Preparation of Zirconia Nanoparticles by Pulsed Laser Ablation in Liquid

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We report on the synthesis of zirconia nanoparticles by nanosecond pulsed laser ablation in water or ammonia at room temperature. Mixtures of tetragonal and monoclinic zirconia nanoparticles were obtained in water, while tetragonal zirconia nanoparticles were synthesized in ammonia. The mechanism of the formation of zirconia nanoparticles was discussed.

Zirconia has three crystallographic phases: monoclinic (m-ZrO_2), tetragonal (t-ZrO_2), and cubic (c-ZrO_2) phases. The monoclinic zirconia is stable at room temperature and transforms to tetragonal zirconia at 1170 °C and cubic zirconia at 2370 °C. The martensitic phase transformation from tetragonal to monoclinic zirconia is accompanied by 5% volume expansion which is important in the application of structural ceramics. In addition, tetragonal zirconia is extensively used as catalysts, catalyst supports, oxygen sensors, and fuel cells.[1–4] Therefore, synthesis of tetragonal zirconia at room temperature attracts the ongoing interest. Adding impurities, such as Y_2O_3, is one way to synthesize tetragonal zirconia. Due to effect of a critical particle size on the stability of tetragonal zirconia, reducing particle size is another way to stabilize tetragonal zirconia.[5,6] Additionally, the aggregation of zirconia nanocrystallites can improve the stability of tetragonal zirconia significantly.[7] Many methods were used to synthesize tetragonal zirconia, while all these methods need calcination at high temperature.[6–8]

Recently, pulsed laser ablation in liquid (PLAL) has attracted great attention in the synthesis of metastable nanomaterials.[9,10] High temperature and high pressure can be created in a local region in the liquid by pulsed laser ablation which leads to the formation of metastable nanomaterials. Moreover, the products are quenched quickly and can be frozen and preserved. In this letter, we report the synthesis of zirconia nanoparticles using a simple method of pulsed laser ablation in water or ammonia at room temperature.

A zirconium metal plate submerged in deionized water or ammonia was irradiated by a third harmonic (355 nm) of a Nd:YAG pulse laser for 60 min. Other parameters of the laser were: pulse width $\tau = 7$ ns, repetition rate $\nu = 10$ Hz, and pulse energy $= 100$ mJ. The target was fixed on the bottom of a glass vessel, and then water or ammonia was poured into the vessel. The depth from the liquid surface to the target was 5 mm. The ammonia was chemically pure, and the concentration was 25 wt %. The laser beam was focused onto the target surface using a lens with a focal length of 100 mm. The samples were collected after evaporating the solutions at 80 °C. X-ray diffraction analysis (XRD) and Raman spectra were used to study the crystal phases of the samples. Transmission electron microscopy (TEM) was used to study the shape and size distribution of the synthesized nanoparticles. High-resolution TEM (HRTEM) was used to analyze the crystal phases.

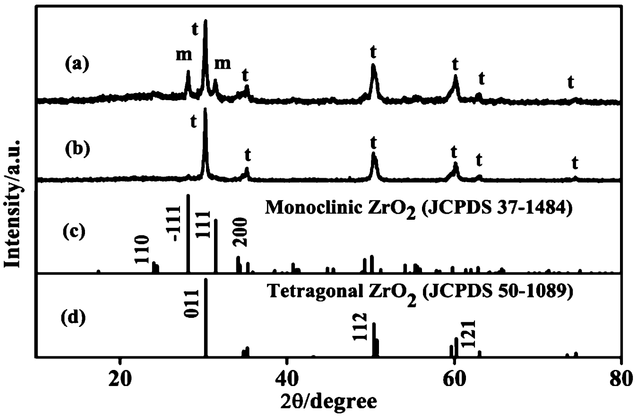

Figure 1. XRD patterns of ZrO_2 produced by pulsed laser ablation in water (a) and ammonia (b). The standard JCPDS card data for monoclinic (c) and tetragonal (d) ZrO_2 are provided as references.

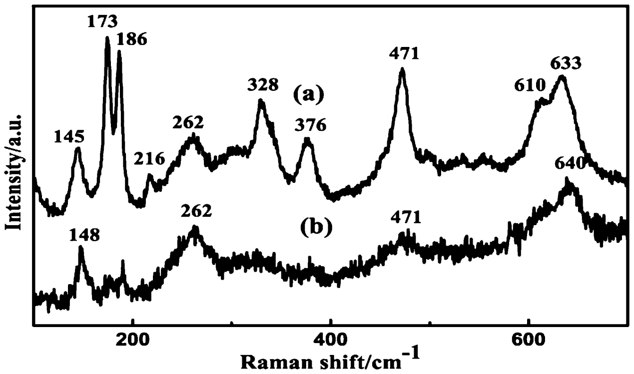

Figure 2. Raman spectra of ZrO_2 produced by pulsed laser ablation in water (a) and ammonia (b).

XRD patterns in Figure 1 show that the sample produced in water is a mixture of tetragonal and monoclinic zirconia, while the sample obtained in ammonia is mainly tetragonal zirconia.

The differences in component with different starting solutions can be further proved by Raman spectra. As shown in Figure 2, the Raman peaks at 173, 186, 216, 328, 376, and 610 cm^{-1} are the characteristic bands of monoclinic zirconia, and the Raman peaks at 145, 262, 471, and 633 cm^{-1} can be assigned to tetragonal zirconia.[11,12] Therefore, both of tetragonal and monoclinic zirconia were produced in water, while the sample obtained in ammonia is mainly tetragonal zirconia. No apparent peak at 610 cm^{-1} assigned to characteristic band of cubic zirconia is observed in the Figure 2b, which indicates the absence of cubic zirconia.[11] The Raman spectra were consistent with the XRD results.

