Dangling Bonds-Assisted Synthesis of Arborization Silica

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Novel arborization silica is fabricated with dangling bonds (Si-)-assisted growth manner by the hydrothermal method without any metallic catalyst and its surface morphology, microstructure and composition are characterized and analyzed. The results show that the samples display arborization morphology with amorphous structure and the average growth rate and average characteristic length of each branch are different. The branching degree of arborization silica is higher. The concentration of dangling bonds (Si-) may mainly influence silica morphology. The dangling bonds-assisted growth mechanism is proposed.

Key Words: Arborization silica, Branching degree, Growth mechanism.

INTRODUCTION

With the rapid development of preparation technology, testing technology and nanotechnology, research and exploitation on SiO_2 materials with different structures and many potential special functions have endowed their new uses, also indicated their potential application as nano-functional materials. The excellent performances of SiO_2 depend strongly on its morphology structure, therefore people deeply concern about its studies on the structural and performance differences. The key of preparation of SiO_2 products with high technology content and high added value is how to control its morphology structure reasonably. Commercial price of SiO_2 products has great disparity in different forms, ranging from 3,000 yuan per ton to 6,000,000 yuan per ton. In order to excavate the special functions of different structural forms, researchers have exploited the corresponding special technologies, such as special morphology, nano-ization, surface modification and high dispersibility. Integration on preparation, processing applications and composite technology of multiple functions of SiO_2 material is an innovation which researchers seek. For example, SiO_2 as catalyst carrier applies to refining of petroleum, photoluminescence properties of SiO_2 nanowires have potential applications in nano-optoelectronic devices[1] and X-type, Y-type and tree-type nano-silica will serve as functional building blocks of nano-optoelectronic devices[2]. In recent years, plenty of works have been carried out on controlling SiO_2 morphology and formation mechanism, synthesizing of a number of different morphologies and special arrangement

of SiO_2 in accordance with the design requirements. For example, single helix and double helix mesoporous nano-silica fiber[3] synthesized using low molecular weight gel self-assembly, also mesoporous silica helical bundle[4] and coiled mesoporous silica band[5]. Hu[6] have synthesized SiO_x nanostructures with different morphologies (feather, pen-shaped, bamboo-like) in different temperature zone with eroding Ge target by laser and evaporating SiO powder. Pan[7] collected the sandwich-like nano-SiO_2 on alumina substrate using Ga as the catalyst, heating SiO powder. As well SiO_2 nanoflower[8], SiO_2 nano-brush and SiO_2 nanotubes[9], SiO_2 nanowire bundles[10], tree-like and tadpole-like SiO_2 nanofibers[11], lantern-like amorphous SiO_2[12] and ordered macroporous microspheres SiO_2[13], *etc*. Among the different morphologies (sphere, wire, tube, rod, band, branching type, *etc.*) of SiO_2 material, branching materials are promising materials for polymer, carrier, building structure electronic devices[14,15] and photocatalysis due to their unique morphologies with some fantastic performances, such as high dispersion and high adsorption, high specific surface area and transmission channel with mutual throughout.

However, low-melting metal catalysts, providing a solid/liquid interface for silica nucleation and growth, were used in most synthesizing methods of branch-type silica[6-12]. These catalysts not only affect silica shape, structure and performance, but also limit the scope of its application. In this study, arborization silica was synthesized *via* a hydrothermal method without any catalyst, the dangling bonds-assisted growth mechanism is proposed. This study is of practical significance

on controlling the preparation of SiO_2 special morphology and polymerization controlled and expanding the application of SiO_2 material. The arborization silica may be used as catalyst carrier, the building block for organic-inorganic composite functional materials, functional nano-optoelectronic devices and interconnects in future nanoscale integrated optical devices.

EXPERIMENTAL

Silicon monoxide powder (purity: 99.99 %, particle size: *ca.* 88 nm) is used as the starting materials, GCF-1L reaction kettle is major experimental facility. The synthesis of arborization silica is briefly described as follows. First, the cavity of reaction kettle was washed several times to ensure no residue. Second a mixture of 2.5 g silicon monoxide powder and 47.8 mL ultra-pure water were put into the reaction kettle with 1000 mL, then the reaction kettle was sealed and heated to 450-470 °C and 10-13 MPa and kept for 12-14 h. During the reaction, the rotating speed for the stirrer equipped in the reaction kettle was maintained at 200 rpm. After the reaction kettle was naturally cooled down to room temperature, a lot of white powders were harvested onto the top of upper surface of the reaction kettle. Then a JEOL JSM-6700 field emission scanning electron microscopy (FESEM) equipped with energy-dispersive spectroscope (EDS) and a JEOL JEM-3010 high-resolution transmission electron microscope (HRTEM) equipped with selective area electron diffraction (SAED) as well as energy-dispersive spectroscopy (EDS) were used to characterize structure, morphologies and chemical compositions of the products. Rigaku D-max 2500 X-ray diffraction (RXD) was used to investigate crystalline structure of the products.

