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Sol-Gel Synthesis of Yb-Er Co-doped TiO₂-ZnO Heterostructures for Enhanced Photocatalytic Degradation of Methylene Blue: Performance and Mechanism

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Abstracts

Water pollution is a pressing global issue, and photocatalysis is a promising approach for degrading organic pollutants in printing and dyeing wastewater. Enhancing solar utilization and clarifying reaction mechanisms are core goals of heterogeneous photocatalysis. TiO₂ is limited by its wide bandgap (UV-only activation) and rapid photogenerated charge recombination. Herein, a Yb³⁺/Er³⁺ co-doped TiO₂-ZnO composite was prepared via sol-gel method. Structural/morphological analyses confirmed enlarged specific surface area, narrowed bandgap and improved light absorption, with optimal calcination at 550 °C for 2 h. The TiO₂-5%ZnO/1%Yb-1%Er composite achieved 76.31% methylene blue (MB) degradation under visible light for 6 h (vs. 33.20% for pure TiO₂) and 98.58% degradation under UV light for 2 h (vs. 52.82% for pure TiO₂), outperforming P25. This work verifies that rare-earth co-doping effectively boosts the photocatalytic performance of TiO₂ based composites.

Keywords: titanium dioxide; Photocatalysis; Composite semiconductor; Rare earth co-doping

1 Introduction

The textile printing and dyeing industry has a high water consumption rate and contains high concentrations of organic pollutants and colourants, which have a serious impact on regional water quality^{[1][3]}. The molecular structure of organic pollutants in water is highly stable^[4], but prolonged contact with the human body can result in cleavage and the release of carcinogenic aromatic amines. Therefore, the efficient treatment of wastewater containing organic pollutants is of great practical importance in order to prevent health risks. Photocatalytic technology is widely used in the treatment of difficult-to-biodegrade organic wastewater. Among the photocatalytic materials, TiO₂ is a widely used n-type semiconductor; however, due to its wide forbidden bandwidth (between 3.0 and 3.2 eV)^{[5][8]}, it can only be excited by ultraviolet light with wavelengths below 387 nm. The photogenerated electron pairs are easily compounded, resulting in lower photonic

efficiency^{[9][10]}. Consequently, the photocatalytic efficiency of TiO₂ is greatly limited in practical applications.

Ratanathavorn Wittawat^[11] prepared TiO₂/ZnO composite spherical particles. The absorption of visible light and the catalytic activity of the TiO₂ composite were greatly improved compared to the single component. Zn²⁺ and Ti⁴⁺ are similar in size; Zn²⁺ can easily enter the crystal lattice of TiO₂ without destroying its structure. Moreover, ZnO and TiO₂ have similar forbidden bandwidths (TiO₂ E_g=3.2 eV and ZnO E_g=3.37 eV), and their staggered energy band positions^[12]. When these two materials are combined, a semiconductor-semiconductor heterojunction system is formed, which not only inhibits the crystalline transition process and particle growth of TiO₂, but also enhances the UV absorption ability of the composite semiconductor^[13]. Meanwhile, doping TiO₂ with rare earth ions that exhibit upconversion luminescence properties is an effective way to utilise infrared light^[14]. Chen and Xiang et al.^[15] synthesised TiO₂ photocatalytic materials with different amounts of Er³⁺ doping by using the sol-gel method. They found that the forbidden band widths decreased and the light absorption range expanded significantly^[16]. Yb³⁺ ions have attracted much attention among many rare earth elements for their unique energy level structure^{[17][18]}, especially in relation to the energy levels of Er³⁺ ions. This enables Yb³⁺ to effectively act as a sensitising ion, providing Er³⁺ with an efficient energy transfer mechanism (Yb³⁺ → Er³⁺). Yb³⁺, Er³⁺-doped TiO₂ can absorb more visible or even near-infrared light, improving the efficiency of photodegradation^{[19][26]}. Furthermore, Yb₂O₃ and Er₂O₃ are broad-band rare-earth oxides that exhibit excellent stability and possess a wide spectral absorption range. They possess large conduction band offsets, a property that makes them highly promising photocatalytic materials.

In this paper, TiO₂-ZnO heterostructures were prepared using the sol-gel method. On this basis, rare earth elements were doped to create a novel nano-TiO₂-ZnO/Yb-Er heterojunction photocatalytic material, exploiting the synergistic effect between the components. The catalysts were analysed and discussed using various characterisation methods, and the photocatalytic activity was examined in terms of the methylene blue (MB) degradation rate to investigate the effect of rare earth concentration, calcination time and temperature on photocatalytic performance^[27].

2 Experimental component

2.1. Instruments and materials

Electronic balance (FA/JA); Magnetic stirrer (SN-MS-3D); Muffle furnace (SX2-12-10A); Vacuum drying box (DZF-6020BZ); Ultraviolet-visible spectrophotometer (TU-1810S-T6); X-ray

diffractometer (D8 Advance); Scanning electron microscope (Zeiss EVO MA 10/LS); Infrared spectrometer (Spectrum 100); Uv-visible diffuse reflectance spectrometer (Shimadazu UV2450); High-pressure mercury lamp (125W); Long arc Xenon lamp (500W).

Butyl titanate [Ti(OC₄H₉)₄] (Shanghai Maclin Biochemical Technology Co., LTD.); Zinc acetate [C₄H₆O₄Zn] (Aladdin Reagent Shanghai Jingchun Biochemical Technology Co., LTD.); Ytterbium oxide [Yb₂O₃] (Aladdin Reagent Shanghai Jingpure Biochemical Technology Co., LTD.); Erbium oxide [Yb₂O₃] (Aladdin Reagent Shanghai Jingpure Biochemical Technology Co., LTD.); Anhydrous ethanol [CH₃CH₂OH] (Aladdin Reagent Shanghai Jingchun Biochemical Technology Co., LTD.); Glacial acetic acid [CH₃CO₂H] (Aladdin reagent Shanghai Jingchun Biochemical Technology Co., LTD.).

2.2 Preparation of photocatalytic materials

Ytterbium nitrate solution and erbium nitrate solution were prepared

Ytterbium nitrate solution and erbium nitrate solution were prepared by weighing 0.2g ytterbium oxide powder with an electronic balance, adding it into an appropriate amount of dilute nitric acid solution, heating and stirring until the mixed solution was completely clarified and transparent, and then using a 50mL volumetric bottle to form 0.25mol/L ytterbium nitrate solution. The dissolution procedure of erbium oxide is the same as above, and 0.125mol/L erbium nitrate solution is prepared in a 50mL volumetric bottle and reserved for backup.

Experimental steps of preparation of photocatalytic materials by sol-gel method

To prepare solution A: add 7mL tetrabutyl titanate into 20mL anhydrous ethanol and stir thoroughly until evenly mixed. Preparation of solution B: Appropriate amount of zinc acetate, ytterbium nitrate, and erbium nitrate, 2.5mL acetic acid, and 2.5mL deionized water were added into 10mL anhydrous ethanol, and fully stirred to obtain evenly mixed solution B. Sol-gel preparation: Solution A is slowly dropped into solution B at a rate of one drop per second using a dropping funnel under mechanical stirring conditions. Continue stirring at room temperature for 2 hours until transparent sol is formed. Subsequently, it is left to age at room temperature for 24 hours to gradually transform the sol into a gel state. Drying and calcination: The obtained gel is dried at 100°C for 3 hours to obtain a dry gel. After grinding the dry gel into a powder, it is placed in the Muffle furnace. It is slowly heated to 550 °C at a rate of 5 °C per minute and calcined at this temperature for 2 hours to complete the preparation process of the material. Finally, it is naturally cooled to room temperature,

and through this series of steps, photocatalytic materials with different doping composite ratios are prepared.

Rare earth single-doped and rare earth co-doped photocatalysts were prepared using $\text{TiO}_2\text{-ZnO}$ (5%ZnO) as the basis, and $\text{TiO}_2\text{-5%ZnO/1%Yb-1%Er}$ samples were selected for calcination at different calcination temperatures and different calcination times to prepare photocatalytic materials with different influencing factors (doping concentration, calcination temperature and calcination time).

The preparation flowchart of the $\text{TiO}_2\text{-ZnO/Yb-Er}$ photocatalyst is shown in Figure 1.

