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ARTICLE

Preparation and characterization of SiC@CNT coaxial nanocables using CNT as template

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Novel one-dimensional SiC@carbon nanotube (CNT) coaxial nanocables have been successfully fabricated in large scale by using a carbothermal, chemical vapor deposition method. Sol-gel-derived silica xerogels containing commercial multi-wall carbon nanotubes (MWCNT) were used as silicon source and carbon source. The obtained product was characterized by SEM, HRTEM, Raman and XRD. The coaxial nanocables have been found to be composed of a 40–100nm diameter carbon nanotube as the core, surrounded by thick SiC out layer. The inner nanotube corresponded to the multi-walls of the carbon nanotube with lattice spacing of 0.34 nm. The PL spectrum reveals that SiC@CNT nanocable have two broad emission bands centered at 461 nm and 573 nm which can be attributed to quantum confinement effect and the morphology effects. The morphology of the product was tuned by simply altering the reaction temperature. And the formation of SiC@carbon nanotube coaxial nanocables was proposed that CNT acted as a template to confine the reaction, which resulted in SiC out layer continuous growth on the CNT surface to form cable-type growth.

Introduction

SiC is a wide-bandgap semiconductor and has various excellent properties such as high electron mobility, high thermal conductivity, and high tolerance to electrical breakdown, high hardness, and high mechanical strength.[1,2] These excellent properties make SiC a good candidate for electronic and photonics devices designed for high-temperature, high-power, and high frequency applications.[3,4] Many researches effort have been devoted to the design and synthesis of SiC-related one dimensional (1D) nanostructures.[5-7]

As a unique kind of one-dimensional (1D) nanoarchitecture, nanocable is a coaxial core-shell heterostructure that can provide the possibility to enhance functionality and multifunctional properties compared with those of their limited single-component counterparts.[8] Coaxial nanocables can be fabricated by first forming nanotubes of nano-sized diameter, then depositing a material dissimilar to that of the nanotubes over the surfaces of the nanotubes.[9,10] Such nanocables possess one-dimensional features of both nanowires and nanotubes in the axial direction. Because of the morphological integrity of carbon nanotubes, which are able to spatially confine reactions, CNTs have been used as ideal templates to synthesize one-dimensional nanostructures with similar diameters, lengths, and orientations close to their own.[11] Hence, many efforts have been devoted on the direct synthesis of special 1D coaxial nanocable by using CNT as the template. For example, well defined silica-coated CNT coaxial nanocables have been synthesized at room temperature by using sonication with sol-gel techniques.[12] The CNT@SnO_2-Au nanocables were successfully prepared by a simple one-pot synthetic route.[13] There has also been a report on the direct reaction between CNT and Si powders via thermal evaporation process in vacuum to form SiC@CNT composite nanotubes.[14] Nevertheless, significant difficulties still exist in directly fabricating well-defined SiC@CNT coaxial nanocables which can maintain the skeleton of the CNT template in the final product.

Carbothermal reduction of silica is the most useful method of SiC nanowire synthesis owing to its efficiency and simplicity. Herein, SiC based nanocables can possibly be achieved by subsequent forming SiC outlayer on the surface of CNT template via direct reaction between CNTs and silica. Such heterostructures may offer great potential for applications in field effect transistors, light emitting diodes, solar cells, gas sensors, magnetic sensors and optical nanodevices.[7]

In this work, we report the fabrication of SiC@CNT coaxial nanocables on $Co(NO_3)_2$-catalyzed Si substrate by using a carbothermal, chemical vapor deposition method (CVD). The structure and properties, and the possible growth mechanism of the SiC@CNT heterostructure on the Si substrates are discussed.

Experimental

Sol-gel-derived silica xerogels and commercial multi-wall carbon nanotubes (purchased from Shenzhen Nanotech Port

Co., Ltd, China) were used as silicon source and carbon source, respectively. The preparation method of silica xerogels containing MWCNTs was similar to that described in our previous work.[15] Monocrystalline n-type Si (100) substrate was etched in molten KOH at 500 °C for 5 min in muffle furnace. After the etching process, the Si substrate was cleaned with deionized water, and then immersed into $Co(NO_3)_2$ ethanol solution (0.04M), and dried naturally. The raw materials and Si substrates with a thin layer of $Co(NO_3)_2$ were placed in a alumina boat located in central hot-zone of the furnace. The system was heated in Argon gas (Ar, purity 99.999%) flow (200 sccm) to 1450 °C at a rate of 5 °C /min and maintained at this temperature for 6 h. The as-grown samples with gray-black color deposited on Si substrate were taken out for the following measurements.

