Preparation and Properties of Nanoparticle-Coated ZrW2O8 Hollow Structure Postprint

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Abstract

Single-phase zirconium tungstate (ZrW2O8) hollow spheres were prepared using a coating method. Colloidal carbon spheres synthesized via hydrothermal method were employed as templates, and a zirconium tungstate precursor gel with network structure was prepared through a sol-gel process. A subsequent simple coating procedure yielded a core-shell structure comprising colloidal carbon spheres and zirconium tungstate gel, which upon calcination (held at 610°C for 10 h) with removal of the carbon templates afforded ZrW2O8 hollow spheres. The obtained ZrW2O8 hollow spheres possessed an average diameter of approximately 3 m and an average shell thickness of 1.5 m; the nanoscale ZrW2O8 particles forming the shell were rod-shaped irregular polyhedra measuring approximately 500 nm × 50 nm × 50 nm. FTIR and TG-DTA analyses demonstrated that the product was cubic-phase ZrW2O8 hollow spheres with a density of 2.8 g/cm^3, representing a 45% reduction from the theoretical value. The hollow spheres exhibited favorable negative thermal expansion characteristics; within the temperature range of room temperature to 200°C, the negative expansion coefficient was slightly lower than the theoretical value, with an average coefficient of thermal expansion of -11.4$×10^{-6}$ K^{-1}.

Full Text

Preparation and Properties of ZrW_2O_8 Hollow Structures Coated with Nanoparticles

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Abstract

Colloidal carbon microspheres were prepared from aqueous glucose solutions via a hydrothermal synthesis procedure, then used as templates to fabricate submicron core/shell structured precursors of carbon spheres/ZrW_2O_8 through a sol-gel method. These templates provided reactive surfaces that facilitated the deposition of nano-sized ZrW_2O_8 particles. Hollow spheres of ZrW_2O_8 were subsequently produced by calcining the precursors at 610°C for 10 hours to remove the colloidal carbon sphere templates. The final ZrW_2O_8 spheres, with an average size of approximately 3 m, were composed of single-phase nano-sized ZrW_2O_8 particles. Their density was measured to be 2.8 g/cm^3, approximately 45% lower than the theoretical value. FTIR and TG-DTA analyses confirmed the formation of cubic-phase ZrW_2O_8 hollow spheres. The product exhibited excellent negative thermal expansion characteristics, with an average thermal expansion coefficient of -11.4$×10^{-6}$ K^{-1} in the temperature range from room temperature to 200°C, which is slightly lower than the theoretical value.

KEYWORDS: inorganic non-metallic materials, colloidal carbon spheres, nano-layered structures, NTE, ZrW_2O_8

Introduction

As material applications continue to expand, performance requirements have become increasingly demanding. Beyond excellent mechanical properties, materials must also satisfy stringent thermal performance criteria, particularly regarding dimensional stability. To meet special requirements for thermal geometric stability and thermal shock resistance, the development of low-thermal-expansion and zero-expansion materials has emerged as a new branch of materials research. Negative thermal expansion (NTE) materials, which contract with increasing temperature, can be used as additives with positive thermal expansion matrix materials to fabricate composites with controlled thermal expansion coefficients. Such composites are valuable for high-precision optical systems, fiber optic systems, electrical devices, and thermal packaging materials for Bragg gratings.

Cubic-phase ZrW_2O_8 exhibits isotropic behavior and a large negative expansion coefficient (-8.9$×10^{-6}$ K^{-1}) across a broad temperature range from -273°C to 777°C, providing a foundation for widespread applications. However,

ZrW_2O_8 has a narrow thermodynamic stability range, existing only between 1105-1257°C. It decomposes into ZrO_2 and WO_3 between 780-1105°C, and forms a ZrO_2-WO_3 amorphous glass phase at higher temperatures. Consequently, solid-state synthesis requires prolonged high-temperature reactions. Additionally, because WO_3 is volatile at high temperatures, preparing single-phase ZrW_2O_8 is challenging. Wet chemical methods offer better compositional homogeneity and reliable process control. Various techniques have been employed to synthesize ZrW_2O_8 powders and films, including solid-state methods, sol-gel methods, combustion synthesis, microwave methods, chemical co-precipitation, and hydrothermal synthesis. The sol-gel method enables molecular-level mixing of reactants, reducing reaction temperatures and improving product purity.

