Low-Temperature Transformation of C/SiO₂ Nanocomposites to β-SiC with High Surface Area

Xiong-Fei Zhang, † Zhouchuan Chen, † Yi Feng, † Jianhao Qiu, † and Jianfeng Yao*, †, ‡, †

† College of Chemical Engineering and ‡ Jiangsu Key Lab for the Chemistry & Utilization of Agricultural and Forest Biomass, Jiangsu Key Lab of Biomass-based Green Fuels and Chemicals, Nanjing Forestry University, 159 Longpan Road, Nanjing, Jiangsu 210037, China

ABSTRACT: Mesoporous silicon carbide (SiC) nanostructures were synthesized by magnesiothermic reduction of carbon–silica (C/SiO₂) nanocomposites at a low temperature of 700 °C by using furfuryl alcohol as the carbon source. The phase, morphology, and structure of the samples were characterized by a combination of X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectra, X-ray photoelectron spectroscopy, thermogravimetric analysis, and N₂ adsorption. The starting C/SiO₂ composites exhibited an interpenetrating network and the resulting SiC preserved the mesoporous properties of the original templates. The SiC products were of β-SiC phase and showed a high surface area of 786 m²/g. The reaction mechanism and role of intermediate species (Mg₃Si) were explored in detail. Furthermore, the resulting β-SiC exhibits remarkable electromagnetic wave absorption performance with a minimum reflection loss of −17.2 dB and reflection loss bandwidth less than −10 dB of 3.7 GHz.

KEYWORDS: Magnesiothermic reduction, β-SiC, High surface area, Microwave adsorption

INTRODUCTION

Silicon carbide (SiC) functional nanomaterials have numerous potential applications in semiconductors, catalysts, functional ceramics, high-frequency electronics, and wave-absorbing devices because of outstanding thermal stabilities, large avalanche breakdown field, excellent mechanical properties, high electron saturation velocity, and superior chemical inertness.¹⁻³ To date, overwhelming breakthroughs in growth of SiC nanomaterials have been achieved and numerous techniques were developed to fabricate nanostructured SiC, including laser ablation, chemical vapor deposition, autogenic pressure reactions, pyrolysis of polymeric precursors, nanocasting, arc-discharge, and carbothermal reduction.¹,⁴⁻⁵ Problems appeared in some of the processes, such as the use of toxic precursors, complicated equipment, and heavy agglomeration of the products. In our previous work, we have reported that SiC nanoparticles and nanofibers can be produced via carbothermal reduction of C/SiO₂ nanocomposites.⁶⁻⁸ However, the carbothermal reduction process involves complicated equipment and always performs at very high temperature (>1300 °C).⁹,¹⁰

Moreover, the conventional carbothermal reduction is not a pseudomorphic transformation process.¹¹ The generation of gaseous silicon monoxide (SiO) intermediate destroys the starting network and causes particle aggregation.¹² Problems related to control of grain growth and sintering make it difficult to produce SiC with high surface area and regular morphological forms. However, in most applications of SiC, surface area is thought to be an important consideration. It is therefore desirable to develop new methods to convert C/SiO₂ composite to the corresponding SiC materials without losing the pristine nanostructure and morphology of the precursors.¹³⁻¹⁵

To this end, increasing attention has been paid to alternative magnesiothermic reduction.¹⁶⁻¹⁸ For example, Shi et al. developed a template approach for directly converting C/SiO₂ composites to hierarchical SiC nanomaterials via a magnesiothermic reaction at a relatively low temperature.¹⁴ They adopted Pluronic F127 block copolymer and polystyrene spheres as dual templates to prepare the precursor. After the magnesiothermic reduction, the structure of the SiC products was consistent with the precursor. A similar approach was taken to synthesize SiC nanomaterials by Mojarad et al. but using mesoporous carbon or zeolites (SBA-15/KIT-6) as hard templates.¹⁰ Herein, we report the fabrication and characterization of SiC with high surface area and well-defined porosity from interpenetrating C/SiO₂ precursors.¹⁷ Furfuryl alcohol (FA) was chosen as the carbon source, and it is one of the most important furanic derivatives that have been industrially converted from renewable saccharidic biomasses.²⁰,²¹ Synthesis of SiC nanomaterials using biobased resources has drawn increasing attention as it is an environmentally-friendly and cost-effective route.²² The prepared SiC nanoparticles were of β-SiC phase with sizes of 40–100 nm. The generation of SiO gas was avoided and thus the original morphology and structure regularity were preserved. The reaction mechanism was
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discussed in detail. In addition, the electromagnetic (EM) wave absorption performance of the SiC nanoparticles was investigated and a remarkable performance was observed.

