Synthesis, characterization and photocatalytic activity of Co^{2+}-doped titania

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Abstract. Photocatalyst of Co^{2+}-doped titania was simply prepared, and the photocatalytic activity was tested under UV irradiation for methyl orange degradation. The influence of doping quantity, calcination temperature, calcination time and quantity of catalyst was investigated for photocatalytic efficiency of the photocatalyst. The sample was characterized by UV diffuse reflectance spectra (UV/DRS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and IR. The results showed that the photocatalytic activity Co^{2+}-doped TiO₂ which calcined at 200 °C for 5 h is high, and which diameter is about 4-7 nm presents anatase phase. The sample absorption band of UV/DRS moves to visible region and reaches 580 nm. This kind of catalyst is also effective for degradation other organic dyes and beer wastewater.

Keywords: sol-gel; titanium oxide; photocatalytic degradation; visible light.

1. Introduction
In 1972, Fujishima and Honder reported the first photoelectrochemical cell water splitting, by using a rutile TiO₂ photoanode and Pt counter electrode [1]. The interest in developing artificial systems capable of converting solar to chemical or electrical energy is increasing [2-5]. One of the most active photocatalytic areas is that semiconductor particles as photocatalysts for the oxidation of organic pollutants in the water or air [6-8]. In spite of this, the active phase-anatase, do not absorb significantly over 387 nm, and the activity decrease when only visible light is used. The efforts to achieve a more efficient photocatalytic process, are in direction to improve the TiO₂ response, people look for new materials with ion doped, etc.

The biggest challenge is getting high activity catalysis. The method is doping ions to increase the efficiency of TiO₂. The doping ions include transitions metal ions, rare earth metal ions, inorganic function ions, etc. Metal ions doped to TiO₂ have been frequently reported [9-12]. Photocatalytic activity of metal doped TiO₂ depends on its preparation method [13-14], which affected the physicochemical properties of the photocatalyst. Therefore it is necessary to develop a simple method of catalyst synthesis, which doped transition metal ions. In this work, we reported the synthesis and characterization of Co^{2+} doped TiO₂ by simple preparation, which use cheap raw material TiCl₄. We studied the photocatalytic activity of the catalyst by degradation of methyl orange in aqueous dissolution. The result showed that the photocatalytic activity of samples was high when it calcined at lower temperature.
2. Experimental

2.1 Synthesis
Take 2 mL TiCl₄ in beaker, water and solution of CoCl₂ were added under stirring. Then an aqueous solution of NH₄OH was added under continuous stirring to adjusted pH value of the solution to ca. 7. The reaction mixture was maintained at room temperature until a gel was formed, and then colloid was stirred gently for about 1.5 h. It was dried in the oven at 85 °C. Finally the sample was calcined at different temperature in muffle.

2.2 Photocatalysis
Photocatalytic activity was evaluated by degradation of methyl orange solution. A quantity of 50 mg of the catalyst was added to a vessel containing 20 mL of methyl orange aqueous solution (C₀ = 0.02 g/L). The solution was irradiated with mercury lamp (250 W). During the process of the photocatalysis tests, the concentration of methyl orange was detected by a visible spectrophotometer (Shanghai 722s) at $\lambda_{\text{max}} = 464$ nm.

The decontamination of wastewater was evaluated by COD degradation in beer wastewater.

2.3 Characterization
TEM images were recorded on a H-800 transmission electron microscope. DR-UV-Vis spectra was recorded on a Cary 500 UV-VIS-NIR spectrometer. XRD patterns were recorded on a Shimadzu XP-7000 with Cu-Kα radiation ($\lambda = 0.154178$ nm) and XPS patterns were recorded on a PHI 5300 ESCA X-ray photoelectron spectroscopy. IR images were obtained on a HITACHI 260-10 IR spectrometer. COD were detected on an AQUA LYTIC AL-32 COD vario.

3 Results and discussion

3.1 Optimization of photocatalyst

3.1.1 Influence of calcination temperature
In this paper, we discussed the influence of the calcination temperature of Co²⁺ doped titania. The samples were calcined at 150, 200, 300, 400, 500, 600 and 700 °C for 5 h. The degradation results were shown in Fig. 1. From Fig. 1, it can be seen that from 150 °C to 700 °C, the activity of Co⁴⁺-TiO₂ is higher than TiO₂. The sample which calcined at 200 °C preserved high degradation. As the calcination temperature is above 400 °C, the activity of Co²⁺-doped TiO₂ decreased quickly.

3.1.2 Influence of doping quantity
CoCl₂ solution (0.03 mol/L) was added to titania gel, the quantity of CoCl₂ is 0.05, 0.075, 0.1, 0.125, 0.15, 0.2, 0.3 mL respectively. Then the samples were calcined at 200 °C for 5 h. The methyl orange degradation experiments were shown in Fig.2. The degradation gradually increased along with the increment of the doping ion quantity (Co²⁺ ≤ 0.003 mmol), and the photocatalytic activity of sample containing 0.003 mmol Co²⁺ is high.

![Fig. 1 Photocatalytic activity of catalyst calcined at different temperature](image1)

![Fig. 2 Photocatalytic activity of different contents Co²⁺-doped titania](image2)

3.1.3 Influence of calcination time
A quantity of 0.1 mL CoCl₂ solution (0.03 mol/L) was added to titania gel. Then the samples were calcined at 200 °C for 3h, 4h, 5h, 6h, 7h respectively. The methyl orange degradation experiments result was shown in Fig.3. From Fig.3, it can be seen that with the calcination time increasing, the photocatalytic activity of sample was high. However, the optimum time was 5h by considering energy resource.