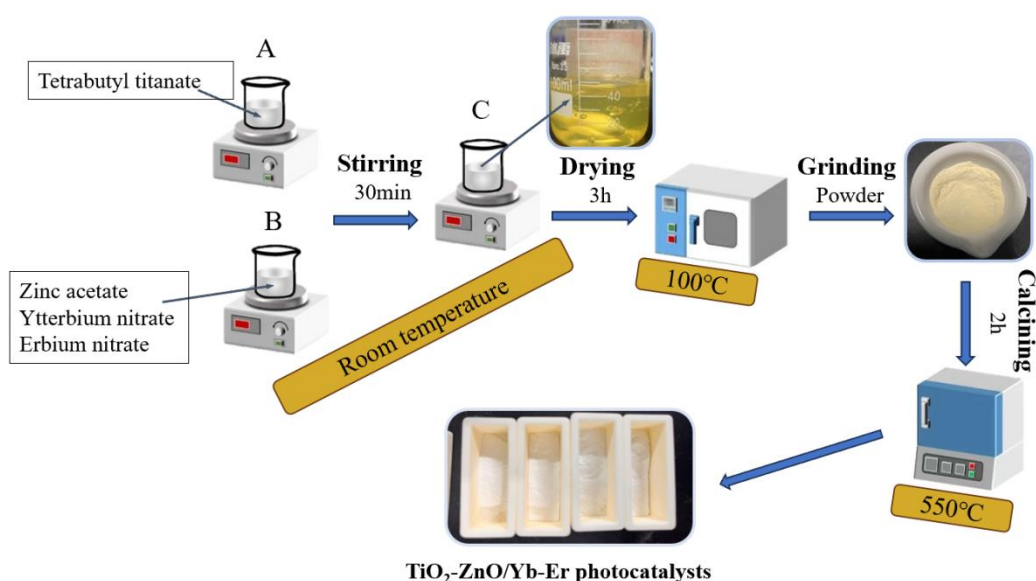


Fig. 1. Preparation flow chart of $\text{TiO}_2\text{-ZnO/Yb-Er}$ photocatalyst

2.3 Photocatalyst activity test

The photocatalytic activity of the photocatalyst was evaluated by the degradation of methylene blue. 200mL of methylene blue solution with an initial concentration of 4mg/L was measured in a 500mL beaker, and 20mg of powder photocatalyst was weighed and dispersed in the methylene blue solution. The photocatalyst was first stirred away from light for 30min to establish adsorption/desorption balance. First, the UV light source of 125W high-pressure mercury lamp and 500W xenon lamp were irradiated with ultraviolet light. After a certain interval, 2 to 3mL reaction liquid was taken. The samples were centrifuged for 10min at a rotational speed of 10000r/min, and the supernatant was taken. The absorbance of the supernatant was measured by UV-VIS

spectrophotometer at the maximum absorption wavelength of 665nm. The photocatalytic degradation efficiency was calculated by equation^{Error! Reference source not found.} (1) :

$$\eta = A_0 - A_t / A_0 \times 100\% \quad (1)$$

(Where A_0 is the initial absorbance of methylene blue solution, and A_t is the absorbance of methylene blue solution after the reaction time t).

3 Results and Discussion

3.1 Analysis of particle structure and valence state of catalyst

The XRD analysis pattern of each sample is shown in Fig 2. The XRD diffraction peak is compared with the standard spectrum of the anatase phase TiO_2 (JCPDS21-1272) card^[28], and the rutile phase diffraction peak appears near 27.5° and 27.4° for pure TiO_2 and TiO_2 -5% ZnO , respectively. Obviously, the peak strength of pure TiO_2 anatase diffraction peak is stronger than that of TiO_2 -5% ZnO , and the purity is particularly high. The samples doped with rare earth Yb and Er show anatase characteristic diffraction peaks near $2\theta=25.3^\circ(101)$, $37.8^\circ(004)$, $48.0^\circ(200)$, $55.0^\circ(211)$, $62.6^\circ(204)$, $68.9^\circ(220)$, $75.0^\circ(215)$, $82.6^\circ(224)$. No rutile phase diffraction peak was found, indicating that the crystal phase of TiO_2 -5% ZnO /1%Yb-1% prepared in this experiment belongs to the anatase type. Doping of rare earth Yb and Er can inhibit the occurrence of the TiO_2 rutile phase. Compared with pure TiO_2 , doped rare earth reduces the peak intensity of TiO_2 , and the diffraction peak becomes wider from sharp. The results show that the conversion of anatase crystal can be inhibited by adding rare earth ions.

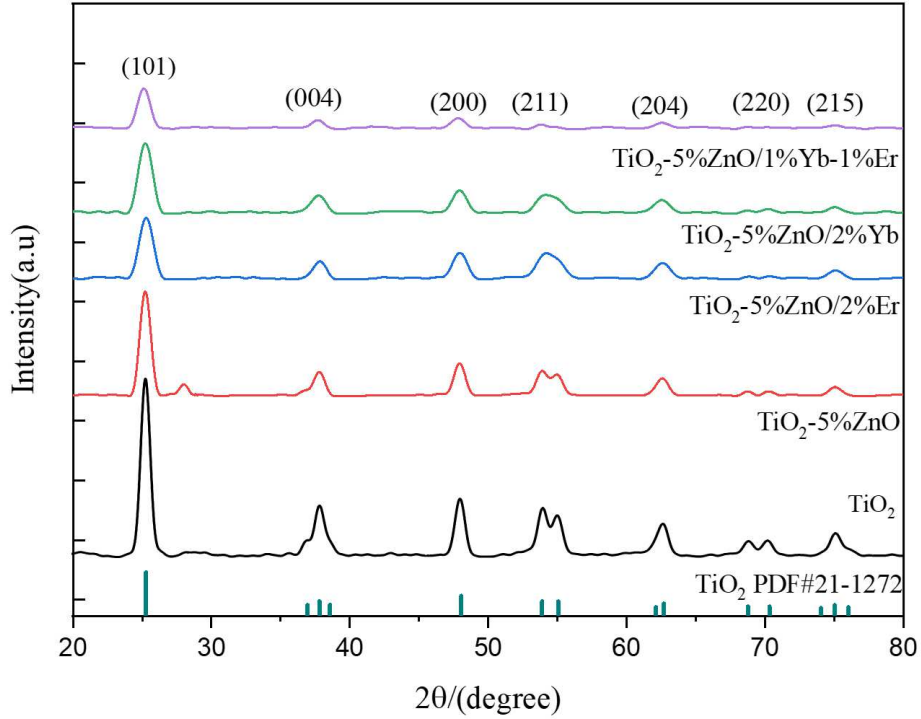


Fig 2. XRD of photocatalysts with different doping systems

The XRD of the powder of $\text{TiO}_2\text{-5\%ZnO/1\%Yb-1\%Er}$ photocatalysts calcined at different temperatures with different times of calcination is shown in Fig. 3. As can be seen from Fig. 3(a), the five XRD spectral lines from the bottom to the top ($650^\circ\text{C} \rightarrow 600^\circ\text{C} \rightarrow 550^\circ\text{C} \rightarrow 500^\circ\text{C} \rightarrow 450^\circ\text{C}$), the peak intensity of the characteristic diffraction peak of anatase at $2\theta = 25.3^\circ$ (crystallographic plane 101) gradually decreases with the decrease of the temperature in the ($650^\circ\text{C} \rightarrow 600^\circ\text{C} \rightarrow 550^\circ\text{C}$) temperature interval, while the peak width of the peaks in the ($550^\circ\text{C} \rightarrow 500^\circ\text{C} \rightarrow 450^\circ\text{C}$) temperature interval, the peak intensity of the characteristic diffraction peak of anatase at $2\theta = 25.3^\circ$ (crystal plane 101) gradually increased with the decrease of temperature, and the peak width gradually became narrower. calcined within 1 h, the photocatalyst was difficult to become a powder state, so four time points of 2 h, 4 h, 6 h and 8 h were set to observe. As can be seen from Fig. 3(b), the peak intensities of the characteristic diffraction peaks of anatase with 4 spectral lines from bottom to top ($8\text{h} \rightarrow 6\text{h} \rightarrow 4\text{h} \rightarrow 2\text{h}$) $2\theta=25.3^\circ$ (crystallographic plane 101) gradually decrease and the peak widths gradually become wider. According to Scherrer's formula $D=0.89k\lambda(b \times \cos\theta)^{[29]}$, the grain size gradually becomes smaller. The shorter the diffusion of photogenerated carriers from the interior of TiO_2 to the surface, the lower the electron-hole complexation and the higher the catalytic activity of the sample. From the XRD spectrum analysis, no rare earth wave peaks were detected, which may be due to the low content. From the scientific point of view, anatase TiO_2 has a wider bandwidth than

rutile, which makes the electron-hole pairs formed by the anatase TiO_2 have stronger oxidation ability, and thus gives it a higher photocatalytic activity. In addition, the lattice structure of anatase phase TiO_2 is rich in defects and dislocations, and these structural properties lead to the generation of more oxygen holes, which effectively traps electrons. This mechanism helps to inhibit carrier complexation, which in turn significantly enhances the photocatalytic efficiency^[30].

