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Original Research Paper

A general approach to monodisperse perovskite microspheres

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ABSTRACT

$BaTiO_3$, $PbTiO_3$, $SrTiO_3$, and $Pb(Zr,Ti)O_3$ microspheres with uniform size and narrow size distribution have been successfully synthesized by a novel hydrothermal and annealing approach. In this approach, the chemical reaction and crystallization process of the ABO_3 perovskite oxides were separated in two steps. Spherical particles containing the B-site ions were obtained first via a controlled hydrolysis and aging process. Then, during hydrothermal treatment, the A-site ions were incorporated *in situ* into the microspheres to form amorphous perovskite microspheres. The particles were further crystallized with preserved spherical morphology under subsequent annealing treatment. The BET surface areas of the TiO_2 gel particles, the amorphous $PbTiO_3$ and the as-annealed $PbTiO_3$ microspheres were 245.7 m^2/g, 41.67 m^2/g and 4.53 m^2/g, respectively, showing a significant change of the surface feature in the preparation process. This approach also allowed the microspheres diameters to be manipulated from 100 nm to 1500 nm in a controlled manner. Most of the microspheres were composed by closely packed nanosized particles. Furthermore, the $Pb(Zr,Ti)O_3$ microspheres with an average diameter of 200 nm exhibited single crystal features, indicating highly oriented growth in the crystallization process. The microspheres were very stable, and still maintained spherical shape after higher temperature calcination.

1. Introduction

Perovskite oxides with the general formula ABO_3 have attracted sustained scientific and technological interest due to their outstanding physical and chemical properties [1–3]. For instance, $BaTiO_3$ is widely used as a dielectric material in multilayered ceramic capacitors (MLCCs) because of its high dielectric constant [4], while $SrTiO_3$ is often used as a dielectric and photoelectric material [5]. As typical ferroelectric materials, the Pb-based perovskite oxides, e.g. $PbTiO_3$ and $Pb(Zr,Ti)O_3$, have significant applications in electronics such as piezoelectric actuator, sensors, nonvolatile memories, and ultrasonic transducers for their high spontaneous polarization and large piezoelectric displacement [6].

The formation of high quality perovskite ceramics is determined to a large extent by the powder characteristics. It has been commonly believed that spherical powders with a fine particle size, a non-agglomerated state, and a narrow size distribution are the most desirable for the compacting and sintering of ceramics [7–9]. Moreover, these monodisperse perovskite particles can also be served as ideal building blocks to construct other complex functional composites with ordered structures and coupling properties [10]. Until now, perovskite oxide particles with novel morphologies such as cubes [11], needles [12], rods [13,14], wires [15,16], tubes [17–19], and nanoparticles [20,21] have been successfully fabricated by different methods. However, it is still difficult to obtain monodisperse microspheres because of the instinct cubic crystal structure and anisotropic growth behavior of the perovskite particles. Reports on the synthesis of perovskite microspheres were mostly based on hydrothermal treatment of amorphous gel particles with metal hydroxides under alkaline conditions [22,23]. As the high solubility of the amorphous gel particles under alkaline conditions and elevated temperatures, perovskite microspheres were obtained only in a very limited range of hydrothermal synthesis conditions. Moreover, these microspheres were usually composed of weakly bonded primary particulates, and were losing the spherical shape by disintegrating into nanosized particulates during ultrasonic treatment. Recently, Demirörs and Imhof [24] presented a method for synthesizing monodisperse perovskite microspheres by postsynthesis addition of metal hydroxides to amorphous and porous titania colloids. However, as the titania colloids and the metal hydroxides were mixed by ultrasonic vibration, the stoichiometry of the *A*/*B* ratio was hard to control.

In this study, we report a novel approach for the fabrication of monodisperse perovskite microspheres by a combined hydrothermal

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Table 1
Detailed synthesis conditions for the preparation of typical samples.

Perovskite oxide	A-site ion source	*A* (mol/L)	*A*/*B* ratio	Hydrothermal temperature (°C)	Hydrothermal time (h)	KOH (mol/L)	Annealing temperature (°C)
$BaTiO_3$	$Ba(OH)_2{\cdot}8H_2O$	0.1	2:1	90	6	0	700
$PbTiO_3$	$Pb(NO_3)_2$	0.1	1:1	100	3	0.18	600
$SrTiO_3$	$Sr(OH)_2$	0.1	2:1	60	6	0	700
$Pb(Zr,Ti)O_3$	$Pb(NO_3)_2$	0.1	1:1	120	4	0.18	700

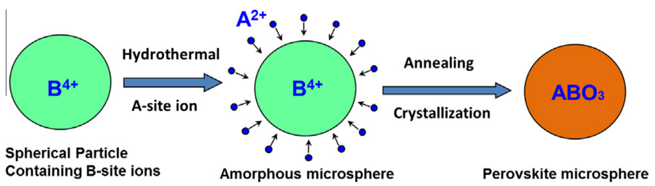

Fig. 1. Schematic illustration of the combined hydrothermal and annealing approach to the synthesis of perovskite microspheres.

and annealing process. Using this method, various kinds of perovskites microspheres like $BaTiO_3$, $PbTiO_3$, $SrTiO_3$ and $Pb(Zr,Ti)O_3$ have been successfully prepared in a relatively wide range of the synthesis conditions.

