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Preparation of mesoporous yttria-stabilized zirconia (YSZ) and YSZ–NiO using a triblock copolymer as surfactant

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Mesoporous yttria-stabilized zirconia (YSZ) and YSZ–NiO have been prepared for the first time using Pluronic P103 as a structure-directing agent and inorganic chlorides as precursors in a nonaqueous medium. After being fired at 500 °C for 2 h, mesostructured YSZ has a BET surface area of about 146 $m^2\ g^{-1}$, with an average pore size of 3.8 nm, while mesostructured YSZ–NiO has a BET surface area of about 108 $m^2\ g^{-1}$, with an average pore size of 4.5 nm.

1 Introduction

The successful preparation of the M41S family of mesoporous molecular sieves using a supramolecular templating approach has stimulated an explosion in research on the preparation of highly ordered mesoporous or nanostructured materials through templating techniques.[1–3] The ordering in these materials is a consequence of a self-assembly process that occurs spontaneously in an aqueous solution containing organic surfactants (anionic, cathodic, or neutral) and inorganic (oligo-) cations or anions.[4–8] The use of surfactant species to organize mesoporous silica has been widely explored. However, extension of the surfactant templating process to the formation of non-silica mesoporous oxides, especially complex transition metal oxides, has been much less successful, although these compounds display very interesting functionality for electrochemical and catalytic applications such as catalysis, separation, batteries and fuel cells.

Recently, it has been discovered that non-ionic alkyl poly(ethylene oxide) (PEO) surfactants and amphiphilic block copolymers (such as Pluronic surfactants) can be used to organize, not only mesostructured silica, but also mesostructured non-silica oxides.[9–13] This discovery represents a significant advance in the area of synthesis of mesoporous complex metal oxides. Pluronic surfactants are PEO–poly(propylene oxide) (PPO) triblock copolymers with the formula $(PEO)_n(PPO)_m(PEO)_n$, in which the PPO linkages act as the hydrophobic segments while the PEO linkages act as the hydrophilic segments. Since the chain length of the triblock copolymers can be tuned to balance the hydrophobic and hydrophilic portions in the ampliphilic surfactants, pore size and pore size distribution can be readily tailored using such surfactants. Using Pluronic surfactants as structure-directing agents and inorganic chlorides as precursors in non-aqueous solutions, Yang *et al.*[12,13] have recently prepared a series of thermally stable, ordered, large-pore mesoporous metal oxides and composites. In this article, we report our findings using Pluronic P103 surfactant as structure-directing agents for the preparation of mesoporous yttria-stabilized zirconia (YSZ) and YSZ–NiO composite for electrochemical applications such as in solid oxide fuel cells (SOFCs).[14]

2 Experimental

The starting materials for preparation of mesoporous YSZ and YSZ–NiO are zirconium dichloride oxide, yttrium chloride, nickel chloride, and Pluronic P103. In a typical synthesis, 1 g Pluronic P103 was dissolved in 15 ml ethanol. To this solution, 0.01 mol of the appropriate inorganic chloride precursors were added and stirred until a clear solution was obtained. The resulting sol solution was gelled in an open porcelain dish for 3 days at 40 °C in an oven with saturated water vapor. The resulting gel was then dried in a vacuum oven. The dried gel was pulverized and calcined in air at 500 to 800 °C for 2 h with a heating and cooling rate of 2 °C min^{-1}. Low-angle and wide-angle X-ray powder diffraction patterns were obtained on a Scintag X1 diffractometer using Cu-Kα radiation. A Rheometric Scientific STA 1500 instrument was used for simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) with a heating rate of 2 °C min^{-1}. Transmission electron microscopy (TEM) studies were performed on a Hitachi HF2000 electron microscope operating at 200 keV. The samples were prepared by directly dispersing fine powders of the products onto holey carbon nickel grids. The

