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Synthesis and Characterization of Zirconia Nanorods

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ZrO_2 nanorods are prepared by annealing precursor powders produced in the novel inverse microemulsion system. The length and diameter of ZrO_2 nanorods are a few micrometers and 40–100 nm, respectively. The microstructure of the resultant nanorods are studied by XRD, TEM, selected area electron diffraction, and Raman spectroscopy. The ZrO_2 nanorods are single crystalline and have monoclinic structure. The formation of ZrO_2 nanorods is discussed.

I. Introduction

ZIRCONIA (ZrO_2) has attracted much attention in the fields of electrochemical devices, structural ceramics, oxygen sensors, catalytic systems, and magnetic and thermal fields.[1–3] For example, ZrO_2, with a melting point of 3100 K, is one of the most important refractories, and fine-grained ZrO_2 ceramics have important applications where superplasticity and transformation toughening are highlighted.[4–6] Today, ceramic fibers and whiskers have been increasingly used as reinforcements for advanced composite materials. The mechanical properties of these reinforcements significantly affect the strength of composite materials. Single-crystal fibers show very high mechanical strength because of their crystalline perfection and small dimensions, which minimize the occurrence of defects. It is well-known that the strength of ceramic fibers and whiskers is size-dependent.[7–10] As the diameter decreases, the strength of ceramic fibers and whisker increases. Meanwhile, the fracture of a single crystal of a brittle material is initiated through the formation of high stress concentrations at a particular imperfection or combination of imperfections in the structure. However, the smaller whiskers approach a condition of being almost free of imperfections.[11–13] If ZrO_2 nanorods and whiskers can be synthesized, their strength is bound to be excellent. Although many methods have been developed to synthesize ZrO_2 powders, including precipitation,[14] sol–gel,[15] thermal decomposition,[16] and hydrothermal treatment,[17] there are few methods for preparing ZrO_2 ceramic nanofibers and nanowhiskers. In the present work, the synthesis of ZrO_2 nanorods is accomplished by annealing precursor powders in which NaCl and $Zr(OH)_4$ particles are homogeneously mixed. Inverse microemulsion techniques have been used to prepare the precursor powders.

An inverse microemulsion (IμE), which consists of an oil phase, a surfactant, and an aqueous phase, is a thermodynamically stable isotropic dispersion of the aqueous phase in a continuous oil phase.[18] Unlike conventional emulsions, however, IμE domains fluctuate in size and shape and undergo spontaneous coalescence and breakup. They can exhibit water-continuous structure, with typical equilibrium domain sizes ranging from 10 to 100 nm. These domains are ideal for the preparation of extremely fine particles.[18] In the last decades, nanoparticles of metal oxides have been prepared in IμE.[19,20] Most recently, IμE systems have found utility as templates for synthesis of hollow polymer shells[21] and nanocrystal superlattices.[22] Here, we employ IμE systems to prepare the precursor powders of ZrO_2 nanorods.

II. Experimental Procedures

The starting materials used in the present work included a high-purity zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), sodium chloride (NaCl), and sodium hydroxide (NaOH). A high-purity cyclohexane, mixed polyoxyethylene (5) nonylphenol ether (NP5) with volume ratio 1:1, polyoxyethylene (9) nonylphenol ether (NP9), p-octyl polyethylene glycol phenyl ether (OP), and polyoxyethylene alkyl ether (AEO) were used in the volume ratio 4:2:1:1. All chemical reagents were analytical grade. Three microemulsion compositions were prepared: (a) 48 wt% cyclohexane + 48 wt% NP5/NP9/OP/AEO (hereafter referred to as NPPA) + 4 wt% 1 mol/L $ZrOCl_2$ aqueous solution (hereafter expressed as "A"); (b) 46 wt% cyclohexane + 46 wt% NPPA + 8 wt% 2 mol/L NaOH aqueous solution (hereafter expressed as "B"); and (c) 41.7 wt% cyclohexane + 41.7 wt% NPPA + 16.6 wt% 2 mol/L NaCl aqueous solution (hereafter expressed as "C"); First, 26 mL of "A" was added to 36 mL of "C" while being stirred magnetically to produce "D." Subsequently, 27 mL of "B" were added to "D" while being vigorously magnetically stirred to produce mixture "E." Mixing was achieved by vigorously magnetically stirring "E" >30 min to produce precipitates. Next, the precipitates were repeatedly washed by using anhydrous acetone then centrifuged. The precursor powders were then dried in an oven at 80°C before they were calcined at 820°C for 3 h to form ZrO_2 nanorods.

