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Uniformity's influence of silica xerogel on synthesis efficiency of SiC nanorods by carbothermal reduction

Huynh Thi Ha¹, Cao Tuan Anh², Nguyen Thi Thu Ha¹, Phan Viet Phong¹, Dao Tran Cao¹, Le Quang Huy¹ and Nguyen The Quynh¹

¹ Institute of Materials Science, Vietnam Academy of Science and Technology,
18 Hoang Quoc Viet Road, Cau Giay Distr., Hanoi, Vietnam

² Institute of Physics, Vietnam Academy of Science and Technology,
10 Dao Tan Street, Badinh Distr., Hanoi, Vietnam

E-mail: haht@ims.vast.ac.vn

Abstract. Silica xerogels containing nanocarbon were milled for several hours before the carbothermal reduction processing. The formation of SiC nanorods was investigated at different annealing temperatures. It is shown that the formation temperature of SiC nanorods can be decreased if the powder size of milled silica xerogels is lower than 100 nm. The morphology, structure and production efficiency of synthesized SiC were determined by scanning electron microscopy SEM, X-ray diffraction XRD and thermo-gravimetric analysis TGA measurements. It is evident that production efficiency of synthesized SiC nanorods clearly depends on uniformity of precursor materials.

Keywords: Silica xerogel, SiC nanorods, carbothermal reduction, grinding.

1. Introduction

Nanostructured silicon carbide has unique properties in microelectronics, optoelectronics as well as mechanical engineering. Nowadays, nanostructured SiC material manufacturing with high efficiency is an attraction in nanotechnology's application. SiC nanowires have been produced by several methods: carbothermal reduction of silica [1], reaction between silicon halides and CCl_4 [2], etc. An advantage of carbothermal reduction of silica is the relatively low cost in mass production. Some researchers successfully synthesized SiC nanowires by using precursor materials like nano-sized SiO or SiO_2 to react with carbon nanotubes under catalysts such as Fe, Al, etc. [3, 4]. However, under working conditions without any catalyst, the production efficiency of this method depends significantly on the size and uniformity of silica precursors. In current works, silica xerogel containing carbon nanoparticles has been produced from tetraethoxysilane and saccharose. In order to investigate the uniformity's influence of silica xerogel containing carbon particles on synthesis efficiency of SiC nanorods, grinding processes were carried out before and after formation of xerogel.

In this work, the synthesis of SiC nanorods via a two-step reaction in carbothermal reduction has been developed. These studies address the overall structure and growth efficiency of SiC nanorods.

2. Experimental

The first stage in preparation of silica xerogel containing carbon particles is the silica sol making. It was done as follows: 100 ml $\text{Si}(\text{OC}_2\text{H}_5)_4$ (p.a), 100 ml ethanol (p.a) and 100 ml deionized water were

firstly mixed together by magnetic stirring for 15 minutes. A few drop of concentrated nitride acid (~ 5 ml, MERKC, p.a) was then added into the mixture under continuous stirring for another 15 minutes. In order to obtain carbon nanoparticles in silica gel, saccharose $C_{12}H_{22}O_{11}$ was next gradually added into the solution under vigorous stirring. The amount of saccharose was adjusted to get molar ratio of C to Si of 4.1:1. The stirring was done for 20 hours in ambient air to achieve homogeneity in gel.

In the second stage, gel was dried at 90°C in a dry box and then was calcined at 700°C for 2 hours in flowing N_2 atmosphere to completely decompose saccharose into carbon and water vapor. Gel was then divided into smaller pieces to undergo different experiments. A part was grinded before calcination. Another part was grinded after xerogel formation. After the grinding, they were then divided again and milled for 5, 10, and 15 hours respectively in ambient air. Another part of xerogel was milled for 5 hour in ethanol. SiO_2 xerogel containing carbon particles was milled by high-energy horizontal vibrating ball mill SPEX 8000D in using Tunsten carbide (WC) grinding vial.

