

## 低温下溶胶凝胶法制备 $\text{TiO}_2$ 纳米晶

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**摘要:** 从含过量水的溶胶出发, 在室温下得到了  $\text{TiO}_2$  纳米晶。通过红外光谱, 透射电子显微镜法和 X 射线粉末衍射法对含有过量水的溶胶体系中  $\text{TiO}_2$  纳米晶的室温形成机理进行了研究。与传统的溶胶凝胶法相比, 在改良的溶胶凝胶体系中, 在缩聚反应之前由于水过量使得钛的先驱体快速且充分的水解, 从而生成  $[\text{TiO}_6]$  基团, 随之形成  $\text{TiO}_2$  纳米晶。晶粒的尺寸为约 3.5 nm, 该法得到的  $\text{TiO}_2$  纳米晶比传统溶胶凝胶法得到的  $\text{TiO}_2$  纳米晶和商用光催化剂德固赛 P25 具有更好的光催化活性。

**关键词:**  $\text{TiO}_2$  纳米晶; 改良的溶胶凝胶体系; 机理; 光催化活性

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## Preparation of Nanocrystalline $\text{TiO}_2$ by Sol-Gel-Method at Room Temperature

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**Abstract:** Nanocrystalline titania( $\text{TiO}_2$ ) particles were obtained at room temperature by a modified sol-gel method starting from a solution with large amount of water. The nanocrystalline  $\text{TiO}_2$  particles prepared with large amount of water at room temperature were characterized by IR, TEM and XRD. Comparing with conventional sol-gel method, the present system offers quick and complete hydrolysis of titanium precursor before polycondensation, thus resulting in  $[\text{TiO}_6]$  units, and the formation of nanocrystalline  $\text{TiO}_2$  particles with an average grain size of 3.5 nm. Moreover, the as-prepared nanocrystalline  $\text{TiO}_2$  powders exhibit a better photocatalytic activity than both of the powders prepared by conventional sol-gel method and the commercial photocatalyst Degussa P25.

**Key words:** nanocrystalline  $\text{TiO}_2$ ; modified sol-gel method; mechanism; photocatalytic activity

## 0 Introduction

Crystalline titania( $\text{TiO}_2$ ), as one of the most important oxide semiconductor material with a wide energy band gap, has attracted much attention for its wide applications as key material in gas sensors, dielectric ce-

ramics, and photocatalysts<sup>[1-4]</sup>, and in the field of photocatalysis and photoelectrochemistry<sup>[5-9]</sup>. So far, a variety of methods have been successfully applied for the synthesis of  $\text{TiO}_2$  nanoparticles, for example, hydrothermal method<sup>[10]</sup>, magnetron sputtering technique<sup>[11]</sup>, chemical vapor deposition<sup>[12]</sup> and sol-gel method<sup>[13]</sup>. Among them,

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sol-gel method has been employed most widely due to its inexpensive equipment required, highly pure product produced, product shape controlled<sup>[14]</sup>. In the conventional sol-gel system, the molar ratio of water to titanium precursor is often smaller than 15<sup>[15-16]</sup>. Such prepared gel particles are amorphous and further heat treatment is generally required to induce crystallization. However, heat treatment frequently leads to particle growth and agglomeration.

In the last decades, many efforts have been devoted to the formation of nanocrystalline TiO<sub>2</sub> particles at lower temperature. The nanocrystalline TiO<sub>2</sub> can be derived from sols containing large amount of water. For example, spherical-shaped TiO<sub>2</sub> particles with a size of about 4 nm were obtained by Hu et al.<sup>[17]</sup> by refluxing the solution containing titanium-n-butoxide, ethanol and distilled water at 75 °C for 24 h, and the molar ratio of water to titanium precursor was 151. Kanna et al.<sup>[18]</sup> reported that nanocrystalline TiO<sub>2</sub> materials with size of 4~20 nm were prepared by adding TiCl<sub>4</sub> to the excessive deionized water, followed by heat treatment at 80 °C. Chen et al.<sup>[19]</sup> showed that pure anatase type TiO<sub>2</sub> nanocrystallines with size of 3~7 nm were prepared by adding Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> to excessive water ( $n_{\text{H}_2\text{O}}/n_{\text{Ti}^{+4}}=100\sim 400$ ) with pH value of 1 adjusted by dilute HNO<sub>3</sub>. However, much of the work was focused on the preparation of nanocrystalline TiO<sub>2</sub>, the photocatalytic activity and doping modification. To the best of our knowledge there

