

# A Facile Route to Construct SiCO Nanospheres with Tunable Sizes

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We report a facile route to synthesize SiCO nanospheres using Pluronic F127/polyvinylsilazane (PVSZ) mixed micelles as a template, in which PVSZ selectively swells with the PEO core of the F127 micelles. The thermal degradation of the F127/PVSZ mixed micelles leads to the formation of SiCO nanospheres. The size of the resultant SiCO nanospheres can be tuned in the range from 25 nm to 75 nm by controlling annealing time at 70°C.

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## Introduction

Block copolymers have attracted considerable attention as a building block to assemble nanoscale micelles in selective solvents.<sup>1–4</sup> The self-assembled micelles of block copolymers are a result of the phase separation of immiscible blocks. The morphology of self-assembled block copolymer micelles depends on the relative block length,<sup>5,6</sup> the chemical nature of the repeat unit,<sup>7</sup> and solution condition.<sup>8,9</sup> The co-assembly of low molecular thermosetting resins and block copolymers has been proven to be a powerful method in the synthesis of hybrid materials in which the thermosetting resin selectively swells with one of the blocks.<sup>10,11</sup> Well-defined mesophases can be formed by systematically increasing the resin to block copolymer volume fractions.

Recently, the self-assembly method has been applied to the mixture of amphiphilic block copolymers and preceramic polymers. The combination of two initially separated research areas of polymer-derived ceramic<sup>12,13</sup> and block copolymer microphase separation<sup>14</sup> enables to synthesize nanostructured ceramics. The PEO-based amphiphiles, such as PI-b-PEO,<sup>15,16</sup> PB-b-PEO,<sup>17,18</sup> PS-b-PEO,<sup>19–21</sup> PEO-b-PHMA,<sup>22</sup> PEO-PPO-PEO,<sup>23,24</sup> and alkyl-PEO alcohols,<sup>25</sup> have been used in the conjunction with ceramic precursors in sol-gel processes to obtain nanostructured organic–inorganic hybrid materials, in

which heat treatment is used to transform the preceramic polymer into ceramic materials, while retaining the original shape. Thus, the resultant materials have polymer-derived structures and ceramic-like properties. Wiesner demonstrated that polysilazane (Ceraset) was chemically compatible with the PEO microdomains of the block copolymer PI-b-PEO<sup>15</sup>. After cross-linking, the lamellar morphology was obtained. Kamperman<sup>16</sup> reported that PI-b-PEO and liquid polymeric precursor could be self-assembled to form ordered mesoporous silicon carbonitrides. Wan<sup>17,18</sup> presented that nanostructured nonoxide ceramics were synthesized by the cooperative self-assembly of PB-b-PEO and polyvinylsilazane (PVSZ).

Herein, we report a facile synthesis of SiCO nanospheres with tunable sizes through a simple micellar-templating route. In this work, we use Pluronic F127 triblock copolymer (PEO<sub>106</sub>-PPO<sub>70</sub>-PEO<sub>106</sub>) as a structurally directing agent and PVSZ as a ceramic precursor. The thermal degradation of mixed F127/PVSZ micelles, in which PVSZ selectively swells with the PEO core of F127 micelles, leads to the formation of SiCO nanospheres. The size of the SiCO nanospheres can be tuned in the range from 25 nm to 75 nm by controlling annealing time at 70°C.

## Experimental

Polyvinylsilazane (PVSZ, Mw = 500 g/mol) from Sigma-Aldrich (St. Louis, MO) was used as a ceramic

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precursor and its chemical structure can be ideally represented by  $[(\text{CH}_2=\text{CH})\text{SiCH}_3\text{NHSiHCH}_3\text{NH}]_n$ . Block copolymer Pluronic F127 (PEO<sub>106</sub>-PPO<sub>70</sub>-PEO<sub>106</sub>; Sigma-Aldrich) was used as a structurally directing agent. Dicumyl peroxide (DCP; Sigma-Aldrich) was used as a radical initiator. Tetrahydrofuran (THF) and chloroform (CHCl<sub>3</sub>) purchased from Aldrich were used as solvents. These chemicals were used as-received without further purification.

