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Fabrication of novel hydrophobic SiC/SiO_2 bead-string like core-shell nanochains *via* a facile catalyst/template-free thermal chemical vapor deposition process

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HIGHLIGHTS

- Novel SiC/SiO_2 bead-string like core-shell nanochains are successfully synthesized.
- No catalysts or templates are used during the synthesis process.
- These nanochains exhibit hydrophobicity with a water contact angle of about 140.5°.

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ABSTRACT

Novel SiC/SiO_2 bead-string like core-shell nanochains have been fabricated *via* a thermal chemical vapor deposition process without using any catalysts and templates. These SiC/SiO_2 bead-string like core-shell nanochains are made up of SiO_2 spheres as beads and SiC/SiO_2 core-shell nanowires as strings, respectively. A Vapor–Solid growth mechanism is proposed to explain the formation of these SiC/SiO_2 hetero-nanostructures in the absence of catalysts on the basis of the characterization results, the possible reactions among the solid phases, intermediate gas phases and surface energy minimization. Moreover, these SiO_2-SiC bead-string like nanochains exhibit good hydrophobicity with a water contact angle over 140°, which is caused by the special surface composition. This hydrophobicity makes these SiO_2-SiC bead-string like nanochains promising candidates as surface protective or self-cleaning materials in harsh environments.

1. Introduction

In the past decades, one-dimensional (1D) nanostructures, such as nanowires, nanotubes, nanobelts, nanochains and nanocables, have attracted considerable attention due to their potential applications as interconnects or functional components in nanoscale electronic, optoelectronic, or mechanical devices [1–3]. Variety of 1D nanomaterials including carbon nanotubes [4,5], silicon nanotubes [6], boron nitride nanotubes [7,8], molybdenum disulfide nanowires [9], titanium oxide nanotubes [10], gallium nitride nanowires [11], silicon carbide nanowires [12,13], and silicon carbide/silica (SiC/SiO_2) core-shell nanowires [14,15], have been fabricated. Among these 1D nanostructures, SiC nanowires have attracted intensive interest because of their unique properties, such as large bandgap, outstanding mechanical properties, excellent chemical inertness, high thermal stability and conductivity, and good field emission properties [12,16–19]. These unique properties make them very attractive in various fields from reinforcements in ceramic, polymer or metal matrix composites to the areas of nanoelectronics, photocatalysts, field emitters and nanosensors [12,17,19–26]. Till date, diverse methods such as chemical vapor deposition (CVD) [13], carbon thermal reduction [27], arc discharge [28], thermal evaporation [29], solvothermal synthesis [30] and polymer pyrolysis [31], have been developed to grow SiC nanowires. However, undesired SiO_2 layer is usually formed as a by-product on the surfaces of SiC nanowires forming SiC/SiO_2 core-shell nanostructures owing to the existence of trace oxygen during the preparation of SiC nanomaterials [14,32,33]. SiO_2 is an insulator and its nanostructure has been one of the most widely explored building blocks in multicomponent hybrid structures due to its easy fabrication and high physicochemical inert properties [34–36]. Moreover, it has been reported that optimum SiO_2 coatings on SiC nanowires can effectively improve the field emission and electromagnetic microwave absorption properties of SiC

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nanowires [37–39]. In this regard, the fabrication of these 1D SiC/SiO_2 core-shell nanostructures becomes increasingly important in the building blocks of complex electronic, photonic and multifunctional nanodevices because of the excellent properties of both SiC cores and SiO_2 shells.

An increasing number of researches have been done on the synthesis of 1D SiC/SiO_2 core-shell nanowires. For example, Zhang Haifeng et al. have synthesized helical crystalline SiC nanowires covered with SiO_2 sheath (SiC/SiO_2) *via* CVD technique [15]. This SiC core typically has diameter in the range of 10–40 nm with a helical periodicity of 40–80 nm covered by a uniform layer of 30–60 nm thick amorphous SiO_2 shell [15]. Wu Renbing et al. present a simple vapor deposition method for one-step synthesis of SiC/SiO_2 core-shell nanowires which consist of single crystalline SiC cores of 20–30 nm in diameter covered by uniform amorphous SiO_2 shells with thickness of about 15 nm [14]. Chen Kai et al. have fabricated several hundreds of micrometers long SiC/SiO_2 core-shell nanowires on Si substrates by thermal evaporation method using iron nitrate as catalyst, and the typical SiC core diameter is 50–100 nm while the SiO_2 shell thickness is 5–10 nm [40], respectively. Hu Ping et al. have developed a catalyst-assisted chemical vapor reaction process to large scale fabrication of SiC/SiO_2 core–shell nanowires with the lengths ranging from several tens to several hundreds of micrometers using silicon and carbon black as raw materials [27]. The diameter of these as-fabricated SiC/SiO_2 core-shell nanowires is in the range of 40–120 nm consisting of β-SiC cores coated with thickness of 2–3 nm amorphous SiO_2 shells [27]. Li Zhenjiang et al. have fabricated a novel SiC/SiO_2 chain-like nanostructure *via* a simple template/catalyst-free chemical vapor reaction approach using Si-SiO_2 mixed powder and CH_4 as precursors [41]. These SiC/SiO_2 core-shell nanowires exhibit chain-like structure with the length up to tens of micrometers and diameter of 20–30 nm [41], respectively.

