

Synthesis, Characterization and Application of Single and Mixed Oxides Nanomaterials

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Abstract: Single and mixed oxides have been widely used for various applications such as a semiconductor in dye-sensitized solar cell, catalysts, fuel cells, resistors, gas sensors, transparent optical device, optical coatings and so on. The efficiency of materials is influenced by many factors such as crystallinity of structure, particle size, surface area, and the method of preparation. The sol-gel synthesis is promising a new material fabrication method for nanoscale materials and nanotechnology. Mesoporous high surface area and high crystallinity MO₂ (M = Ti, Ce, Zr, and Hf) nanopowders were synthesized by a modified sol-gel method using laurylamine hydrochloride, metal alkoxide and acetylacetone. The prepared powders had crystalline size of about 5-15 nm, specific surface area of 44-80 m²/g, and a narrow pore size distribution with average pore diameter of about 3-6 nm. Mesoporous TiO₂-CeO₂ nanopowders responding to visible wavelength were also obtained by using the same process. A small addition (5 mol %) of CeO₂ did not affect anatase phase. However, further addition of CeO₂ increased fluorite-CeO₂ structure while anatase TiO₂ decreased. These synthesis methods provide simple route to fabricate nanostructured materials under mild conditions.

Keywords: Mesoporous oxides, Characterization, Sol-gel, TiO₂-CeO₂, Mild Conditions.

Introduction

Metal oxides with wide or moderate band gap, such as TiO₂, CeO₂, ZrO₂, and HfO₂, 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 [1-4]. Their functional properties are influenced by many factors such as crystallinity, particle size, surface area, and preparation [5]. In previous works, mesoporous TiO₂-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 [6]. This process has also been applied to a semiconductive material in dye-sensitized solar cells [7].

In this article, our recent studies on the surfactant assisted process have been overviewed for several metal oxides. Mesoporous TiO₂, CeO₂, ZrO₂, HfO₂, and mixed oxides of TiO₂-CeO₂ were synthesized using laurylamine hydrochloride(LAHC) / metal alkoxide modified with acetylacetone (ACA) system. The characterization of nanopowders will be reported.

Experimental Procedure

Mesoporous TiO₂ 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 [6-9]. 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. Mesoporous CeO₂, SnO₂, ZrO₂, and HfO₂ nanopowders were synthesized using the same route of TiO₂ by changing alkoxide precursors.

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.

Results and Discussion

Mesoporous TiO₂ [6]

Fig.1 shows the X-ray diffraction pattern of the TiO₂ sample calcined at 400°C for 4 h, demonstrating the formation of anatase phase. The peaks were rather sharp, which indicated the obtained TiO₂ had relatively high crystallinity

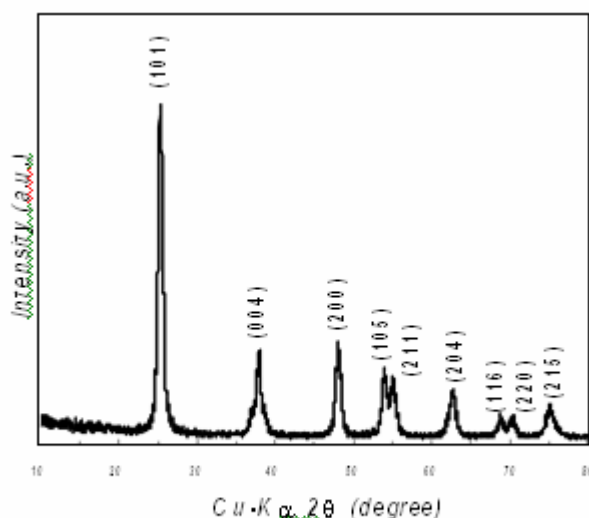


Fig. 1 XRD pattern of TiO_2 calcined at 400 °C for 4 h [6].