RESULTS AND DISCUSSION

FESEM images of arborization SiO_2 (Fig. 1), revealing that the products consist of trunks and branches. The length of the trunks is in the range of 1.2-13 μm and their average diameter is *ca.* 2 μm. They are smooth and bend. The branches have a length of 20-11 μm and a diameter of 2-8 μm from the root to tip, becoming smaller and most branches are very straight. There are many branches on the trunk, in particular, as can be seen in Fig. 1(c), a branch forest is observed. The branches spread in all the directions and present the hyperbranched structure. The surface of branches is very smooth without any metal catalyst particles. The branches of the tree-like SiO_2[11] with the catalyst film grew from the end of Si nano-rods, quantity of the branches was fewer and the branching degree is not high.

In order to determine the white product which is SiO_2 rather than other element, the chemical elements are analyzed. EDS spectrum of the trunk in SEM, shown in Fig. 2(a), reveals that the trunks are composed of Si and oxygen except for a small amount of C element from the conductive adhesive. The chemical composition of the branch consists of silicon and oxygen as determined by EDS in TEM [Fig. 2(b)] except for a small amount of copper from the copper micro-grid. Further quantitative calculation shows that the atomic ratios of Si:O in both the trunk and the branch are about 1:2, indicating that the products are silica. Then the morphology and structure of branches
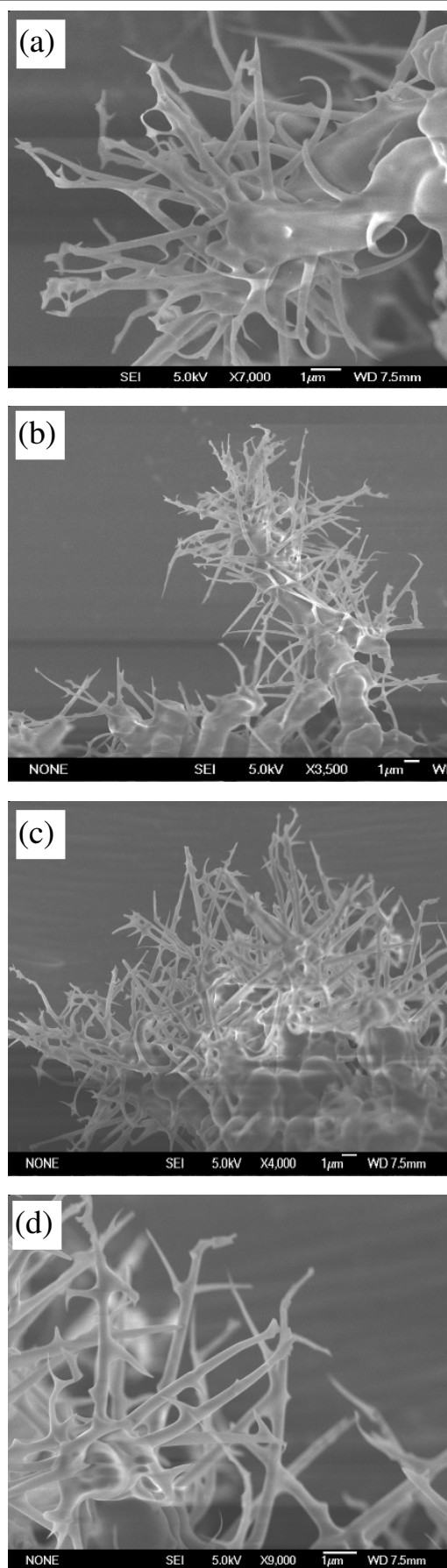