However, the studies on the properties of above-mentioned SiC/SiO_2 core-shell nanostructures are mainly focused on their photoluminescence, field emission or electronic properties, and rare work discusses the surface wettability. Usually, SiC/SiO_2 core-shell nanowires are hydrophilic and need to be modified by the low energy polymers to achieve hydrophobicity [42]. The incorporation of water-repellent properties into SiC/SiO_2 core-shell nanowires can not only enhance the stability and life of them when they are used in humidity environment, but also hold great promise for application as self-cleaning materials. Herein, in current research, novel SiC/SiO_2 bead-string like core-shell nanochains were fabricated *via* a thermal CVD process at 1500 °C without using any catalysts and templates. The morphology, composition, and microstructure of the as-fabricated nanochains were then characterized. The possible growth mechanism was also proposed to explain the formation of these novel hetero-nanostructures in the absence of catalysts on the basis of the characterization results, the possible reactions among the solid phases, intermediate gas phases and surface energy minimization. Furthermore, the surface wettability of these as-fabricated nanochains was investigated by measuring the static water contact angles (CAs).

2. Experimental procedures

Carbon cloth, silica gel solution (10–20 nm, 40%) and ammonia borane were used as raw materials. The ammonia borane was synthesized according to the method reported in the literature [43]. Typically, experiments were carried out as follows: Initially, 5 g of ammonia borane and 50 g of silica gel solution were dispersed into 50 ml of deionized water (0 °C) under ultrasonication. When the solution changed into uniform white gel, the carbon cloth was immersed into it for one minute to let the gel completely covered onto the carbon cloth surface. After being dried at 95 °C, the gel covered carbon cloth was transferred into a tube furnace for heating treatment. Before heating, the high purity argon gas (99.999%) was introduced into the furnace at a flow rate of 100 ml/min for ten minutes to purge the tube under atmospheric pressure. Then, the furnace was heated up to 1500 °C from room temperature with a heating rate of 3 °C/min and then maintained for 1 h. High purity argon was kept during all the experimental process. When the heating treatment process was terminated, the furnace was naturally cooled down to room temperature. Finally, light-blue product was found on the surface of carbon cloth.

The photographs of the carbon cloth and as-fabricated products were taken by a digital camera. The high magnification photograph of the carbon cloth was detected by YYT-540E optical microscope. The X-ray diffraction (XRD) spectrum of the as-fabricated products was obtained on a Rigaku X-ray diffractometer with Cu Kα radiation, and the diffraction points were recorded from 10° to 90° with a scan step size of 0.04°. Raman spectrum was recorded from 700 to 1100 cm^{-1} on a microscopic confocal Raman spectrometer (Renishaw) using a 532 nm laser. The scanning electron microscopy (SEM) images of the as-fabricated products were performed on TESCAN VEGA II electron microscope equipped with an energy dispersive X-ray spectroscope (EDS). The transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images of the as-fabricated products were collected on a JEM-2100 electron microscope equipped with an energy dispersive X-ray spectroscope (EDS, Oxford Instrumenta). The surface wettability of the as-fabricated products was examined using a JC2000D (Powereach) contact angle goniometer. The surface bonding state of the as-fabricated products was investigated by fourier transform infrared spectroscopy (FTIR, PerkinElmer).

3. Results and discussion

Fig. 1a and b displays the photographs of the used rectangular carbon cloth in which the rough and black surface can be observed. After thermal CVD process, the products can directly grow on the surface of carbon cloth as shown in Fig. 1c, in which mass light blue products can be found. Fig. 1d presents the low-magnification SEM image of the as-fabricated products, showing that lots of bead-string like nanostructures randomly distribute on the substrate. The amount of the bead-string like nanostructures in the sample exceeds 90%, indicating the relatively high amount and purity quotient of the products [41]. Fig. 1e exhibits the high-magnification SEM image of the as-fabricated products, clearly showing that bead-string like nanostructures with string of tens of nanometers and beads of 2–4 μm in diameter are obtained. Fig. 1f and g depict the EDS spectra collected from the bead (area I) and string (area II) as marked with red squares in Fig. 1e, respectively. Fig. 1f reveals that the bead is mainly composed of Si and O elements while the string between adjacent beads comprised of Si, C and O elements (Fig. 1g), respectively. Based on this result, we could roughly infer that the bead-string like nanostructures are composed of SiC/SiO_2 core-shell nanowires (strings) and SiO_2 microspheres (beads).

Fig. 2 shows the XRD pattern of the as-fabricated products in which four sharp diffraction peaks at $2\theta = 36.0°$, 41.9°, 60.2° and 72.1° can be observed. These peaks well match with the known values for 3C-SiC (JCPDS Card No.29–1129), and can be indexed to the planes of (111), (200), (220), and (311) reflections of cubic 3C-SiC [14], respectively. Additionally, the broad XRD peak at low diffraction angle (10–30°) can be assigned to the amorphous phase of SiO_2 [33]. Raman spectrum (Fig. 3) collected from the strings as highlighted in Fig. 3b shows that three peaks located approximately at 795, 947 and 972 cm^{-1} are observed. The two peaks at 795 and 972 cm^{-1} correspond to the transverse optical (TO) phonon mode and longitudinal optical (LO) phonon mode of 3C-SiC [44], respectively. The shoulder peak centered at 947 cm^{-1} can be assigned to the peak of amorphous SiO_2, which is similar to the value reported by Li Ming [45]. The results of XRD and Raman analysis clearly demonstrated the existence of SiC and SiO_2 phases in the as-fabricated products.

Fig. 4a presents the typical low magnification TEM image of the string of the as-fabricated SiC/SiO_2 bead-string like core-shell nanochains, clearly showing that the diameter of the string is about