Fig. 2 gives the nitrogen adsorption isotherm of the TiO_2 sample calcined at 400 °C for 4 h. The isotherm shows a typical IUPAC type IV pattern with sharp inflection of nitrogen adsorbed volume at P/P_0 about 0.65 (type H2 hysteresis loop), indicating the existence of mesopores. The pore size distribution of the sample, as shown in the inset of Fig. 2, showed that the prepared material had mesopores 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

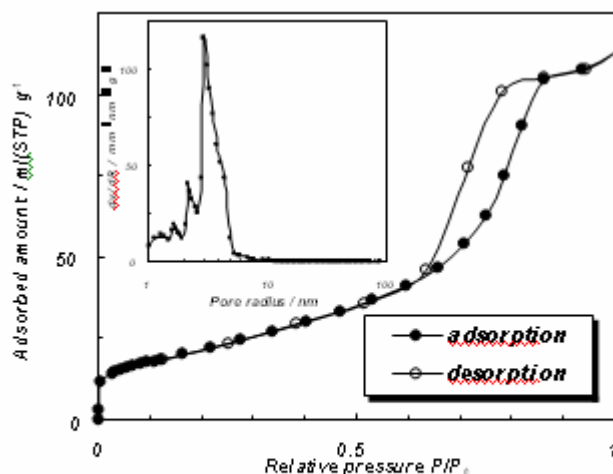


Fig. 2 Nitrogen adsorption isotherm pattern of TiO_2 calcined at 400 °C for 4 h, and the pore size distribution of sample with pore diameter about 5-6 nm (inset) [6].

Fig.3 shows a representative SEM image of the prepared TiO_2 calcined at 400 °C for 4 h. The image indicates that the particles are spherical in nature. Larger particles in this figure should be aggregates of the smaller particles. TEM image of the prepared TiO_2 calcined at 400 °C for 4 h in Fig. 6 (a) shows nano size crystalline structure, which had the crystalline size about 7-15 nm. The electron diffraction pattern shown in the inset of Fig. 6 (a) supported that the prepared TiO_2 crystalline structure was anatase-type TiO_2 . High resolution TEM

image of the prepared TiO_2 is shown in Fig. 6 (b). The lattice fringes of the nanoparticles appearing in the image ($d = 0.35 \text{ nm}$) also allowed for the identification of the anatase phase.

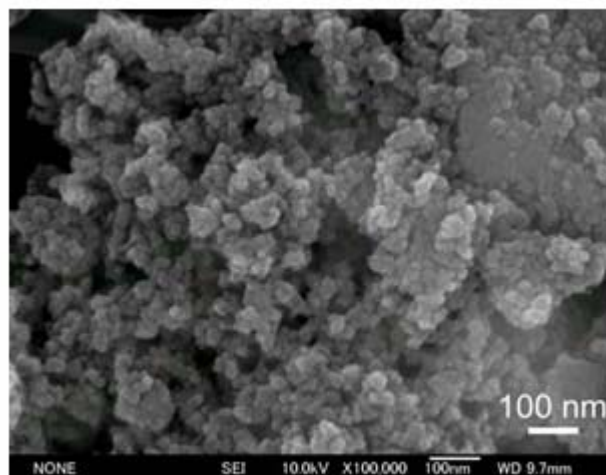


Fig. 3 SEM image of TiO_2 calcined at 400°C for 4 h [6].

Mesoporous CeO_2 and other metal oxides [6]

The X-ray diffraction pattern of the CeO_2 sample calcined at 400°C for 4 h showed peaks corresponding to the cubic fluorite structure as shown in Fig. 4.

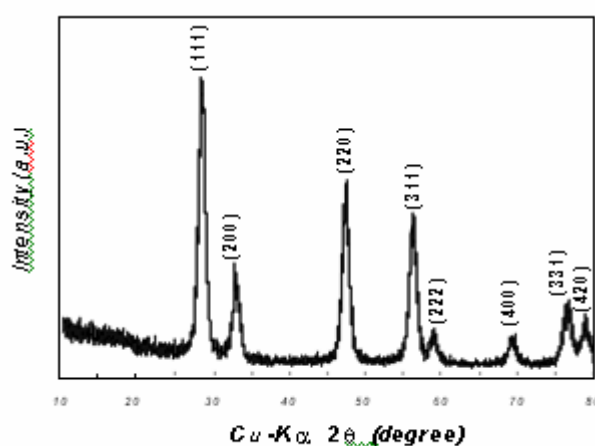


Fig. 4 XRD pattern of CeO_2 calcined at 400°C for 4 h [6].

