ELSEVIER

# Efficient production of nanoporous silicon carbide from rice husk at relatively low temperature

### Jianjun Gao, Li Li, Juan Liu, Fei Liu, Yanqiu Han, Xiao Zhu and Kai Ma*

*Heze University Shanxian, 274300 Shanxian, Heze, Shandong, P. R. China. E-mail: iakam@mail.ustc.edu.cn*

**Nanoporous silicon carbide with a specific surface area of up to 186.45 m² g⁻¹ has been efficiently synthesized from waste rice husk using a magnesiothermic reduction at 950 °C as a key step. Throughout the entire process, the recovery rates of silicon, potassium and phosphorus from rice husk can reach 88.46, 91.5 and 65.5%, respectively. Turning rice husk waste into a real treasure, this promising method for producing porous SiC protects the environment and brings economic benefits.**
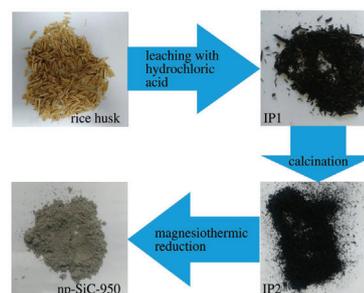
Silicon carbide (SiC) materials are commonly used in ceramic ball bearings, valves, semiconductor materials, gyroscopes, measuring instruments, aerospace and other fields due to their high modulus of elasticity, moderate density, low coefficient of thermal expansion, high thermal conductivity, thermal shock resistance, high specific stiffness, high dimensional stability and isotropic thermal and mechanical properties as well as several other excellent physical properties.[1] It is known that silicon carbide contains vacancies in the silicon and carbon sublattices. A decrease of carbide particles to a nanometer size is accompanied by an increase in the concentration of vacancies. These vacant lattice sites or vacancies play an important role in the atomic transport and the electrical, magnetic or mechanical properties of solids.[2–4]

Numerous methods of fabricating nano-SiC have been developed. However, these methods often have some disadvantages, such as expensive raw materials, complicated processes and difficulty in mass production. Even nanometallocarbosilanes have been used as precursors for SiC ceramic composites modified with refractory metal carbides.[5] As a non-trivial solution to the above problems, many researchers have synthesized SiC from rice husk (RH).[6–14] RH is a renewable resource, contains about 6 wt% silicon and about 35 wt% carbon and has a naturally porous structure. All the above methods for preparing SiC from RH are based on carbonization reduction, and the reaction temperature is very high what results in destroying the naturally porous structure of RH. In this work, we proposed a new magnesiothermic reduction method to produce porous SiC from RH efficiently. When reacting with magnesium metal powder at a relatively low temperature, the rice husk's natural cellular structure is retained in the final SiC products. Hence, RH is an excellent raw material for SiC production, which reduces environmental pollution and creates economic benefits.

We synthesized nanoporous silicon carbide (np-SiC) from RH in four steps. In step 1, the RH starting material was leached with hot 20 wt% hydrochloric acid, then filtered and dried to give intermediate product 1 (IP1). In step 2, IP1 was calcined at 700 °C under argon atmosphere to obtain intermediate product 2 (IP2). Reduction of IP2 with magnesium powder at different temperatures in step 3 produced intermediate product 3 (IP3). In final step 4, IP3 was calcined at 600 °C in the air to remove excess carbon.[†] The appearance of the starting RH and obtained powders IP1, IP2 and np-SiC is shown in Figure S1. The products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS), selected area electron diffraction (SAED), X-ray diffraction (XRD), BET specific surface area and pore size distribution, as well as elemental analysis.[†]

In the first step, 100 g of RH was refluxed with hydrochloric acid to obtain 55.04 g of IP1 as a dried filter cake and 0.85 g of final product 1 (FP1) after evaporation of the filtrate and calcining. According to elemental analysis, potassium and phosphorus content in FP1 (as $K_2O$ and $P_2O_5$) is 32.3 and 10.6 wt%, respectively, which makes it a high-quality phosphorus–potassium compound fertilizer. The elemental composition of RH and IP1 is shown in Table S1.[†] It can be seen that the content of metal ions in RH is significantly reduced after leaching with hydrochloric acid, and in this step, these impurity ions are prevented from entering the final SiC product, thereby ensuring its purity. The hydrochloric acid treatment can effectively recover the beneficial potassium and phosphorus from RH, and FP1 can be used as a valuable compound fertilizer. In this step, the recovery rates of potassium and phosphorus are 91.5 and 65.5%, respectively.