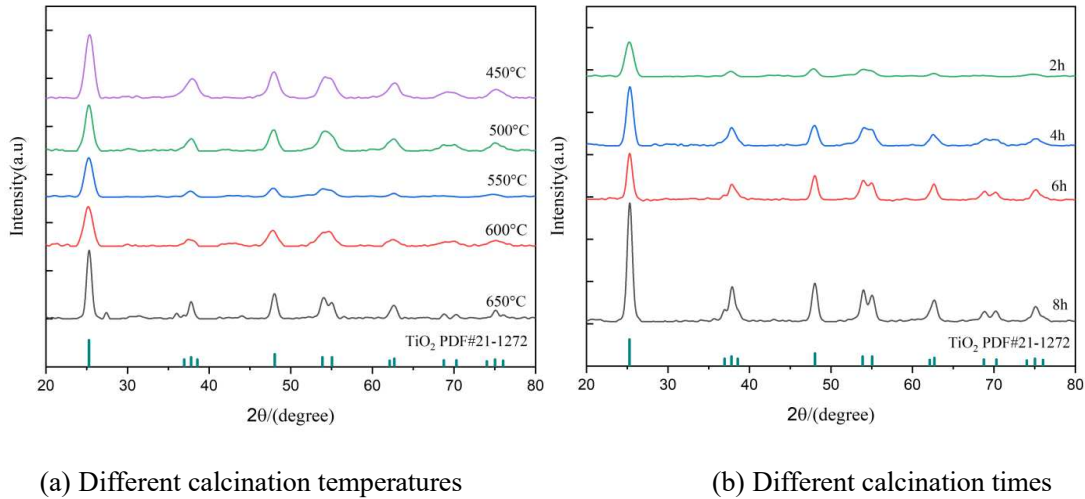


Fig 3. TiO_2 -5% ZnO /1% Yb -1% Er photocatalysts calcined at different temperatures and times.

In order to further determine the surface element composition and chemical state of TiO_2 -5% ZnO /1% Yb -1% Er heterojunction photocatalytic material samples, X-ray photoelectron spectroscopy (XPS) tests were conducted on pure TiO_2 and TiO_2 -5% ZnO /1% Yb -1% Er samples respectively, and the test results are shown in Fig. 4. From the total spectrum 4(a) of pure TiO_2 and the total spectrum 4(b) of doped composite photocatalyst^[31], it can be found that 4(b) has two more peaks than 4(a), corresponding to the peaks of $\text{Zn } 2p_{1/2}$ and $\text{Zn } 2p_{3/2}$ respectively, which proves that ZnO is successfully supported on the surface of TiO_2 . 4(c) is the high-resolution electron energy spectrum signal of $\text{Ti}2p$, two peaks at 458.48eV and 464.30eV, and the binding energy corresponds to the $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ orbitals, respectively, which fully indicates that Ti in the sample exists in the form of Ti^{4+} in the TiO_2 lattice. 4(d) The characteristic peaks of $\text{Zn}2p_{3/2}$ and $\text{Zn}2p_{1/2}$ at 1021.75eV and 1044.81eV indicate the existence of Zn in the form of Zn^{2+} . According to 4(e) and (f), the electron binding energy of the Yb element on the sample surface corresponds to the electron binding energy of $\text{Yb}4d_{3/2}$ and $\text{Yb}4d_{1/2}$ at 185.24eV and 192.47eV, and the electron binding energy of Er element corresponds to the electron binding energy of $\text{Er}4d$ at 168.50eV. It shows that Yb and Er on the surface of the sample are mainly incorporated into the TiO_2 lattice in trivalent form to form Ti-O-Yb and Ti-O-Er bonds.

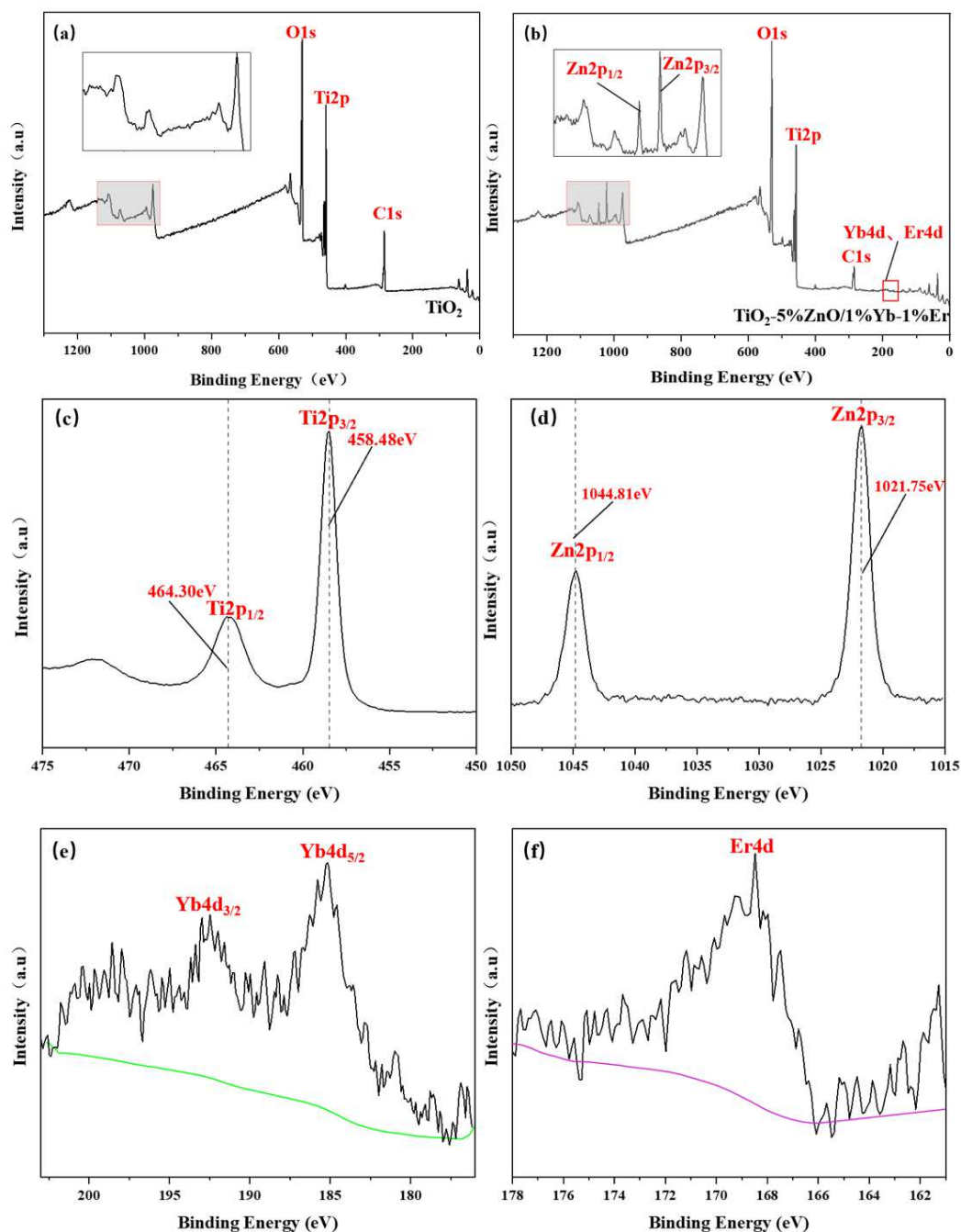


Fig 4 XPS spectra of pure TiO_2 and TiO_2 -5%ZnO /1%Yb-1%Er: (a) Total spectrum of pure TiO_2 ; (b) Total spectrum of TiO_2 -5%ZnO/1%Yb-1%Er; (c)Ti2p; (d) Zn2p; (e)Yb4d; (f)Er4d

