

## Photoluminescence of Tetragonal ZrO<sub>2</sub> Nanoparticles Synthesized by Microwave Irradiation

Jiahe Liang,<sup>†</sup> Zhaoxiang Deng,<sup>†</sup> Xin Jiang,<sup>‡</sup> Fuli Li,<sup>‡</sup> and Yadong Li<sup>\*†</sup>

Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China, and Department of Physics, Capital Normal University, Beijing 100037, P.R. China

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Polymer-stabilized tetragonal ZrO<sub>2</sub> nanopowders with average size of ca. 2.0 nm have been prepared by microwave heating in an aqueous solution containing Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O, PVA, and NaOH. The photoluminescence of the synthesized ZrO<sub>2</sub> fine particles has been investigated.

In recent years, there has been considerable interest in photoluminescent properties of many metal oxides such as TiO<sub>2</sub>,<sup>1</sup> ZnO,<sup>2</sup> WO<sub>3</sub>,<sup>3</sup> and In<sub>2</sub>O<sub>3</sub>,<sup>4</sup> because they could possibly be used, for example, as nanoscopic optical storage elements or as probes in living systems.<sup>5</sup> However, comparatively few studies,<sup>6</sup> to the best of our knowledge, have been carried out concerning the luminescence of nanoscale ZrO<sub>2</sub> crystallites.

Nanometric ZrO<sub>2</sub> particles are a technologically important class of materials with a wide range of applications.<sup>7</sup> ZrO<sub>2</sub> has three polymorphs: monoclinic(m), tetragonal(t), and cubic(c) phases. The monoclinic phase is thermodynamically stable up to 1100 °C, the tetragonal phase exists in the temperature range 1100–2370 °C, and the cubic phase is found above 2370 °C.<sup>8</sup> The existence of metastable t-ZrO<sub>2</sub> at low temperature has been reported, and fine powders of t-ZrO<sub>2</sub> at mild temperature have been prepared by many methods, including forced hydrolysis,<sup>8,9</sup> sol–gel method,<sup>10</sup> hydrothermal method,<sup>11</sup> thermal decomposition,<sup>12</sup> coprecipitation,<sup>13</sup> surfactant templating method,<sup>14</sup> and spray pyrolysis.<sup>15</sup> However, it is very beneficial for us to find a fast, simple, and energy efficient approach to produce fine t-ZrO<sub>2</sub> powders.

Microwave-assisted synthesis is another way to produce inorganic compounds since 1986. Compared with conventional methods, microwave synthesis has the advantages of very short reaction time and production of small particles with narrow size distribution and high purity.<sup>16</sup> Only a few publications reported studies on microwave-assisted inorganic synthesis, and some of them describe the fabrication of zirconia particles by microwave heating.<sup>17</sup> However, it is a challenge to find an efficient way to prepare ZrO<sub>2</sub> powders with particle size about several nanometers by using the microwave method, and there have been no reports on the luminescent properties of nanoscale ZrO<sub>2</sub>.

In the present work, a microwave-assisted method for the preparation of polymer-stabilized nanocrystalline t-ZrO<sub>2</sub>, without addition of any mineralizer, is reported, and its luminescent property is investigated. We think PVA has an important influence on the stabilization of the as-prepared t-ZrO<sub>2</sub> nanoparticles.

ZrO<sub>2</sub> nanoparticles were successfully prepared by means of hydrolysis of Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (Tianjin chemical, AR) under microwave irradiation in NaOH (Beijing chemical, AR) aqueous solutions. In a typical synthesis, an aqueous solution containing 0.10 mol L<sup>-1</sup> Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O and 5 mol L<sup>-1</sup> NaOH was exposed to microwave radiation at a power of 650 W. The microwave irradiation was operated in 30-second cycles (on for 10 s, off for 20 s) for 6 min, and then,

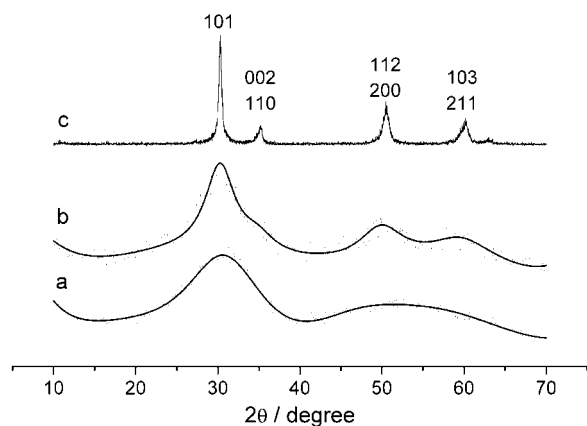
\* To whom correspondence should be addressed. E-mail: ydli@tsinghua.edu.cn. Fax: +86-10-62788765. Phone: +86-10-62772350.

