

## Synthesis of SiC@SiO<sub>2</sub> Nanocables *via* a Catalyst-free Carbothermal Reduction Method

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**Abstract:** SiC@SiO<sub>2</sub> nanocables (NC), as a new functional nanocomposite, have captured widespread attention due to their excellent performances and widely application prospects. Therefore, it is significant to develop a kind of effective, economical and environmental method to prepare SiC@SiO<sub>2</sub> NC. Herein, a catalyst free carbothermal reduction method was developed to synthesize SiC@SiO<sub>2</sub> NC fast and efficiently, through heating the mixture of silicon powder and silica sol at 1500 °C in Ar. The NC is composed of single-crystal  $\beta$ -SiC core and amorphous SiO<sub>2</sub> sheath, with the length of hundreds of micrometers and the diameter of 60–80 nm. And the size of the core-shell can be adjusted by the holding time. The formation of the NC is explained based on the experimental data and the vapor-solid (VS) mechanism. The experiment results can also enrich the mechanism, and offer inspiration for their industrial-scale production.

**Key words:** SiC; nanocables; carbothermal reduction; catalyst-free

In recent years, nanocables, a newly type of one-dimensional (1D) nanostructures, have already attracted the attention of many researchers, as their applications could be further enhanced by fabricating the core with sheath of different materials. The “nanocables” is firstly referred to the coaxial structures of several layers of nanotubes and clusters<sup>[1-2]</sup>. Among the 1D nanomaterials sheathed with an outer layer, SiC NC with different coating materials, such as SiC/SiO<sub>2</sub><sup>[3-4]</sup>, SiC/Al<sub>2</sub>O<sub>3</sub><sup>[5]</sup>, SiC/C<sup>[1, 6]</sup> and SiC/BN became particularly significant, since they showed outstanding excellent field emission characteristics<sup>[3]</sup>, photoluminescence performance<sup>[5]</sup>, and enhanced electrical properties<sup>[7]</sup>.

It is well known that SiC@SiO<sub>2</sub> core-shell NC exhibits excellent super hydrophilic properties and mechanical strength<sup>[8-9]</sup>, holding great promise for application as self-cleaning materials and functional ceramic reinforcements, respectively. To date, various strategies have been developed to obtain SiC/SiO<sub>2</sub> NC<sup>[10]</sup>. Ryu, *et al*<sup>[11]</sup> has synthesized the core-shell SiC@SiO<sub>2</sub> nanowires by using NiO catalyst. Cai and collaborators<sup>[12]</sup> produced SiC@SiO<sub>2</sub> NC through an organic precursor method using dimethylsiloxane as raw material. By arc-discharge method, Yao, *et al*<sup>[13]</sup> fabricated large-scale SiC@SiO<sub>x</sub> nanocables. Li, *et al*<sup>[14]</sup> also developed an iron-catalysis chemical vapor deposition (CVD) method to obtain

SiC@SiO<sub>2</sub> coaxial nanowires using C<sub>3</sub>H<sub>6</sub> as carbon source. However, usage of the metal catalyst, such as NiO<sup>[11]</sup> which is difficult to be removed from the product, is not matching the rule of convenience; the application of the expensive raw material and the complex process is not conforming with the principle of economization; and usage of the polluting gas, CH<sub>4</sub> or C<sub>3</sub>H<sub>6</sub>, is not according with the law of environment protection. Therefore, it is significant to develop an effective, economical and environmental method to synthesize SiC@SiO<sub>2</sub> NC.

In this study, we developed a modified method to synthesize long SiC@SiO<sub>2</sub> NC. In the process, the mixture of silicon powder (500 nm) and silica sol, coupled with carbon felt (CF) were heated at 1500 °C in Ar without any catalyst. The growth mechanism of SiC@SiO<sub>2</sub> NC was discussed, and the formed structure and optical properties were characterized.

