



Ce and Er Co-doped TiO₂ for rapid bacteria-killing using visible light

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ABSTRACT

Bacterial infection and related diseases are threatening the health of human beings. Photocatalytic disinfection as a simple and low-cost disinfection strategy is attracting more and more attention. In this work, TiO₂ nanoparticles (NPs) were modified by co-doping of Ce and Er using the sol-gel method, which endowed TiO₂ NPs with enhanced visible light photocatalytic performance but not pure ultraviolet photocatalytic properties compared the untreated TiO₂. Our results disclosed that as the doping content of Er increased, the photocatalytic activity of modified TiO₂ NPs initially increased and subsequently decreased. The same trend occurred for Ce doping. When the doping dose of Er and Ce is 0.5 mol% and 0.2 mol%, the 0.5Ce0.2Ti-O calcined at 800 °C presented the best antibacterial properties, with the antibacterial efficiency of 91.23% and 92.8% for *Staphylococcus aureus* and *Escherichia coli*, respectively. The existence of Er ions is thought to successfully turn the near-infrared radiation into visible region, which is easier to be absorbed by TiO₂ NPs. Meanwhile, the addition of Ce ions can effectively extend spectral response range and inhibit the recombination of electrons and holes, enhancing the photocatalytic disinfection activity of co-doped TiO₂.

1. Introduction

Bacteria can cause enormous health problems for human beings. Some reports have revealed that bacterial infections and related complications are the second leading cause of death, affecting 15 million people approximately each year [1–3]. As we all known, since the invention of penicillin by Alexander Fleming, antibiotics were widely utilized to cope with diseases caused by bacteria. Nevertheless, the misuse and overuse of traditional antibiotics have already led to the appearance of bacterial resistance and even the occurrence of multi-drug-resistant (MDR) bacteria of “superbugs” [4]. A recent study predicts that superbugs may cause the death of over 10 million people by 2050 [5,6]. On this basis, the development of antibiotics-free disinfection strategy is urgently needed [7,8]. Among these strategies, visible light disinfection can effectively kill bacteria as a nonresistant and minimally invasive process [9,10]. Compared with antibiotics, it can destroy physiological activities of bacteria in a shorter time through

the radical oxygen species (ROS), such as ·O₂⁻, ·OH, ¹O₂ and H₂O₂, which are produced by photocatalysts [11–13]. Among various photocatalysts, TiO₂ is the most common one thanks to its low toxicity and long-term photostability. However, TiO₂ possesses a wide band gap of 3.0, 3.13, and 3.2 eV for rutile, brookite and anatase, respectively, which makes it can only be driven by ultraviolet (UV) light [14–16]. Long time irradiation under strong UV light is harmful for health. In addition, UV only accounts for less than 5% of the whole sunlight. Hence, much effort has been made to modify TiO₂ NPs to broaden light absorbance, including element doping, noble metal deposition, heterojunction construction, and so on [15,17–20]. Recently, Guayaquil-Sosa et al. synthesized Pt on mesoporous TiO₂ using a non-thermal assisted sol-gel and reduced the band gap to 2.34 eV [21]. Zhu et al. prepared a new class of red phosphorus (RP) decorated TiO₂ and largely extended the optical light harvesting ability [22]. The rapid recombination of photogenerated electron-hole pairs is another problem which limits the photocatalytic property of TiO₂. Up to now, Ce doping

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has been extensively studied and proved to be effective on reducing the band gap and suppressing the recombination of electron–holes, thanks to its incompletely occupied 4f and 5d electron orbitals [23,24]. Er-doping have received considerable attention for frequency up-conversion of infrared radiation into visible light with the suitable host matrix and ion concentration [25–27]. However, few studies have reported the dual elemental doping for TiO₂ NPs.

In this work, TiO₂ photocatalysts with different dopant contents of Ce and Er were synthesized using a sol–gel process. Furthermore, their photocatalytic properties were investigated through the degradation of methyl orange (MO) and their antibacterial performances were assessed by spread plate using *E. coli* and *S. aureus*.

2. Experimental

2.1. Materials preparation

Anhydrous ethanol, glacial acetic acid, titanium butoxide (Ti(O(C₄H₉))₄), cerium nitrate hexahydrate, erbium nitrate pentahydrate and polyethylene glycol (PEG 400) were all purchased from Aladdin Shanghai. Deionized water (DI) was used for washing. And all the chemicals were used as received without any purification.

