around 120 nm from the TEM images. Interestingly, in the presence of 5 mg of RB (Fig. 2 b,e) rod-shaped MSNs (aspect ratio is ~1.5) was obtained. Doubling of the RB amount (10 mg) increases the aspect ratio of particles to ~1.9 (Fig. 2 c,f). Average particle width and length for rod-shaped MSNs prepared using 10 mg of RB were determined to be around 75 nm and 145 nm, respectively from TEM images. Further increasing the RB amount (20 mg), however, result in a mixture of polydisperse spheres and very long helical rods with aspect ratios even larger than 10 (see ESI<sup>†</sup>, Fig. S1).

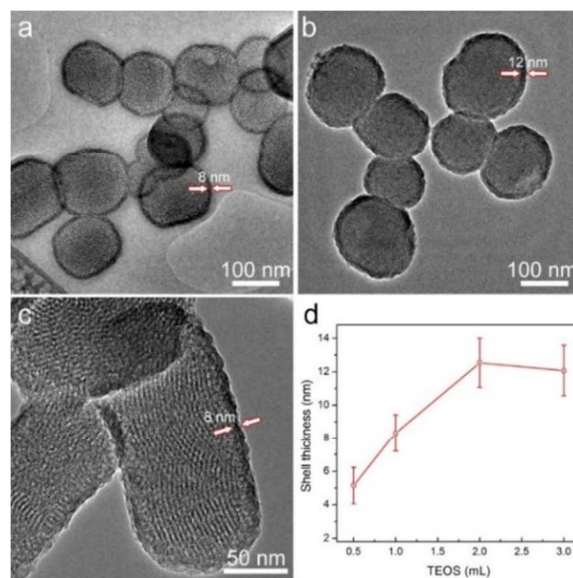


**Fig. 2** TEM (left panel) and SEM (right panel) of MSNs prepared using different amounts of RB. (a, d) No RB, (b, e) 5 mg RB and (c, f) 10 mg RB. In the presence of RB, rod-shaped MSNs are formed and with the increasing RB amount longer rods can be obtained.

It is known that morphology of the mesoporous silica materials are highly dependent to the synthesis conditions. Even a slight change in the reaction parameters such as temperature and pH may significantly alter the size, shape and pore structure of the MSNs by affecting the nucleation, growth and dissolution rates of silica and the thermodynamics of surfactant-silica assembly.<sup>39</sup> For instance, Mou *et al.*,<sup>40</sup> demonstrated the significant impact of the pH on the size of MSNs; decreasing the pH from 11.38 to 10.86 reduced the particle size almost 6 fold (170 to 30 nm). Also, Yang *et al.*,<sup>41</sup> reported that addition of acetate esters result in a rapid decrease in the pH of the reaction mixture and change the shape of the particles from spheres to helical rods by changing nucleation and growth rates of silica and interactions between silicates and surfactant molecules. Similarly, we hypothesized that dissolution of the RB molecules may change the pH of the reaction solution and this may be the reason of the rod-shape MSN formation in the presence of RB. Accordingly, we measured the pH of the reaction solutions before and after addition of different amounts of RB. However, we did not observe any significant change in the pH of the reaction mixture (~11.75) even after addition of 20 mg of RB. Apparently, a pH drop based shape transformation mechanism is not applicable for our case. On the other hand, He *et al.*<sup>42</sup> reported that negatively charged ibuprofen molecules incorporate into the surfactant micelles and affects the pore morphology of the particles. Although, RB is also negatively charged, TEM images did not indicate any difference in the pore structure of the MSNs prepared in the

presence or absence of RB. Therefore, incorporation of RB molecules into the surfactant micelles did not change the mesostructure of surfactant micelle assembly at least in the studied concentration region. Based on these results, it is believed that, the shape transformation in the presence of RB is due to the effect of negatively charged RB molecules on the assembly between silica and surfactant micelles. The negatively charged RB may electrostatically assemble with cationic surfactant micelles and accordingly can change the final shape of the silica-surfactant assembly.

