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Rapid synthesis of nanostructured porous silicon carbide from biogenic silica

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Abstract:

Nanostructured silicon carbide (SiC) is an exceptional material with numerous applications e.g. in catalysis, biomedicine, high performance composites, and sensing. In this study, a fast and scalable method of producing nanostructured SiC from plant materials by magnesiothermic reduction via self-propagating high-temperature synthesis (SHS) route was developed. The produced biogenic material possessed a high surface area above 200 m²/g with a SiC crystallite size below 10 nm, which has not been done previously by SHS. This method enables affordable synthesis of the material plant-based precursors in a reaction that only takes a few seconds, thereby paving a way for nanostructured silicon carbide production in high volumes using renewable resources. The material was also functionalized with carboxylic acid and bisphosphonate moieties, and its use as metal adsorbent in applications such as wastewater remediation was demonstrated.

Keywords: adsorption/adsorbents • biomass • composites • nanostructures • silicon carbide

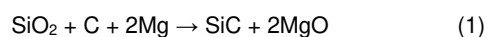
Introduction

Silicon carbide is a remarkable material because of its unique mechanical, thermal, chemical and electric properties.¹ For example, it is a semiconductor, one of the hardest known materials and has a very high thermal stability. It is also highly inert against numerous chemical reactions and is shown to be both bio- and hemocompatible.^{1,2}

Nanostructured SiC has, in addition to the beneficial properties of bulk SiC, size-dependent features which have made it an attractive material for e.g. biomedical applications, catalysis, coatings, composites and as a precursor for sintering bulk bodies.^{1,3-7} Common processes for production of nanostructured SiC include chemical vapor deposition (CVD), sol-gel and plasma processes.⁸ Depending on the method, nanostructured SiC can be made in several forms such as nanoparticles, nanowires, nanoflakes, and nanoflowers.⁶ Nanostructured SiC can also be prepared as mesoporous microparticles.^{7,9} Because of the excellent chemical and thermal stability, mesoporous SiC has an advantage over more commonly used mesoporous materials such as mesoporous silica and silicon in applications involving aqueous environments, corrosive chemicals, or high temperatures.

New processes to prepare nanostructured SiC with improved structural and functional properties are frequently reported. Ortega-Trigueros et al. produced high surface area SiC by CVD using hierarchical mesoporous silica template obtaining mesoporous SiC with 118 m²/g surface area.⁷ An et al. obtained an even higher surface area (162 m²/g) monolithic SiC aerogel by carbothermal reduction of catechol-formaldehyde/silica aerogel precursor.¹⁰ Shcherban et al. compared the use mesoporous silicas with different nanostructures as templates in synthesis of mesoporous SiC by carbothermal reduction.¹¹ They found that the nanostructure of the carbon/silica composite precursor significantly affected the morphology of the SiC product yielding surface areas of up to 410 m²/g when using the highest surface area precursor. Despite the progress in obtaining various SiC nanostructures, it is still challenging to produce nanostructured SiC in large quantities.⁸

Recently, a new method of producing porous nanostructured SiC was developed based on converting precursors comprising of mesoporous SiO₂ and carbon into nanostructured SiC by magnesiothermic reduction at a relatively low temperature of approximately 600 °C.^{9,12} The reduction takes place according to the following highly exothermic reaction.



A prerequisite for the success of this reaction is a high contact area between the SiO₂ and C phases since the diffusion of the reactants through the solid materials becomes very slow already after only few nanometers thick SiC layers have been formed.¹³ Therefore, synthetic ordered mesoporous silicas with high surface areas up to 1000 m²/g have been used as precursors. Recently, nanostructured SiC was produced from rice husks, a widely available agricultural residue, using magnesiothermic reduction.¹⁴ Making nanostructured SiC by magnesiothermic reduction requires heating the precursors in small batch sizes for several hours at a temperature above 600 °C. It is not possible to increase the batch size to high volumes because of the highly exothermic nature of the reaction, making it poorly scalable. One way of accomplishing magnesiothermic reduction is through the so called self-propagating high-temperature synthesis (SHS). In this method, a high temperature reaction front propagates through the precursors and the products are formed in a short time frame. SHS is an advantageous way of producing SiC because of low energy consumption and high purity of the products. Few reports have shown that SHS is possible for SiC production from biogenic silica obtained from rice husks, corn cob ash, and bagasse ash.¹⁵⁻¹⁷ However, very fine nanostructures (< 50 nm) of SiC have not been reported and remains a

very significant synthetic challenge, presumably because the high temperature generated during the reaction causes excessive crystal growth and sintering of the SiC structures.

In this study, magnesiothermic reduction via SHS is used for the first time to produce porous SiC (PSiC) with very fine (<10 nm) crystallite size from biogenic silica. The conversion of SiO₂ from tabasheer¹⁸ (extracted from bamboo) to SiC can be done in just a few seconds at a relatively low temperature to yield very fine SiC crystals possessing a high surface area. This combination of biogenic silica precursor and fast reaction time opens the possibility of producing the material sustainably in high volume from affordable and renewable source materials. Other plant-based silica precursors from e.g. husk and straws of wheat, barley and rice could also be utilized in this method. These precursors are found in large volumes in various agricultural residues but are rarely utilized. These kinds of processes are important for transition to circular economy in the future.

