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以 OTS 自组装单分子膜为探针研究 TiO₂ 液相空穴氧化机理

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摘要: 通过引入十八烷基三氯硅烷(OTS)自组装单分子膜作为氧化反应的探针,在排除反应物的吸附和扩散的条件下研究溶胶-凝胶制备的 TiO₂ 薄膜表面光催化空穴氧化初始过程. 研究表明,在紫外光照下,水溶液中 OTS 部分覆盖的 TiO₂ 表面能够很快从憎水变成亲水. 存在空穴捕获剂后, TiO₂ 表面 OTS 自组装单分子膜碳链的脱除受到明显抑制,水接触角随光照时间变化非常小;而水中羟基自由基捕获剂或者 F⁻ 的存在则对 TiO₂ 表面 OTS 自组装单分子膜碳链的脱除几乎无影响. 这表明,空穴氧化在 TiO₂ 表面 OTS 自组装单分子膜碳链的脱除中占主要地位.

关键词: 光催化; 机理; 空穴氧化; 牺牲剂; 自组装单分子膜

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Hole Oxidation on TiO₂ Films in Aqueous Solutions Studied by Using OTS SAMs as a Probe

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Abstract: An approach was developed to investigate hole oxidation on TiO₂ films in aqueous solutions by using octadecyltrichlorosilane (OTS) self-assembled monolayers (SAMs) as a probe, in which the adsorption and surface diffusion of the reactants were excluded. Under UV irradiation, the water contact angle of the OTS SAMs on TiO₂ films in water decreased obviously. In the presence of hole scavengers, the decrease of water contact angle for the OTS SAMs on TiO₂ films with UV irradiation was inhibited apparently, while the effect of ·OH radical scavengers and fluoride on the decrease of water contact angle was very small. It indicated that direct hole oxidation played a major role in photocatalytic removal of alkyl chains on TiO₂ films in aqueous solutions.

Key Words: Photocatalysis; Mechanism; Hole oxidation; Scavenger; SAMs

TiO₂ photocatalysis is a promising method for purifying the environment because most organic pollutants can be decomposed for its strong oxidation ability^[1-4]. The mechanism of this oxidative reaction has been studied intensively, but the role of the main active species causing the initial photooxidation including photo-generated positive holes (h⁺) and hydroxyl radicals (·OH) is still one of the controversial issues for photocatalysis^[15]. Hydroxyl radicals are often assumed to be the principal oxidizing species and should be responsible for the photocatalytic oxidation in

many studies^[6-12]. Moreover, mechanisms involving both ·OH radicals and positive holes have also been suggested^[13-15]. However, there also exists a significant body of literature supporting the idea that the direct reaction of the photo-generated positive holes with organic compounds on the TiO₂ surface plays an important role in the photooxidation process^[16-18]. Ishibashi *et al.*^[17] suggested that photocatalytic reactions developed mainly *via* photogenerated holes by comparing the quantum yields of holes with that of ·OH radicals. However, the previous reports have indicated

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that the adsorption intensity, adsorbate configurations and surface diffusion of reactants on TiO₂ surface greatly influenced the hole oxidation process in the heterogeneous photocatalysis^[19–22]. Therefore, an effective way to investigate the surface reaction excluding the adsorption and surface diffusion of the reactant could give deeper insights into the mechanism of the heterogeneous photocatalysis.

SAMs are thin organic films, which form spontaneously on solid surfaces with chemical bonds, and are considered to be a good model system for photocatalysis^[23]. In gas phase, the alkylsiloxane SAMs on TiO₂ can be decomposed through the photocatalytic oxidation of the alkyl chains^[24]. And the factors that affect the adsorption and surface diffusion of the reactant could be excluded in the process of the degradation of alkylsiloxane SAMs on TiO₂. Furthermore, previous studies have shown that the increase in the hydrophilicity is accompanied by a decrease in the amount of carbon, reflecting the removal of alkyl chains on the OTS-coated surface^[24,25]. This indicates that the value of water contact angle could correspond to the residue of alkyl chains on the surface.

In this article, the hole oxidation mechanism in aqueous solutions was studied by applying OTS SAMs on sol-gel TiO₂ films. Hole and ·OH scavengers were used to distinguish the effect of holes and ·OH radicals. And the hydrophilicity of OTS SAMs-coated TiO₂ surface was characterized by measuring the water contact angle.