<sup>†</sup> Tsinghua University.

<sup>‡</sup> Capital Normal University.

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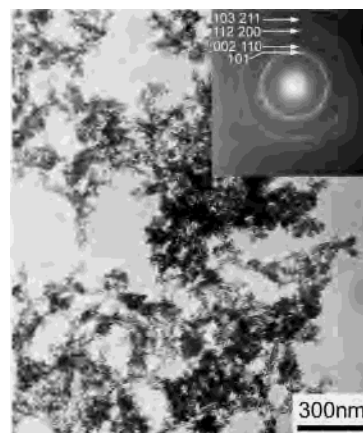


**Figure 1.** XRD patterns of the microwave synthesized  $\text{ZrO}_2$  samples in the absence (a) and presence (b) of PVA, and the  $\text{ZrO}_2$  products annealed at  $320\text{ }^\circ\text{C}$  for 6 h (c). The noisy curves in a and b are experimental results, and the smooth curves in a and b are simulated results.

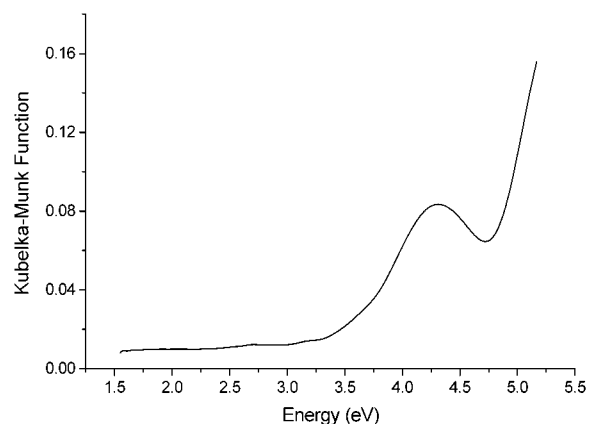
the solutions were allowed to cool to room temperature naturally. The resulting precipitates were collected, washed with distilled water and absolute alcohol, and dried in air for 2 h. The product obtained in this procedure is referred to as sample a. For the synthesis of polymer-stabilized  $\text{ZrO}_2$  nanoparticles (referred to as sample b in the following text), the procedure was the same except that PVA (Beijing chemical, AR) was existent in 30 wt % along with other reactants. Heating treatments of the synthesized  $\text{ZrO}_2$  nanoparticles were conducted at  $320\text{ }^\circ\text{C}$  in air.

X-ray diffraction (XRD) patterns of the obtained samples were recorded on a Bruker D8-advance X-ray powder diffractometer. Morphology analysis of the samples was conducted with H-800 transmission electron microscopy (TEM) operated at 200 kV. The photoluminescence (PL) of as-prepared sample was observed under excitation by UV light at 254 and 412 nm in air with a Perkin-Elmer LS-50B fluorescence spectrophotometer. Optical diffuse reflectance of the samples were recorded on Shimadzu UV-2100S spectrophotometer based on the procedure described in the literature.<sup>18</sup>

XRD patterns of the samples obtained directly by microwave synthesis in the absence or presence of PVA are given in Figure 1 a,b, respectively. Both of them exhibit broad diffraction peaks, implying the extremely small dimensions of the prepared  $\text{ZrO}_2$  powders. Using PowderCell 2.3,<sup>19</sup> the two experimental XRD results (noisy curves in Figure 1) were fitted by simulated XRD profiles (smooth curves in Figure 1) for tetragonal  $\text{ZrO}_2$ , and an average crystallite size of ca. 2.0 nm for sample b could be derived from the simulation results. On the basis of the XRD reflectances, it could be found that sample b (Figure 1b) crystallizes better than sample a (Figure 1a). These facts prove that PVA played a significant role in the formation and stabilization of the t- $\text{ZrO}_2$  phase via the current microwave method. The XRD pattern of the annealed sample obtained by microwave



**Figure 2.** TEM image of the as-synthesized  $\text{ZrO}_2$  product (sample b). Inset shows an electron diffraction (ED) pattern taken on a selected area of the sample.