has been little report on the formation mechanism of the nanocrystalline TiO<sub>2</sub> at low temperature. We report here the preparation of nanocrystalline TiO<sub>2</sub> materials by the modified and conventional sol-gel method using starting solutions with large amount of water and small amount of water, respectively. The products were characterized by IR, TEM and XRD techniques. The photocatalytic property of the prepared samples were also studied.

## 1 Experimental

### 1.1 Preparation of powder TiO<sub>2</sub> samples

Powder TiO<sub>2</sub> samples were prepared by the modified sol-gel method and the conventional sol-gel method. The differences between the two synthesis procedures were the molar ratio of the starting materials, the dropping order of the solution preparation, and the heat-treatment of the prepared sol samples. For the modified sol-gel method, the starting solution was with large amount of water, hereafter called as TiO<sub>2</sub>-L system. The experimental procedure is shown in Fig.1(a). The molar ratio of the starting materials was  $n_{\text{Ti}(\text{OC}_4\text{H}_9)_4} : n_{\text{C}_2\text{H}_5\text{OH}} : n_{\text{H}_2\text{O}} : n_{\text{HNO}_3} = 1 : 15 : 100 : 0.2$ . Firstly, solution A was prepared by mixing [Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>] with two-thirds of amount of ethanol as shown in the above molar ratio setting. Secondly, solution B was prepared by mixing the distilled water with nitric acid, and the rest one-third of the ethanol. Then solution A was added dropwise to solution B under vigorous stirring. After aging

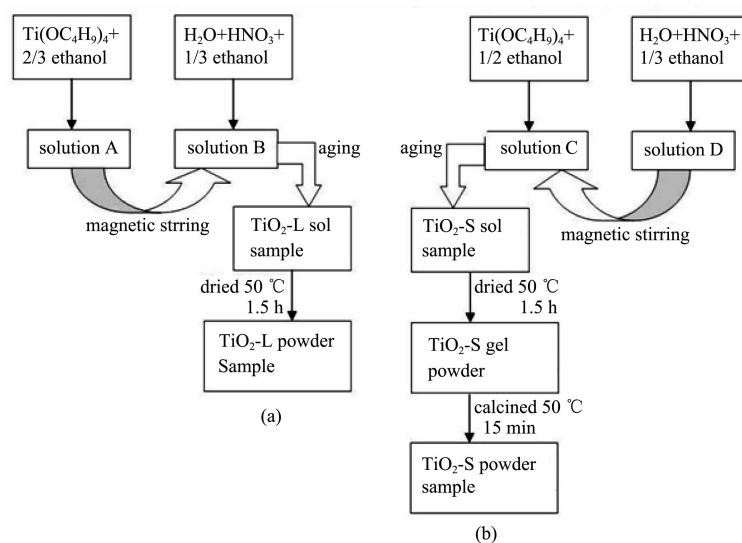


Fig.1 Procedures used to prepare the TiO<sub>2</sub>-L powder sample (a) and TiO<sub>2</sub>-S powder sample (b)