The crystalline structure was characterized by using an X-ray diffractometer (Bruker AXS D8 Advance) with Cu Kα radiation. Field emission scanning electron microscopy (FESEM, JSM-6700F) equipped with an energy dispersive X-ray spectroscope (Hitachi, S-4200) was employed to investigate the morphology of the products. Further structure characterization was performed on a high resolution transmission electron microscopy (HRTEM, JEM-2010) at 200KV. Raman spectroscopy (RENISHAW inVia) was carried out with 30-mW Ar + green light (λ = 514 nm) laser as an excitation source. Photoluminescence (PL) spectrum was recorded on a Hitachi F-4500 fluorescence spectrometer at room temperature with the 325 nm line from He-Cd laser.

Results and discussion

3.1 Structure and morphology

Typical SEM images of as-prepared coaxial nanocables grown on Si substrate are shown in Fig. 1 at different magnifications. Low-magnification SEM image in Fig. 1(a) shows large-scale uniform nanowires have densely stacked on the substrate, which is essential in potential applications in future nanodevice design. Fig. 1(b) reveals that the nanowires possess coaxial nanocable structure. High-magnification SEM observations (Fig. 1(c) and (d)) further indicate that the inner nanotube are obviously observed at the top end of the nanostructures. The nanostructures had a cross section with clear concentric circles which further confirmed the coaxial cable structure. The nanocables exhibited uniform dimensions along their entire lengths. The diameter of the CNT was in the range 40-100 nm. The out layers on CNT were continuous and uniform, the thickness of the out layers ranged from 200 to 400 nm which were larger than the size of inner nanotube.

A typical XRD pattern of the as-prepared products is shown in Fig. 1(e). As can be seen, the characteristic peaks of SiC can be easily indexed as the (111), (200), (220), (311), and (222) reflections of 3C-SiC (JCPDS, No. 29-1129). In addition, the chemical composition of SiC@CNTs was determined by energy-dispersive X-ray spectroscopy (EDS). As shown in Fig. 1(f), the corresponding EDS spectra of the products demonstrate the presence of silicon and carbon. It can be inferred that the thick out layer coated on the inner nanotube were SiC. The inner nanotube was CNT which was used as carbon source in the reaction. The result would be further confirmed by TEM analysis.

Further characterization of the nanostructures was carried out by using transmission electron microscopy (TEM), as shown in Fig.2 (a-e). The surface of coaxial nanocable was