The samples prepared were examined by XRD using a diffractometer (Model D/MAX-RA, Rigaku, Japan) with Cu$K\alpha$ radiation and a graphite monochromatic crystal. TEM was performed using a micrometer (Model JEM–200CX, JEOL, Tokyo, Japan) to characterize the ZrO_2 nanorods. The samples for TEM measurements were prepared by dispersing some products in ethanol, immersing them in an ultrasonic bath for 30 min, then putting a few drops of the resulting suspensions onto a copper grid coated with a layer of amorphous carbon. Crystal structures were determined by selected area electron diffraction (SAD) using an accelerating voltage of 200 kV and a double-tilt sample holder.

Measurements of Raman spectra were performed on a spectrometer (Model 1403, Spex Industries, Edison, NJ) under backscattering geometry. The blue line (514.5 nm) of an Ar^+ laser was taken as the excitation source. ZrO_2 nanorods were weighed and compressed into disks 12 mm in diameter and 0.5 mm in thickness under a pressure of 3×10^8 Pa.

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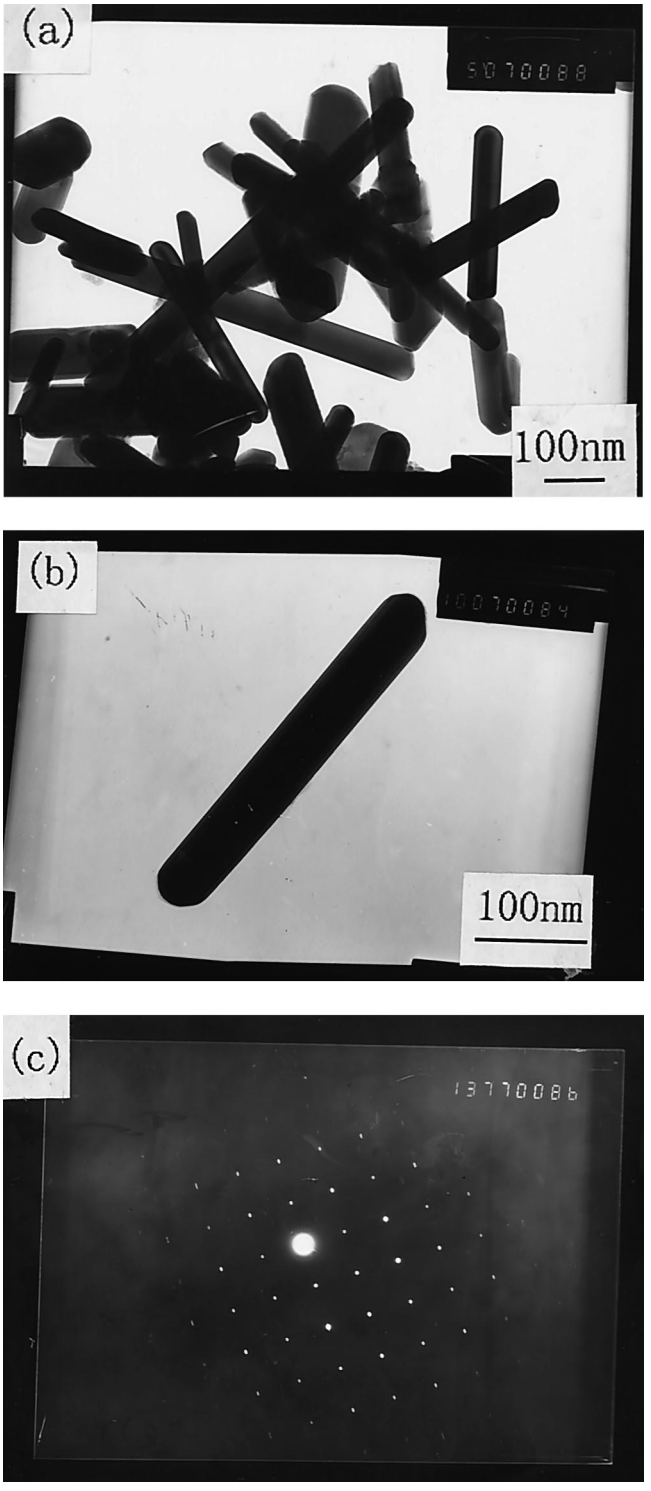

