Synthesis of Mesoporous Ce-doped TiO_2 with High Thermal Stability

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Mesoporous Ce-doped TiO_2 with a high thermal stability was prepared by using inexpensive glycerin as a pore former via sol-gel and hydrothermal processes. The product has a high specific surface area (129.7 m^2/g) and a pore volume (0.41 cm^3/g) even after calcination at 600 °C for 2 h.

Special attention has been paid to TiO_2 as a potential candidate for high-performance electrorheological (ER) materials because of its high dielectric constant.[1–3] It was reported that doping Ce^{3+} could increase the ER activity of anatase TiO_2 significantly.[4] Recently, researchers further believed that the slow polarization, in particular the interfacial polarization of particles in suspensions was especially important for a strong ER effect.[5–7] Based on this, J. B. Yin et al. prepared mesoporous Ce-doped TiO_2 and studied the corresponding ER effects.[8,9] The suspension of these mesoporous Ce-doped TiO_2 in silicone oil had a good dispersion stability due to the presence of wormhole-like mesopores and showed an extraordinarily strong ER activity, which was twice as high as that of Ce-doped TiO_2 without mesopores. It was also found that the thermal stability of mesoporous Ce-doped TiO_2 was important to a good reversibility in repeating temperature effect tests.

Different strategies have been developed using surfactants or amphiphilic block copolymers as templates to prepare mesoporous titania.[10–13] In order to obtain mesoporous anatase TiO_2 with high porosity which is indispensable for most applications, removal of the template as well as growth of anatase domains is usually performed by heat treatment below 350 °C. Higher calcination temperature mostly results in a total collapse of pores. Therefore, a challenge remains in the preparation of mesoporous anatase titania with a high thermal stability. Here, we report a simple method to prepare mesoporous Ce-doped TiO_2 by using inexpensive glycerin as a pore-forming agent via sol-gel and hydrothermal processes. The resultant mesoporous Ce-doped TiO_2 shows a high thermal stability, which has a specific surface area (129.7 m^2/g) and a pore volume (0.41 cm^3/g) even after calcination at 600 °C.

Mesoporous Ce-doped TiO_2 was prepared as follows. After 50 mL tertrabutyl orthotitanate was dissolved in 126-mL ethanol, 3-mL acetylacetone was added with stirring for 30 min. Then 6.2 mL of 4.76 M HNO_3 was added dropwise into the above solution with stirring for 1 h at room temperature. 5.428 g $Ce(NO_3)_3 \cdot 6H_2O$ was added (Ce/Ti = 8.5 mol %, verified as the optimal doping amount for ER activity).[9] At last, glycerin was added according to the desired amount (glycerin/TiO_2 = 20/80, 30/70, 40/60, 50/50, 60/40 by weight) and the solution was stirred for 1 h. The beakers were sealed by para-film that was stabbed with a few pinholes. After gelation, the aerogel was dried at 90 °C for 12 h, ground and sieved to a particle size finer than 100 μm. Then 5-g xerogel powders suspended in 30-mL distilled water were put into an autoclave and held at 120 °C for 24 h (xerogel powders are denoted as TC-*x*, where TC and *x* represent the Ce-doped TiO_2 and glycerin content, respectively). Crystalline powders after hydrothermal treatment were recovered by filtration, washed with water and ethanol, and dried at 110 °C overnight. The recovered powders were calcined at 400, 500, 600 °C for 2 h, respectively. As-synthesized samples were labeled as TC-*x*-*y*, where *x* and *y* represent glycerin content and calcination temperature, respectively. Transmission electron microscopy (TEM) images were obtained on a JEOL-200CX electron microscope. Nitrogen adsorption data were collected on a Micromeritics ASAP 2010 nitrogen adsorption apparatus. X-ray diffraction (XRD) patterns were obtained on an automated diffractometer D/max 2550V. Simultaneous differential scanning calorimetric analysis (DSC) and thermogravimetric analysis (TG) were carried out on a NETZSCH STA 449C instrument in air with a heating rate of 10 °C/min. The content of Ce ions was determined by chemical analysis.

