



One Step Synthesis and Photocatalytic Activity of Rare Earths/Rutile TiO₂

LIANG BIAN^{1,2,3,*}, MIANXIN SONG^{2,*}, TIANLIANG ZHOU⁴, JINBAO XU¹ and LEI WANG¹

¹Xinjiang Institute of Physics and Chemistry Technics, CAS, Wulumuqi 830011, Xinjiang, P.R. China

²Key Laboratory For Advanced Building Materials of Sichuan Province, South West University of Science and Technology, Mianyang 621010, Sichuan, P.R. China

³Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621009, Sichuan, P.R. China

⁴University of Science and Technology Beijing, Beijing 100018, P.R. China

*Corresponding author: Tel: +86 991 3835096; +86 816 6089036; E-mail: bianliang555551@126.com; songmianxin@swust.edu.cn

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Rutile TiO₂ and 12 rare earths (RE)/rutile TiO₂ were synthesized by one-step method at 80 °C. Subsequently, they were characterized using XRD, SEM, particle size, DRS and Zeta (ζ) potential. The results indicated that the rare earth/rutile TiO₂ was successfully synthesized at 80 °C and rare earth obviously improved the parameters of photocatalytic activity of rare earth/rutile TiO₂, such as crystalline lattice diameters, particle size, band gap and ζ potential.

Key Words: Rutile TiO₂, One-step method, Rare earth, Low temperature, Photocatalytic activity.

INTRODUCTION

It was evident that the band gap for rutile, which was usually synthesized under high temperature^{1,2} is 3.0 eV. The absorbing wavelength of rutile TiO₂ is much longer than that of anatase TiO₂ (3.2 eV) with a similar crystal grain size³. Zhao *et al.*⁴ synthesized the small grain size and pure rutile TiO₂ using a novel, low temperature based, one-step method. At present, there has been a growing interest in the studying of photocatalytic activity of rutile TiO₂ from a doped materials view⁵.

The influence of rare earth on photo catalytic activity of anatase TiO₂ had been confirmed, several examples of simulation can be found in the literature^{6,7}. Therefore, rare earth improved the band gap of anatase TiO₂, but it had not been applied to study on rutile TiO₂. Recently, the band gap and photo catalytic activity of rare earth/rutile had been studied using DFT⁸. However, it has been, until recently, a lack fundamental experimental study on small particle size rare earth/rutile TiO₂ under low temperature.

In the present paper, rare earth/rutile TiO₂ was synthesized using one-step method and the corresponding crystal phase and photocatalytic activity were investigated using the XRD, SEM, particle size, DRS and ζ potential methods^{9,10}.

EXPERIMENTAL

Experimental methods were shown in Fig. 1 and rutile phase appears at (b) step. The volume ratio of Ti(OC₄H₉)₄, 2.0

mol L⁻¹ ammonia and 65 % HNO₃ was 1:1:1. The gel was washed by centrifugalization and rare earth oxide in HNO₃ was added into the solution. Therefore, quality ratios of rare earth oxide were 0.0, 0.5, 1.0, 1.5 and 2.0 wt %, respectively. Following vigorous magnetic stirring, the rare earth/rutile TiO₂ was obtained at 80 °C⁴ and the total synthesis time was dominated by its enthalpy of formation. Finally, the rare earth/rutile TiO₂ powders were dried at 90 °C for 2 h.

RESULTS AND DISCUSSION

Synthesis time: Fig. 2 shows that surface morphology of rare earth/rutile TiO₂ depends on its growth ratio and crystalline degree, therefore, its growth ratio is faster than that of rutile TiO₂. Typically, rare earth improves the crystal degree and grain size of total system⁷.

The synthesis time (t) of rare earth/rutile TiO₂ is dominated by enthalpy of formation (E) of system, in accordance with its calculated data⁸, is directly proportional as eqn. 1. When the E of rare earth/rutile TiO₂ increases, its synthesis time will increase in line.