3.2 Analysis of catalyst particle morphology

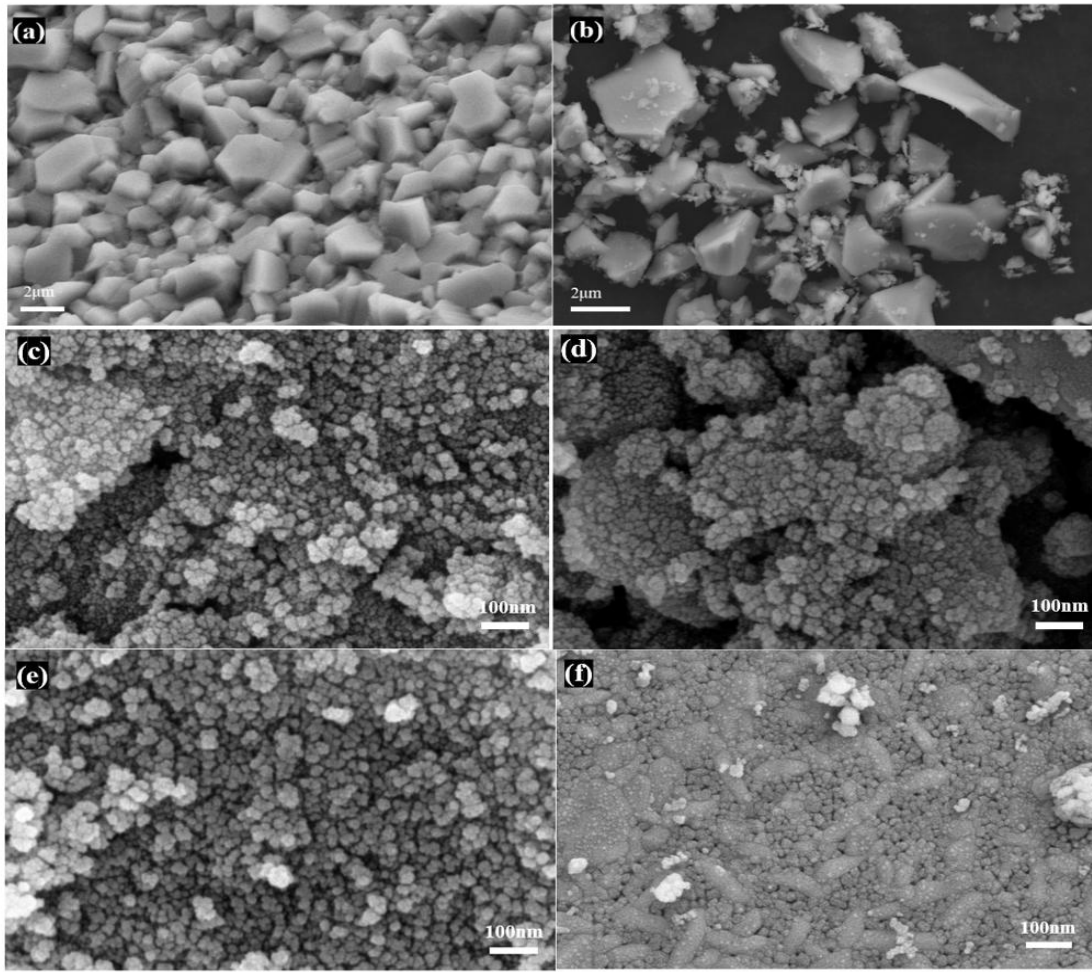


Fig. 5. SEM images of photocatalysts with different doping concentrations

(a) Pure TiO_2 ; (b) TiO_2 -5% ZnO /2% Yb ; (c) TiO_2 -5% ZnO /2% Er ; (d) TiO_2 -5% ZnO /1% Yb -1% Er ; (e) 500nm TiO_2 -5% ZnO /2% Yb (f) 500nm TiO_2 -5% ZnO /1% Yb -1% Er

The SEM images of different systems of photocatalysts are shown in Fig. 5. In Fig. 5(a), TiO_2 particles show a more regular shape. Compared with Fig. 5(a), more fine particles appear on the surface of TiO_2 - ZnO in Fig. 5(b), which is because ZnO and rare earth ions have been doped into TiO_2 - ZnO . Fig. 5(c) and (d) show the morphologies of Yb^{3+} and Er^{3+} doped single rare earths. After rare earth doping, the thermal stability is enhanced, which causes the lattice distortion of TiO_2 and changes its surface morphology^[32]. From Fig. 5(d), it can be found that TiO_2 has obvious lattice distortion and a wider gap, indicating that the doping effect of Yb^{3+} is more significant than that of Er^{3+} . As can be seen from (e)(f), after enlarging to 100nm, it can be clearly seen that a rod shape completely different from the previous one appears in (f), which should be a TiO_2 - ZnO binary composite semiconductor, which is loaded with small round particles, there are also many small

particles in it, and there are many holes, and the specific surface area is relatively large. During degradation, the contact area between the catalyst and the degradation product is larger, and the more active sites provided, the better catalytic performance^[33].

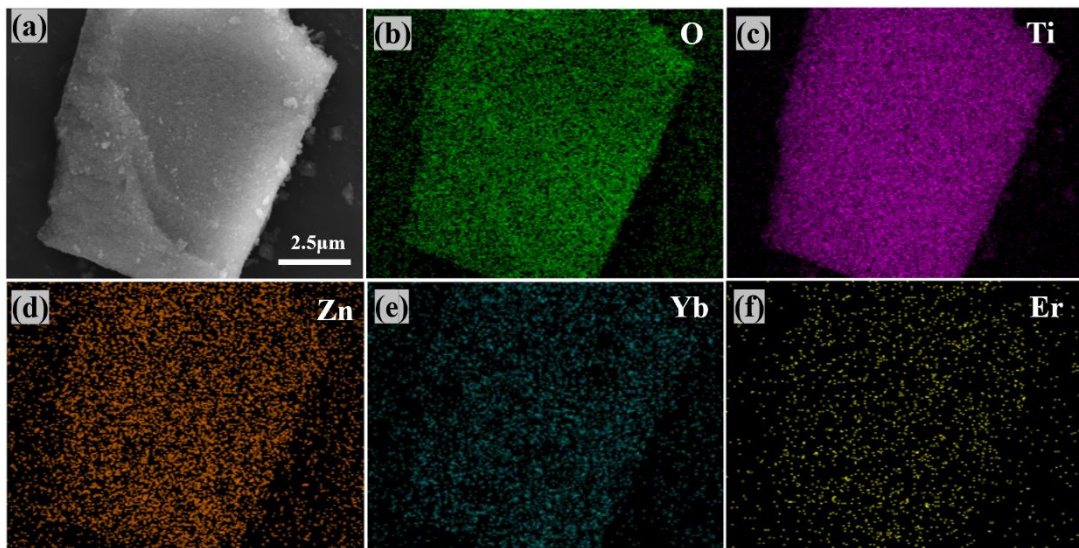


Fig. 6. Distribution of different elements (a) TiO_2 -5% ZnO /1% Yb -1% Er ; (b) Ti distribution; (c) Zn distribution; (d) Yb distribution; (e) Er distribution

In order to further determine the physical phase dispersion state of TiO_2 , ZnO , and ytterbium erbium ions in the composite photocatalytic material, SEM-Mapping was chosen to analyze the elemental distribution of the composite photocatalytic material, and the results of the EDS spectroscopic analysis are shown in Fig. 6. (b) is the distribution of Ti, which can be seen that the distribution space of TiO_2 is dense and more uniform. (c) Zn is distributed in the rod-like region, and some are also enriched on the surface of TiO_2 , which indicates that the Zn element has a well-dispersed state, and also to a certain extent indicates that the TiO_2 and Zn composite forms a new physical phase ZnTiO_3 with a high degree of dispersion. Fig. 6(d) points of the density of the reaction element content is small, it can be seen that Yb and Er elements are also uniformly distributed on the surface of TiO_2 or into the Ti to produce lattice distortion to generate a new phase Yb_2TiO_5 , Er_2TiO_5 , $\text{Er}_2\text{Ti}_2\text{O}_7$, $\text{Yb}_2\text{Ti}_2\text{O}_7$ consistent with the XRD elemental analysis, the rare earth elements inhibit the reorganization of the lattice of TiO_2 , to ensure that the stability of the anatase phase, to improve the photocatalytic degradation efficiency.