SiCO nanospheres was performed by one-pot synthesis. F127 (5 wt%) was dissolved in a THF/CHCl<sub>3</sub> mixed solvent (1:1 v/v). PVSZ (5 wt%) and DCP (2 wt%) were then added into the F127 solution. The mixture was stirred for 5 h at room temperature. F127 triblock copolymer contains two hydrophilic poly(ethylene oxide) chain (PEO) and a hydrophobic poly(propylene oxide) chain (PPO).<sup>26,27</sup> Due to different polarity nature between the block PEO and the PPO block, F127 self-assembles into micelles with cage-like structure, in which the block PEO is the core surrounded by the PPO shell.<sup>24</sup> PVSZ ceramic precursor selectively swells with the PEO core due to the hydrophilic nature of the PEO. F127/PVSZ micelle solution was poured into a Teflon dish. The evaporation of organic solvents leads to the formation of micelle films with a thickness of 0.2–0.5 mm, in which DCP was used as a thermal initiator to cross-link the PVSZ swelled by the PEO core of F127 micelles. The micelle films were annealed in an oven for different periods of time at 70°C. The temperature was subsequently ramped up to 130°C for 1 h to cross-link the PVSZ. After the cross-linking, the films turn to yellow color. The yellow films with a thickness of ~ 0.5 mm were peeled off from the dish and then transferred into a furnace with flowing nitrogen. Finally, the samples were thermally decomposed at 500°C for 4 h (heating rate = 0.5°C/min) and then pyrolyzed at 1000°C for 1 h (heating rate = 0.2°C/min) to form ceramic films.

The samples were characterized using differential scanning calorimeter (DSC, DSC204C; Netzsch, Selb, Germany). Fourier transform-infrared spectra (FT-IR) were recorded between 4000 and 400 cm using a Nicolet-360 spectrometer (Thermo Nicolet, Madison, WI) by the KBr pellet method. The pyrolytic process of ceramic precursors was investigated using thermal gravimetric analysis (TGA, STA 409 EP; Netzsch) and differential thermal analysis (DTA, DIL 404; Netzsch). The morphology of the resultant ceramic films was characterized with scanning electron microscope (SEM, LEO1530; Oberkochen, Germany) and transmission electron microscope (TEM, JEM-2100 HR; JEOL, Tokyo, Japan). The phase compositions were determined by X-ray diffraction (XRD, PANalytical X'Pert PRO diffractometer;

PANalytical, Almelo, the Netherlands), using CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The elemental analysis of the ceramic films was performed by electron probe microanalyzer (EPMA, JEOL-8100; JEOL) in the wavelength dispersion mode.

## Results and Discussion

Figure 1 shows DSC plots of pure F127 block copolymer, together with the yellow films formed by the cross-linking of the PVSZ swelled in the PEO core of F127 micelles. The pure triblock copolymer shows a strong melting peak at 58°C (Fig. 1a), while the yellow films display a weak melting peak at 54°C (Fig. 1b). This result suggests that the crystallization of the PEO phase is suppressed in the yellow films due to the selective swelling of the PVSZ in the block PEO phase.<sup>21,23</sup>

Transmission electron microscope (TEM) measurements show that the micelles formed by F127 in mixed THF/CHCl<sub>3</sub> solvent have a diameter of ~ 125 nm (Fig. 2a). After the addition of PVSZ ceramic precursor, the diameter of F127 micelles increases to ~ 310 nm (Fig. 2b). The increased diameter of F127 micelles is a result of the swelling of PVSZ in the PEO core of the micelles.