Figure 1 depicts XRD patterns of the powders. As-synthesized TC-30 xerogel was amorphous (Figure 1a), while the broad anatase TiO_2 peaks appeared after hydrothermal treatment (Figure 1b). After TC-30 xerogel with hydrothermal treatment was calcined at 400, 600 °C for 2 h, the intensity of the anatase TiO_2 peaks became stronger (Figures 1c and 1d), indicating that particles became larger. No peaks of the second phase can be found. Probably large radius cerium ions substitute for the Ti rather than forming independent phase in the calcination process.[8] The atomic ratio of Ce/Ti in TC-30-400 is about 8.88%, which is in good agreement with the designed atomic composition (8.5%). This indicates that the atomic ratio of Ce/Ti changes slightly during hydrothermal treatment. Figure 2 shows TG-DSC curves of TC-30 xerogel after hydrothermal treatment. The endothermic peak at 99.5 °C represents the loss of the absorbed water and solvent. The exothermic peak at 281 °C is attributed to the combustion of organic compounds and the decomposition of nitrate ions. Weight loss between 350 and 800 °C is extremely small, indicating that organic compounds can be completely removed by calcining the powders above 350 °C.

The N_2 adsorption–desorption data of as-synthesized samples were shown in Table 1. The pore properties of mesoporous Ce-doped TiO_2 calcined at 400 °C change slightly with the increase of glycerin content. Moreover, mesoporous Ce-doped

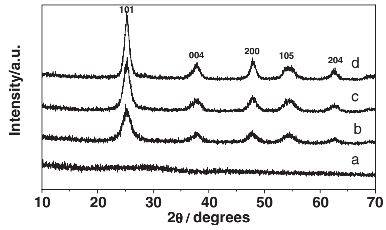

Figure 1. XRD patterns of (a) TC-30 xerogel, (b) TC-30 xerogel after hydrothermal treatment, (c) TC-30-400, (d) TC-30-600.

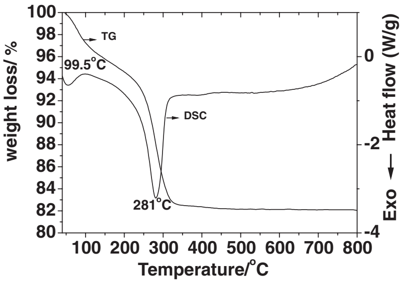

Figure 2. TG-DSC curves of TC-30 xerogel after hydrothermal treatment.

Table 1. Physicochemical properties of mesoporous Ce-doped TiO$_2$

Sample	Specific surface area/m^2/g	Pore volume /cm^3/g	Average pore diameter/nm
TC-20-400	189.7	0.32	6.5
TC-30-400	199.1	0.40	7.8
TC-40-400	185.9	0.41	8.3
TC-50-400	189.7	0.44	8.7
TC-60-400	149.6	0.29	7.3
TC-30-500	154.5	0.36	8.9
TC-30-600	129.7	0.41	12.4
T-40-400[a]	139.6	0.17	4.7
TC-40-400-*n*[b]	56	0.02	3.0

[a]T-40-400 represents mesoporous undoped TiO$_2$ synthesized by the same procedure as that of TC-40-400, [b]TC-40-400-*n* represents the powders obtained by calcining TC-40 xerogel without hydrothermal treatment (calcination temperature is 400 °C).

TiO$_2$ (TC-40-400) has larger specific surface area and pore volume than those of mesoporous undoped TiO$_2$ (T-40-400), owing to the stabilizing role of Ce^{3+}.[14] It was found surprisingly that TC-30-600 has a specific surface area (129.7 m^2/g) and a pore volume (0.41 cm^3/g). The type IV isotherm with type H2 hysteresis loop shown in Figure 3 indicates the existence of mesopores in TC-30-400. Also, TC-30-600 has a narrow BJH pore size distribution, indicating that the obtained powders can retain mesoporous structure even after calcination at 600 °C. Figure 4 gives TEM image of TC-30-400. It clearly displays that wormhole-like pores exist throughout the aggregate. The corresponding pore sizes are estimated to be in the 6.0–10.0 nm range, which are in agreement with the inserted BJH pore size distribution shown in Figure 3.