High-power transmission electron microscopy (HRTEM) Fig. 7 is a high-power transmission electron microscopy image of TiO_2 -5% ZnO /1% Yb -1% Er heterojunction sample. As can be seen from Fig. 7, the sample presents a granular shape of 10~20nm. It can be seen from Fig. 7 that the lattice stripes of 0.247nm, 0.274nm, and 0.153nm belong to $\text{ZnO}(101)$ crystal face, $\text{Yb}(200)$ crystal

face, and Er(200) crystal face, respectively, which proves that all three are successfully deposited on the surface of TiO₂. The results of XRD, SEM, and HRTEM confirm that Yb, Er, and Zn are uniformly dispersed on the surface of TiO₂.

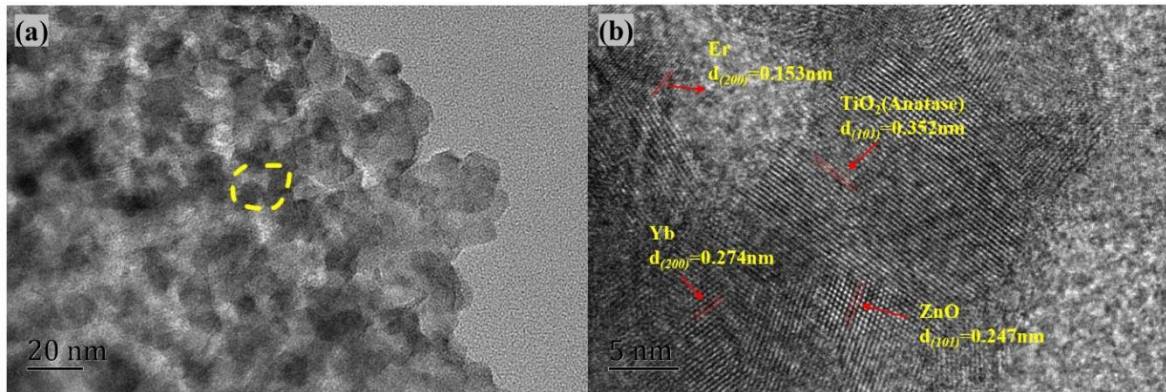


Fig 7. HRTEM images of TiO₂-5%ZnO/1%Yb-1%Er heterojunction samples

3.3 Analysis of optical properties of catalyst particles

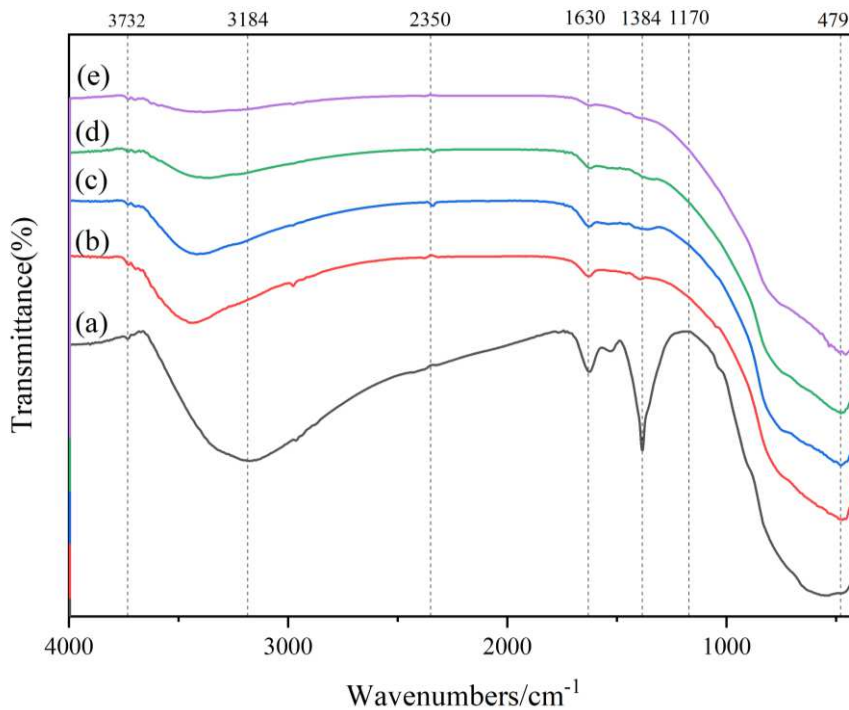


Fig. 8. Infrared profiles of photocatalysts with different doping systems

(a) pure TiO₂; (b) TiO₂-5%ZnO; (c) TiO₂-5%ZnO/2% Er; (d) TiO₂-5%ZnO/2% Yb; (e) TiO₂-5%ZnO/1%Yb-1%Er;

The molecular structure and functional group information of pure TiO₂ and TiO₂ photocatalytic materials modified by composite doping were obtained by FT-IR spectroscopy. FT-IR spectra of different composite doped samples are shown in Fig 8. According to relevant literature, there is a wide absorption peak in the vicinity of 3184cm⁻¹-3732cm⁻¹, which is the stretching vibration peak of the O-H bond between hydroxyl group and adsorbed water on the sample surface, and a relatively

obvious absorption peak in the range of 1530cm^{-1} - 1655cm^{-1} is the bending vibration of hydroxyl group and adsorbed water O-H on the catalyst surface^[34]. These all prove the presence of hydroxyl groups on the catalyst surface. In addition, there are two possible absorption peaks at 1384cm^{-1} one is the bending vibration peak of C-H, which may come from the solvent in the catalyst preparation process. The other is that they are unstable O^{2-} 、 O_2^{2-} species. After rare earth doping, the peaks become wider and redshifted significantly, and TiO_2 can absorb more O-H. Rare-earth Yb and Er are dispersed to the intercellular space of TiO_2 in the form of oxides, which can increase the OH on the surface of the powder. The stretching vibration of the Ti-O bond and the bridge stretching vibration of the Ti-O-Ti bond cause the strong absorption peak of $400\text{-}700\text{cm}^{-1}$ in the Fig. Compared with undoped TiO_2 , TiO_2 catalysts doped with Yb and Er were deformed to different degrees at $400\text{-}700\text{cm}^{-1}$, which may be due to the fact that Ti^{4+} was replaced by Zn^{2+} 、 Yb^{3+} and Er^{3+} at the boundary of TiO_2 lattice, forming Ti-O-Zn, Ti-O-Yb and Ti-O-Er bonds. This confirms the conclusion that Ti-O-Zn, Ti-O-Yb, Ti-O-Er, and other chemical bonds are formed at the lattice boundary in the XRD pattern.

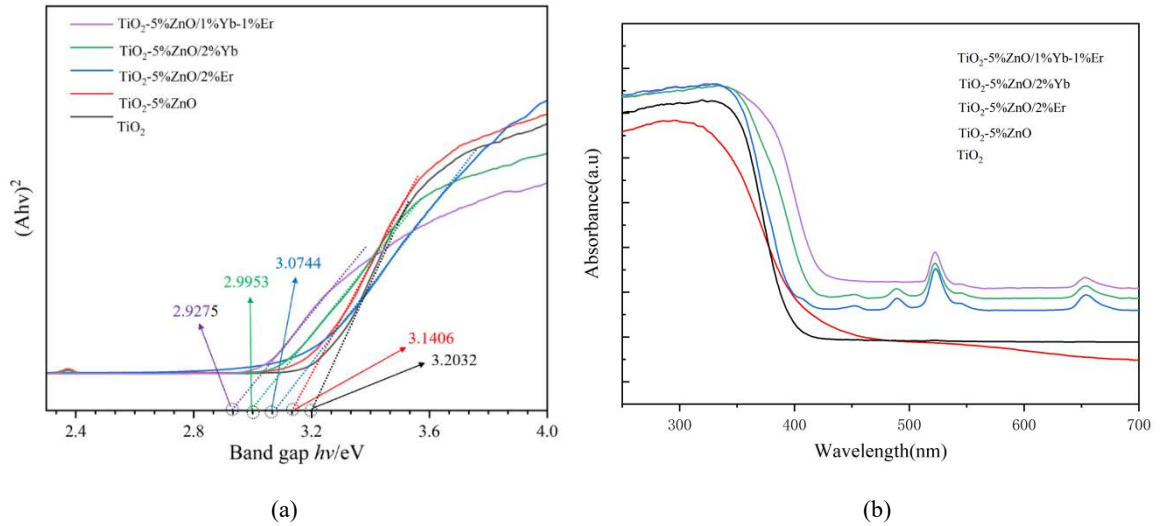


Fig. 9. UV-vis diffuse reflectance spectra of different samples and Tauc diagrams of $\text{TiO}_2\text{-ZnO}$ doped with Yb^{3+} and Er^{3+} at different concentrations