As depicted in Fig. 3, the E of rare earth/rutile TiO₂ increases with shifting in the atomic number of rare earth. Therefore, the E of La (Y)/rutile TiO₂ is less than that of rutile TiO₂ and is similar to each other, because of the similar outer electrical energy.

$$t = t_R + \zeta \cdot (E - E_R) / \Delta E \quad (1)$$

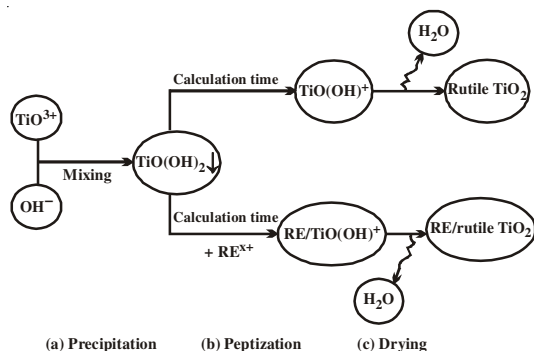


Fig. 1. Flow chart of rare earth/rutile TiO_2 by one-step method. Where the model parameters were based on reported by Bian *et al.*¹⁰. The total energy was calculated using the PBE-GGA method. A kinetic energy cutoff of 350 eV and Fermi energy was chosen for 0-energy point

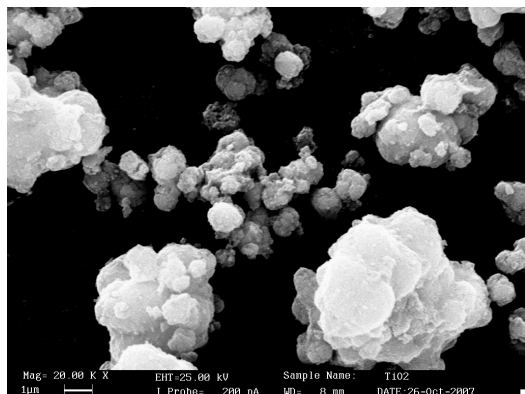


Fig. 2. Illustration of scanning electron microscope (SEM) to La/rutile TiO_2 . It was character by LEOS440, Leica Cambridge LTD company. Large size powder was possibility rare earth/rutile TiO_2 and small powder was rutile TiO_2

where t_r and E_R are the synthesis time and energy of rutile TiO_2 , respectively; ζ is the ratio of band gap between DFT simulation and experiment and ΔE is the time and energy separation using orthogonal test.

X ray diffraction studies: As shown in Fig. 3, the crystal phase of different content rare earth/ TiO_2 is rutile and the dopant different content is not effective on the crystal phase. According to the Scherrer formula in eqn. 2, the crystalline aberrance increases as follows based on the change in its d-spacing^{3,9,10}.

The crystal plane spacing of rare earth/rutile TiO_2 is altered obviously, according to eqn. 3, includes the master growth surface diameters d_{110} , d_{101} and d_{111} . Its crystalline lattice diameter is shown in Fig. 3 and less than that of rutile TiO_2 . Rare earth is also effective on the (211) and (002) faces, but they are not sensitive to photocatalytic activity⁵.

