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Preparation and characterization of monodisperse zirconia spherical nanometer powder *via* lamellar liquid crystal template method

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ABSTRACT

Cubic phase spherical zirconia nano-powder was prepared by a direct template route in the lamellar liquid crystal formed by polyoxyethylene *tert*-octylphenyl ether (Triton X-100)/sodium dodecyl sulfate (SDS)/H_2O. The precursor powder and zirconia powder were characterized by XRD, FT-IR, TG/DSC, TEM, and SEM methods. Results show that the stability of the lamellar liquid crystal is controlled by $NH_3 \cdot H_2O$ concentration. The size of nanoparticles is greatly affected by $NH_3 \cdot H_2O$ and $ZrOCl_2 \cdot 8H_2O$ concentrations. The zirconia nanoparticles show narrow particle size distribution of 10–30 nm.

1. Introduction

As an important engineering material with outstanding mechanical properties, strong toughness, low thermal conductivity and high ionic conductivity at high temperature, zirconia is widely applied as structural component, fuel cell electrolytes, catalysts, and oxygen sensors [1–5]. The packing density, sintering temperature, and microstructure of ceramic are notably affected by the morphology and size of particles [6–9]. It is desirable to prepare ceramic powder with spherical morphology and narrow size distribution, giving high packing density, low sintering temperature, and uniform microstructure [10]. Controlling the particle size and shape of precursor particles is particularly important to produce high-quality ceramics.

Extensive researches have been carried out to control the morphology of zirconia [11,12]. Monodisperse spherical zirconia particle has been prepared by sol–gel reaction between zirconium isopropoxide and zirconium-chloride at 340 °C [13]. However, the high reaction temperature limits its large-scale production. Thermal hydrolysis of zirconium slat solution in a bulk solution is another way to produce colloidal particles. For example, Tai *et al.* have prepared spherical zirconia particles in the thermal hydrolysis of zirconyl nitrate solution at 95 °C in a stable microemulsion [14]. Microemulsion solution is a transparent, isotropic and thermodynamically stable system with nanosized droplets dispersed in a continuous oil phase [15]. Recently, spherical zirconia nanoparticles are successfully produced in a microemulsion [16,17]. Generally, liquid synthesis routes of ZrO_2 mainly involve in microemulsion [18]. Emulsions are dispersions of one liquid in another, both liquids being mutually immiscible, so emulsions are thermodynamically unstable. Since non-equilibrium nature of emulsions determines its lifetime, droplet size and polydispersity are highly dependent on the preparation method. Moreover, the structure of dispersed and continuous phases is a topic recently for the production of specialty materials [19].

Compared with microemulsion, lamellar liquid crystal is a suitable candidate for template and self-assembling of nanoscale materials due to its order and mobility at the molecular level [20,21]. Much scientific and technological effort has been dedicated to the preparation of zirconia by lytropic liquid crystal template. Ding *et al.* synthesized monodisperse zinc gluconate nanoparticles using the lamellar liquid crystal formed by Triton X-100/*n*-$C_{10}H_{21}OH/H_2O$ system [22] and showed that the shape and size of nanoparticle are nearly independent of the composition of lamellar liquid crystal. Freitas *et al.* reported directional growth of macroscopic ceramic needles by combining a thermoresponsive sulfated hydroxy zirconyl hydrosol with a swollen hexagonal liquid crystal [23]. Santos *et al.* reported the synthesis of zirconia microneedles by direct nucleation of particles inside a hexagonal swollen liquid crystal [24]. However, little attention has been paid to the stability and instability effects of precursor on the lamellar phase.

In this work, a lamellar liquid crystal composed of polyoxyethylene *tert*-octylphenyl ether (Triton X-100)/sodium dodecyl sulfate (SDS)/H_2O is used to prepare monodisperse spherical zirconia nano-powder *via* the reaction between ammonia water and zirconium salt solved in nano-reactors. The stability and microstructure of the lamellar liquid crystal are investigated. The effect of concentrations of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) and ammonia water ($NH_3 \cdot H_2O$) on the size of ZrO_2 particles is discussed.

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2. Experimental

2.1. Materials

Triton X-100 (polyoxyethylene tert-octylphenyl ether with an average number of EO units of 9.5, >99%), $ZrOCl_2 \cdot 8H_2O$ (purity 99.5%), ethanol and $NH_3 \cdot H_2O$ were purchased from Sinopharm Chemical Reagent Limited Corporation, and SDS was purchased from Tianjing Fine Chemical Factory (China). The chemicals were used as received without further purification. Water used was deionized and distilled.