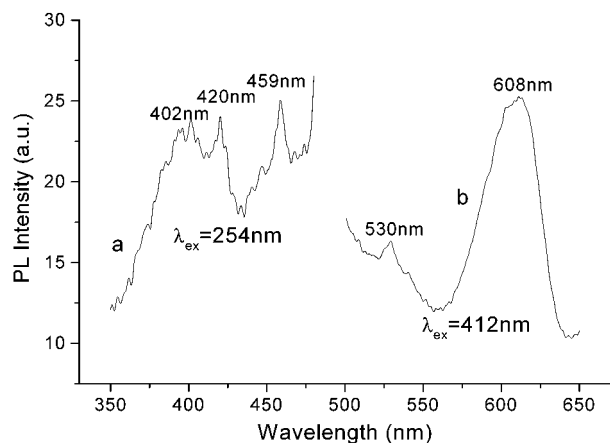
**Figure 3.** UV-vis absorbance of the microwave synthesized  $\text{ZrO}_2$  samples.

synthesis in the absence of PVA was shown in Figure 1c. On the basis of the Debye-Scherrer equation, the particle sizes calculated from the fwhm (full width at half-maximum) of the four strong reflectance peaks are 18 ([101]), 11.6 ([002], [110]), 9.7 ([112], [200]), and 10.1 nm ([103], [211]). The smaller values derived from the latter three peaks were in agreement with the fact that all of them are composed of two reflectances, which is characteristic of tetragonal  $\text{ZrO}_2$ . Therefore, the real particle size of the annealed product is about 18 nm calculated from the fwhm of [101] reflectance. Similar results were also obtained when sample b was treated in the same way. The good crystallinity of the tetragonal  $\text{ZrO}_2$  product obtained only through heating at  $320\text{ }^\circ\text{C}$  for 6 h, along with the good fitting between the simulated and experimental XRD results as shown in Figure 1, reveals that the initial product through microwave synthesis is nanosized tetragonal  $\text{ZrO}_2$ .

TEM and ED pictures of sample b are shown in Figure 2. Because the particle size is only about 2 nm as judged from the XRD results, it is reasonable that the TEM does not show individual particles under the magnification used. The ED pattern shows well-defined quasicontinuous diffraction rings, which is consistent with the fact that the particles are much smaller than the radius of the electron beam employed for the electron diffraction.

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**Figure 4.** PL spectra of the  $\text{ZrO}_2$  samples excited at 254 nm and 412 nm.

The diffusive reflectance spectrum of the as-synthesized  $\text{ZrO}_2$  nanoparticles is given in Figure 3. Because the individual particle size is much less than the thickness of the sample layer, an ideal diffuse reflectance with constant scattering coefficient could be expected. The Kubelka–Munk function,<sup>20</sup> which is the ratio between the absorption and scattering factors, is then used for the absorbance plotting, which shows a clear absorption onset arising at about 3.5 eV. The photoluminescence (PL) spectra obtained at two different excitations for the nano- $\text{ZrO}_2$  samples are shown in Figure 4. Figure 4a shows the PL spectrum with an excitation wavelength of 254 nm; three fluorescence emis-

sions at 402 nm, 420 nm, and 459 nm, respectively, could be observed. The PL spectrum in Figure 4b was obtained at 412 nm excitation, exhibiting a maximum at 608 nm, with a weak satellite peak at 530 nm. Although the detailed PL mechanism for the nano- $\text{ZrO}_2$  is still under research, we could ascribe the emissions that appear at short wavelength excitation to the near band-edge transitions. In the case of the emission in Figure 4b, it should be due to the involvement of mid-gap trap states, such as surface defects and oxygen vacancies.<sup>21</sup> Large amounts of surface defects should exist on the as-synthesized nano- $\text{ZrO}_2$  particles because of their high surface area.

In conclusion, a microwave-assisted method has been successfully used for the preparation of ultrafine polymer-stabilized nanocrystalline  $t\text{-ZrO}_2$  powders. Photoluminescence of the as-synthesized  $t\text{-ZrO}_2$  particles was observed and investigated. The microwave method is rapid, simple, and energy-saving, which can be easily extended to the preparations of other oxide nanocrystals.

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