In-situ growth of β-SiC nanofibers from polymer precursors

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Abstract. Silicon powder and different organic polymers were used to in-situ growth of SiC nano fibers on porous SiC ceramic in the current study. SEM analysis showed the most abundant nano fibers were obtained by milling silicon powder for 12 hours, and the highest aspect ratio of nano fibers was obtained by milling for 24 hours. starch, guar gum and collagen were used separately as binding materials for preparing cellulose-silicon powder precursors. The best growth of nano fibers was obtained with addition of collagen. The growth mechanism of nano fibers was proved to be vapor-liquid-solid (VLS). XRD analysis indicated the main crystalline phase is $\beta$-SiC after 1400°C pyrolysis.

1. Introduction
Diesel engines possess low fuel costs, higher transportation efficiency, thermal efficiency and durability compared with gasoline engines. Till now, diesel engines have been widely used in heavy duty trucks, tractors, and ships. However, burning of diesel fuel will emit PM and NOx, which is reported to be harmful to human health [1]. Various after-treatment techniques have been developed in order to reduce PM emissions. DPF is one of the most widely used technology which can achieve efficiency higher than 90% [2]. DPFs need to withstand high temperature, high thermal shock resistance and good anticorrosive ability. Two widely used materials to make DPF substrate are cordierite and silicon carbide. Cordierite is widely used in DPF substrates due to its low price and ease of manufacture. However, cordierite is vulnerable to high temperature, high thermal shock. As a result, pinholes, cracks and melts have been observed during long term DPF running [3].

Silicon carbide, on the other hand, has high mechanical robustness, melting point, thermal shock resistance and chemical stability [4]. Silicon carbide honeycomb ceramics with Pt/Pd catalyst coating have the advantages of high catalytic activity, good thermal stability and long service life, so that are widely used in high temperature gas filtration, chemical catalysis and separation etc.

One-dimensional nano-structures such as nanowires and nano fibers are at the forefront of nanoscience and nanotechnology. In particular, ceramics with 1D nanostructures received increasing interest. A fibrous morphology provides many unique favorable properties, the most prevalent is the increase in surface to volume ratio and excellent mechanical properties, which expands the application of this type of materials. Silicon carbide nano fibers in particular offer potential applications as substrates for catalysis and as well as high temperature filters [5]. nan et al synthesized nanowires modified porous SiC ceramics by CVI, Characterization showed nanowires modified SiC ceramics provided better permeation performance, mechanical properties and thermal conductivity [6].
Several techniques have been developed to synthesize SiC nano fibers, including chemical vapor deposition (CVD), carbothermal reduction process, polymeric precursor pyrolysis. However, most of these methods, involved complicated processes, rigid vacuum conditions and high temperature heat treatment [7]. In this paper, we proposed a facile method to develop porous SiC ceramic with decoration of SiC nano fibers served as DPF material from low cost precursors at 1400 ℃ with platinum nitrate as the catalyst, providing a technical guidance for developing new diesel exhaust filter.

2. Experimental

2.1. Preparation

Silicon powder(average particle size:10μm) was mixed with carbon containing materials after being milled(180rpm) for 0h, 6h, 12h and 24h, the solution was added to the mixture subsequently. The composition of the solution is: an appropriate amount of ethanol was added to tetraethyl orthosilicate(TEOS), then deionized water was added to mixed solution. The volume ratio of ethanol, TEOS and deionized water is 5:5:100, Platinum nitrate solution(15wt%) was added to the mixed solution. When producing the cellulose-silicon powder combination, guar gum, starch, and collagen were used as binders, respectively. Pug was obtained after Stirring well. The specific formulations is shown in Table 1. The pug then was packed into a mold to form a wafer. After being cured at 80 ℃ for 24 hours, the wafer was placed in a alumina oxide tube furnace (SK-G08163-3), then heated the furnace to 1400 ℃ at a rate of 5 ℃/min with an argon gas flowrate of 1L/ min, the samples were then held isothermal for 4 hours. After pyrolysis, the samples were cooled naturally. The samples were analyzed by SEM-EDS and XRD subsequently.

| number | Carbon source | Silicon source | other additives |
|--------|---------------|----------------|----------------|
| 1      | 1g of guar gum| 1g of silicon powder | 10ml solution+0.05%Pt(NO)₃, mill 0h |
| 2      | 1g of guar gum| 1g of silicon powder | 10ml solution+0.05%Pt(NO)₃, mill 6h |
| 3      | 1g of guar gum| 1g of silicon powder | 10ml solution+0.05%Pt(NO)₃, mill 12h |
| 4      | 1g of guar gum| 1g of silicon powder | 10ml solution+0.05%Pt(NO)₃, mill 24h |
| 5      | 5g of Cellulose| 1g of silicon powder | 10ml solution+0.05%Pt(NO)₃+1g of guar gum |
| 6      | 5g of Cellulose| 1g of silicon powder | 10ml solution+0.05%Pt(NO)₃+1g of starch |
| 7      | 5g of Cellulose| 1g of silicon powder | 10ml solution+0.05%Pt(NO)₃+10% collagen |

2.2. Characterization

The morphology was characterized by a scanning electron microscope (SEM, SU3500) equipped with an Electron Dispersive Spectroscopy (EDS). The phase identification of the samples was characterized by an X-ray diffractometer (SHIMADZU XRD-6100).