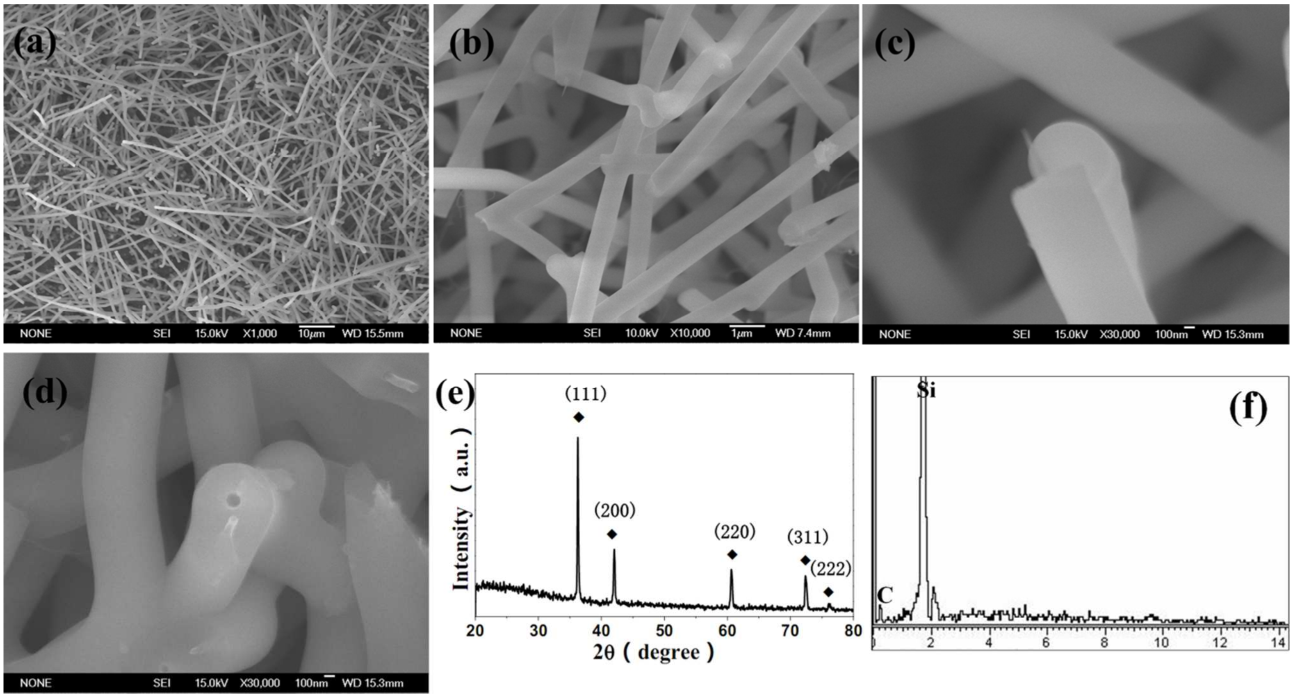

Fig. 1 SEM images of SiC@CNT coaxial nanocables: (a) and (b) at low magnification; (c) and (d) at high magnification; (e) the XRD pattern of SiC@CNT nanocables; (f) EDS spectrum of the SiC@CNT nanocables.

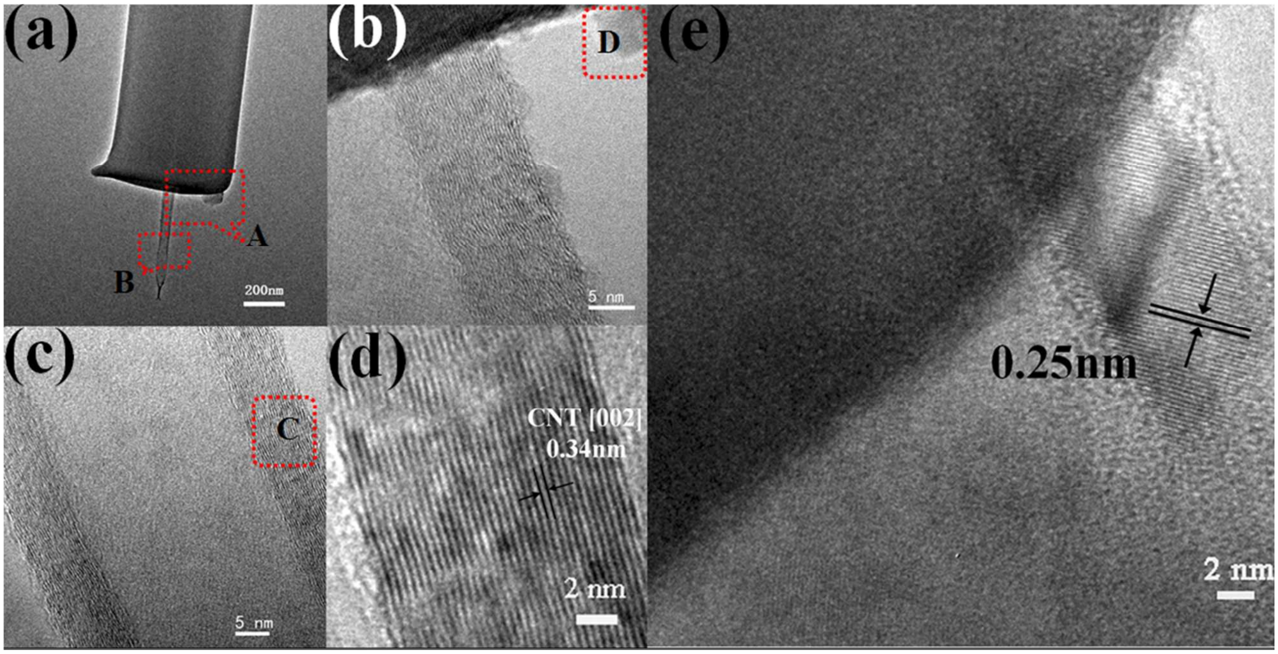

Fig.2 TEM images of SiC@CNT coaxial nanocables on the carbon-coated Cu grid: (a) TEM image of SiC@CNT nanocable at a low magnification. (b) and (c) enlarged TEM images obtained from the top end of SiC@CNT nanocable recorded from the marked area of A and B in (a), respectively. (d) HRTEM image recorded from the areas of C in (c). (e) HRTEM image recorded from the marked area of D in (b).

