



Beaded silicon carbide nanochains via carbothermal reduction of carbonaceous silica xerogel

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Abstract

Novel silicon carbide nanostructures, beaded nanochains, are prepared from the carbothermal reduction of a carbonaceous silica xerogel with cetyltrimethylammonium bromide and lanthanum nitrate as additives. The nanochains consist of a stem with a diameter of about 50 nm and uniform beads with diameters of 100–200 nm. It is demonstrated that the tensile strength of an epoxy composite filled with the SiC nanochains improves significantly due to the unusual morphology of the nanochains.

1. Introduction

The preparation of nanosized building blocks for complex nanostructure assembly and for use in nanodevices is an essential activity nowadays in the nanoscience and nanomaterials community. The morphology-dependent physical or chemical properties open new horizons for their applications in nanotechnology [1]. Silicon carbide, an important functional material with many excellent properties, such as wide band gap, high thermal stability and strong resistance to oxidation and chemical corrosion, has been synthesized as a nanostructured material with various morphologies, such as nanowires [2], nanotubes [3, 4], nanorods [5], nanofibres [6], coaxial nanocables and nanosprings [7–9]. For applications of SiC nanowires in composite materials, the strength of the material is strongly influenced by the interfacial strength between the filler and the matrix. Therefore, beaded nanowires may have applications as reinforcing agents because the mechanical interlocking between beads can produce stronger interfacial adhesion. Singjai and coworkers reported the synthesis of beaded nanofibres with coexistent carbon nanotube and SiC phases [10]. More recently, Wei and coworkers found a necklace-like SiC nanostructure in the straight SiC nanowires produced by the reaction of SiO₂ and graphite powder [11]. The nanostructure has a thread with a diameter of 100–300 nm, and beads with diameters of 0.5–1.0 μm.

SiC materials are frequently prepared via the carbothermal reduction of the carbonaceous silica (C–Si) xerogel prepared from tetraethoxysilane (TEOS) and phenolic resin. Usually the xerogel produces SiC nanowires [12, 13]. However, in our previous studies, C–Si xerogel containing different additives was shown to generate different morphological SiC nanostructures, such as nanoparticles [14], nanowires [15] and mesoporous SiC [14, 16]. When using lanthanum nitrate as an additive to the C–Si xerogel, we obtained bamboolike SiC nanowires which had a stem of cubic β-SiC and nodes consisting of a high number of stacking faults [17]. It was suggested that the stacking faults resulted from sudden segregation of SiC from liquid metallic droplets. This stimulates us to prepare beaded SiC nanowires using different additives with the xerogel.

In this paper, we report the synthesis of a type of SiC nanochain with beads about 200 nm in diameter, simply by using cetyltrimethylammonium bromide (CTAB) and lanthanum nitrate in the sol–gel preparation. CTAB is a surfactant, which is frequently used as a structure directing

agent in the synthesis of silicon-based mesoporous materials [18, 19]. In these systems containing CTAB and TEOS, a self-assembly process occurs between CTAB and silica, usually leading to ordered meso-structured materials. The aim of using CTAB as an additive in the present work is to make primary silica particles form an orderly assembly in the gelation process. The SiC nanochains obtained exhibit an unusual reinforcing property when used as a filler in epoxy composite, a functional material related to its unique morphology.

