



## Research of Co/N/Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> in Sonocatalytic Degradation of Dyeing Wastewater†

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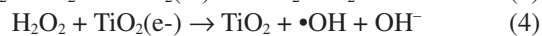
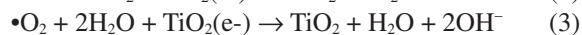
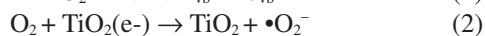
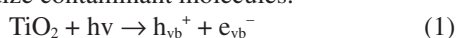
The preparation of the complex Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> film was used sol-gel coating process. The nano powders samples of Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> were characterized by X-ray diffraction, which appeared anatase mine peaks and the peaks of Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> samples appeared broadened. Their SEM photos illustrated that the size of Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> particles were smaller than Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> particles due to Co and N doped. The test of catalytic degradating dye wastewater by using Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> or Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> were done under ultrasonic radiation. Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> sonocatalytic degradation efficiency was improved significantly because of doping Co and N.

**Keywords:** Co/N/Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>, XRD, SEM, Sonocatalytic, Degradation, Dye wastewater.

### INTRODUCTION

The production of dyestuff is very large in China. In the wastewater of the textile and dyeing industry there are very large displacement, high organic matter content, high chroma and complicated composition. So the development of effective solutions to the problems of wastewater treatment is perhaps the most challenging at the present time. Especially along with the rapid development of chemical fiber, chemical dyestuff and widespread applications, the bioavailability of dyeing wastewater has been becoming worse and worse and the degradation of dyeing wastewater became more difficult. Now commonly used treatment methods such as biochemical method, coagulation sedimentation method, electrolytic method, they are all difficult to meet emissions standards.

A new kind of photocatalytic degradation technology of nanometer TiO<sub>2</sub> can make the degradation reactions more effective and the degradation products of the wastewater are CO<sub>2</sub> and H<sub>2</sub>O in the UV or visible light radiation. In the catalytic degradation process, electron-hole pairs generate in the valence band and conduction band of TiO<sub>2</sub>. The holes react with the adsorbed water to produce highly active free radicals (•OH), which oxidize contaminant molecules.



where  $h_{\text{vb}}^+$  and  $e_{\text{cb}}^-$  are electrons in the valence band and conduction band of holes.

The photocatalytic degradation technology of nanometer TiO<sub>2</sub> is green, low cost and the degradation reaction rate is fast *etc.* So it has attracted people's attention. But this technology has three shortcomings: (1) electrons and holes that are stimulated by the light re-combine easily, which low the efficiency of light quantum, (2) the spectral response range of TiO<sub>2</sub> is narrow, TiO<sub>2</sub> absorption band gap of pure titanium ore type is 3.2 eV and spectrum absorption threshold is 387 nm, which can only accounts for about 4 % of ultraviolet light of the sun spectrum range. (3) TiO<sub>2</sub> is not suitable for the degradation of low transparent or non-transparent organic wastewater, which severely restricts its application in the dark dye wastewater treatment. In order to improve the efficiency of TiO<sub>2</sub> photocatalysis, many researchers devote themselves to the research of TiO<sub>2</sub> surface modification and photocatalytic new technology<sup>1,2</sup>.

Some studies have shown that ultrasound mineralization is a very effective way in the degradation of non-transparent or low-transparent dyeing wastewater. Its principle is that the solution generates the cavitation bubbles and cavitation bubbles collapse quickly in ultrasound radiation, so result in instantaneous high temperature and high pressure and generate a strong oxidizing free radicals-•OH, which combine to degrade the organics in the solution. Recently, there are some reports about catalytic degradation of organic pollutants using TiO<sub>2</sub> powder

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in ultrasonic radiation<sup>2-5</sup>. However, due to the wide band gap of TiO<sub>2</sub>, only a small fraction (ultraviolet light) of sonoluminescence can be utilized to sonocatalytic degradation<sup>6</sup>. This means that the insufficient supply of ultraviolet light from sonoluminescence restrains the catalytic activity of TiO<sub>2</sub>. But the up-conversion luminescence agent can convert visible light to ultraviolet light, which can activate the TiO<sub>2</sub> effectively<sup>7</sup>. For further expanding the spectral response range of ultrasound catalysis currently, some semiconductor materials combine some up-conversion luminescence agent to improve the catalytic degradation effect<sup>8,9</sup>.