Fig. 1.   SEM images of SiO_2 products synthesized from silicon monoxide powders under supercritical hydrothermal conditions (A)X7000, (B) X3500, (C) X4000 and (D) X9000
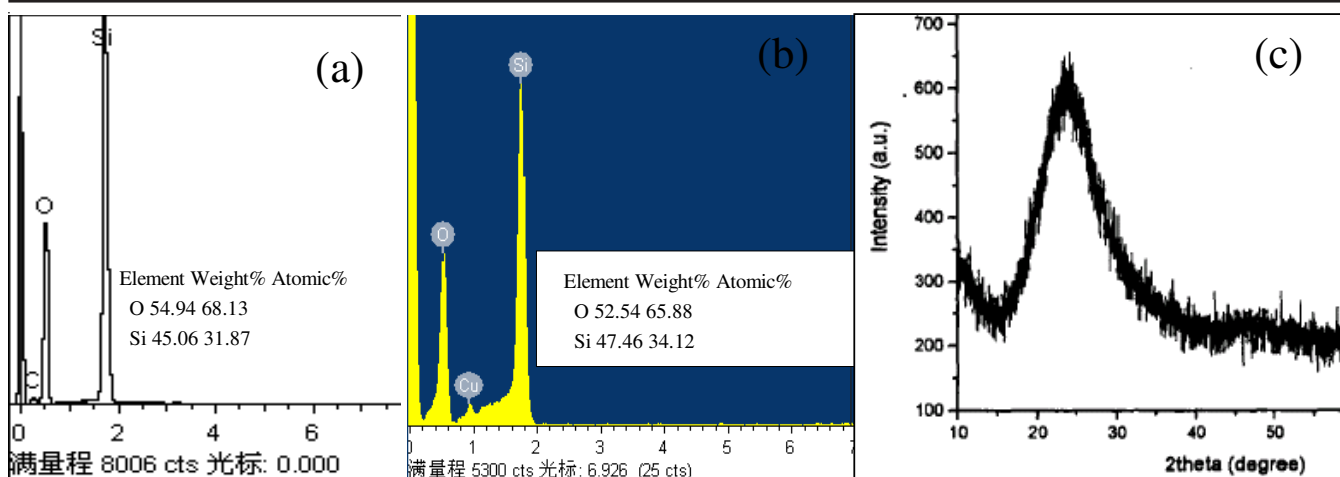
Fig. 2. (a), (b) EDS mage of trunk and branch respectively; (c) XRD pattern of arborization SiO₂
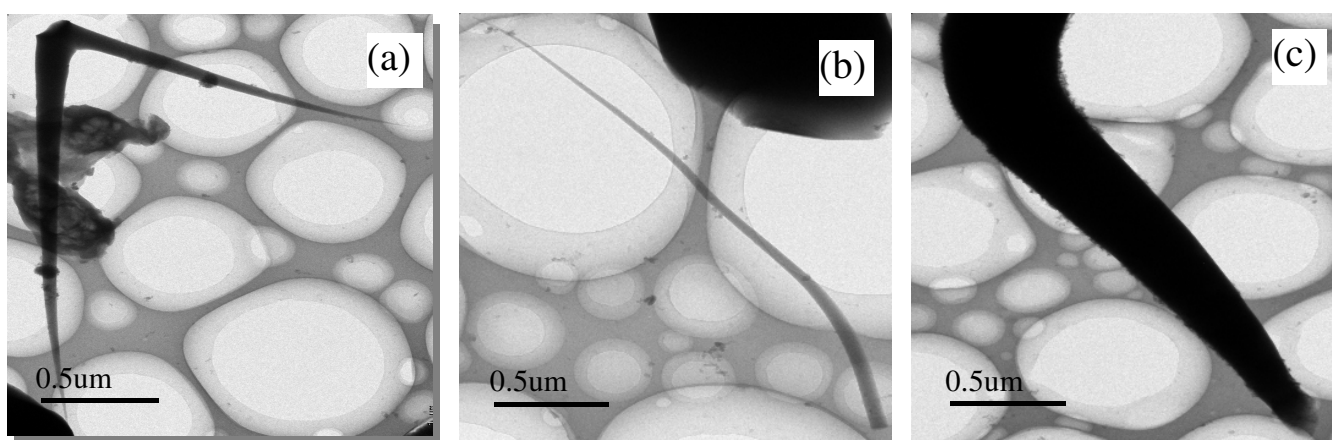

Fig. 3. (a), (b) and (c) HRTEM image of branch

are characterized by HRTEM. The typical HRTEM images of the branches, shown in Fig. 3(a-c), indicate that the diameter of the branches is becoming smaller and smaller from the root to tip, that the angle between the two branches is about 650 and some branches appear bent. Fig. 4(a) and (b) show that the branches are a typical amorphous structure. SAED image shown in Fig. 4(a) reveals that the arborization silica is completely amorphous. XRD pattern of arborization SiO₂ is shown in Fig. 2(c). Only a wide diffraction peak is observed in the range of 15-330, indicating the amorphous characteristics of arborization silica. At the same time, it can be seen that the branches are solid rather than hollow and the tip of branches is smooth and round as shown in Fig. 4(b).