## 1 Experimental

Si powders (500 nm, Jinan Yinfeng Co., China), and silica sol (prepared according to our former work<sup>[15]</sup>) were mixed in an agate pot by ball milling for 60 min. After drying at 80 °C in oven for 2 h, the powder mixtures were transferred into the corundum crucible, covered with carbon felt (TZ-307, Taek. Co., Korea). Then

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the whole “sandwich” was put in the center of horizontal tube furnace. After replacing with high purity Ar, the furnace was heated to 1500 °C, and kept for 4–6 h. Then the furnace was cooled down to room temperature. During the whole process, flowing Ar of 10 sccm was introduced from the furnace.

The crystalline phase of the products was determined by X-ray diffraction analysis (XRD, D8 Advance, Bruker Co., Germany). The microstructure was observed using scanning electron microscope (SEM; Melin, Zeiss Co., Germany) at the accelerating voltage of 15.0 kV. The morphology and the diffraction pattern were detected by high-resolution transmission electron microscopy (TEM; JEM-2100F, JEOL Co., Japan), equipped with energy dispersive spectrum (EDS), operated at the accelerating voltage of 200 kV. Raman spectra were excited using the 633 nm excitation source from He-Ne laser and collected by a micro-Raman spectrometer at room temperature.

## 2 Results and discussion

It is obvious that large quantity of long straight and curved nanowires are synthesized, as shown in Fig.1(a). A typical FESEM image further reveals that the diameter of the nanowires is uniformly ranged from 60 to 80 nm (inset in Fig.1(a)) with smooth surface and the tens of micrometers in length, implying a large aspect ratio (Fig.1(b)). For the hundreds of wires, no spherical caps are observed at the tips of the wires, which reveals that the wires form by the vapour-solid (VS) mechanism.

X-ray diffraction is conducted to investigate the phase and structure of the as-synthesized products. As shown in Fig. 2, the product is identified as the  $\beta$ -SiC structure. The strong intensities and narrow widths of the peaks indicate that the nanowires are crystalline. The major diffraction peaks at  $2\theta=36^\circ$ ,  $41^\circ$ ,  $60^\circ$  and  $72^\circ$ , are attributed to the (111), (200), (220), and (311) respectively, agreed well with  $\beta$ -SiC (PDF 29-1129)<sup>[14]</sup>. The low intensity peak at  $2\theta=33^\circ$  (marked “SF”) is typically observed in XRD pattern of  $\beta$ -SiC, ascribed to stacking faults within the crystals<sup>[16]</sup>. Meanwhile, there is amorphous background and swell in  $2\theta=23^\circ$  of the XRD pattern, which is marked as amorphous  $\text{SiO}_2$ <sup>[14, 17]</sup>.

To further characterize the structure in detail, TEM image and selected area electron diffraction (SAED) are tested. Fig. 3 (a) is the typical TEM image of the core-shell NC with the diameter of 80 nm, obtained by being kept in 1500 °C for 4 h. It clearly reveals that the NC possesses a darker inner core of about 17 nm in diameter and a lighter outer shell with the thickness of nearly 30 nm. There are some slashes in the core, which may be stacking faults<sup>[18]</sup>, and this is in agreement with

the XRD result (Fig. 2). After being kept in 1500 °C for 6 h, the diameter of inner core of the NC grows up to 40 nm and the thickness of outer shell reduces to nearly 20 nm, as shown in Fig. 3(b). Therefore, we can infer that through controlling the holding time in 1500 °C, diameter of the inner core can be regulated. Fig. 3(c) shows the edge of core SiC and shell  $\text{SiO}_2$ . It is obvious that the core SiC shows regular arrangement of atoms, indicating high crystallinity, while the shell  $\text{SiO}_2$  presents atoms are disorder, manifesting the amorphous structure. Fig. 3(d) reveals the interspace of the lattice fringes is 0.25 nm, corresponding to the  $d$ -spacing of the (111) plane in  $\beta$ -SiC,