Figure 3 shows FT-IR spectra of PVSZ ceramic precursor and yellow films formed at different temperatures. The ceramic precursor exhibits the absorption peaks at 3380 cm (N-H, stretching vibration), 3045 cm (CH=CH<sub>2</sub>, stretching vibration), 1625 cm (C=C, stretching vibration), 1410 cm (Si-CH=CH<sub>2</sub>), 1014 cm

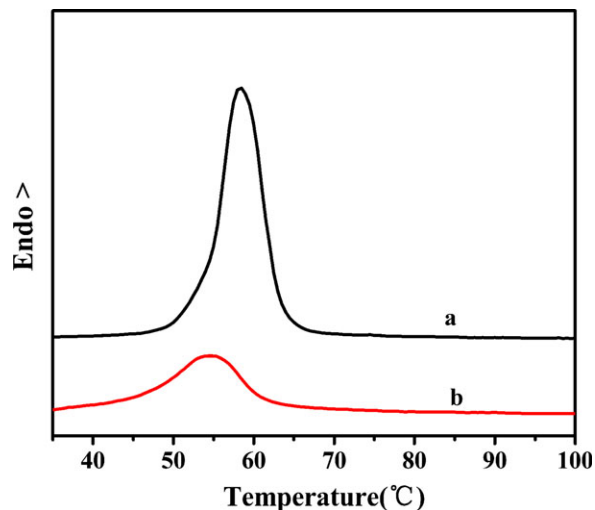


Fig. 1. Differential scanning calorimeter (DSC) measurements of (a) F127 and (b) yellow films.

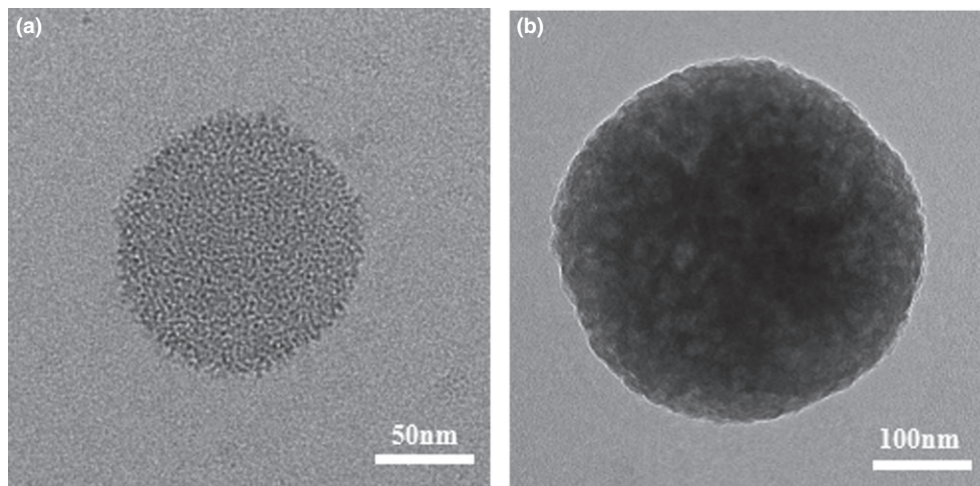


Fig. 2. Transmission electron microscope (TEM) of F127 micelles formed in THF/ $\text{CHCl}_3$  mixed solution without (a) and with (b) PVSZ.

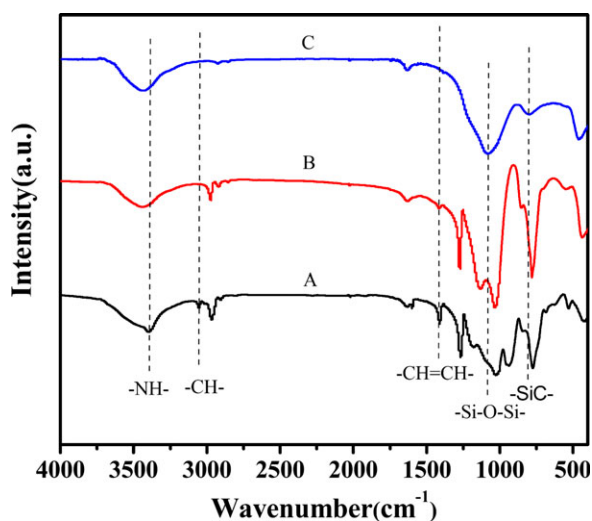


Fig. 3. Fourier transform-infrared spectra (FT-IR) spectra of (A) PVSZ ceramic precursor and yellow films after thermal treatments at (B) 500°C and (C) 1000°C.

