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# Preparation of Rare-earth Doped Titanium Oxides Nano Particles with Modified Sol-gel Synthesis Method

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**Abstract:** Modified sol-gel synthesis method was researched in this paper. The new method was used to prepared rare earth doped TiO<sub>2</sub> nano particles under the same preparation conditions, in which the ratio of Ti and rare earth was RE<sup>n+</sup>: Ti<sup>4+</sup>=0.02 or 0.10. RE<sup>n+</sup> was presented for Nd<sup>3+</sup>, Ce<sup>4+</sup>, La<sup>3+</sup>, Er<sup>3+</sup>. Triethanolamine and water was put into flasks. Then tetrabutyl titanate-n-butanol solution was dropped into flasks for some time. And then the mixed solution of a certain amount of rare earth and citric acid was dropped into flasks for some time. Distillate to remove solvent, dry the remaining sol at 100°C, place the products in a muffle furnace and calcine at 500°C for 5 hours. Changing the ratio of RE<sup>n+</sup>: Ti<sup>4+</sup>, products with different properties was prepared. TG-DTG, XRD, TEM was used to analysis the roast temperature, size, morphology and so on. It was shown that the average cell size of rare earth doped TiO<sub>2</sub> nano particles were around 20 nm and a little rare-earth doped titanium dioxide materials were benefit in dispersion.

**Keywords:** Rare-earth doped; TiO<sub>2</sub> nano particles; Modified sol-gel synthesis

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## Introduction

Nano-TiO<sub>2</sub> as an important inorganic functional material was concerned with its good weather resistance, corrosion resistance and so on. Therefore, the preparation of nano- TiO<sub>2</sub> powder with high purity, small particle size and well dispersion was used to achieve the precondition [1]. Currently, the general methods of preparation of nano-TiO<sub>2</sub> were as follows, hydrothermal synthesis method [2], homogeneous precipitation, sol-gel method, etc. The sol-gel method for its easy to control, fewer side effects, simple process, was widely adopted in recent years. However, this method had a poor dispersion of particles, which could easily lead to the agglomeration [3]. Therefore, it was practical and

necessary to explore better preparation method of TiO<sub>2</sub> nano-particles.

In recent years, the preparation of rare earth doped TiO<sub>2</sub> became a hot spot [4]. Those doped particles were prepared by physical or chemical method. Rare earth ions introduced into the TiO<sub>2</sub> lattice, which was resulting in the introduction of new charge, could also lead to lattice defects or change the type of lattice. These changes would ultimately affect the dispersion of TiO<sub>2</sub>. Rare earth doped nano-materials research had also made a lot of progress [5]. Presently, the research of rare earth elements (La, Ce, Pr, Gd, Er, Nd, Sm, Ho, etc.) doped TiO<sub>2</sub> has also made key progress. The researchers set to RE<sup>n+</sup>:Ti<sup>4+</sup> = 0.01-0.05 (molar ratio) for a small amount of doping.

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## Experiment

The rare earth doped nano-  $\text{TiO}_2$  was prepared with sol-gel method. Put 3 ml triethanolamine and 100 ml water into flasks, 4ml tetrabutyl titanate mixed with 100ml n-butanol is dropped into flasks with magnetic stirring, to react 2 hours. After reaction, drop the mixed solution of a certain amount of rare earth and citric acid into flasks and react another 2 hours. Distillate to remove solvent, dry the remaining sol at  $100^\circ\text{C}$ , place the products in a muffle furnace and calcine at  $500^\circ\text{C}$  for 5 hours. The rare earth doped nano-  $\text{TiO}_2$  particles are prepared above mentioned. Change the ratio of  $\text{RE}^{n+}:\text{Ti}^{4+}$  to make products with different properties (Table 1).

**Table 1 Chemical Composition**

Sample	composition	ratio	Sample	composition	ratio
S-1	$\text{TiO}_2$	0.00	S-5	$\text{Ce}^{4+}:\text{Ti}^{4+}$	0.10
S-2	$\text{Ce}^{4+}:\text{Ti}^{4+}$	0.02	S-6	$\text{La}^{3+}:\text{Ti}^{4+}$	0.10
S-3	$\text{La}^{3+}:\text{Ti}^{4+}$	0.02	S-7	$\text{Nd}^{3+}:\text{Ti}^{4+}$	0.10
S-4	$\text{Nd}^{3+}:\text{Ti}^{4+}$	0.02	S-8	$\text{Er}^{3+}:\text{Ti}^{4+}$	0.10

TG209 F1 for Netzsch company was used to analysis the temperature of calcine.