![Fig. 3 Photocatalytic activity of Co²⁺-doped titania calcined for different time](image1)

### 3.14 Influence of catalyst quantity
Methyl orange solution (0.02 g/L) was degraded by catalyst of 0.03, 0.05, 0.10 and 0.15 g, respectively. The degradation result was shown in Fig. 4. The photocatalytic activity was increased with a rise in dosage of catalyst. However, more than 0.05 g, the photocatalytic activity of catalyst increases slowly. Hence, the quantity of catalyst we chose was 0.05 g.

### 3.2 Activity of Co²⁺-doped TiO₂ for other dyes and beer wastewater
In this work, we choose Rosaniline, Bromophenol blue, Methylene blue to study the activity of Co²⁺-doped TiO₂. The results were listed in Tab. 1. The photocatalytic activity of P25 and TiO₂ is lower when irradiated under visible light.

In addition, beer wastewater was chose to study the activity of Co²⁺-doped TiO₂. A quantity of 50mg of catalyst was added to a vessel containing 20 mL wastewater solution. Under stirring, the solution was irradiated with a Hg lamp for 2 h. The COD was decreased from 1431 to 376, and the COD degradation rate was 73.7%, compared with degradation rate of 69.4% of P25.

### Table 1 Photocatalytic activity of Co²⁺-doped TiO₂ composite for organic dyes degradation.

| Dye             | C(mg/L) | V/(mL) | UV light | Visible light |
|-----------------|---------|--------|----------|---------------|
| Rosaniline      | 20      | 20     | 1        | 95.7          | 5  | 75.2 |
| Bromophenol blue| 20      | 20     | 2.5      | 97.9          | 5  | 67.9 |
| Methylene blue  | 20      | 20     | 2.5      | 89.6          | 5  | 63.8 |
| Methyl orange   | 20      | 20     | 2.5      | 95.6          | 5  | 79.6 |

### 3.3 Characterization

#### 3.3.1 UV diffuse reflectance spectra
The UV/DRS spectra of Co²⁺ doped TiO₂ showed that Co²⁺-doped TiO₂ exhibited broad and strong absorption in the range from 200 to 400 nm, and the red shift was observed compared with pure TiO₂, the absorption peak shift to 580 nm. The result was explained degradation of methyl orange and beer wastewater test.

#### 3.3.2 X-ray diffraction
From the XRD pattern in Fig. 5, it was shown that the effect of calcination temperature to the crystal of TiO₂. As shown in Fig. 5, the peak shapes of the samples calcined at 150 and 200 °C were obviously different from those of 400, 500 and 700 °C. The XRD patterns of 150 and 200 °C had characteristic peak of NH₄Cl phase at 2θ = 23°, 32.7° and had characteristic peak of anatase phase at 2θ
It illustrated that amorphism of TiO₂ had changed into anatase at 150 °C. From 150 °C to 700 °C, it can be seen that the breadth of peak is diminished, with the calcination temperature increased, and the crystal size was enlarged. When temperature higher than 700 °C, the rutile characteristic peaks at $2\theta = 27.4^\circ$, 36.0° and 54.3° appeared in the XRD pattern. Through the calculation by Scherrer the particle size calcined at 150, 200, 400, 500, 700 °C for 5 h was roughly 6, 7, 11, 15, 33 nm, respectively. The temperature of crystallize transform is 150 °C, which was shower than the other report [15-16].

3.3.2 TEM and X-ray photoelectron spectroscopy
The TEM images of Co²⁺-doped TiO₂ calcined at 200, 500 and 700 °C are showed in Fig. 6. From Fig. 6, it can be seen that the average diameter of the sample calcined at 200 °C was about 4-7 nm and the selected area electron diffraction (SAED) was showed that the composite has a uniform polycrystalline structure (Inset in Fig. 6A). When the calcination temperature increased, the average diameter of the sample enlarged gradually. The diameter of the sample calcined at 500 °C was roughly 15-20 nm and the diameter calcined at 700 °C was roughly 30-40 nm. It was also in accordance with the results of XRD.

3.3.3 XPS and Infrared spectroscopy
The XPS images of Co²⁺-doped TiO₂ calcined at 200 °C showed that the bands at 780 and 795.9 eV were corresponding to Co 2p3/2 and Co 2p1/2 of CoO [17], respectively. Because XPS can only detect the photoelectron for several nanometer on the surface of the samples (for inorganic compound as 2-4 nm), Therefore Co²⁺ exists on the surface of the samples.

The IR images of Co²⁺-doped TiO₂ calcined at 200 °C for 5 h showed the NH₄⁺ IR characteristic peaks (3130 cm⁻¹ and 1400 cm⁻¹), and anatase phase TiO₂ peaks (1650 cm⁻¹ and 700 cm⁻¹). It can be deduced that the samples contain NH₄Cl and anatase TiO₂. Otherwise, it illustrated that TiO₂ was crystallized under 200 °C.
4. Conclusion
In this paper, we used TiCl₄ as the raw material to prepare Co²⁺-doped TiO₂, and discussed the factors effect on the activity. The result showed that activity of Co²⁺-doped TiO₂ calcined at 200 °C is high. This crystal type of Co²⁺-doped TiO₂ is anatase and absorption band moves to the visible region 580 nm, and has the utilization of visible-light. The organic dyes and beer wastewater were effectively degraded by the catalyst, and the graduation rate is high.

Acknowledgements
The Natural Science Foundation Council of China (20271007 and 20331010), and Specialized Research Fund for the Doctoral Program of Higher Education (20030007014) are acknowledged for financial support.

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