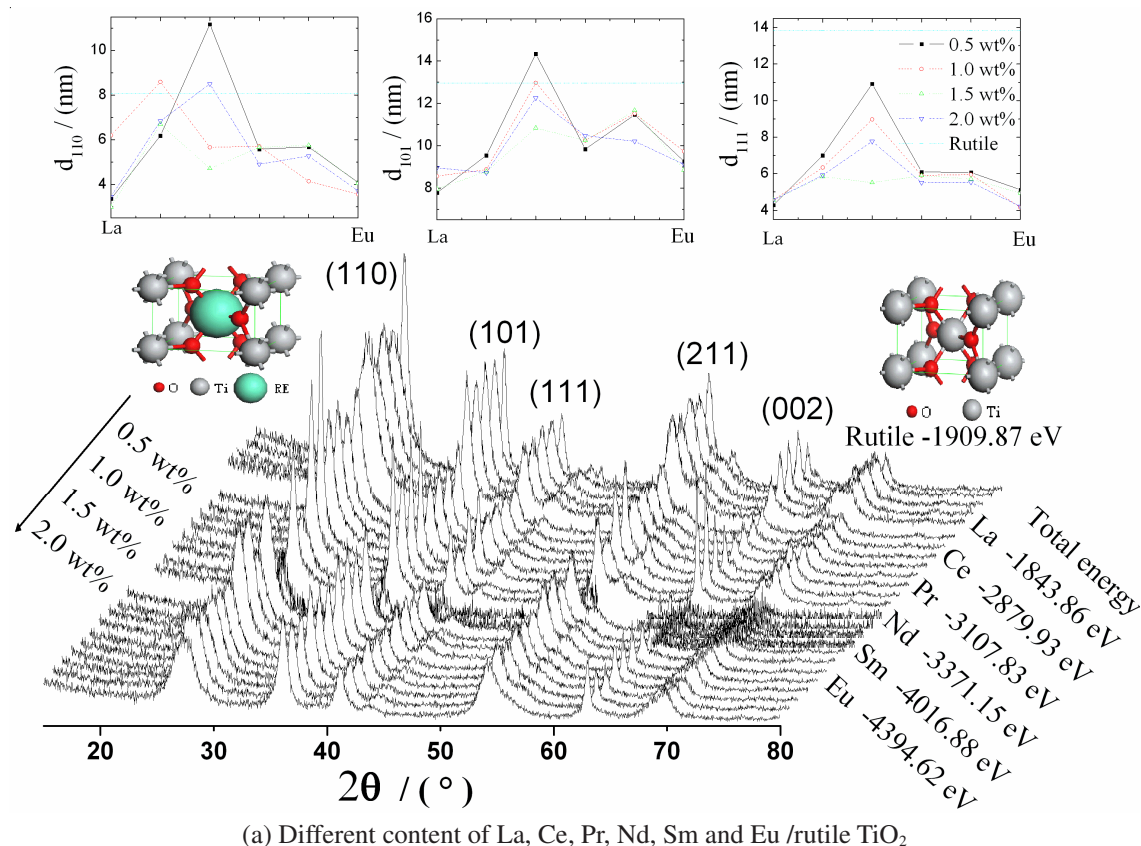
Typically, the crystalline degree of rare earth/rutile TiO_2 reduces with its E increasing. It depends on surface electronic states of rare earth. Thus there are some miscellaneous peaks on the crystal surface of Gd, Tb, Dy, Tm and Er/rutile TiO_2 .

$$D = K\lambda/\beta\cos\theta \quad (2)$$

$$2d\sin\theta = n\lambda \quad (3)$$

Where K is the Scherrer constant; D is the crystal lattice diameter; β is the integral full width at half maximum. d is the interplanar spacing; n is the diffraction order.

Particle size: The particle size is obtained by the volume-average diameter and number-average diameter, according to eqns. 4-5. As shown in Fig. 3, except of La and Y, rare earth causes the agglomeration of rutile TiO_2 ^{9,11}. The agglomeration of Tb/rutile TiO_2 is the most obviously significant and the agglomeration degree of La (or Y)/rutile TiO_2 is the least.