Despite its excellent properties, ZrW_2O_8 must ensure both thermal geometric stability and lightweight characteristics for aerospace applications. With a density of 5.08 g/cm^3, ZrW_2O_8 powder is nearly twice as dense as typical aluminum matrix materials. Therefore, fabricating large-volume, lightweight ZrW_2O_8 hollow sphere structures can reduce composite density while maintaining thermal expansion coefficient, thereby achieving weight reduction. Hollow spheres are primarily prepared through physical methods (solvent methods, swelling methods, gas blowing insertion) and chemical methods (template methods, microemulsion methods, sol-gel methods, hydrothermal methods). Template methods are simple and effective, with sacrificial templates being the main approach. Common templates include latex spheres, microemulsions, and polymer micelles.

Caruso et al. used polystyrene (PSt) latex particles as templates, relying on electrostatic interactions to alternately assemble SiO_2 nanoparticles with PDADMAC onto the outer layer to obtain core-shell particles with ideal shell thickness, then dissolved the PSt template to obtain SiO_2 hollow spheres. Peng et al. used SiO_2 colloidal crystal arrays as templates, infiltrated them with styrene monomer for polymerization, extracted SiO_2 particles with hydrofluoric acid to obtain three-dimensionally ordered mesoporous polystyrene modules, then attached titanium alkoxide hydrolysis products (TiO_2) to the module surfaces, and finally dissolved the modules to obtain three-dimensional arrays of TiO_2 hollow spheres. Shiho used PSt template particles with $FeCl_3$ as iron source, urea as precipitant, and PVP as stabilizer to prepare metallic Fe hollow spheres. These template-based methods typically require surface modification of templates and involve complex coating processes, often necessitating organic solvents, stabilizers, and surfactants. In contrast, colloidal carbon spheres, due to their excellent properties, have been widely used as templates for preparing hollow structures.

Compared with traditional templates, colloidal carbon sphere templates offer simpler synthesis methods using glucose or sucrose as precursors without requiring organic solvents, initiators, or surfactants. Their properties can be optimized by adjusting parameters such as particle size, chemical composition, structure, and crystallinity. The carbon sphere surface structure is similar to polysaccharides, featuring abundant hydroxyl and carboxyl functional groups

that provide excellent hydrophilicity. Carbon sphere templates can be removed by calcination in air or oxygen. Hollow structures of W_2O_3, GaN, Ga_2O_3, SnO_2, and Al_2O_3 have been prepared using carbon sphere templates. This work employs glucose-derived colloidal carbon spheres as templates to prepare ZrW_2O_8 hollow structures via a sol-gel method and investigates their properties.

Experimental Procedures

1.1 Preparation of Colloidal Carbon Spheres Six grams of anhydrous glucose (Sinopharm Chemical Reagent) was dissolved in 40 mL deionized water. After stirring for 30 minutes, the solution was transferred to a 50 mL hydrothermal reactor (Teflon liner) and reacted at 200°C for 4 hours, then cooled to room temperature to obtain a brown colloidal solution. The product was centrifuged and washed three times each with deionized water and absolute ethanol, ultrasonically dispersed, transferred to a petri dish, and dried at 80°C for 5 hours.

1.2 Preparation of ZrW_2O_8 Hollow Spheres The starting materials were analytical-grade zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, Aladdin) and ammonium metatungstate ($(NH_4)_6W_{12}O_{39} \cdot xH_2O$, Alfa Aesar). Appropriate amounts of $(NH_4)_6W_{12}O_{39}$ and $ZrOCl_2 \cdot 8H_2O$ were weighed according to the stoichiometric W:Zr ratio of 2:1 and dissolved to prepare 50 mL solutions of 1 mol/L and 0.5 mol/L, respectively. Under magnetic stirring, both solutions were simultaneously added dropwise to 25 mL deionized water, immediately forming a white precipitate. After continuous stirring for 10 hours, 125 mL of 6 mol/L hydrochloric acid was added to the mixture, which was then refluxed for 48 hours. After cooling to room temperature, the supernatant was decanted and the remaining liquid was filtered. The gel was allowed to stand at room temperature for 7 days. An appropriate amount of colloidal carbon spheres was added with stirring, left to stand at room temperature for 12 hours, centrifugally separated, and then transferred to a 60°C oven for drying to obtain the core-shell structure of zirconium tungstate precursor coated carbon spheres. The precursor powder was placed in an alumina crucible in a muffle furnace for calcination to completely volatilize water and other volatile substances. During calcination, the heating rate was 1°C/min, with a hold at 500°C for approximately 2 hours, followed by heating to 610°C and holding for 10 hours.