The apparatus for the synthesis of SiC nanorods is a horizontal tube vacuum furnace GLX1600-80X. The milled xerogels were loaded in a graphite boat and placed at the center inside the alumina tube. The samples were heated at different temperatures at 1400, 1450, 1500 and 1550 °C for 3 hours under continuous flow of high-purity argon gas.

Upon completing the reaction, the collected SiC nanorods were characterized by X-ray diffraction (XRD Siemens D5000), transmission electron microscopy (TEM JEM1010 JEOL), scanning electron microscopy (SEM Hitachi S-4800), and thermo-gravimetric analyzer (TG-DTA/DSC Setaram Instrumentation).

3. Results and discussion

In our work, the size of silica xerogel containing carbon nanoparticles grinded by different conditions was carefully tested. Figure 1 displays SEM images of silica xerogel containing carbon nanoparticles.

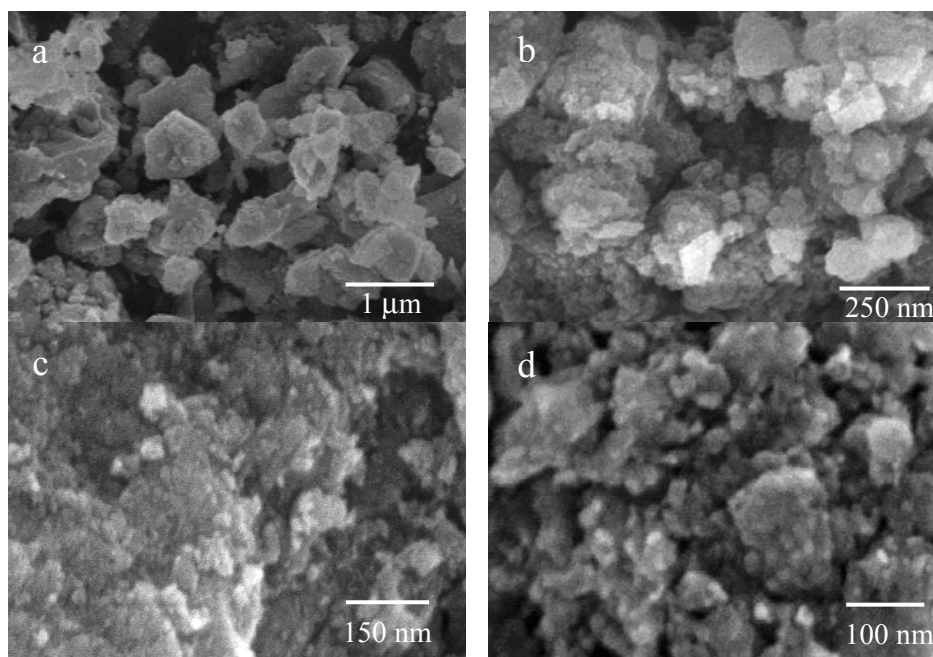


Figure 1. SEM images of silica xerogel containing carbon nanoparticles under:
 a) HEM for 5 hours after xerogel formation,
 b) rough grinding before calcination of gel+HEM for 15 hours after xerogel formation,
 c) fine grinding before calcination of gel+HEM for 15 hours after xerogel formation,
 d) rough grinding before calcination of gel+HEM for 05 hours after xerogel formation in ethanol.

If there was only high-energy mill (HEM) for 5 hours after xerogel formation, the size of xerogel was around several hundred nanometers (figure 1a). In the case where there was a rough grinding before calcination of gel, the size of xerogel appreciably decreased below 100 nm (figure 1b). When there was a fine grinding before calcination of gel, the size of xerogel was smaller than 50 nm though the boundaries were still not clear (figure 1c). In the case where there was a rough grind before calcination of gel and high-energy mill carried out in ethanol, the size of xerogel was smaller and grain boundaries became more evident (figure 1d).

XRD spectrum and diffraction pattern of the product in figure 2 show two constituents. The analysis from figure 2a indicates that the product was mainly β -SiC and contained part of remaining amorphous carbon and silicone oxide. The result from figure 2b reveals that the product was a mixture of predominantly β -SiC with crystalline WC. The appearance of WC particles was due to the WC grinding vial when xerogel was milled in ethanol. The result also shows that at heating temperature 1450 °C the crystal β -SiC could be received.

