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Photocatalytic removal of methyl orange in an aqueous solution by a WO_3/TiO_2 composite film

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Abstract−WO_3/TiO_2 composite film was prepared by microarc oxidation technique and characterized by SEM, XRD, UV-vis spectra and Zeta-potential. The photocatalytic activity of WO_3/TiO_2 composite film was evaluated by examining the degradation of methyl orange. The influence of solution pH and inorganic anions on removal ratio of methyl orange was investigated. Removal ratio of methyl orange decreased with an increase of pH value in acidic solution, while it increased with the pH value in alkaline solution. The influence of added anions on the removal ratio is divided into two aspects. Addition of Cl^- and SO_4^{2-} resulted in a decrease in photocatalytic removal ratio of methyl orange, while it was facilitated by PO_4^{3-}, HCO_3^- and NO_3^-.

Key words: Photocatalysis, Microarc Oxidation, Solution pH, Inorganic Anions

INTRODUCTION

The large amount of textile dyeing wastewater, accounting for one-tenth of the total industrial wastewater emissions, is directly discharged without treatment annually [1], leading to serious environmental harm and threatening the health and existence of humanity [2-4]. A great deal of effort has been devoted to treat textile dyeing wastewater. Among the most commonly used treatment technologies, biodegradation, or physicochemical method, still faces some shortcomings. For example, dye toxicity usually inhibits bacterial growth and limits, therefore, the efficiency of the decolorization in biological treatments [5], Physicochemical methods usually need additional chemicals that sometimes produce a secondary pollution and a huge volume of sludge [6-8].

TiO_2 photocatalysis, an advanced oxidation technology, is widely studied to treat environmental contaminants without secondary pollution, especially difficult biodegradable substrates because of its no-choice and powerful oxidation capacity [9-11].

However, the composition of the textile dyeing wastewater is rather complex, which usually contains many different inorganic anions [12], such as chloride ion, sulfate ions, carbonate ion, nitrate ion and phosphate ion. These inorganic anions can affect the removal ratio of dye molecules through competitive adsorption on the TiO_2 photocatalyst surface, capturing hydroxyl radical or hole [1]. In addition, fluctuating pH of textile dyeing wastewater could affect its removal greatly, which has been confirmed by some studies [2, 13]. So, study on the effect of inorganic anions and solution pH on the photocatalytic removal of organic waste is of great significance for the practical application of TiO_2 photocatalysis.

In this work, WO_3/TiO_2 composite film is prepared in tungstate electrolyte via microarc oxidation (MAO) technique. The influence of inorganic anions and solution pH on the photocatalytic activity of TiO_2 film is investigated.

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EXPERIMENTAL

1. MAO Process

A purity titanium (99.9%) sheet with dimensions of 20 mm×20 mm×2 mm was selected as anode. A stainless steel plate was used as the counter electrode. The experiment was conducted using a high frequency (700 Hz) bipolar pulse current mode. The positive voltage, negative voltage and duty cycle were 400 V, −30 V and 0.3, respectively, during the MAO process. Sodium tungstate was chosen as the major electrolyte to obtain WO_3/TiO_2 composite film photocatalyst because WO_4^{2-} will decompose into WO_3 under high temperature caused by microarc discharge. The electrolyte consisted of 0.05 M $NaWO_4$, 2 $g \cdot l^{-1}$ NaOH and 2 $g \cdot l^{-1}$ NaF. The temperature of the electrolyte was kept under 40 °C and the treatment time was 5 min.

2. Analyses of Oxide Film

The microstructure and morphology of film were characterized by Quanta-200 scanning electron microscopy. The phase composition was estimated by XRD analysis using a D/Max-IIIB diffractometer (Cu K_α radiation). The UV-vis absorption spectra of TiO_2 film were recorded on a Shimadzu UV-2550 spectrophotometer. The zeta-potential of TiO_2 film was measured in 0.1 M NaCl solution by using a Zahner IM6eX electrochemical workstation.