**EXPERIMENTAL SECTION**

**Materials.** P123 (EO20–PO70–EO20) was purchased from Adamas, China. Tetraethoxysilane (TEOS, 99%) was obtained from Shanghai Lingfeng Chemical, China. Anhydrous ethanol and FA (99%) were purchased from Sinopharm Chemical, China. All chemicals were used as received without further purification.

**Preparation of C/SiO2 Composites.** C/SiO2 nanocomposites were fabricated according to our previous method with minor changes.8,22 In a typical synthesis, 5.0 g of H2O, 3.3 g of ethanol, and 0.5 g of HCl (1 M) were mixed in a capped polypropylene bottle. P123 (4.1 g) was then added to this solution under continuous agitation. After that, 10.0 g of TEOS and 5.0 g of FA were added slowly under vigorous agitation. The resulting mixtures were stirred at room temperature for 3 h and subsequently aged for 4 days and dried at 80 °C for another 3 days. The acquired black monoliths (silica–P123–FA) were ground into powders and carbonized in N2 at the heating rate of 1 °C min⁻¹ and kept at 550 °C for 5 h to form C/SiO2 composites. As comparison, the silica–P123–FA was also calcined under air using the same heating program to produce SiO2.

**Preparation of SiC Nanoparticles.** The obtained C/SiO2 composites were mixed and ground with magnesium powder (C/SiO2: Mg weight ratios of 1:1, 1:2, 1:3, and 1:4), and then transferred into a sealed tube furnace. Before heating, the furnace was vacuumed to evacuate air for 0.5 h. Afterward, the composites were heated under an argon atmosphere with a heating rate of 5 °C min⁻¹ to 700 °C. The samples were kept at the setting temperature for 6 h and then cooled down. Finally, the SiC in high purity was acquired after etching the mixture with HCl (2 M) for 2 h to remove residue compounds and subsequently subjected to carbon burnoff at 500 °C for 5 h. The acquired samples were denoted as SiC-1, SiC-2, SiC-3, and SiC-4 according to the Mg addition.

**Characterization.** The phase structure of the samples was recorded on an X-ray diffractometer (XRD) using Rigaku MiniFlex II with Cu Kα radiation. Nitrogen adsorption—desorption experiments were performed at 77 K with a Micromeritics ASAP 2020. Fourier transform infrared spectra (FT-IR) were conducted by an FT-IR spectrophotometer (Thermo Electron Nicolet-360, USA) using the KBr wafer technique. The morphology of the samples was observed by scanning electron microscopy (SEM) utilizing a JSM-7600F (JEOL Ltd., Japan) with an operating voltage of 30 kV. Thermogravimetric analysis (TGA) (PerkinElmer, Pyris 1 thermogravimetric analyzer) was conducted at a heating rate of 10 °C min⁻¹ to 1000 °C. X-ray photoelectron spectroscopy (XPS, AXIS UltraDLD, Japan) was employed to determine surface electronic states of the samples. All the binding energies were referenced to the C 1s peak of the surface adventitious carbon. Microstructural observations were performed using a transmission electron microscope (TEM, Model 2100F, JEOL Ltd., Tokyo, Japan) operating at 200 kV, and elemental mapping images were obtained by using energy-dispersive X-ray spectroscopy (EDX) attached to the JEOL 2100F microscope.

**Wave Absorption Performance.** For EM wave absorption measurement, the as-synthesized samples were dispersed into paraffin (as substrate) with a weight ratio of 5:5 to fabricate the corresponding composite. The composite was then molded into a ring shape with an inner diameter of 3 mm and an outer diameter of 7 mm. The EM parameters were determined by using an E5071C series vector network analyzer (Agilent, USA) at EM frequencies of 2–18 GHz. The analyzer was in operating mode for at least 30 min before calibration and subsequent data collection. All measurements were carried out in triplicate.

