

Preparation and application of nano-TiO₂ catalyst in dye electrochemical treatment

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Abstract

This paper reports results of an investigation into the removal of ARB (Acid Red B) dye in an electrochemical oxidation reactor with semi-conductor suspended in the electrolyte. TiO₂ nano-powders spiked with various elements, including Si, Co, Zn, La, Ag, Ce, W and Bi, were prepared by sol-gel method to improve colour removal efficiency. Through the $L_{16}(4^4)$ orthogonal experiment, the optimised preparation conditions of nano-TiO₂ catalyst were obtained, namely prepared at 400°C and spiked with 10% Co (in molar ratio). The XRD (X-ray diffraction) analysis indicated that TiO₂ prepared at 400°C occurred predominantly in the anatase crystalline form and the particle size was below 20 nm. The BET (Brunauer, Emmet and Teller) surface area was 69.2 m²/g. The decolourisation efficiency using Co (10%)/TiO₂ as catalyst was 33.1% and increased by 5.7% (about 1.21 times) compared with the colour removal without catalyst. The DRS (diffuse reflectance spectroscopy) demonstrated that the improvement of colour removal of Co(10%)/TiO₂ compared with pure TiO₂ was probably due to its better light absorption and photocatalytic activity in the visible region.

Keywords: electrochemical oxidation; titanium dioxide; Acid Red B; wastewater treatment

Introduction

Increasingly, electrochemical technology is receiving more and more attention, for its success in removing colour without the production of a secondary pollutant and due to its convenience and simplicity (Chen XJ et al., 2005; Chen XM et al., 2003; Chen GH, 2004; Brillas and Casado, 2002; Wang et al., 2004). The exact mechanisms, which occur during the electrolysis, are complicated and not entirely clear. Based on the intermediate products and radicals that can be determined in the electrolysis, such as O₃, H₂O₂, Cl₂, O₂, •OH, ClO⁻ and other oxidants, it is postulated that organic pollutants could be oxidised directly or indirectly (Chen GH, 2004; Panizza and Cerisola, 2001).

However, the high energy consumption of electrochemical oxidation process confines its utilisation to a large scale. It is herewith reported that the presence of a catalyst in the electrical field can enhance the treatment efficiency. Chen WG (Chen WG and Zhu, 1998) has used metal dioxide to remove three types of organic pollutants, phenol, phenylamine and di-mephtalate from wastewater. The presence of H₂O₂ and •OH was verified during the electrolytical catalysis process. The results showed that the removal efficiency depended on the reactive intermediate yield in the system. Organic pollutants were effectively removed by increasing the H₂O₂ yield. Notable removal efficiency was reached when the H₂O₂ yield was more than 0.3 mg/l. A semiconductor catalyst can be used in electrochemical processes as well as in a photo-degradation system (Qamar et al., 2005; Shen et al., 2002). The removal of xenobiotic compounds, such as chlorophenols and pesticides, from municipal and industrial wastewater is very important because of their toxicity and their bioaccumulation tendency. Among the several methods

proposed, photo-degradation catalysed by suspending inorganic semiconductors (i.e. TiO₂) has lately received wide attention because this process leads to non-toxic final products and shows high degradation efficiency (Lo et al., 2004; Bessekhouad et al., 2004). TiO₂ is a semiconductor catalyst that has been widely studied since the seventies and over the past century. The TiO₂ electrode has been used to degrade 4-chlorophenol and dyes (Azzam et al., 2000; Carneiro et al., 2004). In our previous study (Shen et al., 2002) it was shown that pure TiO₂ could not achieve successful catalytic results.

In the electrical field, many metal ions with variable valences, such as Fe³⁺ and Co³⁺, are added to expedite the oxidation process by indirect oxidation. However, it is difficult to recycle these ions. Nano-composite TiO₂ mixed with metal ions with variable valences may have a higher catalytic effect. In order to study the effect of a semiconductor catalyst mixed with metal elements with variable valences in the electrical field, preparation and application of nano-composite TiO₂ catalyst have been studied in this research. The objective was to enhance the electrolysis efficiency.