3. Evaluation of Photocatalytic Activity

The photocatalytic activity of WO_3/TiO_2 composite film was determined by measuring the removal ratio of methyl orange aqueous solution. Sample of 20 mm×20 mm×2 mm was immersed into 20 ml of methyl orange aqueous solution. The solution pH was adjusted by H_2SO_4 or NaOH. An ultraviolet germicidal lamp, whose power and wavelength are 300 W and 365 nm, was used as light source and hang perpendicularly above the vessel. The processing time was 2 hours and the distance between the lamp and the film was 10 cm. The solution was constantly supplied with air during

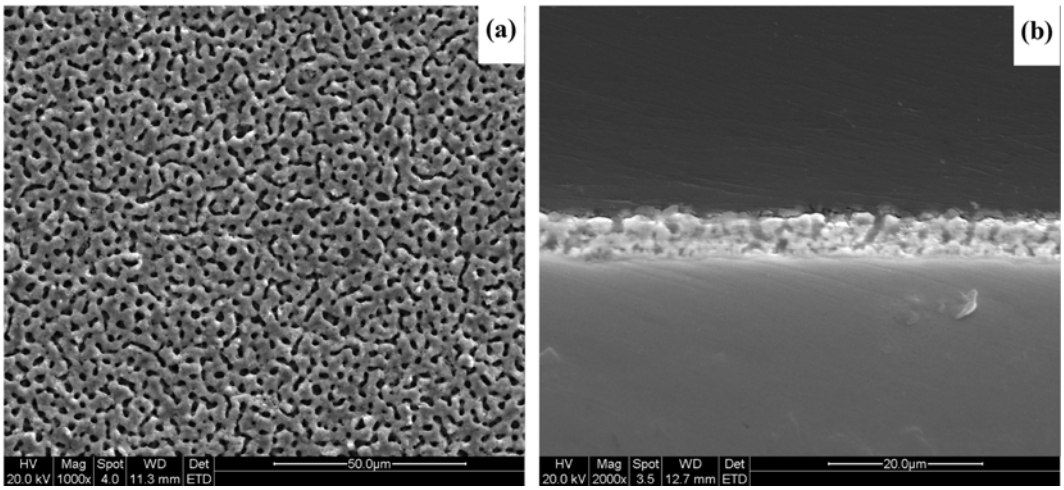

Fig. 1. Morphologies of WO_3/TiO_2 composite film: (a) surface morphology; (b) cross-section morphology.

the irradiation. The concentration of methyl orange before and after irradiation was measured by a UV spectrophotometry.

RESULTS AND DISCUSSION

1. Characterization of Film Structure

Fig. 1 shows the morphology of WO_3/TiO_2 composite film. A porous and rough film forms on the titanium substrate. All the pores are well separated and homogeneously distributed over the film. The pore size is 2-10 μm and the thickness of film is 5-6 μm. There is no apparent discontinuity between the deposited film and the underlying substrate. It appears that the TiO_2 film is well adhered to the titanium substrate, which is beneficial to long-term removal of pollutants.

The XRD pattern of WO_3/TiO_2 composite film is listed in Fig. 2. A mixture phase of anatase and rutile is clearly identified. The intensity of rutile phase outclasses that of anatase phase. The relative content of anatase can be determined by the formula $W_A=1/(1+1.265I_R/I_A)$, where I_A and I_R are the diffracted intensities for the major peak of anatase and rutile phase, and the crystal sizes of anatase and rutile can be calculated by Scherrer formula. The calculated content of anatase and rutile is 18% and 82%, respectively, and the crystal sizes of anatase and rutile are 30 nm and 37 nm, respectively. The appearance of WO_3 peak means that WO_3/TiO_2 composite film could be achieved by microarc oxidation technique. The Ti peaks are detected from Ti substrates.