**RESULTS AND DISCUSSION**

**Characterization of the Materials.** To confirm the crystal structure of samples, the XRD pattern of the C/SiO2 composite (Figure 1a) shows a broad hump in the range of 21°–26°, which corresponds to the amorphous silica and carbon. The XRD pattern of SiC without purification (Figure 1b) exhibits several intense diffraction peaks. Some of them are assigned to typical (111), (200), and (220) peaks of cubic MgO phase (JCPDS No. 45-0946), representing the existence of MgO nanocrystals.23,24 The peaks centered at 44.6° and 78.1° are attributed to residual Mg powder. In addition, the weak peak located at 24.2° and 28.1° are indexed to Mg2Si, indicating the presence of a trace amount of Mg2Si.12 It is worth noting that the diffraction peaks of Si were not observed, which can be ascribed to the excess carbon used.

After acid etching and carbon burnoff, the sharp peaks at 2θ = 35.6°, 41.4°, 60.0°, 71.7°, and 75.8° are attributed to the (111), (200), (220), (311), and (222) planes of β-SiC (JCPDS No. 29-1129), respectively.25,26 The slight peak at 33.6° marked with S.F. is ascribed to the stacking faults in the crystalline β-SiC structure. XRD patterns of SiC products synthesized with different Mg addition show the same peaks but with different intensity, which indicates that amorphous C/SiO2 precursor was transformed into SiC via low-temperature magnesiothermic reduction. No evidence of phases associated with other impurities is observed, implying that Mg2Si and MgO were both completely removed by HCl treatment. It should be highlighted that HF or HNO3 is not used in the purification process, as there is no residual SiO2 in the resulting products. The average crystallite size of the β-SiC was calculated to be 7.9 nm by Scherrer analysis.

The microstructure of the SiC products were further characterized by the N2 adsorption—desorption analysis. As illustrated in Figure 2, all samples present a representative type IV isotherm with a hysteresis loop at P/P0 of 0.4–0.8, indicating the presence of mesoporous structures. The samples possess higher N2 adsorption capacity than that of most other SiC nanomaterials reported previously.9,14 The BET surface area of the mesoporous SiC initially increases from 704 to 786 m²/g when the weight ratio changes from 1:1 (SiC-1) to 1:2 (SiC-2), and then decreases to 586 m²/g when the weight ratio becomes 1:3 (SiC-3). The decrease of the surface area might be attributed to the abrupt and massive heat release caused by addition of excess Mg powder. The heat generated in the contact zone between Mg and C/SiO2 composite ruins the pristine porous structure to some extent and leads to rapid growth of SiC crystals. With further increasing of the Mg addition, the specific surface area of SiC-4 decreases substantially to 170 m²/g, confirming the sintering and

![Figure 1. XRD patterns of the C/SiO2 composite (a) and the products before purification (b), SiC-1 (c), SiC-2 (d), SiC-3 (e), and SiC-4 (f).](Image 363x584 to 526x716)
aggregation of SiC nanoparticles. N₂ adsorption isotherm of C/SiO₂ composites also display type IV curves (mesoporous structures) and have a BET specific surface area of 1022 m²/g. As compared with the interpenetrating C/SiO₂ precursor, the obtained SiC products inherit the sufficient mesoporosity and preserve the high surface area. The relatively weaker order of mesopores in SiC products is due to the slight collapse of part framework during the synthesis process. It is concluded that the mesoporous C/SiO₂ nanocomposite serves as matrix template and Mg powder plays a crucial role in determining the surface area.

Figure 3 illustrates the FT-IR spectra of the as-synthesized C/SiO₂ precursor and SiC products. All samples show an obvious broad peak at around 3450 cm⁻¹, which is associated with the O–H stretching vibration mode of the adsorbed water. And the absorption bands centered at 1645 cm⁻¹ are caused by the O–H bending vibration mode. For C/SiO₂ nanocomposite, the strong bands at 1080 and 460 cm⁻¹ are ascribed to the asymmetric Si–O–Si stretching vibration. Upon reduction treatment and purification process, the peak belonging to the mesoporous silica is significantly weakened. But a pronounced band centered at 830 cm⁻¹ corresponding to the vibration of Si–C bond appears. Consistent with XRD results, the FT-IR spectra verified the successful formation of SiC from the initial C/SiO₂ composites.