Experimental

Preparation and characteristics of nano composite TiO₂ catalyst

Nano-composite TiO₂ catalysts were prepared through a proprietary sol-gel method. Tetrabutyl titanate and diethanolamine were dissolved in ethanol. After stirring for 2 h at room temperature, an ion additive was added to the sols, including cobaltous, cerous, lanthanum and tungstate salts etc. To this solution a mixed solution of water, nitric acid and ethanol was added with a burette while stirring. The ratio of Ti(OC₄H₉)₄/C₂H₅OH/H₂O/HNO₃ of this solution was 1:30:1:0.03 in molar. The resultant alkoxide solution was kept at room temperature for about 10 h after which it was heated at 400~700°C for 3 h. All the reagents

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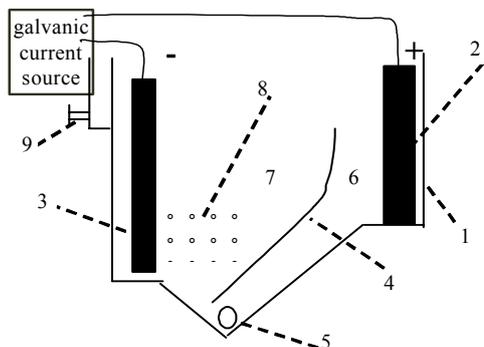


Figure 1

Scheme of catalytic electrolysis equipment

1. tank; 2. anode; 3. cathode; 4. guide plate; 5. water (gas) inlet; 6. ascending area; 7. deposition area; 8. catalyst; 9. outlet

used were analytical reagents (AR) and all the aqueous solutions were prepared by de-ionised water.

The prepared catalyst was then ground to powder and detected by an X-ray powder diffractometer (D8 advance, Bruker, German). The average crystal size of the powders was determined by the Scherrerl equation. The surface area and the pore size were characterised by nitrogen adsorption-desorption isotherms obtained with an automatic adsorption instrument (ASAP 2000, Micromeritics, USA) at 77 K. The resulting isotherms were analysed using the BET method, while pore size calculations were carried out using the BJH (Barrett, Joyner and Halenda) method (Roquerol et al., 1998). The DRS spectra of the catalyst were recorded by a dual beam UV-Vis spectrometer (TU-1900, Beijing Purkinje General Instrument Co. Ltd), equipped with an integral ball. The wavelength of the light beam used in this experiment ranged from 230 to 850 nm. The integral ball collected all of those light beams reflected from the surface of the catalyst, and the spectrometer reported the percentage of those reflected lights. The reflectance of BaSO₄ was adopted as the base line.

Electrolysis and analytical measurement

ARB (Acid Red 14, an azo dye) was used as electrolysis indicator in this paper with 60 mg/l ARB (commercially available) solution containing 55 mg/l Na₂SO₄(AR) as supporting electrolyte.

Figure 1 shows the scheme of electrolysis equipment used in this study. Graphite was used as anode and activated carbon felt electrode as cathode. Air was pumped into the equipment from the bottom so as to stir the solution. Graphite anode had an effective area of 40 cm². Catalyst (1 g/l) was used as suspending powder in the electrolysis system. For the presence of the airflow and the guide plate, catalyst flowed between anode and cathode, which improved the contact between catalyst and solution.

When the catalytic electrolysis equipment was used, ARB solution was pumped into the equipment with 1 g/l TiO₂ catalyst. A potential of 8V was applied on the electrodes. The electrolysis time was 40min. Electrical current density was detected over time.