for a certain period of time, the transparent sol was obtained, hereafter called as TiO<sub>2</sub>-L sol sample. TiO<sub>2</sub>-L sol sample was dried under infrared lamp at about 50 °C to obtain TiO<sub>2</sub>-L powder sample. For the conventional sol-gel method, the starting solution was with a small amount of water, hereafter called as TiO<sub>2</sub>-S system. Its experimental procedure is schematically described in Fig.1(b). The molar ratio of the starting materials was  $n_{\text{Ti}(\text{OC}_4\text{H}_9)_4} : n_{\text{C}_2\text{H}_5\text{OH}} : n_{\text{H}_2\text{O}} : n_{\text{HNO}_3} = 1 : 15 : 1 : 0.002$ . Firstly, solution C was prepared by mixing [Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>] with half of the above fixed amount of ethanol. Secondly, solution D was prepared by mixing the distilled water with nitric acid, and the rest half of the ethanol. Then solution D was added dropwise to solution C under vigorous stirring. After aging, the transparent sol sample was obtained. The TiO<sub>2</sub>-S sol sample was dried under infrared lamp at about 50 °C for 1.5 h to obtain the TiO<sub>2</sub>-S gel powders, which were heated at 500 °C for 15 min to obtain the TiO<sub>2</sub>-S powder sample.

## 1.2 Characterization

Infrared spectra were recorded by using the Avatar 360 infrared Spectrometric Analyzer. The IR samples were prepared by dropping the same volume of prepared sols on the surface of the KBr tablets, followed by drying under infrared lamp. The crystal behavior and morphologies of the sol samples were observed using a JEM 200CX transmission electron microscope. The crystal behavior of the powder samples was measured by a D/MAX-rA diffractometer using nickel filtered Cu K $\alpha$  radiation ( $\lambda = 0.154\ 18\ \text{nm}$ ) with a scanning angle ( $2\theta$ ) of 15°~75°, and a voltage and current of 40 kV and 40 mA. The specific surface area was measured with a Micromeritics ASAP 2020 M+C instrument, using the adsorption of N<sub>2</sub> at the temperature of liquid nitrogen.

## 1.3 Photocatalytic activity measurement

The photocatalytic activity of the TiO<sub>2</sub>-S and TiO<sub>2</sub>-L powder samples was evaluated by degrading the methyl orange from its aqueous solution under UV light. Three strip tungsten lamps with intensity of 15 W·m<sup>-2</sup> were used as the light source, whose characteristic emission wavelength is 290 nm. The distance between the light source and the solution level was kept as 12

cm. An amount of 0.1 g of photocatalyst was added into a 10 mL aqueous solution of 10<sup>-4</sup> mol·L<sup>-1</sup> methyl orange with a maximum absorption at about 466 nm. Before irradiation, the solution was stirred for 30 min in the dark until adsorption-desorption balance was reached. After illumination, the solution was centrifuged and filtered, and the supernatant was used for the UV-Vis absorption test at the absorption peak (466 nm) before and after photodegradation. A<sub>0</sub> is the absorbance of the initial methyl orange solution at 466 nm and A is the absorbance of methyl orange solution at 466 nm when t is 3 h, 6 h, 9 h, 12 h, respectively. The photocatalytic activity is characterized by apparent rate constant K, which could be calculated by the equation below<sup>[15]</sup>

$$K = \frac{1}{t} \ln\left(\frac{A_0}{A}\right) \quad (1)$$

The absorption spectra of the photodegraded methyl orange solution were recorded by a Hitachi U-4100 UV-Vis spectrophotometer.

## 2 Results and discussion

### 2.1 Formation mechanism of nanocrystalline TiO<sub>2</sub> in sol with large amount of water

Fig.2 shows the IR transmission spectra of the prepared TiO<sub>2</sub>-S and TiO<sub>2</sub>-L sol samples. Both TiO<sub>2</sub>-S and TiO<sub>2</sub>-L sol samples show bands around 1 636 and 3 200 to 3 600 cm<sup>-1</sup>, which correspond to the vibration of hydrogen bonded OH groups<sup>[20]</sup>. The ethanol evaporated IR test samples prepared were dried, therefore it can be concluded that the OH groups are due to the Ti-OH from the hydrolysis of Ti (OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>. The much stronger