2. Experimental section

2.1. Materials preparation

All chemicals used were AR grade, and the water was deionized. The synthesis included xerogel preparation and subsequent carbothermal reduction. The preparation started from an ethanol solution of phenolic resin (16.0 g), TEOS (50 ml), lanthanum nitrate (1.0 g) and CTAB (5.4 g), where the approximate molar ratio of the four substances was 3:1:0.014:0.07. 8 ml of oxalic acid (3.4 wt%) and a few drops of dense hydrochloric acid (~0.5 ml) were added to the solution under stirring to enhance the hydrolysis of TEOS. After 24 h, hexamethylenetetramine aqueous (35.8 wt%, 10 ml) solution was dropped into the above mixture to accelerate the gelation. The gel was then dried at 110° C for 12 h to obtain a xerogel. In the carbothermal reduction, the xerogel was heated at 1300° C in argon flow for 5 h in a horizontal tubular reactor. The raw product was purified by air oxidation at 700° C to remove residual carbon, and by acid treatment (first nitric acid, then hydrofluoric acid) to remove unreacted silica and other impurities. The purified sample was a light-green powder. We usually used 5 g of the xerogel for the carbothermal reduction and obtained about 0.1 g of purified sample. Details of the carbothermal reduction can also be found elsewhere [17].

Fabrication of the SiC-reinforced composites was similar to that described in the literature [20]. Firstly, 20 g of epoxy resin was mixed with 0.1 g of milled SiC powder (0.5 wt% of the resin, the same as in the following) by mechanical grinding. Secondly, a given amount of acetone (20 wt%) and triethylenetetramine (10 wt%) were added into the mixture under strong stirring. The above mixture was infused into a silicone mould, which had a length, width and thickness of 50, 9 and 5 mm respectively, and was then vacuumized to eliminate air bubbles. Finally, the composite was dried at 130° C for 4 h. For comparison, samples with straight SiC nanowires and without filler were also prepared. Tensile tests of three groups of epoxy composites (epoxy only, nanowire-reinforced and nanochain-reinforced; 3 samples for each group) were performed on a materials testing machine (SANS, Shenzhen, China). The machine has a loading rate of 1.0 mm min⁻¹ and an extensometer of gauge length 9.5 mm.

2.2. Characterization

The sample was characterized in a Philips CM 200 FEG TEM operated at 200 kV and equipped with a Gatan Image Filter. Scanning electron microscopy (SEM) images were acquired with an S4800 FEG microscope (Hitachi). The acceleration voltage was set to 5 kV and the working distance to 10 mm. X-ray diffraction (XRD) measurements were done at room temperature on a STOE STADI-P focusing monochromatic transmission diffractometer equipped with a Ge(111) monochromator and a position sensitive detector. Cu K_α radiation was used. The phase analysis was performed with the STOE Win XPOW software package (version 1.06; Stoe Darmstadt, Germany).

3. Results and discussion

An SEM image of the light-green sample is shown in figure 1. The most evident characteristic of the sample is that it mainly consists of beaded nanochains with a diameter of 100–200 nm. The ratio of the nanochains in the sample is estimated to be more than 60%. A low magnification SEM image shows that the length of the nanochains ranges from several to tens of microns. The x-ray diffraction pattern (figure 2) demonstrates that the sample is pure cubic SiC with some stacking faults [21]. Most of the nanochains have a uniform periodic structure. Figure 3(A)

shows an extremely straight SiC nanochain with a length of several microns. The nanochain (figures 3(A) and (B)) has beads with a diameter of 150 nm, and a thinner stem with a diameter of 50 nm. The distance between two neighbouring beads is 200 nm, which is almost invariable,

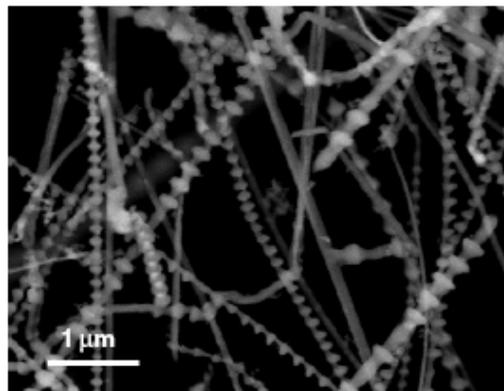


Figure 1. SEM image of beaded SiC nanochains.