In this work, we also demonstrate that the material can be functionalized with suitable organic moieties such as bisphosphonates.^{19,20} Because of its metal adsorbing properties, high surface area, and chemical stability, such material has potential applications e.g. in treatment of wastewater.

Experimental procedures

Detailed experimental procedures are given in the Supporting information including description of the characterization methods. The Sample preparation methods are summarized below. Tabasheer powder was commercially obtained from Bristol Botanicals Ltd. and purified in 10 % hydrochloric acid at 100 °C for 2 h. After washing with deionized water, the powder was calcined at 500 °C in air for 4 h to remove organic components.

Composites of SiO₂ and C were prepared with a method similar to the method used by Zhao et al.²¹ First, 119 mg, 238 mg or 476 mg of sucrose was dissolved in 1 ml of 2.7 % H₂SO₄. The solution was then mixed with 400 mg of the purified SiO₂ powder and the mixture was heated slowly up to 160 °C for 5 h in order to dehydrate the sucrose and form a SiO₂/C composite. Finally, the samples were heated at 700 °C in an argon atmosphere for 2 h.

The SiO₂/C composites were mixed with 400 or 800 mg of Mg powder and placed in a quartz boat as a 10 cm long and 1 cm wide powder bed. The samples were then heated in a tube furnace from room temperature up to 650 °C, 725 °C or 800 °C in an Ar atmosphere in order to reduce the SiO₂ into SiC. The average heating rate up to 650 °C was 74 °C/min and the total heating time 4.5 h unless otherwise mentioned. After the reduction, the samples were cooled down to room temperature and washed with 40 ml of 37 % HCl at 70 °C for 2 h to dissolve any MgO, Mg₂Si and Mg phases. The samples were then filtered, washed with deionized water and dried overnight under vacuum. Finally, the samples were immersed in 1M NaOH for two days to remove SiO₂ and Si phases leaving only SiC and carbon phases in the samples. Three replicates were prepared for each sample type. Samples are named according to the Mg amount, reduction temperature, and initial carbon amount as shown in Fig. 1.

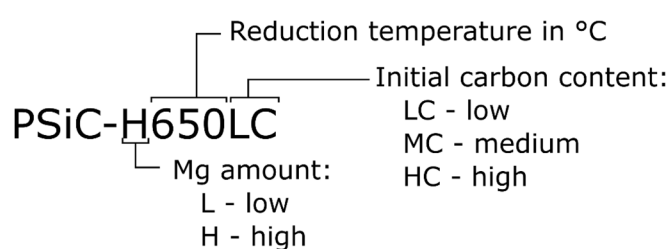


Figure 1. Sample codes explained. L, low Mg amount in reduction (1:1 Mg:SiO₂ in mass); H, high Mg amount in reduction (2:1 Mg:SiO₂ in mass); 650, 725 or 800: reduction temperature in °C; LC, low initial carbon amount (m(sucrose)/m(SiO₂)=0.3); MC, medium initial carbon amount (m(sucrose)/m(SiO₂)=0.6); HC, high initial carbon amount (m_{sucrose}/m_{SiO₂}=1.2). Sample label with a -Q at the end means a shorter reaction time.

The NaOH washed PSiC-H650MC was functionalized with undecylenic acid (Fig. 2a) via a two-step method. First, 30 mg of the PSiC particles was heated at 400 °C under argon atmosphere for 30 min. Then the particles were cooled down to room temperature while maintaining the argon flow and neat undecylenic acid was added on the particles while maintaining an Ar atmosphere. The sample was then heated at 120 °C for 19 h. Finally, the particles were washed with dichloromethane to remove excess undecylenic acid and dried under ambient conditions.

Bisphosphonate molecules (Fig. 2b) containing protective trimethylsilyl groups (Tetrakis(trimethylsilyl) 1-(trimethylsilyloxy) undec-10-ene-1,1-diylbisphosphonate) were synthesized as described elsewhere²⁰. The bisphosphonates were grafted on the PSiC-H650MC by first heating 60 mg of the PSiC powder at 150 °C under N₂ atmosphere. The powder was cooled down to room temperature while maintaining the N₂ flow and 120 mg of the bisphosphonate mixed in 5 ml of mesitylene was added on the particles. The sample was then heated at 120 °C for 19 h followed by washing with methanol to remove excess bisphosphonates and the protective trimethylsilyl groups. All the samples were dried under ambient conditions.

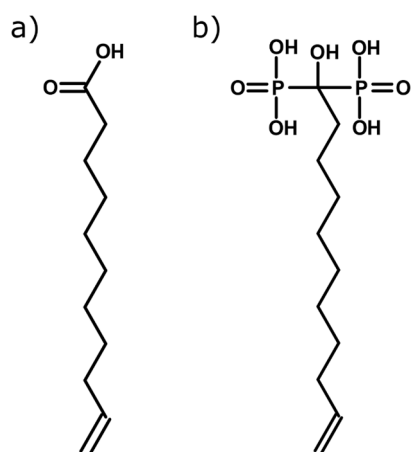


Figure 2. Functional molecules grafted on PSiC a) undecylenic acid b) a bisphosphonate. The depicted bisphosphonate structure does not include the protective trimethylsilyl groups present on the bisphosphonate during the grafting reaction. The protective groups were removed by washing after grafting.