X-ray diffraction (XRD) patterns were obtained by D/max-2000x for Rigaku company instrument using diffracted beam monochromator. The crystallite size of the samples was calculated from the Scherrer equation.

Transmission electron microscopy (TEM) micrographs are obtained by jeol2100 for Hitachi company. Copper grid coated with a holey carbon support film was used to prepare samples for the TEM observation. A powdered sample was dispersed in ethanol and the suspension was treated in ultrasonic bath for 10 min.

## Result and discussion

### Analysis of TG-DTG

The phase transformation of rare earth doped  $\text{TiO}_2$  nanoparticles could be analyzed by TG-DTG. The phase transition temperature was determined by the analysis of crystallization process in order to obtain for the pure anatase or rutile. The Fig. 1 is shown the product  $\text{Ce}^{4+}:\text{Ti}^{4+}=0.10$  by TG-DTG.

The characteristic peak was shown as Fig. 1. There were significant peaks at temperature of  $260^\circ\text{C}$ ,  $340^\circ\text{C}$ ,  $530^\circ\text{C}$ . The small peak before  $100^\circ\text{C}$  was due to heat absorption of gel melting and gel dehydration. Peak at  $260^\circ\text{C}$  corresponds to the decomposition of organic groups. Peak at  $340^\circ\text{C}$  is the strongest endothermic peak accompanied by weight loss. Generally speaking, the transition temperature of  $\text{TiO}_2$  from amor-

phous to anatase was about  $300^\circ\text{C}$ . So the temperature of  $340^\circ\text{C}$  is the crystallization process, which the  $\text{TiO}_2$  particles transferred from amorphous to anatase. There was a clear endothermic peak at  $530^\circ\text{C}$  with a stabilized weight loss, which indicated the phase transition of  $\text{TiO}_2$  from anatase to rutile. The peak is wide because of the slow phase change process. This result determined that the calcination temperature was  $500^\circ\text{C}$ .

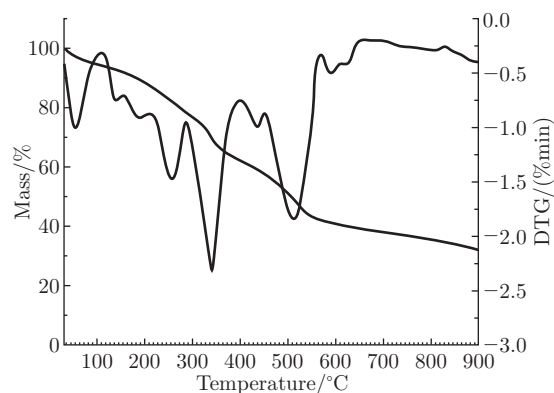


Fig. 1 TG-DTG of  $\text{Ce}^{4+}:\text{Ti}^{4+}=0.10$

### Analysis of XRD

The cell size of nano particles and the lattice distortion were analyzed by Parameters of XRD (Table 2). According to Scherrer formula:  $B = k\lambda/L \cos\theta$ , the cell size of nano particles was calculated. According to the lattice distortion formula:  $E = \Delta d/d = L/4tg\theta$ , the lattice distortion was calculated.

**Table 2 Cell size and lattice distortion**

Sample	name	Average cell size/nm	lattice distortion
S-1	$\text{TiO}_2$	16.00	0.689
S-2	$\text{Ce}^{4+}/\text{TiO}_2(0.02)$	20.70	0.673
S-3	$\text{La}^{3+}/\text{TiO}_2(0.02)$	14.89	0.713
S-4	$\text{Nd}^{3+}/\text{TiO}_2(0.02)$	15.28	0.747
RE <sup>n+</sup> : Ti <sup>4+</sup> =0.02, average cell size=16.95			
S-5	$\text{Ce}^{4+}/\text{TiO}_2(0.10)$	18.11	0.573
S-6	$\text{La}^{3+}/\text{TiO}_2(0.10)$	18.33	0.707
S-7	$\text{Nd}^{3+}/\text{TiO}_2(0.10)$	15.61	0.630
S-8	$\text{Er}^{3+}/\text{TiO}_2(0.10)$	16.12	0.662
RE <sup>n+</sup> : Ti <sup>4+</sup> =0.10, average cell size=17.04			

Compare the pure  $\text{TiO}_2$  particles and rare earth doped nano-  $\text{TiO}_2$  particles (see Table 2). Doped products had not significant increase or decrease of their average cell sizes. The rare earth doped process was not caused the sudden increase or decrease in cell size, which would not affect the adsorption of pure  $\text{TiO}_2$  itself and its self-cleaning properties.