and thus can be regarded as the period of the nanochain ($L = 200$ nm). Of course, some of the nanochains have variable periods (figure 4). As shown in figure 1, the beads and stems are very homogeneous in one nanochain, but vary between different nanochains. Many of the nanochains have an amorphous thin shell (figure 3(C)). Electron energy loss spectrum (EELS) analysis demonstrates that the shell contains silicon and carbon, but no oxygen (not shown). As with most SiC nanowires, the nanochains grow along the [111] direction. The concentration of stacking faults is observed to be higher in the beads compared with the stems of the nanochain (figure 3(D)). A high-resolution transmission electron microscopy (HRTEM) image shows the stacking faults in the stems (figure 3(E)). This is also confirmed with selected area electron diffraction (SAED) of the nanochains (figure 4).

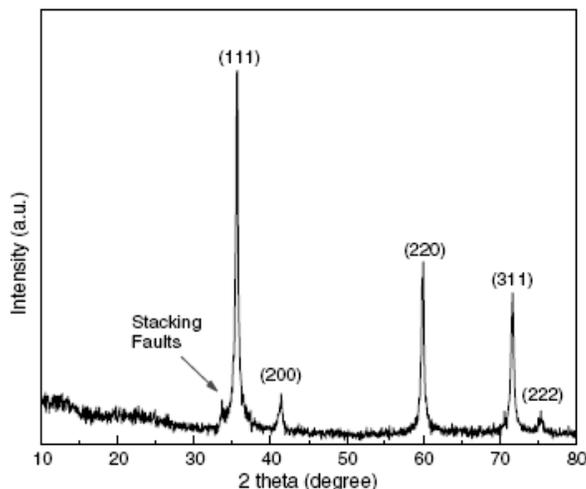


Figure 2. XRD patterns of the SiC sample consisting of beaded nanochains.

The growth mechanism of SiC whiskers or nanowires has been discussed by different authors [22, 23]. The SiC nanowires generally grow along the [111] direction due to the lowest surface energy of the (111) plane. For the beaded SiC nanowires grown without a catalyst, Wei *et al* suggested a two-step process to explain the formation of the beaded structure [11]. According to their suggestion, smooth SiC nanowires are formed first, then SiC beads are generated by deposition. In addition, beaded morphology was also observed in the synthesis of carbon

nanotubes [24] and polymer nanofibres [25]. Heer *et al* suggested that the amorphous beads over carbon nanotubes were formed due to the cooling of viscous liquid carbon [24]. In the two cases, the distance between two neighbouring beads may vary, nevertheless the shape of the beads is closely symmetrical along both vertical and horizontal nanowire axes. However, the beads in the present work are asymmetrical along the direction perpendicular to the nanowires. This may indicate another different formation route.

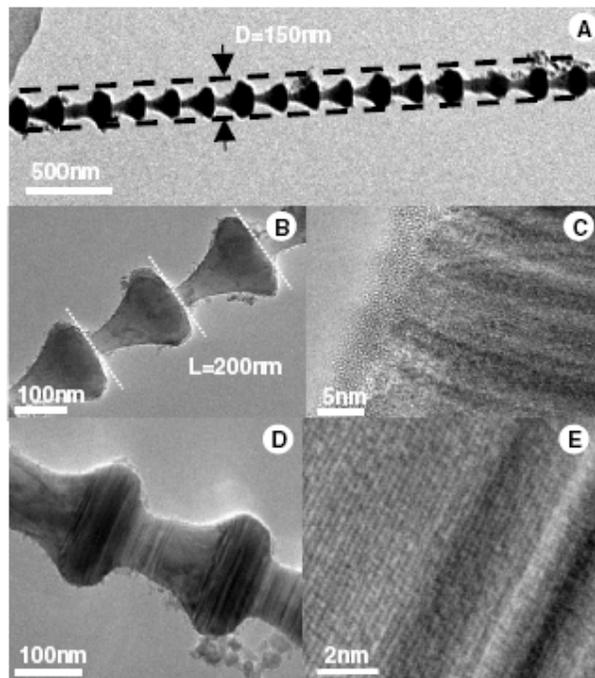


Figure 3. ((A), (B)) TEM images of the alternately changed ‘stem-and-bead’ structure of the nanochains. (C) Amorphous SiC shell and the growth direction [111] of the nanochains. (D) Stacking faults are observed in the beaded nanochains. (E) HRTEM image of cubic SiC (left) and stacking faults (right).