(a) Different content of La, Ce, Pr, Nd, Sm and Eu /rutile TiO_2

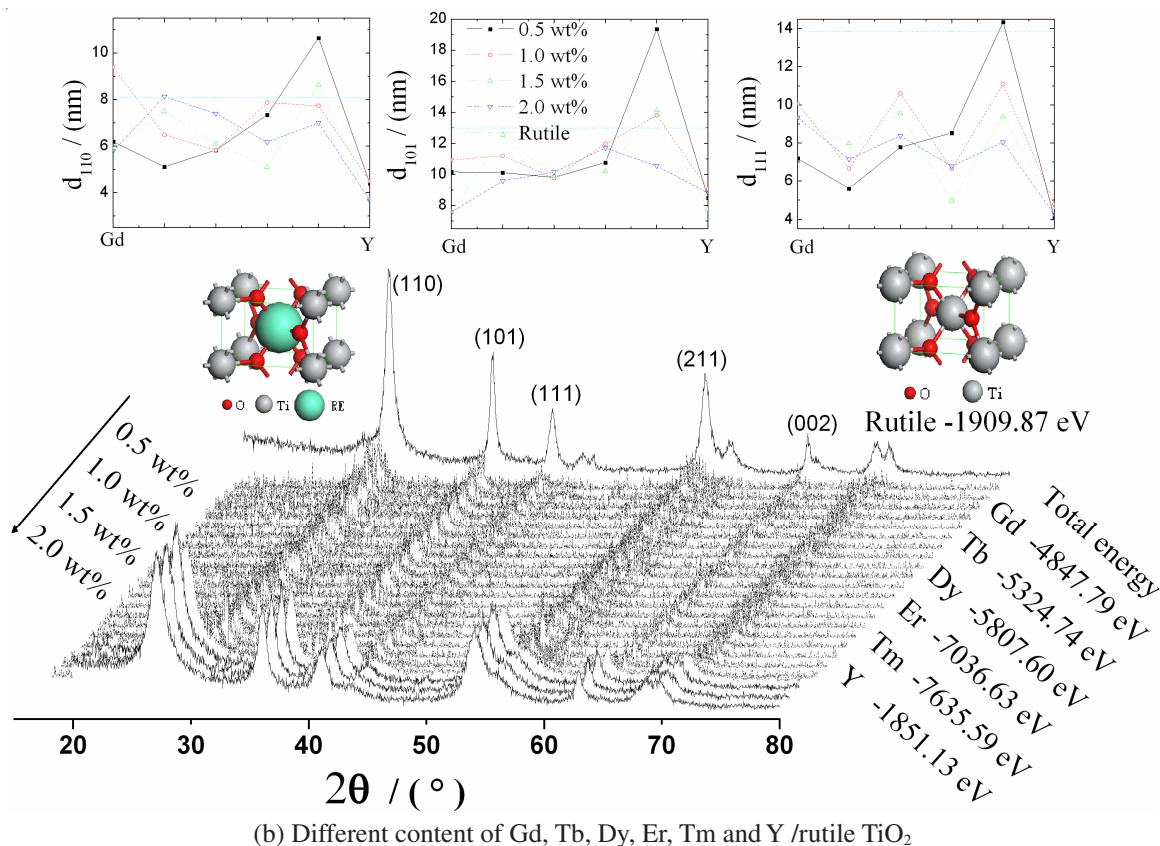
(b) Different content of Gd, Tb, Dy, Er, Tm and Y /rutile TiO₂

Fig. 3. XRD patterns of rare earth/rutile TiO₂. It was character by X'PertPro, PANalytical Company, NL. Where rare earth/rutile TiO₂ is tetragonal; its crystal group is P4₂/mmm.

Rare earth improves average diameter of rutile TiO₂ because of increasing E of system. With increasing the dopant content of rare earth⁴, the average diameter of rare earth/rutile TiO₂ increases. This means that rare earth decreases the total particle size, however, increases the local structural agglomeration. Therefore, particle size of 1.5 wt % rare earth/rutile TiO₂ is the least according to Fig. 3.

$$E_{(\theta,\psi)} = 2\pi A a^2 C J_1(ka\theta)/(ka\theta) \quad (4)$$

$$I_{(\theta)} = I_{a(\theta)} + I_{b(\theta)} \quad (5)$$

where πa^2 is the hole area; C is the delayed phase position; others are phase position difference. I is the diffracted intensity; I_a is the vertical polarized light; I_b is the level polarized light.

Diffuse reflection spectroscopy: According to eqn. 6, DRS results include the initial adsorbing position and wavelength removal^{9,10,12}. Therefore, electron translates from 4fⁿ (or 4fⁿ⁻¹) to O2p and adsorbing wavelength increases with reducing E of rare earth/rutile TiO₂. Fig. 4 depicts, with the exception of Ce and Nd, rare earth improves the red shift of the adsorbing wavelength; its band gap is similar to the results using DFT⁴. The corresponding optimized dopant content is 1.5 wt %, its particle size is less than others as shown in Fig. 3.