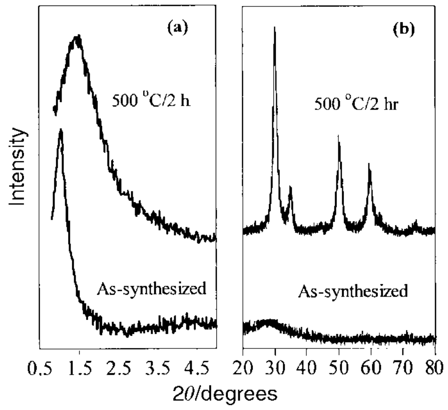

Fig. 1 (a) Low-angle and (b) wide-angle X-ray diffraction (XRD) patterns of as-synthesized (40 °C/3 days) and as-calcined (500 °C/2 h) mesoporous YSZ.

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nitrogen adsorption and desorption isotherms at 77 K were measured using a Coulter SA 3100 surface analyzer after degassing of the samples at 200 °C for 24 h with dry nitrogen.

3 Results and discussion

3.1 Preparation of mesoporous YSZ

Fig. 1 shows several typical XRD patterns for mesostructured YSZ prepared using Pluronic P103 as the structure-directing agent. In the low angle range, only one peak was observed for the as-synthesized YSZ inorganic/polymer mesostructure, corresponding to $d = 84$ Å, indicating that the surfactant molecules were organized into a hexagonal structure after being aged at 40 °C for 3 days. When the as-synthesized YSZ was calcined at 500 °C for 2 h, the small angle diffraction peak shifted to a higher angle, corresponding to $d = 59$ Å, suggesting that the mesoporous superstructure was preserved after the surfactant was removed by calcination. However, the pores contracted from 84 to 59 Å, as evidenced from the shift of the XRD peak. When the calcination temperature was increased to 600 °C, the low angle XRD peak disappeared, implying that the ordered mesostructure had been destroyed. The XRD patterns shown in Fig. 1(b) indicate that the as-synthesized YSZ is amorphous while the calcined YSZ is crystalline (Fluorite structure).

The TG and DSC curves obtained from an as-synthesized YSZ sample (inorganic/polymer mesostructure) are shown in Fig. 2. The TG curve shows that most weight loss occurred below 490 °C, indicating that the block copolymer can be completely removed upon calcination in air at 500 °C for 2 h. The two exothermal events observed from the DSC curve correspond to the release of H_2O, CO and CO_2 from the decomposition of the surfactant.

A representative TEM image of a YSZ sample calcined at 500 °C for 2 h is shown in Fig. 3. Mesostructures with short-range hexagonal order can be seen and the pore size determined from the TEM micrographs is in good agreement with that determined from the XRD pattern. Thus, we have obtained mesoporous YSZ (without surfactant) stable up to 500 °C.

A typical nitrogen adsorption–desorption isotherm curve and the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution curve for a YSZ sample calcined at 500 °C for 2 h are shown in Fig. 4. The calculated Brunauer–Emmett–Teller (BET) surface area is about 146 $m^2\,g^{-1}$. The nitrogen isotherm curve has a well-defined step for the relative pressure P/P_0 ranging from 0.4 to 0.8, characteristic of the filling of the framework-confined mesopores,[15] confirming that the YSZ sample is still mesoporous after calcination at 500 °C for 2 h.

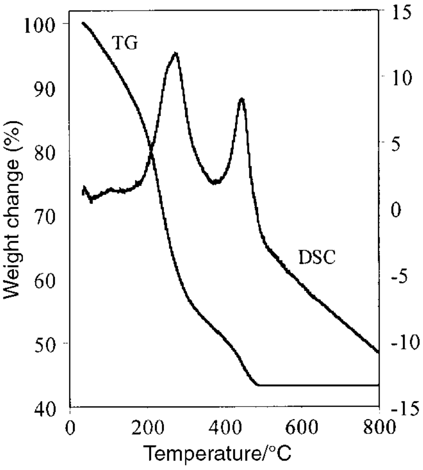

Fig. 2 Weight change and heat flow recorded for as-synthesized mesostructured YSZ. The heating rate was 2 °C min^{-1}.