Fig. 1. TEM and SAD images of ZrO_2 nanorods. (a) Pictures of ZrO_2 nanorods annealed at 820°C for 3 h, (b) morphology of one single ZrO_2 nanorod annealed at 820°C for 3 h, and (c) SAD of one such single-crystalline ZrO_2 nanorod.

III. Results and Discussion

Figure 1(a) shows a typical micrograph of ZrO_2 nanorods, in which ZrO_2 nanorods are straight with diameters of 40–100 nm and lengths up to a few micrometers. One of the nanorods with 40 nm diameter is shown in Fig. 1(b), and its SAD pattern is shown in Fig. 1(c), indicating that it is a single crystal. The SAD patterns can be indexed according to the monoclinic structure.

Figure 2 shows XRD patterns of ZrO_2 nanorods. All peaks are indexed as the monoclinic lattice of ZrO_2 (their *hkl* indexes are given in figure). The diffraction data are consistent with Powder Diffraction File 37-1484, National Centre for Diffraction Data, Newtown Square, PA. No tetragonal ZrO_2 is detected.

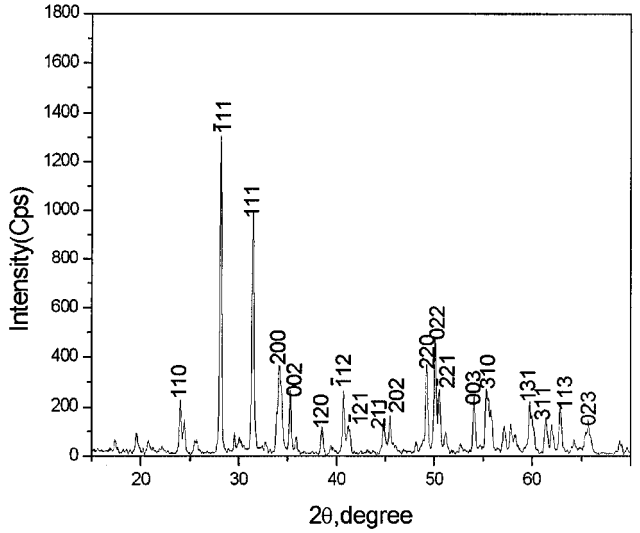

Fig. 2. XRD pattern of ZrO_2 nanorods annealed at 820°C for 3 h.

Figure 3 shows the Raman spectra of the as-prepared ZrO_2 nanorods; they are similar to those for bulk monoclinic ZrO_2,[23,24] with the exception of a redshift in frequency and the Raman line at 142 cm^{-1} belonging to tetragonal ZrO_2. The Raman lines at 186.65, 302.80, 343.95, 471.54, 554.32, and 634.21 cm^{-1} can be assigned as the A_g modes of the monoclinic phase. The Raman lines at 215.31 and 329.18, 379.30, 498.14, and 611.76 cm^{-1} can be ascribed to the B_g modes, and the line at 173.72 cm^{-1} is derived from the $A_g + B_g$ mode of monoclinic ZrO_2. This further proves that the as-prepared nanorods have a monoclinic phase and show long-range order structure. XRD usually reveals the long-range order of the materials and gives structural information within several unit cells. Raman scattering, as a local probe, is very sensitive to the crystallinity and microstructures of the materials. The very weak Raman line at 142 cm^{-1} implies that ZrO_2 nanorods contain a little tetragonal phase and that ZrO_2 nanorods are not phase-pure, although no tetragonal ZrO_2 is detected by the XRD measurement. However, from the XRD measurement and the weak peak of the Raman spectrum for the monoclinic ZrO_2, the major phase of the ZrO_2 nanorods is a monoclinic structure.