( $\text{CH}_2$ ,  $\text{CH}_2$  deformation in  $\text{Si-CH}_2\text{-Si}$ ), 934  $\text{cm}^{-1}$  ( $\text{Si-N}$ , stretching vibration), and 760  $\text{cm}^{-1}$  ( $\text{Si-C}$ ,  $\text{Si-CH}_3$  deformation and  $\text{Si-C}$  stretching), respectively. After the thermal decomposition of yellow films at 500°C, the absorption peaks of the  $\text{C=C}$  bond disappeared because of the polymerization reaction of vinyl groups. When the temperature ramped up to 1000°C, the absorption peak of  $\text{Si-CH}_3$  group completely disappeared. However, the absorption peaks of the  $\text{C=C}$  (1625  $\text{cm}^{-1}$ ),  $\text{Si-O-Si}$  (1080  $\text{cm}^{-1}$ ), and  $\text{Si-C}$  (760  $\text{cm}^{-1}$ ) bonds appear at 1000°C, suggesting the formation of ceramic films at 1000°C.

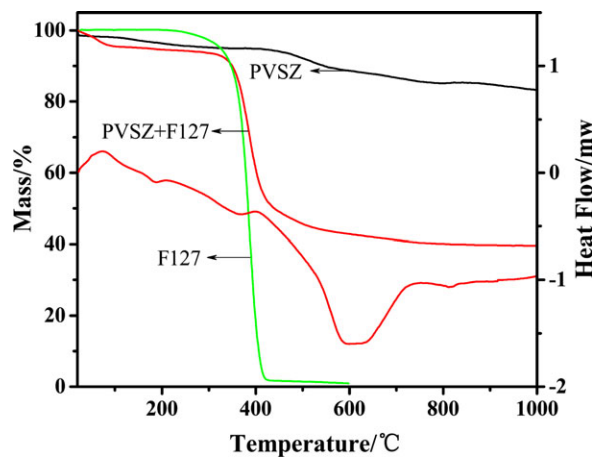


Fig. 4. TG and DTA curves of as-made films after cross-linking at 130°C, together with TG curves of F127 and PVSZ.

Figure 4 shows the TG and DTA curves of yellow films after cross-linking at 130°C, together with the TG curves of F127 and PVSZ in a nitrogen atmosphere with a heating rate of 10°C/min. The pyrolysis of yellow films after cross-linking has four stages. In the first step from 30 to 100°C, the film loses 4% of its initial mass by the evaporation of residual organic solvent and low molecular weight oligomers. The second step occurs from 100 to 410°C with a weight loss of 43%, which is due to the thermal decomposition of F127 triblock copolymer. The transformation to ceramic films appears in the range from 410 to 750°C. Above 750°C, a further of 1.2% weight loss occurs. The overall ceramic film yield at 1000°C is approximately 39.6%. The corresponding DTA curve shows four peaks, including an endothermic peak and three exothermic peaks. The endothermic peak