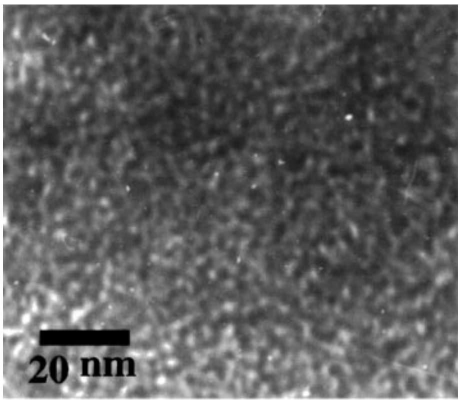

Fig. 3 A representative TEM micrograph of mesoporous YSZ calcined at 500 °C for 2 h.

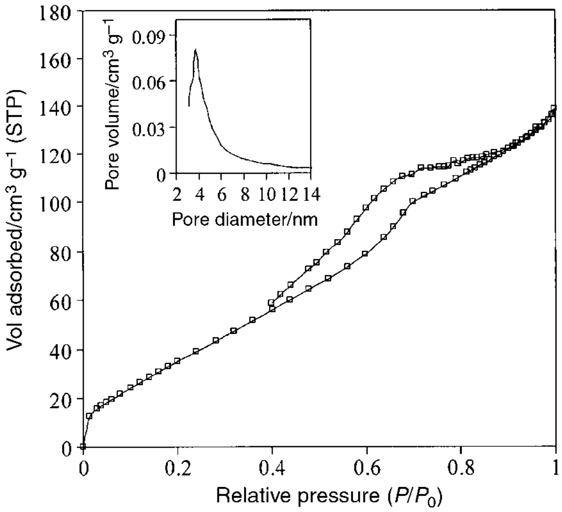

Fig. 4 Nitrogen adsorption–desorption isotherms for mesoporous YSZ calcined in air at 500 °C for 2 h. The corresponding BJH pore size distribution is shown in the inset.

As shown in the inset in Fig. 4, the average pore size in the YSZ sample is about 3.8 nm.

3.2 Preparation of mesoporous YSZ–NiO

Fig. 5 shows representative XRD patterns for mesostructured YSZ–NiO composite prepared using Pluronic P103 as the structure-directing agent. In the low angle range, one diffraction peak (corresponding to $d = 79$ Å) was observed for the as-

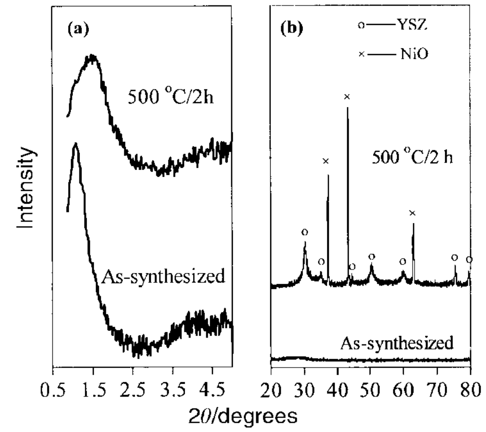

Fig. 5 (a) Low-angle and (b) wide-angle X-ray diffraction (XRD) patterns of as-synthesized (40 °C/3 d) and as-calcined (500 °C/2 h) mesoporous YSZ–NiO.

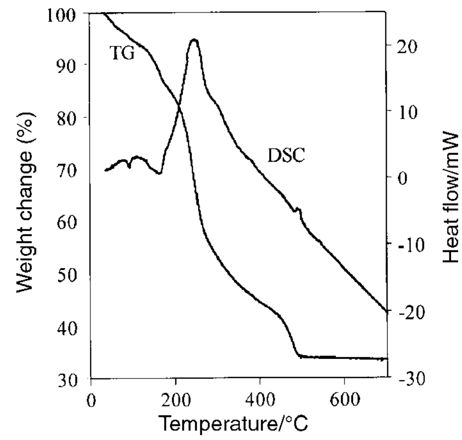

Fig. 6 Weight change and heat flow recorded for as-synthesized mesostructured YSZ–NiO composite. The heating rate was 2 °C min^{-1}.