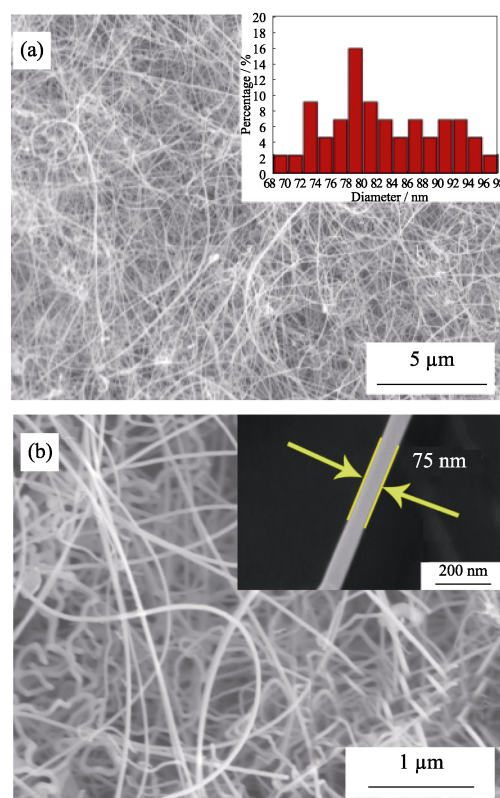


Fig. 1 SEM images of core-shell SiC@SiO<sub>2</sub> NC (a) Low-magnification image, with inset showing distribution of the SiC@SiO<sub>2</sub> NC diameters; (b) High-magnification image, with inset showing the corresponding image of a single NC

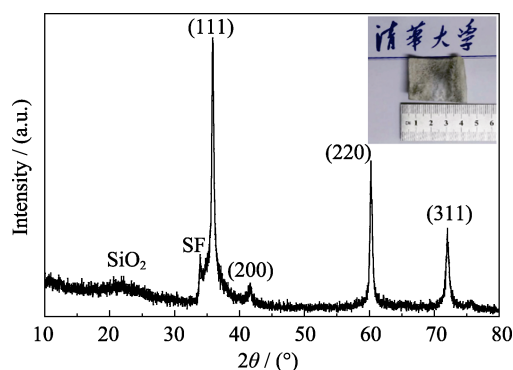


Fig. 2 Typical XRD pattern obtained from the core-shell SiC@SiO<sub>2</sub> NC

as indicated in the insert SAED pattern. It is generally accepted that the SiC nanowires should grow preferentially along the [111] direction to maintain the lowest growing energy, as the surface energy of (111) plane is much lower than those of the other planes<sup>[11, 19]</sup>.

Furthermore, we investigated the mapping mode of the EDS to indicate the distribution of the elements to insure the core and sheath. As shown in Fig. 4(c), the element of O mainly distributes in the sheath, while the core is “dark”, manifesting the lack of O element. It is obvious that the element of C mainly enriches in the core, shown in Fig. 4(d). In Fig. 4(b), the core is brighter than the sheath, manifesting the higher content of Si element in the core, as the molar percentage of Si in SiC 50%, while 33.3% in SiO<sub>2</sub>.

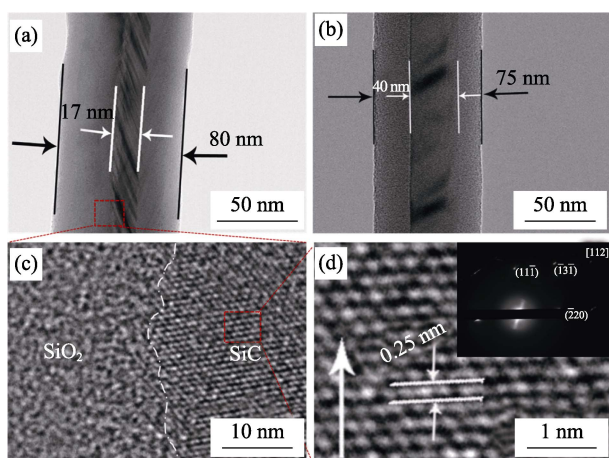


Fig. 3 TEM images of the core-shell SiC@SiO<sub>2</sub> NC kept in 1500 °C for 4 (a) and 6 h (b), the corresponding SAED (c), and HRTEM image (d)