After electrolysis, the dye solution was analysed by a spectrophotometer (U-3010 Hitachi, Japan). Each dye solution was scanned and its maximum absorbency visible wavelength was detected. The colour removal ratio was calculated as follows:

$$R_{\text{colour}} \% = (ABS^M_0 - ABS^M) / ABS^M_0 \times 100\% \quad (1)$$

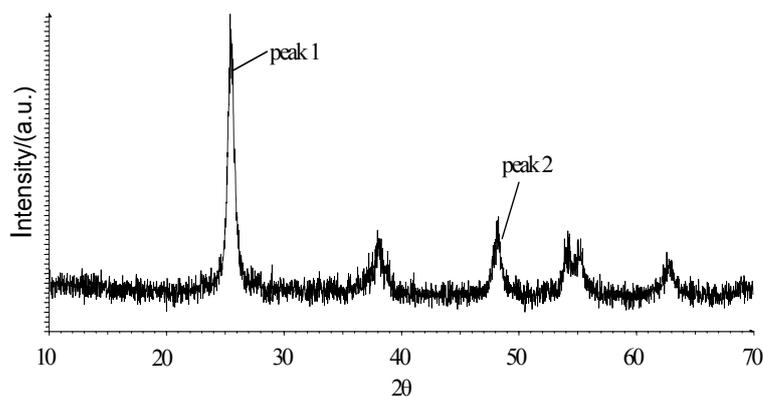


Figure 2

Typical X-ray diffraction of nano-TiO₂ prepared at 400°C

where:

ABS^M: Average of absorbency values at its maximum absorbency visible wavelength

ABS^M₀: ABS^M value before electrolysis.

ABS^M: ABS^M value after electrolysis.

Results and discussion

The characteristics of nano TiO₂

Figure 2 illustrates a typical XRD spectrum of nano TiO₂ prepared at 400°C with 2θ diffraction angles between 10° and 70°. Three primary peaks can be seen at 25.4°, 37.8° and 48.1° and can be assigned to diffraction from (1 0 1), (0 0 4), and (2 0 0) planes of anatase respectively (JCPDS No. 21-1272, 1988); the other peaks can all be attributed to the anatase TiO₂, which is in agreement with the findings of Ozkan et al., 1998. These results showed that the prepared nano-material consisted mainly of the anatase structure. From the XRD data, the particle size has been calculated and is presented in Table 1. Its average particle size was less than 20 nm.

Peak	1	2
Half peak width	0.649	0.663
2θ(°)	25.438	48.124
Particle size (nm)	12.572	13.177
Average (nm)	12.875±0.428	

The nano TiO₂ prepared at 400°C was desiccated for 1 h at 90°C and for 5 h at 350°C. Then it was tested on ASAP 2000, V3.01 (Micromeritics Instrument Corporation). Its BET surface area reached 69.2 m²/g; the single-point area was 66.0 m²/g; the single-point volume was 0.1108 cm³/g; the average aperture was 6.402 nm.

Electrolysis results of spiked TiO₂

Nano-composite TiO₂ catalysts spiked with 5% (mol/mol) other elements, including Si, Co, Zn, La and W etc., were prepared through the said sol-gel method and then used in the dye electrolysis treatment as described above. Figure 3 shows electrolysis results of these catalysts. The colour removal

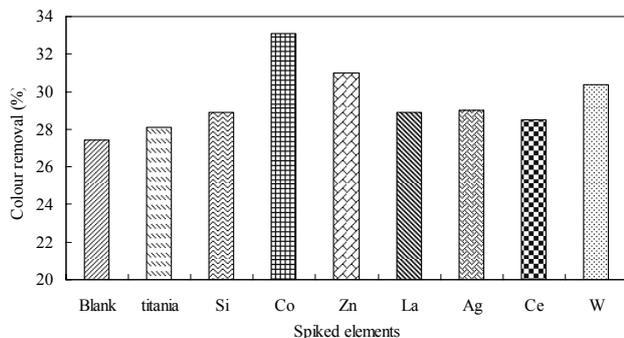


Figure 3
Electrolysis results of nano-TiO₂ catalyst spiked with 5% (mol/mol) other elements

efficiency without catalyst was 27.4% and that of TiO₂ was 28.1%, which demonstrates that pure TiO₂ has little significant catalysis effect in this electrolysis experiment. However, the colour removal efficiencies of TiO₂ spiked with Co, Zn and W are 33.1%, 31% and 30.4%, respectively. Evidently, spiking TiO₂ with Co, Zn and W into can enhance dye removal efficiency.