Typically, the lowest band gap widths of Gd (Tb)/rutile TiO₂ may be too small to be character and some energy levels of Gd (Tb) 4f states are barrier by Ti 3d states. Their actual experimental results are higher than the estimated data.

$$F_{(R)} = K / S = \epsilon C / S = b C \quad (6)$$

where b is the constant; C is the component concentration; S is the scattering coefficient; K is the absorptivity.

Zeta (ζ) potential: Based on the Helmholtz-Smoluchowski equation of ζ potential, rare earth can improve the surface electric state and adsorbing ability of rutile TiO₂, this is related to the surface electric activity as shown in eqn. 7. When the data of 4fⁿ states (or 4fⁿ⁻¹ states) and O2p state is greater than 0, the isoelectric point can easily be shifted in the alkaline direction and it is little affect by the dopant content.

As seen in Fig. 5, Pr, Sm, Er and Eu causes double isoelectric points, it increases the uniformity of particle size that is related to surface defects. The rare earth, such as La, Ce, Dy, Gd, Tb, Tm and Y, reduces specific double isoelectric point of rutile TiO₂ to a single-point; it improves the surface adsorption action between organic matters and rutile TiO₂.

The isoelectric point of Ce (Dy, Gd and Tb)/rutile TiO₂ shifts in the acidic direction and the isoelectric point of La (Tm and Y)/rutile TiO₂ shifts towards the alkaline direction. However, there is no isoelectric point in the plots of ζ potential of Nd/rutile TiO₂ that may be rapid inactivation.

$$\zeta = \eta \Lambda_0 (dEz) / [\epsilon_0 \epsilon_r (dAP)] \quad (7)$$

where ζ is the solution viscosity; Λ₀ is the electrical conductivity; ε₀ is the dielectric constant of free space; ε_r is the dielectric constant of electrolyte solution.

