

Synthesis of Controllable Crystalline Nano-TiO₂ at Low Temperature

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TiO₂ catalysts of high surface area and different anatase/rutile ratios have been prepared at low temperature with microemulsion method. The contents of anatase and rutile have been successfully controlled by simply changing the proportion of Cl⁻ and SO₄²⁻ in aqueous phase of microemulsion. The photocatalytic activity of TiO₂ was tested with photodegradation of Methyl Orange. Anatase and rutile were confirmed having a synergistic effect in enhancing the photocatalytic activity of TiO₂ and the catalyst containing 74.2% anatase showed the highest photocatalytic activity.

Many efforts have been devoted to improving the photocatalytic activity of TiO₂ since the discovery of photoelectrochemical splitting of water on n-TiO₂ electrodes.¹ It is widely considered that the mixed phase of titania is beneficial in reducing the recombination of photogenerated electrons and holes and in enhancing photocatalytic activity.^{2,3} However, synthesis of controllable crystalline nano-TiO₂ was recently reported. Luo et al.⁴ synthesized bicrystalline and tricrystalline mesostructured titania through varying the solvent and cosolvent, and Liu et al.⁵ prepared rutile-anatase mixtures by controlling the contents of toluene-*p*-sulfonic acid (TSA) in homogeneous hydrolysis system and the heat-treatment temperature. In order to get crystalline titania, both of their synthetic methods need heat treatment in high temperature and so result in the decrease of the surface area and the increase of crystalline size. In this study, tetrabutyl titanate (Ti(OC₄H₉)₄) was used as the Ti source and reverse microemulsion media described by Wu et al.⁶ as the reaction surroundings. By simply varying the proportion of anion in aqueous phase of microemulsion, controllable crystalline nano-TiO₂ with high surface area was successfully synthesized at low temperature.

For the preparation of the reverse microemulsion system, Triton X-100 (*tert*-octylphenoxypolyethoxyethanol) was used as the surfactant, *n*-hexanol as the cosurfactant, and cyclohexane as the continuous oil phase. Tetrabutyl titanate and (NH₄)₂SO₄ dissolved in hydrochloric acid as the aqueous phase. The synthetic procedure was as follows. Firstly, 10 mL of Triton X-100, 6 mL of *n*-hexanol, and 16 mL of cyclohexane were mixed under magnetic stirring. Secondly, 3.4 mL of tetrabutyl titanate and 0.0682 g of (NH₄)₂SO₄ were dissolved in 4 mL of 10 M hydrochloric acid solution, making up the aqueous phase. Then the aqueous phase was added dropwise to the oil phase, forming clear microemulsion. The microemulsion was transferred to a 100 mL Teflon-inner-liner stainless-steel autoclave. The autoclave was kept for 13 h under 120 °C and then precipitate was got at the bottom of the autoclave. The precipitate was washed repeatedly with ethanol and water, then dried for 12 h in an infrared oven to obtain the final sample S-1.28, in which the number "1.28" refers to the mole percentage of SO₄²⁻ in the Cl⁻ and

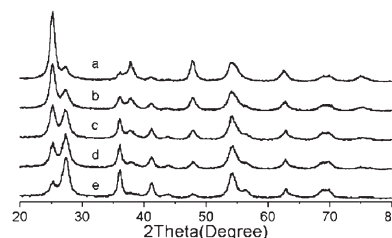


Figure 1. XRD patterns of TiO₂: (a) S-1.28, (b) S-1.12, (c) S-0.96, (d) S-0.80, and (e) S-0.64.

SO₄²⁻ ($n_{\text{SO}_4^{2-}}/(n_{\text{Cl}^-} + n_{\text{SO}_4^{2-}})$). Different samples of S-1.12, S-0.96, S-0.80, and S-0.64 were also prepared through varying the addition of (NH₄)₂SO₄ with the same method.

The X-ray diffraction patterns in Figure 1 illustrate the crystalline phase of different samples. As is shown in the Figure 1, the contents of anatase decrease in the order of S-1.28, S-1.12, S-0.96, S-0.80, and S-0.64. That is to say, the more sulfate ions are in aqueous phase of microemulsion, the higher the contents of anatase phase are formed in the TiO₂ powders. The average crystalline sizes of anatase and rutile in the samples can be calculated by applying the Debye-Scherrer formula on the anatase (101) and rutile (110) diffraction peaks and are showed in Table 1.

Table 1. Synthetic conditions and physicochemical properties of TiO₂ particles

Sample	Crystalline Size of Anatase /nm	Crystalline Size of Rutile /nm	Contents of Anatase/%	S _{BET} /m ² g ⁻¹
S-0.64	15.9	11.2	15.3	162
S-0.80	15.0	11.6	36.0	169
S-0.96	12.0	10.5	52.4	147
S-1.12	13.0	12.1	74.2	131
S-1.28	12.5	15.9	89.3	113

The phase contents of the samples were also estimated from the X-ray intensities of the anatase (101) and the rutile (110) diffraction peaks, respectively.⁷ The calculated anatase content of the samples was showed in Table 1. In order to study the relationship between the addition of anion and the contents of anatase, we carried out a fit with these data. It is very interesting that the relationship between the mole percentage of SO₄²⁻ in the Cl⁻ and SO₄²⁻ and the contents of anatase in TiO₂ powder can be reasonably described by a linear function (Figure 2). It strongly implies that the contents of anatase and rutile can be well controlled around the anatase contents of 15–90% by simply varying the proportion of the Cl⁻ and SO₄²⁻ in aqueous phase of microemulsion.