smooth and homogeneously. A thick and solid tubular-like structure attached to the surface of inner nanotube. The hollow feature of such heterostructure was clearly revealed by the exposed top end. The nanocable was too thick to obtain clear HRTEM images, but good images were obtained in the exposed top end. Fig.2 (b and c) shows the HRTEM micrograph of the top end of the nanocable marked by dotted red rectangle in Fig.2 (a). Two parallel walls indicated that the inner core is nanotube. The lattice plane spacing was about 0.34 nm, which was attributed to the (002) planes of MWCNTs as shown in Fig. 2(d). Fig. 2(e) shows the HRTEM images of the outer layer marginal regions recorded from the marked area of D in (b). According to the HRTEM image, the lattice plane spacing of 0.25nm corresponded to the SiC (111) crystal plane. The morphology and composition analysis implied that they were obtained as a result of carbon-nanotube confined reaction, CNT served as the template for the continuous growth of SiC nanolayer to form SiC@CNT coaxial nanocable.

3.2 Raman and PL spectrum

The Raman spectrum was recorded at room temperature using an excitation wavelength of 514 nm from an Ar$^+$ laser (as shown in Fig3). The peaks at 804 cm^{-1} and 972 cm^{-1} correspond to the transversal optical phonon (TO) and longitudinal optical phonon (LO) at the Γ point of 3C–SiC, respectively. The Raman spectrum of the SiC nanostructure is different from that of bulk SiC or thick SiC film.[16] It is speculated that the peak shift of the TO lines of SiC in the Raman spectrum is possibly caused by the defects and size confinement effect. The two peaks at around 1368 and 1582 cm^{-1} are typical Raman peaks of CNTs. The peaks at 1368cm^{-1} (D-band) indicate the existence of defective graphite layers in CNT.[17] The peak at 1582 cm^{-1} (G-band) appears due to the C—C stretching Raman-active Eg mode for CNTs.[18] The coexistence of SiC phase and the graphite phase in the Raman measurement again strengthens the possibility of coaxial nanocables structure of SiC@CNT.

Fig. 4 shows the room-temperature PL spectrum of the as-prepared SiC@CNT coaxial nanocable under the 260 nm ultraviolet fluorescent light excitation. The PL spectrum reveals that SiC@CNT nanocables have two broad emissionbands centered at 461 nm and 573 nm, respectively. The strong green emission band centered at 573 nm is similar to the previously reported irregular SiC tubes or SiC film.[19] It may be associated with C-related deep level defects formed during the reacting process. The emission peak at 461 nm is attributed to the blue emission luminescence from SiC. The PL bands in present SiC nanostructures are also blue-shifted relative to the bulk SiC,

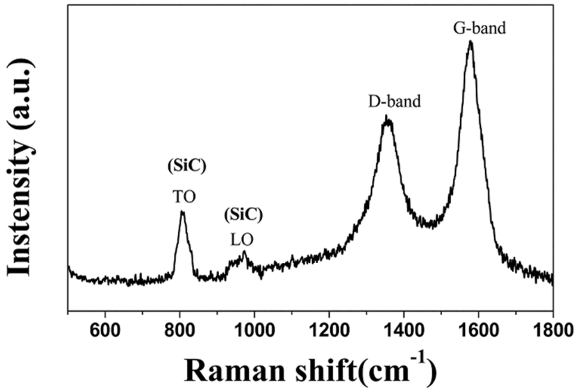

Fig.3 The Raman spectrum of SiC@CNT nanocables

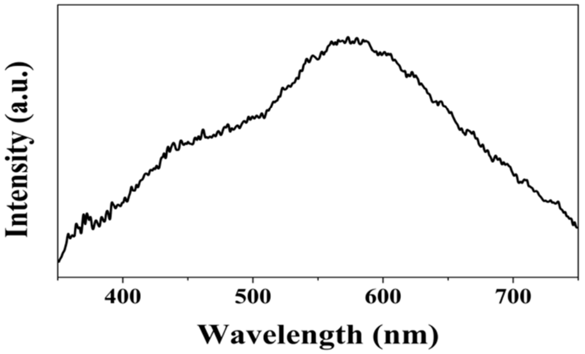

Fig.4 PL spectrum of the synthesized SiC@CNTs coaxial nanocable

which was attributed to the quantum size effects of SiC nanocables[20].