Results

Biogenic silica was purified from tabasheer powder by HCl washing and calcination. The purified SiO₂ had a white color, high surface area of 302 m²/g, and average pore size of 10 nm (Table 1).

Reduction of the SiO₂/C composite was performed at three temperatures (650 °C, 725 °C and 800 °C) with either a 1:1 or 2:1 mass ratio of Mg to SiO₂. The X-ray diffractograms (Fig. 3a) show that with a low Mg amount, very little crystalline SiC and Si were

produced (samples PSiC-L650MC, -L725MC and -L800MC, see explanation of sample codes in Fig. 1). However, with higher amounts of Mg, broad diffraction peaks from nanocrystalline SiC were observed as well as narrower Si peaks (samples PSiC-H650MC, -H725MC and H800MC). The SiC diffraction patterns resembled 3C-SiC polytype patterns with triangular peak shapes, implying that populations of crystallites with different sizes were present in the sample. However, a closer inspection revealed that the SiC samples also contained at least one other polytype. Positive identification of the SiC polytypes was not possible because SiC has numerous polytypes with similar diffraction patterns, the measured diffraction peaks were very broad, and the peaks had an unconventional shape. Generally, a good fit was obtained by using two commonly observed SiC phases, 3C with larger crystallites and 15R with smaller crystallites. The calculated crystallite sizes are shown in Table 1. The average crystallite size of the 3C phase was approximately 5 nm with samples reduced with higher Mg amount and approximately 3 nm when lower Mg amount was used. Similarly, larger 25-31 nm Si crystallites were produced with higher Mg amount and smaller 9-11 nm Si crystallites with lower Mg amount. It is noteworthy that halos in the 2θ 20-30° typical for amorphous silica are also clearly visible, especially for samples with low Mg contents.

