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Iron-Assisted Vapor-Phase Hydrothermal Method: A Low-Temperature Approach To Synthesize Blue Light Emissive SiO_x Nanowires with Single-Crystal Structure of $P2_12_12$

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There is increasing research into the synthesis of nanoscale one-dimensional (1D) materials because of their characteristic physical properties, as well as their potential applications in electromechanical, optoelectronic, electrochemical, and other nanodevices.[1] On the basis of its remarkable optical properties,[2] the 1D silicon oxide nanowire (SiONW) is of great significance in the fields of photoluminescence (PL), localization of light, near-field optical microscopy, low-dimensional waveguide, nano-inter-connection integrated optical devices, etc.[3−5] In the past decade, several methods, including chemical vapor deposition,[3,6] carbon-assisted method,[4,7,8] laser ablation,[5,9] and thermal evaporation,[10] have been developed to prepare amorphous SiONWs. Recently, Rao and co-workers[11] synthesized for the first time α-cristobalite nanowires by a carbon-assisted method at 1300 °C, for a possible application in the area of optical data transmission. However, the complex conditions used in all of these methods,[3−11] such as high temperature (>900 °C), the need to pre-evacuate the chamber, and the necessity of having precise control of carrier gas composition, flow rate, and pressure, have limited the large-scale manufacture and application of such materials. Some groups have tried to develop low-temperature routes, such as the hard template method,[12] to fabricate SiONWs. However, the high cost and complexity associated with the introduction of templates has limited the practical application of this approach.

In this communication, we present a novel iron-assisted vapor-phase hydrothermal method to fabricate SiONWs with a new single-crystalline structure at mild temperature. By treating various Fe pre-embedded silica sources, such as bimodal silica (BMS),[13] fumed silica, or SBA-15,[14] in the vapor of ethylenediamine at 200 °C for 24 h, followed by washing in 1 M HCl to remove Fe species, a high yield of white SiONWs was obtained. Compared with the previous methods, here, many complicated factors in preparation, such as high temperature, pre-evacuation, carrier gases, or introduction of the templates, are successfully avoided, and thereby provide a possible approach for large-scaled preparation of SiONW. Importantly, this method produces a new single-crystalline SiONW with a space group of $P2_12_12$ and an intense blue light emission, which may bring some new opportunities for research and application of such materials.

Figure 1a depicts a typical scanning electron microscope (SEM) image of SiONW product using BMS as the silica source. The diameter and length of the SiONWs were estimated as <150 nm and >40 μm, respectively. No Fe species could be detected in the product by energy-dispersive X-ray spectroscopy (EDS) after HCl washing, and its Si:O atomic ratio is about 1:1.68. Accordantly, the inductively coupled plasma atomic emission spectrometer (ICP-AES) shows that the Si:O atomic ratio is 1:1.66, while the Fe content is <0.5 wt %. The growing process of SiONWs was explored by observing the morphological evolution of the samples

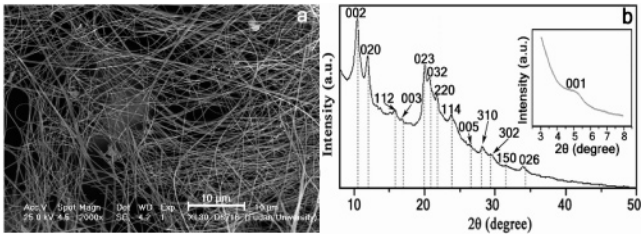

Figure 1. (a) SEM (Philips XL30, scale bar = 10 μm) image, and (b) XRD pattern (Rigaku D/max PC2550, Cu Kα radiation, λ = 1.54056 Å) of SiONWs by using BMS as the silica resource.

prepared from Fe-embedded BMS with alkali-treated time (Supporting Information). After being treated in amine vapor for 3 h, the surface of BMS spheres becomes obviously coarse, and then nanowires gradually grow from BMS spheres by consuming the silica nutrition in BMS. Finally, all the BMS spheres are exhausted, and the pure SiONWs are obtained.

Figure 1b is the X-ray diffraction (XRD) pattern of the obtained SiONW shown in Figure 1a. The broad diffractive peaks could be attributed to the nanosize of the sample. After being refined by the MDI/JADE6 program (Supporting Information) and searched in ICDD PDF database, the SiONWs exhibit a new crystalline structure of the orthorhombic system with $P2_12_12$ space group, and no diffractive peaks due to impurities are detected. The unit cell parameters are $a = 9.685$, $b = 14.870$, and $c = 16.898$ Å. This structure can be validated by transmission electron microscope (TEM) image and its attached selected area electron diffraction (SAED) pattern. The high-resolution TEM (HRTEM) images recorded in low-dose mode (Figure 2a and b) clearly display the single-crystalline structure of the SiONWs, with the lattices extending throughout the whole nanowire. Their SAED patterns (Figure 2c and d) can be well indexed referring to the refinement result of XRD. It is noted that the $h = 2n + 1$ in $h00$ reflections and the $k = 2n + 1$ in $0k0$ reflections are absent, which match well with the system absence principle of the $P2_12_12$ space group. The inverse Fourier transformations (IFFTs) for the squares in Figure 2a and b are shown in Figure 2e and f. The *d*-spacings of the crystalline lattices are 0.49, 0.74 nm and 0.49, 0.84 nm, respectively. Both of them meet at right angles and could be respectively indexed as (200), (020) and (200), (002) planes, based on the data of XRD results. This suggests that the growth direction for SiONWs should be along the [100] zone axis. To further confirm our conclusion, we also simulated XRD peaks based on SAED and HRTEM results. The main simulated peaks are shown in Figure 1b as the dashed lines. It is clear that the simulated diffractive peaks fit very well with those obtained from the XRD experiment.