PL properties of SiC nanostructures depend strongly on the growth conditions, microstructure, and morphology. The wide PL spectrum SiC@CNT coaxial nanocable may be attributed to the existence of the special rough core-shell interface, the quantum confinement effect and the morphology effects.[21] However, the detailed explaining for photoluminescence in SiC@CNT coaxial nanocable is yet unknown, and further study is necessary to be continued. The intensive blue-green emission properties of the SiC@CNT nanocable are of significant interest for their potential blue-green emitting device applications.

3.3 Growth mechanism

To investigate the formation mechanism of SiC@CNTs coaxial nanocable, temperature-dependent growth was investigated by carbothermal reaction at 1370°C(a), 1400°C(b), 1450°C(c) , 1480°C(d) for 6h in Fig. 5. When the reaction temperature was 1370°C, it was found that only a few SiC nanowires were obtained, as shown in Fig. 5(a). There still existed a large amount of CNTs still maintain the original state after reaction. For the products obtained at 1400°C, cracked nanocable structures can be clearly seen in Fig. 5 (b), and were densely populated on the Si substrate. With the growth temperature increased further to 1450°C, similar nanocable structures marked by dotted red rectangle in Fig. 5(c) were again seen. Large amount of bent and intertwined CNTs converted to straight and relatively decentralized coaxial nanocables structures which are covered by SiC layer. At the reaction temperature of 1480°C, nanocables structures were almost disappeared and replaced by solid rod-like structure marked by dotted red rectangle in Fig. 5(d), revealing that higher temperature will accelerate the SiC nanorods growth and increase the yield of SiC