In this experiment, the absorption spectrum of Shimadzu UV2450 UV-visible diffuse reflection spectrometer (UV-Vis) in $200\text{nm}\text{-}900\text{nm}$ was used for sample detection. Fig. 9 UV-vis diffuse reflection spectra of different samples. As shown in the figure, all five samples have strong absorption in the ultraviolet region with wavelength $<388\text{nm}$, and the ultraviolet absorption intensity of the modified samples after ZnO composite and rare earth Yb and Er doping is stronger than that of pure sample TiO_2 . The strength of sample $\text{TiO}_2\text{-5\%ZnO/1\%Yb-1\%Er}$ is the highest. In the visible region, the spectra of the samples modified by ZnO composite and rare earth doping show a redshift, which is enhanced to a certain extent compared with pure TiO_2 absorption, indicating that the photoresponse

range of the photocatalyst after ZnO composite and rare earth doping moves to the visible region, narrowing the band gap, which can effectively enhance TiO₂'s absorption of ultraviolet light and visible light, and improve its ability to absorb visible light. The photocatalytic degradation ability of methylene blue was enhanced. The Tauc diagram of band gap of TiO₂-5%ZnO/1%Yb-1%Er photocatalyst determined by Tauc Plot method is shown on the right in Fig 9. The formula is shown in^[35] (2) :

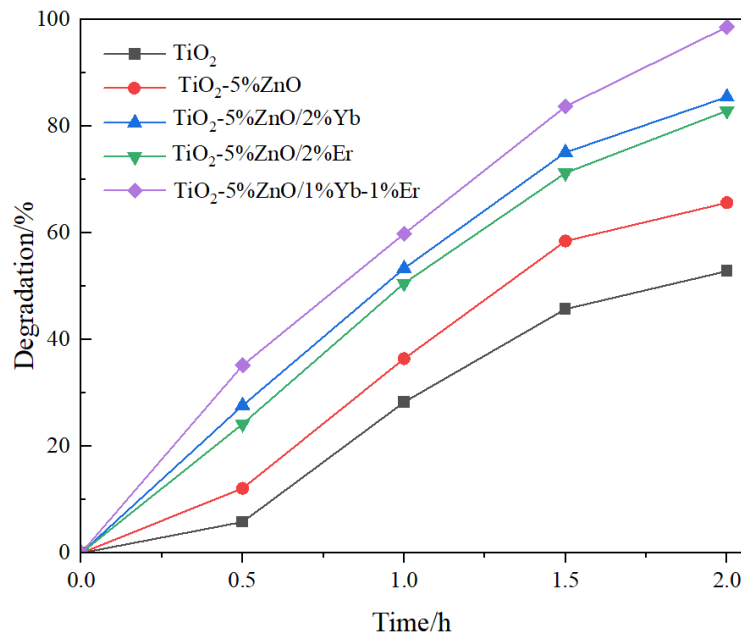
$$(\alpha\alpha\nu) = A(h\nu - E_g) \quad (2)$$

Where α is the absorption coefficient, $h\nu$ is the photon energy and relation constant, and E_g is the optical band gap. The band gaps of TiO₂-ZnO are 2.995, 3.074, and 2.927 eV when the single doping content of Yb and Er is 2% and the codoping content is 1%, respectively. This indicates that the band gap energy (3.203eV) of TiO₂ is reduced, which facilitates the transfer of charge from the valence band (VB) to the conduction band (CB) ^[36]. At the same time, compared with TiO₂-ZnO without Yb and Er doping, the band gap energy is further reduced, indicating that the doping of rare earth ions can reduce the band gap energy and improve the visible light absorption capacity. At present, similar trends have been reported, which can further confirm that the interaction between rare earth ions and TiO₂ is closely related, resulting in higher photocatalytic degradation efficiency.

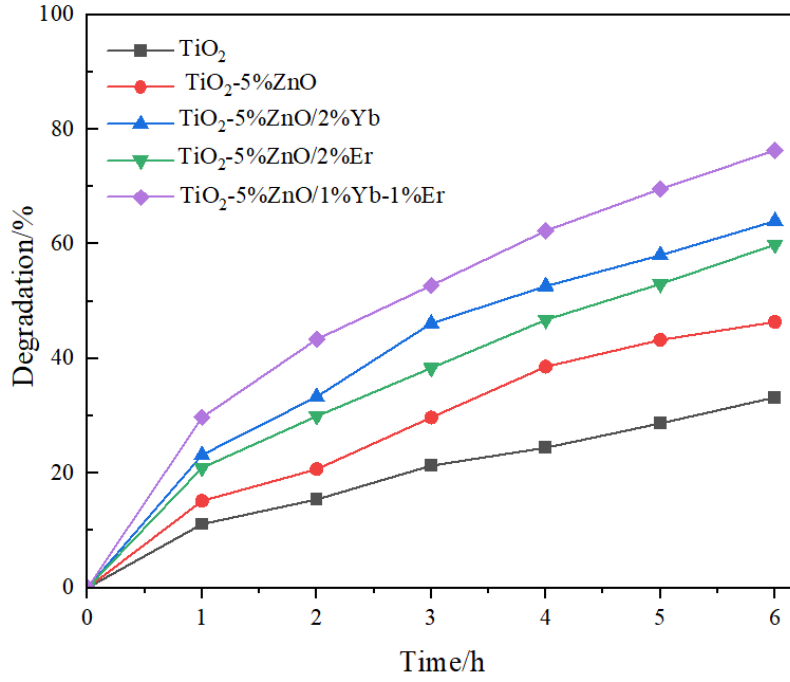
3.4 Photocatalytic activity studies

3.4.1 Effect of different doping systems on photocatalytic performance

The activity curves of different samples for photodegradation of methylene blue under UV and visible light are shown in Fig. 10.



(a) Under ultraviolet light



(b) Visible light

Fig. 10. Photocatalytic degradation curves of methylene blue under UV and visible light with different photocatalysts

As can be seen from Fig. 10(a), different samples have different degradation efficiencies for methylene blue solution under ultraviolet light, and the photocatalytic activity of the samples doped with ZnO composite and rare earth is higher than that of pure TiO₂^[37]. The photodegradation rates of pure TiO₂, TiO₂-5%ZnO/2%Yb, TiO₂-5%ZnO/2%Yb-1%Er to methylene blue solution were 52.82%, 65.64%, 85.46%, 82.87% and 98.58%, respectively. Rare earth doping is more obvious to improve the performance of TiO₂ photodegradation methylene blue solution^[38]. As can be seen from Fig. 10(b), rare earth co-doped TiO₂-5%ZnO/1%Yb-1%Er samples showed a higher photodegradation rate of 74.31% after 6h of visible light irradiation. It is higher than 46.36% of TiO₂-5%Zn, 63.98% of TiO₂-5%ZnO/2%Yb, and 59.88% of TiO₂-5%ZnO/2%Er.

According to the analysis, the photocatalyst TiO₂-5%ZnO/1%-Yb-1%Er has the highest photocatalytic degradation activity of methylene blue solution under ultraviolet and visible light, and the photodegradation efficiency is significantly improved compared with the photocatalyst doped only rare earth Er ions^[39], and the photocatalytic performance is also better than that of the photocatalytic material with only composite semiconductor ZnO. The excellent photocatalytic activity of the photocatalyst in this paper is mainly attributed to two aspects: First, the catalyst has a

complete anatase phase structure and a large specific surface area, which provides abundant catalytic sites^[40]; Second, the TiO₂ surface is loaded with a large number of ultrafine Yb/Er/ZnO heterojunctions, which act as active centers and can effectively inhibit the recombination of photogenerated electrons and holes^[41]. The synergistic effect of these two aspects significantly improves the photocatalytic activity of the catalyst, and fully demonstrates the good coordination effect between TiO₂, ZnO and Yb/Er.