Thermogravimetric (TG) analysis was conducted and TG curve of SiC-2 is shown in Figure 4a. The measurement result implies that the as-prepared SiC has oxidation resistance and thermal stability. There is no drastic weight gain or loss below 700 °C. The slight weight increase above 700 °C could be attributed to the partial oxidation of nanocrystalline SiC under oxidative atmosphere, which is in line with prior reports. Besides, the molar ratio of C:Sio₂ in the precursor C/SiO₂ composite was calculated to be 3.4:1 by burnoff of the carbon in air at 550 °C for 5 h. As illustrated in Figure 4b, the morphology of SiC-2 shows uniform particle size of about 40–100 nm. Although slight aggregation of nanoparticles was observed, the original nanostructures of precursors are fairly well retained after magnesiothermic reduction. By contrast, in the carbothermic reduction, the SiC nanoparticles are subjected to severe agglomeration because of the high reaction temperature and intense exothermic process. There is no detectable structural shrinkage occurring in magnesiothermic reduction. Three reasons are summarized: (1) interpenetrating C and SiO₂ in the composite contributes to a rigid framework, which acts as stable support or a barrier against aggregation. (2) Structure and porosity preservation is favored by a low temperature. (3) There is no evidence of SiO gas produced during the reaction; thus, the SiC products exhibit very low sinterability.

The prepared SiC samples were gray green in color, which was consistent with the color of SiC obtained in industries using coke as the carbon source. A representative TEM image of SiC-2 is shown in Figure 5a, which evidently appears that the product is mainly composed of nanoparticles with sizes of 40–100 nm. As illustrated in Figure 5b,c, elemental mapping images of SiC-2 nanoparticles reveal the presence of Si and C. In addition, the weak O element signal in the mapping image (not shown) is attributed to the inevitable oxidation on the surface of SiC nanoparticles.

XPS analysis was performed to study the chemical state of SiC nanoparticles and the results are presented in Figure 6. The
XPS spectrum of Si 2p (Figure 6b) region shows two peaks. The peak located at 100.4 eV can be assigned to Si in SiC form, while the weak peak centered at 102.0 eV corresponds to Si in SiO₂. This is in agreement with XRD and FT-IR results. As illustrated in Figure 6c, the C 1s peak can be deconvoluted into two subpeaks at 282.7 and 286.3 eV associated with SiC particles and trace residual carbon, respectively.

**Reaction Mechanism.** With respect to the specific reaction process, several mechanisms have been proposed and the detailed mechanism is still underway. Shi et al. stated that SiO₂ is reduced to Si and then Si reacts with C to produce SiC,¹⁴ while other researchers thought that Mg reacts with C initially to generate Mg₂C₃ or MgC₂ intermediate and subsequently MgC₂ interacts with SiO₂ to form SiC.¹¹ Some other studies suggested that Mg₂Si is the possible intermediate species.¹² However, available studies mostly lack insights into the basic thermodynamics of reactions.³¹,³² Thermodynamics calculations have proven to be a useful tool for explaining and understanding the reactions steps at the atomistic level.³³ As shown in Figure 7, the Gibbs free energy changes (ΔG) for reaction (5) is more negative in 700 °C, demonstrating the thermodynamic possibility of formation of Mg₂Si based on the theory.

