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Synthesis of Silicon Carbide Nanostructures via Simplified Yajima Process - Reaction at the Vapor-Liquid Interphase

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Silicon carbide is a wide bandgap semiconductor material with many potential high technology applications.[1] There are many ways to prepare silicon carbide powders and thin films. These include cabothermic reduction of silica, sol-gel synthesis, and various chemical vapor deposition techniques.[2-5] In 1975, Yajima reported a preceramic polymer route to prepare β-SiC fibers industrially.[6] In the process, Na was employed to couple $SiMe_2Cl_2$ monomers in hydrocarbon solvents into polydimethylsilane, -$(Me_2Si)_n$-. The preceramic polymer -$(Me_2Si)_n$- was further decomposed thermally into the β-SiC fibers. Now, we wish to demonstrate that the original Yajima process can be simplified to generate β-SiC nanostructures efficiently. Cubic cages, cubic shells and nanoparticles of β-SiC are formed via the reactions involving vapors of methylchlorosilanes, $SiMe_2Cl_2$ and $SiMeCl_3$, and liquid Na.

At 623 K and under 1 atm of Ar, NaH powders were decomposed to form small droplets of liquid Na. Then, the liquid Na was reacted with the vapors of $SiMe_2Cl_2$ and $SiMeCl_3$ to generate particle precursors **Pre-I** and **Pre-II**, respectively. After the precursors were decomposed at 1273 K under vacuum, fine powders were collected as the final products. Black powders **I** and yellow powders **II** were obtained from **Pre-I** and **Pre-II**, respectively.

As shown by the scanning electron microscopic (SEM) images in Fig. 1, the particles of **I** display two types of morphology. The major type, **Ia**, appears as hollow cubic cages with an edge length of 60 - 400 nm (Fig. 1a). Many of the cages show an edge thickness of ca. 40 nm. An energy dispersive spectrum (EDS) suggested that **Ia** contains Si, C, and some O atoms. The minor type, **Ib**, is cubes with an edge length of 1 - 2 μm as shown in Fig. 1B. The EDS of **Ib** suggests that the cages are composed of Si, C and a small amount of O also. Transmission electron microscopic (TEM) images of **Ia** and **Ib** are shown in Figs. 1C and 1D, respectively. The TEM image of **Ia** confirms that the inner space defined by the cage's edges is empty. The electron diffraction (ED) study of **Ia** shows a diffused ring pattern indicating that the structure is polycrystalline. The ED rings can be indexed to the (111), (220) and (311) planes of a cubic structure. The lattice parameter a is estimated to be 0.251 nm, close to the value of β-SiC.[7] The TEM image in Fig. 1D shows that **Ib** is composed of hollow cubes with a wall thickness of ca. 20 nm. The ED pattern and the derived lattice parameter, a = 0.251 nm, suggest that **Ib** is polycrystalline β-SiC too.[7] Furthermore, X-ray diffraction (XRD) and other spectroscopic data, such as Fourier transform infrared (FT-IR), [29]Si solid-state nuclear magnetic resonance (^{29}Si SSNMR)

and X-ray photoelectron spectroscopy (XPS), support that **I** is β-SiC.
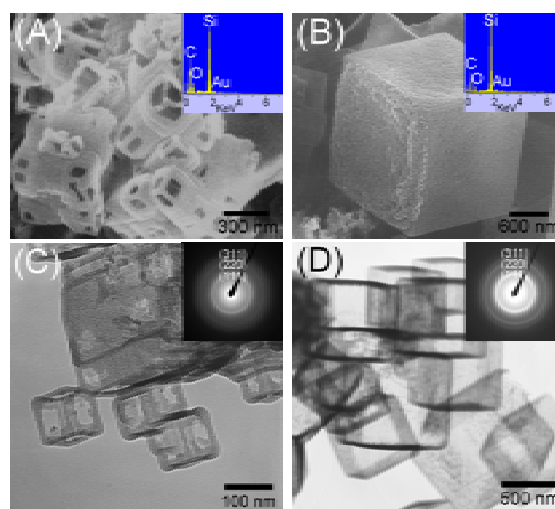

Figure 1. Images of **I**, prepared from $SiMe_2Cl_2$. SEM and EDS (inset) of (A) **Ia** and (B) **1b**. TEM and ED (inset) of (C) **Ia** and (D) **1b**.