Pure TiO₂, a series of Er doped TiO₂ and Er–Ce co-doped TiO₂ photocatalysts were synthesized by sol–gel method [28–30]. The preparation process was schematically diagrammatized in Scheme 1. Briefly, 10 ml of titanium butoxide (Ti(O(C₄H₉))₄) was added into 20 ml of anhydrous ethanol and 5 ml of glacial acetic acid with for 30 min stirring to form solution A. In the preparation process of mono-doped and co-doped TiO₂ NPs, calculated amounts of cerium nitrate hexahydrate and erbium nitrate pentahydrate were added into solution A. 10 ml of absolute ethanol, 1.8 ml of DI and 1 ml of PEG 400 were mixed to get solution B. In the followed step, solution B was dropped into solution A with constant stirring condition to obtain homogeneous sol. The final solution was heated up to 60 °C and reacted for 2 h to transform into gel. The gel was then aged at room temperature for a day and dried at 80 °C in vacuum. Subsequently, the samples were washed to remove residual chemicals, dried in a vacuum and annealed for 3 h.

2.2. Characterization

Scanning electron microscope (SEM, Hitachi S-4800, Japan) analysis equipped with an energy dispersive X-ray spectroscopy (EDS, Oxford X-max20, UK) and transmission electron microscope (TEM, JEM-2100F, Japan) were used to characterize the sample morphologies. X-ray diffractometer (XRD, D8 Advanced, Germany) was used to identify the crystal structure of TiO₂ with Cu- α radiation ($\lambda = 1.5406 \text{ \AA}$), operated with the step size of 2°/min in the range of $2\theta = 20\text{--}80^\circ$. The Raman spectra were obtained to prove the presence of surface defects using a Raman microscope (DXR2, Thermo Scientific, USA) under

532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) analysis was utilized to determine the surface chemical species of the particles (ESCALAB 250Xi, Thermo Scientific, USA). The diffuse reflectance ultraviolet–visible (DR UV–vis, UV-2700, Japan) spectrum was carried out to achieve the absorption spectra of photocatalysts in the range of 200–800 nm with BaSO₄ as a reference. The band energy gap can be calculated using the following formula [17]:

$$(Ah\nu)^{1/2} = C(h\nu - E_g), \quad (1)$$

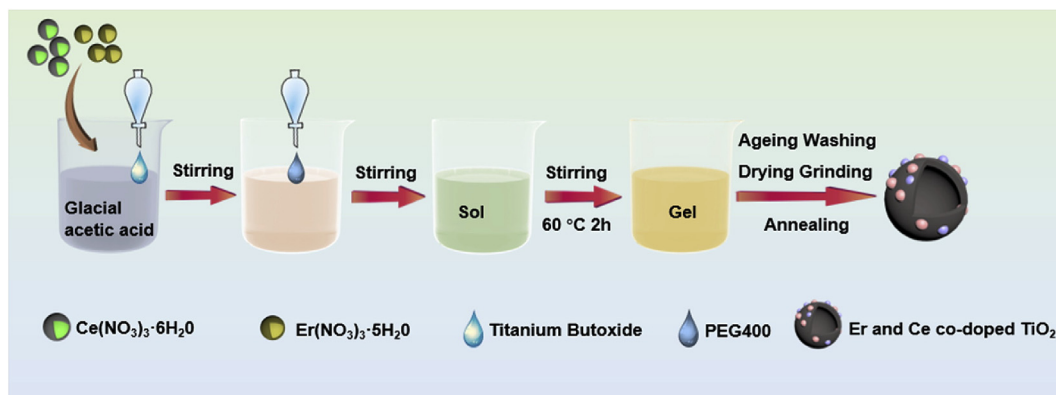
where A is the absorption coefficient, C is a parameter that associated with the valence and conduction band, $h\nu$ is the absorption energy, and E_g is the band gap. To analysis the tendency of carriers recombination, photoluminescence (PL) spectra were recorded by a fluorescence spectrophotometer (LS-55, American) with an excitation wavelength of 425 nm. To explore the up-conversion performance, luminescence emission spectrum of as-prepared nanoparticles was detected by using a fluorescent spectrometer (FLS980, UK) under 808 nm and 980 nm semiconductor solid laser excitation.