3.4.2 Effect of different calcination temperatures on photocatalytic performance

Fig. 11 shows the photocatalytic degradation rate of methylene blue by sample TiO₂-5% ZnO/1% Yb-1% Er at different calcination temperatures under visible light.

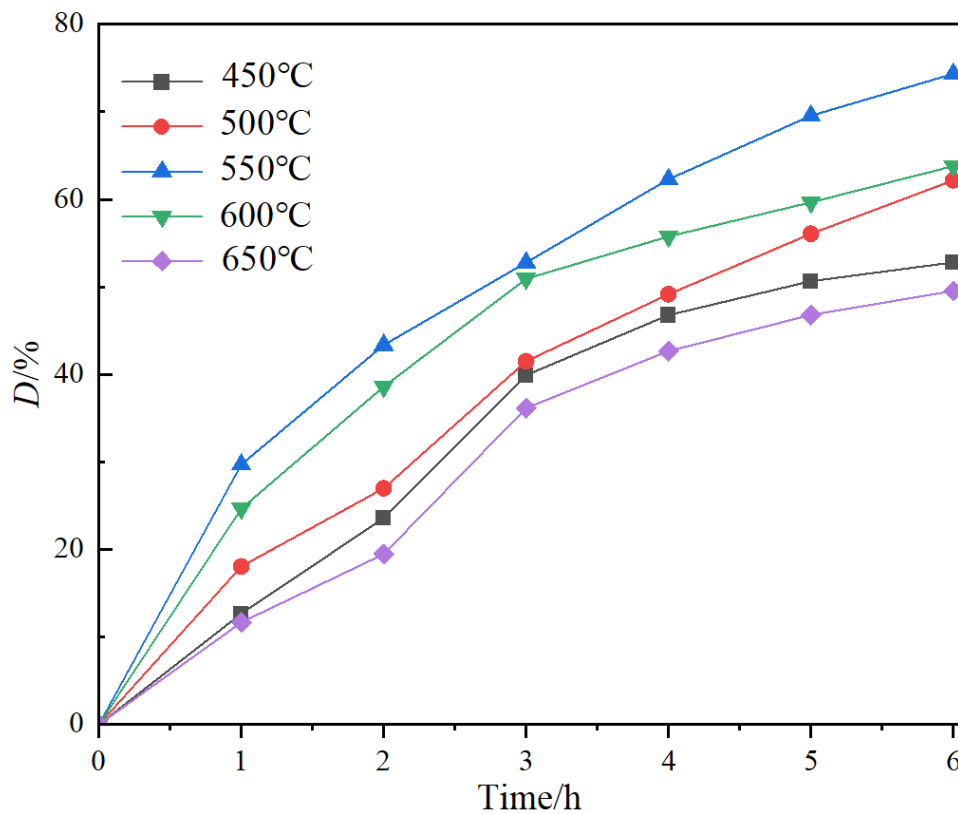


Fig. 11. Photocatalytic degradation curves of methylene blue at different calcination temperatures

52.74% (450 °C), 62.17% (500 °C), 74.31% (550 °C), 63.78% (600 °C), 49.53% (650 °C). The calcination temperature has a significant effect on the catalyst activity. In the range of 450°C~650°C, the photocatalytic activity of TiO₂-5%ZnO/1%Yb-1%Er powder increases first and then decreases. According to XRD in Fig. 2 (a), at 450°C~550°C, with the increase of calcination temperature, the catalytic activity increases, and the decolorization rate can reach 100%. The increase in calcination temperature promotes the loading of nano-crystalline ZnO on the surface of TiO₂, which effectively

separates photogenerated electrons and holes, thus improving photocatalytic activity. However, when the calcination temperature was further increased to the range of 550 °C~650 °C, although the crystallization degree of the catalyst increased, the peak strength increased, and the peak width narrowed, the photocatalytic activity decreased. This is mainly due to the appearance of rutile phase TiO_2 at high temperatures, which has lower photocatalytic activity than the anatase phase. In addition, high-temperature roasting may also lead to sintering of the catalyst, reducing the active site, and thus reducing the photocatalytic activity.

3.4.3 Effects of different calcination times on photocatalytic performance

Fig.12 shows the photocatalytic degradation rate of methylene blue by sample TiO_2 -5%ZnO/1%Yb-1%Er at different calcination times under visible light.

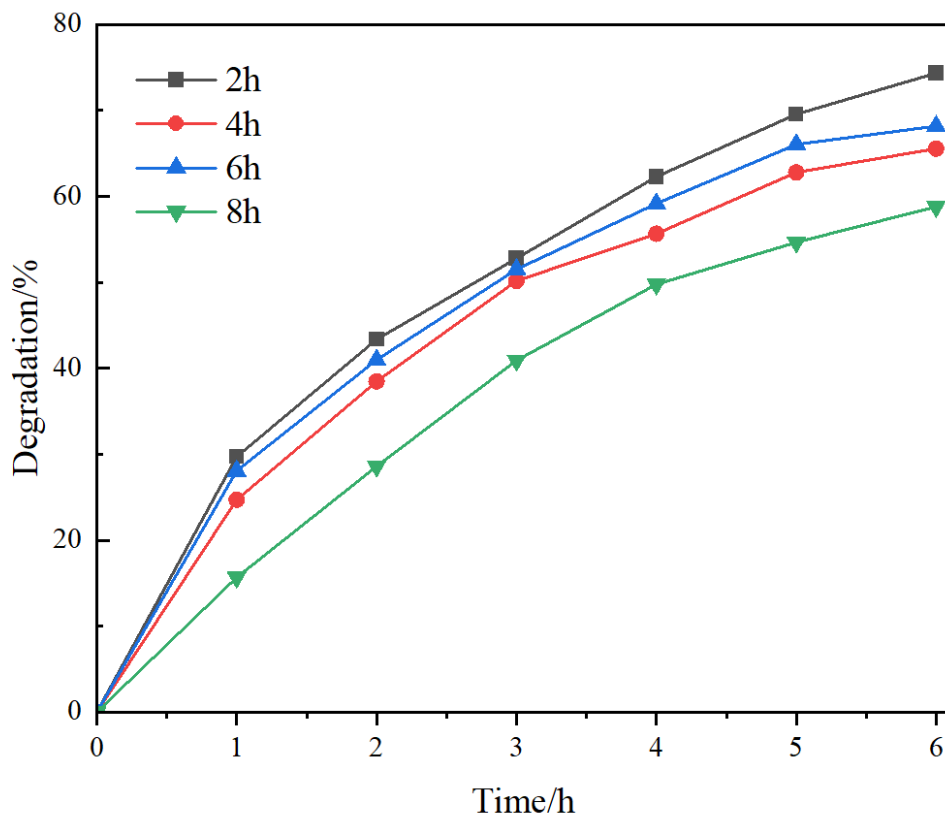


Fig. 12. Photocatalytic degradation curves of methylene blue at different calcination temperatures

The degradation rates were 74.31% (2h), 65.53% (4h), 68.15% (6h), and 58.75% (8h), and the calcination temperature had a significant effect on the catalytic activity, and the degradation rate was highest at the calcination time of 2h, and with the prolongation of the calcination time, the catalytic activity showed a gradual decrease, combined with the XRD of Fig. 3(b), it is known that the prolongation of calcination temperature was not conducive to the improvement of the catalytic activity in the stage of 2-8h. The prolongation of the calcination temperature is not conducive to the

improvement of the catalytic activity, mainly due to the fact that the TiO_2 samples are prone to agglomeration phenomenon under prolonged high-temperature calcination with enhanced crystallisation, and it is not conducive to the formation of heterogeneous structure. This led to the decrease of photocatalytic activity.

3.5 Study on photocatalytic reaction kinetics

$\ln(C_0/C_t)$ was used to plot the reaction time t , and the kinetics curves of different photocatalysts for photocatalytic degradation of methylene blue organic pollutants under UV and visible light obtained after linear fitting were shown in Fig.13 was used to plot the reaction time t , and the kinetics curves of different photocatalysts for photocatalytic degradation of methylene blue organic pollutants under UV and visible light obtained after linear fitting were shown in Fig.13.

