Synthesis and characterization of ultrasmall zirconia particles via nonhydrolytic solvothermal technique

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Zirconium oxide (ZrO$_2$) or zirconia has been studied with much interest due to its wide variety of applications such as in catalysis [1][2], gas sensing[3][4], fuel cell technology [5][6], and ceramics [7]. These are made possible due to its intrinsic properties that are governed by its atomic and bulk characteristics [8]. Recently, there have been much interest on the nanoparticles with less than 10 nm in size which are ruled by quantum confinement effects caused by the finite size of the particles [9]. However, synthesis of such particles with good control over the size and phase purity is not easily done. One way is to use nonhydrolytric route which is advantageous in terms of size controllability and narrow size distribution [10] done in solvothermal technique [11]. In our current work, we were able to synthesize well crystallized ultrasmall zirconia particles using a modified alcohol based nonhydrolytic route without any surfactant. Average structural and morphological characterizations via classical X-ray diffraction and transmission electron microscopy were done on the samples. Results show that we were able to manipulate the phase purity of our samples from dual phase (m-ZrO$_2$ and t-ZrO$_2$) to single phase (t-ZrO$_2$). Also, we observed a good control over the average apparent size of our particles which are in the nanoscale range from 4.0 nm to 1.0 nm and appears to favor a spherical shape. Furthermore, the modified nonhydrolytic approach allowed us to produce nanocrystals at low temperatures from 210°C down to 80°C with good compositional purity. One of the reasons why we were able to achieve these results is due to the fine tuning of the ratio of precursors to adjust the alkalinity of the solution. For the ultrasmall zirconia particles (~1.0 nm), the atomic-pair distribution function analysis reveals that the structural characteristics does not conform strictly to any of the four polymorphs of bulk zirconia with fluorite derived structure. This suggests a structural distortion with large disorder in comparison to the bulk polymorphs. In addition, this work presents a plausible mechanism for the formation of the ultrasmall zirconia particles in an alcohol deficient environment.

[10] P. H. Mutin et A. Vioux, Chemistry of journals (2009), 14, 582–596