**Synthesis of Core/Shell MSNs.** Mesoporous core/solid silica shell particles are prepared in a one-pot reaction. Following the polymerization tetraethyl orthosilicate (TEOS) monomer around CTAB micelles to form initial MSNs, excess TEOS monomer was added to prepare solid shells around the particles. Fig. 3 shows the TEM images of core/shell nanospheres and nanorods which were prepared using different amounts of TEOS in the second addition. Uniform solid silica shells around the particles reflect clear contrast difference from the porous cores. Fig. 3a and b show the nanospheres prepared using 1 and 3 mL of additional TEOS which have 8 and 12 nm thick very uniform shells, respectively. Similarly, 8 nm thick uniform silica shell was observed around the nanorods (Fig. 3c) when 1 mL TEOS was used in the second step showing that the shell thickness is independent from the particle morphology. Fig. 3d demonstrates the effect of second TEOS addition amount on the silica shell thickness of nanospheres. We observed that between 0.5 and 2 mL of TEOS addition, shell thickness gradually increased to 12 nm from 5 nm. Further increase in the TEOS amount (3 mL) did not change shell thickness significantly indicating that shell growth is self-limiting.

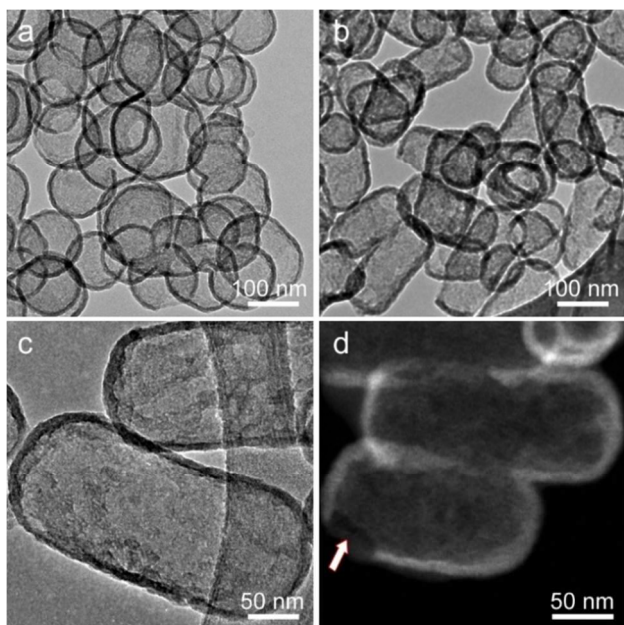


**Fig. 3** Morphology and shell thickness of core/shell MSNs. (a-c) TEM images of spherical MSNs prepared using 1 mL of additional TEOS (a), spherical MSNs prepared using 3 mL of additional TEOS (b), rod-shaped MSNs prepared using 1 mL of additional TEOS (c). Arrows indicates the shells of the particles. (d) Shell thickness of spherical particles are determined by the additional TEOS amount.

**Selective Dissolution of Porous Cores in PBS.** Porous cores of the core/shell particles were selectively dissolved by incubating the particles in PBS at 65 °C for one day (Fig. 4).

After hollowing process, the particles were calcinated at 550 °C to remove the CTAB surfactant and RB molecules. It should be noted that, particle concentration in PBS solution was 0.5 mg/mL for nanospheres and 1 mg/mL for nanorods. We observed that partially etched particles are formed at the higher particle concentrations than 1 mg/mL (will be discussed below) suggesting that an equilibrium is reached for silica dissolution.

Fig. 4 shows the TEM images of fabricated hollow nanospheres (prepared using 1 mL of additional TEOS) and nanorods (prepared using 10 mg of RB and 1 mL of additional TEOS). There is a clear contrast difference between interior and exterior parts of the particles indicating core dissolution after PBS incubation. The efficiency of hollowing process is almost 100% (see low magnification TEM image of the hollow nanospheres in ESI<sup>†</sup>, Fig. S2). Importantly, the shell thickness remained almost intact after the hollowing process; around 8-9 nm, for both nanospheres and nanorods which suggests that only cores of the particles dissolved.

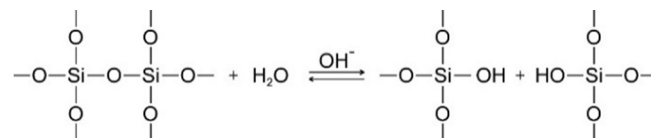


**Fig. 4** TEM images of hollow nanoparticles. (a) Hollow nanospheres prepared using core/shell particles with 8 nm shell thickness, (b) hollow nanorods prepared using core/shell particles with 8 nm shell thickness. Shell thickness of hollow particles remained same after hollowing process, indicating that cores were completely dissolved. (c) Close-up TEM image of nanorods. (d) High magnification STEM image of hollow nanorods that shows the mesoporous shells of particles. Arrow indicates a crack formed on the hollow nanorod shell during core dissolution and calcination processes.

