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Hydrothermal synthesis of monodisperse single-crystalline alpha-quartz nanospheres†

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Uniformly-sized, single-crystal alpha-quartz nanospheres have been synthesized at 200 °C and 15 atm under continuous stirring starting from uniform, amorphous Stöber silica colloids and using NaCl and alkali hydroxide as mineralizers. Quartz nanosphere size is controlled by the colloid particle size *via* direct devitrification. Uniform, high-purity nanocrystalline quartz is important for understanding nanoparticle toxicology and for advanced polishing and nanocomposite fabrication.

Synthesis of high purity, well-dispersed, and monosized single-crystalline quartz nanospheres remains a challenging problem. Devitrification of amorphous silica is facilitated when the silica is contaminated with impurities[1,2] or in contact with alkali halide crystal grains.[3,4] Higher purity polycrystalline quartz has been formed from amorphous silica in seawater and distilled water at 50 to 900 °C and 50 MPa to 3 GPa to enhance both nucleation and growth rates,[5] but, under hydrothermal conditions, high temperatures and pressures result in rapid coarsening.[3,6] In comparison, at only 145 °C and 100 MPa, 90 days are required for crystallization.[7] Alkali hydroxides and alkali halides are effective mineralizers for hydrothermal synthesis of silica polymorphs, allowing greater control of nucleation and growth.[7,8] The rate of crystallization is proportional to the square of the hydroxyl ion concentration.[9] Various crystalline silica varieties[10–12] can be generated depending on the alkaline concentration, temperature and duration. However it is difficult to control crystal growth, and the quartz particles are often large and strongly aggregated[13] as a consequence of the high pressure and temperatures needed for practical growth times.[3,14] Bertone *et al.*[15] prepared sub-micrometre-sized quartz powders using hydrothermal methods in alloy Parr bombs and classified them to get nanrrower size fractions of nanocrystalline quartz. In a subsequent report

this group[16] found the toxicity of the α-quartz nanoparticles to be independent of the particle size, however the role of metallic impurities was uncertain. To solve the puzzles of nanoparticle toxicity, metal alloys should be avoided as the container material to prevent potential contamination, and a facile synthesis method needs to be developed for producing high quality, non-aggregated, monodisperse quartz nanospheres.

The hydothermal synthesis of quartz by precipitation from aqueous solutions saturated with silica has been studied for over fifty years.[9] In order to prepare nanocrystals, the general concept is to establish conditions under which there is rapid nucleation followed by slow crystal growth. However as pointed out previously[15] these conditions are difficult to achieve for quartz due to its extremely fast growth rate at the temperature and pH required for nucleation. Additionally Ostwald ripening (driven by the differential solubility of large and small particles according to the Ostwald Freundlic equation) under typical basic hydrothermal conditions can lead to rapid coarsening.[17] These combined factors cause the size, shape, and crystal structure of quartz to be hard to control *via* hydrothermal synthesis.[18]

To overcome these previous issues, our approach is to use hydrothermal conditions to devitrify unifom amorphous silica nanoparticles according to the pathway: hydrated amorphous silica → anhydrous amorphous silica → alpha-quartz. By employing aqueous basic conditions with high concentrations of NaCl, we suppress significantly amorphous and crystalline silica solubility,[19] eliminating secondary quartz nucleation and growth and Ostwald ripening. Under such conditions the nanocrystal size and shape are dictated by the size and shape of the parent nanoparticle template–by using uniform Stöber silica colloids as the nanoparticle precursors we form equiaxed single crystal quartz nanoparticles with uniform size.

