

# Low-Temperature Synthesis of Mesoporous SiC Hollow Spheres by Magnesiothermic Reduction

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**Mesoporous silicon carbide hollow spheres (SiC-HS) with a large specific surface area ( $690.2 \text{ m}^2 \text{ g}^{-1}$ ) are synthesized at a relatively low temperature of  $650^\circ\text{C}$  by magnesiothermic reduction using the template of carbon-coated mesoporous silica hollow spheres and molten salt as the heat absorbent and solvent. The mesoporous SiC-HS comprising many small primary crystals (2–4 nm) with a well-maintained microstructure have good thermal stability and adsorption ability, and are promising as adsorbents to remove organic pollution from water. The synthesis technique can be extended to other nanostructured carbide ceramic materials.**

**Keywords:** silicon carbide; hollow sphere; mesoporous; adsorbent

## I. Introduction

BECAUSE of the excellent mechanical strength, good thermal stability, high chemical inertness, nontoxicity, small thermal expansion coefficient, large active sites, and good thermal-shock resistance, nanostructured silicon carbide (SiC) such as nanowires, nanotubes, and nanospheres have many applications, for instance, drug carriers, catalyst carriers, waste removal, microwave absorption, and photocatalysts.<sup>1–4</sup> In particular, nanostructured hollow spheres have attracted much attention due to the large surface area and high permeability, which can be exploited in applications such as removal of organic contamination from waste water.<sup>5–9</sup> SiC hollow spheres (SiC-HS) are usually synthesized by carbothermal reduction employing silica oxide hollow spheres as the precursor.<sup>10–12</sup> For example, Noh et al. have prepared SiC-HS with a SiO<sub>2</sub> nanoparticle template and carbon coating followed by carbothermal reduction at  $1300^\circ\text{C}$  and HF etching to remove the residual SiO<sub>2</sub>.<sup>9</sup> However, owing to the strong covalent bond in SiC, a high temperature is needed to form the Si–C chemical bond often resulting in defects and sintering.<sup>13,14</sup> In this respect, magnesiothermic reduction (MR) can circumvent these drawbacks such as the high temperature because the exothermic reaction can be activated at a relatively low temperature.<sup>13–15</sup> However, the abrupt and massive heat release in the contact zone may cause rapid growth of SiC and destroy the microstructure. Addition of the proper metal salt is a reason-

able approach to absorb the heat released during the MR process, and the molten salt (MS) can serve as the solvent as well. Liu et al.<sup>13,15</sup> have produced porous SiC nanospheres by mixing silica, carbon, and magnesium powders in LiCl/KCl at a relatively low temperature. Unfortunately, most of the SiC nanospheres have structural defects and it is still challenging to synthesize SiC-HS with good structural integrity, large specific surface, and desirable porosity at a low temperature.

Herein, we report a novel technique combining MR and MS to synthesize mesoporous SiC-HS at a relatively low temperature of  $650^\circ\text{C}$  using carbon-precoated mesoporous SiO<sub>2</sub> hollow spheres (SiO<sub>2</sub>-HS) as the template. The spherical nanostructure has a large specific surface area of  $690.2 \text{ m}^2 \text{ g}^{-1}$ , outstanding ability to remove organic contaminants from water. The SiC-HS also show outstanding cycle ability with adsorption capability retention of 95% after eight times. The technique is promising and can be extended to the fabrication of other nanostructured carbide ceramics.

## II. Experimental Procedures

Synthesis of the SiO<sub>2</sub>-HS followed the procedures described in the literature.<sup>16</sup> The SiO<sub>2</sub>-HS were then coated by polydopamine layer (SiO<sub>2</sub>-HS@PDA) with chemical polymerization method. The process was conducted in 2-amino-2-hydroxy-methyl -propane-1, 3-diol (Tris, 0.24 g), and dopamine (DA, 0.6 g) solution. Subsequently, the carbon-coated SiO<sub>2</sub>-HS (SiO<sub>2</sub>-HS@C) were fabricated by annealing the SiO<sub>2</sub>-HS@PDA at  $750^\circ\text{C}$  for 3 h at a heating rate of  $3^\circ\text{C min}^{-1}$  under Ar atmosphere. Lastly, SiO<sub>2</sub>-HS@C, magnesium powders, and NaCl with a weight ratio of 1:1:10 were mixed and annealed at  $650^\circ\text{C}$  for 4 h. After annealing at  $500^\circ\text{C}$  for 3 h in air and washing with HCl, HF, and distilled water several times to remove MgO, residual SiO<sub>2</sub>, and NaCl, respectively, the mesoporous SiC-HS were obtained.

