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Microstructure and Optical Properties of Scandium Doped TiO_2 Nanoparticles*

Yang Jian (杨 建)*, Qiu Tai (丘 泰), Nie Hengchang (聂恒昌), Shen Chunying (沈春英)
(College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, China)

Abstract: Pure and Sc doped TiO_2 nanoparticles with different molar fractions of Sc were prepared by a sol-gel process, and were characterized by means of XRD, TG-DSC, TEM, UV-Vis and PL spectra. Effects of calcination temperature and Sc content on microstructure and optical properties of as-prepared TiO_2 samples were investigated and the influencing mechanisms were discussed. The results show that Sc dopant greatly inhibits the crystallization from amorphous state to anatase and the phase transformation from anatase to rutile. Retarding effect of Sc on the grain growth of TiO_2 was also observed and the effect becomes significant with the increase of Sc content. Compared with pure TiO_2, the UV-Vis absorption band edge of Sc doped samples shows obvious blue-shift, however, there is no noticeable increase in the shift with increasing Sc content. The ultraviolet absorbing capacity of TiO_2 samples at 200～300 nm is reduced and then enhanced with increasing Sc content. The samples doped with 1.5% and 2% (mole fraction) Sc show stronger ultraviolet absorption than pure one. Photoluminescence peaks at 410 and 460 nm were detected on all the samples, which means that the doping of Sc does not generate new luminescence phenomena, but the luminescence intensity is enhanced with the increase of Sc content.

Key words: TiO_2; doping; Sc; microstructure; photoluminescence; rare earths
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Bulk TiO_2 is a wide band-gap n-type semiconductor material and recently, nano TiO_2 has attracted much attention for their unique properties such as photoelectric convertion, optically nonlinearity and low probability of nonradiative transition due to low phonon energy. It is well known that TiO_2 has two main crystalline modifications, anatase and rutile, which are thermodynamically the stable and metastable, respectively. Moreover, the two modifications show different characteristics in many properties. Nano anatase particles have been found to possess high photoelectric activity and excellent light absorption ability at ultraviolet band. Numerous researches have been reported that the doping of oxides could promote or inhibit the anatase-to-rutile transformation and the doped nanosized TiO_2 may show more superior properties. The addition of rare earths (La, Ce, Er, Pr, Gd, Nd, Sm) may extend the optical response range of TiO_2[1～3]. New energy level of -0.8 and -0.5 eV appears in the surface forbidden band of TiO_2 doped with CeO_2[4] and the materials show heatcatalysis and photocatalysis phenomena[5]. Photooxidation effect was found in WO_x-TiO_2 system[6]. Eu-TiO_2 and (Er, Y)-TiO_2 exhibited interesting photoluminescence characteristics[7,8]. Er-TiO_2 is expected to be a potential integrated optical devices[9]. Sc and its compounds, owing to special properties, are widely used in preparing luminescence materials, electroluminescence materials and laser materials[10～12]. However, study on TiO_2 doped by Sc has not been reported so far. In this paper, pure and Sc doped TiO_2 nanoparticles with different molar fractions of Sc were prepared and effects of doped Sc on the crystalline, phase transformation, grain size and optical properties of TiO_2 were investigated by means of XRD, TG-DSC, TEM, UV-Vis and PL spectra.

1 Experimental

1.1 Preparation of pure and Sc doped TiO_2 nanoparticles

The samples were synthesized by the sol-gel process. In this method, 17 ml tetra-n-butyl titanium ($Ti(O\text{-}Bu)_4$) dissolved in 40 ml of absolute ethanol was added drop-wise under vigorous stirring to a mixture solution containing 10 ml distilled water, 40 ml absolute ethanol, 10 ml acetic acid and 3% dispersant agent (Dodecyl sulfonic acid sodium salt) to carry out hydrolysis. After further stirring for 1 h, the resulting

* **Received date:** 2006-01-06; **revised date:** 2006-06-10
Biography: Yang Jian (1976-), Male, Doctor, Lecturer; Research field: Structural and functional properties integration materials
* **Corresponding author** (E-mail: yangjian1976@163.com)

transparent colloidal suspension was obtained and then it was aged for 2 days till the formation of gel The gel was dried at 343 K for 24 h and then ground The powder was calcined at different temperatures for 2 h, and then pure TiO_2 nanoparticles were obtained Similarly, 0.2%, 0.5%, 1%, 1.5%, 2% and 4% (mole fraction) Sc doped TiO_2 samples were also prepared according to the above procedure by substituting Sc $(NO_3)_3$ solution with certain concentration for 10 ml distilled water.