As nanocrystalline templates our approach uses, high purity, uniform, amorphous hydrated silica colloids of size ranging from 5–50 nm in diameter prepared from tetraethyloxysilane, ultra-pure DI water, 30% analytical pure ammonium hydroxide, and 200 proof ethanol by a variation of the Stöber method.[20] In a typical synthesis, 71.5 g silica colloid solution containing 3.84 wt% of ∼45 nm metal-free silica is premixed with 1.65 g analytical pure KOH or NaOH and 4.3 g analytical pure NaCl at room temperature. The mixture is put in a 200 cm³ Teflon autoclave maintained at ∼200 °C and ∼1.5 MPa and stirred at 1000 rpm over three days with a Teflon-coated

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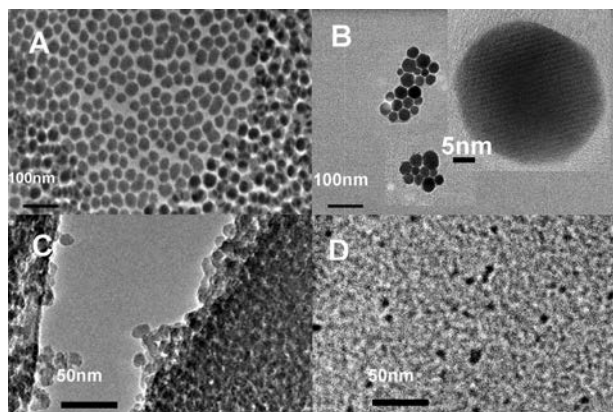
Fig. 1 TEM images of ∼45 nm diameter Stöber silica precursors (A) and corresponding alpha-quartz nanospheres (B), scale bar: 100 nm; ∼10 nm diameter Stöber silica precursors (C) and corresponding alpha-quartz nanospheres (D), scale bar: 50 nm.

magnetic stirring bar (XRD amoprhous products are formed after one and two days). The moderate temperature and high NaCl concentration help to control the solubility and diffusion of silicate species, while maintaining a suitable quartz devitrification rate. The product is centrifuged and washed or purified by dialysis. The quartz nanospheres are quite monodisperse and can be dispersed easily in water. Importantly there is no metal contamination, which is commonly observed for conventional high-temperature methods using stainless steel or alloy reactors.[16]

We find that the size of the Stöber silica colloidal precursors controls the size of the crystalline quartz nanoparticles. Fig. 1 shows representative TEM images of the parent hydrated Stöber silica nanoparticle precursors and the resulting alpha-quartz nanoparticles. The high resolution TEM image (Fig. 1B and 2A) and the selected area diffraction pattern (Fig. S1†) for the uniform multi-faceted silica nanospheres formed from ∼45 nm diameter Stöber silica seeds (Fig. 1A) demonstrate that the alpha-quartz nanospheres are single crystalline. The XRD peaks (Fig. 3) match well with the pattern of alpha-quartz, and the crystallite size based on the Sherrerformula agrees well with the TEM data. Comparing Fig. 1A, B, C and D, we observe that reducing the colloid precursor size reduces the size of the resulting quartz nanoparticles and that the size dispersity of the quartz nanoparticles is comparable to that of the original colloidal particles (see also the dynamic light scattering data Supplementary
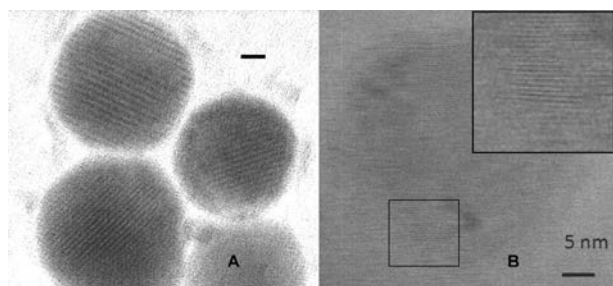

Fig. 2 HRTEM for quartz nanospheres of Fig. 1B (scale bar: 5 nm) (A) and TEM for partially crystallized silica after 48 h treatment at 200 °C (B), the inset is after magnification of the selected region.