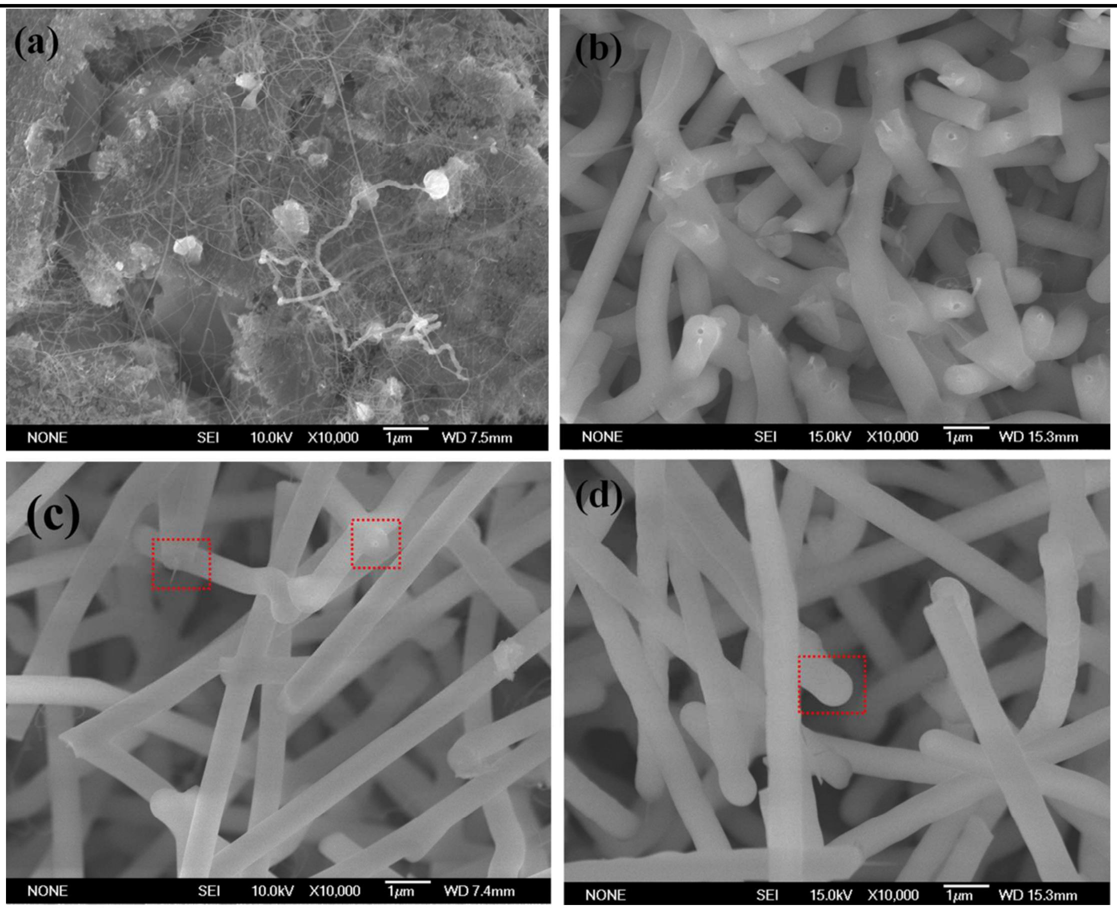

Fig. 5 SEM images of SiC@CNTs coaxial nanocables prepared at different temperatures: (a)1370°C, (b)1400°C, (c)1450°C, (d)1480°C for 6h.

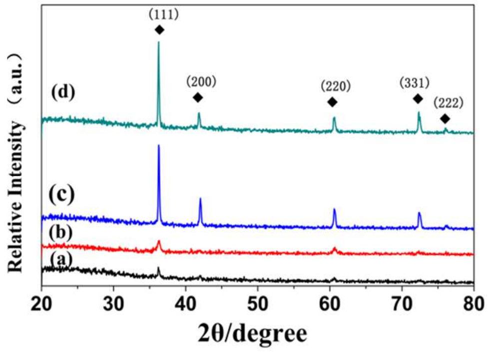

Fig. 6 Representative XRD patterns of SiC@CNTs coaxial nanocables prepared at different temperatures: (a)1370°C, (b)1400°C, (c)1450°C, (d)1480°C for 6h.

nanorods. The diffraction peaks intensity of the XRD patterns presented in Fig. 6 were gradually enhanced and the diffraction peaks became sharper with increasing the reaction temperature. Along with the XRD and SEM analysis, it suggests that the structure evolution of samples can occur when the temperature is increased.

Although the detailed process of nanocable to nanorod conversion is not fully understood at the moment, the above mentioned results surely indicate that SiC@CNT nanocables have been directly formed on the CNT skeleton. CNTs not only serve as carbon source but also act as the templates for the nanocable growth. A high density of nanocables is observed on the Si substrate by introducing the Co catalyst in the growth system. Interestingly, the nanocables are not achieved with Ni catalyst under the same conditions (as shown in Fig. 1S). Therefore, we speculate the existence of Co plays an important role in the growth of the nanocables. In a general, it is difficult for SiC to nucleate on CNTs due to the inert graphene surface and small diameter of CNTs[22]. However, the nanoscale Co droplets can be deposited on the surface of the carbon nanotubes to produce a catalyst layer, which can induce the SiC nanostructures to grow on the CNTs because of high catalytic activity of Co[23].

According to the above-mentioned results, the reasonable growth process of SiC@CNTs nanocable was illustrated inFig.7. At the first stage, the SiO vapor was obtained by carbothermal reduction of silica xerogels by reaction (1). In the nucleation stage, nanosize liquid Si–Co–C droplets are formed by the reaction of the SiO vapors and the carbon atoms in the outer layers of surviving CNTs with the Co catalyst. After Co is sufficiently saturated with the Si and C, SiC crystallites formed by reaction (2) served as nucleus as shown in Fig. 7 (a) which leads to SiC layer growth. However, reaction (2) did not ensure the continuous growth of SiC nanolayer. Once the nanotube was covered with SiC nucleus, the inner CNT would be isolated by the grown SiC layer from the flowing fresh air and keep inner layer intact. Nevertheless, nanocables may thicken if an epitaxial growth on the surface of as-grown SiC layer results from the reaction between SiO and CO gas by-products of reaction (3) in Fig.7(b). The generated CO_2 gas from reaction (3) might react with still existing carbon nanotubes. Thus, Reaction (1) and reaction (4) can provide CO gas source and have a positive feedback characteristic for reaction (3).

$$SiO_2(s)+C(s)=SiC(g)+CO(g) \quad (1)$$

$$SiO(g)+2C(s)=SiC(s)+CO(g) \quad (2)$$

$$SiO(g)+3CO(g)=SiC(s)+2CO_2(g) \quad (3)$$

$$CO_2(g)+C(s)=2CO(g) \quad (4)$$

Layer growth is a general phenomenon associated with supersaturation[25]. SiC was formed layer by layer via surface diffusion of Si atoms and C atoms on the surface of carbon nanotube.[24]As a result, SiC layer continued to grow along the length of the CNT to form nanocable structure (Fig.7 (c). CNTs acted as a template to constrain and determined the shape morphology of the final products. Along with SiC out layer continuous grown on CNT, SiC@CNT nanocable became relatively straight which is obviously different from the starting curved and twisted carbon nanotubes. With the increase of temperature, the flexibility of carbon nanotubes enhances, and relatively straight which is obviously different from the starting consequently weakens the influence that results from the restriction of the bending footpath which provides carbon atoms[26]. Therefore, SiC@CNT nanocables grow straight at a high reaction temperature.