But the peak of the rare earth doped nano-  $\text{TiO}_2$  would be some changes, as shown in Fig. 2.

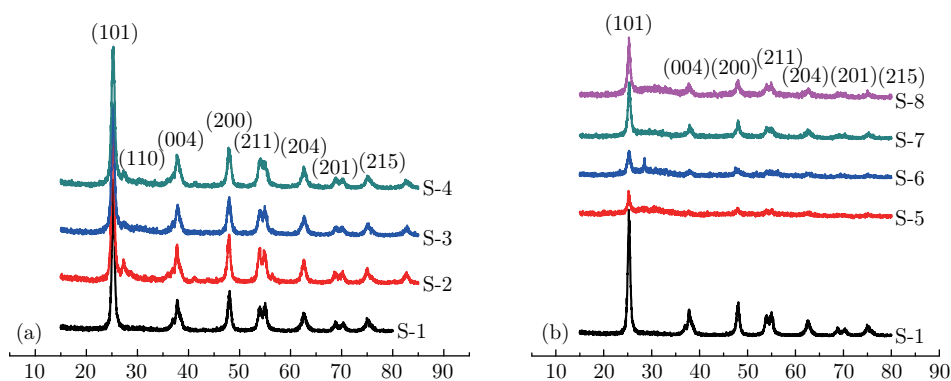


Fig. 2 X-ray diffraction patterns of the same mol ratio of different rare earth doped materials  
 (a)  $RE^{n+}:Ti^{4+}=0.02$ ; (b)  $RE^{n+}:Ti^{4+}=0.10$ .

Figure a of Fig. 2 shown that when  $RE^{n+}: Ti^{4+} = 0.02$ , the samples of rare-earth doped appeared the rutile peak (110). The ratio of this doped particle was easy for anatase nano  $TiO_2$  change to rutile crystal. The reason is that part of the rare earth ions into the  $TiO_2$  lattice, instead of  $Ti^{4+}$ , which let lattice produce a number of new defects and changed the chemical properties of  $TiO_2$ . The rare earth ions instead of  $Ti^{4+}$  was also producing oxygen vacancies, which on the one hand providing the space to rearrangement movement of ions of  $TiO_2$  phase transition and reducing the strain energy, on the other hand reducing the bond breaking of titanium oxygen which is considered conducive to the phase transition [6].

Figure b of Fig. 2 shown that when  $RE^{n+}: Ti^{4+} =$

0.10, the rutile peak of all the samples of rare earth doped particles were not very obvious but  $La^{3+}$  doped. Mackenzie and Melling considered that the presence of oxygen vacancies could promote the change of rutile phase, but the rare earth ions which not entered oxygen vacancies becoming oxides and depositing on the surface of  $TiO_2$ , which inhibited the phase transition of  $TiO_2$  [7]. The increase of the ratio of rare earth doped could inhibit the rutile phase transition.

A small amount of rare earth ions doped nano- $TiO_2$  does not affect the basic peak of  $TiO_2$ , which considered that the rare earth ions entered into the lattice of  $TiO_2$  well and good into crystal properties. When the ratio of rare earth doped increased, the peak of particles grown shorter and wider, but no rare earth element

