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Preparation and characterization of mesoporous MO_2 (M = Ti, Ce, Zr, and Hf) nanopowders by a modified sol–gel method

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Abstract

Mesoporous high surface area and high crystallinity MO_2 powders (TiO_2, CeO_2, ZrO_2, and HfO_2) were synthesized by a modified sol–gel method using laurylamine hydrochloride, metal alkoxide and acetylacetone. The prepared MO_2 powders, characterized by XRD, nitrogen adsorption isotherm, SEM, TEM, and SAED, had crystalline size of about 5–15 nm, specific surface area of 44–80 m^2/g, and a narrow pore size distribution with average pore diameter of about 3–6 nm. This synthesis method provides a new simple route to fabricate nanostructured materials under mild conditions.

Keywords: Mesoporous oxides; Characterization; Sol–gel; Mild conditions

1. Introduction

Metal oxides with wide or moderate band gap, such as TiO_2, CeO_2, ZrO_2, and HfO_2, have been widely used for various applications like semiconductor materials in dye-sensitized solar cell, catalysts, fuel cells, resistors, gas sensors, transparent optical device, and optical coatings [1–8]. Their functional properties are influenced by many factors such as crystallinity, particle size, surface area, and preparation [8–13]. In previous works, mesoporous TiO_2-based nanopowders with pore size about 5 nm were synthesized by a modified sol–gel method in aqueous phase using a surfactant-assisted process, offering a high photocatalytic activity [11]. This process has also been applied to a semiconductive material in dye-sensitized solar cells [12–15].

In this study, the surfactant-assisted process has been expanded to prepare other metal oxides. Mesoporous CeO_2, ZrO_2, HfO_2, as well as TiO_2 were synthesized using laurylamine hydrochloride (LAHC)/metal alkoxide modified with acetylacetone (ACA) system. The nanopowders characteristics will be reported.

2. Experimental

For mesoporous TiO_2 preparation, tetraisopropylorthotitanate (TIPT, Tokyo Chemical Industry Co., Ltd.) was mixed with the same mole of ACA (Nacalai Tesque, Inc.) to slowdown the hydrolysis and the condensation reactions [11–13]. Subsequently, 0.1 M LAHC (Tokyo Chemical Industry Co.) aqueous solution (as the surfactant, pH 4–4.5) was added in the solution (molar ratio of TIPT to LAHC was 4), and it was stirred at room temperature for 1 h. After kept stirring at 40 °C for 24 h, it was put into an oven at 80 °C for 1 week. The alcohol by-product was removed by drying at 80 °C for 24 h, followed by calcinations at 400 °C for 4 h (Fig. 1). Mesoporous CeO_2, ZrO_2, and HfO_2 nanopowders were synthesized using the same route of TiO_2 by changing alkoxide precursors (Table 1).

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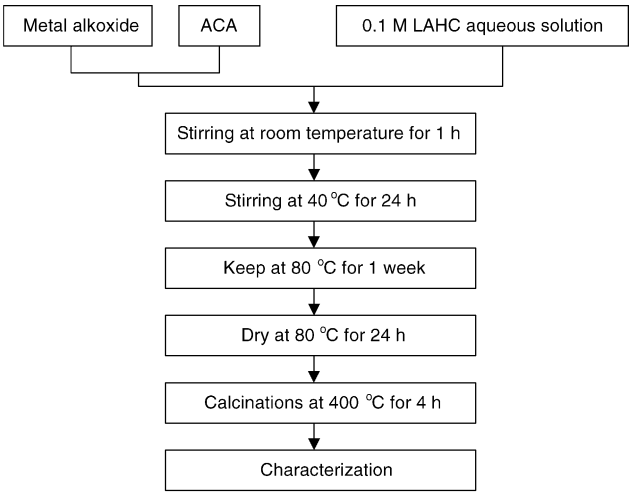
Table 1
Physicochemical properties of the prepared metal oxides calcined at 400 °C for 4 h

Oxide	Inorganic precursor	Crystalline structure	Crystalline size (nm)	Pore size (nm)	Pore volume (cm^3/g)	Surface area (m^2/g)
TiO_2	$Ti(OCH(CH_3)_2)_4$	Tetragonal (anatase)	7–15	5–6	0.197	80
CeO_2	$Ce(O(CH_2)_3CH_3)_4$	Cubic (fluorite-type)	5–10	3–4	0.113	73
ZrO_2	$Zr(O(CH_2)_3CH_3)_4$	Tetragonal	7–15	3–4	0.063	72
HfO_2	$Hf(O(CH_2)_3CH_3)_4$	Monoclinic	7–15	3–5	0.057	44



Condition: [Metal alkoxie] / [ACA] = 1, [Metal alkoxide] / [LAHC] = 4

Fig. 1. Flow sheet of processing steps.