1.3 Material Characterization Thermogravimetric-differential thermal analysis (TG-DTA) was performed on 25 mg samples using a TA Q600 integrated thermal analyzer (TA Instruments) with argon as protective atmosphere at a heating rate of 10°C/min. Sample morphology was observed and analyzed using an FEI Sirion20 scanning electron microscope (SEM). Phase structure was determined using a Bruker D8 Advance X-ray powder diffractometer (XRD) with Cu Kα radiation at a continuous scanning rate of 10°/min. High-temperature X-ray diffraction was used to measure diffraction

patterns at various temperatures for calculating lattice parameters at different temperatures, with a continuous scanning rate of 5°/min. Functional groups of the templates were identified using a Nicolet 6700 Fourier-transform infrared spectrometer (FTIR) with wavenumber range of 4000-400 cm^{-1}. True density of the powder was tested using a DX-120T powder density meter.

Results and Discussion

2.1 Morphology of Colloidal Carbon Spheres/ZrW_2O_8 [Figure 1: see original paper] shows SEM images of the colloidal carbon spheres, which appear as smooth, uniform spheres with an average diameter of approximately 1.5 m. The growth of colloidal carbon spheres under hydrothermal conditions follows the Lamer model: glucose molecules first undergo dehydration polymerization to form long-chain aromatic compounds and oligosaccharides. When the solution reaches critical supersaturation, nucleation occurs instantaneously. Cross-linking reactions between linear or branched oligosaccharide molecules due to dehydration ultimately cause carbonization and agglomeration into spheres. Subsequently, solutes in the solution continuously diffuse to the nucleus surface, resulting in isotropic growth of the formed nuclei until reaching the desired size. While traditional template methods often require surface modification, colloidal carbon spheres have a surface structure similar to polysaccharides, featuring abundant hydroxyl and carbonyl groups that provide excellent hydrophilicity, enabling direct use as templates without surface modification. After dispersing colloidal carbon spheres into solution, precursor species readily adsorb onto the carbon sphere surfaces.

[Figure 2: see original paper] presents SEM images of ZrW_2O_8 hollow spheres, showing diameters of approximately 3 m with relatively thick shells. The nanoscale particles constituting the shell network structure are rod-shaped irregular polyhedra with dimensions of approximately 500 nm × 50 nm × 50 nm. The measured density of the obtained ZrW_2O_8 hollow spheres is 2.8 g/cm^3, representing a reduction of about 45% compared to the theoretical value.

2.2 FTIR Analysis of Colloidal Carbon Spheres/ZrW_2O_8 [Figure 3a: see original paper] shows the FTIR spectrum of colloidal carbon spheres. The absorption peak at 3429 cm^{-1} corresponds to −OH groups, while the peak at 1026 cm^{-1} corresponds to C−OH absorption, indicating abundant hydroxyl groups on the carbon sphere surface. The peak at 1700 cm^{-1} corresponds to C=O stretching vibration, and 1623 cm^{-1} corresponds to conjugated alkene skeleton vibration. Absorption peaks at 1508 and 1384 cm^{-1} indicate aromatization during glucose hydrolysis. Additionally, absorption peaks at 2367/2359 cm^{-1} may correspond to carbon-carbon triple bonds. [Figure 3b: see original paper] and [Figure 3c: see original paper] show FTIR spectra of the colloidal carbon sphere-ZrW_2O_8 core-shell structure and ZrW_2O_8 hollow spheres, respectively. Comparing the spectra before and after coating reveals minimal changes

in the infrared absorption of functional groups on the carbon sphere surface. In the core-shell structure spectrum, the region near 3328 cm^{-1} corresponds to −OH stretching vibration, a bending vibration peak for structural water −OH appears at 1401 cm^{-1}, and C=C is present at 1649 cm^{-1}. Meanwhile, peaks at 960, 851, 749, and 652 cm^{-1} indicate the presence of ZrW_2O_8. In the hollow sphere spectrum, the peak at 3448 cm^{-1} corresponds to physically adsorbed water O−H stretching vibration on the ZrW_2O_8 surface, and the peak near 1428 cm^{-1} represents O−H bending vibration. Peaks at 997, 908, and 876 cm^{-1} can be attributed to symmetric stretching vibrations of WO_4 tetrahedra, while peaks at 803, 741, 699, and 648 cm^{-1} indicate asymmetric stretching vibrations of WO_4. The broad peak near 500 cm^{-1} corresponds to ZrO_2 lattice vibration modes. Based on the XRD pattern of the hollow sphere structure shown in [Figure 4: see original paper], the reaction product is identified as single-phase ZrW_2O_8.

