Crystalline silica nanowires

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α-Cristobalite nanowires of 50–100 nm diameter with lengths of several microns have been synthesized for the first time by the solid-state reaction of fumed silica and activated charcoal. The nanowires have been characterized by x-ray diffraction, electron microscopy, photoluminescence, and Raman scattering. The nanowires are single crystalline as revealed by high-resolution electron microscope images. The crystalline nanowires are clad by an amorphous silica sheath when the carbon to fumed silica ratio in the starting mixture is small. Use of hydrogen along with Ar helps to eliminate the amorphous sheath.

Several strategies have been reported in recent years for the synthesis of inorganic nanotubes[1,2] and nanowires.[3,4] Among the various one-dimensional inorganic nanostructures, much attention has been devoted to the synthesis of nanotubes and nanowires of silica.[1–4] Using molten Ga as the catalyst, the vapor–liquid–solid process has been used to obtain aligned silica nanowires.[5,6] Use of other catalysts such as Sn also yields densely aligned silica nanowires by a similar process.[7] Other methods for the synthesis include the laser ablation of a mixture of Si, SiO_2, and Fe,[8] thermal oxidation of Si wafers,[9] and the oxidation of Si vapor catalyzed by Au.[10] Thermal treatment of Si powder with graphite is also found to yield silica nanowires.[11] A recent report employs the solid-state transformation of silica films to obtain silica nanowires.[12] The transformation of silica nanowires to nanotubes has also been examined.[13] In all the preparations reported previously, the silica nanowires obtained are amorphous, showing intense blue luminescence. We were interested in exploring the possibility of producing crystalline silica nanowires, which might find useful applications in optical data transmission, in areas related to low thermal expansion, as a refractory and in composites. Besides, it would be interesting to establish the exact conditions under which they form. For this purpose, we have used the carbon-assisted process, which has proved effective in the synthesis of nanowires of several oxide materials.[14–16] In this communication, we report the first successful synthesis of single crystalline α-cristobalite nanowires.

The procedure used for the synthesis of the α–SiO_2 nanowires was as follows. Fumed silica (Sarabhai Chemicals, Baroda, India) was thoroughly mixed and ground with activated charcoal (Sarabhai Chemicals, Baroda, India) heated to 700 °C in flowing H_2/He mixture or activated carbon prepared by the decomposition of polyethylene glycol-600 units in an Ar atmosphere at 700 °C. The mixture was placed in an alumina boat and heated to 1300 °C (heating and cooling rates, 3 °C min^{-1}) for 5 h in flowing Ar (50 sccm, sccm = standard cubic centimeter per minute) or a mixture of Ar (50 sccm) and H_2 (20 sccm). The relative molar ratio of the carbon source with respect to fumed silica was varied between 0.5 and 2. The product obtained in the alumina boat was a white or gray powder, which was characterized first by x-ray diffraction (XRD) at 25 °C with a Rich-Siefert 3000-TT diffractometer employing Cu K_{α} radiation. The morphology was analyzed by scanning electron microscopy (SEM) with a Leica S-440I instrument (U.K.). Transmission electron microscope (TEM) images were recorded with a JEOL JEM 3010 instrument (Japan) operated with an accelerating voltage of 300 kV. Photoluminescence studies were carried out at room temperature (Perkin-Elmer LS50B) at an excitation wavelength of 325 nm. Raman spectra were recorded at room temperature with a Nd-YAG laser (532 nm) and an Ar-ion laser (488 nm and 514.5 nm). Differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer instrument employing a heating rate of 20 K min^{-1}.