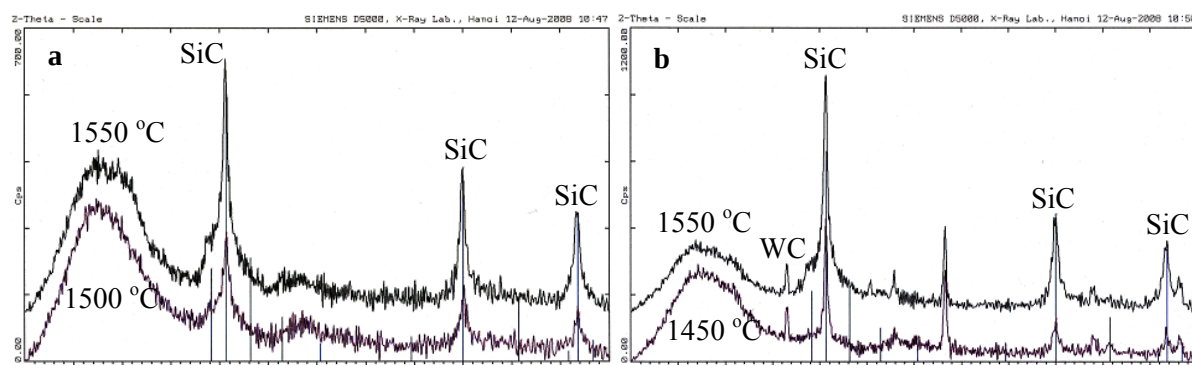


Figure 2. XRD spectrum of SiC product: a) high-energy mill in ambient air; b) high-energy mill in ethanol.

Figure 3 below shows TEM measurements of SiC nanorods heated at 1550°C. The result indicates that outside diameters of SiC nanorods ranged from 10 to 30 nm (figures 3a, b). In the case where high-energy mill was carried out in ethanol, they were smaller (figure 3c, 10 - 20 nm). The morphology of nanorods was straight and solid. Stacking faults were found on SiC nanorods.

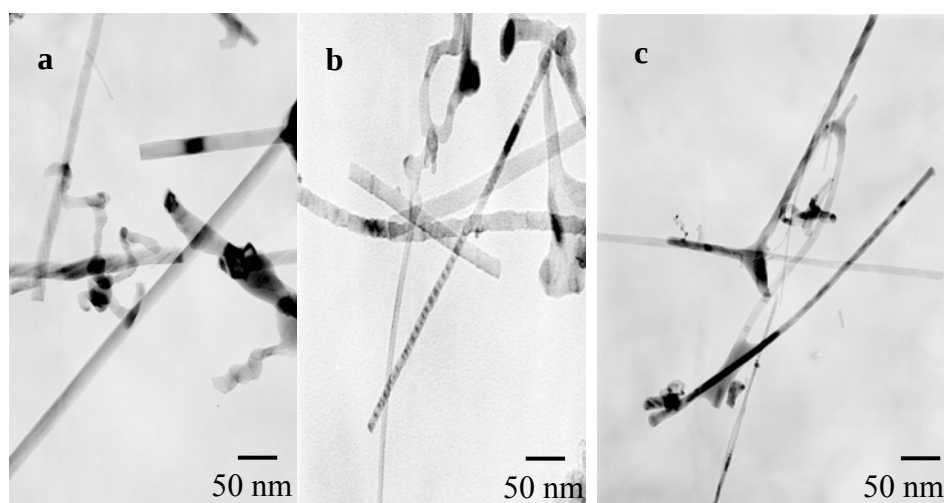


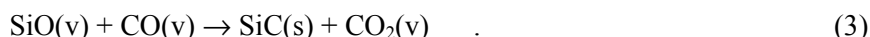
Figure 3. TEM images of SiC nanorods at heating temperature 1550°C with: a,b) high-energy mill in ambient air, c) high-energy mill in ethanol.