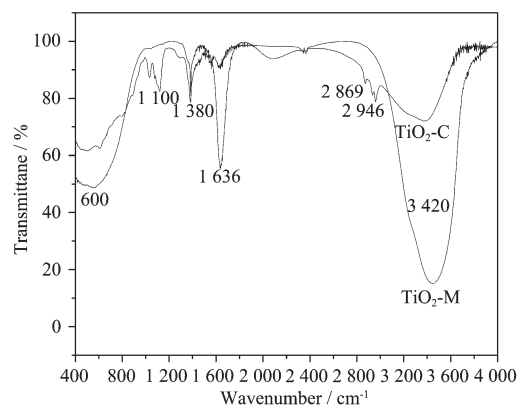


Fig.2 Infrared transmission spectra of the prepared TiO<sub>2</sub>-S and TiO<sub>2</sub>-L sol samples

bands of Ti-OH groups in TiO<sub>2</sub>-L means much more Ti-OH groups in the TiO<sub>2</sub>-L sol sample than that in the TiO<sub>2</sub>-S sol sample. The band at 600 cm<sup>-1</sup> in the two sol samples can be assigned to symmetric stretching vibration of the Ti-O-Ti bonds<sup>[21]</sup>. Again, the band at 600 cm<sup>-1</sup> of the TiO<sub>2</sub>-L sol sample is stronger than that of the TiO<sub>2</sub>-S sample, which suggests that the TiO<sub>2</sub>-L sol sample has more Ti-O-Ti groups than TiO<sub>2</sub>-S sample. The small bands around 1 380, 2 869 and 2 946 cm<sup>-1</sup> in the TiO<sub>2</sub>-S sol sample can be ascribed to the vibration of the C-H groups<sup>[22]</sup>. The weaker band around 1 380 cm<sup>-1</sup> and the absent of bands around 2 869 and 2 946 cm<sup>-1</sup> in the TiO<sub>2</sub>-L sol sample suggest less organic residues or organic groups in TiO<sub>2</sub>-L sol sample than that in TiO<sub>2</sub>-S sol sample. The band at 1 110 cm<sup>-1</sup> only seen in TiO<sub>2</sub>-S sol sample can be assigned to the asymmetric vibration of the Ti-O-C due to unreacted alkoxide groups<sup>[23]</sup>. Accordingly, it can be concluded that in TiO<sub>2</sub>-L sol sample

the starting material Ti (OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> has already reacted completely, Ti groups exist in the form of inorganic substance containing Ti-O-Ti or Ti-OH groups. On the other hand, in TiO<sub>2</sub>-S sol sample, Ti groups exist in the form of not only inorganic substance containing Ti-O-Ti or Ti-OH, but also organic substance containing Ti-O-C.

Fig.3 shows the TEM images of TiO<sub>2</sub>-L and TiO<sub>2</sub>-S sol samples. It can be seen that spherical particles with diameters of 3~7 nm are synthesized in TiO<sub>2</sub>-L sol sample. Fig.3(b) shows the electron diffraction (ED) pattern of TiO<sub>2</sub>-L sol sample. The diffraction rings are indexed, and shown in Table 1, which are in good agreement with the crystal plane indexes of the anatase titania. Accordingly, it can be concluded that the anatase TiO<sub>2</sub> nanocrystalline has already existed in the TiO<sub>2</sub>-L sol sample before any further heat treatment. From Fig.3 (c) and Fig.3 (d), no diffraction ring is observed, indicating that the particles in the sol are amorphous.