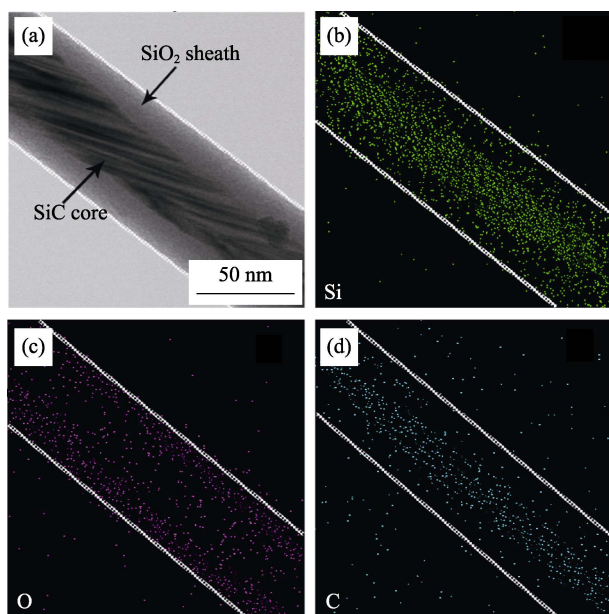


Fig. 4 Mapping mode of the EDS of the elements, Si/C/O in the NC

A typical Raman spectrum of  $\beta$ -SiC@SiO<sub>2</sub> core-shell NC is shown in Fig. 5. Two peaks at around 794 and 916 cm<sup>-1</sup> are observed in the Raman spectrum. The center of 916 cm<sup>-1</sup> is corresponding to the Raman peak of amorphous SiO<sub>2</sub><sup>[14]</sup>, and the peak at 794 cm<sup>-1</sup> is assigned to the TO phonon at the G point of cubic SiC<sup>[20]</sup>. We note that the TO (G) phonon line shows a low number shift of 2 cm<sup>-1</sup> compared with the TO phonon modes of bulk SiC (796 cm<sup>-1</sup> for TO and 980 cm<sup>-1</sup> for LO)<sup>[21-22]</sup>. The reason for this exception may originate from the confinement effect, stacking faults and inner stress from the hetero structure of core-shell SiC NC<sup>[23-24]</sup>. In addition, we have not found the LO phonon of  $\beta$ -SiC in the Raman spectrum. Maybe the LO phonon shifts to the low number, and is coincidentally eclipsed by the amorphous bulge of SiO<sub>2</sub>.

Based on the characterization of the morphologies and crystal structures, the mechanism for the formation of the SiC@SiO<sub>2</sub> core-shell NC is governed by the VS process<sup>[17, 19]</sup>. Fig. 6 shows the schematic illustration of the growth and morphology evolution of the SiC-SiO<sub>2</sub> nanocables. Firstly, in the Si/silica sol mixtures, Si reacts with SiO<sub>2</sub> to form SiO vapour at 1300 according to reaction (1)<sup>[25]</sup>. The as-formed SiO vapour reacts with C and CO vapour in accordance with reaction (2-4)<sup>[25-26]</sup>. In reaction (2), SiC nuclei firstly generates at the active sites of the CF, as no spherical caps at the tips of the wires shown in Fig. 1. Subsequently, the formed SiC nuclei acts as seeds to grow SiC nanostructures<sup>[27-28]</sup>. At the early stage, SiC grows on the surface of the substrate,

