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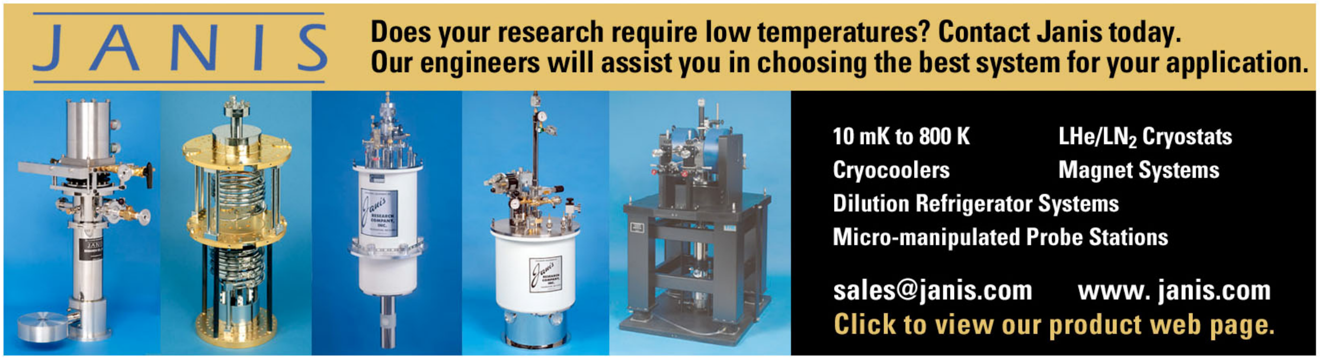

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Reversible blue light emission from self-assembled silica nanocords

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Self-assembled silica nanocords were synthesized through a vapor-solid process without the assistance of catalyst. The rope-like nanostructures were formed by splitting and connecting of lots of amorphous silica nanowires. Appropriate water vapor partial pressure and reaction temperature play critical roles in determining the morphologies. Blue light emission of these nanocords can dramatically be strengthened and weakened in the process of alternative dry and humid treatments. We propose that hydroxyl groups and adsorbed–desorbed ambient water on the nanocords surface are responsible for the reversible blue light emission behavior through analyzing photoluminescence and infrared spectra. Silica nanocords with such blue light emission may be used as effective optoelectronic devices and optical signal humid sensors. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1996846]

One-dimensional (1D) nanostructures have become the subject of extensive research due to their distinctive performances compared to those of the bulk materials not only for scientific importance but also for various potential applications in optics, electronics, and magnetics.[1,2] As an example, 1D silica nanostructures have attracted much attention and achieved abundant morphologies (nanowires,[3,4] highly aligned nanowire assemblies,[5–7] nanoflowers,[8] nanotubes,[9] and nanosprings,[10] etc.) mainly through metal-catalyst vapor-liquid-solid (VLS) mechanism or sol-gel approach. Their various promising properties, especially optics, from intense blue light emission[3] to optical waveguide,[11] were also investigated. Intrinsic structural defects and extrinsic environment influence, such surface adsorbed species as hydroxyl (OH) groups and water molecules, are generally put forward to explain some luminescence properties of silica.[3,4,9,12–15] However, little has been reported on the photoluminescence (PL) characteristics coming from environment variation, which can remarkably affect and further modulate optical properties. Therefore, study of environment effects on the luminescence of silica nanostructures will not only offer overall understanding of their optical properties, but also find various applications related to environment sensitivity.

In this letter, we report the synthesis of self-assembled rope-like silica nanostructures, so-called nanocords, in large quantities by a facile high temperature humid vapor method without any catalyst. More importantly, we find that their blue light emission around 2.7 eV is highly sensitive to humid ambience and reversible in humid and dry environments. PL and fourier-transform infrared (FTIR) spectra at different treatment stages together corroborated that the blue light emission was related to the OH groups-coated silica nanocords and extrinsic adsorbed water molecules.

