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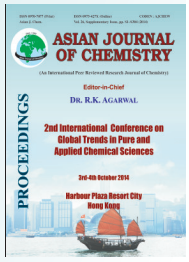

Characteristics and Sonocatalytic Degradation Effect of Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ in Organic Dyestuff Wastewater Treatment

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The role of the composite TiO_2 film in wastewater treatment has been attracted more attention. In this study the preparation of the complex Co/N/ Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ film was used sol-gel coating process. Their composition, morphology and luminescent properties of the powders derived from the precursor calcined at different temperatures were analyzed by X-ray diffraction, the absorption spectra and upconversion emission spectra. The nano powders samples of Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ were characterized by X-ray diffraction, which appeared anatase mine peaks and the peaks of Co/N/ Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ samples appeared broadened. The absorption spectra analysis of crystalline Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ manifested that N doping could cause stretching vibration peak broadening of the adsorption of water or hydroxyl and the Ti-O stretching vibration peak shifted to lower wavenumbers, Co^{2+} ions exist strong absorption at 1-1.7 μm wavelength range, the transition luminescence of Er^{3+} ions just in Co^{2+} ions absorption band. The emission spectra of the test showed that: Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ could launch 500-560 nm of green and red 650-700 nm, which appeared in 525, 550 and 660 nm peaks, corresponding to $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4H_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}. Cobalt and nitrogen doping improved the absorption and upconversion emission effect. The test of catalytic degradating organic dyestuff (Reactive blue 4, methyl orange, rhodamine B) by using Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ were done under ultrasonic radiation. Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ sonocatalytic degradation efficiency was improved significantly because of doping Co and N.

Keywords: Co/N/ Er^{3+}: $Y_3Al_5O_{12}/TiO_2$, XRD, FTIR, Upconversion emission spectra, Sonocatalytic, Degradation, Organic dyestuff.

INTRODUCTION

In recent years, the photocatalyst is widely used for the oxidative decomposition of organic pollutants, sterilization and deodorization. Among the numerous photocatalyst, TiO_2 became the most promising photocatalyst due to low cost, non-toxic, high stability and high efficiency of refractory organic compounds degradation. But because TiO_2 photocatalyst can only absorb UV light and recombination rate of the photo-generated charge carriers is high, which restricts its industrialization. Therefore, how the TiO_2 is modified to improve its catalytic activity, has become the focus of study in recent years[1,2].

The wastewaters discharged from the textile industries contain considerable amounts of inorganic salts and surfactants. The presence of inorganic salts and surfactants has complicated influence on the photocatalytic treatment processes of dye effluents. Some studies have shown that ultrasound mineralization is a very effective way in the degradation of non-transparent or low-transparent dyeing wastewater. Recently, there are some reports about catalytic degradation of organic pollutants using TiO_2 powder in ultrasonic radiation[3-7]. Ultrasonic irradiation generates the phenomenon of acoustic cavitation, *i.e.* nucleation, growth and implosive collapse in liquid. Rapid collapse of microbubbles which entrap gas/vapors (lifetime in the order of microseconds) could produce small localized hot spots (transient temperatures up to 5000 K and pressures higher than 1000 atm)[8]. In these extreme situations, the oxidation pathway will depend on the compound volatility and reactivity under different conditions[9]. However, due to the wide band gap of TiO_2, only a small fraction (ultraviolet light) of sonoluminescence can be utilized to sonocatalytic degradation[10]. This means that the insufficient supply of ultraviolet light from sonoluminescence restrains the catalytic activity of TiO_2. But the up-conversion luminescence agent can convert visible light to ultraviolet light, which can activate the TiO_2 effectively[11]. For further expanding the spectral response range of ultrasound catalysis currently, some

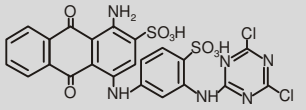
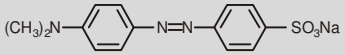
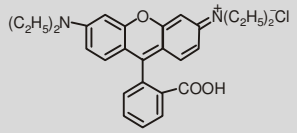
semiconductor materials combine some up-conversion luminescence agent to improve the catalytic degradation effect[12].

This work introduces the preparation of Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$, the characterization of XRD. This study detailed for the effects on crystal structure, spectra, degradation efficiency of organic dyestuff wastewater of Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ due to Co, N doping.

