Synthesis of High-Purity SiC Nanowires via Catalyst-Free Pyrolysis of SiO2/Si and Sponge-Like Graphene Oxide

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ABSTRACT: The large-scale synthesis of high-purity SiC nanowires is a challenge. In this context, sponge-like graphene oxide (GO) was used as a carbon source as well as a reaction template for directly synthesizing SiC nanowires. GO was completely reacted with SiO to prepare high-purity 3C-SiC nanowires by thermal evaporation and carbothermal reduction without the use of any catalyst, rather than by epitaxy. Characterization was conducted using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and selected-area electron diffraction. The SiC nanowires had lengths of several tens of micrometers and a perfect single-crystalline structure with a bamboo-like morphology.

1. INTRODUCTION

In the past few years, one-dimensional silicon carbide (SiC) nanowires (SiCNWs) have attracted considerable attention due to many excellent characteristics, including their field emission optical properties and wide energy band gap. In addition, compared to SiC bulk and powder materials, SiCNWs exhibit greater thermal conductivity, mechanical strength, chemical stability, and mechanical properties.1-3 Currently, SiCNWs are widely used in optoelectronics and power electronic devices because of their unique electrochemical properties. In addition, SiCNWs are also used to toughen ceramic matrix composites due to their superplasticity at low temperatures and relatively high strength.1-5 Therefore, it is of great interest to obtain high-purity SiC nanowires through a simple and low-cost synthesis route.

Many methods for preparing SiCNWs15-17 have been reported. Researchers18-19 have also proposed that SiCNWs with a length of several millimeters or even centimeters could be more suitable to study the properties of nanostructures than the relatively short ones. The vapor-liquid-solid (VLS) and vapor-solid (VS) mechanisms are usually used to explain the formation process of nanowires.19 The main difference between the two mechanisms is whether they involve a catalyst or not. In the case of the VLS mechanism, transition metal catalysts (e.g., Fe and Ni) are widely used to grow 3C-SiCNWs.20-21 However, the residual metal catalyst acts as a contamination and thus affects the electronic and mechanical properties of the remaining SiCNWs, particularly under severe environmental conditions.22-24 Compared with the methods that involve the use of a catalyst, the catalyst-free growth of SiCNWs via the vapor-solid (VS) mechanism could ensure the purity and quality of the nanowires. Many growth methods

with different sources and growth processes have been used to obtain SiCNWs. Dong et al. successfully synthesized SiCNWs by the VS mechanism, and SiCNWs thus obtained lengths of tens to hundreds of micrometers.25 Lin et al. demonstrated the synthesis of single-crystalline β-SiCNWs using a SiO2 sol and carbon fiber felts as the starting materials; these single-crystalline β-SiCNWs had a size of approximately 200 nm and exhibited hierarchical morphology.15 Despite the successful synthesis of one-dimensional SiCNWs, defects such as stacking faults are difficult to avoid. In this context, it is still a challenge for scientists and industrialists to synthesize relatively large-scale and pure SiCNWs by using a simple and rapid method.

In this study, we aim to develop a feasible synthesis of pure SiCNWs without introducing any catalyst. First, sponge-like graphene oxide (GO), owing to its porous characteristics, was used as a C source and provide the reaction space for Si and C sources. Subsequently, SiO and CO gas reacted and formed SiCNWs by thermal evaporation and carbothermal reduction. Finally, high-purity SiCNWs of several micrometers in length were laid flat on graphite paper because these nanowires were directly grown on GO.
2. RESULTS AND DISCUSSION

Figure 1 shows the schematic illustration for preparing SiCNWs. High-purity 3C-SiC nanowires were grown on a GO layer without using any catalyst. GO was prepared by a modified Hummers method, and sponge-like GO having ultraporosity was then obtained by freeze-drying. At the bottom of a custom crucible, SiO$_2$/Si powder was mixed and spread on the bottom layer. Subsequently, a layer of graphite paper was placed on top of the SiO$_2$/Si powder. Finally, sponge-like GO that had been prepared by the modified Hummers method was spread on graphite paper. The graphite

Figure 1. Overview of preparing SiC nanowire films.

Figure 2. SEM images of the SiC nanowires synthesized by pyrolysis of SiO$_2$/Si and graphene oxide with different reaction times ((a) 0 h, (b) 0.5 h, (c) 1.0 h, (d) 1.5 h, (e) 2.0 h, and (f) 3.0 h).
paper was not only used as a substrate for produced SiCNWs but also as a separation layer for SiO2/Si powder and GO to prevent them from being mixed together. The sampled crucible was placed in a tube furnace, and the working pressure was approximately 15 Pa. Subsequently, the temperature of the tube furnace was raised to 1350 °C, and calcination was performed for 0.5–3 h.