1.2 Characterization of TiO_2 nano particles

DSC-TG measurement of the dry gels was performed on a NETZSCH STA 449C thermal analyzer in N_2 with a heating rate of 10 ℃ · min^{-1}. To determine the phase composition and grain size of the prepared TiO_2, XRD analysis was carried out on the ARL X′TRA diffractometer using Cu Kα radiation (λ = 0.15418 nm). The mass fraction of anatase in TiO_2, C_A, was calculated from the Eq.[7]

$$C_A = \frac{1}{1 + 1.26 I_R / I_A} \times 100\% \quad (1)$$

where I_R and I_A are intensities of the most intense line of the respective phases, e.g., d = 0.3245 nm for (110) plane of rutile and d = 0.351 nm for (101) plane of anatase, and 1.26 is a proportionality constant

The average grain size of TiO_2 was calculated with the peak widths using the Scherrer's equation

$$D = \frac{K\lambda}{(\beta_C - \beta_S)\cos\theta} \quad (2)$$

where D is the average grain size of TiO_2; λ is the X-ray wavelength; β_C and β_S are the FWHM of the sample and the standard (single-crystal silicon), respectively; the number K = 0.89 is a coefficient; θ is the diffraction angle.

The investigation of the particle morphology and size was performed on a JEM-200CX transmission electron microscope (TEM) and the micrographs were recorded at 300 kV. The samples were pressed into discs under 3 MPa and their UV-Vis diffuse reflection spectra (DRS) were measured using a UV-Vis scanning spectrophotometer (Shimadzu UV-2401 PC). The photoluminescence (PL) emission spectra of the samples were recorded using PE LS50-B fluorescence spectrometry.

2 Results and Discussion

2.1 DSC-TG

Fig 1 shows the DSC-TG curves of as-synthesized pure and 1% Sc doped TiO_2 dry gels A endothermic peak centered at 90 ℃, accompanied by weight loss in TG curves, was observed for both of the two systems, which is attributed to desorption of adsorbed water and ethanol in the gels The weight loss in the region from 150 to 300 ℃ results from the charring and decomposition of the adsorbed organic matters For pure TiO_2 sample, there are several continuous overlapped exothermal peaks from 300 to 500 ℃, which correspond to the further charring and decomposition of the organic matters and the crystallization of TiO_2 gel from amorphous to anatase[8]. For the doped sample, the exothermic peak at this temperature range is not obvious and the corresponding weight loss process shows a lower rate and higher end temperature compared with the pure one. This suggests that the doping of Sc inhibits the transformation process from amorphous to anatase and increases the crystallizing temperature. XRD results proved that the crystalline process has been fulfilled for the two samples after calcinations at 500 ℃. In the two systems, as can be