EXPERIMENTAL

Reactive blue-4 ($C_{23}H_{14}C_{12}N_6O_8S_2$), methyl orange ($C_{14}H_{14}N_3SO_3Na$) and rhodamine B ($C_{28}H_{31}N_2O_3Cl$) (99.99 % purity, Tianjin Kaiyuan Reagent Corporation, China) were used to undergo the sonocatalytic degradation. The molecular structure of them was shown in Table-1. Y_2O_3 (purity 99 %), Er_2O_3 (purity 99 %), CoO (purity of 99 %) and Al $(NO_3)_3$ $9H_2O$ (AR) and HNO_3 (analytical pure) (Veking Company, China) were used as the Yb, N and Co source to prepare doped Co/N/Er^{3+}: $Y_3Al_5O_{12}$. Tetrabutyl titanate, absolute ethyl alcohol, diethanol amine, polyethylene glycol (PEG-3000), deionized water, glacial acetic acid were used to prepare TiO_2 gel.

TABLE-1
CHARACTERISTICS OF SEVERAL ORGANIC DYES

Dyes	m.w. (g/mol)	Chemical structure
Reactive blue-4	637.43	
Methyl orange	327.34	
Rhodamine B	479.02	

Preparation of Co/N/Er^{3+}:$Y_3Al_5O_{12}/TiO_2$: Y_2O_3 (purity 99 %), Er_2O_3 (purity 99 %), CoO (purity of 99 %) and $Al(NO_3)_3{\cdot}9H_2O$ (AR) were the test materials. the molar ratio of Er^{3+}: Co^{2+}: Y^{3+} equal to 1:9:90 were weighted and dissolved in HNO_3. The excess HNO_3 was evaporated in order to obtain a mixture of dilute nitrate. The Al $(NO_3)_3{\cdot}9H_2O$ that the moles ratio of [Y $(NO_3)_3$ + Er $(NO_3)_3$] to Al $(NO_3)_3$ was 3/5 was added to the above mixed nitrate and put into a certain amount of N,N-dimethylformamide 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_2O:AcOH was equal to l:2:0.002:20:2:0.3. Anhydrous ethanol was added in tetrabutyl titanate and diethanolamine, stirring the mixture. HAc was dissolved in the deionized water, which was dripped in above Er^{3+}: $Y_3Al_5O_{12}$ solution to stir and then put in PEG-3000, stirred again for 3 h. The Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ gel was formed.

The preparation of Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ was the molar ratio of Er^{3+}: Y^{3+} = 1: 9: 90. The other was same as the former method.

Sonocatalytic degradation of organic dyestuff 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 l0-15 min under an infrared lamp 250 W, then the films were drawn again. The temperature was controlled at 90 °C for l h by the drying oven. Then the films were taken out and cooled naturally to room temperature for use.

Then, three samples of a 50 mg/L dyes (reactive blue 4, methyl orange and rhodamine B) solution was prepared, each 100 mL in a reaction vessel, respectively. The slides with Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ films of 8 g each were put into the above solution separately. And the solution was dispersed under sonication for 20 min, with continuous stirring by a magnetic stirrer. Then the solution were placed under ultrasonic irradiation for 120 min, which were sampled once every 20 min and immediately centrifuged 15 min at 6000 rpm. Each experiment was repeated three times and the average values were taken as the result.

The dye concentration of the sample was determined using an Aquamate™ Plus UV-visible spectrophotometer (Thermo Scientific Company) to calculate the degradation efficiency. The concentrations of reactive blue 4, methyl orange and rhodamine B were measured at their respective maximum absorbance of 596, 464 and 554 nm.

Analytical method: The samples of Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Co/N/ Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ nanoparticles were analyzed by powder X-ray diffractometer and scanning electron microscopy.

Hitachi F-4500 fluorescence spectrometer was used to test the upconversion emission spectra of the sample. And the UV-visible/NIR spectrometer spectrometer (Model V-570JASCO) was used to analyzed the absorption spectrum at room temperature. The absorbance of dye solution was measured by Shimadzu 2450 UV-visible spectrophotometer.

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 at1160 °C for 2 h and were cooled to the room temperature. Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ crystalline powders were formed. The X-ray diffraction pattern was shown in Fig. 2. In Fig. 2, 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.

Spectral characteristics: The absorption spectra of crystalline Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ is shown in Fig. 2. N doping could cause stretching vibration peak broadening of the adsorption of water or hydroxyl and the Ti-O stretching vibration peak shifted to lower wavenumbers, Co^{2+} ions exist strong absorption at 1-1.7 μm wavelength range, the transition luminescence of Er^{3+} ions just in Co^{2+} ions absorption band. The absorption peak at 1.55 μm just was corresponding to $^4A_2 \rightarrow {}^4T_1$ (^4F) transition of Co^{2+}. The absorption curve, near 1.47-