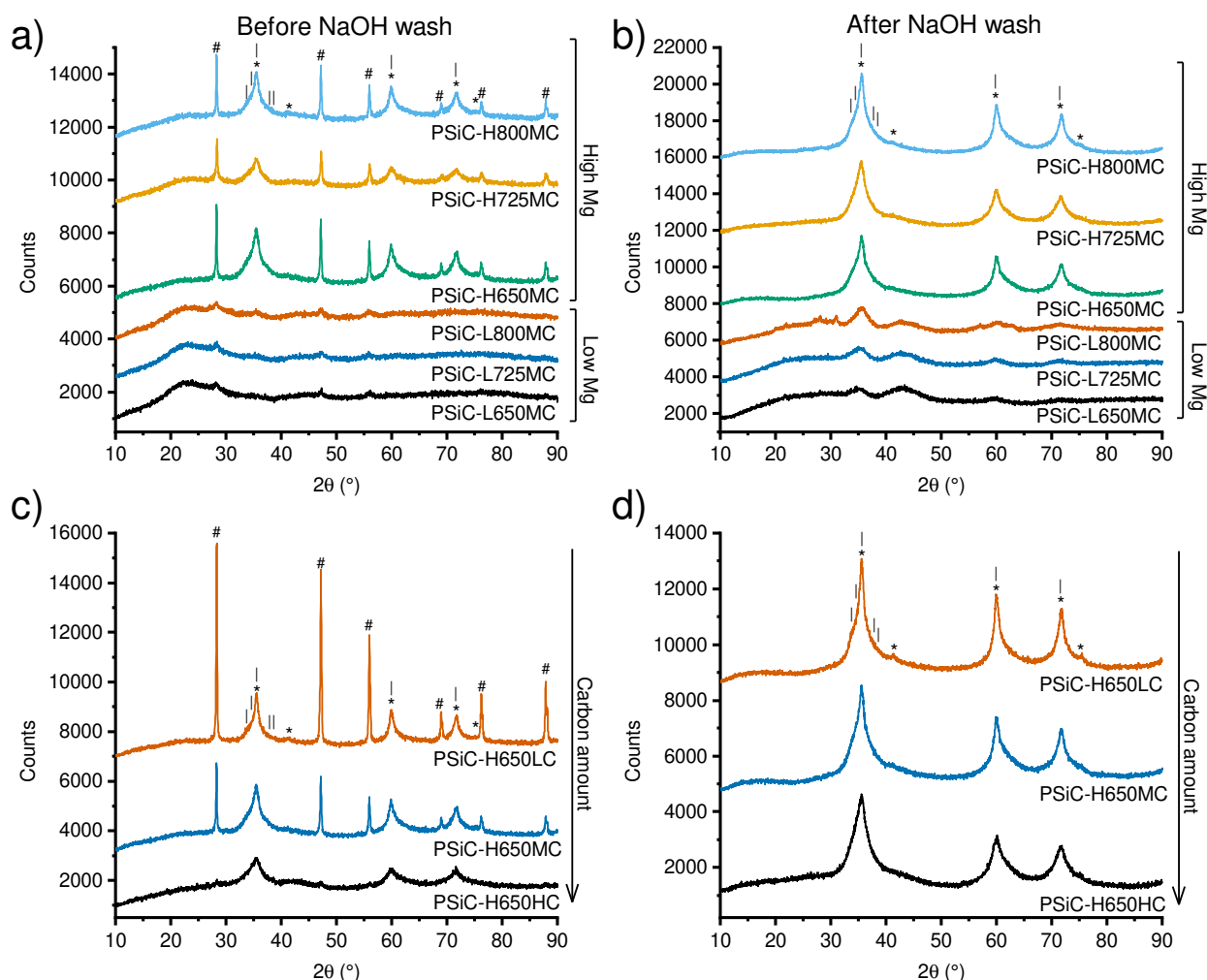


Figure 3. X-ray diffractograms showing the effect of reduction temperature, Mg amount (graphs a and b) and initial carbon amount (c and d). Diffractograms in a and c are measured before and after diffractograms in b and d after dissolving the SiO₂ and Si phases with NaOH wash. The diffraction peaks are labelled as * (3C-SiC), | (15R-SiC), and # (Si).

After washing the samples with 1 M NaOH to dissolve Si and SiO₂ phases, the Si peaks were not observed. The SiC peaks became slightly more intense with the samples reduced with low amount of Mg (Fig. 3b) in part because of the disappearance of the amorphous halo. The materials reduced with relatively low amounts of Mg showed an increased intensity of the SiC peaks with increasing reduction temperature. In contrast, the temperature did not have a significant effect on the diffractograms when samples were reduced with higher amounts of Mg.

Effect of the initial amount of carbon in the SiO₂/C composite was studied by doubling (sample PSiC-H650HC) and halving (sample PSiC-H650LC) the initial carbon amount compared with sample PSiC-H650MC while using the higher 1:2 SiO₂ to Mg ratio and a 650 °C reduction temperature. The diffractograms measured before a NaOH wash show that the amount of carbon has a significant effect on the amount of Si produced during the reduction (Fig. 3c). With high initial carbon amount, almost no crystalline silicon was observed whereas the most intense Si peaks were observed when the lowest amount of carbon was used. After the NaOH wash, the diffractograms of samples with medium (PSiC-H650MC) and low (PSiC-H650LC) carbon content were similar (Fig. 3d). The sample with high initial carbon content showed slightly less intense SiC peaks and also a higher background intensity, especially at low 2θ angles most likely because of high amounts of amorphous carbon remaining in the sample after reduction. The crystallite size of 3C SiC and Si was also dependent on the initial carbon amount with low carbon amount producing the largest crystallites (Table 1).

Amounts of carbon remaining in the samples after NaOH wash was determined by TG measurements in synthetic air (see Table 1 and Fig. S1 in Supporting information). All the samples showed mass loss between 400 and 650 °C because of oxidation of amorphous carbon. The samples reduced with the low amount of Mg had high carbon content varying from 40 to 60 wt% depending on the reduction temperature. The samples reduced with a high amount of Mg had significantly lower content of free carbon, approximately 12 wt%, suggesting a better yield of the reaction. This result was corroborated by XPS measurements showing that the atomic ratio between C and Si to be 5.5 in low Mg sample L650MC and 1.3 in high Mg sample H650MC (Table S1, Supporting information). The TG measurements showed no systematic dependency of free carbon on the reduction temperature with the high Mg samples. Initial carbon amount had an expected effect on the free carbon content after reduction. Low initial carbon content led to 3 wt% of free carbon and high initial carbon amount leading to 29 wt% free carbon content.

The mesoporous texture of the NaOH washed materials was studied by nitrogen sorption (Table 1, and Figs. S2, S3 in Supporting Information). All the isotherms exhibited a hysteresis loop indicating mesoporosity. The samples reduced with low Mg content (Fig. 3a) had very high surface areas between 650 and 900 m²/g depending on the reduction temperature. If high Mg and medium carbon amounts were used, the measured surface area was between 300 and 400 m²/g and no systematic dependency with reduction temperature was observed. All the samples had a wide distribution of pores primarily below 50 nm (Fig. S4, in Supporting Information) and the average pore size was between 12 and 27 nm. Surface areas were strongly dependent on the initial amount of carbon varying from 227 m²/g (low initial carbon amount) to 610 m²/g (high initial carbon amount) when the high Mg amount was used.

The synthesis conditions had a significant effect on the SiC yield. If a low amount of Mg was used, the yield of SiC was quite low, from 13 to 26 % of the theoretical maximum. An increasing trend in the yield with increasing reduction temperature could be seen, although the differences were not statistically significant. If a high amount of Mg was used, the yield was increased up to 51 and 57 %, without significant difference between samples reduced at different temperatures. Initial amount of carbon had a moderate effect on

the yield. The highest yield (60 %) was obtained with the sample reduced with the highest initial carbon amount and the lowest yield (44 %) with the lowest initial carbon amount.

The effect of reduction time was tested by preparing samples similar to PSiC-H650MC but instead of heating the samples for 4.5 h the tube oven was opened immediately after the oven reached 650 °C (heating time 8.5 min) and the samples were let to cool down quickly (labelled PSiC-H650MC-Q). There was no statistically significant difference between any of the measured properties between the samples with different reduction times (Tables 1 and S1, Supporting Information).

Loading the sucrose solution into the pores of the SiO₂ powder by incipient wetness method was also tested. This was done to ensure that all the carbon was in the pores but no effect on the PSiC properties was observed (data not shown).

