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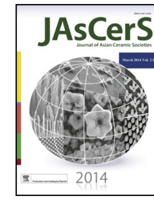

Synthesis and optical property of zinc aluminate spinel cryogels

Lifen Su [a,b,*], Lei Miao [c,**], Jibin Miao [a], Zhengzhi Zheng [a], Bin Yang [a], Ru Xia [a], Peng Chen [a], Jiasheng Qian [a]

[a] Anhui Province Key Laboratory of Environment-friendly Polymer Materials, School of Chemistry and Chemical Engineering, Anhui University, Hefei 230601, China
[b] Key Laboratory of Renewable Energy, Chinese Academy of Sciences, Guangzhou 510640, China
[c] School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China

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ABSTRACT

Zinc aluminate spinel cryogels with various molar ratio of Al/Zn are synthesized by sol–gel technology followed by vacuum freeze drying. The structures and optical properties are both found to be affected by the molar ratios of Al/Zn and annealed temperatures. The peaks of zinc oxide (ZnO) and zinc dialuminum oxide ($ZnAl_2O_4$) are both obtained for the samples with more Zn content annealed at 750 °C or upward. The composites have a large surface area (137 m^2/g) with mesoporous structure after annealing at 750 °C. The SEM images reveal that the $ZnAl_2O_4$ crystals formed a multilayer structure with redundant ZnO particles which deposited on it. Furthermore, the maximum infrared reflectance is about 80% with an improvement of 35% in the infrared region after annealing at 950 °C compared with that of 450 °C, which indicates that these porous cryogels have a potential application as thermal insulating materials at a high temperature.

1. Introduction

Zinc dialuminum oxide composite materials have attracted considerable attention due to their synergetic effect [1] with excellent properties such as wide band gap [2], high stability and high mechanical strength [3,4]. The films of these composites with outstanding optical transmittance [5,6] have been utilized in a wide variety of applications including electric transducers [7], gas sensors [8], window layers and antireflection coatings in solar cells [9–11]. The bulk of these composites with opaque white color may hold the potential applications of optical and thermal resistance.

Aerogels are one of the most popular porous bulk materials owing to their fascinating properties such as low density, large surface area, high porosity, high optical transparency and low thermal conductivity, whose applications have been described well in several outstanding review articles [12–15]. However, the aerogels dried by supercritical drying (SD) must undergo in an autoclave way, which costs expensive [16]. Another promising drying method, vacuum freeze drying [17–19], is carried out to keep the textural properties of a wet gel, avoiding the formation of a liquid–vapor meniscus during the drying process. The dried gel termed as "cryogel" [20] also has similar properties to those of aerogels. This technique is much simpler and cheaper than the SD method, which is appropriate for practical large-scale productions. Most researchers have focused on the preparation and optical properties of alumina-zinc oxide composite (AZO or $ZnAl_2O_4$ spinel) films [21–25]. Few works have been reported on the bulk of these composites because the preparations of ZnO gels doping with aluminum are difficult and the obtained powders have poor optical properties [26]. Charinpanitkul et al. [1] investigated the synthesis and microstructure of zinc aluminate ($ZnAl_2O_4$) with an ethylacetoacetate (EAC) as chelating agent followed by peptizing condensation. Microstructure of the single crystal $ZnAl_2O_4$ with the face centered cubic arrangement was obtained after annealing at the higher temperature than 400 °C. Chen et al. [27] fabricated the $ZnO/ZnAl_2O_4$ core–shell nanostructures through an interfacial solid-state reaction between ZnO and Al_2O_3 involving the Kirkendall effect. Nian et al. [28] reported highly transparent conductive electrode through aqueous solution fabricated Al_2O_3–ZnO nanocrystals. Recently, the $ZnAl_2O_4$ with excellent luminescent

* Corresponding author at: Anhui Province Key Laboratory of Environment-friendly Polymer Materials, School of Chemistry and Chemical Engineering, Anhui University, Hefei 230601, China. Tel.: +86 551 63861480; fax: +86 551 63861480.
** Corresponding author at: School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China. Tel.: +86 773 2316370; fax: +86 773 2316370.
E-mail addresses: ausulf@sina.com (L. Su), Miaolei@guet.edu.cn (L. Miao).

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properties has also been demonstrated [29,30]. Therefore, the synthesis of aluminum-zinc oxides composites bulk in a cost-effective way and the study of the optical properties are still challengeable.

In this study, we report a novel technique to prepare zinc aluminate spinel composites by using a sol–gel method followed by vacuum freeze drying [31]. The wet gels are prepared by dispersing aluminum and zinc precursors into the acid-water without any other gelation initiators or organic solvents followed by the vacuum freeze drying directly, which lowers the cost and simplifies the process greatly. Excellent infrared reflectance is found in the obtained porous cryogels powders, which can make up for the limitations of silica emission in the infrared region [32] while it is used as a thermal insulator at a high temperature [33–35]. Here, the effects of calcination temperatures and molar ratios of Al/Zn on the microstructure and optical properties of the cryogels are investigated in detail.

2. Experimental procedure

2.1. Materials preparation

The chemicals used for the preparation of alcogels were aluminum sec-butoxide (ASB, 97%), zinc acetate [$Zn(CH_3COO)_2{\cdot}2H_2O$, 99.9%], acetic acid (HAc, 99.9%), nitric acid (HNO_3, HPLC) and urea (99.9%) that were purchased from Aladdin Reagent Database Inc. (China). The double distilled water (H_2O) was prepared in the authors' laboratory.

