Solvothermal Preparation of Silicon Nanocrystals

Jun Qiu, Wanqing Shen, Ruijie Yu, and Baodian Yao*
Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

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Silicon nanocrystals have been produced successfully by using silicon monoxide as the starting material via a simple solvothermal preparation method. The temperature needed in the solvothermal preparation is found to be as low as 220 °C when ethylenediamine is used as the solvent. The as-prepared silicon samples are of single-crystal nature with diameters around 5 nanometers and dispersed in an amorphous silica. The silicon nanocrystals became a little larger in size after removing the amorphous silica, according to the results of transmission electron microscope (TEM) characterization.

The first observation of room-temperature luminescence more than a decade ago in silicon-implanted SiO_2[1] or in porous silicon[2] has triggered a strong interest in the fabrication of silicon nanocrystals (Si-NCs) and their properties. Some of this interest arises from scientific curiosity concerning size-dependent optical absorption and photoluminescent response and from the potential applications offered by the seemingly forbidden band gap transition that leads to photoluminescence not manifested in bulk Si. To date, controlled preparation of Si-NCs is still the focus of intense research, and many advances have been achieved in this regard. For Si-NCs confined in matrix, the known methodologies include the formation of Si-NCs by ion implantation,[1,3] by thermal crystallization of amorphous Si/SiO_2 superlattice,[4] and by phase separation of thermal annealed SiO/SiO_2 superlattice.[5] For freestanding Si-NCs, the methods include solution-based silicon precursor reduction,[6] silicon precursor thermolysis, and pyrolysis[7] by using usually hazardous, expensive silicon precursors. It might be imaged that it is essential to tightly control Si-NCs over the size, shape, crystallographic orientation, and surface chemistry. Thus, it is still a challenging work to develop new process and technology, especially by using cheap and non-hazardous silicon precursor, to effectively address all of these issues.

In this contribution, we report one simple solvothermal method for the preparation of silicon nanocrystals with several nanometers in size by using readily available, nonhazardous silicon monoxide (SiO) as precursors. Samples are characterized by X-ray diffraction (XRD) and TEM.

The starting chemicals, 99.9% SiO powders and A. R. reagent ethylenediamine, purchased from Beijing Chemical Factory were used without further purification. In short, 0.2 g of SiO powders and 15 mL of pure ethylenediamine mixture was put into a 20-mL Teflon-lined stainless steel autoclave, which was then thermally treated in a preheated oven at 220 °C for 24 h. The as-prepared samples were filtered, washed with deioned water and dried at 90 °C. Part of the products was treated with concentrated HF to remove SiO_2 and unreacted SiO for transmission electron microscope characterization.

The powder XRD data were recorded on a German Bruker D4 X-ray diffractometer with Ni-filtered Cu Kα X-ray source at 40 kV and 40 mA. TEM images were obtained on a JEM-2010 transmission electron microscope in combination with an energy dispersive X-ray spectroscope (EDX) operating at an acceleration voltage of 200 kV. Sample grids were prepared by sonicating the powdered samples in absolute ethanol for several minutes and evaporating one drop of the suspension on carbon film supported on copper grids.

Figure 1 showed the XRD patterns of SiO source material, and two solvothermal products obtained at 200 and 220 °C, respectively. The starting material of SiO powders are amorphous and no crystal Si could be detected (Figure 1a). For samples solvothermal treated at temperature lower than 200 °C, the XRD result (Figure 1b) showed no Si crystal, too. When the solvothermal temperature increased to 220 °C, diamond-cubic silicon (Joint committee on Powder Diffraction Standard, JCPDS card: 27-1402, $a = 5.43088$ Å) XRD peaks can be clearly seen (Figure 1c), which indicated that the disproportionation reaction of SiO had been initiated:

$$2SiO \rightarrow Si + SiO_2 \qquad (1)$$

Therefore, this solvothermal process endows reaction 1 at very low initiating temperature which is usually higher than 800 °C in the case of vapor decomposition processes.[8] The broad XRD peaks in Figure 1c also indicated the crystallite size of Si products in nanoscale, which was around 5 nm calculated from line-broading of (111) peak by the Scherrer formula.

Deionized water is also adopted as the solvent to produce Si-NCs, however, no Si crystal was detected in samples obtained by a similar procedure at temperatures ranging from 150 to 250 °C. In cases of hydrothermal temperature higher than 220 °C, gas release can be observed from the reacted autoclave after cooling, which implied that certain gaseous products were formed in the autoclave. The following two reactions are

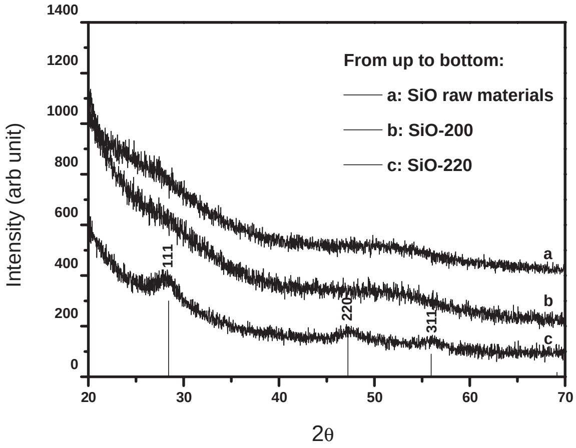

Figure 1. XRD patterns of SiO raw materials untreated (a), solvothermal treated at 200 (b) and at 220 °C (c).