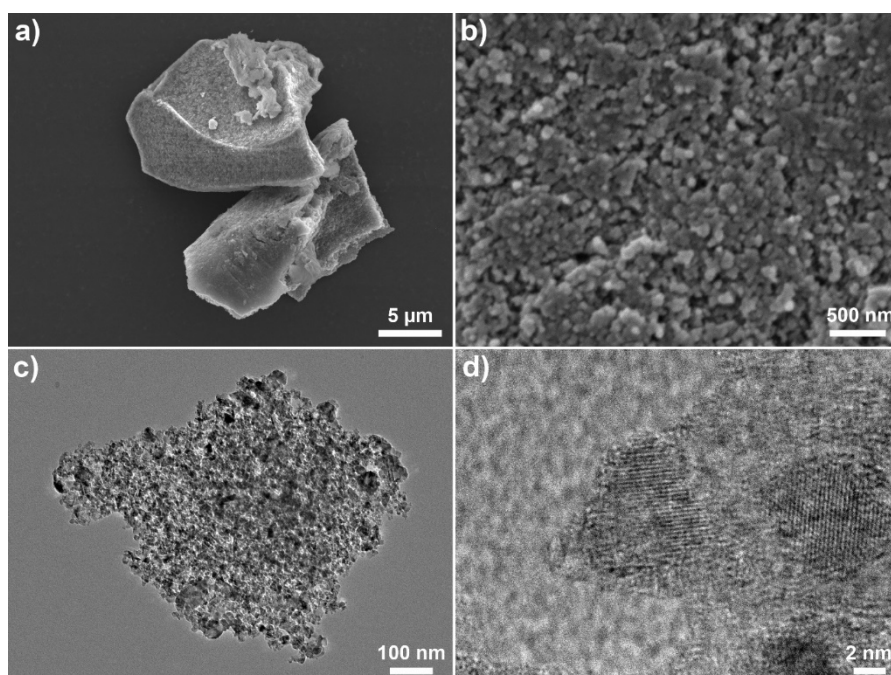


Figure 4. SEM (a and b) and TEM (c and d) images of the sample PSiC-H650 after NaOH wash.

Based on the results, the sample PSiC-H650MC was chosen for further studies. SEM and TEM images of this material are shown in Fig. 4. Microparticles with porous surface were seen in the SEM images. TEM images revealed a porous structure and small crystallites with an average interplanar distance of (0.255 ± 0.004) nm consistent with interplanar distance of (111) planes in 3C-SiC (0.252 nm). The median particle size, measured with laser diffraction, was (18 ± 2) μm and the particle size distribution is shown in Fig. S5 in Supporting Information.

The chemical composition of PSiC-H650MC was studied with solid state NMR, XPS and FTIR. According to XPS, the sample consisted of 29 wt% of carbon, 51 wt% of silicon i.e. atomic ratio of 1.3 (C/Si) (Table S1, Supporting information). The sample also contained 15 wt% of oxygen as well as 4 and 1 wt% of Mg and Na impurities, respectively.

The ²⁹Si CPMAS and ¹³C CPMAS spectra are shown in Fig. 5a. The ²⁹Si CPMAS NMR spectrum reveals that the Si species in the material are mainly SiC (-9 ppm). Minor amounts of oxycarbides and SiO₂ were observed besides the main resonance in the range of -130 to -40 ppm²². The oxides are presumably native oxides known to appear on SiC surfaces under oxygen containing, especially

in nanostructured SiC.^{23,24} The acquisition time of ca. five days was needed to obtain the ^1H - ^{13}C CPMAS NMR spectrum presented in Fig. 5b. However, even with the long acquisition time the signal-to-noise ratio is very low. The reason for the poor signal-to-noise ratio is probably the small amount of carbon species that are located in the vicinity of hydrogen atoms. The ^{13}C CPMAS spectrum (Fig. 5b) shows two resonances at chemical shifts of 26 and 129 ppm. The signal at lower chemical shift corresponds to sp^3 hybridized carbon consistent with SiC and the resonance at higher chemical shift corresponds to sp^2 hybridized carbon in the free carbon²². The higher intensity of the latter resonance is most likely due to the higher abundance of hydrogen in vicinity of the sp^2 hybridized carbon species compared with the sp^3 hybridized carbon found mainly in the SiC phase and does not correspond to relative amounts of these carbon species. The FTIR spectrum of the PSiC-H650MC sample (Fig. S6 in Supporting Information) shows a strong SiC absorption at 820 cm^{-1} as well as surface $-\text{OH}$ groups or water around 3500 cm^{-1} and 1630 cm^{-1} .