Employing $SiMeCl_3$ into the reaction, **Pre-II** was generated first at 623 K. After the precursor was decomposed at 1273 K, **II** was isolated. An SEM image in Fig. 2A shows the morphology of **II**. It consists of spherical nanoparticles with a diameter of ca. 10 nm. The EDS result shows the presence of Si and C atoms. A TEM image in Fig. 2B confirms that **II** has a nearly nonagglomerated spherical shape with an average diameter of 10 nm. An ED study in Fig. 2C shows a ring pattern which can be assigned to the diffractions from the (111), (200), (220), and (311) planes of a cubic phase polycrystals. From the ED, the lattice parameter a is estimated to be 0.251 nm. This is consistent with the literature value of β-SiC.[7] A high resolution TEM (HRTEM) image of a nanoparticle of **II** is shown in Fig. 2D. The particle has an averaged diameter of 10 nm. The fringes, spaced 0.25 nm apart, can be observed clearly. These are assigned to the (111) planes of β-SiC. The value is close to the literature data for β-SiC, 0.252 nm.[7] In addition, **II** is confirmed to be β-SiC based on the results from XRD, FT-IR, Raman, and XPS studies.
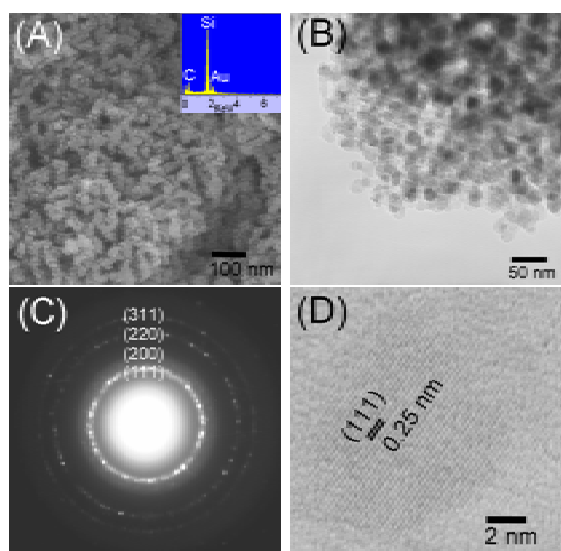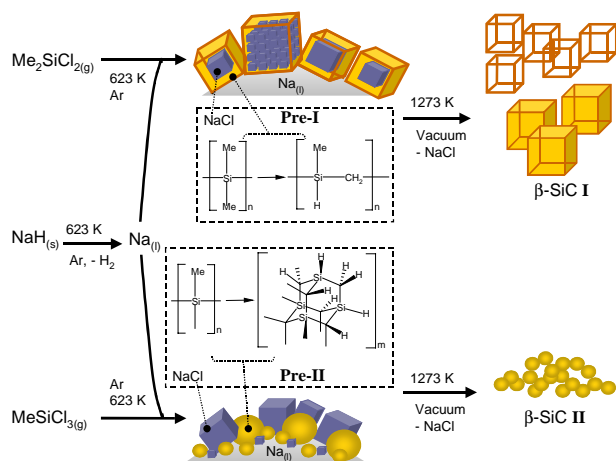
Figure 2. (A) SEM and EDS (inset), (B) TEM, (C) ED, and (D) HRTEM images of **II**, prepared from SiMeCl₃.

Scheme 1. Reaction steps to form **I** and **II**.

We studied how the physical shapes of **I** and **II** were influenced by the precursors **Pre-I** and **Pre-II**. Formed at 623 K, **Pre-I** showed cubic structures under SEM. EDS and XRD studies indicated the presence of NaCl, a byproduct in the reaction. FT-IR and ^{29}Si SSNMR data supported that **Pre-I** was a mixture of polydimethylsilane and polycarbosilane.[8] According to the original Yajima studies, the polydimethylsilane, which was the initial product generated from the coupling of SiMe₂Cl₂ by Na, was transformed into polycarbosilane near the reaction temperature.[6] Based on the above information, we suggest that **Pre-I** had cubic cores of NaCl crystals, which served as self-generated templates, to support flexible shells composed of the linear polymers. At 1273 K under vacuum, the inner cores were vaporized while the outer shells decomposed further into **I**, showing the cubic cage and shell structures of β-SiC. The overall steps to the products are summarized in Scheme 1. For **Pre-II**, the presence of NaCl and polycarbosilane was also supported by XRD, FT-IR and ^{29}Si SSNMR data. However, since **II** were nanoparticles, displaying a physical shape distinctively different from **I**, we speculate that **Pre-II** did not have a tightly attached NaCl/polycarbosilane core/shell structure similar to that observed for **Pre-I**. Instead, the polymer and the salt might grow into phases separated widely and with little physical and structural

interactions. Based on a previous report,[9] the initial coupling product between SiMeCl₃ and Na at 623 K is proposed to be polymethylsilyne, (MeSi)ₙ, a highly cross-linked network polymer. In the ^{29}Si SSNMR spectrum, a broad signal near –60 ppm was observed and assigned to this type of bonding environment for Si. This material probably reacted further into a rigid cross-linked polycarbosilane based nanoparticles of **Pre-II**. Then, at 1273 K, these nanoparticles were converted into β-SiC of **II**.

In conclusion, we have synthesized β-SiC cages, cubes and nanoparticles via vapor-liquid reactions employing methylchlorosilanes and Na. The route is a simplified solvent-free Yajima process. This interesting example shows how nonvolatile products produced at the vapor-liquid interphase may cooperatively influence the physical appearances. Both the precursors **Pre-I** and **Pre-II** were composed of mixtures of organosilicon polymers and NaCl. In **Pre-I**, the more flexible polymers probably wrapped the NaCl crystals, which served as cubic templates. Consequently, the cubic shape was maintained in the final product **I**. In contract, in **Pre-II**, the more rigid cross-linked polymers probably separated from the NaCl crystals completely. The result is that little structural influence and correlation was observed between the two. As a result, the final product **II** stayed as featureless nanoparticles. The differences at the precursor srage generated pronounced shape variations in the final products of β-SiC. Clearly, the appearance difference between **I** and **II** is the consequence of the interaction difference among the phase-separated solid products, generated at the interphase of vapor-liquid/solid reactions. This type of behavior has been observed in other systems.[10,11] Search for potential applications of these new materials is in progress.

Supporting Information Available:. Experimental section. SEM, XRD, FT-IR, Raman, SSNMR and XPS data of the particles isolated from this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Synopsis

By reacting vapors of $SiMe_2Cl_2$ and $SiMeCl_3$ with liquid Na at 623 K, precurosrs containing organosilicon polymers and NaCl were obtained. Decomposition of the precursor from $SiMe_2Cl_2$ at 1273 K under vacuum generated β-SiC cubic cages (edge length 60 - 400 nm, edge thickness 40 nm) and shells (edge length 300 nm, shell thickness 20 nm). Decomposition of the precursor from $SiMeCl_3$ under a similar condition, β-SiC nanoparticles (diameter 5 - 10 nm) were obtained.