NANO LETTERS

2003
Vol. 3, No. 5
655−659

Hydrothermal Synthesis of Quartz Nanocrystals

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Received October 18, 2002; Revised Manuscript Received December 6, 2002

ABSTRACT

This paper describes for the first time a chemical method for the preparation for nanocrystalline quartz. Submicron quartz powders are initially produced in hydrothermal reactions where soluble silica precursors precipitate as pure crystalline silica. To yield nanocrystalline material these particles can be purified and size selected by dialysis, filtration, and centrifugation. Transmission electron microscopy and X-ray diffraction illustrate that the product is pure phase α-quartz, consisting of isolated (i.e., nonaggregated) nanocrystals. Depending on the size selection method, crystallites with average sizes of 10 to 100 nanometers can be recovered.

In nature, quartz is the primary form of silicon and oxygen, elements that together comprise over 70% of the earth's crust.[1] Its properties have been of great interest to geologists for decades, and its superior electrical and thermal insulating properties find applications in many industries.[2−5]

Given the widespread importance of quartz in nature and technology, it is remarkable that there are no reported chemical routes for the production of nanoscale quartz. Such a material would have a range of potential uses. The phase behavior of quartz nanocrystals could provide insight into the fundamental mechanisms responsible for solid-state amorphization and the $\alpha-\beta$ transition, and their solution phase properties would be a valuable model for rock erosion.[6−11] Nanoquartz might also exhibit nanoscale piezoelectric behavior, which could be applied in small-scale actuators and motors. These and other potential applications motivated us to develop a solution-phase route to form nanoquartz.

Quartz possesses features that make a purely chemical approach to its nanoscale formation challenging. First, the amorphous state of silica is nearly equal in energy to that of α-quartz.[12] Thus, the common nanochemical strategy of employing rapid decomposition of molecular precursors to form crystallites generally fails since the resulting product is amorphous. Second, the ideal prescription for nanocrystal formation, fast nucleation followed by slow growth, is difficult to implement in the case of quartz due to its extremely rapid growth rate in conditions required for its nucleation (80 nm/sec at 263 °C in 0.5 M NaOH).[13,14] This rapid growth rate also makes size control problematic.

For these reasons, our strategy relies on both chemical as well as physical methods to form nanocrystalline quartz.[15] We conduct our reactions under hydrothermal conditions where bulk quartz is known to precipitate from aqueous solutions saturated with silica. Hydrothermal reactions have been successful at producing other nanocrystalline oxides such as TiO_2 and $BaTiO_2$, and recent reports have highlighted hydrothermal synthesis of micron sized quartz powders.[8,16−21] Taking these as a starting point, we use high surface area silica precursors and perform the reaction under basic conditions in order to accelerate the quartz nucleation rate.[22−28] The resulting submicron powders can be subjected to simple purification processes which allow for nanocrystal samples of varying average sizes to be generated.

This reaction starts with the hydrothermal dissolution and reprecipitation of silica under conditions designed to encourage rapid nucleation of quartz. In a typical reaction, 3.5 g of a dry amorphous silica precursor is added to 100 mL 0.1 M NaOH in a Parr 4550 minireactor and ramped at 6 °C/min to 200−300 °C (see Supporting Information for detailed reaction procedures). Most of the reactions reported here use fumed silica as the starting material (99.8%, 390 m^2/g, Sigma), though amorphous colloidal silica gives equivalent results. Both of these silica sources have high surface areas which result in rapidly rising soluble silica levels in the reactor. This coupled with strong basic conditions favors quartz nucleation.

After 2 h, the starting product has dissolved and the reaction is quenched to 70 °C in 10−15 min by water circulation through the internal reactor cooling loop. A white powder (90% yield) can be recovered and purified by dialysis. It is crucial during dialysis to maintain a slightly basic pH (∼8). More basic solutions will favor the dissolution of solid phases of silica and may reduce the quartz yield.[29] Even slightly acidic solutions are known to promote the

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10.1021/nl025854r CCC: $25.00
Published on Web 03/27/2003