2.2. Characterization

The birefringence properties of samples were recorded with polarizing optical microscope (POM) (Axio Scope.A1, Ceiss, Germany). Structural analysis was carried out by X-ray diffraction using (Bruker D8 Advance, Germany) equipped with Ni-filtered Cu-K_α radiation (a scan rate of 3(°) · min^{-1} and a step size of 0.02°) and Fourier Transform Infrared (FT-IR) Spectroscopy (Thermo Scientific, Nicolet iS10, USA). Particle size and particle size distribution were determined by NanoZS90 (Malvern Instruments Ltd., England). The morphology of prepared ZrO_2 powder was examined by a transmission electron microscope (TEM) (JEM-2010, Hitachi Ltd., Japan). Surface morphology of ZrO_2 nanostructures was examined by a field emission scanning electron microscope (SEM) (S-3400, Hitachi Ltd., Japan). TG-DTA was measured on a thermoanalyzer (PT1600, Linseis, Germany) in air from room temperature to around 1000 °C at a speed of 10 °C · min^{-1}.

2.3. Experimental method

2.3.1. Determination of lamellar liquid crystal region

The lamellar liquid crystal templates were prepared by mixing Triton X-100, SDS, and H_2O solutions. The ternary diagram was determined by titration of the non-ionic surfactant (Triton X-100) into anionic surfactant SDS aqueous solution. The samples were mixed vigorously using a vortex mixer and stored in a thermostat for 24 h at 298 K. Phase boundary of the lamellar liquid crystal region was determined by using a polarizing microscope, under which anisotropic phases exhibit typical microscopic textures. For example, a lamellar liquid crystalline phase shows a cruciate flower or oily streaks. On the other hand, isotropic phases such as micellar and cubic phases do not present a particular texture but a dark background under the polarizing microscope.

2.3.2. Preparation of zirconia nano-powder

Lamellar liquid crystal samples were prepared by substituting zirconia and $NH_3 \cdot H_2O$ aqueous solution for water in the Triton X-100/SDS/H_2O system. All the samples were prepared by weight in the sealed glass vials. Mixtures were then vigorously stirred at room temperature (25 °C) until the formation of a homogenous and highly viscous gel. Samples were centrifuged at 4000 r · min^{-1} for 2 min to remove air bubbles. When the lamellar phase reached equilibrium state, the sample became transparent with birefringence features under the polarizing microscope. The lamellar phase templates were removed using absolute ethanol and deionized water. The resulting nanoparticles were separated by centrifugation and washed with deionized water and alcohol alternatively. The precursor was calcined at 600 °C in the air.

3. Results and Discussion

3.1. Determination of the lamellar liquid crystal region

A partial phase diagram of the ternary system SDS/Triton X-100/H_2O is shown in Fig. 1. L phase occupies minor part of the phase diagram, extending in the range of 3%–66% SDS, 4%–61% Triton X-100, and 47.6%–78.9% water.

3.2. Stability of the lamellar liquid crystalline templates

For successful template of nanostructured materials, the template should be appropriate to define the synthesis. It is necessary to prove that the composition of inorganic precursors does not disrupt the long-distance order of lamellar liquid crystalline. Therefore, it is important to determine the stable region of lamellar phase.

3.2.1. Stability of the lamellar liquid crystal formed by Triton X-100/SDS/$NH_3 \cdot H_2O$ system

Texture of lamellar phase. The optical textures reveal that the microstructure of the lamellar liquid crystal template does not rupture with $NH_3 \cdot H_2O$. When the content of $NH_3 \cdot H_2O$ increases to 25% (Fig. 2D), lamellar liquid crystal turns from transparent to white-turbid in appearance, indicating that the long-distance order of the lamellar liquid crystal is disrupted.

3.2.2. Stability of the lamellar liquid crystal formed by Triton X-100/SDS/$ZrOCl_2 \cdot 8H_2O$ system

Fig. 3 shows POM images of lyotropic liquid crystal of Triton X-100/SDS/$ZrOCl_2 \cdot 8H_2O$. The samples with different $ZrOCl_2 \cdot 8H_2O$

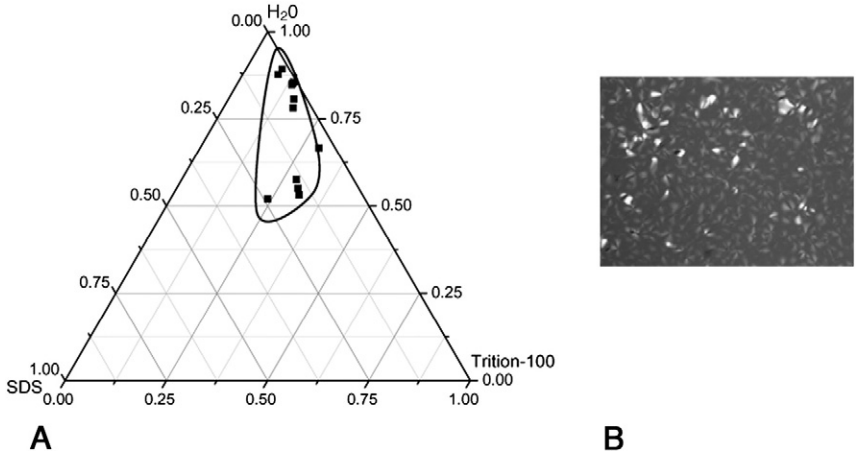

Fig. 1. Partial phase diagram of Triton X-100/SDS/H_2O system (A) and typical POM picture of lamellar liquid crystalline phase (B) at 298 K.