In Fig. 1, we show SEM images of the SiO_2 nanowires obtained under different conditions. Shown in Fig. 1(a) are crystalline silica nanowires obtained on heating a mixture of fumed silica and activated charcoal (molar ratio of 1:2) in 50 sccm Ar. The nanowires have a diameter between 50 and 100 nm, with lengths extending up to tens of microns. We notice the presence of a small quantity ($\leqslant$ 5%) of unreacted carbon as identified by energy dispersive x-ray analysis (EDAX). The carbon
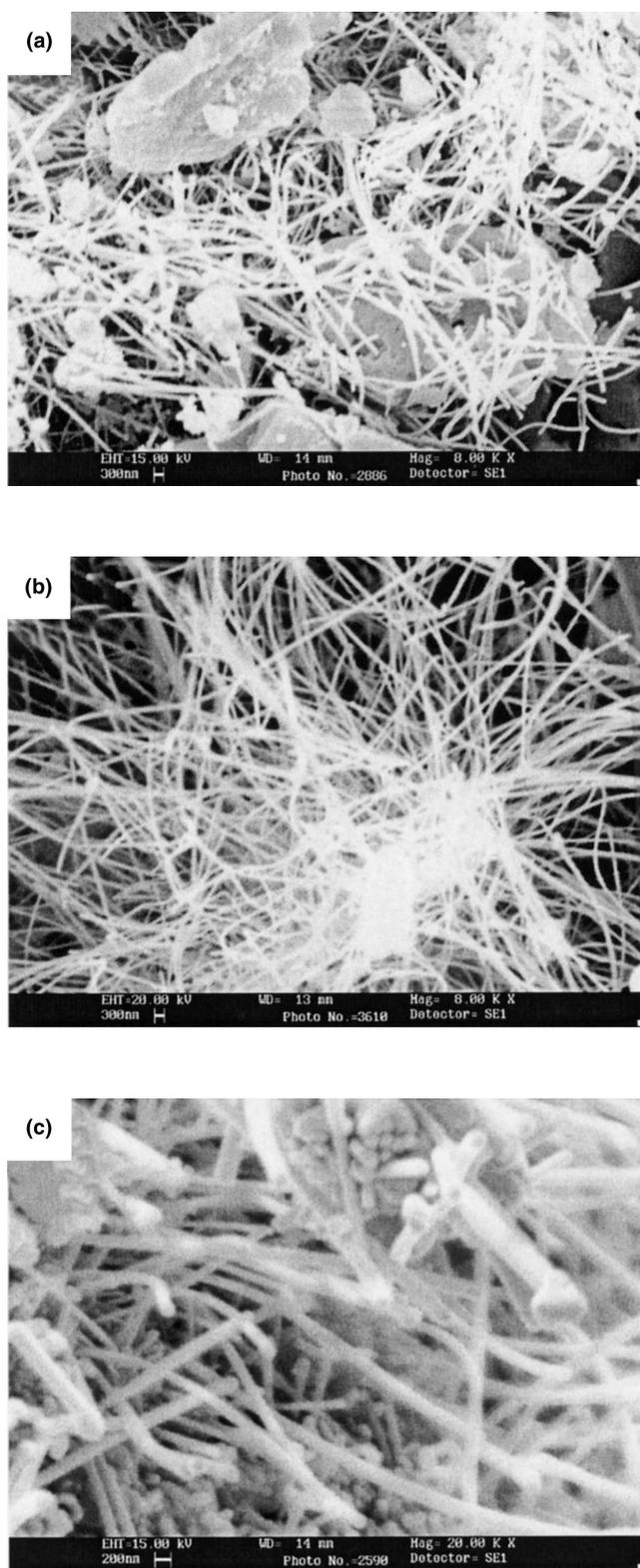
FIG. 1. SEM images of the silica nanowires found in the alumina boat by the reaction of fumed silica with activated charcoal at 1300 °C for 5 h: (a) with silica to carbon molar ratio 1:2 in 50 sccm Ar, (b) with a molar ratio 1:0.5 in 50 sccm Ar, and (c) with a molar ratio 1:2 in 50 sccm Ar and 20 sccm H$_2$.

content is, however, reduced or eliminated by starting with a low carbon:silica ratio. The XRD pattern of the nanowires shown in Fig. 2(a) corresponds to that of α-cristobalite with the tetragonal structure (lattice parameters: $a = 4.97$ Å, $c = 6.92$ Å, JCPDS (NBS, USA) Card No. 39-1425). We observe no peaks due to silicon and other impurities. A low-magnification TEM image of the sample is shown in Fig. 3(a). Selected area electron diffraction (SAED) patterns of several nanowires were recorded at different points along the length of the wires. The inset in the Fig. 3(a) shows a representative SAED pattern with the Bragg spots corresponding to (101), revealing the single crystalline nature of the nanowires.