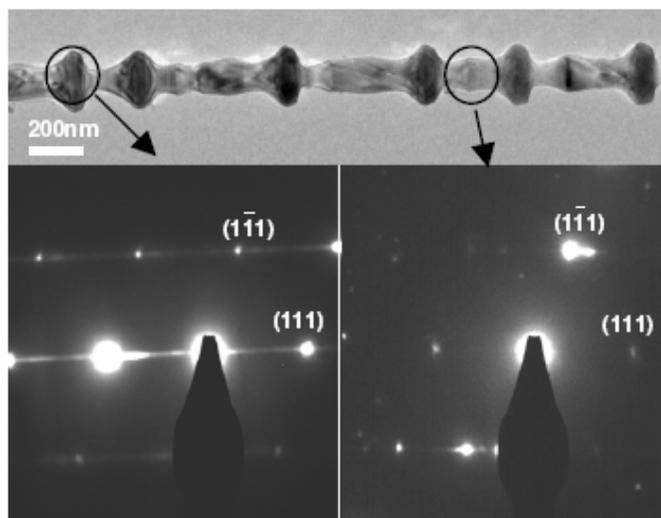


Figure 4. TEM and SAED of the SiC nanochains. The growth direction is observed to be the [111] direction. The streaks observed in the SAEDs are due to the stacking faults in the cubic SiC probed in the selected area for diffraction.

It is well known that SiC whiskers or nanowires are produced according to the vapour–liquid–solid (VLS) mechanism in the presence of metal catalysts, and the driving force for SiC growth by the VLS mechanism is the carbon activity gradient between the VL and LS interfaces [26–28]. Reasonably, we suggest that the beaded SiC nanochains are produced via the VLS mechanism. Under the reaction conditions, silica reacts with lanthanum and forms a eutectic solution, which appears in the reaction system as alloy droplets. The droplets absorb gaseous reactants SiO and CO (or carbon), and precipitate silicon carbide after the concentrations of Si and C elements in the droplets come to saturation. Usually, the absorption rates of Si and C elements are approximately equal to the precipitation rate of SiC. In this case, smooth SiC nanowires are expected. However, the concentrations of Si and C in the droplets could reach a very high degree of supersaturation when the adsorption rates are much larger than the precipitation rate. For a general droplet, the accumulation of C and Si atoms would result in changes in the droplet volume and composition, and would thus lead to a change in the contact angle between the droplet and the wire. This might result in a radial growth together with the axial growth. Note that the precipitation increases, and then the composition of the droplet changes again leading to normal wire growth. The periodically alternating Si and C concentrations in the droplet therefore lead to the formation of the beaded morphology. From our experiments, the lanthanum catalyst without CTAB usually produces bamboo-like SiC nanowires, a few of them with a nodular morphology [17]. It is thus suggested that the lanthanum component in the droplets has changed the carbon activity gradient, and thus resulted in a high supersaturation degree of the Si and C concentrations. The use of CTAB possibly makes silica particles assemble and form an orderly arrangement in the gelation process [18, 19]. This occurs at room temperature, however the mesostructured arrangement can be partially maintained at the reaction temperature, although CTAB has run away at lower temperatures. It is possible that the arrangement of silica and carbon particles enhances the formation of the beaded morphology.