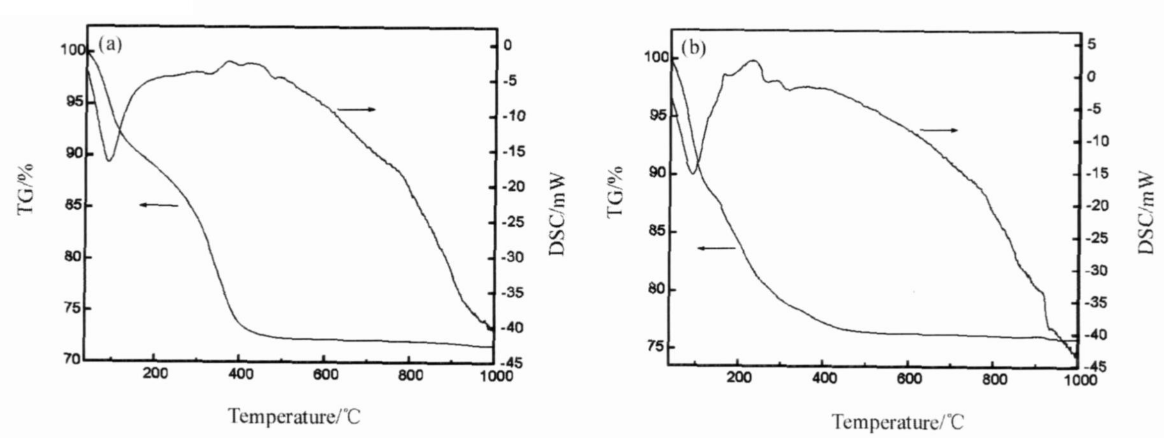

Fig 1 DSC-TG curves of pure (a) and 1% Sc doped (b) TiO_2 dry gel

seen from Fig 1, there is no a remarkable exothermic peak corresponding to the transformation from anatase to rutile, which implies that the transformation is a gradual and temperate process

2.2 XRD

Fig 2 shows the XRD patterns of the samples calcined at 600 and 700 ℃. It can be seen that in all the samples calcined at 600 ℃, only anatase exists When calcined at 700 ℃, diffraction peaks of rutile appear in the pure sample (The percentage of anatase was calculated to be 84.7%), whereas all the doped samples are still complete anatase modification. As a result, a conclusion can be made that the doped Sc inhibits the transformation from anatase to rutile and increases the transformation temperature.

It also can be seen from Fig 2 that all the samples show broad diffraction peaks, which is the general characteristics of nano particles Moreover, the broadening becomes significant with the increase of Sc addition. Fig 3 shows the grain size of all samples calculated using Scherrer's equation. As shown in Fig 3, the grain size of the Sc doped samples is always smaller than that of the pure TiO_2 and decreases with the increasing Sc addition. The results indicate that the doped Sc significantly retards the grain growth of TiO_2 and the effect is intensified with increasing amount of Sc. Fig 4 shows the TEM images of pure and 4mol% Sc doped TiO_2 calcined at 600 ℃. It can be seen that the particles are nearly ball and the average diameter is around 25 and 10 nm, respectively, which are consistent with the grain size presented in Fig 3.

When the ionic radius of the dopant is larger or smaller than Ti^{4+} (0.068 nm), the dopant is introduced substitutionally into the TiO_2 lattice, producing some lattice distortion and accumulating some deformation energy, which inhibits the phase transformation of anatase[13, 14]. The ionic radius of Sc^{3+} is 0.0745 nm[10], which is larger than that of Ti^{4+}. It should be noted from Fig 2 that the values of diffraction angles of the Sc doped samples are almost identical with those of pure TiO_2, which implies that the doped Sc dose not enter into TiO_2 lattice and substitute Ti^{4+}. In addition, no any diffraction peaks of Sc-containing compounds appeared in all XRD patterns These results suggest that the doped Sc may distribute homogeneously in TiO_2 nano particles as small Sc_2O_3 clusters Thus the Ti-O-Sc bond will be formed around anatase microcrystallines during the calcinations process, which results in inhibiting the transformation of anatase and its grain growth[14].