By carrying out the reaction of fumed silica with reduced amounts of carbon (molar ratio of 1:0.5) in 50 sccm Ar, we obtained a high yield of nanowires with no or negligible carbon content. We show a typical SEM micrograph of these nanowires in Fig. 1(b). The
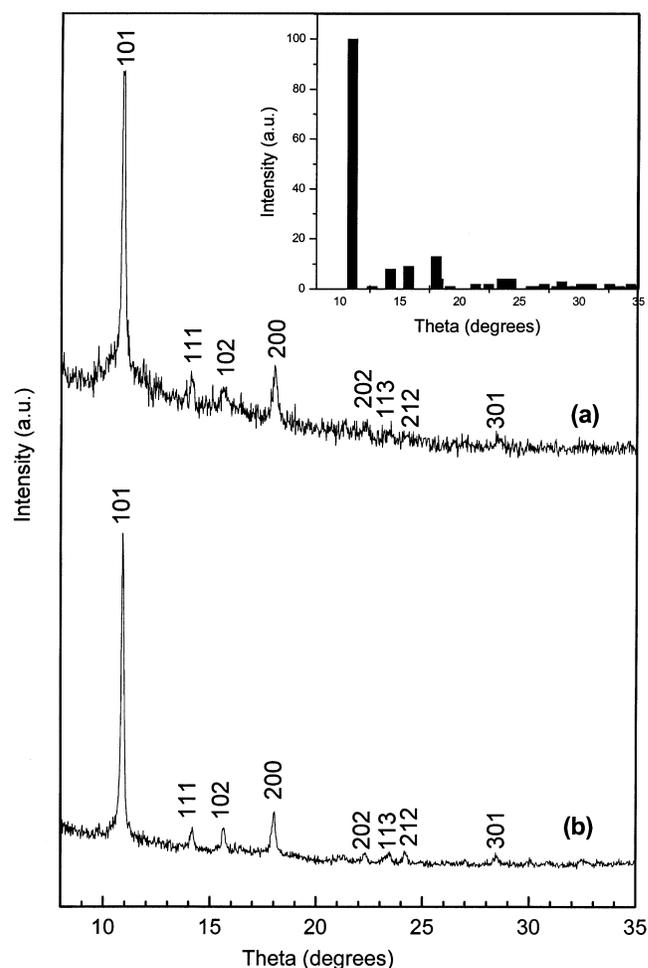