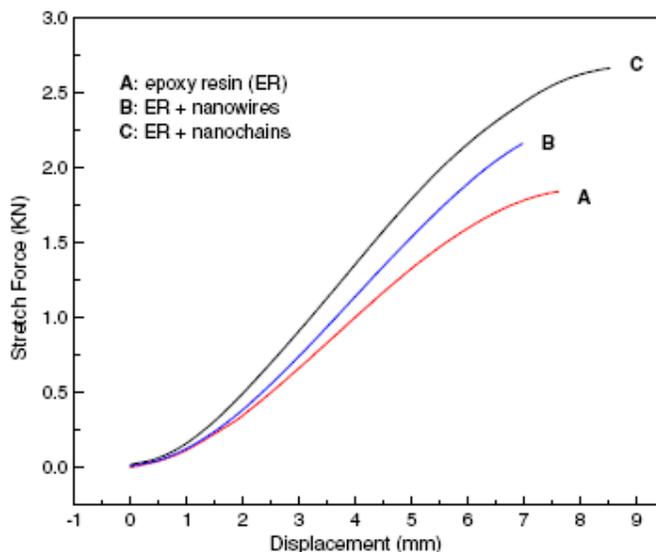


Figure 5. Force–displacement curves of the epoxy composites. The composite reinforced by the nanochains exhibits a remarkable improvement in rigidity.

To investigate the mechanical properties of the composite material reinforced by the nanochains, epoxy composites with 0.5 wt% SiC filler were prepared according to the method described in the literature [20]. Tensile tests of three groups of epoxy composites (epoxy only, nanowirereinforced and nanochain-reinforced; three samples for each group) were tested on a SANS materials testing machine. For each composite sample, the machine can give a force

displacement curve. The measured force and strength values have errors of about 5% for each group of samples. For comparison in figure 5, we selected from each group a set of force–displacement data, which corresponded to the sample with a moderate tensile strength. From the figure, it can be seen that the rigidity of the nanochain-reinforced composite has improved significantly. For each group of samples, three values of the tensile strength were simply averaged. The averaged tensile strength is 38.9 MPa for epoxy only, 44.4 MPa for nanowire-reinforced and 51.4 MPa for nanochain-reinforced composites. Obviously, the tensile strength is increased by 32% for the nanochain-reinforced composite, but 14% for the nanowire-reinforced. The SEM image (figure 6(A)) of the composite fracture demonstrates that the nanowires are pulled out from the matrix. However, no pullout nanochains are found from the fracture, all of them are broken (figure 6(B)). These results further confirm that the unusual reinforcing effect of the nanochains results from the mechanical interlocking between the beads and the matrix.

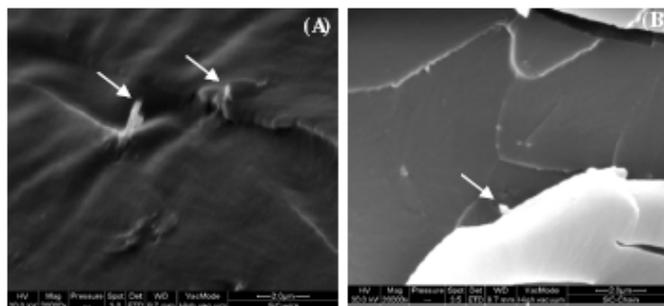


Figure 6. SEM images of the fractures of nanowire-reinforced (A) and nanochain-reinforced (B) epoxy composites. Those arrowed are pull-out nanowires and broken nanochains, respectively.

4. Conclusion

In conclusion, we have demonstrated that beaded SiC nanochains can be simply prepared from the carbothermal treatment of the carbonaceous silica xerogel with CTAB and lanthanum nitrate as additives. Furthermore, it is confirmed that the nanochains have an unusual reinforcing effect due to the mechanical interlocking between beads, which can enhance the interfacial adhesion between the filler and the matrix. The periodically alternating diameter, and thereby resistance, of the nanochains resulting from the beaded morphology are of significant importance for the applications of semiconductor nanowires in nanodevices.