The absorption spectrum of WO_3/TiO_2 composite film is presented in Fig. 3. The absorption edge of TiO_2 film appears at about 425 nm, and its band gap Eg could be calculated by the formula

$$Eg=hc/\lambda=1243.1/\lambda \quad (1)$$

Where Eg is the band gap (eV) of TiO_2 film, λ is the cut-off wavelength of the spectrum (nm) [14]. The band gap energy of TiO_2 film is determined to be 2.92 eV. Obviously, coupling TiO_2 with WO_3 can obtain a slightly red shift of light absorption compared to pure TiO_2 [15].

Fig. 4 shows the zeta-potential of WO_3/TiO_2 composite film. The iso-electric point of TiO_2 film is demonstrated as 3.4. A low iso-electric point means a higher concentration of hydroxide ions on

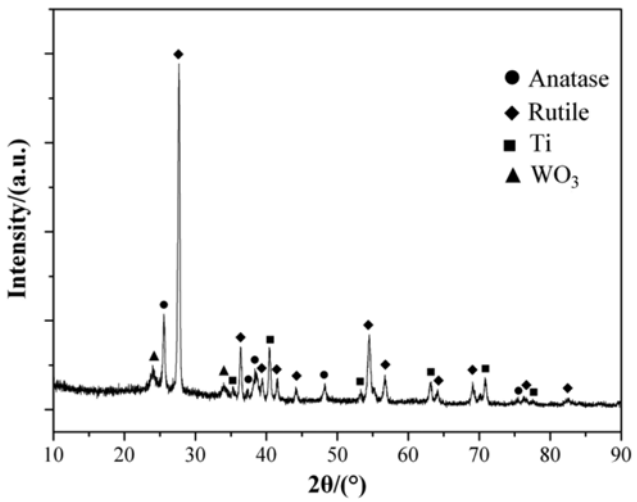

Fig. 2. XRD pattern of WO_3/TiO_2 composite film.

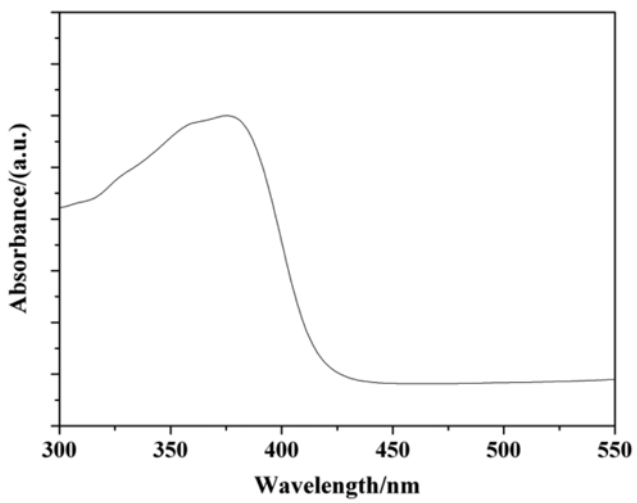

Fig. 3. UV-vis absorption spectra of WO_3/TiO_2 composite film.

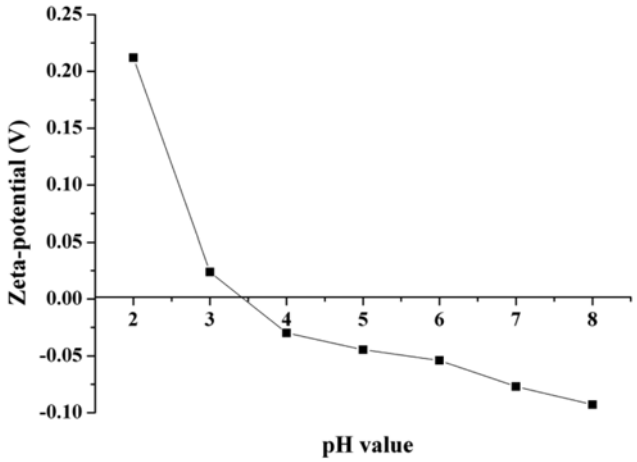

Fig. 4. Plot of the zeta-potential as a function of pH value for WO_3/TiO_2 composite film.

the surface of the photocatalyst [16]. More hydroxide ions may be expected to yield a higher photocatalytic activity. In addition, the iso-electric point would greatly influence the adsorption of methyl orange on the surface of photocatalyst, which plays a very important role in photodecomposition. As an anionic dye, MO can be more effectively absorbed on the TiO_2 film surface when the pH value of MO solution is less than 3.4.