SEM images of SiC nanorods are shown in figure 4. At heating temperature 1400°C, rods randomly appeared (figure 4a) and there were no crystalline phases in XRD analysis. At 1450°C, a number of SiC nanorods were obtained with outside diameters of roughly 100 nm and lengths of 5-10 μm (figure 4b). At 1550°C, a large amount of nanorods were formed with thinner outside diameters and shorter lengths (figure 4c).

In the two-step reaction process, the reaction equations are:



According to suggestions by W. Han [5] the generated CO vapor in reaction (1) can react with SiO vapor on the generated SiC nanorods surface as follows:



In such a case, the epitaxial growth of SiC on the surface of initially produced SiC nanorods from reaction (2) makes the diameter of some final SiC nanorods larger. We think that at lower heating temperature (1450°C), the lost amount of SiO and CO vapours because of argon flow was smaller than that at a higher temperatures (1550°C); therefore the probability of reaction (3) was larger, which explains why in our results the diameters of SiC nanorods produced at 1450°C were larger.

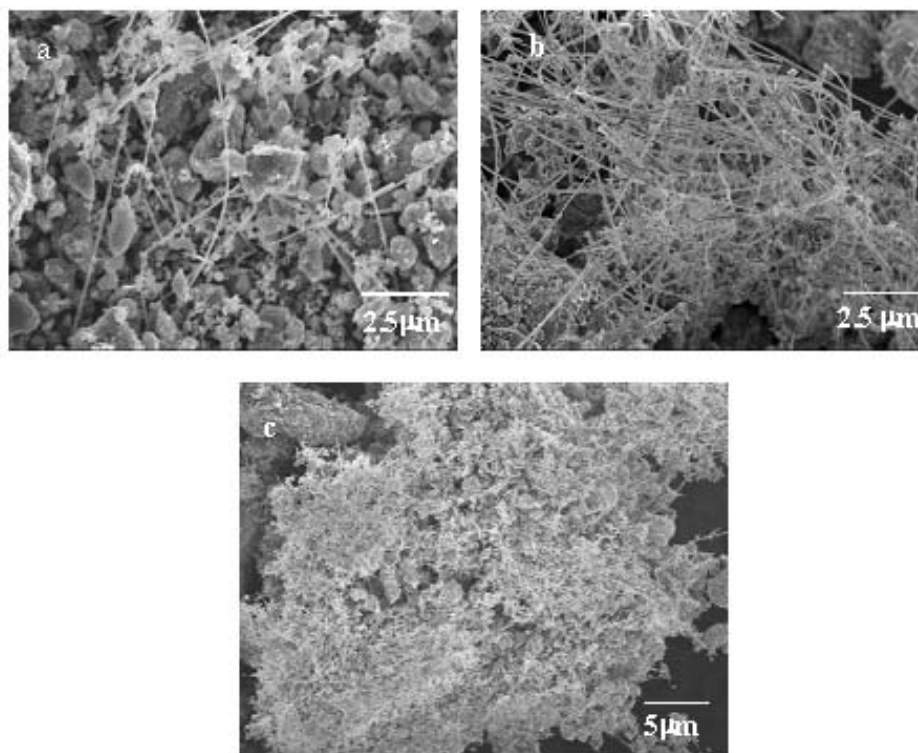


Figure 4. SEM images of SiC nanorods at heating temperature:
 a) 1400°C, b) 1450°C, and c) 1550°C.

Figure 5 is the thermogravimetric analysis (TGA) of SiC product. The measurement was carried out in ambient air in temperature range 20-1350°C with heating rate of 10°C/min. The SiC products under different grinded and heated temperature conditions were tested. The XRD measurements show that a part of amorphous un-reacted carbon still existed in the synthesized product, hence in TGA result it could have been the heat emission process where carbon was burned in a temperature range below 1000°C. The percentage value of lost mass in heat emission implies an indirect relationship between the amount of un-reacted free carbon with Si in solid state and the efficiency of different SiC synthesis processes. Table 1 presents the TGA data of SiC synthesis processes, where TGA

measurements were done with different kinds of grinding: non-grinding before xerogel formation sample (NG), rough grinding before xerogel formation (RG), fine grinding before xerogel formation (FG), high-energy mill in ethanol (E) and at different temperatures 1450, 1500, and 1550°C. After xerogel formation the samples were milled by high-energy mill for 5 or 15 hours.