Acknowledgments

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References

- [1] Xia Y, Yang P, Sun Y, Wu Y, Mayers B, Gates B, Yin Y, Kim F and Yan H 2003 *Adv. Mater.* **15** 353–89
- [2] Gundiah G, Madhav G, Govindaraj A, Seikh M M and Rao C N R 2002 *J. Mater. Chem.* **12** 1606–11
- [3] Sun X H, Li C P, Wong W K, Wong N B, Lee C S, Lee S T and Teo B K 2002 *J. Am. Chem. Soc.* **124** 14464–71
- [4] Pham-Huu C, Keller N, Ehret G and Ledoux M J 2001 *J. Catal.* **200** 400–10
- [5] Dai H J, Wong E W, Lu Y Z, Fan S S and Lieber C M 1995 *Nature* **375** 769–72
- [6] Raman V, Bhatia G, Bhardwaj S, Srivastava A K and Sood K N 2005 *J. Mater. Sci.* **40** 1521–7
- [7] Zhang Y, Suenaga K, Colliex C and Iijima S 1998 *Science* **281** 973–5
- [8] Zhang H F, Wang C M and Wang L S 2002 *Nano Lett.* **2** 941–4
- [9] Zhang D, Alkhateeb A, Han H, Mahmood H, McIlroy D N and Norton M G 2003 *Nano Lett.* **3** 983–7
- [10] Singjai P, Wongjamras A, Yu L D and Tunkasiri T 2002 *Chem. Phys. Lett.* **366** 51–5
- [11] Wei J, Li K Z, Li H J, Fu Q G and Zhang L 2006 *Mater. Chem. Phys.* **95** 140–4
- [12] Meng G W, Cui Y, Zhang L D and Phillipp F 2000 *J. Cryst. Growth* **209** 801–6
- [13] Li X K, Liu L, Zhang Y Z, Shen S D, Ge S and Ling L C 2001 *Carbon* **39** 159–65

- [14] Guo X Y, Jin G Q and Hao Y J 2004 *Mater. Res. Soc. Symp. Proc.* **815** 77–82
- [15] Jin G Q, Liang P and Guo X Y 2003 *J. Mater. Sci. Lett.* **22** 767–70
- [16] Guo X Y and Jin G Q 2005 *J. Mater. Sci.* **40** 1301–3
- [17] Hao Y J, Jin G Q, Han X D and Guo X Y 2006 *Mater. Lett.* **60** 1334–7
- [18] Grosso D, Babonneau F, Albouy P A, Amenitsch H, Balkenende A R, Brunet-Bruneau A and Rivory J 2002 *Chem. Mater.* **14** 931–9
- [19] Boonamnuyvitaya V, Tayamanon C, Seo-ung S and Tanthapanichakoon W 2006 *Chem. Eng. Sci.* **61** 1686–91
- [20] Ci L and Bai J 2004 *Adv. Mater.* **16** 2021–4
- [21] Seo W S, Koumoto K and Aria S 2000 *J. Am. Ceram. Soc.* **83** 2584–92
- [22] Wang L, Wada H and Allard L F 1992 *J. Mater. Res.* **7** 148–63
- [23] Gao Y H, Bando Y, Kurashima K and Sato T 2002 *J. Mater. Sci.* **37** 2023–9
- [24] Heer W A, Poncharal P, Berger C, Gezo J, Song Z, Bettini J and Ugarte D 2005 *Science* **307** 907–10
- [25] Fong H and Reneker D H 1999 *J. Polym. Sci. B* **37** 3488–93
- [26] Bootsma G A, Knippenberg W F and Verspui G 1971 *J. Cryst. Growth* **11** 297–309
- [27] Milewski J V, Gac F D, Petrovic J J and Skaggs S R 1985 *J. Mater. Sci.* **20** 1160–6
- [28] Chaussenda D, Ferro G and Monteil Y 2002 *J. Cryst. Growth* **234** 63–9