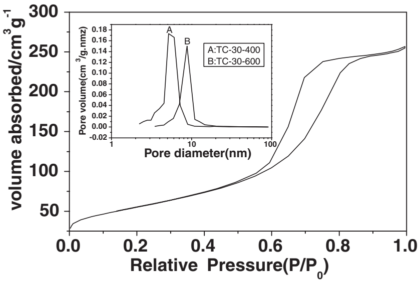

Figure 3. N$_2$ adsorption–desorption isotherm of TC-30-400 and BJH pore size distribution plot (inset) of TC-30-400 and TC-30-600.

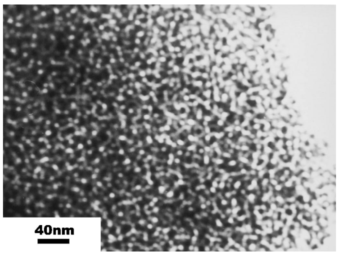

Figure 4. TEM image of TC-30-400.

It is worth noting that hydrothermal treatment plays an important role in obtaining the powders with a high thermal stability. It was found that the specific surface area and the pore volume of the samples with hydrothermal treatment were significantly greater than those of the samples without hydrothermal treatment. For example, TC-40-400-*n* has poorer properties than TC-40-400 as listed in Table 1. Generally, calcination leads to the collapse of mesoporous structure due to crystallization of amorphous TiO$_2$ into anatase. In this work, hydrothermal treatment crystallized amorphous xerogel into an anatase hybrid that can effectively increase thermal stability during calcining process, thus preventing mesopores from collapsing.

In conclusion, mesoporous and crystalline Ce-doped TiO$_2$ was prepared by using inexpensive glycerin as a pore former via sol-gel and hydrothermal processes. Hydrothermal treatment increases the thermal stability of the powders significantly. The resultant mesoporous Ce-doped TiO$_2$ shows a high thermal stability up to 600 °C. When these mesoporous materials are used as ER materials, the activity may be increased.

References

1 P. Atten, J.-N. Foulc, and N. Felici, *Int. J. Mod. Phys. B*, **8**, 2731 (1994).
2 Y. Komoda, T. N. Rao, and A. Fujishima, *Langmuir*, **13**, 1371 (1997).
3 Y. Komoda, N. Sakai, and T. N. Rao, *Langmuir*, **14**, 1081 (1998).
4 X. P. Zhao and J. B. Yin, *Chem. Mater.*, **14**, 2258 (2002).
5 H. Block and P. Rattay, in “Progress in Electrorheology,” ed. by K. O. Havelka and F. E. Filisko, Plenum Press, New York (1995), p 19.
6 F. Ikzaki, A. Kawai, K. Uchida, T. Kawakami, K. Edmura, K. Sakurai, H. Anzai, and Y. Asako, *J. Phys. D: Appl. Phys.*, **31**, 336 (1998).
7 a) T. Hao, A. Kawai, and F. Ikazaki, *Langmuir*, **15**, 918 (1999). b) T. Hao, A. Kawai, and F. Ikazaki, *Langmuir*, **16**, 3058 (2000).
8 J. B. Yin and X. P. Zhao, *Chem. Mater.*, **14**, 4633 (2002).
9 J. B. Yin and X. P. Zhao, *J. Mater. Chem.*, **13**, 689 (2003).
10 R. L. Putnam, N. Nakagawa, K. M. Mcgrath, N. Yao, I. A. Aksay, S. M. Gruner, and A. Navroysky, *Chem. Mater.*, **9**, 2690 (1997).
11 V. F. Stone Jr. and R. J. Davis, *Chem. Mater.*, **10**, 1468 (1998).
12 M. Thieme and F. Schuth, *Microporous Mesoporous Mater.*, **27**, 193 (1999).
13 Y. Yue and Z. Gao, *Chem. Commun.*, **2000**, 1755.
14 W. Zhang and T. J. Pinnavaia, *Chem. Commun.*, **1998**, 1185.

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