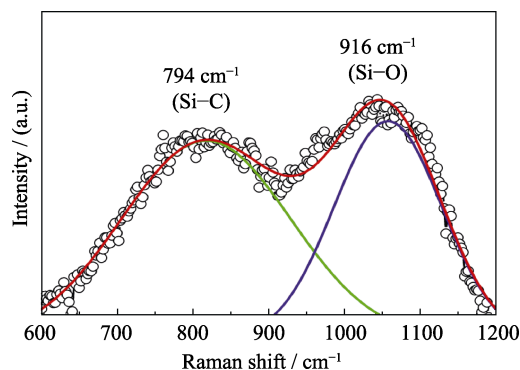


Fig. 5 Raman scattering spectrum of SiC@SiO<sub>2</sub> core-shell NC

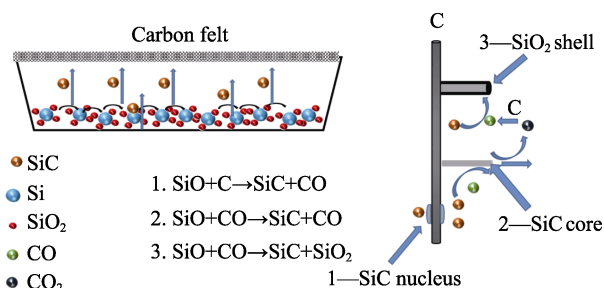
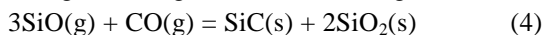
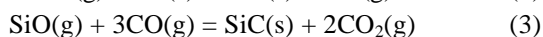
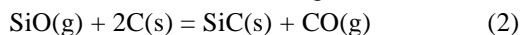


Fig. 6 Schematic illustration of the growth and morphology evolution of the SiC-SiO<sub>2</sub> NC

which can maintain the low energy consumption of the growth system<sup>[26]</sup>. In this part, the nanostructures present a highly defective structure as indicated in Fig. 3(b), which could also be helpful in reducing energy during the growth of SiC nanostructures.

Once the nanostructures protruded from the CF, stable growth conditions can be easily achieved. In this case, the SiC nanostructures begin to grow along the specific direction [111], certified by the HRTEM and SAED images in Fig. 3(d). And the growth of the SiC@SiO<sub>2</sub> NC is no longer controlled by reaction (2), as the growth frontier is far away from the solid carbon source<sup>[29]</sup>. Meanwhile, reactions (3-4) are responsible for further growth of the SiC nanostructures, as all reactants are gases. Thus, the diameter grows with the holding time in 1500 °C increasing, as shown in Fig. 3(c). During the cooling process, SiO<sub>2</sub> formed by reaction (4) deposits on the surface of SiC nanostructures firstly and then gradually condense into solid, forming SiC-SiO<sub>2</sub> core-shell structures<sup>[11]</sup>.



### 3 Conclusions

In this study, we developed a modified catalyst-free carbothermal reduction method to synthesize long SiC@SiO<sub>2</sub> NC, which is effective, economical and environmental. This may offers inspiration for their industrial-scale production. As the diameter of inner core can be regulated by controlling the holding time in 1500 °C, it also enriches the VS mechanism which is employed to interpret the NC formation. What's more, the enriched mechanism could provide great prospect in possible applications to synthesize other long NC.

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## 无催化剂碳热还原法制备 SiC@SiO<sub>2</sub> 纳米电缆

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**摘 要:** SiC@SiO<sub>2</sub> 纳米电缆作为一种新型的功能性纳米复合材料, 以其优异的性能和广泛的应用前景受到了广泛关注。因此, 开发一种有效、经济、方便, SiC@SiO<sub>2</sub> 纳米电缆的制备方法具有重要意义。本研究采用无催化剂的碳热还原法在 1500 °C 的 Ar 气氛下, 通过加热硅粉和硅溶胶混合物从而快速高效地制备了 SiC@SiO<sub>2</sub> 纳米电缆。该核壳的纳米电缆是由单晶  $\beta$ -SiC 核心和无定形 SiO<sub>2</sub> 壳组成, 其长度达几百微米, 直径为 60~80 nm, 而且通过调节保温时间可以调控核壳的尺寸。结合实验数据并依据气-固(VS)机理解释了 SiC@SiO<sub>2</sub> 纳米电缆的形成过程, 同时也进一步丰富了该生长机制, 为其工业化生产提供了参考。

**关 键 词:** 碳化硅; 纳米电缆; 碳热还原; 无催化剂

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