The structure analysis shows that TiO_2 film via micro-arc oxidation technique is suitable as a photocatalyst to remove pollutants.

2. Effect of Solution pH

The influence of solution pH on removal ratio of MO is shown in Fig. 5. Obviously, the removal ratio is smallest in the neutral solution. Both acidic and basic conditions can favor the removal of methyl orange. Hydroxyl radicals (·OH) are the predominant oxidation species in photocatalytic removal of methyl orange, which are generated by two ways: (a) dioxygen (O_2) reduced by electrons in conduction band; (2) hydroxide ion (OH^-) reacted with holes (h^+).

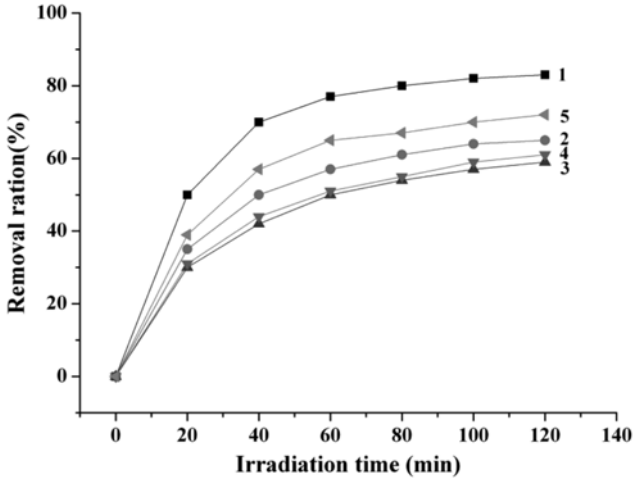

Fig. 5. The influence of solution pH on the removal ratio of MO (curves 1-5 represented the changeable relation of the removal ratios and the irradiation times, and the corresponding pH values were 3, 5, 7, 9 and 11, respectively).

In acidic solution, ·OH can be produced by reducing O_2 through a series of reactions.

$$O_2+e^-\rightarrow O_2^- \quad (2)$$

$$O_2^-+H^+\rightarrow HO_2\cdot \quad (3)$$

$$2HO_2\cdot\rightarrow O_2+H_2O_2 \quad (4)$$

$$H_2O_2+O_2^-\rightarrow\cdot OH+O_2+OH^- \quad (5)$$

$$H_2O_2+hv\rightarrow 2\cdot OH \quad (6)$$

In this circumstance, the number of ·OH increases with the increasing acid strength.

In addition, the functional groups are protonated, and the proportion of the positively charged surface increases in acidic solution. So, the adsorption of methyl orange, an anionic dye, on the surface of WO_3/TiO_2 film gradually increases with decreasing pH value. The increased adsorption could favor the removal of methyl orange [17]. Therefore, the removal ratio increases with increased adsorption of methyl orange and number of ·OH.

In basic solution, more hydroxide ions available on TiO_2 surface can be easily oxidized to form more ·OH by trapping photo-induced holes (h^+), consequently promoting the removal of methyl orange.

$$OH^-+h^+\rightarrow\cdot OH \quad (8)$$

Therefore, high photocatalytic removal ratio of methyl orange is possible in the acid or alkaline solution.