The single-crystalline SiONWs exhibit a high PL peak centered at 452 nm (Figure 3aA), whereas the PL activity of all raw materials used here is negligible. The bright blue light emitted as observed

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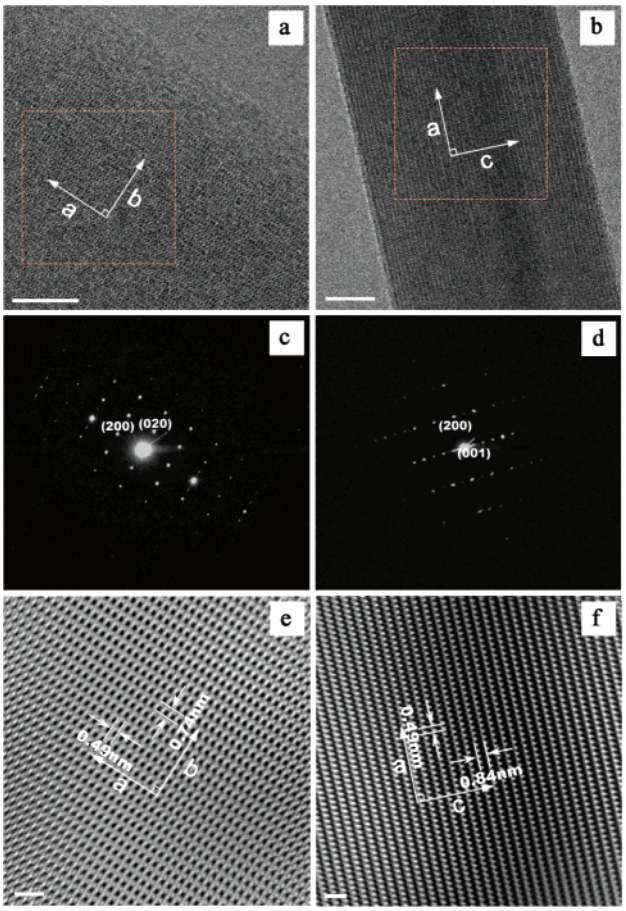

Figure 2. (a and b) HRTEM (JEOL JEM-2011) images of two SiONWs; (c and d) SAED patterns of SiONWs in (a and b); (e and f) IFFTs of areas in the squares in (a and b). The scale bars in HRTEM and IFFT are 10 and 2 nm, respectively.

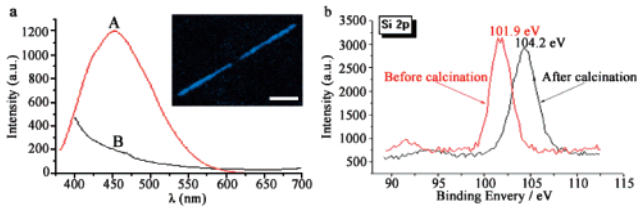

Figure 3. (a) PL spectra (Hitachi F-2500, excitation source: Xe laser, 359 nm) of SiONWs (A), and SiONWs (B) after calcination in air at 800 °C. The inset is the confocal fluorescence microscope (Olympus FV300) image of SiONWs; scale bar = 10 μm; (b) the Si 2p XPS spectra of the product before and after calcination in air at 800 °C.

by confocal fluorescence microscopy (Figure 3a, inset). The uniformity of the PL properties along the SiONW can be confirmed through microphotoluminescence spectra (Supporting Information). However, after calcination in air at 800 °C, their fluorescence activity almost vanished (Figure 3aB). As mentioned above, the as-synthesized SiONWs show clearly the lack of oxygen (Si:O = 1:1.68). After calcination, however, the atomic ratio of Si:O increased to about 1:1.98 (ICP-AES result). These results imply that bright blue light probably emits from the neutral oxygen vacancy in the SiONW as the case of amorphous ones in previous reports.[2,5] This change of neutral oxygen vacancy can also be verified by the result of X-ray photoelectron spectroscopy (XPS), as shown in Figure 3b, in which the binding energy of Si 2p shifts from 101.9 (before calcination) to 104.5 eV (after calcination).

In conclusion, bright blue light emitting single-crystalline SiO_x ($x = 1.68$) nanowires have been synthesized by a novel iron-assisted vapor-phase hydrothermal method at low temperature. The SiONWs obtained possess a new crystalline structure which belongs to an orthorhombic system with space group of $P2_12_12$ and unit cells of $a = 9.685$, $b = 14.870$, and $c = 16.898$ Å. Thanks to the mild reaction conditions, high yield, and environmental benefit (via circularly using the amine solution in the bottom of autoclave), this method may have potential for industrial-scaled application.

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Supporting Information Available: The experimental details, the EDS profiles of the product, the SEM images of the SiONWs growth process, SEM images of the products obtained without Fe, the XRD patterns, SEM and TEM images, and SAED patterns of the products prepared from fumed silica and SBA-15, the microphotoluminescence spectra of a single SiONW, EDS and PL spectrum of product calcinations in N_2, and the detailed cell refinement report of the XRD are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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