Fig. S3 and S4,† which show comparable size distributions for the parent particle and quartz product). The hydrothermal treatment of Stöber silica particles in aqueous NaCl and NaOH solution causes gradual dehydration, densification, nucleation, and crystallisation of alpha-quartz. TGA analysis indicates that the Stöber silica nanoparticle precursors are hydrated containing approximately 3.6 wt% water as internal silanol groups. Dehydration resulting from silanol condensation reactions causes densification and formation of what appear to be internal voids within the colloidal seeds after one day (see TEM image Fig. S2†), after two days of hydrothermal treatment the particles appear to be solid (Fig. 2B). Crystallization of amorphous silica into alpha-quartz begins within the condensed spheres from nuclei identified by lattice fringes (Fig. 2B inset) and proceeds throughout the particles ultimately coalescing into single crystal quartz nanospheres that due to density differences (accompanied by some dissolution) are smaller than their parent precursor particles (Fig. S3, S4†). The as-synthesized sample is a mixture of quartz nanospheres and salts based on XRD analysis (Fig. S5†). The negative surface charge at high pH accounts for the stability of the quartz spheres. However, if the colloid concentration is too high or no stirring is applied, the nano quartz will undergo aggregation and coarsening. Fig. S6† shows the TEM image of unstirred samples. Continuous stirring is required to attain high quality nanospheres.

The extent and rate of these transformations, the particle size, and final quartz nanosphere morphology vary considerably with the starting material and the process parameters: reaction temperature, pressure, time, concentration of mineralizers, and the concentration of particles in the feedstock. Assuming the Stöber silica colloids to be monodisperse and that each Stöber silica precursor particle forms a quartz nanosphere, the final quartz nanosphere size (D_Q) can be controlled by initial size D_0, silica weight ratio in the precursor (w_S), Stöber silica density, ρ_s quartz sphere density, ρ_Q and the solubility, S according to the mass balance applicable for hydrothermal conditions.

$$D_Q = D_0 \sqrt[3]{\frac{\rho_S}{\rho_Q}\left[1 - \frac{(1-w_S)}{w_S}S_\infty \exp\left(\frac{4\gamma M}{RT\rho_Q D_Q}\right)\right]}$$

Here the solubility is expressed as the Ostwald Freundlich equation where S_∞ is the solubility of a planar quartz surface
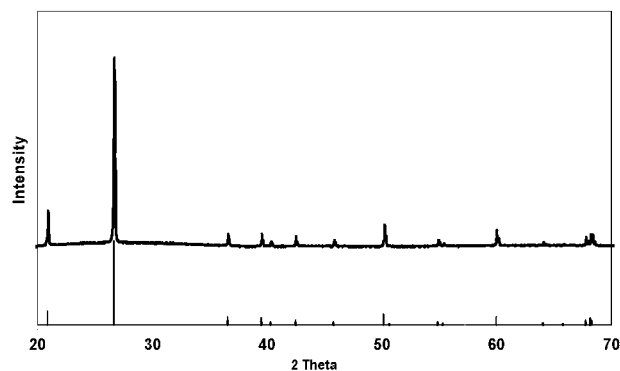

Fig. 3 XRD for dialysed quartz nanospheres. Standard diffraction peaks for alpha-quartz are marked for comparison.

under the hydrothermal conditions, which is a function of the temperature (T) and alkaline and salt concentrations, M is the molar mass of silica, γ is the surface tension, and R is the gas constant. Assuming a density, 1.8–2.0 g cm^{-3} for the hydrated Stöber silica precursor particle and S_∞ to be zero due to the high NaCl concentration, the calculated $D_Q/D_0 = 0.88$–0.91, which is close to that observed experimentally, e.g. 0.91 see supplementary Fig. S4.†

The w_S needs to be controlled to prevent aggregation of silica particles at high temperature and high NaCl concentration especially for nano-sized silica colloids. If the NaOH concentration and the temperature are too high, and/or insufficient NaCl or silica is added, all silica will dissolve, and it will be impossible to practically synthesize crystalline quartz without supplying silica to the system or removing water vapor. To make uniform quartz nanospheres, a proper concentration of Stöber silica colloids is needed, and the Stöber silica should be uniform in size. Furthermore, the temperature and concentrations should be kept uniform during the synthesis. To grow larger quartz nanospheres, soluble silica species can be added to the precursor as an additional silica source or can be supplied continuously. Gradual release/addition of water from/to the reactor also helps to adjust the final quartz size.