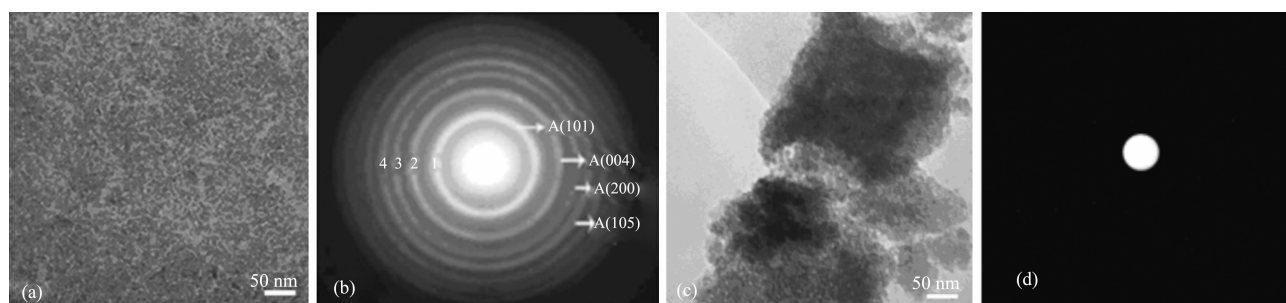


Fig.3 TEM images: (a) TEM image of TiO<sub>2</sub>-L sol sample; (b) Electron diffraction (ED) pattern of TiO<sub>2</sub>-L sol sample; (c) TEM image of TiO<sub>2</sub>-S sol sample, (d) Electron diffraction (ED) pattern of TiO<sub>2</sub>-S sol sample

Table 1 Electron diffraction rings of the TiO<sub>2</sub>-L sol sample

Ring No.	<i>d</i> -spacing <sup>a</sup> / nm	( <i>hkl</i> ) <sup>b</sup>
1	0.352	anatase (101)
2	0.236	anatase (004)
3	0.189	anatase (200)
4	0.168	anatase (105)

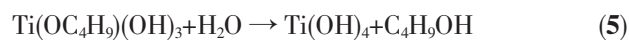
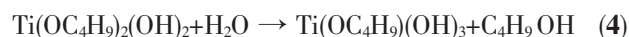
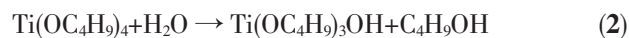
<sup>a</sup>The interplanar crystal spacing of the crystal planes.

<sup>b</sup>The crystal index of the crystal planes.

The water amount plays a key role in the formation of TiO<sub>2</sub> crystal. For the titanium alkoxide, the hydrolysis and condensation both occur by nucleophilic substitution mechanisms, involving nucleophilic addition followed by proton transfer from the attacking molecule to an alkoxide or hydroxo-ligand within the transition state and removal of the protonated species as either alcohol

or water.

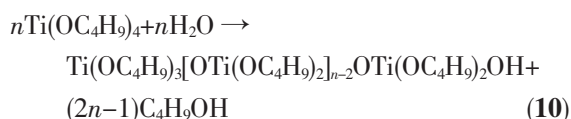
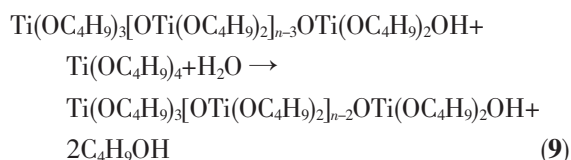
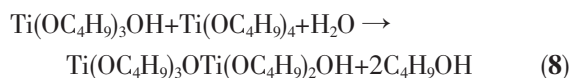
The possible hydrolysis reactions of Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> can be described as follows.



Also, the possible polycondensation reactions can be described as follows.



Usually, the condensation occurs before the completion of hydrolysis. Therefore, the complex processes happen. Reactions among the titanium alkoxide  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ , hydroxo-ligands  $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{OH}$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)_2(\text{OH})_2$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)(\text{OH})_3$  and intermediate products will take place as follows.