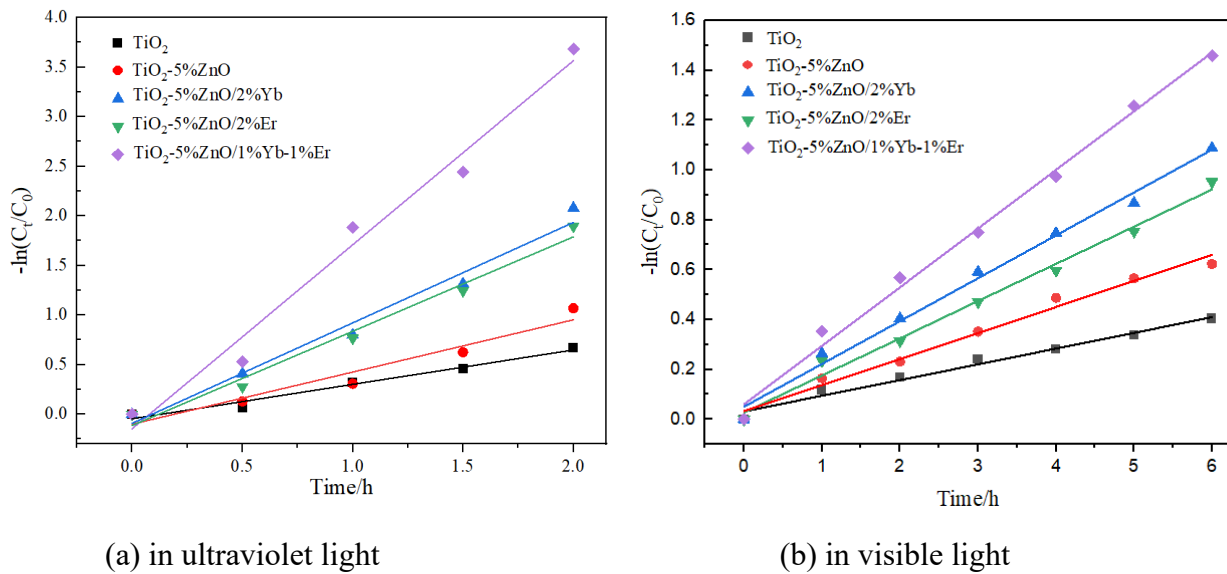


Fig. 13. Kinetics curve of methylene blue degradation under UV and visible light with different photocatalysts

As can be seen from Fig. 13, photocatalytic degradation follows the Langmuir-Hinshelwood equation^[42], whose equation is as follows:

$$\ln(C_0/C_t) = -Kt \quad (3)$$

Where K is the first-order reaction kinetic constant, C_0 is the initial concentration of reactants (mg/L), and C_t is the concentration of reactants at time t (mg/L).

The first-order kinetic constants and correlation coefficients of methylene blue degradation by photodestruction of different samples under UV and visible light are shown in Table 1.

Table 1 First-order kinetic constants and correlation coefficients of photocatalytic degradation of methylene blue

Samples	K_{UV}/h^{-1}	R^2	K_{vis}/h^{-1}	R^2
TiO ₂	0.3474	0.9751	0.0630	0.9813
TiO ₂ -5%ZnO	0.5265	0.9415	0.1046	0.9847
TiO ₂ -5%Zn/2%Yb	0.9784	0.9783	0.1719	0.9917
TiO ₂ -5%ZnO/2%Er	0.9519	0.9824	0.1493	0.9900
TiO ₂ -5%ZnO/1%Yb-1%Er	1.8562	0.9904	0.2354	0.9937

Note: K_{UV} and K_{vis} are apparent rate constants in ultraviolet and visible light, respectively.

As can be seen from Table 1, the apparent rate constant can be derived from the Langmuir-Hinshelwood equation^[43]. The photocatalytic reaction rate of the sample with a high apparent rate constant is faster, and the apparent rate constant under ultraviolet irradiation is greater than that under visible light irradiation. It can also be seen from the reaction rate that the addition of Yb³⁺ and Er³⁺ improves the degradation ability of heterojunction materials, and the improvement effect is most obvious when the doping ratio of Yb³⁺ and Er³⁺ is 1% respectively.

3.6 Heterojunction nanophotocatalyst mechanism

Heterojunction nano catalyzers were prepared by the sol-gel method at the molecular level. According to the experimental and characterization results, the possible reaction mechanism and charge transfer path on the TiO₂-5%ZnO/1%Yb-1%Er heterojunction catalysts are shown in Fig.14. Under the irradiation of the xenon lamp, e⁻ on the valence band (VB) of TiO₂ and ZnO will transition to the conduction band (CB). e⁻ on TiO₂(CB) will migrate to the ZnO(CB) position against the electric field direction, while h⁺ on ZnO(VB) will migrate to the TiO₂(VB) along the electric field direction, realizing the separation of photogenerated electron-hole pairs^[44]. Methylene blue organic molecules will adsorb on the active center of Yb and Er, and then undergo the dehydrogenation process at the (VB) position of TiO₂. The valence band holes themselves have a strong oxidation capacity, and can form strong oxidizing ·OH free radicals with H₂O adsorbed on the surface of the powder. In addition, ·OOH free radicals can form H₂O₂ with water molecules and oxygen. H₂O₂ can react with ·O₂⁻ to generate more ·OH radicals, which participate in the photocatalytic reaction process, and finally degrade methylene blue organic molecules into small molecules of H₂O and CO₂.

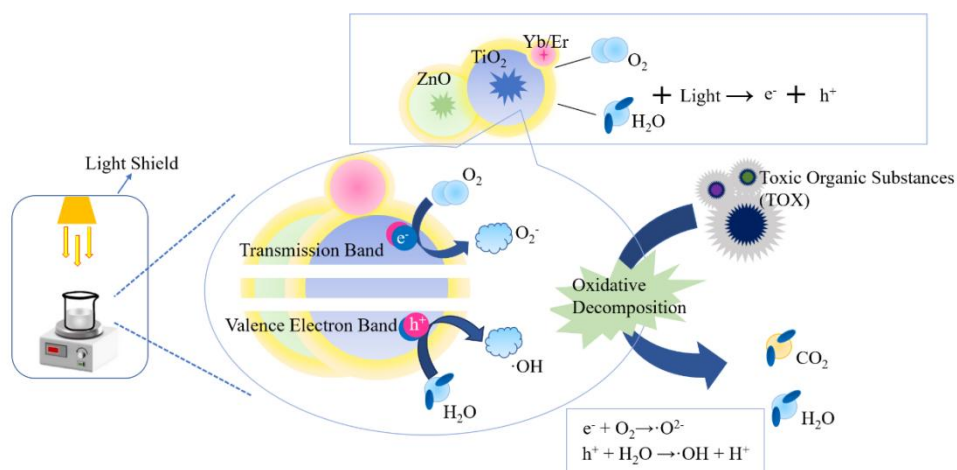


Fig. 14. Mechanism of TiO₂-ZnO/Yb-Er photocatalytic reaction

4 conclusion

Based on the successful sol-gel synthesis of rare earth (Yb, Er) co-doped TiO₂-ZnO composite semiconductors, characterization techniques including XRD, SEM, HTEM, XPS, IR, and UV-Vis DRS revealed that ZnO modification and Yb/Er doping induced TiO₂ lattice distortion, reduced particle size, and narrowed the band gap to 2.927 eV. These structural and optical enhancements improved UV absorption and extended visible-light response, leading to significantly improved photocatalytic degradation of methylene blue. The optimal sample, TiO₂-5%ZnO/1%Yb-1%Er, exhibited a degradation rate increase from 52.82% to 98.58% after 2 hours under UV light, and from 33.20% to 76.31% after 6 hours under visible light. Kinetic analysis confirmed that the degradation rate was higher under UV irradiation than under visible light.

CRedit authorship contribution statement

Tan Mao: Conceptualization, Methodology, Writing - Original Draft, Supervision. **Wei Wang:** Investigation, Data Curation, Writing - Original Draft. **Peilong Liu:** Validation, Formal analysis, Visualization. **Junyan Zha:** Writing - Review & Editing. **Xiran Bu:** Formal Analysis, Validation, Investigation. **Rui Song:** Resources, Software, Investigation, Visualization, Funding acquisition. **Xueke Luo:** Project administration, Supervision, Writing - Review & Editing.

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