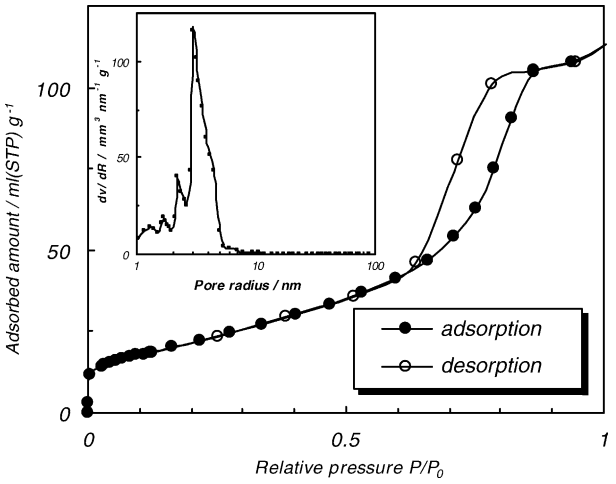


Fig. 3. Nitrogen adsorption isotherm pattern of TiO_2 calcined at 400 °C for 4 h, and the pore size distribution of sample with pore diameter about 5–6 nm (inset).

The crystalline structure of samples was evaluated by X-ray diffraction (XRD, RIGAKU RINT 2100). The microstructure of the prepared materials was analyzed by scanning electron microscopy (SEM, JEOL JSM-6500FE), transmission electron microscopy (TEM, JEOL JEM-200CX), and selected-area electron diffraction (SAED). The nitrogen adsorption isotherm and Brunauer–Emmett–Teller (BET) specific surface area of materials, which were outgassed overnight at 200 °C, were measured with BEL Japan BELSORP-18 Plus equipment.

3. Results and discussion

3.1. Mesoporous TiO_2

The X-ray diffraction pattern of the TiO_2 sample calcined at 400 °C for 4 h, demonstrated the formation of anatase phase as shown in Fig. 2. The peaks were rather sharp, which indicated relatively high crystallinity.

Fig. 3 gives the nitrogen adsorption isotherm of the TiO_2 sample calcined at 400 °C for 4 h, which shows a typical

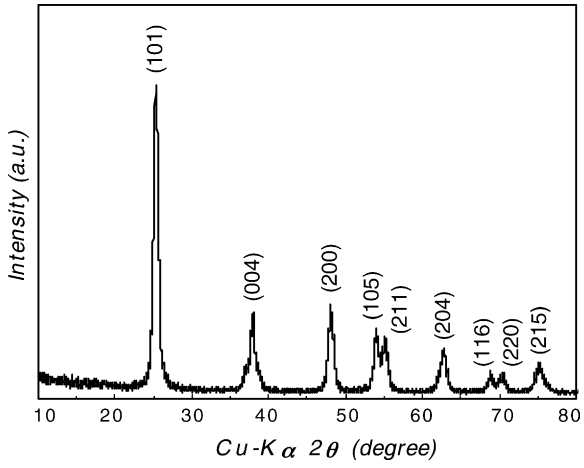


Fig. 2. X-ray diffraction pattern of TiO_2 calcined at 400 °C for 4 h.

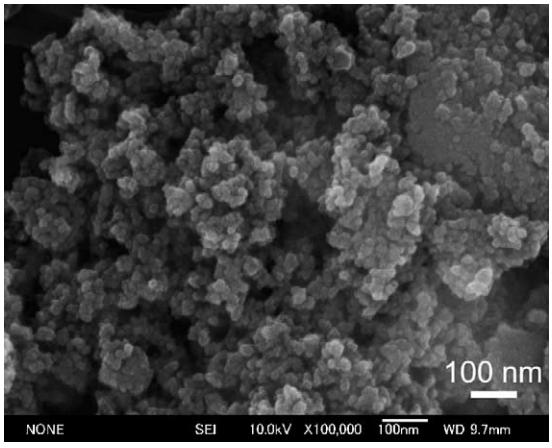


Fig. 4. SEM image of TiO_2 calcined at 400 °C for 4 h.