The mechanism of forming different contents of anatase is

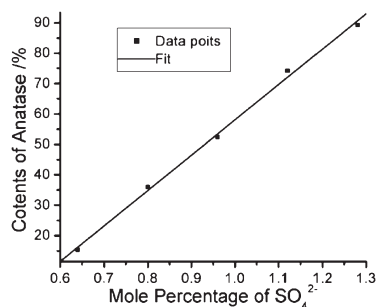


Figure 2. Linear fit of the contents of anatase and the mole percentage of SO_4^{2-} .

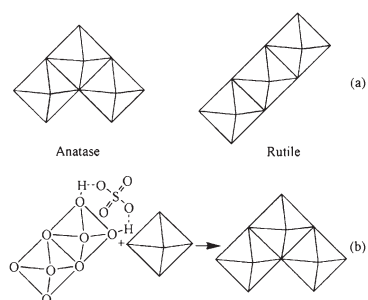


Figure 3. Proposed mechanism for the formation of anatase in the existence of SO_4^{2-} : (a) difference of octahedral arrangement in anatase and rutile, (b) formation of anatase in the existence of SO_4^{2-} .

proposed in Figure 3. All TiO_2 crystal structures consist of TiO_6^{2-} octahedra, which share edges and corners in different manners that result in different crystal phases. For forming anatase and rutile nucleus, the first step is similar and two TiO_6^{2-} octahedra share edge. The placement of the third octahedron determines whether a rutile or an anatase nucleus is formed (Figure 3a).⁸ However, the presence of SO_4^{2-} influence the orientation of the third octahedron. Because of steric effect of SO_4^{2-} , the orientation of the third octahedron more easily forms an anatase nucleus (Figure 3b). The more SO_4^{2-} are, the more anatase nucleus can be formed. On the other hand, there is not steric effect for Cl^- because of its little radius, and the presence of Cl^- makes the structure of titanium(IV) complex ions more symmetrical which is favored to form rutile.⁹ As a result, different rutile–anatase mixtures can be prepared by changing the proportion of Cl^- and SO_4^{2-} in aqueous phase of microemulsion.

Figure 4 shows the decomposition of Methyl Orange (40 mgL^{-1}) after irradiating 80 min on different TiO_2 catalysts. The relationship between the photodegradation of Methyl Orange and the contents of anatase was clearly presented. The sample S-1.12 containing 74.2% anatase has the highest photocatalytic activity, while the photocatalytic activity of the sample S-0.64 containing the least anatase is poor. The BET surface areas of all samples are shown in Table 1. There is a downtrend for the BET surface area with the increase of the anatase contents. The S_{BET} of sample S-1.12 with the highest photocatalytic activity is only $131 \text{ m}^2\text{g}^{-1}$, while the BET surface area of sample S-0.64 with poor photocatalytic activity achieves to $162 \text{ m}^2\text{g}^{-1}$. The reason may be that the electron–hole recombination at the particle surface is enhanced by an increase of surface defects.¹⁰ This result implies that the surface area is not the most important

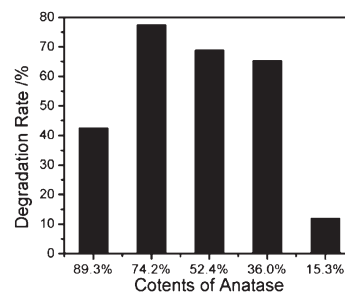


Figure 4. Degradation of Methyl Orange (40 mgL^{-1}) after irradiating 80 min on different TiO_2 catalysts from left to right: S-1.28, S-1.12, S-0.96, S-0.80, and S-0.64.

factor for effect on the photocatalytic activity in our experiments. Therefore, we can conclude that the difference of the photocatalytic activity in the samples is mainly caused by the difference of the anatase contents. That is to say, anatase and rutile have a synergistic effect in enhancing the photocatalytic activity of TiO_2 . The efficiency of most photocatalysts is determined to a large degree by recombination rates and rutile exhibits high rates of recombination in comparison to anatase.¹¹ However, rutile has a more narrow band gap and can extend the useful range of photoresponse. When anatase and rutile form mixed-phase TiO_2 catalysts, the rutile phase can harvest more light and electron transfer from rutile to anatase trapping sites hinders electron–hole recombination.¹² When the content of rutile is too little, it may be loaded with many anatase particles³ and could not be well excited by light. Thus, the rutile phase can not act as a role of extending the photoactive range. However, too much rutile makes electron not efficiently transfer to anatase and mostly recombine in rutile phase. Therefore, the proportion of anatase and rutile exists an optimum value that is about 3:1 in our experiment.

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