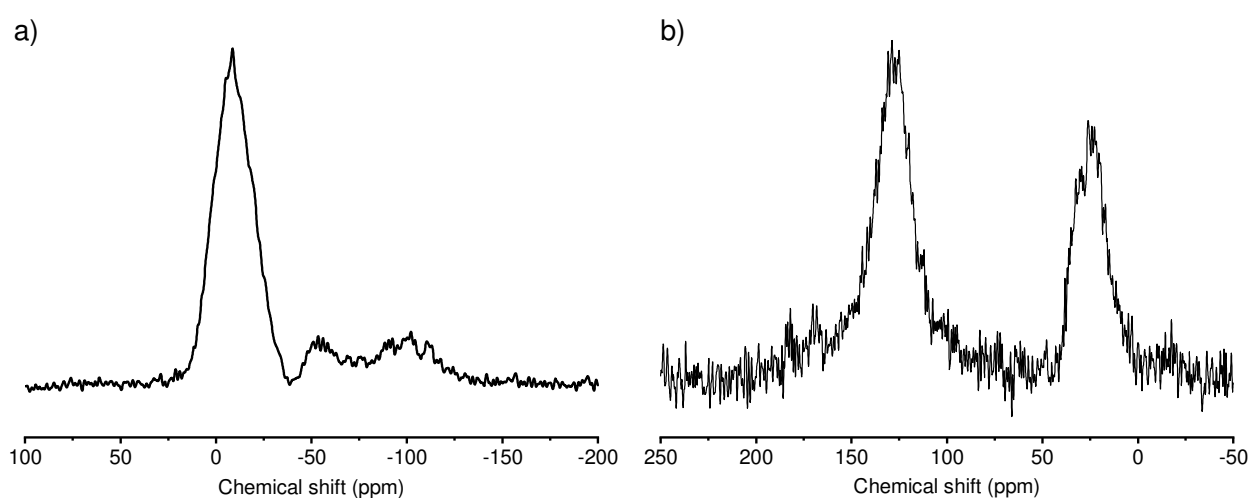


Figure 5. a) ^{29}Si CPMAS NMR and b) ^{13}C CPMAS NMR spectra of PSiC-H650MC.

The possibility to functionalize the material with organic molecules was tested with undecylenic acid and a bisphosphonate molecule (Fig. 2). The functionalization was performed by radical addition at $120\text{ }^{\circ}\text{C}$ in neat undecylenic acid or a mesitylene solution of the bisphosphonate. The amount of organic molecules grafted on the surface was determined by TG. The undecylenic acid functionalization yielded surface coverage of (1.1 ± 0.3) molecules per nm^2 and the bisphosphonate functionalization coverage of (0.26 ± 0.02) molecules per nm^2 . The FTIR spectrum of undecylenic acid functionalized PSiC showed additional peaks attributed to CH_x and $\text{C}=\text{O}$ -groups (Fig. S6 in Supporting Information). There CH_x peaks were also observed in the FTIR spectrum of the bisphosphonate modified material but no clear peaks of the phosphorus groups were detected because of the relatively low amount of the bisphosphonate molecules and overlapping peaks at the $1000\text{--}1300\text{ cm}^{-1}$ range (Fig. S6 in Supporting Information).

The applicability of the bisphosphonate functionalized PSiC was tested in adsorption of lead ions. The functionalized PSiC powder was immersed in a 30 ppm Pb^{2+} solution at pH 2.5. The material adsorbed $(109 \pm 5)\text{ }\mu\text{mol}$ of Pb per gram and the material could be regenerated by desorbing the lead with 1 M HNO_3 .

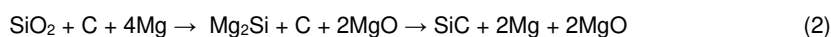
Discussion

Nanostructured silicon carbide was produced from biogenic silica, obtained from tabasheer, by magnesiothermic reduction. High surface area has been shown to be an important factor when choosing a silica precursor in the magnesiothermic reduction.^{12,13} The high surface area (> 300 m²/g) of tabasheer makes it a good choice in this regard.

A higher Mg to SiO₂ mass ratio was clearly beneficial for the formation of SiC. With Mg:SiO₂ mass ratio of 2 (molar ratio of 5) the SiC yield was approximately twice compared to the yield of mass ratio of 1 (molar ratio of 2.5), while demonstrating a significantly lower free carbon amount (Table 1). With the low Mg content, the reduction temperature seemed to improve the conversion to SiC. Even though the temperature dependent differences in each individual parameter had rather low statistical significance, the fact that several parameters (free carbon content, surface area, Si crystallite size and pore volume) exhibited a temperature dependent trend shows that when using low Mg amounts the reduction temperature does affect the material properties. This was also observed in a previous study.¹³

When a high Mg amount was used, the reduction temperature did not have an effect on the properties of the PSiC. In fact, there were no observable changes in the samples after the oven temperature reached 650 °C, even if the samples were heated up to 800 °C for 4.5 h. It was visually observed that when the oven temperature reached 570 °C the highly exothermic reaction was initiated at one end of the SiO₂/C/Mg powder and quickly propagated through the sample in a few seconds (see video in the Supplementary Information). Because the temperature rises rapidly to high values at the beginning of the reaction, keeping the sample at 650-800 °C afterwards does not have an effect on the products. These results show that a high amount of Mg and a fast heating rate enabled production of nanostructured porous SiC by a self-propagating high-temperature synthesis (SHS).

The amount of Mg was critical in initiating the SHS. Even though the molar ratio of 2.5 between Mg and SiO₂ exceeds the stoichiometry of the overall reaction (Eq. 1) it was not enough to produce a high enough reaction rate to increase the temperature of the material sufficiently to initiate SHS in our system. It has been suggested that the magnesiothermic reduction proceeds via an intermediate reaction between magnesium silicide and carbon^{13,25} according to the following equation.