2.3 TG-DTA Analysis of ZrW_2O_8 Precursors [Figure 5: see original paper] presents TG-DTA curves of the synthesized ZrW_2O_8 precursor from room temperature to 800°C. The curve shows two distinct mass loss regions: approximately 12.7% mass loss from room temperature to 233°C, and 6.7% mass loss from 233 to 565.9°C. According to the DSC curve, the first significant weight loss region corresponds to two endothermic peaks. An endothermic peak appears at 73.4°C, corresponding to loss of adsorbed water from the precursor, while a sharp endothermic peak at 187.7°C accompanies obvious mass reduction due to loss of crystallization water and possible volatilization of amorphous phases near this temperature. The second weight loss region corresponds to three exothermic peaks. The exothermic peak at 479.0°C can be attributed to removal of the colloidal carbon sphere template, leading to the selection of a slightly higher treatment temperature (500°C) for template removal calcination. The exothermic peak near 612.8°C corresponds to ZrW_2O_8 synthesis from the precursor.

2.4 Formation Mechanism of ZrW_2O_8 Hollow Spheres Due to the stable network architecture of the ZrW_2O_8 precursor gel, the obtained coating layer is thick, resulting in large particle sizes for the colloidal carbon sphere–ZrW_2O_8 precursor core-shell structure that prevent direct TEM imaging. However, FTIR analysis reveals infrared absorption peaks of ZrW_2O_8 precursor on the carbon sphere surface after coating. Additionally, the appearance of an exothermic peak at 479.0°C for carbon sphere template removal and an endothermic peak at 612.8°C for ZrW_2O_8 synthesis confirms the existence of the core-shell structure. After calcination, the colloidal carbon sphere template is completely removed, yielding single cubic-phase ZrW_2O_8. The measured product density of 2.8 g/cm^3, representing a reduction of approximately 45% compared to ZrW_2O_8 powder prepared directly by sol-gel methods, further corroborates the hollow structure formation.

[Figure 6: see original paper] illustrates the synthesis schematic for ZrW_2O_8 hollow spheres. First, colloidal carbon sphere cores are prepared in one step via hydrothermal synthesis, with surfaces exhibiting excellent hydrophilicity and abundant carboxyl and hydroxyl groups that enable metal ion adsorption. Carbon spheres are ultrasonically dispersed in ZrW_2O_8 precursor sol, where two metal cations (Zr^{4+}, W^{6+}) adsorb layer-by-layer onto the carbon sphere surface. The precursor undergoes heterogeneous deposition on the template surface, forming colloidal carbon sphere/ZrW_2O_8 precursor core-shell composite particles through a process called pre-adsorption. Finally, a simple calcination process removes the carbon sphere template and converts the precursor to pure-phase ZrW_2O_8, yielding the hollow sphere structure.

2.5 Negative Thermal Expansion Properties of ZrW_2O_8 Hollow Spheres [Figure 7: see original paper] shows XRD patterns of sol-gel prepared ZrW_2O_8 powder at different temperatures. The magnified view ([Figure 7b: see original paper]) reveals that ZrW_2O_8 diffraction peaks gradually shift to higher angles with increasing temperature, indicating that the ZrW_2O_8 unit cell volume decreases with temperature. By precisely collecting variable-temperature XRD data and using POWDER X software to calculate ZrW_2O_8 lattice parameters, the relationship between lattice parameters and temperature was plotted ([Figure 8: see original paper]). The results show that smaller particles correspond to smaller lattice parameters. Linear fitting indicates that the negative expansion coefficient of sol-gel prepared powder is higher than literature values, with an average thermal expansion coefficient of -11.4$×10^{-6}$ K^{-1} in the room temperature to 200°C range. This is related to the preparation method and selected temperature range, as an order-disorder phase transition occurs at 157°C, causing an inflection point in the expansion coefficient.

Conclusions

1. Using colloidal carbon spheres with surface-active functional groups as templates, ZrW_2O_8 hollow structures can be prepared via a sol-gel method. The abundant hydroxyl and carboxyl groups on the carbon sphere surface eliminate the need for surface modification, enabling direct ion adsorption. The precursor gel prepared by sol-gel method possesses a stable network structure that can form core-shell structures with colloidal carbon spheres through a simple coating process.

2. The sol-gel method reduces the synthesis temperature of ZrW_2O_8, while the colloidal carbon sphere template can be removed during calcination. Single-phase ZrW_2O_8 hollow sphere structures can be obtained by heat treatment at 610°C for 10 hours. The experimental ZrW_2O_8 hollow spheres exhibit a density of 2.8 g/cm^3, representing a reduction of approximately 45%. The ZrW_2O_8 hollow spheres demonstrate excellent

negative thermal expansion characteristics. Due to the small powder particle size, the negative expansion coefficient is slightly lower than theoretical values, with an average thermal expansion coefficient of -11.4$×10^{-6}$ K^{-1} from room temperature to 200°C.

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