2.3. Photo-electrochemical tests

To research the generation, migration, and recombination of electrons and holes, photocurrent response and electrochemical impedance spectroscopy (EIS) were tested through an electrochemical workstation (Gamry Instrument, INTERFACE 1000) using 0.5 mol/L Na₂SO₄ as the electrolyte. 4 mg photocatalyst was dispersed in 80 μL DI, 20 μL ethanol and 40 μL Nafion and ultrasonically vibrated for 30 min. Then, 50 μL mixed solution was dip-coated onto a 10 \times 10 mm indium tin oxide (ITO) glass electrode and dried. The prepared electrode, platinum electrode, and saturation calomel electrode played the roles of the working electrode, counter electrode, and reference electrode, respectively [31–33].

2.4. Photocatalytic performance

Photocatalytic performances of these nanomaterials were investigated by subjecting them to photocatalytic degradation of MO under the irradiation of Xenon lamp. 0.2 g nanoparticles were dispersed in 100 ml suspension with a concentration of 20 mg L⁻¹, stirring for 30 min in the dark to attain absorption equilibrium. All suspension solutions were irradiated with continuous stirring under the Xenon lamp light with an intensity of simulated double solar radiation, which is about 2 kW/m². The supernatant was collected every 20 min and its absorbance was analyzed by UV–Vis spectrometer at maximum wavelength (465 nm). The linear relationship between the concentration and absorbance of was significant. And the degree of MO degradation could be determined from Degradation degree = $(A_0 - A_t)/A_0 \times 100$, where A_0 and A_t are MO concentrations of initial and after degradation,



Scheme 1. Typical preparation procedure of TiO₂ NPs with sol–gel method.

respectively [33–35].

2.5. Antimicrobial tests

The antimicrobial performance of photocatalysts was assessed using *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). The nanoparticle with a concentration of 5000 ppm was mixed with bacterial solution which was diluted to 1×10^7 colony-forming units (CFU)/mL in a 96-pore plate. For comparison, an experiment without nanoparticle solutions, instead by same amount of liquid medium was done as control groups. Final solutions were irradiated under the Xenon lamp light for 20 min to simulate natural light, with an intensity of double solar light. After irradiation, 20 μ L solution was taken out and diluted. Finally, 20 μ L of diluted solution was dropped into agar plate and smeared equably. All agar plates were cultivated at 37 °C for a day [36–38]. The bacterial-killing efficacy can be counted according to the following formula:

$$\text{Antibacterial ratio (\%)} = (\text{number of CFUs in control group} - \text{number of CFUs in experimental group}) / (\text{number of CFUs in control group}) \times 100\%. \quad (2)$$

3. Results and discussion

3.1. Characterization results of Er doped TiO₂

We first synthesized Er doped TiO₂ with dopant ratio of 0.25 mol%, 0.5 mol%, 0.75 mol% and 1 mol%. Fig. 1 exhibits the UV–vis spectra of the Er–TiO₂ and the pure TiO₂. The UV–vis spectra reveal that the cut-off wavelength doesn't show an evident red shift, which discloses that the band gap has no significant change. However, the absorption of visible region is enhanced along with doping Er, especially in the range of wavelength over 450 nm. In this range, some strong absorption peaks occur at 488 nm, 522 nm, 545 nm, 654 nm, which correspond to electron transition of 4F_{7/2}, 2H_{11/2}, 4S_{3/2} and 4F_{9/2} to ground state, respectively [39]. Among all samples, it is obviously that Er0.5Ti–O shows the best visible light absorption ability. Meanwhile, the Er0.75Ti–O sample presents only tiny difference with Er0.5Ti–O. As the doping content of Er continues to increase, the visible light absorption is decreased gradually with the following trend: Er0.5Ti–O > Er0.75Ti–O > Er1Ti–O > Er0.25Ti–O > TiO₂, which exhibits that the reasonable ratio of Er may be between 0.5 and 0.75 mol%. To evaluate if doped TiO₂ is an efficient up-conversion host material, the up-conversion luminescence properties of these two samples were detected further.