FIG. 2. XRD patterns of the silica nanowires obtained by (a) the reaction of fumed silica and activated charcoal (molar ratio 1:2) at 1300 °C for 5 h in 50 sccm Ar and (b) the reaction of fumed silica and activated charcoal (molar ratio 1:1) at 1300 °C for 5 h in 50 sccm Ar + 20 sccm H$_2$. Inset shows the standard JCPDS pattern (Card No. 39-1425).
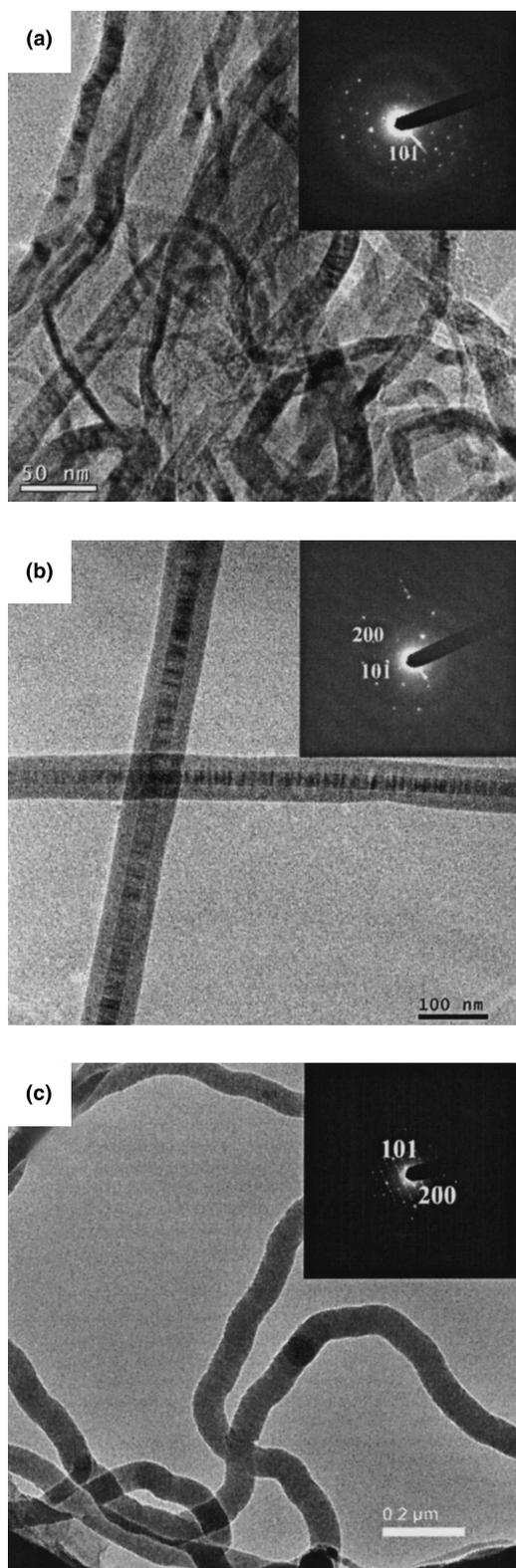
FIG. 3. Low-magnification TEM images of silica nanowires obtained by the reaction of (a) fumed silica with activated charcoal (molar ratio 1:2) in 50 sccm Ar, (b) fumed silica with activated charcoal (molar ratio 1:0.5) in 50 sccm Ar, and (c) fumed silica with activated carbon (molar ratio 1:1) in 50 sccm Ar and 20 sccm H_2 at 1300 °C for 5 h. The insets show the corresponding SAED patterns.

nanowires have a uniform diameter of approximately 70 nm with lengths of tens of microns. The nanowires contain a crystalline core (~30 nm) sheathed by an amorphous layer as can be seen from the TEM image in Fig. 3(b). Reducing the ratio of carbon to fumed silica appears to increase the amorphous coating on the crystalline core, while eliminating or minimizing the carbon content. The amorphous sheath is SiO_2 and not carbon. There is, however, some competition between the magnitude of the amorphous sheath and carbon content in the preparation. Based on independent experiments with nanowires and nanotubes, we have found that any amorphous carbon in the sample is eliminated entirely on heating in hydrogen around 1000 °C. We therefore conclude that no amorphous carbon is present in the silica nanowires subjected to hydrogen treatment at 1000 °C. The sheath is not due to SiC which requires a high $C:SiO_2$ ratio for formation. The SAED pattern, shown as an inset in Fig. 3(b), reveals the nanowires to be single-crystalline α-cristobalite. The Bragg spots in this case arise due to (101) and (200) reflections of the tetragonal structure of α-cristobalite. With a 1:1 molar ratio of fumed silica and activated charcoal, however, we obtained a good crystalline α-cristobalite nanowires of diameters in the 70–100 nm range [Fig. 3(c)]. The diffraction pattern in the inset of Fig. 3(c) reveals the crystalline nature of the nanowires.