1 Experimental

The anatase TiO₂ films were prepared by sol-gel method^[26]. Ethanol and glass were used respectively as solvent and substrate. The molar ratios of ethanol, ethyl acetoacetate, and H₂O to Ti(C₄H₉)₄ were 26, 0.5, and 2, respectively. Surface morphology and the roughness of the films were characterized by an AFM (Autoprobe CP, Veeco, USA). To keep abundant active sites on TiO₂ surface, the partially grown OTS SAMs on both TiO₂ films and fresh mica were prepared. The substrate was immersed into a 2.0 mmol·L⁻¹ solutions of OTS precursor dissolved in toluene at (18.0±1.5) °C in the glove box. The deposition time was about 60 s. The samples were then washed in carbon tetrachloride to remove the excess reactants and dried with pure nitrogen. Then infrared spectra were obtained by the attenuated total reflection spectrometer (Bruker Tensor27, German) because the vibrational frequency of alkyl chains could characterize the coverage of SAMs^[27]. And then the samples were irradiated in aqueous solutions (pH ≈ 7). To check the effect of photolysis of OTS SAMs, the OTS SAMs on mica were irradiated under the same condition as a control experiment. The oxidation mechanism of OTS SAMs on TiO₂ in aqueous solutions was studied by adding excess holes scavengers, 0.1 mol·L⁻¹ KI^[17,28–31], and ·OH radical scavengers, 0.1 mol·L⁻¹ tert-butyl alcohol (TBA)^[9,14,32–34]. And the effects of surface fluorination of TiO₂ on the photocatalytic reaction was investigated by adding 0.1 mol·L⁻¹ NaF^[9,14,18]. Furthermore, the pH values of aqueous solutions ranged from 6.9 to 6.3, and the OTS

SAMs are very stable in these solutions.

The SAMs-coated samples with the same coverage were introduced into a quartz chamber with a 15-W low pressure mercury lamp with total intensity of 5 mW·cm⁻² at a working distance of 2.6 cm. The primary wavelength of the lamp is 254 nm. The water contact angle was employed to measure the hydrophilicity of OTS SAMs-coated TiO₂ films in this work. The sessile drop method was used for contact angle measurements at (20.0±1.5) °C using contact angle meter (Powereach JC2000A, China). The water contact angle of OTS SAMs on TiO₂ films is (97±3)° before UV irradiation while naked TiO₂ films is (20±2)°.

2 Results and discussion

Fig.1 presents the AFM image of TiO₂ films. The films consist of TiO₂ nanoparticles. The root mean square (RMS) roughness of the films measured on an area of 1000 nm×1000 nm averaged out at 1.9 nm. On this smooth surface, the effect of roughness on water contact angle could be negligible. Moreover, two main bands at 2850 and 2920 cm⁻¹ were clearly observed in IR spectrum. These should be assigned to $\nu_s(\text{CH}_2)$ and $\nu_a(\text{CH}_2)$ modes of the OTS alkyl chains, respectively. The peak frequencies for the $\nu_s(\text{CH}_2)$ and $\nu_a(\text{CH}_2)$ modes provide insight on alkyl chain packing in terms of crystalline or liquidlike structure^[27,35–38]. The peak frequency for the $\nu_a(\text{CH}_2)$ mode of an all-trans extended alkyl chain in a crystalline environment is reported to be ca 2915–2920 cm⁻¹, and that for the $\nu_s(\text{CH}_2)$ mode is reported to be ca 2846–2850 cm⁻¹. The frequencies of these peaks increase to ca 2920 cm⁻¹ and 2850 cm⁻¹ for the $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ modes, and are intermediate between crystalline and liquidlike. The vibrational spectra show the shift in vibrational frequency with the coverage of SAMs^[39]. The results of IR and water contact angles indicated that the coverage of OTS SAMs on TiO₂ was about 60% of the maximum^[27,40].

The water contact angle as a function of irradiation time is shown in Fig.2. Few changes are found in contact angle of OTS

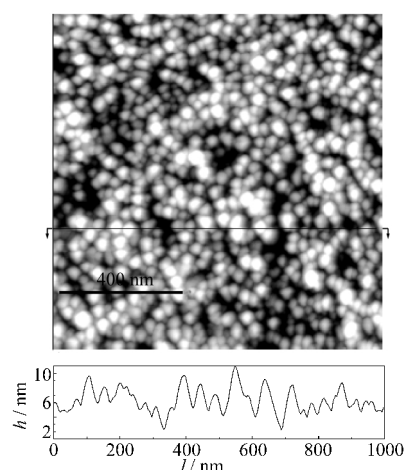


Fig.1 The AFM image (tapping mode) and cross section of TiO₂ films

Scan size is 1000 nm×1000 nm; The RMS roughness is 1.9 nm.