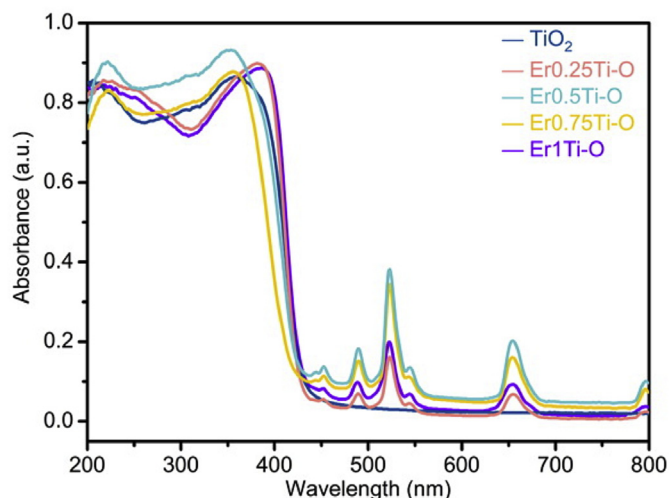


Fig. 1. UV–vis spectra of Er doped TiO₂.

As manifested in Fig. 2(a), the green emission can be observed at 520–570 nm clearly after excited by 808 nm laser, which reveals that TiO₂ is an efficient up-conversion matrix material. When irradiated by 980 nm light source, the green emission decreases but there occurs red emission at 640–690 nm. The synthesized co-doped semiconductors can convert the near-infrared radiation into visible region, which is easier to be utilized by themselves [40,41]. Another discovery is that Er0.75Ti–O sample shows weaker emission than Er0.5Ti–O, which implies that quenching of emission may take place at higher concentration of erbium ions. Therefore, 0.5 mol% is supposed to be the most reasonable ratio and used in our subsequent studies.

As shown in Fig. S1(a), Er0.5Ti–O calcined at 700 °C shows the main characteristic peaks of anatase, namely, the planes (101), (004), (200), (105), (211) and (204) at $2\theta = 25.2, 37.8, 48.3, 53.8, 55.0$ and 62.7 , respectively [42–44]. By contrast, the undoped TiO₂ already transformed into rutile when calcined at 700 °C, and the peaks at $27.4, 36.1, 41.2, 44.1, 54.3$ and 56.6° are associated with (110), (101), (111), (210), (211) and (220) of rutile, respectively. The above results suggest that the addition of Er delays the transition of crystal form as reported elsewhere. To get more information of crystal form, we further investigate the XRD spectra of Er0.5Ti–O annealed at 800 °C and 900 °C. When the annealing temperature is 800 °C, there exist both rutile and anatase. When the temperature is rose to 900 °C, all anatase has been transformed into rutile thoroughly, as shown in Fig. S1(b). It has been reported that the photocatalytic properties of mixed crystal TiO₂ NPs are much better than any single crystal [23,45]. In order to get mixed crystal, 800 °C is selected as calcination temperature for further investigation.

3.2. Characterization results of Er–Ce co-doped TiO₂

The XRD spectra of the Er–Ce co-doped samples are shown in Fig. 3(a), from which we can find that all co-doped TiO₂ NPs are mixed crystal as expected. With the increasing of annealing temperature, the ratio of rutile is lessened, indicating that the transition crystal form is delayed due to the addition of Ce. The inhibition by both dopants may be related to formation of Ti–O–Er or Ti–O–Ce bonds [46]. As revealed in Fig. 3(b), UV–vis spectra indicate that the responsive toward visible light irradiation is obviously enhanced after the addition of Ce. Er0.5-Ce0.2Ti–O exhibits the strongest visible light absorption among all the samples. Hence, it is believed that there is an optimum doping dosage of Ce, similar with Er, which may be about 0.2 mol%. When the concentration is lower than the optimum amount, effective separations of electrons and holes are not achieved. Once the dopant ratio is higher than the optimal concentration, surface barrier becomes higher and space charge regions get narrower, leading to the reduction of catalytic efficiency [47]. Furthermore, compared with the untreated TiO₂, the absorption edge of co-doped samples all show significant red shift (Fig. 3(b)), indicating that band gap of the co-doped catalysts decrease largely, which is related to the incompletely occupied 4f and 5d orbitals of the Ce ions [48]. The characteristic electron orbitals can not only reduce the band energy gap but also inhibit electron–hole recombination rate through providing new energy levels. Consequently, the photocatalytic activities can be enhanced.