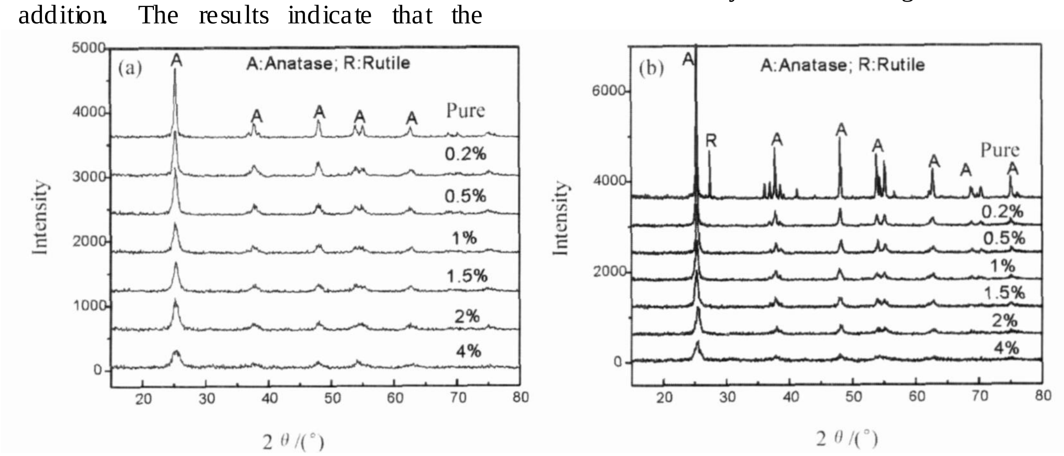

Fig 2 XRD patterns of pure and Sc doped TiO_2 nanoparticles calcined at 600 ℃ (a) and 700 ℃ (b)

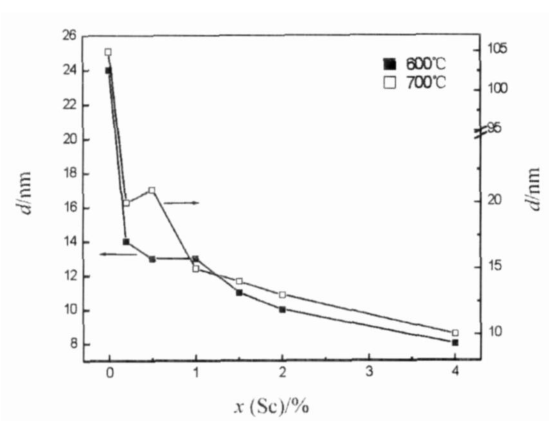

Fig 3 Grain size of TiO_2 nanoparticles calcined at 600 and 700 ℃

2.3 UV-Vis

Fig 5 shows the DRS spectra of the samples calcined at 600 ℃. It can be seen that all the samples show obvious absorption band edge, displaying a typical semi-conductor characteristics However, compared with pure TiO_2, there is evident blue-shift occurred for the doped samples As indicated by the theory of quantum size effect, the smaller the grain size, the wider the band-gap, and the larger the shift of band edge[15]. Therefore, the above results indicate that the Sc doped TiO_2 nanopar-

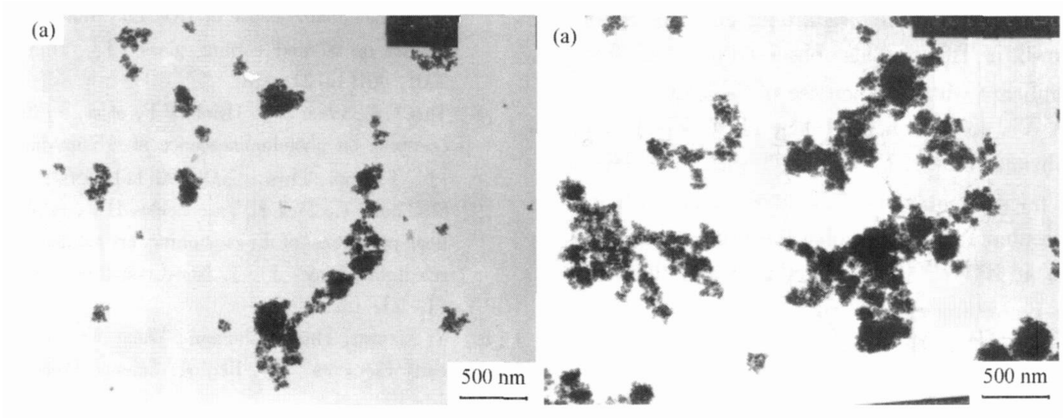

Fig 4 TEM images of pure (a) and 4% Sc doped (b) TiO_2 nanoparticles calcined at 600 ℃