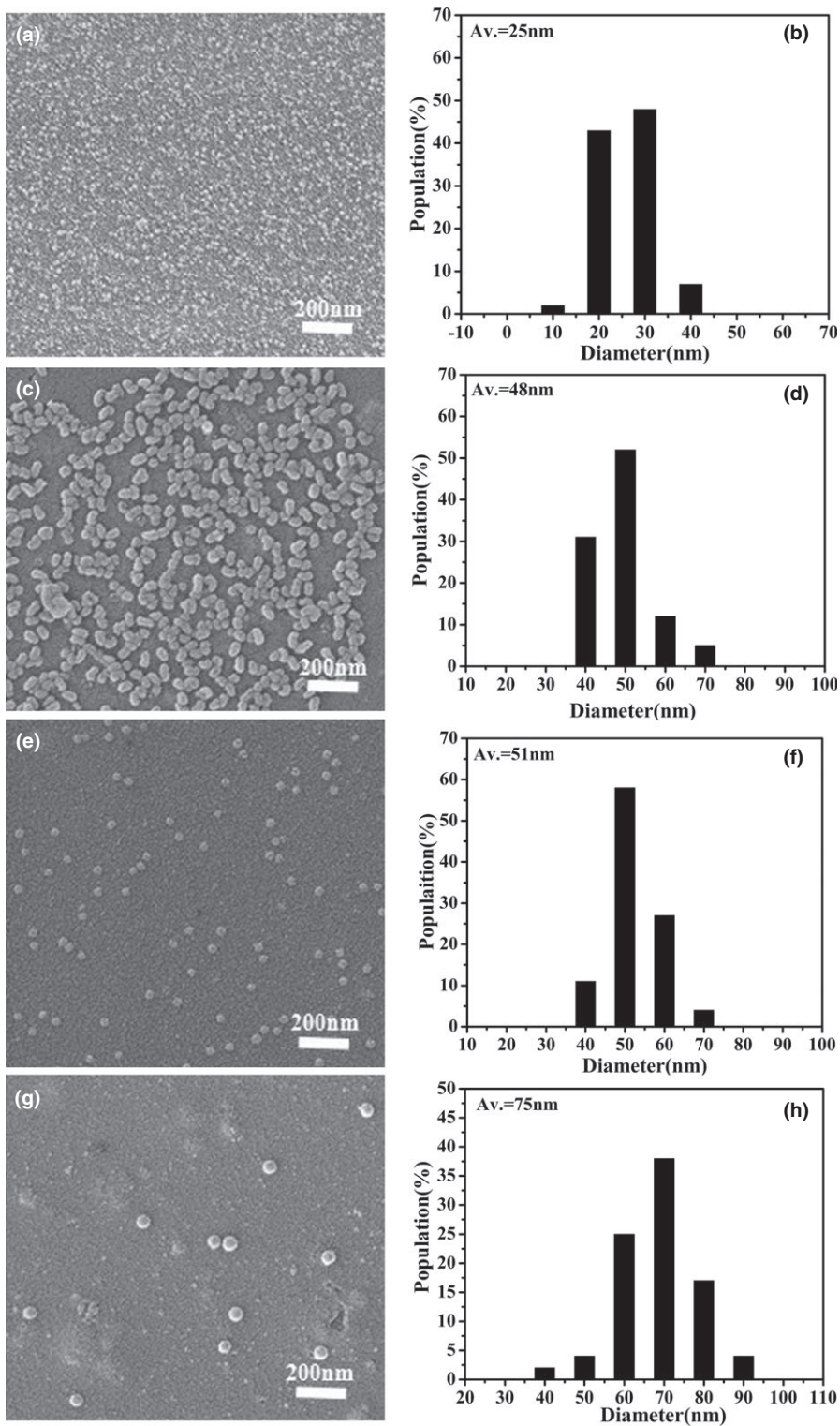


Fig. 5. SEM images and diameter distributions of SiCO nanospheres from 1000 °C pyrolysis with the as-made films holding time 24 h (a,b), 48 h (c,d), 72 h (e,f), and 96 h (g,h) at 70 °C.