This paper studied mainly about the performance of the conversion luminescence: Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> of Co, N doped, combined with TiO<sub>2</sub> in the degradation of dyeing wastewater. The results of the test showed that Co doped could make the absorption band of Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> wider and make the absorption behavior of Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> saturated, N doped could replace the oxygen atom of Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> to extend the absorption spectrum and increase its different electro-negativity and emission spectrum intensity of the oxygen atom radius. This helped Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> absorb a broader scope and a greater amount of visible light. Then, Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> could improve the catalytic performance of TiO<sub>2</sub>.

## EXPERIMENTAL

**Preparation of Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>:** Y<sub>2</sub>O<sub>3</sub> (purity 99 %), Er<sub>2</sub>O<sub>3</sub> (purity 99 %), CoO (purity of 99 %) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (AR) were the test materials. the molar ratio of Er<sup>3+</sup>: Co<sup>2+</sup>: Y<sup>3+</sup> equal to 1:9:90 were weighted and dissolved in HNO<sub>3</sub>. The excess HNO<sub>3</sub> was evaporated in order to obtain a mixture of dilute nitrate. The Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O that the moles ratio of [Y(NO<sub>3</sub>)<sub>3</sub> + Er(NO<sub>3</sub>)<sub>3</sub>] to Al(NO<sub>3</sub>)<sub>3</sub> was 3/5 was added to the above mixed nitrate and put into a certain amount of N, N-dimethylformamide (DMF) to form a solution.

In this experimentation the reagent includes: tetrabutyl titanate (TBOT), absolute ethyl alcohol (EtOH), diethanol amine (DEA), polyethylene glycol (PEG-3000), deionized water, glacial acetic acid (HAc). The molar ratio of TBOT: DEA: PEG: EtOH: H<sub>2</sub>O: HAc was equal to 1:2:0.002:20:2:0.3. Anhydrous ethanol was added in TBT and DEA, stirring the mixture. HAc was dissolved in the deionized water, which was dripped in above Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> solution to stir and then put in PEG-3000, stirred again for 3 h. The Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> gel was formed.

The preparation of Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> was the molar ratio of Er<sup>3+</sup>: Y<sup>3+</sup> = 1:9:90. The other was same as the former method.

**Sonocatalytic degradation of dye wastewater:** First slides were degreased and washed before the films were pulled. The pulling speed of membrane machine (BQD1 005 I stepper motor driving power control) was 5-6 cm/min. The wet film dried at 70 °C for 10-15 min under an infrared lamp 250 W, then the films were drawn again. The temperature was controlled at 90 °C for 1 h by the drying oven. Then the films were taken out and cooled naturally to room temperature for use.

The test wastewater was collected from the tail water of a dyeing factory, which concentration of COD was 200-300 mg/L, pH 8.0-8.5, chroma 1800-2000.

Two samples of the dyeing wastewater were taken, each 100 mL into the containers respectively. The slides with Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films of 8 g each were put into the above wastewater separately. And the wastewater was dispersed under sonication for 20 min, with continuous stirring by a magnetic stirrer. Then the wastewater were placed under ultrasonic irradiation for 150 min, which were sampled once every 0.5 h and immediately centrifuged 15 min at 6000 rpm.

**Analytical method:** The samples of Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> nanoparticles were analyzed by powder X-ray diffractometer and scanning electron microscopy. The standard method for CPPA chroma was used in the Chromaticity analysis. The 5B-I type COD Tester was used in the test of COD of dye wastewater treatment.