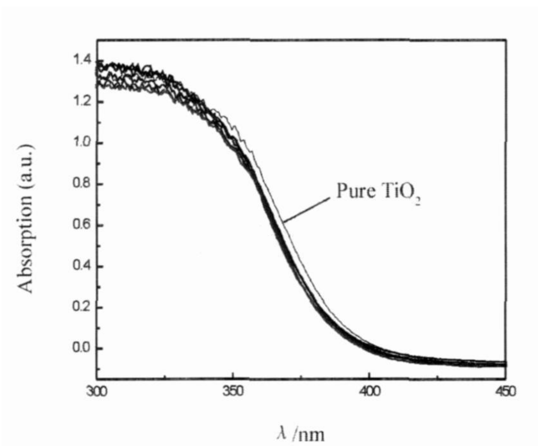

Fig 5 UV-Vis spectra of TiO_2 nanoparticles calcined at 600 ℃

ticles are smaller in size and show obvious quantum size effect, which results in the shift og band edge to the short wavelength side. However, since the decrease of grain size is not obvious enough with increasing Sc addition, which can be easily seen in Fig 3, there is no evident increase in the shift of band edge. It also can be seen from Fig 5 that the ultraviolet absorbing capacity of the samples at 200～300 nm is reduced and then enhanced with increasing Sc content. The samples doped with 1.5% and 2% Sc show stronger ultraviolet absorption than pure one.

2.4 PL

The PL spectra of all the samples calcined at 600 ℃ were measured using the excitation wavelength of 300 nm as shown in Fig 6. It is clearly seen that the energy level of all samples are almost identical, i. e., all samples show obvious PL peaks at 410 and 460 nm, apart from a difference in peak intensity. This suggests that the doping of Sc does not bring about new luminescence bands, but shows influence on fluorescence intensity. It has been known that the photoluminescence of TiO_2 nanoparticles is caused by surface oxygen vacancies and defects. A large number of oxygen vacancies in the surface of TiO_2 nanoparticles and short free-path of electrons owing to small particle size result in a high probability for electrons to be trapped by vacancies to form excitons. Therefore, exciton levels will be formed near the bottom of conduction band, which will in turn generate exciton luminescence bands[16]. The two PL peaks at 410 and 460 nm might be attributed to tie luminescence of free and self-tapped exciton, respectively. Generally, the smaller the particle size, the more the number of oxygen vacancy, the higher the probability of forming exciton, and the more intense the exciton luminescence[17～19]. As shown in Fig 6, the luminescence intensity of TiO_2 nanoparticles is enhanced as the addition of Sc increased, which can be explained by the quantum size effect and increased concentration of oxygen vacancies and defects of Sc doped TiO_2 particles as a result of the fact that the doping of Sc inhibits the phase transformation and grain growth of TiO_2 nanoparticles.

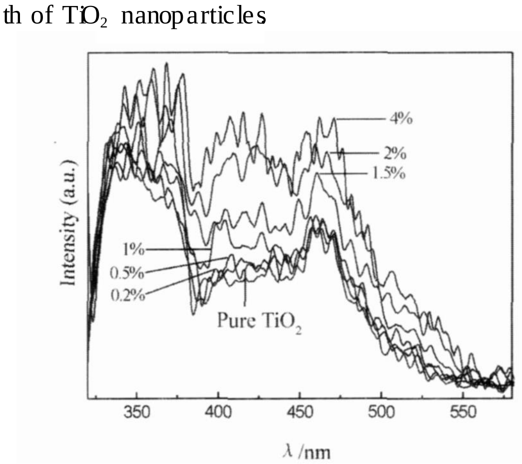

Fig 6 PL spectra of TiO_2 nanoparticles calcined at 600 ℃ (λ_{ex} = 300 nm)

3 Conclusion

The doping of Sc greatly inhibits the crystallization from amorphous state to anatase and the phase transformation from anatase to rutile. Retarding effect of Sc on the grain growth of TiO_2 was also observed and the effect becomes significant with the increase of Sc addition.

The UV-Vis absorption band edge of Sc doped samples show obvious blue-shift compared with pure TiO_2, but there is no noticeable increase in the shift with increasing Sc content. The ultraviolet absorbing capacity of TiO_2 samples at 200～300 nm is reduced and then enhanced with increasing Sc content. The samples doped with 1.5% and 2% Sc show stronger ultraviolet absorption than pure one.

All samples show obvious photoluminescence peaks at 410 and 460 nm, which means that the doping of Sc does not generate new luminescence bands, but the luminescence intensity is enhanced with the increase of Sc content.

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