Fig. 5 gives the nitrogen adsorption isotherm of the CeO_2 sample at 400°C for 4 h. The isotherm of CeO_2 also showed a IUPAC type IV pattern with sharp inflection of nitrogen adsorbed volume at P/P_0 about 0.5 (type H2 hysteresis loop), indicating the existence of mesopores in the prepared material. The inset of Fig. 5 gives the pore size distribution of the sample, which shows the prepared material had mesopores with average pore diameter about 3-4 nm. The BET surface area and pore volume of sample are about $73 \text{ m}^2/\text{g}$ and $0.113 \text{ cm}^3/\text{g}$, respectively.

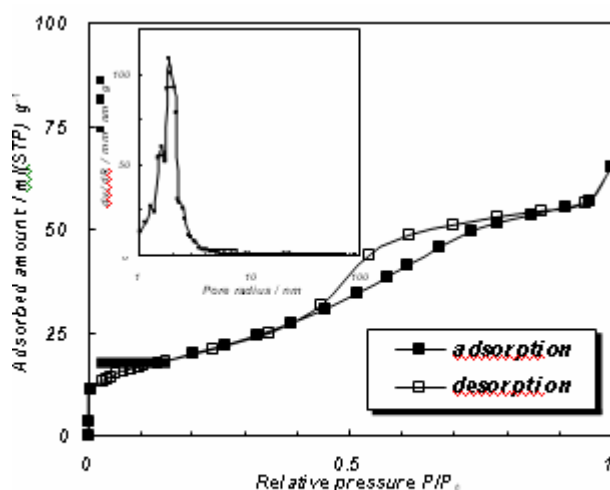
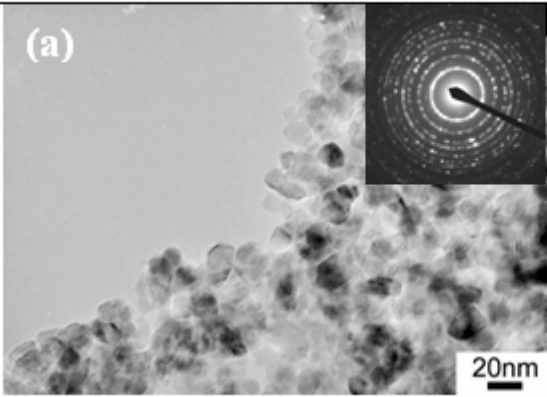
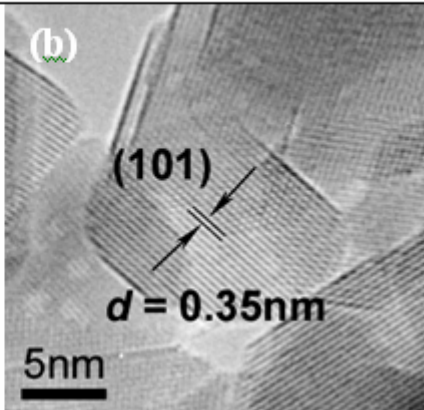
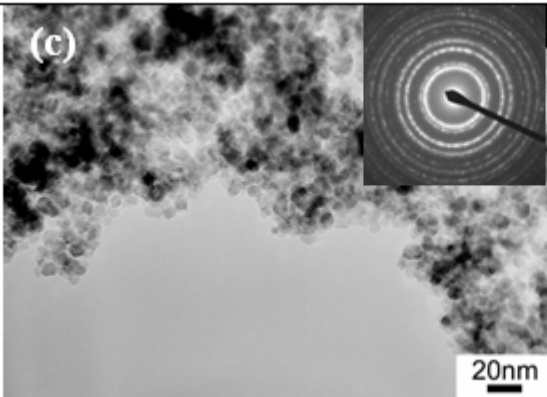
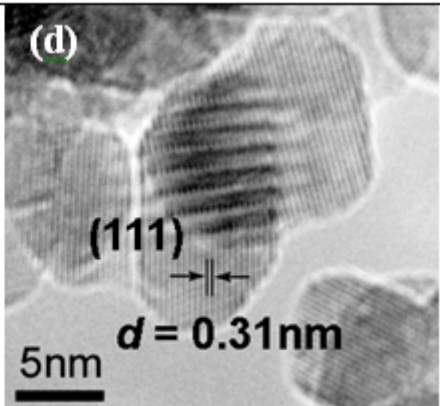


Fig. 5 Nitrogen adsorption isotherm pattern of CeO_2 calcined at 400 °C for 4 h, and the pore size distribution of sample with pore diameter about 3-4 nm (inset) [6].