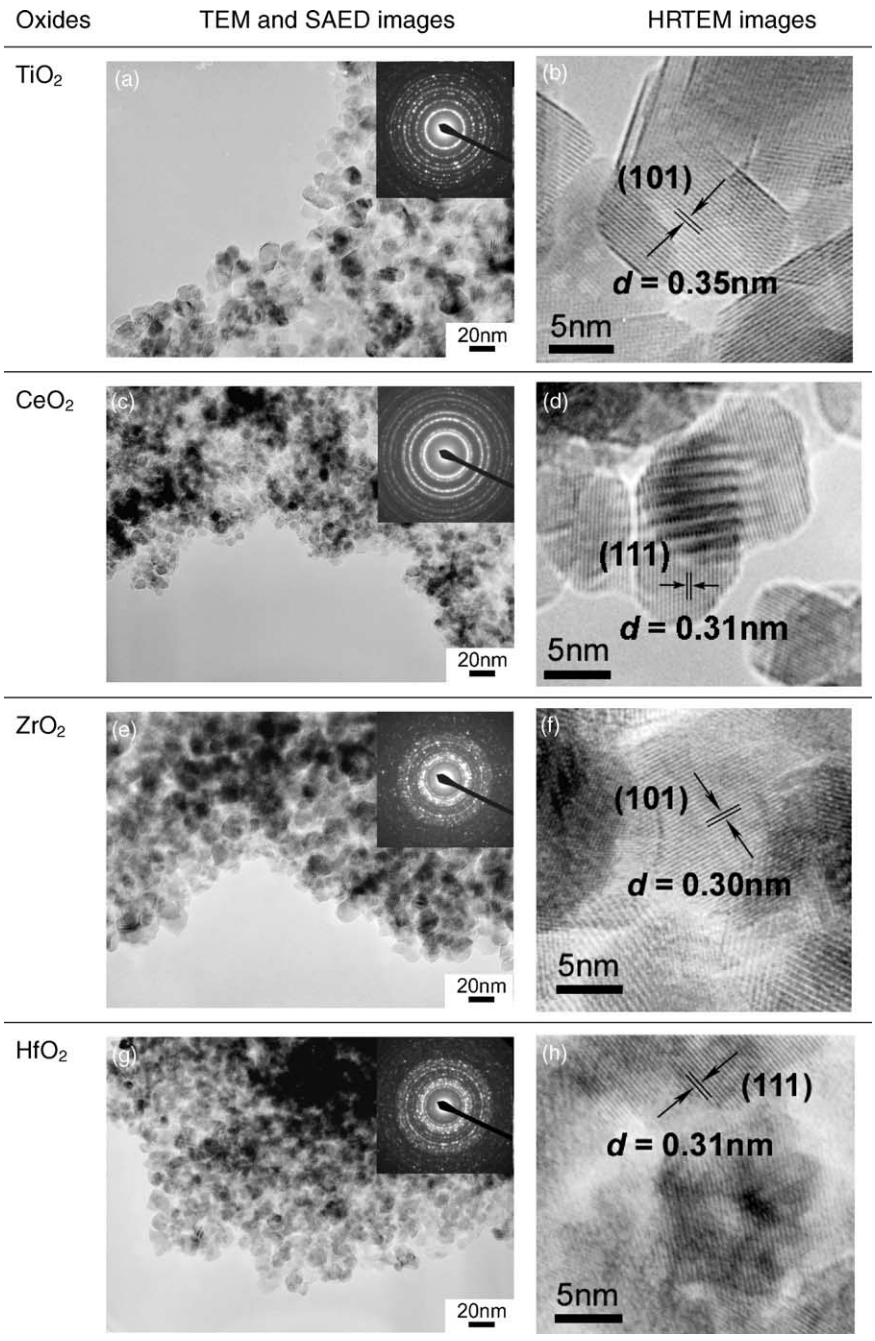


Fig. 5. TEM, SAED, and HRTEM images of the prepared metal oxides.

IUPAC type IV pattern, indicating the existence of mesopores. The pore size distribution of the sample (inset of Fig. 3) showed that the prepared material was mesoporous with narrow pore size distribution (average pore diameter about 5–6 nm). The BET surface area and pore volume of sample are about 80 m^2/g and 0.197 cm^3/g, respectively.