To better understand the properties of RH and IP1, we also performed thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses in nitrogen ($N_2$) and air (Figure S2[†]). There are two exothermic peaks (at 313.22 and 414.3 °C for RH, at 339.74 and 461.46 °C for IP1) on the DSC curves in

---

† For details, see Online Supplementary Materials.

air atmosphere and no exothermic peaks in $N_2$. As the temperature rises, both samples reach a constant weight in the air (18.779% at 468.52 °C for RH, 33.768% at 562.24 °C for IP1), indicating that the carbon has completely oxidized and only silica and minerals remain; therefore, the weight no longer changes with increasing temperature. It is noteworthy that in $N_2$ atmosphere, as the temperature increases, the weight of RH and IP1 continues to decrease, and the heat flow becomes higher and higher. According to published data, this may be mainly due to the chemical reaction of carbon and silica to form volatile silicon monoxide and carbon monoxide gas. The chemical reaction is described by the equation:

$$C + SiO_2 = CO + SiO.$$
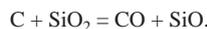
The reaction is endothermic, and up to 1000 °C, the weight is still not constant, indicating that the reaction is still ongoing. From the data of TGA in air, the ash content of RH and IP1 is about 18.779 and 33.768%, respectively.

In the second step, 46.40 g of IP1 prepared from 100 g of RH by acid treatment in the first step was calcined in an inert atmosphere at 700 °C to obtain 31.89 g of IP2. In this step, volatile pyrolysis products containing oxygen and hydrogen are released, and the remaining product in the form of a black powder is mainly composed of carbon and silica. According to chemical analysis, the content of silica and carbon in IP2 is 42.23 and 57.77%, respectively. Thus, the recovery rate of silica in two steps is essentially 100%.

In the third step, a mixture of IP2 with magnesium powder in a weight ratio of 3 : 1 was heated in a sealed stainless steel autoclave at a temperature of 650, 800, 950 or 1150 °C. The reaction product was treated successively with boiling 20 wt% sulfuric acid and then 40 wt% hydrofluoric acid plus 63 wt% nitric acid to remove magnesium oxide, silicon, silica and other by-products. The IP3 intermediate prepared in this step is mainly composed of unreacted carbon and porous SiC.

In the fourth step, the intermediate IP3 was calcined at 600 °C in the air to burn and remove excess carbon, resulting in the np-SiC product as a powder. The products obtained by magnesiothermic reduction at 650, 800, 950 and 1150 °C were designated as np-SiC-650, np-SiC-800, np-SiC-950 and np-SiC-1150, respectively. The yield (or the conversion rate of silica contained in RH to np-SiC) and the purity of np-SiC prepared at different temperatures are shown in Table 1. The content of trace impurities in the final np-SiC products determined according to the standard ISO 9286:1997 (E) is shown in Table 2.

**Table 1** The yield (rate of RH silica conversion to np-SiC) and purity of np-SiC samples prepared by magnesiothermic reduction at different temperatures.

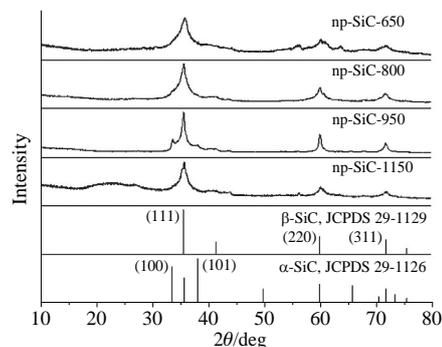| Sample | Weight/g | Yield (%) | Total carbon content (wt%) | SiC content (wt%) |
|---|---|---|---|---|
| np-SiC-650 | 0.268 | 9.52 | 29.84 | 99.3 |
| np-SiC-800 | 1.136 | 40.35 | 29.87 | 99.7 |
| np-SiC-950 | 2.490 | 88.46 | 29.95 | 99.8 |
| np-SiC-1150 | 2.541 | 90.24 | 29.85 | 99.6 |



**Figure 1** The XRD patterns of the np-SiC samples prepared at a temperature of 650, 800, 950 and 1150 °C and standard JCPDS cards for α- and β-SiC.