TEM image of the prepared CeO_2 (calcined at 400 °C for 4 h in Fig. 6 (c)) shows nano size crystallite with the size about 5-10 nm. The electron diffraction pattern shown in the inset of Fig. 6 (c) supported that the prepared CeO_2 crystalline structure was cubic fluorite-type CeO_2 . High resolution TEM image of the prepared CeO_2 is shown in Fig. 6 (d). The lattice fringes of the nanoparticles appearing in the image ($d = 0.31$ nm) also allowed for the identification.

Oxides	TEM and SAED images	HRTEM images
TiO_2	(a) 	(b) 
CeO_2	(c) 	(d) 

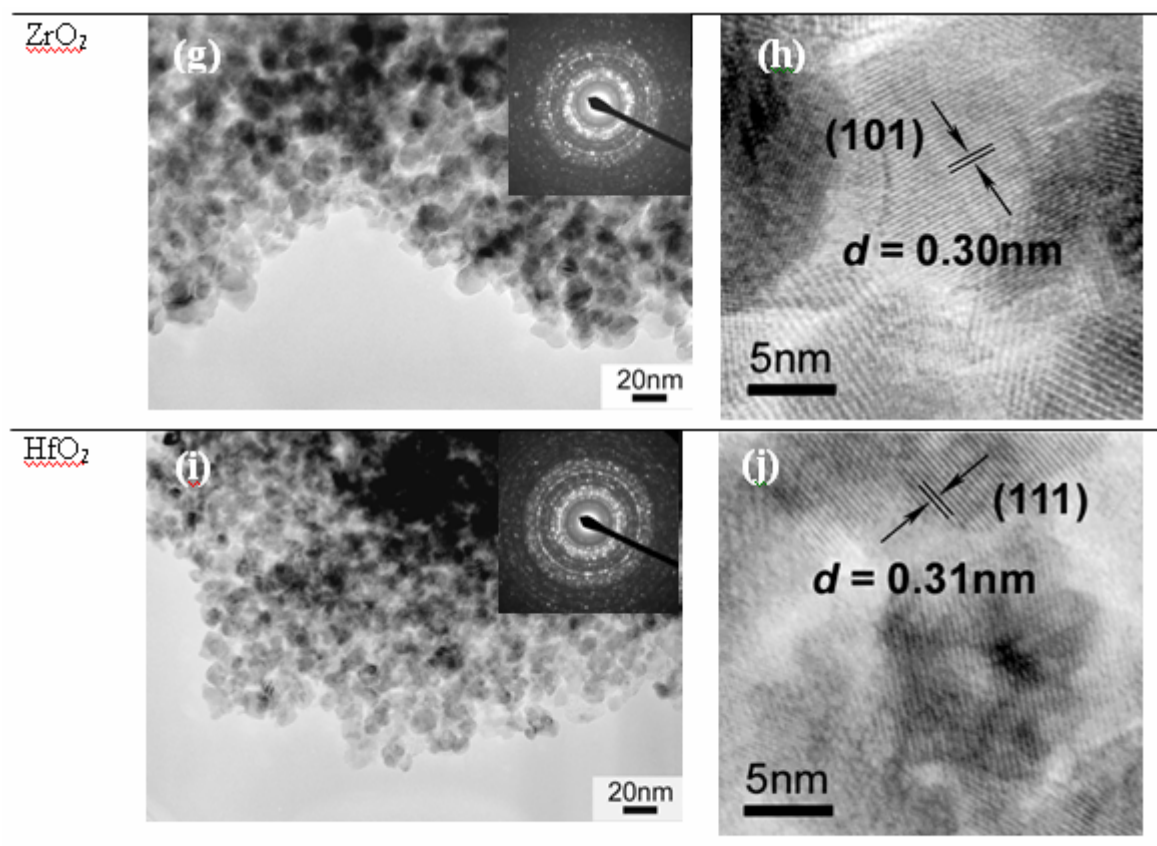


Fig. 6. TEM, SAED, and HRTEM images of the prepared metal oxides [6].