The structure and composition of the SiO<sub>2</sub>-HS, SiO<sub>2</sub>-HS@C, and SiC-HS were determined by field-emission scanning electron microscopy (SEM: Nova Nano 450, FEI, Co. Ltd., Hillsboro, OR), transmission electron microscopy (TEM: Titan 60-300 Cs, FEI Co. Ltd.), X-ray diffraction (XRD: X'Pert PRO MPD, Philips Co. Ltd., Eindhoven, Netherlands), and X-ray photoelectron spectroscopy (XPS: ESCALB MK-II, VG Instruments Co. Ltd., London, U.K.). The specific surface and pore distribution were measured by N<sub>2</sub> adsorption (BET: ASAP2010, Micrometrics Instruments Co. Ltd., Norcross, GA).

Rhodamine B (RB) was utilized to evaluate the adsorption performance of the SiC-HS. Typically, 20 mg of the SiC-HS were added to 50 mL of the RB solution with a concentration of  $20 \text{ mg L}^{-1}$  under stirring in dark

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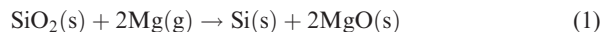
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conditions. A quantity of 5 mL of the solution was taken out and centrifuged every 5 min. After eight extraction experiments, the SiC-HS were recycled by annealing at 400°C in air to remove the organic adsorbates. The adsorbing efficiency was evaluated by UV-Vis spectrophotometry (TU-1810SPC, Beijing PGENERAL Co. Ltd., Beijing, China).

### III. Results and Discussion

The synthesis procedure of the SiC-HS is schematically illustrated in Fig. 1(a). The FE-SEM image and TEM image [Fig. 1(b)] of the SiO<sub>2</sub>-HS show smooth hollow structure with a diameter of 200 nm and a shell thickness of 30 nm. After polymerization and carbonization, the morphology of the SiO<sub>2</sub>-HS@C in Fig. 1(c) is clearly unchanged but the

thickness of the shell increases to 35 nm after carbon coating. Finally, the uniform SiC-HS are obtained by MR at 650°C. The FE-SEM image and TEM [Fig. 1(d)] results indicate that the product inherits the hollow spherical structure of the SiO<sub>2</sub>-HS. The synthesis process can be explained by the following reactions:<sup>17,18</sup>



In the first step, silica is reduced to silicon via the MR in which Mg acts as a reductant, then, the obtained silicon reacts with carbon to form crystalline SiC in virtue of massive exothermic energy from MR.