Moreover, it was suggested that the reaction between Mg₂Si and C takes place in the solid carbon phase. According to this picture, to produce SiC with a 2:1 molar ratio of Mg to Si, four Mg atoms and one SiO₂ moiety first react to produce Mg₂Si and 2MgO. Then the Mg₂Si needs to diffuse into the carbon phase and react with the carbon releasing two Mg atoms. Then the two Mg atoms in the SiC phase need to diffuse back to the SiO₂ phase to continue the process. After the initial phase, the supply of Mg quickly becomes rate limiting in the reaction. Excess Mg with a molar ratio of 4 (Mg to SiO₂) or above allows faster and complete conversion of Si into magnesium silicide without the need for the Mg to be recycled in the reaction. This in turn allows a faster reaction rate which increases the local temperature and further accelerates the reaction, turning it into SHS. Many previous studies have not observed SHS in magnesiothermic reduction of biogenic silica into SiC presumably because of using a low ratio of Mg to SiO₂.

The magnesiothermic reduction via SHS induces a high temperature. However, the high temperature causes crystal growth and sintering which is counterproductive for making materials with fine nanostructures. It is therefore beneficial to quickly increase the temperature to initiate the reaction and then decrease the temperature quickly to hinder crystal growth and sintering. Therefore, the reactant powders were arranged as a long and narrow bed which increases the surface area through which the heat dissipates allowing

for quick cooling and preservation of the nanostructures. However, if the excess heat is not dissipated quickly a microcrystalline material is obtained.^{15,16}

Although SiC formation was low with low Mg amounts, the specific surface area of these samples was very high. These samples also contain a high amount of free carbon which contributes to the total surface area. Indeed, the surface area of the samples is linearly dependent on the amount of free carbon (Fig. S7 in Supporting Information). The surface area extrapolated to zero free carbon amount would be 209 m²/g. This result highlights the importance of measuring or eliminating the free carbon in the produced materials because the measured surface area may be mostly from the free carbon in the material instead of the SiC structures.

The amount of carbon in the SiO₂/C composite had a significant effect on the reduced material. The molar amount of carbon was lower than the molar amount of silicon in all the other reactions except the reaction in which the highest amount of carbon was used (PSiC-H650HC). In this sample, there was very little crystalline silicon observed in the material even though not all SiO₂ was converted into SiC. Therefore, it seems that the high initial carbon amount impeded diffusion of Mg into the SiO₂. However, this did not negatively affect the SiC formation as the highest yield was obtained with the highest initial carbon amount. These observations support the conclusions made in earlier reports that the conversion to SiC takes place within the carbon phase and the limiting factor in the reaction is the diffusion of Si into the carbon.^{13,26} Furthermore, our results show that the SiC crystallite size can be controlled by the initial carbon amount as the crystallite size calculated for the 3C-SiC phase reduced from 27 nm to 12 nm as the initial carbon amount increased. A plausible reason for this is that the initial SiC crystallite size remains smaller when reaction between silicon and carbon is spread over a larger surface area of carbon. Also, in larger amount of carbon, the longer intercrystallite distance between the formed SiC crystallites reduces the likelihood of sintering adjacent crystallites. Furthermore, the local temperature during the reduction is probably lower when more carbon is used because the highly exothermic reduction of SiO₂ into Si is hindered.

The benefits of SHS are that it enables production of materials affordably with low energy consumption and in high volumes.²⁷ In the present setup, the reaction generated 0.1 g of SiC per second which translates to tons of SiC annually in continuous production. It should be noted that in the developed method the time used for the reaction itself was significantly shorter than for preparation of the precursor powder and subsequent dissolution of the side products. Nevertheless, the pre- and postprocessing steps in the production are relatively easy to scale up and perform for larger batches of material. It is the exothermic reduction reaction that has been very challenging to scale up because of its highly exothermic nature. Therefore, this work was focused on developing the reduction part, not on optimizing other parts of the process.

The materials produced here had surface areas above 300 m²/g and crystallite sizes below 7 nm. These finer structures would be beneficial for example in sintering and catalysis.^{3,4} The purity of the present products may be a limitation in some of these applications and will be addressed in future studies.

The large surface area of the synthesized SiC could also be used e.g. to adsorb heavy metals. In the literature, nanoporous SiO₂ has been used in metal adsorption.^{28,29} However, high surface area SiO₂ has limited stability in aqueous solutions restricting its applicability in large scale. In our previous work we have shown bisphosphonate modified nanoporous silicon to be a promising material to be used in metal adsorption.^{20,30} It can be surface stabilized by thermal carbonization and used even several tens of cycles. However, the inherent instability and high cost of the nanostructured Si framework are problematic. Therefore, the PSiC material developed in this work could be an attractive alternative because of the low-cost synthesis and the chemical stability of SiC. To test the applicability of the material, it was functionalized by bisphosphonates with a radical addition reaction. We used the radical addition reaction instead

of a more common silanization because it was shown to create a very stable functional layer on carbonized porous silicon with similar surface chemistry with the PSiC.²⁰ The initial experiments showed a good capability of the material to adsorb lead from a 30 ppm solution and the material could be regenerated with an acid. Further work is ongoing to explore the capabilities of the material in this application in more detail.