The high-resolution TEM image of a single silica nanowire presented in Fig. 4 shows (102) planes with the expected spacing of 0.28 nm between the planes. The normal to the (102) planes makes an angle of approximately 12° with the growth direction of the nanowire.
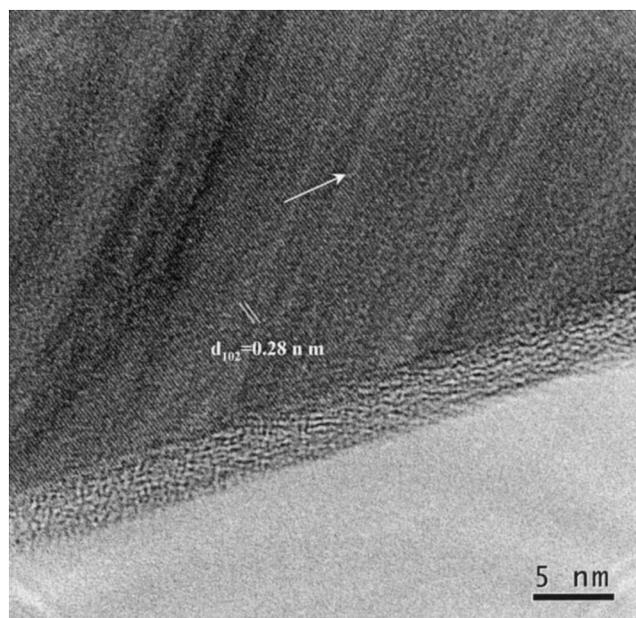

FIG. 4. High-resolution electron microscopy image of a crystalline silica nanowire prepared by the reaction of fumed silica with activated charcoal (molar ratio 1:0.5) at 1300 °C for 5 h in 50 sccm Ar. The arrow denotes the direction of growth of the nanowire.

A good yield of α-cristobalite nanowires was also obtained when 20 sccm of H₂ gas was passed along with 50 sccm Ar while heating a 1:2 mixture of fumed silica to activated charcoal as evident from the SEM image shown in Fig. 1(c). The use of H₂ helps to remove the unreacted carbon, as found by us in repeated experiments. We find a similar situation in the case of carbon nanotubes where again amorphous carbon is best removed by hydrogen treatment at 1000 °C. This can be seen by a comparison of Figs. 1(a) and 1(c). We show a representative XRD pattern of the sample obtained by the reaction of a mixture of fumed silica and activated charcoal (molar ratio of 1:1) heated in a mixture of Ar (50 sccm) and H₂ (20 sccm) in Fig. 2(b). The line-widths of the reflections in this XRD pattern are somewhat narrower suggesting greater crystallinity.

The photoluminescence spectrum of the α-cristobalite nanowires was recorded along with that of fumed silica. As shown in Fig. 5(a), fumed silica exhibits a shoulder in
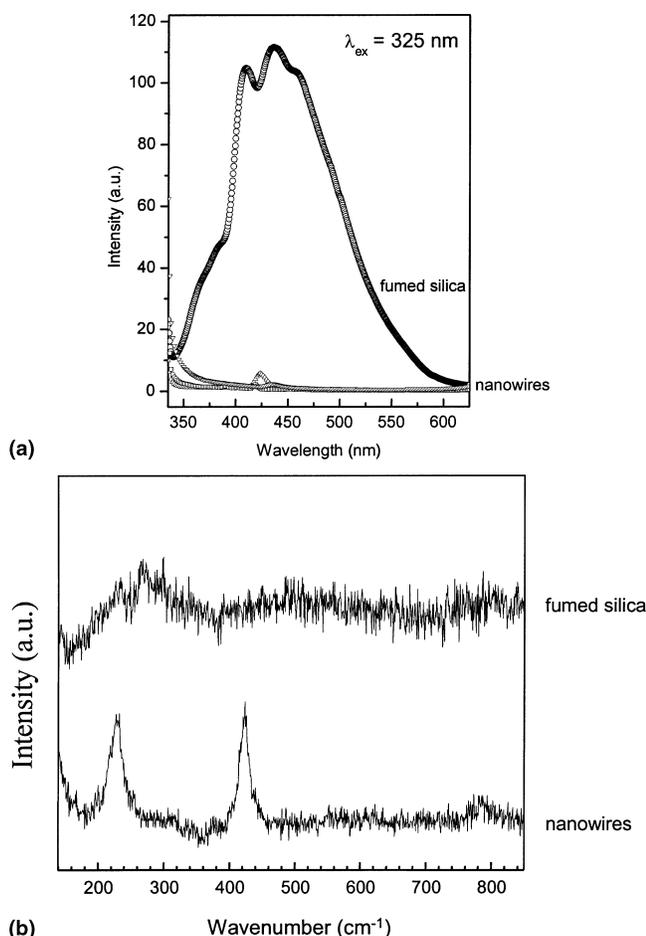