Here, the formation mechanism of SiO₂ is vapour deposition. Under high temperature and high pressure conditions, SiO is evaporated from the silicon monoxide powder and decomposed into gaseous Si and SiO₂: $SiO(g) \rightarrow Si(g) + SiO_2(g)$. When SiO₂ nanoparticles arrive at the top surface of the kettle, they are quenched and deposited on the top surface. This process depends on two conditions: one is driving force of gaseous ions convection. There is strong driving force in an aqueous solution because thermal diffusion rate of water in the supercritical hydrothermal conditions is much higher than in the normal temperature and pressure. At the same time, H₂O vapour is ionized[16] into H⁺ and OH⁻, therefore, five species

(H⁺, OH⁻, SiO, SiO₂ and Si) are contained in the vapour, colliding each other. The gaseous SiO₂ is pushed onto the top surface of the kettle because of the driving force. Another is that the temperature of the top surface of kettle is lower than the bottom of kettle, as the temperature gradient of the kettle existed in the vertical direction. When the gaseous SiO₂ deposit on the top surface of the kettle and immediately quenched into amorphous SiO₂ confirmed by Fig. 4(a) and (b). In addition, according to thermodynamics and growth mechanism of coagulation[17]. When there are large surface area and surface energy in the dispersion nanoparticles, the system will change toward the direction of reducing surface area and lowering surface energy automatically, so as to make SiO₂ nanoparticles cluster and coagulate become final form.

The possible mechanism for the formation of arborization is discussed here. In this study, dangling bonds (Si-)-assisted growth mechanism is suggested. The schematic diagram of dangling bonds-assisted growth of the arborization silica is described (Fig. 5). The growth process consists of a few stages:

Firstly, large amounts of dangling bonds (Si-) are produced in the system with H⁺, OH⁻, SiO, Si and SiO₂. The dangling bonds are obtained through the following three ways: (1) SiO is evaporated and decomposed into gaseous Si and SiO₂ under high temperature and high pressure:
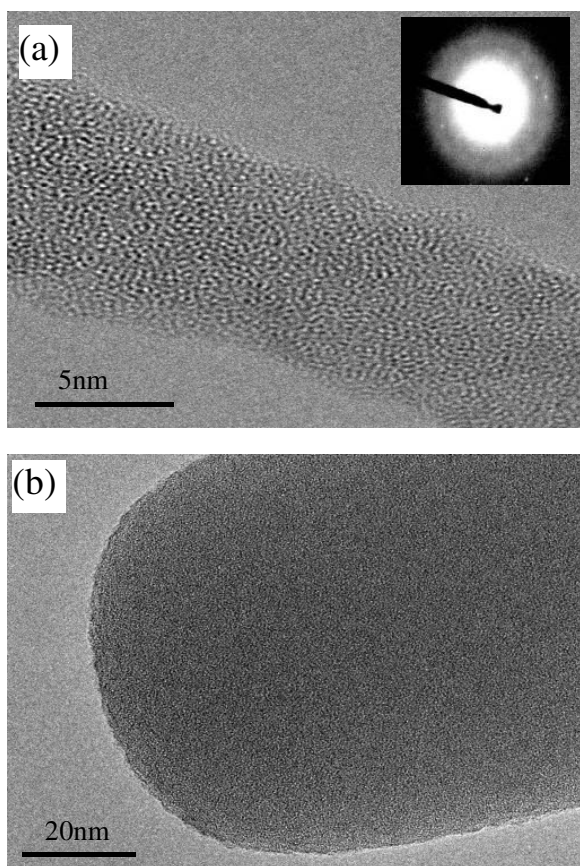
Fig. 4.   (a) HRTEM image of branch and corresponding fourier transform mass spectrum; (b) HRTEM image of peak of branch
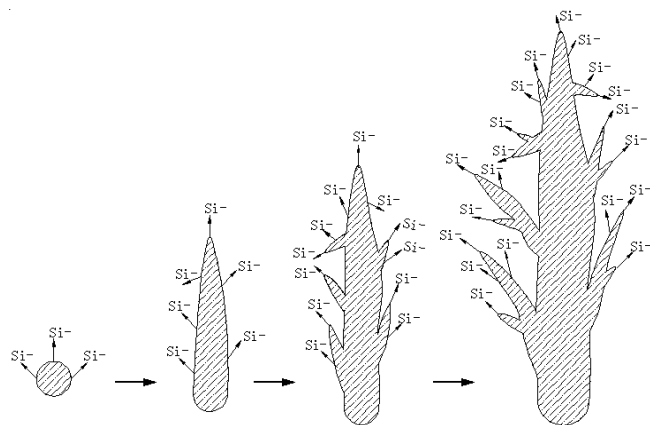