To investigate the selective core dissolution process, FTIR spectra of core particles (MSN), core-shell particles (MSN-ts) and hollow particles (h-MSN) were collected, after the surfactant removal step (see ESI<sup>†</sup>, Fig. S3). The broad band around 1000-1250 cm<sup>-1</sup> is composed of several longitudinal-optical (LO) and transverse-optical (TO) modes of SiO<sub>2</sub> network and peaks of some residual groups bonded to this network.<sup>43</sup> The position and shape of this broad band may provide important information about the cross-linking degree of the silica network.<sup>43,44</sup> The maximum of this band (at 1082 cm<sup>-1</sup>) of MSN blue shifted to around 1085 cm<sup>-1</sup> after silica shell coating (MSN-ts) and further shifted to 1090 cm<sup>-1</sup> after hollowing process (h-MSN). A blue shift in this peak indicates

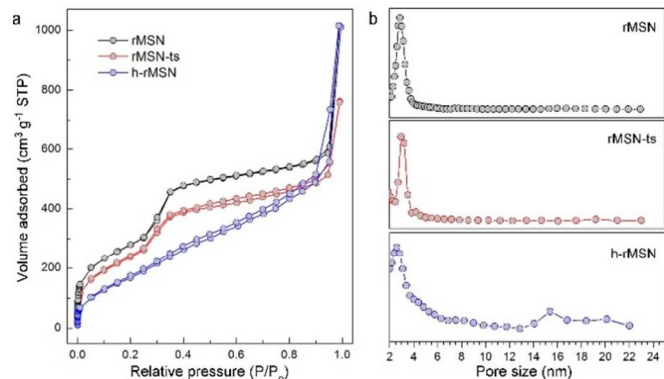
more cross-linked structure with higher internal stress.<sup>44,45</sup> In addition, the intensity of the shoulder around 1200 cm<sup>-1</sup> decreases with the increasing cross-linking degree of the silica network.<sup>43,46</sup> An intense shoulder at 1235 cm<sup>-1</sup> was observed for the MSN indicating a poorly cross-linked silica network for the core particles. After coating the MSN with a thin silica shell (MSN-ts) the intensity of the shoulder decreased and it further reduced after core removal (h-MSN). These results suggest that shell is more cross-linked than the core. Therefore, the less cross-linked and porous core is more susceptible for dissolution and PBS selectively etches the cores of the core/shell particles.

To our surprise, shells of the particles contains mesopores after dissolution which can be clearly seen from Fig. 4c and d. Mesoporosity of the shells was further confirmed using N<sub>2</sub> adsorption-desorption technique (see below). The mesopores can be formed during silica dissolution process in the presence of surfactant molecules.<sup>24</sup> It is well known that dissolution of silica is reversible (Scheme 1) and therefore dissolved silica species can spontaneously regrown.<sup>29</sup> For our case, in the presence of CTAB (leaking from dissolved cores of the particles) dissolved silica can regrown around CTAB micelles to produce mesoporous shell. Another reason of the mesopores can be the residual CTAB molecules which are absorbed to the shell silica network during the synthesis of particles. These residual CTAB molecules can contribute the pore formation during dissolution, regrowth and calcination processes.<sup>24</sup> Besides, we observed cracks on the some of the particles after calcination process (Fig. 4d). Nevertheless, according to the TEM images most of the particles were crack free.