Optimisation of preparation condition

On the basis of the results of above experiments, an orthogonal array experimental design was used to select more efficient catalysts. Co and W that had relatively good catalysis effects were selected (ZnO is unstable in the wastewater) and another metal

TABLE 2
Parameters and levels of the orthogonal array experimental design for nano-TiO₂ catalyst preparation

Column	Factors	Studying levels			
		1	2	3	4
A	Temperature(°C)	400	450	550	750
B	Co(mol/mol)	0%	5%	10%	20%
C	W(mol/mol)	0%	5%	20%	50%
D	Bi(mol/mol)	20%	5%	2%	0%

Bi was introduced into the orthogonal experiments. Additionally, heating temperature was tested here to get the optimum preparation temperature. Hence, four factors, including preparation temperature, Co, W, and Bi, were studied in this experimental design and the interaction between factors was not considered. The various studying levels for each factor are summarised in Table 2. Consequently, a L₁₆(4⁴) orthogonal array was employed for arranging these factors. The characteristic value used in this experimental design was the colour removal of the ARB solution. Table 3 simultaneously lists the design matrix of the L₁₆(4⁴) orthogonal array and the experimental data. Each experiment was done in duplicate and the average was used for the analysis shown below.

Figure 4 shows the average responses of colour removal for these factors in the orthogonal array experimental design. It indicates that preparation temperature and Co amount were

TABLE 3
Design matrix and the experimental results for the L₁₆(4⁴) orthogonal array

Experiment	Factors and their studying levels				Experiment results Colour removal (%)	Square
	A	B	C	D		
1	1	1	1	1	33.8	1 142.4
2	1	2	2	2	35.6	1 263.8
3	1	3	3	3	42.7	1 823.3
4	1	4	4	4	36.8	1 354.2
5	2	1	2	3	30.1	903.0
6	2	2	1	4	38.7	1 497.7
7	2	3	4	1	35.6	1 263.8
8	2	4	3	2	35.0	1 225.0
9	3	1	3	4	31.3	979.7
10	3	2	4	3	27.5	753.5
11	3	3	1	2	34.2	1 169.6
12	3	4	2	1	29.3	855.6
13	4	1	4	2	32.2	1 036.8
14	4	2	3	1	32.2	1 033.6
15	4	3	2	4	31.2	973.4
16	4	4	1	3	33.8	1 139.1
K1	148.9	127.4	140.5	130.8	539.7	18 414.6
K2	139.3	133.9	126.1	137.0		
K3	122.2	143.7	141.2	134.0		
K4	129.3	134.8	132.0	138.0		
Sum	18 303.0	18 235.1	18 240.5	18 209.4	18 201.4	
Sum of squares	101.7	33.7	39.1	8.0	213.2	