Fig. 5.   Schematic diagram describing dangling bonds-assisted growth of the arborization silica

SiO (g)→Si-(g) + SiO$_2$ (g) (1). (2) Amorphous SiO$_2$ structure model is a continuous random network model[18], Si atoms are in Si-O-Si form, also in Si-OH form, Zhuravlev[19] confirmed the existence of Si-OH on silica surface by IR. Actually, in the SiO$_2$ preparation with hydrothermal method, there are lots of Si-H and Si-OH because H$_2$O vapour is ionized into H$^+$ and OH$^-$ in supercritical hydrothermal conditions. Si-H reacts with neighboring Si-O-Si and Si-OH to bring about many dangling bonds (Si-): Si-H + Si-O-Si → 2Si- + Si-OH (2), Si-H + Si-OH → 2Si- (or Si-Si) + H$_2$O (3). (3) Many dangling bonds (Si-) are also produced through reaction equation: H- + Si-OH → Si- + H$_2$O (4). Overall, the dangling bonds (Si-) to be gained

through above reaction equation (1)-(4) can provide large binding activity for forming of arborization micro/nano-SiO$_2$.

Secondly, the trunks grow during heating. With temperature rising, the increase in the concentration gaseous H$^+$, OH$^-$, SiO, Si and SiO$_2$ results in the significant increase in dangling bonds (Si-) and driving force of gaseous ions convection and accelerating the forming speed of the trunks. In Fig. 5, since there are many dangling bonds (Si-) with higher activity on the particles surface of seed SiO$_2$, new generating SiO$_2$ nanoparticles can combine with the dangling bonds (Si-), spontaneously become the lowest energy state with stability in thermodynamical and definitude in structure and form the new trunk or make the original trunks grow up. With the continuous generation of new SiO$_2$ particles and deposition of SiO$_2$, the morphology of amorphous SiO$_2$ will continuously expand in a place of the dangling bonds (Si-) existing, at the same time, new trunks grow too. With temperature increasing, the corresponding increase in growth rate of particles can help to reduce the anisotropic growth[20]. The average growth rate of these trunks in all directions almost is equal and there is little difference in the radial size of the trunks.

Thirdly, the branches mainly grow during insulation-cooling. As insulation and cooling are being carried out, the concentration of gaseous and the driving force of gaseous ions convection decreased slowly and correspondingly the quantity of dangling bonds (Si-) reduced substantially. SEM image in Fig. 1 shows that the small buds first grow on the trunks and then grow into the branch along a certain direction. Large branches are further growing up while new small buds are growing out. Axial growth rate of branches is much greater than the radial growth rate, and thus branches along the axis grow up fast, because droplets of the growth tip with high activity and adsorption[21] are an ideal adsorption sites of Si-dangling bonds, which are expected to have a high efficiency to trap nanoclusters from the vapour and the trapping of the nanoclusters allows the continuous growth of branches. With the temperature and pressure lowering, the symmetry of branches growing in all directions reduced. This conclusion can be confirmed by SEM and HRTEM mage of branch. Obviously, although there was a main trunk in the non-uniform and asymmetric growth system, growth direction of all branches was uncertain. Thus, morphology of the all branches seems more complex and changeable and presents the hyperbranched structure.

Conclusion

In summary, arborization micro/nano-SiO$_2$ with amorphous structure formed in favour of a large number of the dangling bonds (Si-). In the heating process, when the concentration of the dangling bonds is increasing, the amalgamation of nanoparticles is accelerated so as to make the trunks form. When the temperature is becoming lower, the concentration of the dangling bonds decreases so that the growth junctions among the nanoparticles are limited and the particle coalescences are obstructed. Thus, the branches begin to grow. It is interesting to note that the morphology structure of arborization silica may relate not only to temperature and pressure but also to SiO weight and heating rate. The arborization silica with special features will be expected to applied to catalyst carrier,

organic-inorganic functional materials and functional nano-optical devices.

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