3. Effect of Inorganic Anions

The effects of 10 mM added inorganic anions on the pH value

Table 1. Relation between solution pH and inorganic anions

Solution pH	Inorganic anions (10 mmol/L)				
	Cl^-	SO_4^{2-}	HCO_3^-	PO_4^{3-}	NO_3^-
MO	7.2	7	8	10.4	6.8

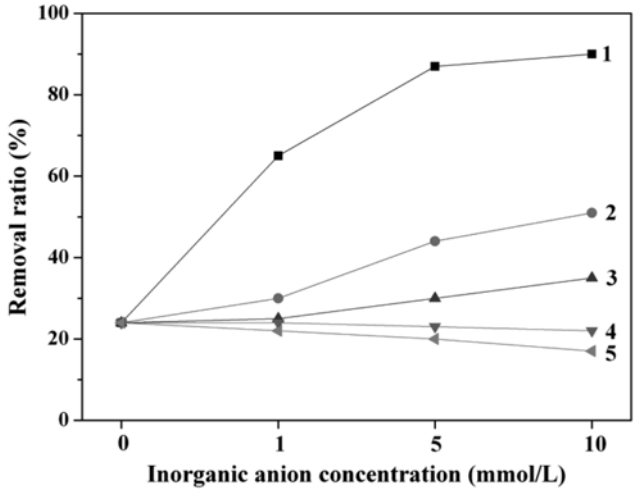

Fig. 6. The influence of inorganic anions on the removal ratio of MO (curves 1-5 represented the changeable relation of the removal ratios and the inorganic anions, and the corresponding anions were NO_3^-, PO_4^{3-}, HCO_3^-, SO_4^{2-} and Cl^-, respectively).

of MO solution are shown in Table 1. The pH value of distilled water is 6.76. Obviously, the pH value of MO solution is changed.

The effect of added inorganic anions on the removal ratio of MO is listed in Fig. 6. HCO_3^-, PO_4^{3-} and NO_3^- promote the removal of MO, while SO_4^{2-} and Cl^- inhibit its removal. The reasons are divided into two aspects.

3-1. Facilitation Effect

The removal ratio of MO increases with addition of NO_3^-, PO_4^{3-} and HCO_3^-, and the order of facilitation is $NO_3^- >> PO_4^{3-} > HCO_3^-$, seen in Fig. 6. This phenomenon could be interpreted as follows.

On the one hand, added NO_3^- could react with H_2O to produce many ·OH under UV irradiation [18], subsequently accelerating photocatalytic removal of methyl orange.

$$NO_3^- + H_2O \xrightarrow{h\nu(\lambda>290\ nm)} NO_2 + OH^- + \cdot OH \quad (9)$$

On the other hand, added HCO_3^- or PO_4^{3-} could hydrolyze to produce many OH^-. The number of OH^- in solution containing PO_4^{3-} is much more than that in solution containing HCO_3^- because hydrolysis of PO_4^{3-} outclassed that of HCO_3^-. This could be confirmed by Table 1.

$$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^- \quad (10)$$

$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^- \quad (11)$$

$$HPO_4^{2-} + H_2O \rightarrow H_2PO_4^- + OH^- \quad (12)$$

OH^- generated by hydrolysis of HCO_3^- or PO_4^{3-} could interact with photo-induced hole to form hydrogen oxygen free radical, which increases the removal of methyl orange.

3-2. Inhibition Effect

The number of ·OH decreases because ·OH could be trapped by added Cl^- and SO_4^{2-}.

$$\cdot OH + Cl^- \rightarrow Cl + OH^- \quad (13)$$

$$\cdot OH + SO_4^{2-} \rightarrow \cdot SO_4^- + OH^- \quad (14)$$

The oxidative ability of generated Cl and $\cdot SO_4^{2-}$ is lower than that of ·OH. So, the removal ratio of MO is reduced.

CONCLUSION

WO_3/TiO_2 composite film was prepared in tungstate electrolyte via MAO technique and used to remove MO in aqueous solution. The effect of solution pH and inorganic anions on the removal ratio of methyl orange was investigated. The obtained results showed the removal ratio of MO increased in acid or alkaline environment. The influence of inorganic anions on the removal ratio of MO was divided into two types: facilitation or inhibition. All of these are beneficial to the practical application of TiO_2 photocatalysis on the treatment of dyeing wastewater.

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