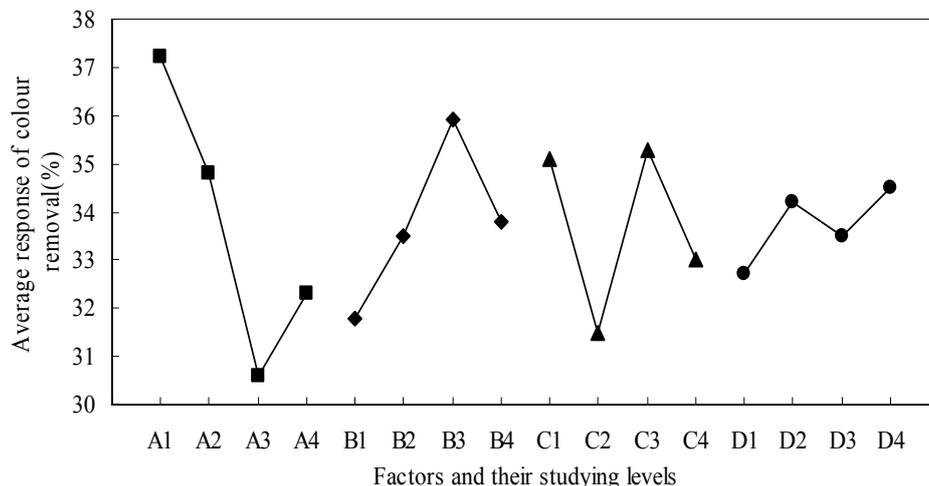


Figure 4
Calculated average responses of the colour removal of different factors

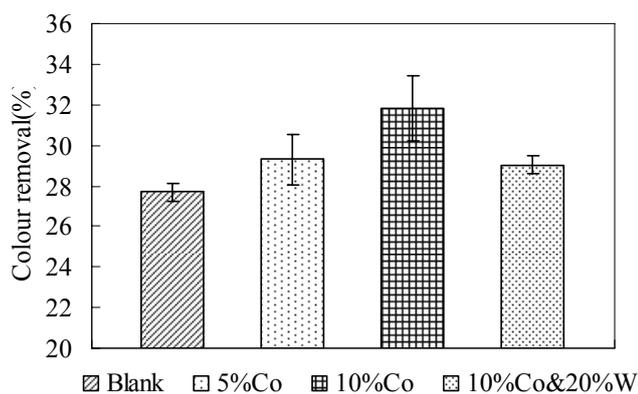


Figure 5
Catalysis effect of three kinds of nano-TiO₂ catalysts prepared at 400°C

more important in the catalysis effect of nano-TiO₂ than the amount of W and Bi. The preparation temperature can determine the crystal structure of the catalyst. When TiO₂ was produced at relatively high temperature, it occurred mainly in the rutile crystalline form; however, the anatase crystalline form was the superior catalyst (Cao et al., 1999). From the orthogonal experiments, the optimal conditions were found to be a temperature of 400°C and spiked with 10% Co.

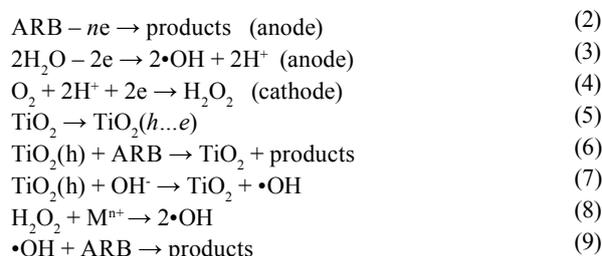
To confirm the result of the orthogonal experiments, three nano-composite catalysts (spiked with 5% (mol/mol) Co, 10% Co and 10% Co & 20% W) were prepared at 400°C. Their catalysis effect is shown in Fig. 5. All three catalysts had some catalysis effect compared to the blank experiment; however, the catalyst spiked with 10% Co was most efficient, which was in accordance with the result of orthogonal experiments. The decolourisation effect of catalyst with 10% Co increased by 5.7% and was about 1.21 times higher than the colour removal without catalyst.

Electro-oxidation and catalytic mechanism

When air is pumped into the electrolysis system, O₂ can be reduced to H₂O₂ on the cathode by a two-electron pathway. The electro-generated H₂O₂ can be further changed into the OH radical, *in situ*, in the presence of transition metal ions. Thus, the electrochemical degradation mechanism of organic pollutants in this electrolysis system is postulated to be the indirect oxidation of the electro-generated H₂O₂ and ·OH.