1D silica nanocords were synthesized via a vapor-solid process in a horizontal tube furnace. Silicon monoxide powders (SiO, purity: 99.99%) loaded in a ceramic boat were placed in the hot zone of ceramic tube, and silicon slices (100) were placed downstream as the deposition site. The reaction temperature and time duration were 1200 °C and 1 h, respectively. During the reaction, high purity argon (20 sccm) was adopted as carrier gas. Water was introduced into the reaction system by placing a ceramic boat filled with distilled water (about 10 ml) in the upstream inlet (about 80 °C) of the tube furnace. After reaction, water was taken away when the temperature at heating center was 600 °C. The wool-like products deposited on the Si slices were then characterized by field emission scanning electron microscopy (FESEM SIRION, FEI), energy dispersive x-ray spectroscopy (EDX INCA, OXFORD), transmission electron microscopy (TEM JEOL 2010), PL spectroscopy (Edinburgh luminescence spectrometer FLS 920, excitation source: Xe lamp), and FTIR spectroscopy (Nicolet NEXUS). Room temperature PL and FTIR spectra were all recorded under the same experimental conditions and similar ambient humidity to prevent the disturbance of environmental water.

Figures 1(a) and 1(b) are typical SEM images of the as-synthesized silica nanocords at low and high magnification respectively, showing high yields and the morphology uniformity. The lengths and diameters of the nanocords are typically hundreds of micrometers and several micrometers, respectively. Every nanocord was self-bunched by lots of silica nanowires. An enlarged image of a single nanocord [Fig. 1(c)] reveals that almost all nanowires split into branches, and the branches further split into subbranches. A similar phenomenon was also observed on silica nanowires obtained by Ga (Refs. 5–7) and Sn (Ref. 16) catalysts. However, the nanocords reported here have been prepared without any catalyst (suggested by the bald nanocord tip), shown in the inset of Fig. 1(c). Furthermore, the nanowires, including branched nanowires, in each nanocord are interconnected. This phenomenon, implying their particular surface state, should be a key behavior in the formation of self-assembled nanocords. The EDX spectrum [Fig. 1(d)] taken from the nanocords shows that O and Si were in atomic ratio of about 2:1. The splitting and connection of nanowires (or branched nanowires) were further verified in TEM images [Figs. 2(a) and 2(b)]. In addition, their smooth surface and uniform diameters were also observed. The selected area electron diffraction pattern [inset Fig. 2(b)] suggests their amorphous nature.

Previously, SiO was extensively adopted to prepare various silicon-based nanostructures through high temperature

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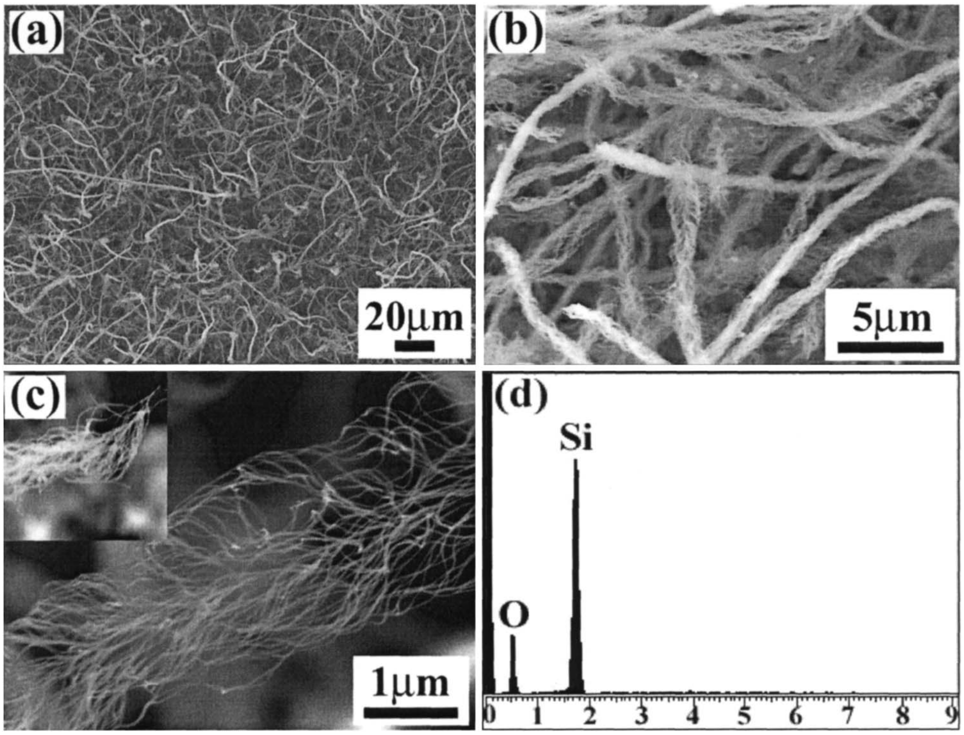