On the basis of our experimental results, a two-step reaction mechanism is given as follows:

\[
\text{SiO}_2 + \text{Mg} \rightarrow \text{Mg}_2\text{Si} + 2\text{MgO} \quad (1)
\]

\[
\text{Mg}_2\text{Si} + \text{SiO}_2 + \text{C} \rightarrow 2\text{SiC} + 2\text{MgO} \quad (2)
\]

The overall reaction can be described as:

\[
\text{SiO}_2 + 2\text{Mg} + \text{C} \rightarrow \text{SiC} + 2\text{MgO} \quad (3)
\]

As the reaction temperature was over the melting point of Mg (~650 °C), Mg₂Si was formed at the Mg–SiO₂ interface. This is supported by the XRD pattern of magnesiothermic reduction performed at a lower temperature of 650 °C (Figure 8), in which the peaks corresponding to Mg₂Si were clearly observed.²⁹ In addition, this process preserved the nanostructure of SiO₂ templates by avoiding the formation of gaseous SiO that breaks down the initial structure.¹⁴

The formation process of SiC was proposed in Figure 9, where the in situ-formed Mg₂Si encounters C and subsequently

![Figure 5. TEM image of SiC-2 (a) elemental mapping images of C (b) and Si (c).](image)

![Figure 6. XPS survey spectrum of the SiC-2 (a), and high-resolution scans of Si 2p (b) and C 1s (c) XPS spectra with the fitted results.](image)

![Figure 7. Gibbs free energy changes as a function of the temperature (calculated by Software HSC Chemistry 6.0).](image)

![Figure 8. XRD patterns of the product before purification (650 °C).](image)

![Figure 9. Schematic illustration of the reaction mechanism for SiC formation.](image)
converts to SiC. In our syntheses, the C/SiO₂ composites were synthesized via infiltrating FA into the mesochannels of SiO₂. Ethanol and HCl were used to slow down the cationic polycondensation process of FA for keeping pace with the hydrolysis of TEOS. Therefore, interpenetrating C/SiO₂ composite makes it possible for the Mg_{2}Si intermediate to directly react with nearby C species. The well-dispersed C species in the self-supporting C/SiO₂ framework prevents the SiC products from aggregating and sintering further. The excess amount of C and its good contact with SiO₂ facilitating SiC formation are crucial for maintaining the integrity of the mesoporous structure. Using Mg not only reduces the reaction temperature but also allows preparation of SiC materials with a high mesoporosity. Mg powder acts as reagent in the first step and serves as catalyst in the second step. The amounts of Mg addition decide the violence of the reaction, and thus influence the final morphology and structure of SiC products.

Microwave Absorption Performance. As displayed in Figure 10, the sample (SiC-2 was tested as an example) shows considerable EM wave absorption with a minimum reflection loss of −17.2 dB and absorption bandwidth less than −10 dB (over 90% microwave absorption) of 3.7 GHz (between 8.1 and 11.8 GHz). All these values are superior to that in the (over 90% microwave absorption) of 3.7 GHz (between 8.1 and 11.8 GHz). These values are superior to that in the literature, demonstrating that the prepared SiC materials have excellent electromagnetic-wave-absorbing performance. The resulting SiC products preserved the mesoporous properties of the original templates. The excellent microwave absorption performance of SiC-2 is attributed to multidielectric polarization arising from the high surface area and the mesoporous structures. This provides a high density of stacking faults and polarized centers, thus making the space charge polarization and relaxation process easier by trapping space charges.

CONCLUSION

In this study, mesoporous β-SiC with a high surface area of 786 m²/g has been prepared at a relatively low temperature of 700 °C via the magnesiothermic reduction. This method provides greater control of the structural ordering and the products preserve the nanostructure and mesoporosity of the interpenetrating precursor. Moreover, the reaction mechanism was explored in detail and some new insights were delivered. We have provided conclusive evidence that SiO₂ is first reduced to the intermediate product Mg_{2}Si, and then SiC is formed from the metathesis of Mg_{2}Si and C. The approach presented here is expected to be a general way for various nanostructured carbide materials at relatively low temperature by carefully designing structures of their precursors. Sample SiC-2 exhibits remarkable EM wave absorption with a minimum reflection loss of −17.2 dB and reflection loss bandwidth less than −10 dB of 3.7 GHz. This material has great potential in the application of high-temperature EM wave absorbers because of its high surface, good thermal stability, excellent chemical resistivity, and low density.

AUTHOR INFORMATION

Corresponding Author
*E-mail: jfyao@njfu.edu.cn (J.F.Y.).

ORCID
Jianfeng Yao: 0000-0002-3619-6741

REFERENCES