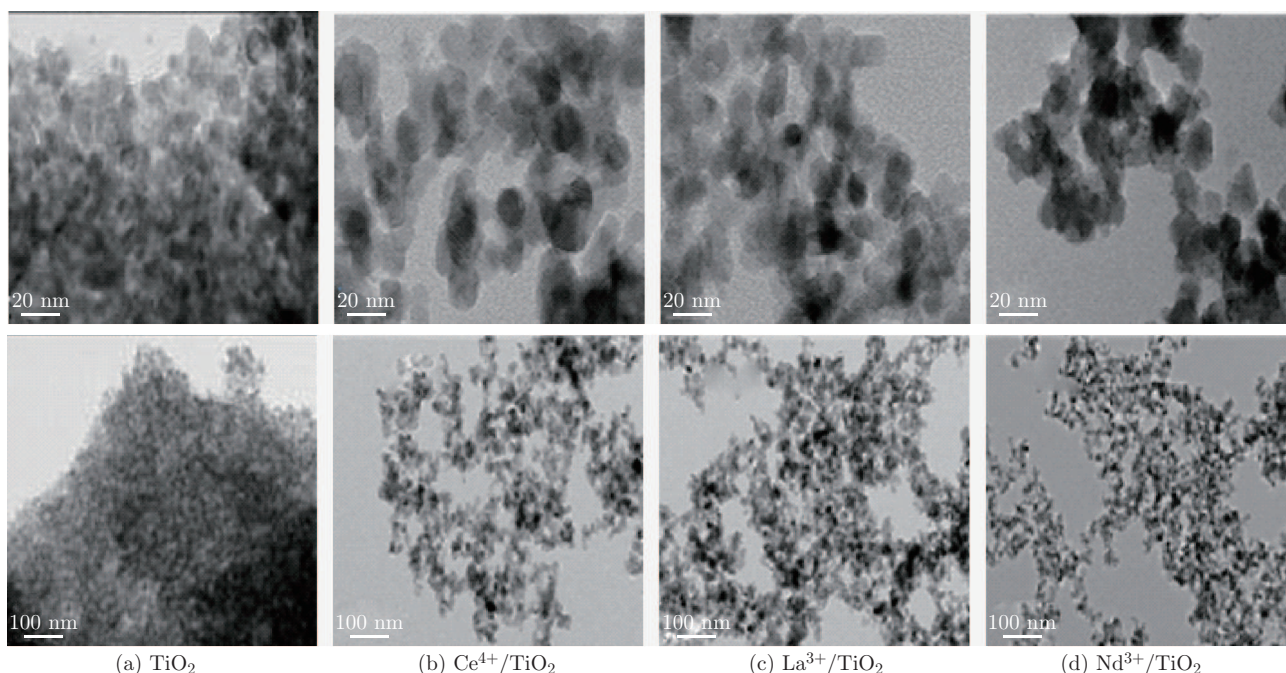


Fig. 3 TEM of  $RE^{n+}: Ti^{4+}=0.02$   
 (a)  $TiO_2$ ; (b)  $Ce^{4+}/TiO_2$ ; (c)  $La^{3+}/TiO_2$ ; (d)  $Nd^{3+}/TiO_2$

peak, which considered that the rare earth ions could also enter into the lattice of  $\text{TiO}_2$  but poor into crystal properties.

### Analysis of TEM

For a small amount of rare earth doped does not affect the formation of crystal of  $\text{TiO}_2$ . The dispersion of different doping and crystal morphology could be characterized by TEM. The experimental results were shown in Fig. 3.

The crystal morphology was shown as Fig. 3. The unit cell dimensions were about 20 nm, whose conclusion was the same as the analysis of parameters calculated of XRD. TEM for the 100 nm scale image could be seen that the rare earth doped  $\text{TiO}_2$  had better dispersion than pure  $\text{TiO}_2$ . Therefore, the rare earth ions doped could have a great effective on  $\text{TiO}_2$  dispersion.

### Conclusion

1) The average cell size of rare earth doped  $\text{TiO}_2$  nano particles were around 20 nm. Rare earth doped had no significant effect on the size, but improved the

dispersion of nano- $\text{TiO}_2$ .

2) A small amount of rare earth doping could appear some rutile phase in nano-anatase  $\text{TiO}_2$ , and the crystalline was well as pure  $\text{TiO}_2$ . When the rare earth doped increased, it would inhibit the production of rutile and reduce forming nano-crystalline.

### References

- [1] Feng X L, Wang Q Y, Wang G Y, Qiu F L. Chinese Journal of Catalysis, 2006, 27(3): 195
- [2] Andrea T, Ignazio R B, Vincenzo B, Carmen C, Massimiliano D'A, Stefano P, Roberto S, Franca M. J. Am. Chem. Soc., 2007, 129 (12): 3564.
- [3] Dong S F. Journal of Shandong University of Technology(Science and Technology), 2005, 19(5): 94.
- [4] Gao L, Liu H Y, Sun J. The Materials Science Forum, 2005, 486-487: 53.
- [5] Hong G Y.. Functional Material, 2004, 35: 2639.
- [6] Jing L G, Sun X J, Xin B F, Wang B Q, Cai W M, Fu H G. Materials Science and Technology, 2004, 12: 148.
- [7] Huang Y L, Li D Z, Fu X Z, Wang X X. Chinese Journal of Inorganic Chemistry, 2008, 24(1): 61.