From Tables S1,[†] 1 and 2, it can be seen that the SiC yield increases with increasing temperature. However, the increase in yield is no longer significant after exceeding 950 °C, and the impurity content of the resulting product grows when the temperature rises from 950 to 1150 °C. These outcomes can be because too high temperature causes impurities to sinter and are difficult to remove by subsequent acid processing steps. Thus, in terms of yield, purity and energy consumption, the optimum temperature is 950 °C.

The XRD patterns (Figure 1) of the four samples show individual peaks at 35.6, 60.0 and 71.8°, corresponding to the (111), (220) and (311) planes of cubic SiC (JCPDS 29-1129), respectively. Unlike other samples, the XRD pattern of np-SiC-950 also exhibits two weak peaks of hexagonal SiC (JCPDS 29-1126) at 33.5 and 38.2°, corresponding to the (100) and (101) planes, respectively, indicating that the prepared product contains a small amount of hexagonal SiC.

The porous and crumbly structure of SiC is unequivocally visible from Figures 2(*a*),(*b*), and the pore diameter is several tens of nanometers. In the HRTEM image [Figure 2(*c*)], we can see clear streaks of the SiC lattice, and the pitch of 0.252 nm corresponds to the (111) plane of SiC, which is in good agreement with the one calculated from the XRD pattern. The EDS results (Figure S3[†]) indicate that there are some impurities such as oxygen, fluorine and magnesium, which is consistent with the results of ICP-AES analyses.

The surface area and mesoporosity of np-SiC-950 were investigated by analyzing the $N_2$ adsorption–desorption isotherm [Figure 3(*a*)]. The prepared SiC products exhibit a representative type IV curve characteristic of mesoporous materials. The BET specific surface area of np-SiC-950 is 186.45 $m^2 g^{-1}$. According to the BJH analysis, the porous structure of np-SiC-950 is characterized by BJH adsorption average pore diameter (4V/A) of 13.7 nm and BJH desorption average pore diameter (4V/A) of 13.3 nm.

In summary, we synthesized nanoporous SiC with high specific surface area and high purity using RH as raw material. Treatment of RH with hydrochloric acid can effectively remove other metal impurity ions from it and prevent these impurity ions from entering the final SiC product, resulting in its purity of up to 99.8%. The naturally porous structure of RH can be
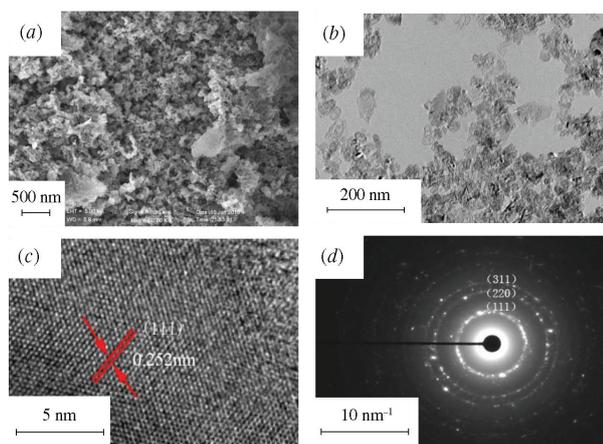
**Table 2** The content of trace impurities in the final np-SiC products determined according to the standard ISO 9286:1997 (E).

| Sample | Trace impurity/$\mu g\ g^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | Unbound Si | Unbound C | Fe | Al | Ca | Mg | F |
| np-SiC-650 | 0.42 | 10.32 | 20.34 | 30.48 | 20.57 | 5.78 | 1205.75 | 1002.4 |
| np-SiC-800 | 0.38 | 9.57 | 18.69 | 20.57 | 19.52 | 4.28 | 1408.62 | 1167.5 |
| np-SiC-950 | 0.25 | 5.62 | 12.37 | 20.65 | 14.82 | 5.62 | 120.61 | 150.8 |
| np-SiC-1150 | 0.40 | 6.23 | 16.53 | 50.62 | 23.56 | 8.69 | 984.43 | 1200.3 |