In summary, by using monodisperse Stöber nanoparticles as templates, employing a moderate temperature and pressure, and adding a large amount of NaCl to the system to suppress silica solubility and crystal growth rate, we succeeded in the synthesis of well dispersed, uniformly sized, single-crystalline quartz nanospheres. The method avoids high pressure and temperature hydrothermal synthesis,[21] and is practical for industrial manufacture. High pH, proper silica colloid concentration, and continuous stirring prevent settling and aggregation of the nanospheres. Under these conditions, the Stöber silica nanoparticles serve as uniformly sized templates that form quartz by direct devitrification preserving the nanoparticle shape and minimizing formation of new stable nuclei in the solution outside the silica nanospheres. The above measures are necessary, especially for growth of nano-sized quartz spheres with size monodispersity. More experiments are in progress to systematically study the effect of Stöber silica size, silica concentration, NaCl, temperature, NaOH/KOH concentration and duration on final silica morphology, phase, size and size distribution. The method for high-quality quartz nanospheres is not only important for on-going research on silica nanotoxicology, but also to provide guidelines for growth of other uniform nanocrystals.

Notes and references

1 H. Nanri, N. Takeuchi, S. Ishida, K. Watanabe and M. Wakamatsu, J. Non-Cryst. Solids, 1996, 203, 375.
2 M. Okabayashi, K. Miyazaki, T. Kono, M. Tanaka and Y. Toda, Chem. Lett., 2005, 34, 58.
3 N. Horii, M. Kamide, A. Inouye and N. Kuzuu, J. Ceram. Soc. Jpn., 2010, 118, 318.
4 D. R. Bassett, E. A. Boucher and A. C. Zettlemoyer, J. Mater. Sci., 1972, 7, 1379.
5 W. L. Huang, Eur. J. Mineral., 2003, 15, 843.
6 T. Moxon and M. A. Carpenter, Mineral. Mag., 2009, 73, 551.
7 James, I. Corwin and A. C. Swinnerton, J. Am. Chem. Soc., 1951, 73, 3598.
8 P. R. Hervey and J. W. Foise, Miner Metall Proc., 2001, 18, 1.
9 W. S. Fyfe and D. S. Mckay, Am Mineral, 1962, 47, 83.
10 O. Schaf, H. Ghobarkar, A. Garnier, C. Vagner, J. K. N. Lindner, J. Hanss and A. Reller, Solid State Sci., 2006, 8, 625.
11 B. Martin, Eur. J Mineral, 1995, 7, 1389.
12 O. Y. Kwon, S. Y. Jeong, J. K. Suh and J. M. Lee, B. Kor. Chem. Soc., 1995, 16, 737.
13 K. J. Lee, K. W. Seo, H. S. Yu and Y. I. Mok, Korean J. Chem. Eng., 1996, 13, 489.
14 V. S. Balitsky, L. V. Balitskaya, T. M. Bublikova, A. G. Kalinichev, E. A. Marina, H. Iwasaki and F. Iwasaki, J. Supercrit. Fluids, 1998, 13, 357.
15 J. F. Bertone, J. Cizeron, R. K. Wahi, J. K. Bosworth and V. L. Colvin, Nano Lett., 2003, 3, 655.
16 David, B. Warheit, Thomas R. Webb, Vicki L. Colvin, Kenneth L. Reed and Christie M. Sayes, Toxicol Sci., 2007, 95, 270.
17 R. K. Iler, The Colloid Chemistry of Silica and Silicates, Cornell University Press, Ithaca, New York, 1955, p. 248.
18 V. S. Balitsky, T. M. Bublikova, L. V. Balitskaya and A. G. Kalinichev, J. Cryst. Growth, 1996, 162, 142.
19 R. C. Newton and C. E. Manning, Geochim. Cosmochim. Acta, 2006, 70, 5571.
20 W. Stöber, A. Fink and E. Bohn, J. Colloid Interf. Sci., 1968, 2662.
21 A. G. Kalinichev, E. A. Marina, H. Iwasaki and F. Iwasaki, J. Supercrit. Fluids, 1998, 13, 357.