Efficient Degradation of Methyl Orange Over TiO₂ and Poly(styrene sulfonate) Thin Films Supported on Glass Slides

XIAOLIN QU

Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong (Dezhou University), Dezhou 253023, P.R. China

Corresponding author: Tel: +86 534 8987865; E-mail: xiaolinqu@126.com

Photocatalytic nanocomposite films with different number of bilayers were prepared on microscopic glass slides *via* an electrostatic layer-by-layer self-assembly method. Atomic force microscopy measurement was used to observe surface morphology of layer-by-layer films. The atomic force microscopy results prove that TiO₂ nanoparticles are successfully incorporated into the thin films. Photocatalytic activity of TiO₂-containing multilayer films was evaluated by measuring the degradation efficiency of methyl orange. Examination of the effects of experimental factors shows that photodegradation efficiency of methyl orange increases with increasing the number of bilayers of (PSS/TiO₂)ₙ films and the highest removal efficiency is obtained when the acidity of solution is 2. The kinetic data demonstrate that the photocatalytic degradation of methyl orange conforms to the apparent first-order reaction dynamics. Immobilization of catalysts on glass slides solves the problem of recovery and may lower the costs of wastewater treatment.

Key Words: Nanocomposite films, TiO₂, Photocatalytic degradation, Methyl orange.

INTRODUCTION

In 1972, Fujishima and Honda[1] found that TiO₂ electrode could split water into H₂ under UV illumination. In the following decades, photocatalytic degradation of toxic dyes in water by TiO₂ nanomaterials is concerned increasingly. Titanium dioxide as a photocatalyst has the advantages in low cost, innoxiousness, chemical inertness and high photocatalytic performance[2,3]. To meet the requirements of the practical applications, photocatalysts must be easily reclaimed and very cheap in addition to superior catalytic activity. However, the use of TiO₂ nano-particles in photocatalytic field has been limited because the ultrafine particles, which have higher photocatalytic activity than that of larger ones, are difficult in separating from reaction environment[4]. Various morphologies of nano-structured TiO₂ such as nanotube[5], nanofiber[6], mesoporous spherical aggregate[7] or polymer-titania microcomposite[8] have been made to solve this problem. The TiO₂ catalysts obtained from above methods can be recovered through centrifugal or gravity separation. However, the layer-by-layer self-assembly method developed by Decher[9] can make the recovery of catalysts become more easier[10]. And no further treatment step is needed after the films are used. This method, based on the electrostatic attraction of oppositely charged building blocks, is a very effective and simple method to fabricate nanocomposite films. The films prepared by this method are stable and reusable[10].

In the last decade, the photocatalytic activity of TiO₂ hybrid films constructed by the layer-by-layer method has been investigated by many researchers[10-12].

Azo dyes are one of the largest and the most important groups of commercial dyes and account for roughly half the amount of global production of dyes[13]. The release of industrial wastewater containing azo dyes is very dangerous to humans and animals health due to their high toxicity, slow biodegradation and potential carcinogenicity[13]. Numerous approaches including biodegradation, coagulation, adsorption, advanced oxidation process and the membrane process have been developed to handle the dye degradation and mineralization. The most promising method among them is the advanced oxidative process, though which organic contaminants can be entirely removed[13,14]. However, to our knowledge, no reports have focused on the influence of pH value and the reaction kinetics of the TiO₂-containing nanocomposite films until now.

In order to test the photocatalytic ability of the nanocomposite films, methyl orange was used as a contaminant model for the photocatalytic degradation. To achieve the optimal photocatalytic efficiency, the influence of number of bilayers and pH value of dye solution on photodegradation of methyl orange was investigated. In addition, the reaction kinetics of methyl orange photodegradation in the presence of (PSS/TiO₂)ₙ was also studied.