FIG. 1. (a); (b) FESEM micrographs of the silica nanocords in low and high magnification, respectively; (c) FESEM image of a single nanocord, and inset is a typical tip of a nanocord; (d) EDX spectrum taken from the nanocords.

vapor routes,[17–19] and such nanostructures are affected greatly by SiO_x clusters, which are the high temperature decomposition product of SiO. Theoretical calculations reveal that silicon suboxide clusters prefer to form Si–Si bonds, while oxygen-rich SiO_x clusters favor the formation of Si–O bonds.[17] Therefore, we propose herein that appropriate water vapor partial pressure will promote the formation of oxygen-rich SiO_x clusters, which combine with other controlled external conditions, such as proper reaction temperatures, and determine the nucleation and growth of the self-assembled silica nanocords. As characterized and analyzed above, the splitting and connection are primary phenomena of the silica nanocords. During the continuous growth, the new formed SiO_x clusters will be adsorbed on the side surface of amorphous nanowires, nucleate, and steer the growth of new branches. Such characteristic shows splitting morphologies. The connecting behavior may be originated from abundant surface dangling bonds of amorphous silica and high reaction temperatures.

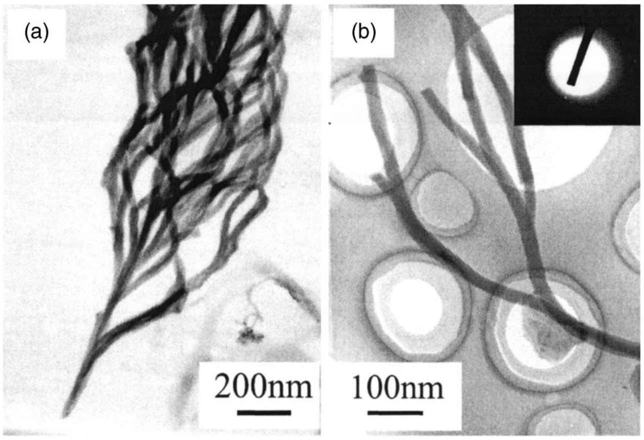

FIG. 2. (a), (b) TEM images of silica nanocords. The splitting and connection behaviors can be seen. Inset of (b) is the corresponding SAED pattern.

Another striking characteristic of the silica nanocords is that their blue light emission is highly sensitive to humid environment and even reversible upon post-treatments. Figure 3(a) is the PL spectra corresponding to three successive stages. All the curves were recorded with the excitation wavelength of 250 nm. All the PL bands have symmetrical distribution. In each case, only one peak with no shoulder can be observed. It is obvious that the intensity of PL band becomes much weaker after the freshly prepared sample being stored in humidistat with the relative humidity of 70% for 3 h. By simply drying the product in air at 200 °C for 3 h again, the primitive PL band can rearouse and the peak position almost does not change. This process has been repeated several times, and good reversibility of the blue light emission has been obtained, as presented in Fig. 3(b). Water molecules and surface hydroxyls are found to be responsible for the PL characteristic owing to the specific presence of water in both processes of preparation and post-treatment. During the preparation, H_2O may not only modulate partial pressures of the heating system but also react with the silica nanowires and be adsorbed on their surface to form $\equiv Si-H$ or/and $\equiv Si-OH$.[13] The silica nanocords coated with these groups should be responsible for the blue light emission of 460 nm.[14] It is known that ambient water molecules, even at room temperature, can be adsorbed on the silica nanocords surface, thereby, may form charge trapping centers and decrease the overlapping of electron and hole wave functions. Consequently, the blue light emission becomes weak owing to the change of recombination probability under optical excitation. However, the heat treatment will desorb surface water molecules, leaving only OH groups on the silica surface; therefore, the blue light was strengthened again. FTIR spectra were further used to explore the OH groups and adsorbed water on the nanocords surface, as discussed below.