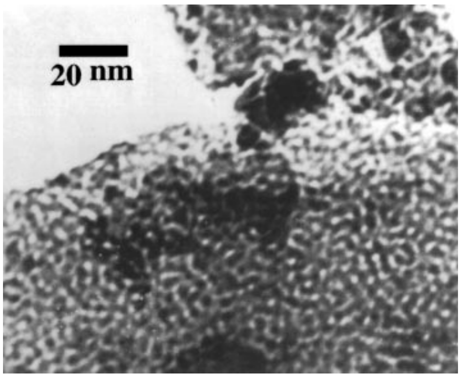

Fig. 7 A representative TEM micrograph of mesoporous YSZ–NiO composite calcined in air at 500 °C for 2 h.

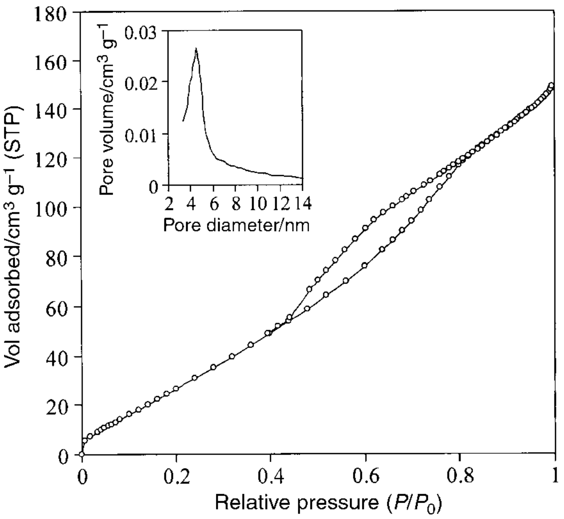

Fig. 8 Nitrogen adsorption–desorption isotherms for mesoporous YSZ–NiO composite calcined in air at 500 °C for 2 h. The corresponding BJH pore size distribution is shown in the inset.

synthesized YSZ–NiO inorganic/polymer mesostructure. After being held at 500 °C for 2 h, the diffraction peak for the as-calcined sample shifted to a higher angle, corresponding to $d = 56$ Å. However, when the calcination temperature was increased to 600 °C, the low angle XRD peak disappeared, indicating that the ordered mesostructure of YSZ–NiO became disordered. The XRD patterns shown in Fig. 5(b) indicate that the as-synthesized YSZ–NiO is amorphous while the calcined YSZ–NiO is crystalline.

TG and DSC curves for an as-synthesized YSZ–NiO sample are shown in Fig. 6. The TG curve indicates that all weight loss occurred below 500 °C, suggesting that the block copolymer is completely removed upon calcination in air at 500 °C for 2 h.

A TEM image of YSZ–NiO composite calcined at 500 °C for 2 h is shown in Fig. 7. Mesostructures with short-range hexagonal order can be seen and the pore sizes determined from the TEM micrographs are in good agreement with those obtained from the XRD patterns. Consequently, we have obtained mesoporous YSZ–NiO stable up to 500 °C.

A representative N_2 adsorption–desorption isotherm curve and the corresponding BJH pore size distribution curve for a YSZ–NiO sample calcined at 500 °C for 2 h are shown in Fig. 8. A hysteresis loop that resembles typical H1-type isotherms is observed for the mesoporous YSZ–NiO sample.[16] The calculated BET surface area is about 108 $m^2 g^{-1}$. BJH analysis shows that the calcined hexagonal mesoporous YSZ–NiO exhibits mean pore sizes of 4.5 nm.

4 Summary

Mesoporous YSZ and YSZ–NiO composite have been successfully prepared using Pluronic P103 as the structure-directing agent and the corresponding metal chlorides as precursors in an alcoholic medium. The surfactant can be completely removed by firing the mesostructured inorganic/polymer powders in air at 500 °C for 2 h. Mesostructured YSZ and YSZ–NiO materials with crystalline walls stable up to 500 °C have been obtained.

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