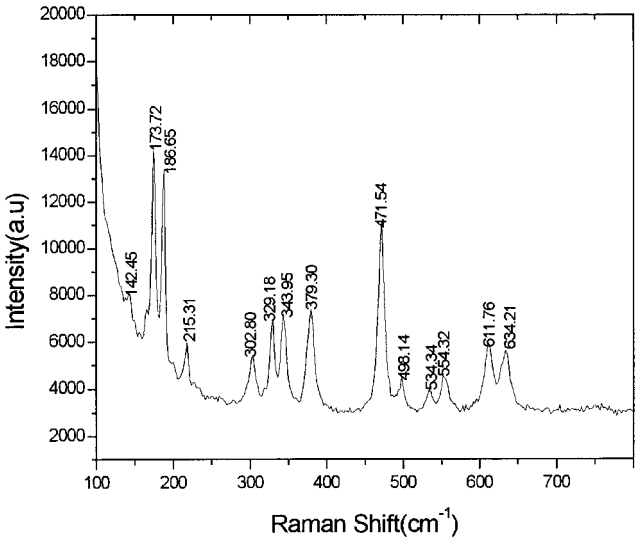

Fig. 3. Raman spectra of ZrO_2 nanorods annealed at 820°C for 3 h.

Temperature has a stronger effect on the formation of ZrO_2 nanorods. After annealing at $<780°C$, no ZrO_2 nanorods are detected, whereas annealing at $>820°C$ produces a few ZrO_2 nanorods and bulk ZrO_2 crystals.

In addition, the influence of surfactants on the formation of ZrO_2 nanorods is investigated. Under the same conditions, without AEO or OP, only very short ZrO_2 whiskers are observed. The development of the morphology of the products is related to the growth environments. There is a strong correlation between the formation of ZrO_2 nanorods and the existences of OP, NP, and AEO. The effects of AEO or OP on the formation of ZrO_2 nanorods are not clear. Further study is in progress.

Based on these experiments, it is suggested that the formation mechanism of ZrO_2 nanorods is similar to that occurring in molten salt synthesis (MSS) approaches,[25] which are similar to those in VLS and SLS approaches.[17] Nanorod growth requires a fluid phase in which elements of the crystal phase can easily move for a certain distance. Another advantage of the fluid phase is that the materials for nanorod formation are homogeneously distributed. Such homogeneity, which is ascribed to the microemulsion, leads to uniform nanorod water/oil (W/O) microemulsions consisting of nanosized water droplets dispersed in a continuous oil medium and stabilized by surfactant molecules accumulated at the W/O interface. The highly dispersed water pools are an ideal nanostructural reactor[18] for producing monodispersed nanoparticles, which make the precursors decompose easily to form ZrO_2 nanorods. The formation process of the ZrO_2 nanorod is as follows: the precursors are fired at a temperature above the melting point of the salt to form a flux of the salt composition. At this temperature, the oxides rearrange and then diffuse rapidly in the liquid salt. In the heating process, the ZrO_2 nanorods are formed through nucleation and growth. At higher synthesis temperatures, the ZrO_2 nanorods become larger in diameter and even become bulk ZrO_2. The formation reaction for the ZrO_2 nanorod in MSS is very fast. The action can be completed in a very short time because of the short diffusion distance and the high mobility of species in the liquid state. In this case, below 780°C, NaCl does not melt. Therefore, no molten phase forms, and no nanorods are detected.

In summary, ZrO_2 nanorods have been successfully prepared by calcining the precursors, which are produced in an IμE.

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