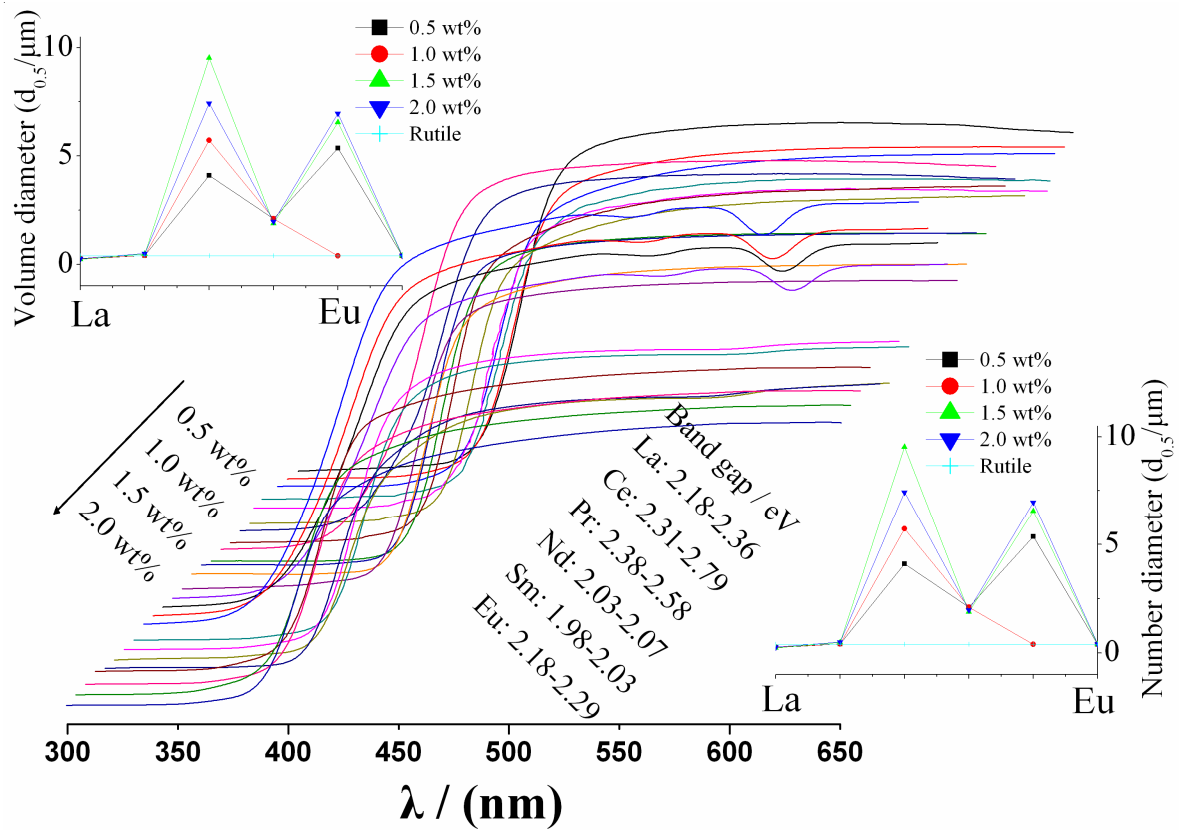
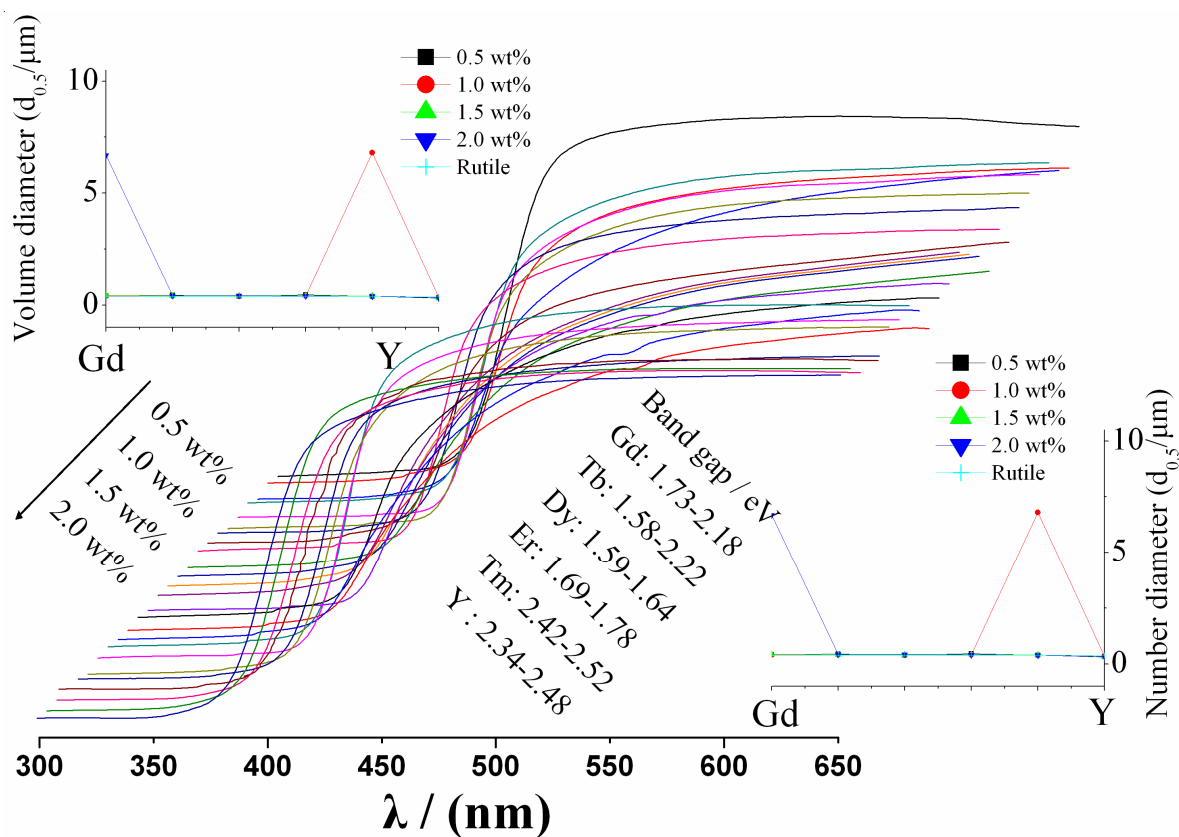
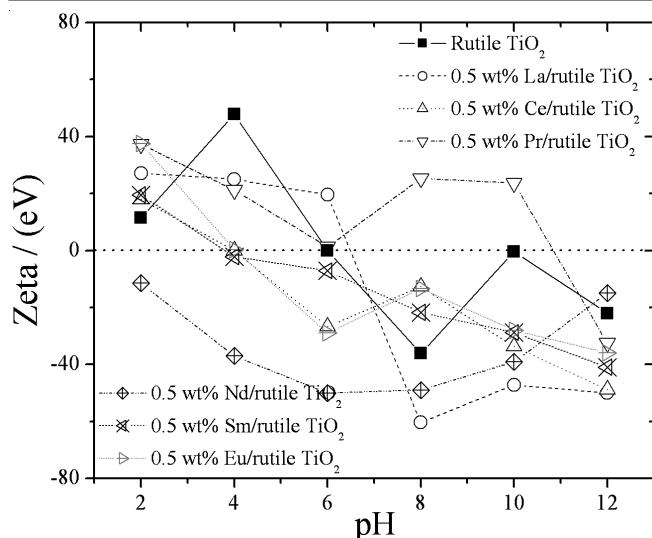
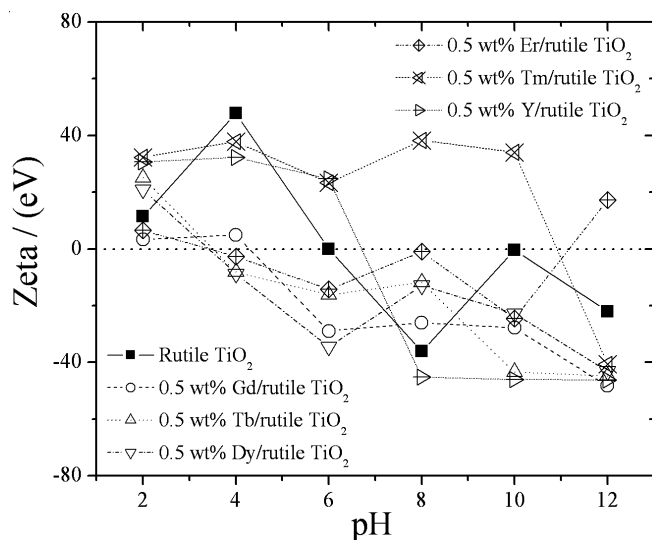
(a) Different content of La, Ce, Pr, Nd, Sm and Eu/rutile TiO_2 (b) Different content of Gd, Tb, Dy, Er, Tm and Y/rutile TiO_2

Fig. 4. Diffuse reflection spectroscopy patterns and average diameters of rare earth/rutile TiO_2 . The band gap of rutile TiO_2 is 2.96 eV. Diffuse reflection spectroscopy was character by UV-3150, Shimadzu Company, Japan. And particle size was character by Mastersizer 2000, Malvem Company, UK

(a) Different content of La, Ce, Pr, Nd, Sm and Eu/rutile TiO₂(b) Different content of Gd, Tb, Dy, Er, Tm and Y/rutile TiO₂Fig. 5. Plots of ζ potential of rare earth/rutile TiO₂. ζ potential was characterized by 3000HS, Malvern Company, UK

Conclusion

(1) Rutile TiO₂ and rare earth/rutile TiO₂ were synthesized using one-step method at 80 °C; their synthesis times are in direct ratio with calculated data.

(2) Particle size of rare earth/rutile TiO₂ was smaller than that of rutile TiO₂ and its crystalline distortion degree depends on surface electronic states and atomic number of rare earth.

(3) Rare earth improves the adsorbing wavelength and iso-electric point of rutile TiO₂, except Y.

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