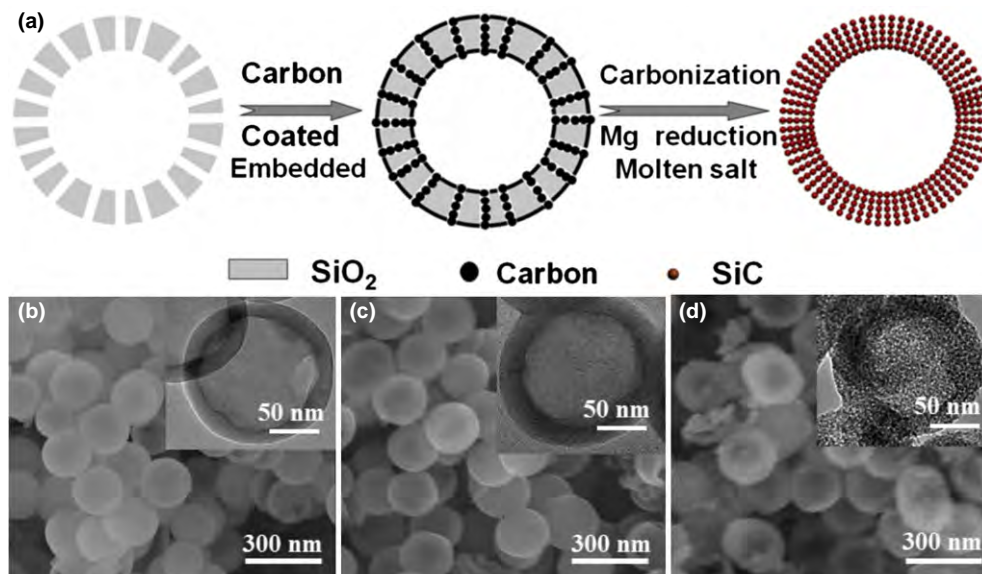


Fig. 1. (a) Schematic illustrating the fabrication procedures of the SiC-HS; FE-SEM images of (b) SiO<sub>2</sub>-HS (c) SiO<sub>2</sub>-HS@C, and (d) SiC-HS with insets being the corresponding TEM images.

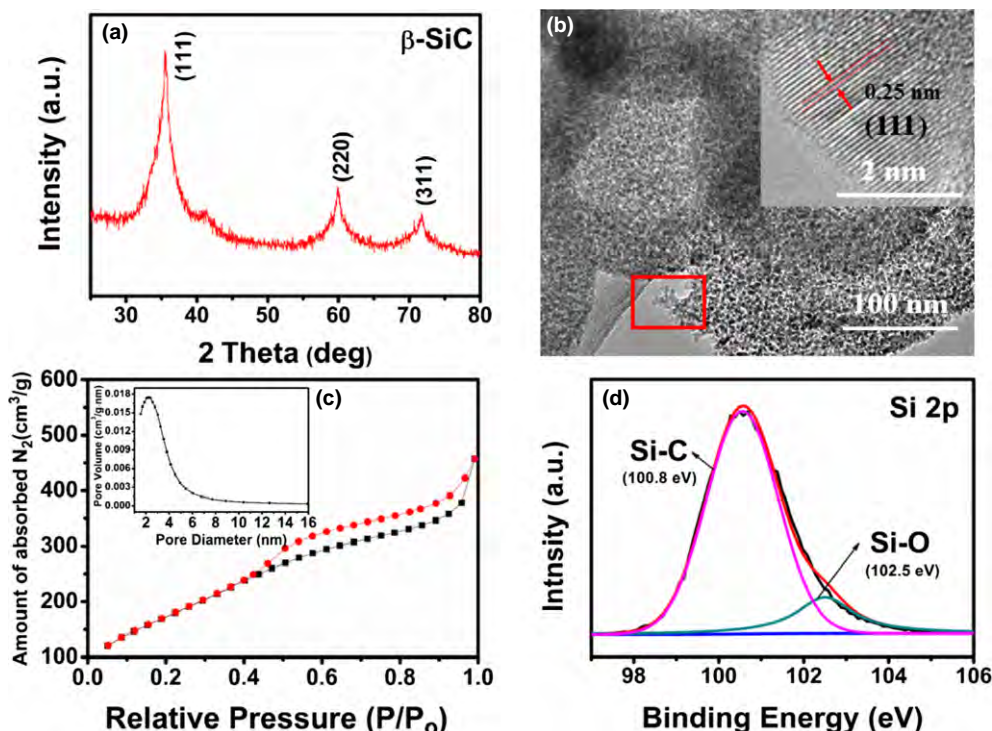


Fig. 2. (a) XRD pattern and (b) HR-TEM image of the SiC-HS; (c) Nitrogen adsorption–desorption isotherm of the SiC-HS with the inset image showing the corresponding pore size distribution; (d) High-resolution XPS spectrum of Si 2p.