**Scheme 1.** Mechanism of hydroxide ion catalyst silica dissolution and regrowth

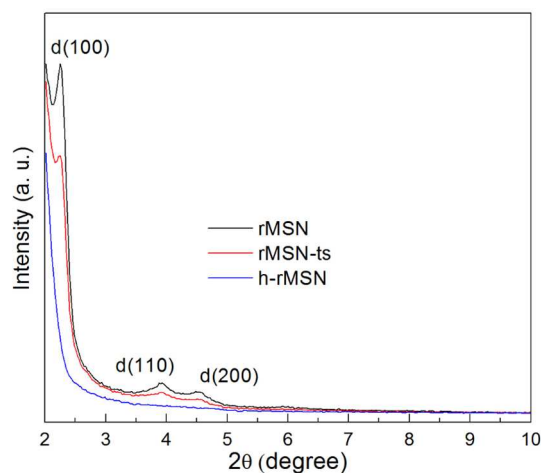
Pore structure, volume, and size and specific surface area of rod-shaped particles were characterized using N<sub>2</sub> adsorption-desorption and XRD techniques. Fig. 5a shows the N<sub>2</sub> adsorption-desorption curves of nanorods (rMSN), core/shell nanorods (rMSN-ts), and hollow nanorods (h-rMSN). rMSN and rMSN-ts revealed type-IV nitrogen sorption curve with a sharp capillary condensation step in nitrogen adsorption amount at relative pressures P/P<sub>0</sub> between 0.2 and 0.4 indicating the presence of mesopores with narrow size distribution.<sup>11,30</sup> On the other hand, this step almost disappeared for h-rMSN reflecting the dissolution of ordered mesoporous core. Corresponding pore size distributions of the particles, which were obtained from N<sub>2</sub> adsorption-desorption curves using DFT method, are given in Fig. 5b. rMSN and rMSN-ts revealed similar narrow pore size distribution with mesopores; 2.9 nm and 3 nm, respectively. The pore size distribution of h-rMSN, on the other hand, was wide between 2 and 6 nm which may be due to the random nature of the silica dissolution and regrowth process and pore widening during core dissolution and calcination processes. Also, second wide peak was observed in the h-rMSN pore size distribution between 13 and 22 nm which may be correspond to the cracks formed on the shell during dissolution and calcination processes.



**Fig. 5** (a)  $N_2$  adsorption and desorption curves of rod-shaped nanoparticles. The step in nitrogen adsorption amount at relative pressures  $P/P_0$  between 0.2 and 0.4 was disappeared for hollow particles indicating the loss of mesoporous core. (b) Pore size distribution of particles calculated using the  $N_2$  adsorption and desorption curves. rMSN and rMSN-ts showed narrow pore size distribution, on the other hand, h-rMSN have broad pore size distribution. (rMSN; rod-shaped MSNs, rMSN-ts; rod-shaped core/shell MSNs, and h-rMSN; rod-shaped hollow MSNs)

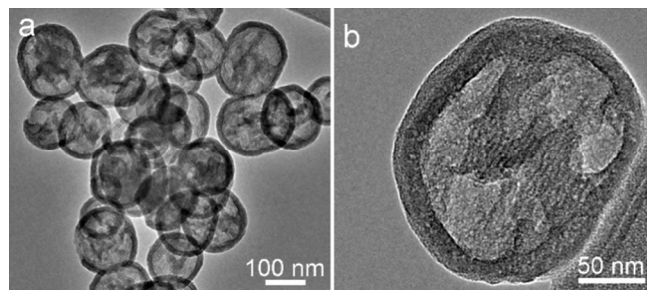
Surface area and pore volume of the particles were calculated using BET and DFT methods, respectively. Surface area of rMSN is  $1008 \text{ m}^2/\text{g}$  and it is reduced to  $862 \text{ m}^2/\text{g}$  after coating the particles with solid silica shell (rMSN-ts). Surface area further reduced to  $598 \text{ m}^2/\text{g}$  after core dissolution (h-rMSN) due to loss of highly ordered and mesoporous cores. Pore volume of rMSN is  $1 \text{ cm}^3/\text{g}$  and it is again slightly reduced ( $0.87 \text{ cm}^3/\text{g}$ ) after silica coating. As expected, pore volume increases more than two fold ( $1.94 \text{ cm}^3/\text{g}$ ) after etching the core of the particles.

Fig. 6 shows the XRD spectra of the rod-shaped particles. rMSN and rMSN-ts, exhibited characteristic diffraction peaks, (100), (110), and (200), of the highly ordered hexagonal pore structure of MCM-41 type mesoporous materials; whereas no order was observed for h-rMSN. Based on TEM,  $N_2$  adsorption-desorption and XRD observations, it can be concluded that shells of hollow particles contains non-ordered mesopores with large pore size distribution.