EXPERIMENTAL

Titanium dioxide (TiO_2) colloid with positive charge was prepared according to method reported by Caruso *et al.*[15]. X-ray diffraction analysis confirmed the appearance of anatase structure of TiO_2 (average particle size of 4 nm). Commercial polyelectrolytes, poly(sodium 4-styrenesulfonate) (PSS, Mw-70 000 g/mol) and poly(allylamine hydrochloride) (PAH, Mw-70 000 g/mol) used for films preparation, were purchased from Sigma-Aldrich (USA). Perchloric acid was obtained from Shanghai Jinlu Chemical Co. Ltd., China. Methyl orange was provided by Jining Chemical Engineering Research Institute. All regents were used without any further treatment.

Assembly of multilayer films: The fabrication of the multilayer film was carried out as follows. The solid substrates, such as silicon wafers and microscopic glass slides, were treated to make their surfaces become clean and hydrophilic[16]. The hydrophilic substrates were firstly immersed in aqueous solution of poly(allylamine hydrochloride) for 20 min, then rinsed by diluted $HClO_4$ solution at pH 2.5 and dried by N_2 to remove the adhering water. The concentration of poly(allylamine hydrochloride) was 2.0 g/L with 0.5 M NaCl and the pH was *ca.* 2.5 adjusted by 3 M hydrochloride acid aqueous solution. Subsequently, the poly(allylamine hydrochloride)-coated substrates with positive charge were alternately dipped into negative charged poly(sodium-4-styrene sulfonate) solution (2.0 g/L with 0.5 M NaCl, pH *ca.* 2.5) and positive charged TiO_2 colloid (16 g/L, pH 2.0) for 20 min, respectively, until the desired number of bilayers was obtained. Rinsing with diluted $HClO_4$ solution at pH 2.5 and drying by nitrogen stream were conducted at each deposition cycle. The multilayer films with desired numbers were described as $(PSS/TiO_2)_n$, where n is the number of bilayers.

Characterization of thin films: Atomic microscopic measurment was performed in air on a Digital Nanoscope IIIa Instrument with the tapping mode. Atomic force microscopic images can provide the detail information on surface morphology of the composite films.

Measurement of photocatalytic activity: Photocatalytic degradation of methyl orange was performed on XPA-system photoreactor, which was purchased from Xujiang electro-mechnical plant, Nanjing of China. The light source, 300W medium-pressure mercury lamp (output mainly at 365 nm) surrounded by double-quartz glass for water cooling, was located inside the inner tube. The photocatalytic decontamination of methyl orange was carried out in air at ambient temperature. All the experiments reported were carried out in culture dish. Briefly, 20 mL of methyl orange solution was mixed with six pieces of glass slides (12.7×38.1 mm^2/piece) coated with $(PSS/TiO_2)_n$ films and then exposed to UV light. The concentration of methyl orange was fixed at 10 mg/L. The change of methyl orange absorbance was monitored by Shimadzu 2450 UV-VIS spectrophotometer at a set time intervals after irradiation. The conversion rate can be calculated according to the following equation:

$$\text{Conversion }(\%) = \frac{A_0 - A}{A_0} \times 100\%$$

where, A_0 represents the original absorbance of methyl orange solution at its maximum absorption wavelength (λ_{max}), A is absorbance of methyl orange at t min.

RESULTS AND DISCUSSION

Characterization of composite films: Atomic force microscopy investigation was taken to provide detailed information about the surface morphology and topography of the multilayer films deposited on the single-crystal silicon substrate. Fig. 1 presents atomic force microscopic images of $(PSS/TiO_2)_4$ multilayer film. It can be seen from Fig. 1 that the surface of $(PSS/TiO_2)_4$ film appears to typical spherical or granular patterns with size ranged from 40 to 60 nm[17,18]. The formation of these patterns seems to be due to the aggregation of TiO_2 colloidal nanoparticles. The root-mean-square (RMS) roughness of $(PSS/TiO_2)_4$ film is determined as 5.667 nm in an area of 1.0×1.0 μm^2, which is increased after adsorption of TiO_2 and poly(sodium-4-styrene sulfonate). The vertical grain structure of $(PSS/TiO_2)_4$ film can be seen clearly in the three-dimensional atomic force microscopic image. It is found that the distribution of aggregated nanoclusters in the surface of multilayer film is uniform. TiO_2 nanoparticles aggregates to a certain level in thin films since the anionic polymer poly(sodium-4-styrene sulfonate) reduces the coulombic repulsion of adjacent TiO_2 nanoparticles[16].
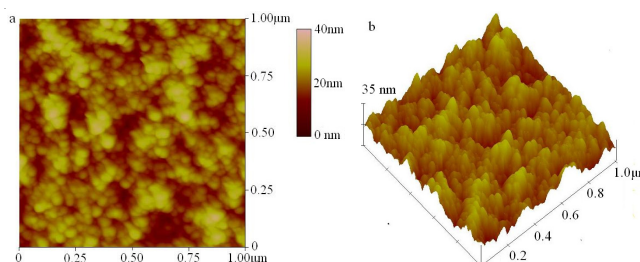