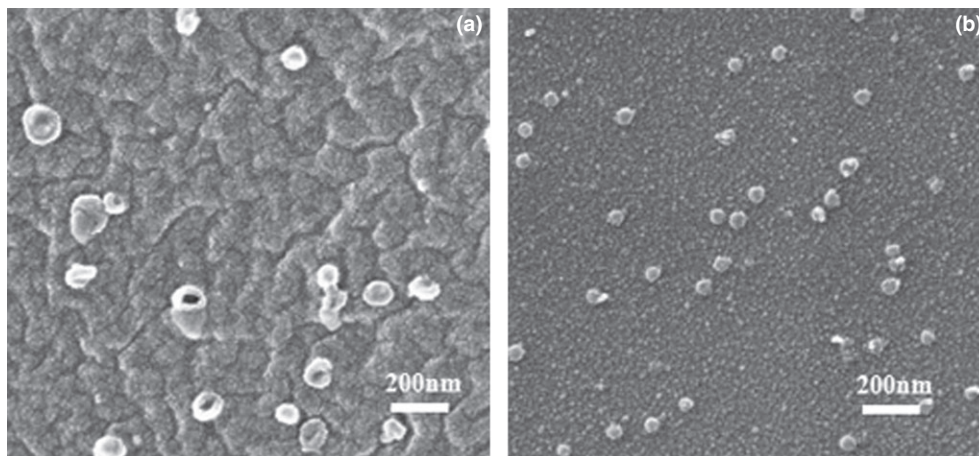


Fig. 6. (a) SEM images of hollow nanospheres from 500°C pyrolysis with the as-made films holding time 72 h at 70°C, (b) the hollow nanospheres collapse after 1000°C thermal decomposition.

at  $\sim 60^\circ\text{C}$  is attributed to the crystalline melting of F127, which is consistent with the DSC shown in Fig. 1. The first exothermic peak at  $180^\circ\text{C}$  is ascribed to the further cross-linking of PVSZ, while the second exothermic peak at  $\sim 370^\circ\text{C}$  is due to the thermal decomposition of F127. The last exothermic peak is attributed to the formation of ceramic films.

After the thermal treatment at different temperatures, the morphology of the resultant films was imaged with SEM. In our experiments, the as-made films after solvent evaporation were held for different periods of time at  $70^\circ\text{C}$ . We find that the ceramic films formed by the pyrolysis at  $1000^\circ\text{C}$  consist of densely packed SiCO nanospheres. The diameter of SiCO nanospheres depends on the holding time at  $70^\circ\text{C}$  (Fig. 5). When the holding time increases from 24 h to 96 h, the size of SiCO nanospheres increases from 25 nm to 75 nm after the pyrolysis. The increased size of SiCO nanospheres is a result of the increase in the amount of PVSZ permeating into the PEO core of F127 micelles. If the holding time is more than 72 h, hollow nanospheres are observed after the thermal decomposition at  $500^\circ\text{C}$  (Fig. 6a). They collapse when temperature ramped from 500 to  $1000^\circ\text{C}$  (Fig. 6b).

The ceramic films obtained were analyzed using XRD. Regardless of the pyrolysis temperature, the XRD patterns of all materials reveal no diffraction peaks, suggesting the ceramics are amorphous with the pyrolysis temperature range. Fig. 7 is a typical EPMA spectrum of the ceramic films formed by the pyrolysis at  $1000^\circ\text{C}$ , which shows C, O and Si peaks. The composition was calculated from the EPMA spectrum using the Oxford Instruments INCA software package (INCA Energy 200; Oxford Instruments, Buckinghamshire, U.K.). The

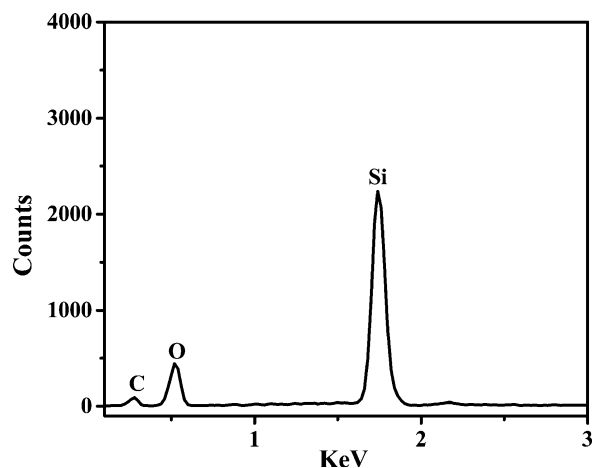


Fig. 7. Electron probe microanalyzer (EPMA) of the ceramic films formed by the pyrolysis at  $1000^\circ\text{C}$ .