## RESULTS AND DISCUSSION

**Characterization:** The aforementioned two parts of gel were heated to 90 °C for 1 h and then were ground into fine powders. Then they were put into the OVEN to calcine at 1160 °C for 2 h and were cooled to the room temperature. Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> crystalline powders were formed. The X-ray diffraction pattern was shown in Fig. 1. In Fig. 1, the main characteristic diffraction peaks appeared at 2θ = 18.2°, 25.6°, 27.4°, 29.8°, 33.6°, 41.1°, 46.6° and 55.1°. Compared JCPDS card, they were the characteristic diffraction peaks of the anatase and the up-conversion luminous agent respectively. The characteristic diffraction peaks appeared broadened due to Co and N doped in curve 2 of Fig. 1.

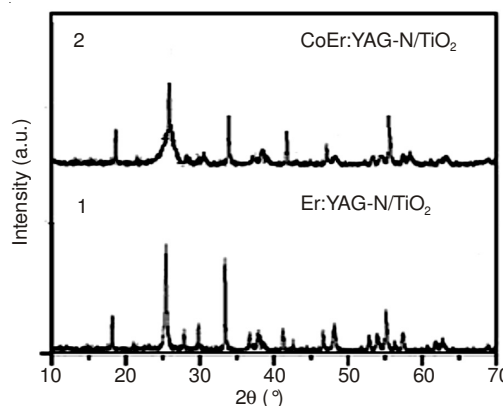


Fig. 1. XRD pattern of the samples of Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> nanoparticles

The two samples' morphologies of Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> were photographed by SEM, as shown in Fig. 2. The average particle diameter of Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> was about 130 nm and the average particle diameter of Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> was about 110 nm. This was because Co could substitute Ti<sup>4+</sup> of TiO<sub>2</sub> crystals and distribute disorderly at Ti<sup>4+</sup> position in the lattice to formed CoO-TiO<sub>2</sub> solid solution, the formation of a solid solution inhibited the growth of TiO<sub>2</sub> grains. So the particle size reduced and so the specific surface area increased, which resulted a large number of active sites that contributed to the catalytic reaction in the Co/N/Er<sup>3+</sup>: Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> surface and the improvement of catalytic efficiency.

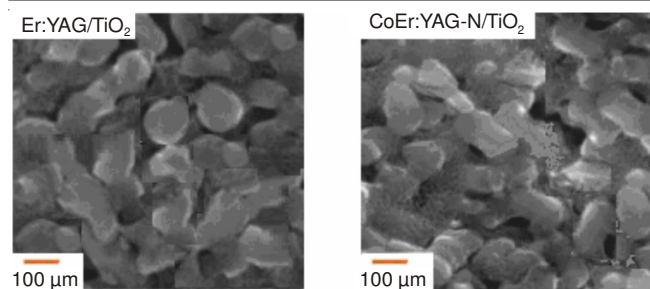


Fig. 2. SEM images of Er:YAG/TiO<sub>2</sub> and Co/N/Er<sup>3+</sup>:YAG/TiO<sub>2</sub> samples

### Efficiency and analysis of sonocatalytic degradation:

According to the standard method for determining CPPA chroma, the formulas of Chromaticity were as follows:

$$\text{Chromaticity (CU)} = 500 \frac{A_2}{A_1} \quad (5)$$

where A<sub>1</sub> was photometric absorbency of 500 CU platinum-drill the standard fluid in 465 nm wavelength, the value was 0.132. A<sub>2</sub> was photometric absorbency of waste water in 465 nm wavelength.

$$\text{Chromaticity removal ratio} = \frac{(A_{21} - A_{22})}{A_{21}} \times 100 \% \quad (6)$$

where A<sub>21</sub> was photometric absorbency before degradation of the waste water, A<sub>22</sub> was photometric absorbency after degradation of the wastewater.