The aluminum-zinc oxides wet gels were synthesized via a sol–gel technology using a co-precursor method. For the alumina part, ASB as a precursor was dispersed in the hot water (80 °C) and stirred for 5 min, then a diluted HNO_3 (1.0 mol/L) was added under constant stir for 30 min at 80 °C to get a translucent alumina sol. The molar ratio of ASB:H_2O:HNO_3 was kept in 1:100:0.2. Specially, the reaction temperature of the alumina sol was required 80 °C at least to induce the hydrolysis of the precursor for following polycondensation of the gel network, which prevented the decomposing of the precursor to form the white $Al(OH)_3$ precipitate. For the zinc solution [36], $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved in water using HAc (0.01 mol/L) as a catalyst under continuous stir for 30 min at 60 °C with the molar ratio of $Zn(CH_3COO)_2{\cdot}2H_2O$:$H_2O$:HAc = 1:40:1.0 × 10^{-3}. Then the zinc solution was added into the aluminum sol corresponding to [Al]/[Zn] molar ratios of 7:1, 5:1, 3:1, 1:1 and 1:3 under vigorous stir for 30 min, followed by the addition of urea with molar ratio to ASB as 0.67:1 for condensation. The obtained homogeneous mixed solution was transferred to a culture dish (inner diameter is 100 mm, the height is 15 mm) and gelation occurred after aged at 80 °C for 5 h. The transparent gels were dried by a vacuum freeze dryer (Christ Alpha 2-4 *LSC*, Germany). Finally, the obtained cryogel powders with opaque white color were annealed at 450 °C, 750 °C and 950 °C for 4 h, respectively. The nanocomposites were denoted as A1Z1 for the sample of [Al]/[Zn] = 1:1 and the same for other samples with different molar ratios.

2.2. Characterization methods

The thermal stability of the zinc aluminate spinel cryogels was estimated by thermo gravimetric and differential analyses (TG–DTA, NETZSCH STA 409, Germany), in nitrogen during heating to 1400 °C at 10 °C/min. The crystallizing nature of the cryogel powders was examined by X-ray diffraction (XRD, X'Pert Pro MPD, Holland). The porous properties of the cryogels were characterized by nitrogen absorption/desorption measurement (Autosorb-iQ, Quantachrome, USA). The specific surface area and pore size distributions were analyzed by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method, respectively. The microstructure of the aluminum-zinc oxide cryogels was observed by a Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi S-4800, Japan). The atomic percentage of the annealed composites was investigated by energy dispersive X-ray spectroscopy (EDS, HORIBA EMAX, Japan). The hemispherical reflectance spectra of the cryogel powders were measured by a UV/VIS spectrometer (Lambda 750, Perkin Elmer, USA) in combination with a Fourier Transform Infrared spectroscopy (FT-IR, Bruker TENSOR 27, Germany) with the integrating sphere.

3. Results and discussion

3.1. Formation of aluminum-zinc oxides cryogel powders

The aluminum-zinc oxides nanocomposite cryogels can be synthesized by using a sol–gel method followed by vacuum freeze drying as shown in Fig. 1. Stable sols with homogeneously dispersed particles (Al^{3+} and Zn^{2+}) were obtained by using water as a solvent in this technique.

Gelation occurred after the addition of base-catalyst (urea) due to the condensation reaction of the alumina gel networks with disperse zinc oxides sols, which promotes the formation of aluminum-zinc oxides gel. The merits of our synthesis are as follows. First, gels were formed by using H_2O as a reaction solvent for dissolution of precursors without any other organic solvent [6,37] and gelation initiator [5,26,38,39] which are usually applied in the reported preparation of Al_2O_3 and ZnO gel. It makes the cost decrease dramatically and is friendly to human and environment. Second, the gels can be dried directly in the freeze dryer without any solvent exchange steps due to the high freezing point of water (0 °C) compared with those of traditional solvents such as ethanol (−97.8 °C) and methanol (−117.3 °C), which simplifies the process greatly. Therefore, this new technique provides a cost-effective way for productions of such nanocomposites in a large scale.

3.2. Thermal analysis of aluminum-zinc oxides cryogel powders

The TG–DTA data of aluminum-zinc oxides cryogels for a typical sample as A1Z1 is presented in Fig. 2. The steady weight loss is about 5% up to 200 °C as a result of the evolution of physically

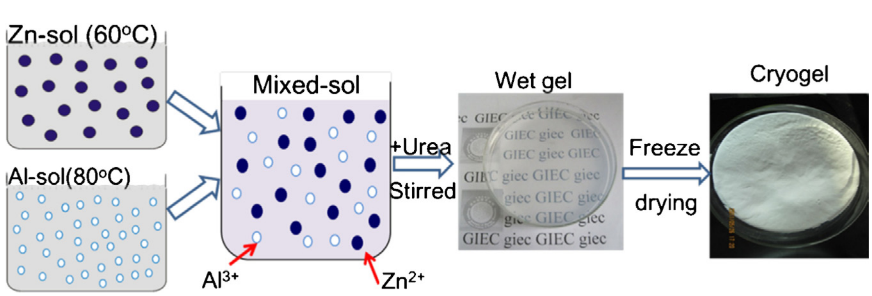

Fig. 1. Schematic illustration of the preparation of aluminum-zinc oxides cryogels.