SiO was first formed after the reaction of SiO2 with Si and sublimated by thermal evaporation under low-vacuum conditions to pass through the graphite paper. Subsequently, SiO reacted with sponge-like GO to form SiCNWs. SiO2/Si and GO were used as the Si source and C source, respectively. The expected result of our experiment was that SiO first reacts with GO to form SiC nanodots attached to the surface of graphene, and SiCNWs then grow perpendicular to the graphene direction by using the graphite paper as a substrate. Our expected result was similar to the previously reported result for the method of generating SiCNWs by thermal evaporation. However, our experimental results show that the generated nanowires did not grow in the direction perpendicular to the graphite paper, but they grew directly on the GO layer while the GO layer was somewhat melting. In addition, the remaining GO adhered to the generated SiCNWs. In order to further verify this interesting phenomenon, several experiments were conducted to accomplish the SiO and GO reaction process for the formation of SiCNWs.

For the purpose of conducting the experiments, the samples were taken out at different reaction times, and SEM observations were performed to investigate the product morphology at different reaction times. The results of SEM observations are shown in Figure 2. These results show that numerous SiC nuclei were formed on the GO layer surface when the sampled crucible was placed in a tube furnace and reacted at 1350 °C for 0.5 h under low-vacuum conditions (15 Pa). In order to confirm the formation of “SiC nanodots”, more experiments were conducted. The samples were taken out with the reaction times of 15 and 30 min, respectively. SEM observations of the samples are shown in Figure S1 in the Supporting Information. These results show that SiC nuclei were formed on the GO layer surface when the sampled crucible was placed in a tube furnace and reacted at 1350 °C for 15 min. With the extension of the reaction time, the number of SiC nanodots gradually increased. Furthermore, after reacting for another half-hour, the GO layer began to partially melt, and SiCNWs appeared on the surface and inside the GO layer. Figure 2b shows the SEM image of the SiC nuclei, which sit on the GO film and act as the seeds for the growth of SiCNWs. As the reaction time is further increased, the amount of SiCNWs formed on the GO increased, and the GO was continuously consumed and collapsed. The amounts and lengths of these wire-like and curvature nanostructures exhibited a significant increase. As the calcination time was prolonged to 3 h, it was found that the reaction was close to completion and almost all of the GO had reacted with SiO to be converted into a large amount of SiC. Therefore, it can be concluded that the formation of SiCNWs is dominated by the VS mechanism, and gaseous SiO and CO act as active substances in the synthesis of SiCNWs. The related reactions are illustrated as follows:

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\begin{align*}
\text{Si} (s) + \text{SiO}_2 (s) & \rightarrow 2\text{SiO}(g) \quad (1) \\
\text{SiO}_2 (s) + \text{C} (s) & \rightarrow \text{SiO}(g) + \text{CO}(g) \quad (2) \\
\text{C} (s) + \text{CO}_2 (g) & \rightarrow 2\text{CO}(g) \quad (3) \\
\text{SiO}(g) + 2\text{C} (s) & \rightarrow \text{SiC} (s) + \text{CO}(g) \quad (4) \\
\text{SiO}(g) + 3\text{CO}(g) & \rightarrow \text{SiC} (s) + 2\text{CO}_2 (g) \quad (5)
\end{align*}
\]

SiO vapor and CO gas are formed in eqs 2–3. The generated SiO vapor fills the pores and arrives on the surfaces of the GO films, which can react with C atoms to generate SiC nuclei (eq 4) under 1350 °C. As the SiO vapor and CO gases are continuously supplied and reacted, the SiC nuclei reach a supersaturation state. They tend to grow along the (111) direction because of their low surface energy. SiC nanowires (eq 5) are formed during these processes.8

In order to further verify this process, we took the products obtained after 0, 1, 2, and 3 h for thermogravimetric (TG) analysis. The results of TG analysis are shown in Figure 3. From the TG curves, we found that, as the reaction time...
increased, the thermal stability of the product continued to improve. As shown in Figure 3, the GO underwent a rapid weight loss of 97% at 300−700 °C, which can be ascribed to the oxidation of carbon components in air. In the case of SiC samples synthesized by pyrolysis of SiO2/Si and GO for 1.0, 2.0, and 3.0 h, a weight loss of 86.00, 12.50, and 2.50% occurred, respectively, indicating that the amount of the SiC product increased with the extension of the reaction time. Remarkably, the SiC samples remain stable over the entire temperature range studied from room temperature to 800 °C.

The crystallite structure of synthesized SiCNWs was investigated using X-ray diffraction (XRD), and the corresponding XRD spectrum is shown in Figure 4. The XRD spectrum indicates that synthesized SiCNWs have a relatively perfect crystallinity and no other impurities. Figure 4 shows one broad weak diffraction peak at 21.68°, which is assigned to the diffraction plane of GO. The five diffraction peaks at 35.35°, 41.39°, 59.97°, 71.77°, and 75.58° were indexed to the (111), (200), (220), (311), and (222) diffraction planes of SiC, respectively, which are well matched with the cubic structure of β-SiC (ICDD data, JCPDS card no. 29-1129).26 Small stacking faults were found within crystals during the growth of SiCNWs. These faults matched the weak shoulder peak marked with SF, which emerged at the left side of the peak for the (111) diffraction plane. Moreover, such stacking faults were also found by other researchers.9,11 No other peaks were detected, indicating that no obvious impurity was formed.