From Figs. 3 and 4, decolorization rate and COD removal rate of Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> were 72.2 and 71.8 % separately, Co/N/Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> were 84.3 and 82.1 % separately. The sonocatalytic degradation rate of Co/N/Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> was higher than them of Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub>. This might be because doping transition metal Co helped for the formation of the Ti<sup>4+</sup>, which could reduce the forbidden band width and widen spectral response range effectively. The electronic valence band would be inspired to the conduction band and form the negatively charged highly reactive electron e<sup>-</sup>, at the same time the positively charged hole h<sup>+</sup> appeared in price bring, that is generated electronic-hole. The electronic-hole would decompose many organic pollutants into CO<sub>2</sub> and H<sub>2</sub>O through a series of process. And N doping introduced a new impurities level, which made the absorption edge of TiO<sub>2</sub> red shift and also could maintain well the balance of charge of the system at the same time. Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> as a recognized up-conversion luminescence agent could absorb the visible light in sonoluminescence induced by ultrasound and then emitted ultraviolet light. And (VB) of TiO<sub>2</sub> semiconductors were transitioned to the conduction band (CB) under ultraviolet light excitation the electrons in the valence band. The principle of ultrasonic degradation mainly was the acoustic cavitation. Beside pyrolysis of water vapor molecules to form various reactive radicals (e.g. •OH) during extreme conditions, cavitation also resulted in the phenomenon called sonoluminescence. The formation of flash light/energy dissipated by acoustic cavitation which equaled or exceeded the band gap energy of the TiO<sub>2</sub> was able to excite the TiO<sub>2</sub> nanotubes, making them acting as a sonocatalyst. A valence band electron could be promoted to the conduction band, leaving behind holes at the valence band<sup>10</sup>.

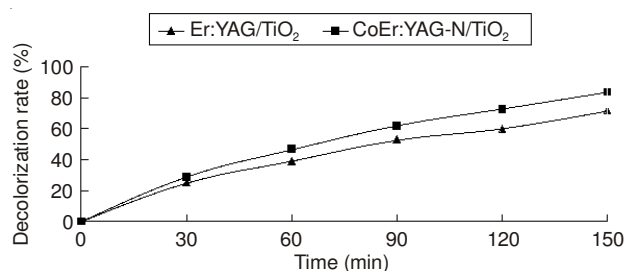


Fig. 3. Decolorization rate of Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Co/N/Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films under ultrasonic irradiation

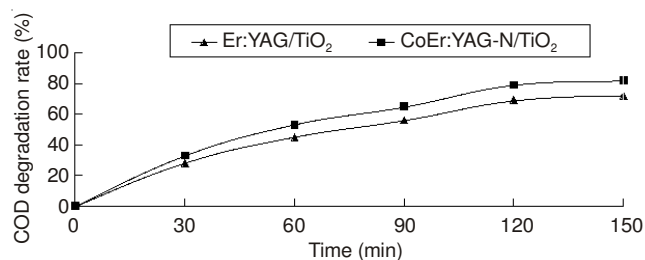


Fig. 4. Degradation rate of COD of Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Co/N/Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> films under ultrasonic irradiation

### Conclusion

Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> and Co/N/Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> were prepared by sol-gel coating process. Degradation rate of dye wastewater of Co/N/Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> film was higher than Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> under ultrasonic irradiation. The reason might be that the Co doped made for the formation of Ti<sup>4+</sup>, so as to reduce the band gap and to broaden the spectral response effectively. The doping of N led to a new impurity level and shifted the red absorption edge of TiO<sub>2</sub>. So the system charge balance could better be maintained. Moreover, ultrasonic irradiation produced cavitation and high temperature and pressure were produced inside the cavitation bubbles where volatile organic solutes and water vapor could be pyrolysis directly. Meanwhile, non-volatile and hydrophilic species such as organic dyes could be degraded through the generation of •OH inside the cavitation bubbles. Therefore, Er<sup>3+</sup>:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/TiO<sub>2</sub> could improve the degradation rate of printing and dyeing wastewater due to doping Co and N.

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