The results show that when the size of xerogel was in the range of several hundred nanometers (with HEM for only 5 hours) the lost mass of free carbon was rather large 33-39%, while with the size in the range of several ten nanometers, the lost mass of free carbon was significantly smaller, even at lower heating temperatures (24.05 %, 1450°C).

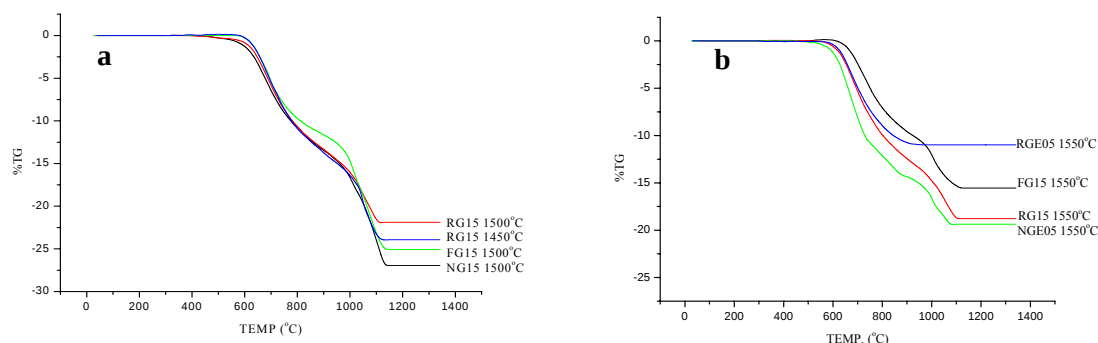


Figure 5. TGA measurements of synthesized production heated at: a) 1450°C and 1500°C, b) 1550°C.

The results also indicate that the products of fine grinding and the rough grinding before xerogel formation gave similar loss on free carbon, while non-grinding before xerogel formation gave larger ones. The loss mass of free carbon in the case of rough grinding before xerogel formation with high-energy mill in ethanol for 5 hours was the least of all. It corresponded to the best uniformity and smallest size of prepared xerogel powder.

Table 1. Relationship of remaining free carbon in SiC product with grinding regimes of SiO₂ xerogel containing carbon nanoparticles.

Heating temperature (°C)	Remaining free carbon, %								
	0.7 MPa Ar pressure ^a		1.4 MPa Ar pressure ^a	NG15 ^b	RG15 ^b	FG15 ^b	NGE05 ^b	RGE05 ^b	
1450	no detected	nanorod	no detected			-24.05			
1500	no detected	nanorod	no detected	-26.94	-21.88	-25.08			
1550		-39		-33		-18.81	-15.25	-19.36	-10.93

^a -hundred-nm size xerogel based

^b -ten-nm size xerogel based (at 0.7 MPa Ar gas pressure)

Through all the results obtained above, it can be seen that in carbothermal reduction of SiO₂ without any catalyst the uniform small size of silica xerogel containing carbon nanoparticles plays an important role in production efficiency of SiC nanorods. Of course, high-energy milling produces smaller grain size, possibly higher surface area, which should contribute a reduced reaction on vaporization temperature and a higher chemical reactivity in SiC nucleation, but it is obviously seen that the different grind regimes give different size and uniformity of xerogel, therefore different production efficiencies in result.

4. Conclusion

The morphology of SiC products synthesized in a two-step carbothermal reduction process of SiO₂ without any catalytic particles was investigated.

- The β -SiC nanorods were 10-100 nm in diameter and 1-10 μ m in length dependent on the uniformity and the size of silica xerogel containing carbon nanoparticles.
- With fine uniformity and small-size (<100 nm) silica xerogel precursors, the formation temperature of SiC nanorods decreased.
- The production efficiency of synthesized SiC nanorods clearly is affected by uniformity of precursor materials and grinding regimes.

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