Fig. 1.   Atomic force microscopy images of the $(PSS/TiO_2)_4$ multilayer film assembled on silicon slides

Photocatalytic performance of composite films: The photocatalytic performance of composite films was evaluated by the photocatalytic degradation of methyl orange in aqueous solution under UV light irradiation. Methyl orange is used as a probe for the photocatalytic degradation since it is widely used in textiles, foodstuffs, papers and leathers industries. Its release gives rise to environmental concern due to its toxicity, carcinogenicity, mutagenicity and slow biodegradability. Fig. 2 shows the influence of bilayers number of $(PSS/TiO_2)_n$ films. In the dark, degradation of methyl orange is hardly observed in the presence of multilayer films. When the dye is exposed to UV radiation for 1 h in the absence of catalyst, only 12.91 % methyl orange is removed. It can be found in Fig. 2 that exposure of the dye solution to both multilayer films and UV light results in fast degradation of methyl orange. Furthermore, the conversion rate of methyl orange increases with bilayers number of $(PSS/TiO_2)_n$ multilayer film. After exposure to UV light for 1 h, the removal of methyl orange in the presence of $(PSS/TiO_2)_n$ thin films is 35.85, 48.18, 54.43, 67.35 and 81.20 % with n = 2, 4, 6, 8, 10, respectively. However, it is worth mentioning that the conversion rate of methyl orange is

not linearly increased with the number of bilayers. This finding is consistent with the previous studies[10]. The results obtained also account for that the contribution of TiO$_2$ nanoparticles in inner and outer layers to methyl orange photocatalytic degradation is different.
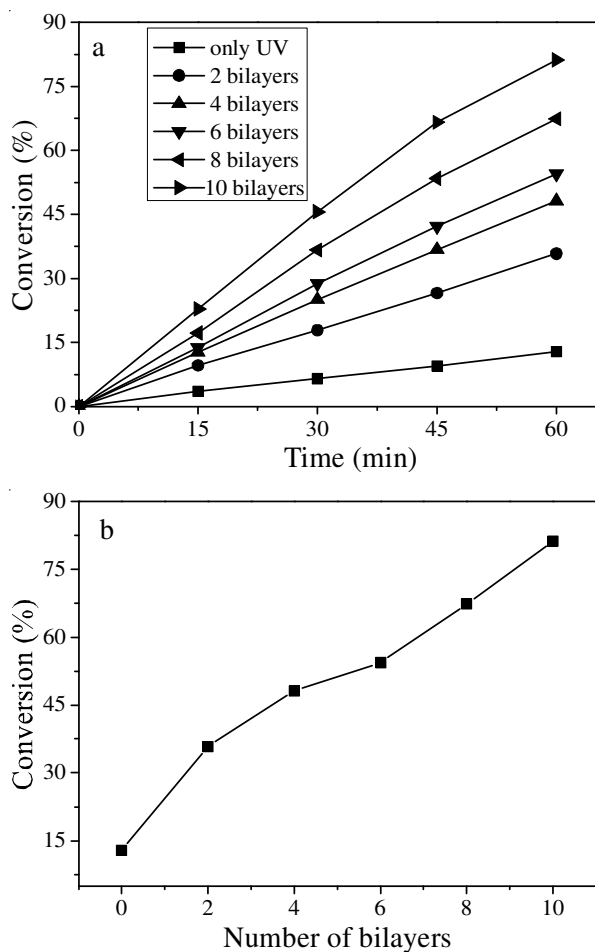