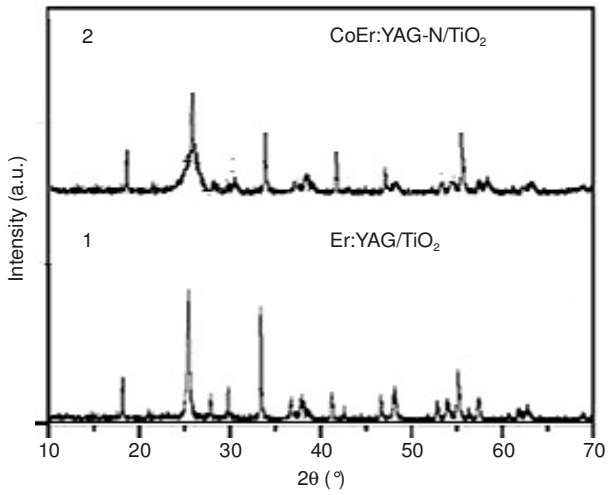


Fig. 1. XRD pattern of the samples of Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ nanoparticles

1.55 μm was not gentle mainly because of the absorption transition of Er^{3+} ions, In Fig. 3, the emission spectra of the test showed that: Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ could launch 500-560 nm of green and red 650-700 nm, which appeared in 525, 550 and 660 nm peaks, corresponding to $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4H_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}. Co and N doping improved the absorption and upconversion emission effect.

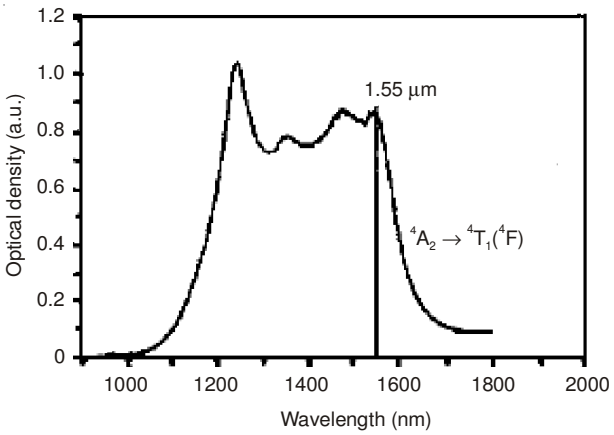


Fig. 2. Absorption spectra of Co/N/Er^{3+}: YAG crystal

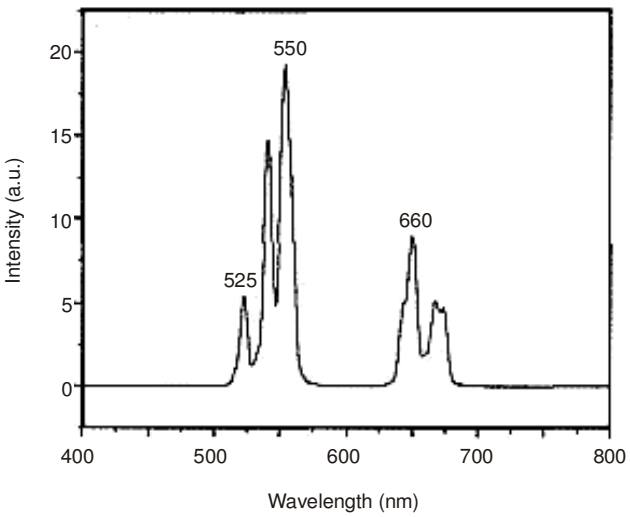


Fig. 3. Upconversion emission spectra of nanoparticles under the excitation of 980 nm diode laser

Efficiency and analysis of sonocatalytic degradation: From Fig. 4-6, the removal efficiency of reactive blue 4, methyl orange and rhodamine B by using Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ were 84.1, 88.6 and 81.9 % separately, Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ were 92.2, 96.3 and 91.7 % separately. The sonocatalytic removal efficiency of Co/N/ Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ was higher than them of Er^{3+}: $Y_3Al_5O_{12}/TiO_2$. This might be because doping transition metal Co helped for the formation of the Ti^{4+}, 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^-, at the same time the positively charged hole h^+ appeared in price bring, that is generated electronic-hole. The electronic-hole would decompose many organic pollutants into CO_2 and H_2O through a series of process. Doped-N could form a new bond enrgy level above the valence band of TiO_2 which can extend the adsorption edge. In addition, doped-N could be beneficial for TiO_2 dispersion. Er^{3+}:$Y_3Al_5O_{12}$