Table 1 Physicochemical properties of the prepared metal oxides calcined at 400 °C for 4 h [6]

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 ⁿ Bu) ₄	Cubic (fluorite-type)	5-10	3-4	0.113	73
ZrO ₂	Zr(O ⁿ Bu) ₄	Tetragonal	7-15	3-4	0.063	72
HfO ₂	Hf(O ⁿ Bu) ₄	Monoclinic	7-15	3-5	0.057	44

ZrO₂ and HfO₂, mesoporous nanopowders were also successfully obtained by the modified sol-gel method. The X-ray diffraction patterns showed that these metal oxides calcined at 400 °C for 4 h were composed of tetragonal SnO₂, tetragonal ZrO₂, and monoclinic HfO₂. The nitrogen adsorption isotherms of these metal oxides also showed typical IUPAC type IV patterns with hysteresis loop, indicating that there exist mesopores (3-8 nm) in the prepared material. The BET surface area of the prepared ZrO₂, and HfO₂ were about 72, and 44 m²/g, respectively (Table 1). The particles of these metal oxides are spherical in nature. The nano size crystalline structure of these metal oxides were also confirmed by TEM images with crystalline size about 7-15 nm as shown in Fig. 6 (e)-(h)

Mesoporous $\text{TiO}_2\text{-CeO}_2$ nanopowders respond to visible wavelength [9]

Fig. 7 shows the XRD patterns of the prepared $\text{TiO}_2\text{-CeO}_2$ nanopowders calcined at 400 °C for 4 h. The 95 mol% TiO_2 -5 mol% CeO_2 system yielded single anatase phase, i.e., no cubic CeO_2 was detected. The 75 mol% TiO_2 -25 mol% CeO_2 system showed both peak of TiO_2 anatase and cubic CeO_2 but lower crystallinity than each pure component. A further addition of the CeO_2 content (50 and 75 mol% CeO_2) increased cubic fluorite CeO_2 structure while anatase TiO_2 decreased.

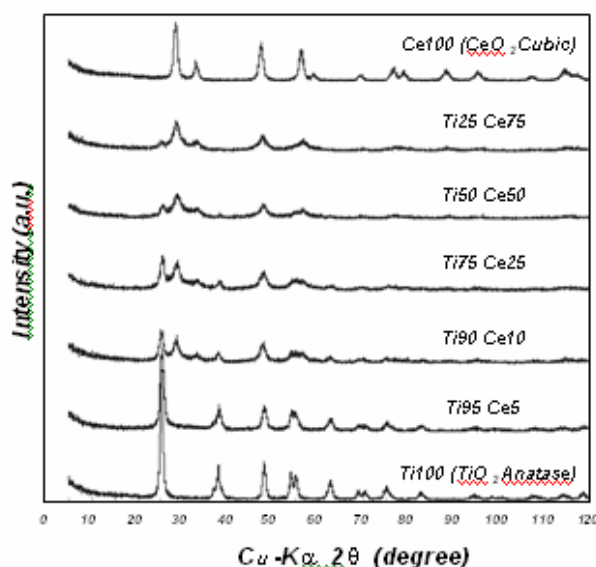


Fig. 7 XRD patterns for the $\text{TiO}_2\text{-CeO}_2$ nanopowders calcined at 400 °C for 4 h [9].

The BET specific surface area of the $\text{TiO}_2\text{-CeO}_2$ system calcined at 400 °C for 4 h (Fig. 8). A small addition of CeO_2 to the TiO_2 system by this method increased the specific surface area of the prepared materials. Using a larger amount of CeO_2 , the specific surface area decreased, may be due to the CeO_2 segregation, contributing to the reduction of the total surface area [8-9]. Addition of 25, 50, and 75 mol% CeO_2 , did not affect the surface area very much.