For  $\text{TiO}_2$ -S sol sample, the molar ratio of water to  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  is 1. As shown in Fig.1(b), the small amount of water is added dropwise into the ethanol solution of  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ , so the hydrolysis of the  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  is very slow, the polycondensation proceeds simultaneously with the hydrolysis, as shown in the above equations. Hence the Ti group in  $\text{TiO}_2$ -S sol sample mostly exists as Ti-O-C (see Fig.2), which acts as structural impurities and inhibits the formation of regular structure. So Ti-O-Ti and Ti-O-H groups in the sol can not connect with each other freely, therefore, no crystalline  $\text{TiO}_2$  is found in  $\text{TiO}_2$ -S sol sample (see Fig.3).

For  $\text{TiO}_2$ -L powder sample, the molar ratio of water to  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  is 100. As shown in Fig.1(a),  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  is added dropwise into the large amount of water, so the water is always in excess. Hence every  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  molecule is surrounded by massive  $\text{H}_2\text{O}$  molecules, which makes the titanium precursor hydrolyze quickly and completely as follows.



After  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  hydrolyzes completely, the polycondensation proceeds as follows.



Therefore the Ti groups in  $\text{TiO}_2$ -L sol sample exist

in the form of inorganic substance containing Ti-O-Ti or Ti-OH groups, and there is no Ti-O-C groups in the sol (see Fig.2), which is beneficial for the connection of the Ti-OH or Ti-O-Ti and formation of the unit- $[\text{TiO}_6]$  octahedron. With the rearrangement of the  $[\text{TiO}_6]$  octahedron units after aging for a certain time, the  $\text{TiO}_2$  nucleates and grows, resulting in the formation of nanocrystalline  $\text{TiO}_2$  in  $\text{TiO}_2$ -L sol sample.

## 2.2 Properties of nanocrystalline $\text{TiO}_2$ powders derived from sol with large amount of water

Fig.4 shows XRD patterns of  $\text{TiO}_2$  powder samples. As shown in the figure, no peak is found in pattern a, which is  $\text{TiO}_2$ -S sol derived powder dried under infrared lamp. While typical anatase type  $\text{TiO}_2$  peaks are found in pattern c, i.e. the pattern for  $\text{TiO}_2$ -L sol derived powder dried under infrared lamp. The size of the formed anatase  $\text{TiO}_2$  crystals is calculated using the Scherrer equation from the half-width of the (101) anatase reflection.

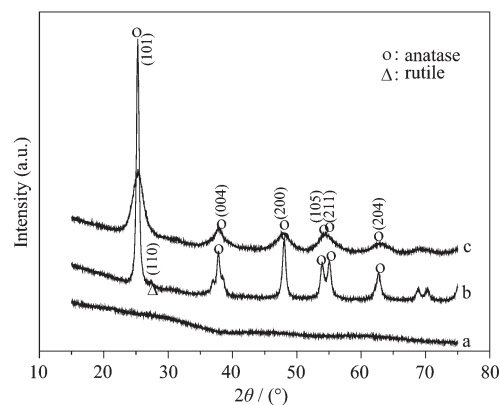


Fig.4 XRD patterns for  $\text{TiO}_2$  powder samples: (a)  $\text{TiO}_2$ -S gel powders prepared by drying the  $\text{TiO}_2$ -S sol sample under infrared lamp at about 50 °C; (b)  $\text{TiO}_2$ -S powder sample prepared by calcining the  $\text{TiO}_2$ -S gel powders at 500 °C, (c)  $\text{TiO}_2$ -L powder sample prepared by drying the  $\text{TiO}_2$ -L sol sample under infrared lamp at about 50 °C

The grain size of  $\text{TiO}_2$ -L powder is 3.5 nm, fairly in agreement with the TEM result (see Fig.3(a)). This indicates that crystal growth does not occur during infrared lamp drying, confirming that nanocrystalline  $\text{TiO}_2$  particles are formed in  $\text{TiO}_2$ -L sol before any heat-treatment.

b in Fig.4 is the XRD pattern for  $\text{TiO}_2$ -S sol derived powder heated at 500 °C. It can be found that not



only strong and sharp peaks of anatase TiO<sub>2</sub> appear, but also small peak at  $2\theta=27.5^\circ$  corresponding to rutile type TiO<sub>2</sub> (110) appears. The grain size of anatase and rutile in TiO<sub>2</sub>-S powder heated at 500 °C is 16.8 and 12.3 nm, respectively, both are much larger than that in TiO<sub>2</sub>-L powder.