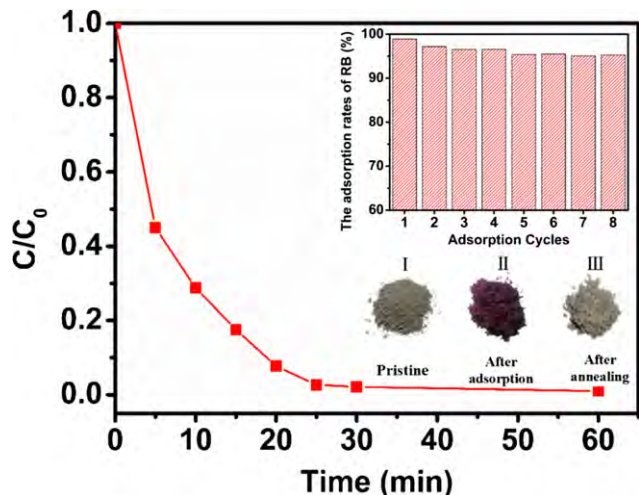


Fig. 3. Adsorption rates of SiC-HS on RB; Insets are recycled adsorption rate of centrifuged RB aqueous solutions after mixing the SiC-HS for 30 min and images of color change of the SiC-HS (I) pristine, (II) after adsorption, and (III) after annealing in air at 400°C.

Figure 2(a) shows that all the diffraction peaks can be indexed to crystalline  $\beta$ -SiC (JSPDS No. 29-1129) and the broad half-peak width implies a small crystal size. HR-TEM [Fig. 2(b)] indicates that the shell of the hollow sphere consists of many crystalline grains with a diameter of 2–4 nm resulting in a large specific surface and the 0.25 nm lattice spacing of the crystal grain assigned to the (111) plane of SiC is confirmed by XRD. The microstructure is further characterized by the  $N_2$  adsorption–desorption analysis. Figure 2(c) shows a typical type IV isotherm with a hysteresis loop in a relative pressure  $P/P_0$  range of 0.4–1.0 indicative of a mesoporous structure. The specific surface area of the SiC-HS is about  $690.2 \text{ m}^2 \text{ g}^{-1}$  and pore volume is  $0.71 \text{ cm}^3 \text{ g}^{-1}$  which is much larger than that of most of other porous SiC nanostructures.<sup>17,18</sup> Barrett–Joyner–Halenda curve indicates that the pore-size distribution of the SiC-HS in the inset is about 2.2 nm in diameter. Figure 2(d) displays the high-resolution XPS Si2p spectrum which can be fitted by two peaks, a strong one associated with Si–C at a binding energy of 100.8 eV and a weak one related to Si–O at 102.5 eV, which indicates the nanosized SiC-HS is a little oxidized inevitably upon exposure to air.<sup>19,20</sup> The nanosized SiC-HS present extreme thermal stability when the temperature is below 500°C (TG and DTA data are not shown).

Mesoporous SiC-HS with good thermal stability and a large specific surface are promising as adsorbents in removal of RB from water, showing a very good adsorption rate in Fig. 3 and over 99% of the RB can be adsorbed in 30 min during the first cycle. The adsorption ability of is investigated after recycling by annealing at 400°C in air to remove the adsorbed RB, 95% of the adsorption rate is recovered suggesting a superb recycle ability due to the high porosity and thermal stability.

#### IV. Conclusion

Mesoporous SiC hollow spheres with a large specific surface area ( $690.2 \text{ m}^2 \text{ g}^{-1}$ ) are synthesized using a template of carbon precoated  $\text{SiO}_2$ -HS at a relatively low temperature of 650°C by the MR technique in the presence of a salt. The precoated carbon facilitates the MR reaction and the salt absorbs the large amount of heat released to avoid collapse of the nanostructure and also serves as the solvent for the

MR reaction. The mesoporous SiC-HS composed of small primary crystalline SiC nanoparticles have a large specific surface and proper pore distribution and are suitable for extracting organic contaminants from water. Owing to the high thermal stability and porosity, the SiC-HS have potential applications such as a ceramic additive, photocatalyst support, as well as drug carrier. The technique can be readily extended to the synthesis of other types of nanostructured carbide ceramics.

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