**Figure 2** (*a*) SEM, (*b*) TEM and (*c*) HRTEM images and (*d*) SAED pattern of the np-SiC-950 sample.

maintained so that the prepared SiC has a high specific surface area of up to 186.45 $m^2 g^{-1}$, which is very advantageous when used as a catalyst carrier. Compared with the conventional SiC production process, such as the carbothermal reduction method, the magnesiothermic reduction process can significantly reduce the temperature required for SiC formation and remarkably decrease energy consumption. In terms of productivity, energy consumption and product purity, the optimum reaction temperature for magnesiothermic reduction is 950 °C. As a result of the entire production process, the recovery rate of silicon from RH can reach 88.46%, and those of valuable elements of potassium and phosphorus are 91.5 and 65.5%,
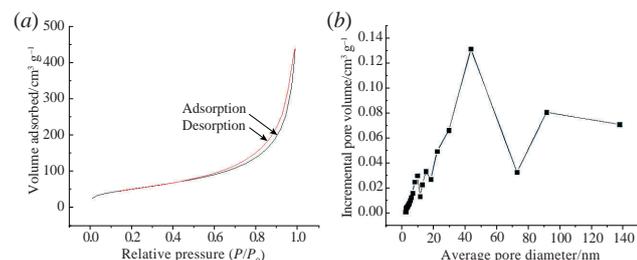
respectively. A highly efficient phosphorus–potassium compound fertilizer can also be obtained as a by-product in the production of porous SiC. This process can turn waste RH into treasures and thus protect the environment and generate economic benefits and is also a promising method for the production of porous SiC.

*Online Supplementary Materials*
Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.041.



**Figure 3** (*a*) The nitrogen adsorption–desorption isotherm and (*b*) the BJH pore size distribution for the np-SiC-950 sample.

**References**

1 H. Toktamiş and P. O. Hama, *Appl. Radiat. Isot.*, 2019, **148**, 138.
2 A. A. Rempel and H.-E. Schaefer, *Appl. Phys. A: Mater. Sci. Process.*, 1995, **61**, 51.
3 A. A. Rempel, W. Sprengel, K. Blaurock, K. J. Reichle, J. Major and H.-E. Schaefer, *Phys. Rev. Lett.*, 2002, **89**, 185501.
4 A. A. Valeeva, A. A. Rempel, S. V. Rempel, S. I. Sadovnikov and A. I. Gusev, *Russ. Chem. Rev.*, 2021, **90**, 601.
5 G. I. Shcherbakova, P. A. Storozhenko, D. V. Zhigalov, M. S. Varfolomeev, M. Kh. Blokhina and N. B. Kutinova, *Russ. Chem. Bull., Int. Ed.*, 2020, **69**, 875 (*Izv. Akad. Nauk, Ser. Khim.*, 2020, 875).
6 C. Makornpan, C. Mongkolkachit and T. Wasanapiarnpong, *Suranaree J. Sci. Technol.*, 2014, **21**, 79.
7 J. Chen, Q. Kong, Z. Liu, Z. Bi, H. Jia, G. Song, L. Xie, S. Zhang and C.-M. Chen, *ACS Sustainable Chem. Eng.*, 2019, **7**, 19027.
8 D. Radev and I. Uzunov, *Solid State Phenom.*, 2010, **159**, 153.
9 A. S. Vlasov, A. I. Zakharov, O. A. Sarkisyan and N. A. Lukasheva, *Refractories*, 1991, **32**, 521 (*Ogneupory*, 1991, no. 10, 15).
10 P. Gorthy and M. Pudukottah G., *J. Am. Ceram. Soc.*, 1999, **82**, 1393.
11 S. K. Singh, B. C. Mohanty and S. Basu, *Bull. Mater. Sci.*, 2002, **25**, 561.
12 M. L. G. Pereira, D. S. S. Figueira, B. R. Girolamo and F. Vernilli, *Cerâmica*, 2020, **66**, 256.
13 S. T. Alweendo, O. T. Johnson, M. B. Shongwe, F. P. L. Kavishe and J. O. Borode, *Procedia Manufacturing*, 2019, **35**, 962.
14 V. Rodriguez-Lugo, E. Rubio, I. Gomez, L. Torres-Martinez and V. M. Castano, *Int. J. Environ. Pollut.*, 2002, **18**, 378.