Fig. 4 shows a representative SEM image of TiO_2 calcined at 400 °C for 4 h. The image indicates spherical nature of the particles, with lager particles being aggregates of the smaller ones. TEM image of the same powder, Fig. 5(a), shows a 7–15 nm nano-size crystalline structure. The SAED pattern (inset of Fig. 5(a)) and high resolution TEM image (Fig. 5(b)) demonstrated that the nanoparticles consisted of the anatase phase.

3.2. Mesoporous CeO_2 and other metal oxides

The XRD pattern of the CeO_2 sample calcined at 400 °C for 4 h showed peaks corresponding to the cubic fluorite structure (Fig. 6).

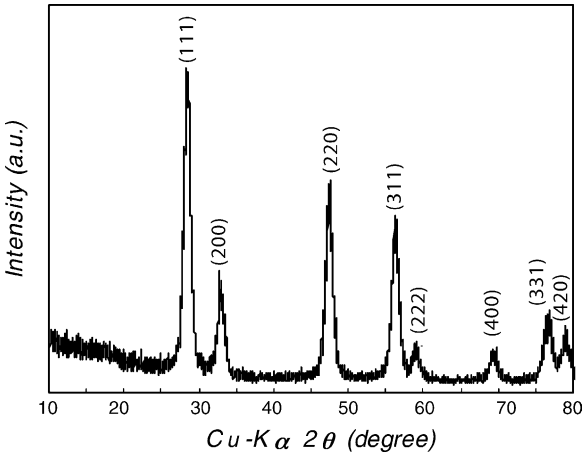


Fig. 6. X-ray diffraction pattern of CeO_2 calcined at 400 °C for 4 h.

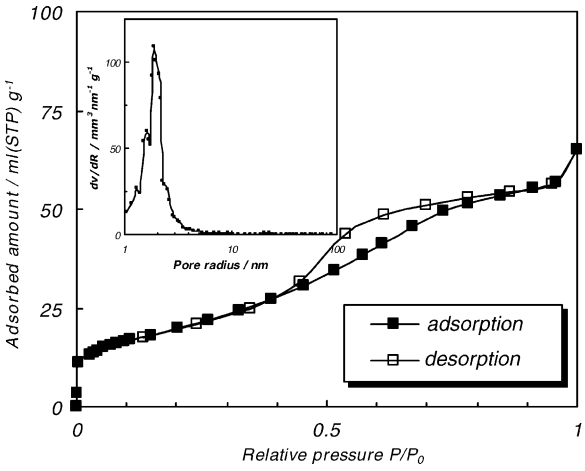


Fig. 7. Nitrogen adsorption isotherm pattern of CeO_2 calcined at 400 °C for 4 h, and the pore size distribution of sample with pore diameter about 3–4 nm (inset).

Fig. 7 gives the nitrogen adsorption isotherm of the same CeO_2 sample. The isotherm also showed an IUPAC type IV, as that of TiO_2, and the pore size distribution (inset of Fig. 7) was about 3–4 nm. The BET surface area and pore volume of sample are about 73 m^2/g and 0.113 cm^3/g, respectively.

TEM image of the CeO_2 nanopowder (Fig. 5(c)) had crystal size about 5–10 nm. The SAED pattern (inset of Fig. 5(c)) and high resolution TEM image (Fig. 5(d)) showed that the nanoparticles were composed of cubic fluorite type CeO_2.

ZrO_2 and HfO_2, mesoporous nanopowders were also successfully obtained by the modified sol–gel method. The nanopowders calcined at 400 °C for 4 h were composed of tetragonal ZrO_2 and monoclinic HfO_2, having mesopores of 3–5 nm. BET surface area of ZrO_2 and HfO_2 was about 72 and 44 m^2/g, respectively (Table 1). The particles of these metal oxides are spherical in nature, with crystalline size about 7–15 nm (Fig. 5(e)–(h)).

4. Conclusions

The modified sol–gel process using a surfactant enabled to fabricate various metal oxides with controlled mesopores. All products possessed high crystallinity with crystal size about 5–15 nm, high surface area (44–80 m^2/g), and average pore diameter about 3–6 nm. These materials are promising for chemical and energy-related applications such as photocatalysts, and semiconductors in dye-sensitized solar cell.

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