results reveal that the ceramic films contain 32.57 at.% C, 44.20 at.% O, and 23.23 at.% Si. It is seen that the nitrogen content of the ceramic films was not detected by EPMA, which could have been oxidized completely. It is also seen that the ceramic films contain a large amount of oxygen, which was likely introduced into the materials during precursor handling and heat treatment.

Figure 8 shows a schematic illustration for the formation of SiCO nanospheres. If the holding time at  $70^\circ\text{C}$  is  $<48$  h, dense nanospheres are observed after the thermal decomposition at  $1000^\circ\text{C}$ . If the holding time is more than 72 h, both hollow nanospheres and dense nanospheres are observed after the thermal decomposition at  $500^\circ\text{C}$ . The hollow nanospheres collapse when temperature ramped from 500 to  $1000^\circ\text{C}$ , while dense nanospheres still retain dense spheres. When the PVSZ was

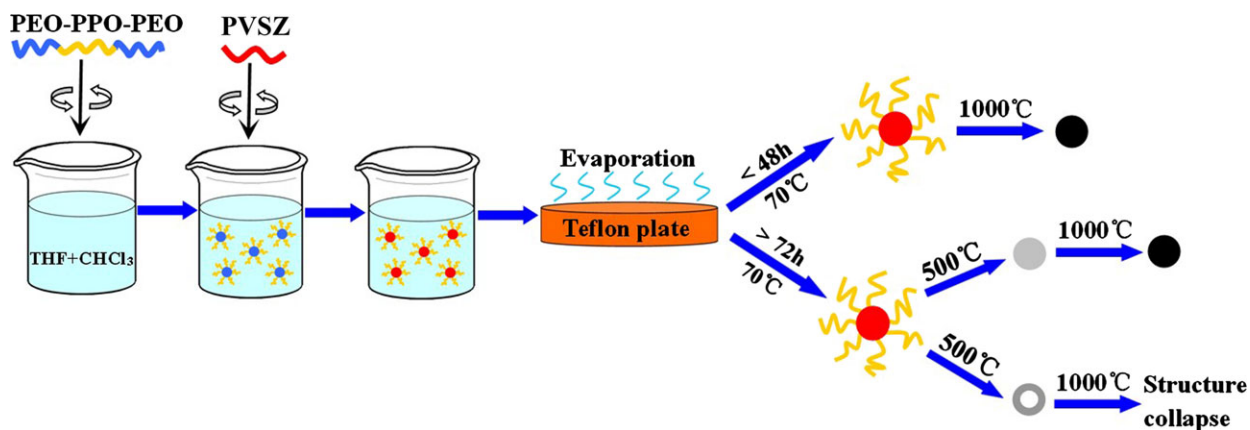


Fig. 8. Schematic illustrating the synthetic procedure of SiCO nanospheres.

added into F127 micelles, the diameter of the obtained F127/PVSZ micelles was  $\sim 310$  nm. After the thermal decomposition at high temperature, the micelles shrank from  $\sim 300$  nm to  $\sim 50$ – $70$  nm in an average diameter. The high shrinkage indicates a high level of densification and is usually ascribed to the organic–inorganic transformation.

## Conclusions

In this study, we have reported a facile method for synthesizing SiCO nanospheres with tunable size using F127/PVSZ mixed micelles as templates, in which PVSZ selectively swells with the PEO core of F127 micelles. After the thermal decomposition of F127 micelles, SiCO nanospheres were obtained. The size of the resultant SiCO nanospheres can be tuned in the range from 25 nm to 75 nm by controlling annealing time at 70°C.

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