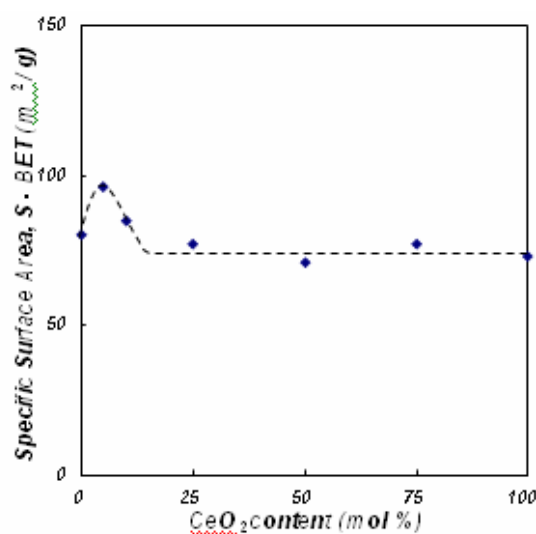


Fig. 8 Specific surface area, for the $\text{TiO}_2\text{-CeO}_2$ nanopowders (molar percent of ceria was varied from 0 to 100) calcined at 400 °C for 4 h [9].

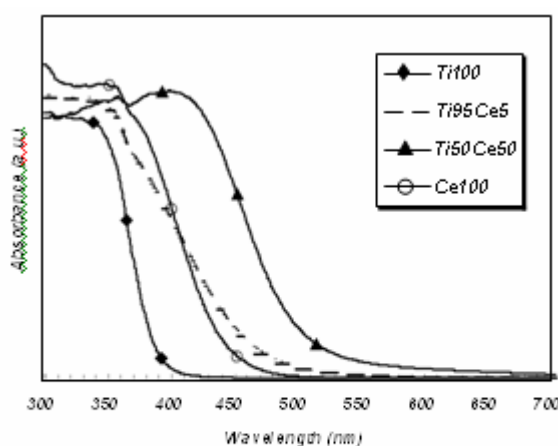


Fig. 9 Diffuse reflectance spectra of the 100 mol% TiO_2 (Ti100), the 95 mol% TiO_2 -5 mol% CeO_2 (Ti95 Ce5), the 50 mol% TiO_2 -50 mol% CeO_2 (Ti50 Ce50), and the 100 mol% CeO_2 (Ce100) [9].

The diffuse reflectance spectra for the TiO_2 - CeO_2 nanopowders are shown in Fig. 9. The 100 mol% TiO_2 absorbed light with wavelength shorter than 400 nm, because the TiO_2 anatase phase has band gap about 3.2 eV. Interestingly, only 5 mol% CeO_2 addition showed red shift of light absorption and can absorb light with the wavelength longer than 400 nm. The best red-shift-light-absorption of mixed oxides was the 50 mol% TiO_2 -50 mol% CeO_2 system and it absorbed visible wavelength more than pure component of TiO_2 and CeO_2 [8-9]. The 100 mol% TiO_2 powder was white, the 100 mol% CeO_2 was pale yellow and the mixed oxides of 50 mol% TiO_2 -50 mol% CeO_2 was orange-yellow, and therefore the 50 mol% TiO_2 -50 mol% CeO_2 system had intensive visible light absorption more than the pure component.

Conclusion

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 ($44\text{-}80\text{ m}^2/\text{g}$), and average pore diameter about 3-6 nm. The mesoporous TiO_2 - CeO_2 nanopowders prepared by the modified sol-gel process (surfactant assisted technique) respond to visible wavelength. A small addition (5 mol %) of CeO_2 did not affect anatase phase. However, further addition of CeO_2 increased fluorite- CeO_2 structure while anatase TiO_2 decreased. Addition of 25, 50, and 75 mol% CeO_2 , did not affect the surface area very much. This system could control the band gap energy with changing the composition.

In this study, the operation of synthesis is a simple method and all the reactions of the synthetic process are carried out in aqueous solution under mild conditions. These materials are promising for chemical and energy-related applications such as catalysts, and semiconductors in dye-sensitized solar cell.

Acknowledgements

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