**Fig. 6** XRD spectra of rod-shaped particles. rMSN and rMSN-ts, demonstrated characteristic diffraction peaks, (100), (110), and (200), of the highly ordered hexagonal pore structure of MCM-41 type mesoporous materials. On the other hand, pore order disappeared after core dissolution (h-rMSN).

Using the porosity difference based selective dissolution method, it is possible to prepare particles with different morphologies. For instance, Fig. 7 shows the TEM images of the partially hollowed nanospheres. These particles contain a few large pores in their cores. Also, it is still possible to observe ordered mesopores in the non-dissolved parts (Fig. 7b). To prepare the half-etched particles we increased the particle concentration to  $5 \text{ mg/mL}$  and we kept the dissolution time and temperature constant. Note that reaction is spontaneously quenched at this particle concentration; further increasing the reaction time does not change the particle morphology. Therefore, it is possible to partially dissolve the cores of core/shell particles simply changing the particle concentration in the PBS solution.



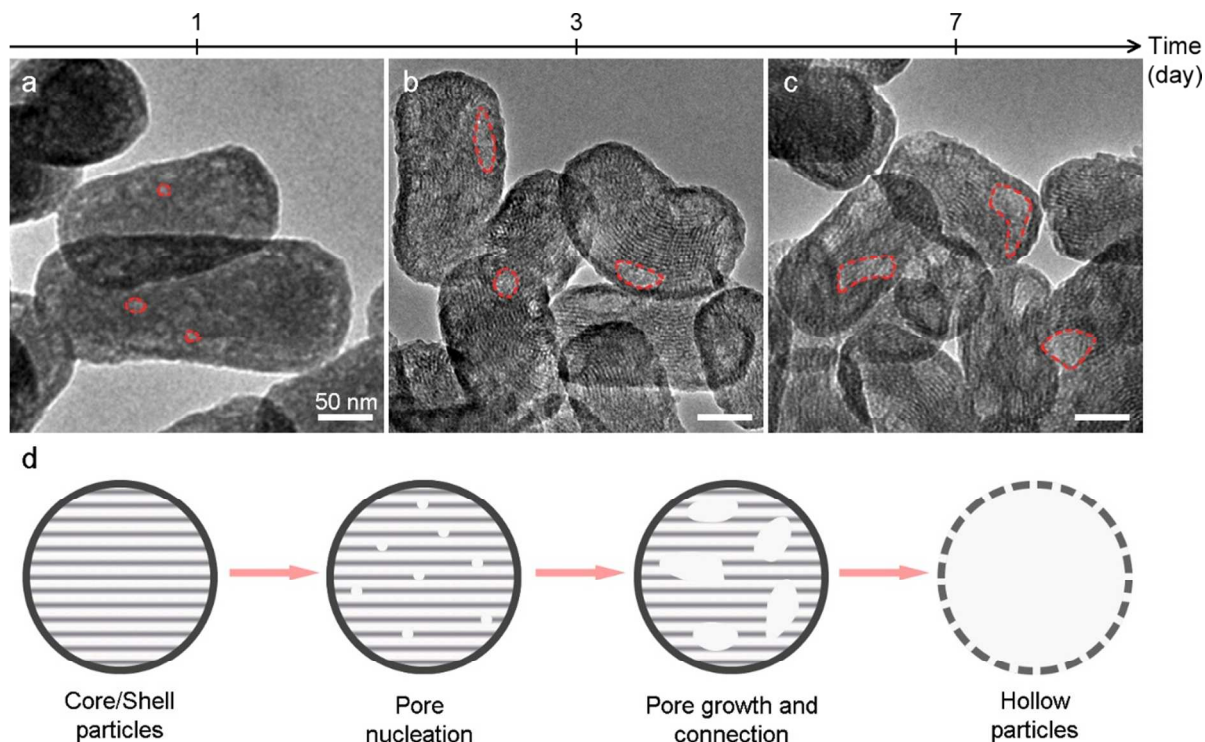
**Fig. 7** TEM images of partially hollowed spherical particles (a) low magnification and (b) high magnification. Partially hollowed particles contain a few large pores in their cores and it is still possible to observe ordered mesopores in the non-dissolved parts.