Conclusion

Porous silicon carbide with very small (< 10 nm) crystallite size and high surface area was produced from biogenic silica for the first time by magnesiothermic reduction via self-propagating high-temperature synthesis. An excess amount of magnesium was necessary to initiate the self-propagating high temperature synthesis. The reaction was finished within just few seconds and no changes in the structure of the material were observed during a prolonged time at temperatures up to 800 °C. We have shown that nanostructured porous silicon carbide can be produced from affordable precursors in a fast and scalable synthetic process that is clearly promising for industrial scale production. Importantly, the silica precursors can be obtained from plants including various agricultural residues such as husks and straws.

Furthermore, this material can be functionalized with organic molecules which further increases its applicability. One such application is to use the PSiC functionalized with metal chelating bisphosphonates as metal adsorbents. We have shown here that such a material can adsorb and desorb lead ions even from relatively low concentrations.

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Figure 1. Sample codes explained. L, low Mg amount in reduction (1:1 Mg:SiO₂ in mass); H, high Mg amount in reduction (2:1 Mg:SiO₂ in mass); 650, 725 or 800: reduction temperature in °C; LC, low initial carbon amount (m(sucrose)/m(SiO₂)=0.3); MC, medium initial carbon amount (m(sucrose)/m(SiO₂)=0.6); HC, high initial carbon amount (m_{sucrose}/m_{SiO2}=1.2). Sample label with a -Q at the end means a shorter reaction time.

Figure 2. Functional molecules grafted on PSiC a) undecylenic acid b) a bisphosphonate. The depicted bisphosphonate structure does not include the protective trimethylsilyl groups present on the bisphosphonate during the grafting reaction. The protective groups were removed by washing after grafting.

Figure 3. X-ray diffractograms showing the effect of reduction temperature, Mg amount (graphs a and b) and initial carbon amount (c and d). Diffractograms in a and c are measured before and after diffractograms in b and d after dissolving the SiO₂ and Si phases with NaOH wash. The diffraction peaks are labelled as * (3C-SiC), | (15R-SiC), and # (Si).

Figure 4. SEM (a and b) and TEM (c and d) images of the sample PSiC-H650 after NaOH wash.

Figure 5. a) ²⁹Si CPMAS NMR and b) ¹³C CPMAS NMR spectra of PSiC-H650MC.

Table 1. Results of XRD, nitrogen sorption and TG measurements

Sample	Yield ^[a] (%)	C ^[b] (%)	A ^[c] (m ² /g)	V ^[d] (cm ³ /g)	D _{pore} ^[e] (nm)	d _{3C-SiC} ^[f] (nm)	d _{15R-SiC} ^[g] (nm)	d _{Si} ^[h] (nm)
SiO ₂	-	-	302 ± 2	0.871 ± 0.003	12.0 ± 0.2	-	-	-
L650MC	13 ± 8	60 ± 20	900 ± 200	2.0 ± 0.4	16 ± 2	-	-	9 ± 9
L725MC	17 ± 6	50 ± 20	800 ± 200	1.7 ± 0.3	12 ± 7	3.2 ± 0.3	1.25 ± 0.08	11 ± 6
L800MC	26 ± 10	40 ± 20	600 ± 200	1.5 ± 0.1	17 ± 3	3 ± 2	3 ± 2	10 ± 20
H650MC	54 ± 3	10 ± 10	330 ± 40	0.8 ± 0.1	21 ± 1	5 ± 1	1.43 ± 0.04	27 ± 3
H725MC	51 ± 11	14 ± 7	400 ± 100	0.9 ± 0.3	19 ± 3	4.6 ± 0.9	1.45 ± 0.08	25 ± 5
H800MC	57 ± 3	11 ± 2	307 ± 5	0.72 ± 0.04	21.8 ± 0.2	5.3 ± 0.8	1.41 ± 0.07	31 ± 5
H650LC	44 ± 13	3.6 ± 0.5	227 ± 3	0.652 ± 0.007	26.6 ± 0.5	6.7 ± 0.1	1.48 ± 0.05	39 ± 4
H650HC	60 ± 7	30 ± 4	610 ± 40	1.0 ± 0.1	11.8 ± 0.7	3.5 ± 0.4	1.6 ± 0.2	10 ± 3
H650MC-Q	58 ± 5	9.3 ± 0.5	320 ± 10	0.67 ± 0.02	21.5 ± 0.4	5.6 ± 0.2	1.44 ± 0.05	28 ± 1

[a] SiC yield as percentage of theoretical maximum.

[b] Amount of free carbon in NaOH washed samples determined from TG curves.

[c] Surface area of NaOH washed samples determined by the BET model applied to the N₂ sorption isotherms.

[d] Pore volume of NaOH washed samples determined from a single point (p/p₀ = 0.98) of the N₂ sorption isotherm.

[e] Average pore diameter of NaOH washed samples determined by BJH from adsorption branch of the N₂ sorption isotherm.

[f] Crystallite size of 3C SiC polytype in NaOH washed samples determined by XRD.

[g] Crystallite size of 15R SiC polytype in NaOH washed samples determined by XRD.

[h] Crystallite size of Si before NaOH wash determined by XRD.

Graphical abstract