The strong intensities and sharp peaks of SiC compared with the background indicates good structural integrity.18 As revealed by the XRD spectra, the resulting SiC samples had high purity and a well-developed cubic crystal structure. β-SiC nanowires were synthesized from graphene without the assistance of any catalyst and without post-processing. Figure 5 indicates that the as-grown ultralong nanowires are pure and have little impurity. Figure 5a presents an overall image at low magnification of the cross section of the film of SiCNWs. In addition, Figure 5a shows that large quantities of linear and curvature nanowires of a few millimeters in length are formed, and these nanowires are randomly oriented. Moreover, the nanowires appear to have evolved into an extensive network structure. It can be seen from the high-magnification image shown in Figure 5b that the diameter of the SiCNWs varies from 40 to 90 nm, and the average diameter is approximately 60 nm. The surface of the as-grown SiCNWs is smooth and flat along the direction of length, and no particles are attached to their surface.

To further investigate the morphology and detailed crystalline structure of SiCNWs, representative transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and selected-area electron diffraction (SAED) were conducted. The corresponding results obtained by using these characterization techniques are presented in Figure 6. From the typical low-magnification TEM image shown in Figure 6a,b, individual nanowires appear...
to have a very interesting bamboo-like morphology with a stem-mode structure. Moreover, these nanowires also appear to have a uniform diameter along their entire length. No spherical caps are observed on the tips of the nanowires. The alternate bright and dark striations of the SiC stem can be attributed to the stacking faults. The formation of stacking faults is very common in SiC nanostructures, and these faults are generally formed due to the change of stacking sequences.
under the fluctuation of kinetic growth conditions.\textsuperscript{5,27} The stacking faults thermodynamically contribute to the decrease in the total free energy of SiCNWs. Figure 6 c,d shows the high-magnification TEM image of the SiCNW tip. In this image, we could see that the tip of the SiCNW has regularly arrayed fringes with an interspacing of 0.25 nm corresponding to the $d$ spacing between the (111) planes in the $\beta$-SiC crystal. This indicates that SiCNWs have grown on the (111) plane along the [111] direction, which is in good agreement with the strongest diffraction peak in the XRD patterns, corresponding to the (111) plane of $\beta$-SiC. The SAED pattern of the lattice-resolved image obtained from HRTEM can also be indexed to the cubic SiC structure. Figure 6e,f represents typical HRTEM images of a single nanowire stem. In contrast to the tip of the nanowire, dense stacking faults along the [111] direction are clearly observed in the stem region of the nanowire. The sharp bright spots and diffuse streaks in the SAED pattern indicate that the stem of the nanowire has a single crystalline structure but contains stacking faults.

3. CONCLUSIONS
In summary, high-yield single-crystal SiCNWs were synthesized via a simple and convenient method in which SiO\textsubscript{2}/Si and sponge-like GO were used as raw materials. An interesting aspect of this study is that GO was not only used as a C source but also as a reaction template, similar to melting to form the nanowires. SiCNWs obtained through this method had diameters of approximately 60 nm and lengths of several tens of micrometers. Structural characterization confirmed that these nanowires had a single-crystalline structure, and it also confirmed that the nanowires were cubic SiCNWs with nanowire growth in the [111] direction. Furthermore, it was found that stacking faults existed perpendicular to the growth direction. The successful synthesis of SiCNWs provides an effective route to synthesize SiCNWs and opens new opportunities for the further preparation of nanowire-reinforced ceramic composites.

4. EXPERIMENTAL SECTION
4.1. Materials. Commercially available Si, SiO\textsubscript{2} (both with a purity of $>$99% and supplied by Anyang Dingxing Metallurgical Refractories Co., Ltd., China), and graphene oxide (GO, single-slice diameter: 0.5–5 $\mu$m, layer thickness: 0.6–1 nm, supplied by Zhongsen Navigation Technology Co., Ltd., China) were used as the raw materials.

4.2. Characterizations. The XRD phase analysis of SiC nanowire films was conducted using a MERCURY CCD X-ray diffractometer (RIGaku, Ultima-IV, Japan, $\lambda = 0.15$ mm) with Cu $K\alpha$ radiation. The 2$\theta$ angle range was 5 to 80$^\circ$, and the scan rate was 2$^\circ$/min. The morphologies of the samples were analyzed using a scanning electron microscope (SEM; HITACHI, SU8010, Japan). The microstructure of the SiC nanowires was characterized by a high-resolution transmission electron microscope (FEI, Tecnai F20, U.S.A.). An energy-dispersive X-ray spectroscopy attachment was equipped and operated at 300 kV. The samples for HRTEM and SAED observations were first dispersed in an alcohol solution using ultrasonic vibrations and then dropped onto a copper grid for natural drying before analysis. The TG analyses of SiCNWs under the growth process were performed using a TG analyzer (TA Instruments, NETZSCH, STA449C, U.S.A.) in the range of 25–800 $^\circ$C under a nitrogen atmosphere with a flow rate of 100 mL/min and a heating rate of 10 $^\circ$C/min.

## Associated Content

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03619.

SEM images of the SiC nanowires synthesized by pyrolysis of SiO\textsubscript{2}/Si and graphene oxide with different reaction times (PDF)

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**Notes**

The authors declare no competing financial interest.

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