3. Results and Discussions

3.1. Effect of different ball-milling treatment

Figure 1 displays the particle size distribution of silicon powder after different ball-milling treatments. The particle size distribution of silicon powder decreases with the increase of ball-milling time. The effect of different ball-milling treatment of silicon powder on the growth of SiC nano fibers
was investigated and is shown in Figure 2. The corresponding precursors formulations are number 1-4 in the table 1. It is obvious that the matrix possesses a porous structure with pore sizes ranging from hundreds of nanometer to tens of micrometer, the growth direction of nano fibers is distributed randomly. As the milling time increases, the abundance of SiC nano fiber increases first and then decreases. When the milling time is 12h, the most abundant nano fibers were obtained, the shape of the nano fibers changed from rod to fiber, nano fibers with highest aspect ratio was obtained by milling for 24h, and nano fibers are intertwined with each other together to form a networked structure.

**Figure 1.** silicon powder particle size distribution with different ball-milling treatment: (a) 0h, (b) 6h, (c) 12h, (d) 24h.

**Figure 2.** SiC nano fibers matrix with different ball-milling treatment: (a) 0h; (b) 6h; (c) 12h; (d) 24h.
3.2. Effect of different binders

The SEM images of nano fibers produced with different precursor materials are shown in Figure 3. The corresponding precursor formulations are number 5-7 in the table 1. It is obvious that the cellulose-guar gum combination created the least SiC nano fibers, only a few short rod-like nano fibers were attached to the SiC particles. The cellulose-starch combination formed a small amount of SiC nano fibers compared with former combination, the average length was longer but the diameter increased simultaneously, and partial of nano fibers possessed a string of bead-like shape with diameter of 3 μm. The cellulose-collagen combination provided the most abundant SiC nano fibers, which grows in a straight line. It is speculated that the nano fibers growth inherited the structure of cellulose, and the average diameter was 500nm. In addition, starch and guar gum have a polymer polysaccharide structures, while collagen extracted from animals, has a polymer protein structure. Different structures lead to different growth conditions of nano fibers, and the specific growth mechanism needs to be further studied.

![Figure 3](image)

EDS analysis indicates that a high concentration of silicon in the spherical structure (60wt%, Carbon element is automatically ignored by the equipment), followed by Pt (10wt%), and few amount of impurity elements in the catalyst. The same element was also found in nano fibers body. However, the different Si/Pt ratio proved metal catalyzed nanofibers growth by VLS [8].

![Figure 4](image)

Figure 5 shows XRD pattern of wafer before and after thermal treatment. Only the crystalline Si phase was detected before treatment, as guar gum doesn’t possess crystal structure. The main
crystalline phase after pyrolysis is the $\beta$-SiC, followed by minor crystalline phases of Si. The sharp peak of SiC indicates that $\beta$-SiC has a high crystallinity.

![XRD profiles of wafer before and after pyrolysis.](image)

**Figure 5.** XRD profiles of wafer before and after pyrolysis.

Figure 6 shows a schematic diagram of SiC nano fibers growth by VLS reaction. Firstly, Pt particles were dispersed and melted into metal droplets at high temperature. Subsequently, the precursors produce silicon-containing vapor and carbon-containing vapor, which are absorbed by catalyst droplet. Finally, the nano fibers grew from the solid-liquid interface, which explained the aggregation of Pt elements in the spherical structure at the top of the nano fibers. The reaction proposed as follow:

$$3\text{Si}(vapor) + 2\text{CO}(vapor) \xrightarrow{\text{Pt}} 2\text{SiC}(solid) + \text{SiO}_2(solid)$$

![Schematic diagram of the growth of SiC nano fibers](image)

**Figure 6.** Schematic diagram of the growth of SiC nano fibers [9].

4. Conclusion

In this paper, silicon powder and low cost polymer precursors such as guar gum and cellulose, with platinum as catalyst, were proposed to in-situ grow SiC nano fibers at 1400°C. SEM figure indicates that the SiC matrix possesses a porous structure. When compared with ball-milling treatment of silicon powder, it is found that the most abundant SiC nano fibers can be obtained by milling for 12h, and the highest aspect ratio was obtained by milling 24h. When producing SiC nano fibers by cellulose-silicon powder, guar gum, starch and collagen were used as a binder respectively, collagen combination produced the best matrix. The VLS mechanism was confirmed by EDS, as nano fibers tip contained high concentration of Pt. XRD results showed that SiC with high crystallinity was synthesized. In general, this paper provides a low cost, facile synthesized and high porous SiC with decoration of SiC nano fibers, which is a potential material in the treatment of diesel particulate filter.

5. Acknowledgments

This work was financially supported by Project of Technology Innovation in Hubei Province (No.2016ACA161).
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