The excitation of the suspended TiO₂ particles in the electrolysis system can lead to the release or acceptance of an electron. The positively charged holes at the surface of TiO₂ particles have considerable oxidising ability. It has been shown (Taghizadeh et al., 2000) that TiO₂ pre-adsorbs organic compounds at the particle/solution interface before degradation. Then, TiO₂ oxidises the compounds directly or indirectly by direct oxidative transformation of the compounds that need to diffuse from the bulk solution to the semiconductor particle surface; and by oxidative radicals, such as ·OH and ·O₂, generated by the oxidation of water and/or hydroxide ions by the valence band holes on the surface area of semiconductor particles. As the ionic radius of Co²⁺ and Ti⁴⁺ is 69 pm and 72 pm, respectively, Co²⁺ can enter the crystal lattice of TiO₂ and promote the formation of rutile TiO₂ (Zhang et al., 2003). The presence of some rutile TiO₂ in anatase TiO₂ can enhance the catalytic effect of TiO₂ (Ohno et al., 2003). Furthermore, it can be seen (Fig. 6) that the reflectance of TiO₂ in the visible range of 400 to 850 nm decreases dramatically by spiking with Co. Figure 6 presents typical DRS spectra of TiO₂ and Co (10%)/TiO₂ prepared at 400°C. This result proves that upon addition of Co to TiO₂, the absorption of the composite powders in the visible spectrum range increases markedly compared to the unspiked TiO₂. This shows that the Co/TiO₂ catalyst is sensitive to visible light, which was also demonstrated by Dvoranová et al., 2002. Hence, Co can improve the colour removal efficiency in the electrolysis system.

The major electrochemical reactions initiating redox processes in the electrolysis system can be summarised as follows (An et al., 2002):



Conclusion

In this study, various nano-composite TiO₂ catalysts were prepared by sol-gel method to expedite colour removal in a catalytic electrolysis system. Through the L₁₆(4⁴) orthogonal experiment, the optimised conditions for the preparation of the nano-compos-

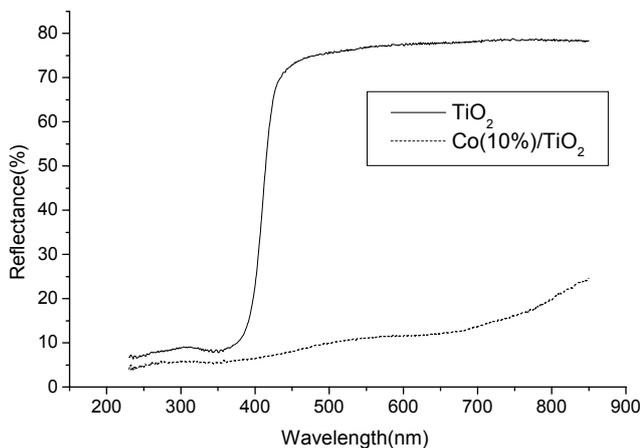


Figure 6
Typical DRS spectra of TiO_2 and $\text{Co}(10\%)/\text{TiO}_2$
prepared at 400°C

ite TiO_2 catalyst were obtained, namely, a temperature of 400°C and a 10% addition of Co (in molar ratio). The XRD results of TiO_2 prepared at 400°C indicated that the particle size was below 20 nm and that the TiO_2 occurred mainly in the anatase crystalline form. The BET surface area was $69.2 \text{ m}^2/\text{g}$. The decolourisation efficiency using $\text{Co}(10\%)/\text{TiO}_2$ as catalyst was 33.1% and increased by 5.7% (about 1.21 times) compared with the colour removal without catalyst. The DRS spectra demonstrated that the improvement of colour removal of $\text{Co}(10\%)/\text{TiO}_2$ compared with pure TiO_2 was probably due to its better light absorption and photocatalytic activity in the visible region.

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