(a)

(b)

FIG. 5. (a) Photoluminescence spectra of fumed silica and crystalline nanowires obtained by the different routes using 325 nm as the excitation wavelength and (b) Raman spectra of fumed silica and the nanowires prepared by the reaction of fumed silica with activated carbon (molar ratio 1:1) at 1300 °C for 5 h in a mixture of Ar (50 sccm) and H₂ (20 sccm).

the UV region at 375 nm and a broad band in the blue region centered at 440 nm. These features are nearly absent in the spectrum of the nanowires. The presence of intense blue emission in fumed silica arises from the high density of defects and oxygen related vacancies. We have recorded the Raman spectrum of the sample and observed two bands at 200 cm^{-1} (A_1) and 424 cm^{-1} (A_1 or B_2) in addition to a weak band around 790 cm^{-1} (E) [Fig. 5(b)]. There is a lot of controversy regarding the band assignment in the literature of the α- and β- phases of cristobalite.[17,18] The spectrum resembles that of the α-phase reported in the literature. DSC of the crystalline nanowires revealed a reversible transformation from the α-form to the β-form at 240 °C. This α–β transition is known to occur in cristobalite around this temperature.[19] Under the preparation conditions used by us, the nanowires are first formed in the β-form, and are then converted to the α-form on cooling to room temperature.

We could obtain α-cristobalite nanowires only with fumed silica but not with other sources of silica. This may be because fumed silica is amorphous, containing very tiny particles with a high surface area. Carbon plays a crucial role in the reaction in reducing silica to its reactive suboxide SiO_x. The presence of a high proportion of carbon relative to silica and use of hydrogen give rise to good crystalline nanowires. A lower proportion of carbon or the absence of hydrogen results in crystalline SiO_2 nanowires coated with an amorphous silica layer. The exothermic nature of the reduction of silica by carbon may give rise to considerable local heating, which may help the crystallization of fumed silica into the cristobalite form. The reaction involved in the formation of crystalline silica can be written as follows

$$SiO_2 + C \rightarrow SiO + CO \quad , \qquad (1)$$
$$2SiO + O_2 \rightarrow 2SiO_2 \quad . \qquad (2)$$

We do not feel that disproportionation of SiO occurs since elemental Si is not formed in the product. The SiO vapors deposited on the walls of the alumina boat react with the oxygen contained in the reaction system to form crystalline nanowires. Such oxidation reactions are well documented.[16,20,21] The growth of the nanowires is likely to occur by the vapor–solid mechanism[3,4] since no metal catalyst has been used in the synthesis. Accordingly, microscopic investigations do not reveal the presence of catalyst/liquid droplets at the ends of the nanowires.

In conclusion, we have, for the first time, synthesized good single-crystalline nanowires of silica in the α-cristobalite form by a simple carbothermal procedure. The nanowires might find useful applications.

ACKNOWLEDGMENT

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