Fig. 2. Photocatalytic degradation of methyl orange by varying number of bilayers of PSS-TiO$_2$ composite films

The wastewater discharged from textile industries usually has a wide range of pH values. And the pH value of solution has an obvious influence on the photodegradation efficiency of different catalyst. Many investigations have been carried out and different influential tendency of pH value on the photodegradation of methyl orange was found[19-22]. These studies have concluded that the photocatalytic performance of catalysts is closely relevant to raw material, preparation and the test parameter. In this paper, the effect of pH value of solution was also examined by varying pH of methyl orange solution from 2.0 to 12.0 and the results are shown in Fig. 3. Methyl orange is an indicator in aqueous solution, which remains quinone structure and azo structure as pH is below 3.1 and above 4.5, respectively, corresponding to the colour of methyl orange solution change from red to yellow. The removal efficiency is calculated based on the absorbance of methyl orange measured the maximum absorption wavelength (λ_{max}) and the λ_{max} is 507 nm at pH 2 and 487 nm at pH = 4 and 463 nm at pH above 4.5. The conversion rate of methyl orange is 81.20 % at pH 2, 59.69 % at pH 4, 24.92 % at pH 6.4,

25.92 % at pH 8 and 51.76 % at pH 12. It is found that photocatalytic degradation efficiency is higher in both acidic and alkaline media than under neutral condition. Furthermore, lower pH is in favour of enhancement of the photocatalytic degradation of methyl orange. Under acidic conditions, the multilayer film catalyst has a positively charged surface[19,22], which is more favourable for the migration of photo-induced electrons to catalyst surface. These electrons can react with O$_2$ adsorbed on catalyst surface to produce $^{\bullet}$O$_2^-$ or H$_2$O$_2$ reactive oxygen species. In addition, the reaction between holes and water can generate more $^{\bullet}$OH. The reactive oxygen species produced are strong and unselective oxidants, which can completely oxidize and degraded organic contaminants in aqueous media to carbon dioxide and inorganic salts. Similarly, alkaline media (pH > 7) makes the surface of catalyst negatively charged due to the reaction of TiO$_2$ with OH$^-$, which can accelerates holes transfer[19,22]. Holes can react with adsorbed water to produce $^{\bullet}$OH, which is responsible for the enhanced degradation of methyl orange. However, at neutral pH, the surface of multilayer film has no charge and they are neutral, which makes the separation of electron-hole pairs less favourable. Consequently, neither $^{\bullet}$O$_2^-$ nor $^{\bullet}$OH can be produced in this condition. A plausible reason for higher degradation of methyl orange obtained under acidic conditions may be that methyl orange is prone to change to a quinone structure when pH is below 3.1. Quinone structure reduces the bond energy and makes methyl orange be easier degraded[19].
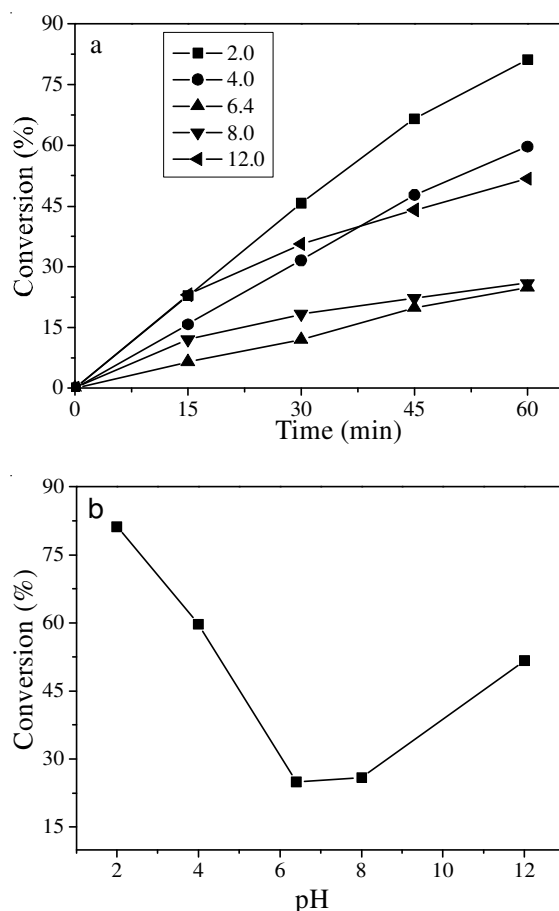