2. Experimental

2.1. Preparation of amorphous TiO_2 and $ZrTiO_4$ microspheres

Amorphous TiO_2 microspheres were prepared by controlled hydrolysis of $Ti(SO_4)_2$ as described by the literature [25]. In a typical synthesis, 4 mmol of $Ti(SO_4)_2$ was dissolved in 40 ml of deionized water and 2.0 g of polyvinylpyrrolidone(PVP) was dissolved in a mixed solution of 1-propanol (75 ml) and deionized water (35 ml). The two solutions were mixed together, and stirred for 3 h at 70 °C. After washed several times, the as-synthesised microspheres were aged in high alkaline solution at 60 °C for 12 h (KOH, 1 mol/L).

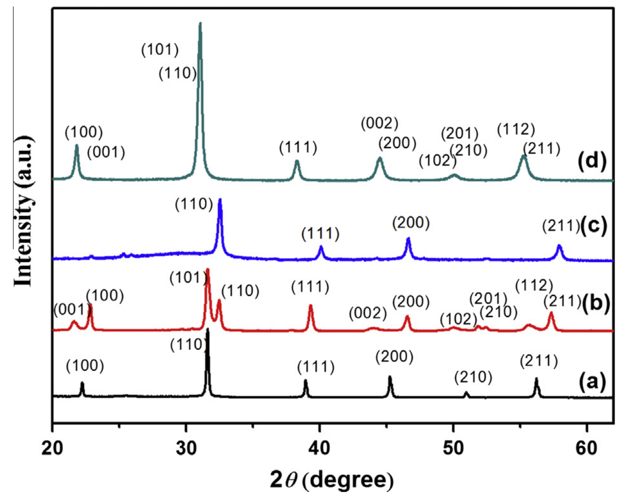

Fig. 3. XRD patterns of the perovskite microspheres: (a) $BaTiO_3$, (b) $PbTiO_3$, (c) $SrTiO_3$ and (d) $Pb(Zr,Ti)O_3$.

For the preparation of $ZrTiO_4$ microspheres, 2 mmol of $Ti(SO_4)_2$, 2 mmol of $ZrOCl_2$, 6 g of $CO(NH_2)_2$ and 2.0 g of PVP were dissolved in 150 ml deionized water. The mixed solution was stirred for 3 h at 90 °C. After washed several times, the as-synthesised powder was aged in high alkaline solution at 60 °C for 12 h (KOH, 1 mol/L).

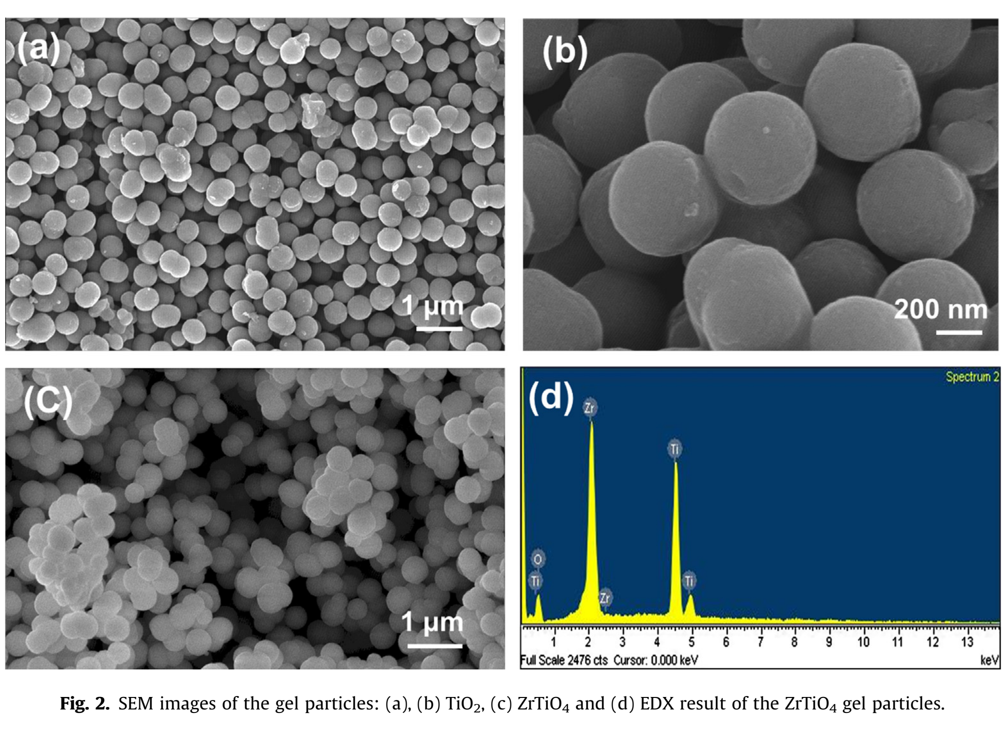

Fig. 2. SEM images of the gel particles: (a), (b) TiO_2, (c) $ZrTiO_4$ and (d) EDX result of the $ZrTiO_4$ gel particles.