Fig.5 shows  $\ln(A_0/A)-t$  plots of TiO<sub>2</sub>-L powder, TiO<sub>2</sub>-S powder heated at 500 °C and the commercial Degussa P25 crystalline TiO<sub>2</sub>. The degradation of methyl orange aqueous system containing TiO<sub>2</sub> powders follows the pseudo-first order kinetics. The result shows that the photocatalytic activities are in the order: P25 < TiO<sub>2</sub>-S powder < TiO<sub>2</sub>-L powder. In addition, the  $S_{\text{BET}}$  values of the P25, TiO<sub>2</sub>-S and TiO<sub>2</sub>-L sample are 55, 74, 120 m<sup>2</sup>·g<sup>-1</sup>, respectively. Comparing with that of P25, the higher photocatalytic activity of TiO<sub>2</sub>-S powder can be ascribed to its higher specific surface area. So the TiO<sub>2</sub>-S powder shows better photocatalytic activity than P25. On the other hand, the particle size of TiO<sub>2</sub>-L powder is about 3.5 nm, which is smaller than that of TiO<sub>2</sub>-S powder. So TiO<sub>2</sub>-L powder owns higher specific surface area than TiO<sub>2</sub>-S powder. Moreover, the size of TiO<sub>2</sub>-L nanocrystalline (3.5 nm) approaches the Bohr radius of anatase type TiO<sub>2</sub><sup>[24-25]</sup>, which causes quantum-size effect. The quantum-size effect results in split of the energy level of TiO<sub>2</sub>, which causes an increase in its photocatalytic oxidation-reduction potential and thus enhances the photocatalytic activity. Accordingly, the TiO<sub>2</sub>-L powders show better photocatalytic activity than

TiO<sub>2</sub>-S powders although the crystal intensity of the TiO<sub>2</sub>-L powder is much weaker than that of TiO<sub>2</sub>-S powder.

### 3 Conclusions

The formation mechanism of nanocrystalline TiO<sub>2</sub> derived from sol with large amount of water was studied. It is found that the nanocrystalline TiO<sub>2</sub> has already existed in the sol. The large amount of water makes the titanium precursor hydrolyze quickly and completely before polycondensation. [TiO<sub>6</sub>] units are formed during polycondensation, thus favoring the formation of nanocrystalline TiO<sub>2</sub>. The grain size derived from the sol with large amount of water is 3.5 nm. The fine nanocrystalline sample shows better photocatalytic activity than powders derived from the conventional sol-gel method and commercial photocatalyst Degussa P25.

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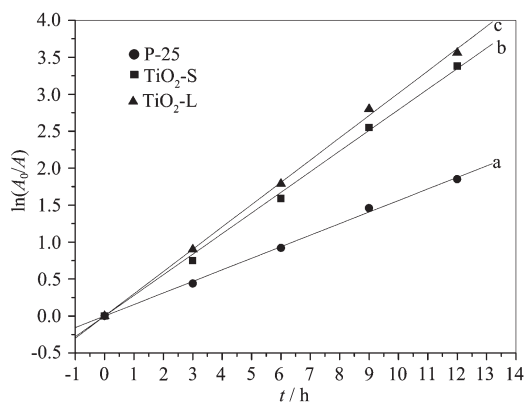


Fig.5 Photocatalytic degradation of methyl orange on P-25(Fig.5a) and prepared TiO<sub>2</sub>-S powder sample (Fig.5b) and prepared TiO<sub>2</sub>-L powder sample (Fig.5c)

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