Fig. 3. Dependence of conversion rate of methyl orange on pH in the presence of (PSS/TiO$_2$)$_{10}$ composite films

Kinetics of methyl orange degradation over multilayer film: The kinetics of photocatalytic degradation of methyl orange solution was investigated. The plots of ln c_0/c (where c_0 is the initial concentration, c is the residual concentration at time t) *versus* time for methyl orange photodegradation (Fig. 4). The straight lines are obtained in presence of multilayer films with different bilayers number, indicating that photocatalytic degradation of diluted methyl orange solution fits well with apparent first-order kinetics. The first-order rate constants (k) can be determined from the slope of linear regression. The values are listed in Table-1. The initial reaction rate of methyl orange at different photocatalysts is also shown in Table-1, which is calculated based on the following equation[23]:

$$r_0 = k_{app}c_0 \qquad (1)$$

where: r_0 = the initial degradation rate of the reactant (mg/L min).

It can be clearly seen that rate constants and initial degradation rate increase with increasing number of bilayers. It is found that the highest photocatalytic degradation rate is obtained when the bilayers number of $(PSS/TiO_2)_n$ is 10.
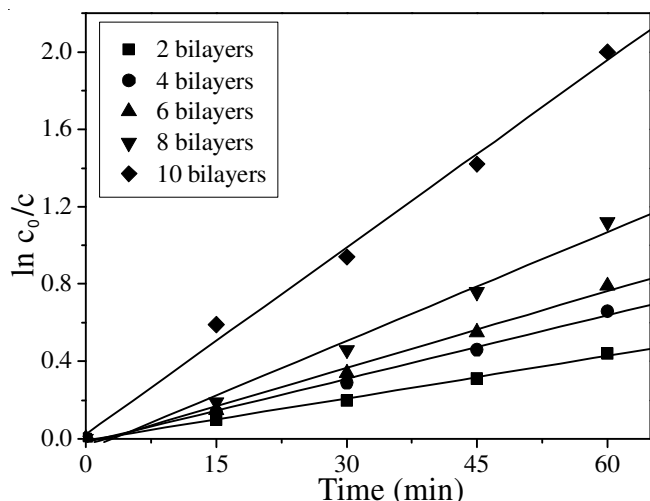

Fig. 4. Reaction kinetic studies of photocatalytic degradation of methyl orange (pH = 2.0) by $(PSS/TiO_2)_n$

TABLE-1
KINETIC ANALYSIS OF THE METHYL ORANGE PHOTODECOMPOSITION

Bilayers number	k (min^{-1})	R^2	r$_0$ (mg/L min)
2	0.0073	0.9984	0.073
4	0.0109	0.9973	0.109
6	0.0132	0.9964	0.132
8	0.0187	0.9938	0.187
10	0.0322	0.9969	0.322

Conclusion

In summary, the TiO$_2$-PSS multilayer films were successfully fabricated by layer-by-layer self-assembly method. Their photocatalytic performance was evaluated by the photocatalytic degradation of methyl orange in aqueous solution under UV light irradiation. The photocatalytic efficiency of $(PSS/TiO_2)_n$ composites films highly relies on film thickness and increases with increasing of bilayer number. Acidic media provided higher degradation efficiency than both neutral and alkaline condition. The results show that the photodegradation of methyl orange by $(PSS/TiO_2)_n$ composites films fitted well to the apparent first-order kinetic equation. In addition, immobilization of catalysts by layer-by-layer method solved the problem of recovery, sharply curtailed the cost of wastewater treatment and avoids the secondary contamination by loss of catalysts, which is very important in the application of TiO$_2$ photocatalytic technique for wastewater purification.

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