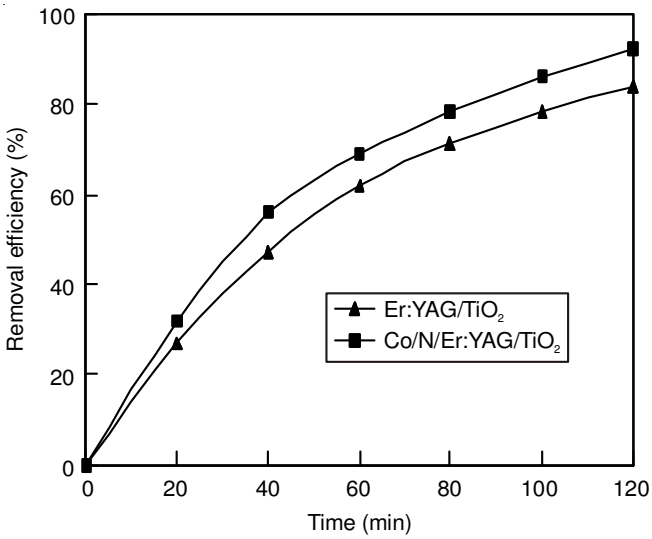


Fig. 4. Removal efficiency of reactive blue 4 by using Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Co/N/ Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ films under ultrasonic irradiation

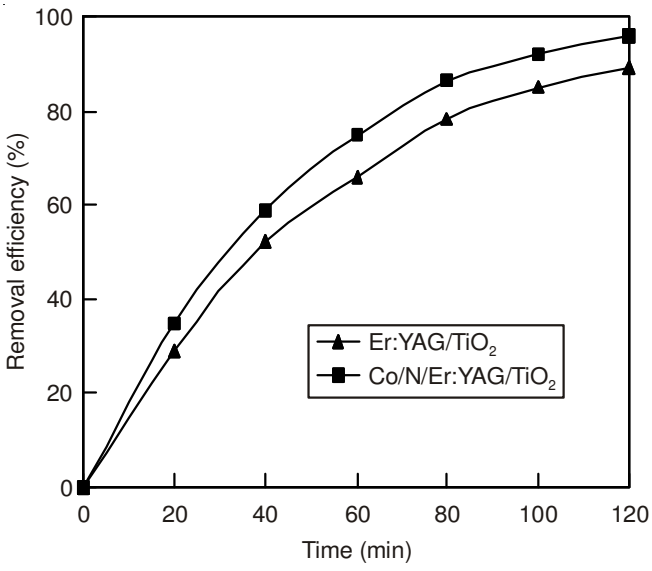


Fig. 5. Removal efficiency of methyl orange by using Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Co/N/ Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ films under ultrasonic irradiation

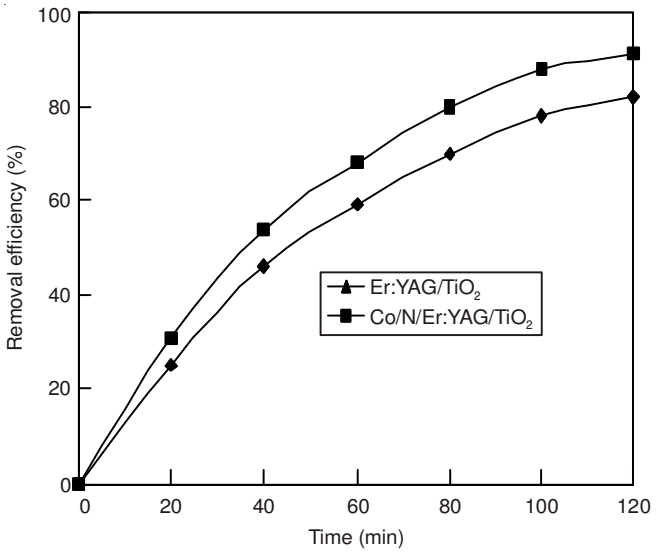


Fig. 6. Removal efficiency of rhodamine B by using Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Co/N/ Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ films under ultrasonic irradiation

as a recognized up-conversion luminescence agent could absorb the visible light in sonoluminescence induced by ultrasound and then emitted ultraviolet light. The principle of ultrasonic degradation mainly was the acoustic cavitation. Beside pyrolysis of water vapor molecules to form various reactive radicals (*e.g.* $^{\bullet}OH$) during extreme conditions, cavitation also resulted in the phenomenon called sonoluminescence[12,13]. The formation of flash light/energy dissipated by acoustic cavitation which equaled or exceeded the band gap energy of the TiO_2 was able to excite the TiO_2 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.

Conclusion

Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ and Co/N/Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ were prepared by sol-gel coating process. Removal rate of reactive blue 4, methyl orange and rhodamine B by using Co/N/ Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ film was higher than by using Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ under ultrasonic irradiation. The reason might be that the Co doped made for the formation of Ti^{4+}, so as to reduce the band gap and to broaden the spectral response effectively. Doped-N could form a new bond energy level above the valence band of TiO_2 which can extend the adsorption edge. In addition, doped-N could be beneficial for TiO_2 dispersion. 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 $^{\bullet}OH$ inside the cavitation bubbles. Therefore, Er^{3+}: $Y_3Al_5O_{12}/TiO_2$ could improve the removal efficiency of reactive blue 4, methyl orange and rhodamine B due to doping Co and N.

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