The coaxial nanocable structure was only a transient state morphology. This kind of one-dimensional growth process

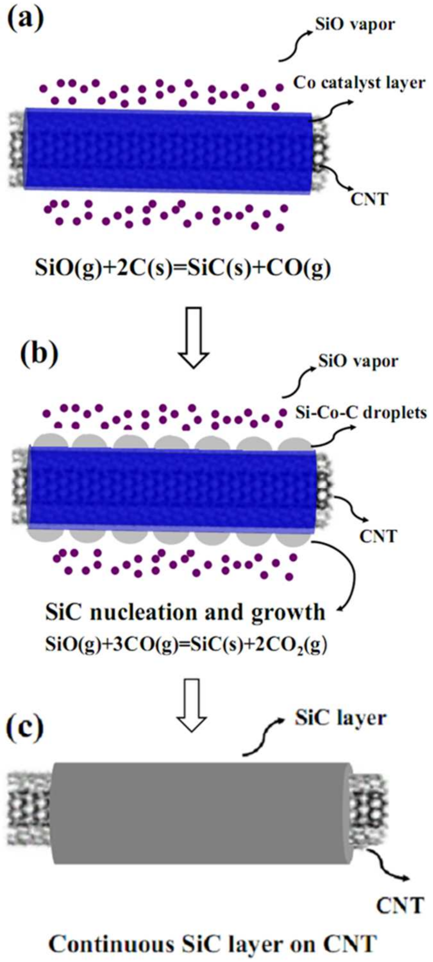

Fig. 7 Schematic illustration of a SiC@CNTs coaxial nanocable: (a) SiO vapor reaction of carbon atoms. (b) Formation of SiC nucleation on the CNT. (c) Formation of SiC layer on CNT.

continued up to the depletion of carbon atoms available in CNTs by the reaction with silicon atoms at higher temperatures. Higher reaction temperature may make the carbon atoms of CNTs become so active that they can more easily react with SiO_2 to produce supersaturated SiO and CO vapors. Thus, the final product became straight solid SiC nanorod. Therefore, we propose that the high growth temperature and carbon source play a key factor for preparing the SiC nanocable and nanorod.

Conclusions

In summary, novel SiC@CNT coaxial nanocables were designed and synthesized via chemical vapor deposition (CVD) reaction by using carbothermal reduction of silica xerogels and CNTs. The investigations of SiCnanostructures have been performed at the temperature range between 1370°C and 1480°C, and the as-prepared products have been characterized with XRD, SEM, TEM, Raman and PL spectra. The growth of the SiC@CNT nanocable is attributed to the reaction of SiO with CO on excess CNT surface assisted by Co catalyst. The SiC outer layer is continuous and uniform on CNT template. Such carbon related core-shell semiconductor hetrostructure would be expected as potential building blocks in nanodevices.

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Notes and references

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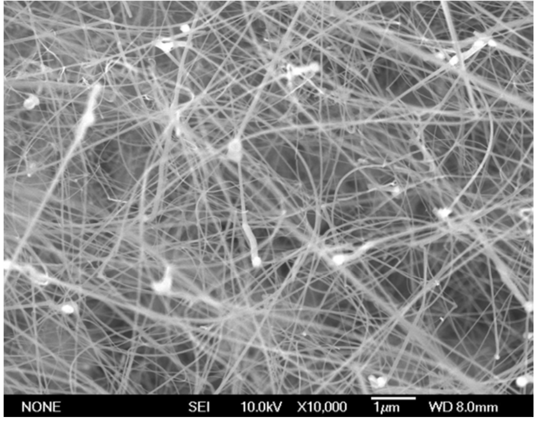

Fig. 1S The SEM image of SiC nanowires on Si substrate by using $Ni(NO_3)_2$ (0.04M) as catalyst prepared at 1450℃ for 6h

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