Curves a, b, and c in Fig. 4 were recorded under the same consecutive treatment sequences as those of the PL curves. Three FTIR spectra all exhibit strong absorption

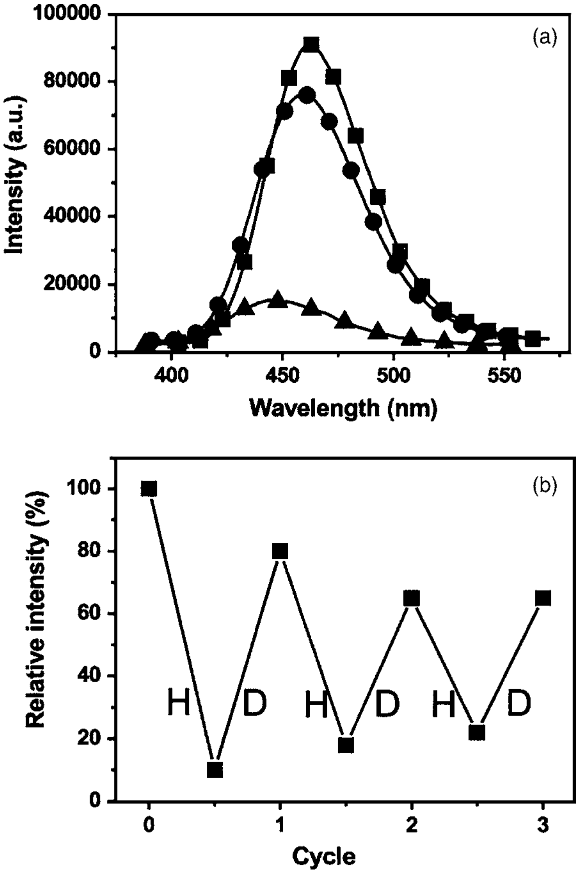

FIG. 3. (a) Room temperature PL spectra of the silica nanocords. (-■-) freshly prepared sample recorded immediately. (-▲-) PL recorded after the sample being stored in humidistat for 3 h. (-●-) PL recorded after the sample being dried for 3 *h* again; (b) the reversible blue light intensity under the alternation of humid (**H**) and dry (**D**) treatments.

bands associated with the characteristic stretching, bending, and wagging vibrations of silica groups at 1130, 802, and 466 cm^{-1}, respectively.[20] The narrow band at 3747 cm^{-1} is attributed to the vibration of surface free OH groups,[20] while the broad band around 3500 cm^{-1} is several types of vibration modes corresponding to adsorbed water molecules on the surface OH groups.[13] The band at 1636 cm^{-1} is due to the bending vibration of the water molecule.[20] The peak position and intensity at 3747 cm^{-1} are almost fixed during the consecutive post-treatments. As to the broad band, only an inconspicuous signal is shown in the freshly prepared samples. However, the intensity changes dramatically, which even disturbs the free hydroxyl vibration peak after the humid treatment. Expectably, the broad band after dry treatment at 200 °C goes back to similar state to that of the freshly prepared samples. This observation verifies the variation of the amount of water molecules and OH groups on silica nanocords surface during post-treatments. The change on FTIR spectra coupled with PL spectra convinced that the reversible blue light emission is indeed influenced by the adsorption–desorption of water molecules.

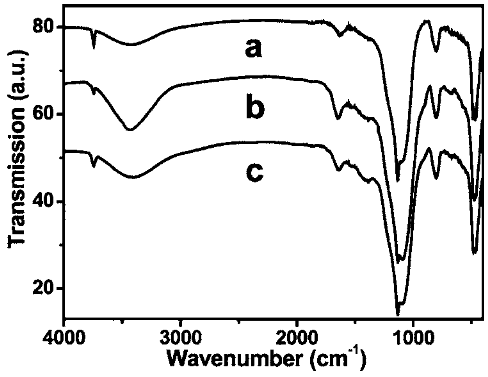

FIG. 4. FTIR transmission spectra of the silica nanocords: (a) Freshly prepared sample recorded immediately; (b) recorded after the sample being stored in humidistat for 3 h; (c) recorded after the sample being dried for 3 h.

In conclusion, self-assembled silica nanocords with reversible blue light emission were synthesized by using a simple chemical vapor process. The splitting and connection behaviors lead to such rope-like nanostructures. PL and FTIR spectra cooperatively elucidate that the OH groups and surface adsorbed water molecules were responsible for the reversible blue light emission. We believe that the silica nanocords may not only facilitate to understand the complicated growth and luminescence mechanism of silica nanostructures, but also find various applications in nanodevices, such as optical switching and sensitive humid sensors based on optical signal.

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