Figure 3 shows the TEM and HRTEM images of ZrO_2 produced by pulsed laser ablation in water (a), (b) and ammonia (c),

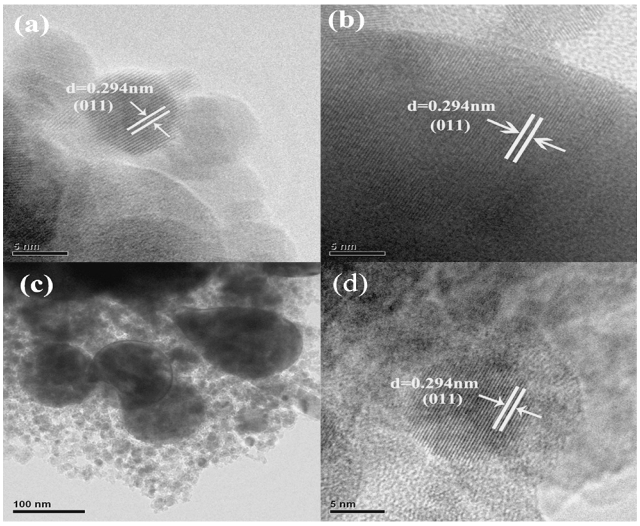

Figure 3. TEM and HRTEM images of ZrO_2 produced by pulsed laser ablation in water (a), (b) and ammonia (c), (d).

(d). The TEM image of ZrO_2 synthesized in water shows that the particles are almost spherical. Tetragonal zirconia lattices (with interplanar spacing of 0.294 nm) are observed in the products in water, as shown Figures 3a and 3b, which confirm the presence of tetragonal zirconia. Figure 3c is a TEM image of ZrO_2 nanoparticles synthesized in ammonia which shows the size of particles distributed mainly in two regions: 10–15 and 100–150 nm. The lattice (with interplanar spacing of 0.294 nm), as shown in Figure 3d, confirms the presence of tetragonal zirconia nanoparticles.

To understand the formation and stability mechanisms of tetragonal zirconia nanoparticles, it is necessary to examine the mechanism of pulsed laser ablation in liquid and to consider factors affecting the stability of tetragonal zirconia. Pulsed laser ablation in liquid is a highly nonequilibrium process. When the laser pulse irradiates the interface between the solid target and liquid through the liquid, species will be ejected out with large kinetic energy. Then a plasma plume will be generated on the interface. The plasma plume expands quickly while the liquid confines it. The confinement of liquid could drive the plasma plume into an extreme thermodynamic state in which the temperature can reach several thousand K and the pressure goes into the order in magnitude of GPa.[9] These conditions are favorable for the formation of metastable phases. Moreover, the cooling of liquid can lead to quenching of the plasma plume which freezes and preserves metastable phase in the final products.

In our case, tetragonal zirconia is a metastable phase at room temperature. Ablated species from the zirconium target reacted with the water molecules at high temperature. Tetragonal zirconia was produced and reserved after quenching of the plasma plume. The fundamental mechanism of pulsed laser ablation has not been fully understood, and the reason for the absence of cubic phase is not clear.

According to the surface energy theory, the critical size for stabilized tetragonal zirconia is 30 nm.[5] In our case, many single spherical tetragonal zirconia particles smaller than 30 nm were produced in water and ammonia, as shown in Figures 3a and 3d. Tetragonal particles larger than 30 nm were also present, as shown in Figures 3b and 3c, which contradicted the prediction about the critical size.

Many factors, such as particle size, hydrostatic strain energy, hard aggregation tendencies, and surface energy could affect the stability of tetragonal zirconia.[13] The phase transformation from tetragonal to monoclinic is accompanied by 5% volume expansion. Shukla et al. suggested that this transformation would induce hydrostatic stresses and improve the stability of tetragonal zirconia.[13] Then the critical size can be larger than 30 nm. Meanwhile, small nanocrystallites aggregated to form larger hard aggregated particles, as shown in Figure 3c. The aggregation of zirconia nanocrystallites could improve the stability of tetragonal zirconia.[7] All these factors could explain the presence of tetragonal nanoparticles larger than 30 nm.

We now discuss the difference between the products prepared in water and ammonia. Mitsuhashi et al. reported that OH^- played an important role in stabilizing tetragonal zirconia.[14] According to the study by Shukla, OH^- could be present on the particle surface which enhanced the interfacial difference between tetragonal and monoclinic phases. OH^- could also be inside tetragonal lattice and then induced hydrostatic stresses.[13] These factors could improve the stability of tetragonal zirconia. In our case, the pH measurements revealed that the solution changed from the initial neutral to an acidic state (pH 3.8) after laser ablation in water, while in ammonia, the pH value (12.8) almost remained unchanged. These results suggested that there could be more OH^- adsorbed on tetragonal zirconia surface and inside tetragonal lattice in ammonia than water. These may result in better stability of tetragonal zirconia in ammonia than water.

In conclusion, mixtures of monoclinic and tetragonal zirconia were prepared in water by pulsed laser ablation, while tetragonal zirconia was synthesized in ammonia. The stability resulted from the inherent advantages of pulsed laser ablation in liquid, hydrostatic stresses, and hard aggregation. Additionally, OH^- may play an important role in the stabilization of tetragonal zirconia in ammonia.

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