**Possible Mechanism of Selective Dissolution Process.** In order to investigate the selective dissolution mechanism, we collected samples at different time intervals during the incubation of rMSN-ts in PBS at  $65^\circ\text{C}$  (particle concentration is  $1 \text{ mg/mL}$ ). However, we noticed that at this temperature core dissolution is very fast; cores of the particles were completely etched after 30 min, which prevent us from the observation of dissolution steps. To slow down the reaction we decreased the dissolution temperature to the room temperature and increased the particle concentration to  $5 \text{ mg/mL}$ . As expected, the core dissolution is very slow at these conditions. At the beginning of the dissolution process (after 1 day), many small pores around  $10 \text{ nm}$  was observed (Fig. 8a). After 3 days (Fig. 8b) pore sizes increased and it further increased after 1 week (Fig. 8c). This indicates that core etch starts from multiple points, and these sites became wider with time and then interconnected with each other. At the end of the process all of the pores were interconnected to form the hollow core (Fig. 8d).

To explore the role of PBS in the dissolution process, we replaced the PBS with water and incubated rMSN-ts at  $65^\circ\text{C}$  for one day. We observed that in water some of the cores were not fully dissolved (see ESI<sup>†</sup>, Fig. S4) indicating that dissolution in water is slower than in highly salted PBS environment. In fact, it is well known that silica dissolution is faster in salted solutions,<sup>33,47</sup> which is in accordance with our observations. Nevertheless, cores of particles can be dissolved in water by decreasing the particle concentration.

We also investigated effect of calcination on the selective dissolution process. In this case, first we calcinated the particles at  $550^\circ\text{C}$  for 5 h in order to strengthen the silica network, then we incubated the particles in PBS at  $65^\circ\text{C}$  for one day. One can expect no or partially dissolved cores for this case due to the improved condensation degree of silica after high temperature treatment.<sup>48</sup> On the contrary, we observed that cores of the

particles dissolved similar to the non-calcinated particles (see ESI<sup>†</sup>, Fig. S5). However, shell thickness of the pre-calcinated particles are almost two times thicker (14 nm) than non-pre-calcinated particles.



**Fig. 8** Mechanism of core dissolution process. (a-c) TEM images taken at different time intervals during the hollowing of rod-shaped MSNs at room temperature. (a) 1 day, (b) 3 days and (c) 7 days. After 1 day, many small pores around 10 nm was observed. The size of these pores increased with time. Some dissolved areas outlined in red in all TEM images. (d) Schematic representation of core dissolution process.

## Conclusions

In summary, a facile porosity difference based selective silica dissolution strategy to prepare hollow MSNs is reported. First, it was demonstrated that in the presence of the RB dye shape of the MSNs were tailored from spheres to rods with controlled aspect ratio. Then, in the presence of excess silica monomer (TEOS) growth of uniform and dense silica shells around MSNs was demonstrated. In PBS, mesoporous cores of these core/shell nanoparticles selectively dissolve due to their higher surface area and less condensed nature compared to the dense shell. After hollowing process, the shells of the nanoparticles contain mesopores on their surfaces which are non-ordered and broad in size distribution which was proved using N<sub>2</sub> adsorption-desorption and XRD techniques. The possible selective dissolution mechanism was investigated and it was concluded that dissolution of porous core starts from multiple nucleation sites, these small dissolved sites become larger over time and interconnected with each other until complete core dissolution. We envisage that the porosity difference based selective dissolution route may be applied to synthesize hollow nanoparticles from a wide range of materials with tailored morphologies for many applications including, catalysis, batteries, bioimaging, drug and gene delivery, and optical coatings.

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## Notes and references

<sup>a</sup> UNAM-National Nanotechnology Research Center, Bilkent University, 06800 Ankara, Turkey

<sup>b</sup> Institute of Materials Science and Nanotechnology, Bilkent University, 06800 Ankara, Turkey

<sup>c</sup> Department of Physics, Bilkent University, 06800, Ankara, Turkey

\* E-mail: yildirim.adem83@gmail.com, ademy@bilkent.edu.tr (A. Y.).

\* E-mail: bayindir@nano.org.tr. Phone: +90 312 2903500. Fax: +90 312 266 4365 (M. B.).

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## Table of Contents

A general method to prepare hollow mesoporous silica nanoparticles with tailored morphology is reported.