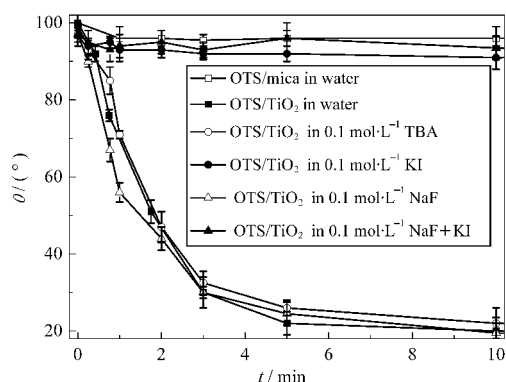


Fig.2 Water contact angle (θ) as a function of UV irradiation time (t) for the OTS SAMs

SAMs on mica as a control experiment. However, the curve got on TiO₂ films showed that the water contact angle of OTS SAMs on TiO₂ films in aqueous solutions decreased greatly. It suggested that the removal of alkyl chains of the OTS SAMs on TiO₂ films with UV irradiation was efficient in aqueous solutions

Fig.2 shows that the decreasing rate of contact angle of OTS SAMs-coated TiO₂ is in order of NaF \approx water \approx TBA \gg NaF+KI \approx KI. In the presence of TBA as \cdot OH radical scavenger^[9,14,32-34], UV irradiation time course of the water contact angle of OTS SAMs-coated TiO₂ is similar to the case in pure water. It suggested that the removal of alkyl chains of the OTS SAMs with photocatalytic oxidation in aqueous solutions was hardly affected by the \cdot OH radical. Whereas, in the presence of KI as hole scavenger^[17,26-31], the decrease of water contact angle with UV irradiation was inhibited apparently, and the water contact angle kept at the range of the high value even after 10 min of UV irradiation. This implied that the removal of alkyl chains on TiO₂ films was predominately initiated by direct hole oxidation in aqueous solutions. However, I⁻ is a scavenger which reacts with positive hole as well as adsorbed \cdot OH radical^[28,31]. Therefore, the effect of F⁻ was investigated because the fluoride adsorption on TiO₂ surface was well known to replace the surface hydroxyl groups with Ti-F species, and then could enhance generation of mobile free \cdot OH radicals and positive hole^[7,14,34,41]. The addition of NaF had slightly positive effects on the decrease of contact angle, which implied that the effect of adsorbed \cdot OH radical on the removal of alkyl chains could be negligible. However, in the presence of both NaF and KI, the decrease of contact angle was efficiently inhibited, and just similar to the case of KI. It might be concluded that direct hole oxidation played a major role in photocatalytic removal of alkyl chains on TiO₂ films in aqueous solutions. In addition, OTS SAMs are directly connected with TiO₂ by chemical bond, which would lead to the higher quantum yield values for hole oxidation of OTS SAMs^[42]. On the other hand, the whole alkyl chains of one OTS molecular could be removed completely by the hole oxidation in aqueous phase because the holes can not leave TiO₂ surface and may attack the groups of OTS SAMs which are close to TiO₂ surface^[43]. Therefore, the residue of alkyl chains or the water contact angle on the TiO₂

surface is highly sensitive to the effect of hole oxidation. And the system of OTS SAMs on TiO₂ could provide a new way to investigate the hole oxidation in aqueous solutions.

3 Conclusions

In summary, excluding the adsorption and surface diffusion of reactants, the hole oxidation on TiO₂ was investigated by OTS SAMs and water contact angle. The water contact angle of OTS SAMs on TiO₂ films in aqueous solutions was remarkably decreased with UV irradiation. In the presence of hole scavengers, the decrease of water contact angle for the OTS SAMs with UV irradiation was inhibited apparently, while \cdot OH radical scavengers and F⁻ had little effect on the removal of alkyl chains on TiO₂. The results indicated that direct hole oxidation played a major role in photocatalytic removal of alkyl chains on TiO₂ films in aqueous solutions.

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