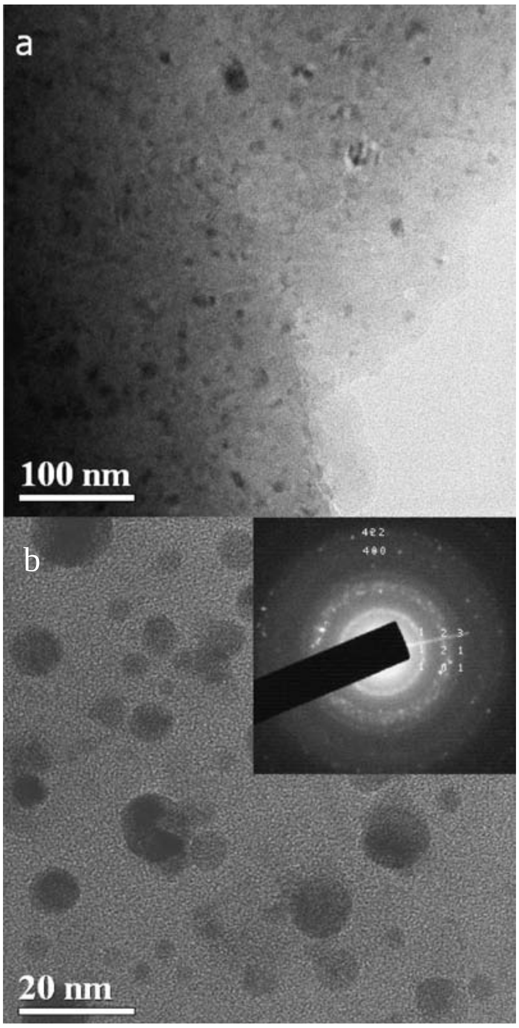

Figure 2. TEM images of as-prepared (a) and HF treated (b) Si-NCs. The inset is the selected area electron diffraction pattern of Si-NCs in (b).

possible and tentatively suggested: one is that the starting material SiO reacts directly with water (eq 2), the other is that Si nanoproducts from reaction 1 will be further consumed by their reaction with water (eq 3):

$$\mathrm{SiO} + 2\mathrm{H_2O} \rightarrow \mathrm{SiO_2} + \mathrm{H_2} \tag{2}$$

$$\mathrm{Si} + 2\mathrm{H_2O} \rightarrow \mathrm{SiO_2} + 2\mathrm{H_2} \tag{3}$$

Though further investigations are needed to confirm the actual reactions, it is reasonable to conclude that the gases involved hydrothermal process is disadvantageous to Si mass production even when Si products can be obtained.[9,10] In this regard, the present solvothermal preparation of Si-NCs using ethylenediamine as solvents is helpful to mass production of Si-NCs because only reaction 1 could occur in the reaction system.

In another attempt to obtain Si products by using phenol as an acidic organic solvent, Si crystal was also not obtained in samples prepared at temperatures ranging from 150 to 250 °C. Therefore, it seems that the basic organic reagent ethylenediamine is likely helpful to catalyze the initiation of reaction 1 at considerable low temperatures.

Figure 2 shows the TEM images of as-prepared and HF-treated Si-NCs. It can be clearly seen that the as-prepared Si-NCs were dispersed in an amorphous matrix (Figure 2a) and seemingly became more regular in shape after HF treatment (Figure 2b). The diameters of Si-NCs were all below 20 nm in sizes and most of them around 8 nm (Figure 2b), which was larger than that calculated from XRD results based on the Scherrer formula. The elemental analysis showed only Si existence in HF-treated samples according to the EDX spectrum (not shown here). The selected area electron diffraction (SAED) pattern (inset of Figure 2b) can be well indexed with diamond-cubic silicon, which further confirmed the crystalline nature of as-prepared Si products.

In summary, we demonstrated for the first time the low-temperature solvothermal formation of Si-NCs using readily available, nonhazardous SiO as Si raw material. Compared to hydrothermal process, silicon nanoproducts could be expected to be mass-produced by solvothermal process. Further work is ongoing to explore the optical properties of as-prepared Si-NCs, as well as the possiblity of solvothermal preparation of one-dimensional silicon nanomaterials, such as nanowires and nanotubes.

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