Raman spectroscopy is taken to detect the change of surface structural before and after doping. Considering that samples calcined at 800 °C show two crystal forms, which may lead to the peaks of spectrum too complicated to be identified, so we prefer the samples annealed at 700 °C. As revealed in Fig. 3(d), TiO₂ as well as all co-doped TiO₂ show spectra centered in $144 \text{ cm}^{-1}, 192 \text{ cm}^{-1}, 400 \text{ cm}^{-1}, 519 \text{ cm}^{-1}$ and 639 cm^{-1} , corresponding to the Raman-active modes of anatase Eg(1), Eg(2), B1g, A1g and Eg(3). Compared with the undoped TiO₂ sample, vibration peaks in doped samples show blue shift, which is induced by some minor structural deformation of TiO₂ [49,50]. Meanwhile, there exist some new Raman bands at $290 \text{ cm}^{-1}, 340 \text{ cm}^{-1}$ and 520 cm^{-1} , which may result from the RE ions located at different

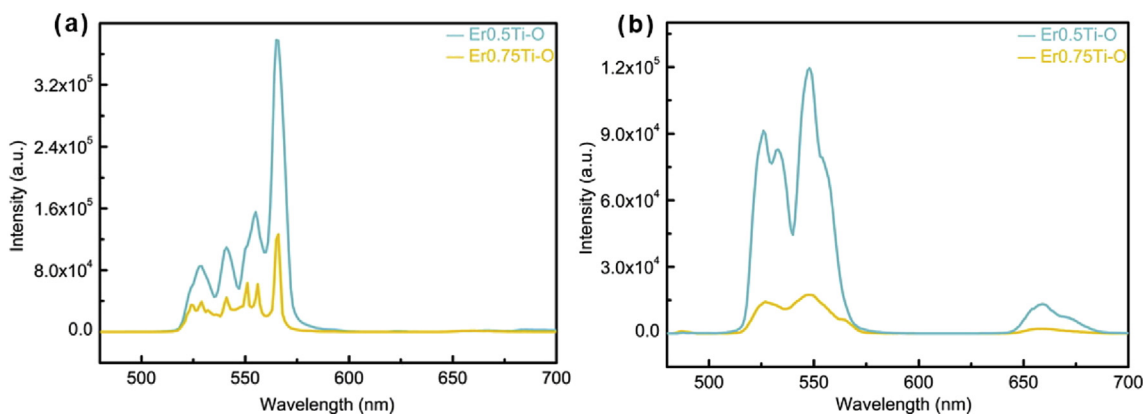


Fig. 2. Up-conversion luminescence spectra for Er_{0.5}Ti-O and Er_{0.75}Ti-O under 880 nm (a) and 980 nm (b) excitation.

sites within the TiO₂ framework [51]. Although there are relatively great differences between radii of Ti ions, Ce ions and Er ions, it has been proposed that there are interstitial channels in anatase crystalline, so that Ce³⁺/Ce⁴⁺ and Er³⁺ can gain access to substitute some Ti⁴⁺ [48].

Fig. 4(a) presents the SEM morphologies of Er_{0.5}Ce_{0.2}Ti-O sample and its EDS composition spectrum is shown in Fig. 4(b). The SEM image shows that the Er_{0.5}Ce_{0.2}Ti-O we prepared are spherical particles with uneven radius, which may be caused by slight aggregation. And the EDS composition spectrum discloses the existence of O, Ti, C, Ce and Er element on the surface. TEM image of Er_{0.5}Ce_{0.2}Ti-O is shown in Fig. 4(c), from which polyhedral structures mainly constituted of hexagonal and rhombus can be seen, with an average size of 30 nm. The HRTEM image is demonstrated in Fig. 4(d), in which the (112) crystal spacing of anatase and the (110) of rutile is marked. And the SAED

pattern shown in Fig. 4(e) exhibits polycrystalline rings corresponding to (101) and (105) planes of anatase and (101) of rutile, which confirm the existence of two crystals, agreeing with the results of XRD spectra.

The surface chemical composition of Er_{0.5}Ce_{0.2}Ti-O investigated by XPS is demonstrated in Fig. S2. From the survey of full scan spectra, O 1s, Ti 2p, and C 1s are detected. The adventitious C 1s peak may be led by the contamination because the samples were exposed to atmosphere. As for Ce and Er, the doping amount is too low to identify their signal peaks in the full scan spectra. The high resolution spectra have been fitted. The binding energy centered in 458.5 eV and 464.2 eV correspond to the 2p_{3/2} and 2p_{1/2} core level of Ti⁴⁺ [33,41]. Fig. 5(c) displays the O 1s spectra with peaks at 529.0 eV, 531.2 eV, and 533.0 eV. The first one is attributed to oxygen lattice, while the peak at 531.2 eV is correlated to surface hydroxyl groups, and the peak at 533.0 eV is associated with surface adsorbed oxygen species [33]. The

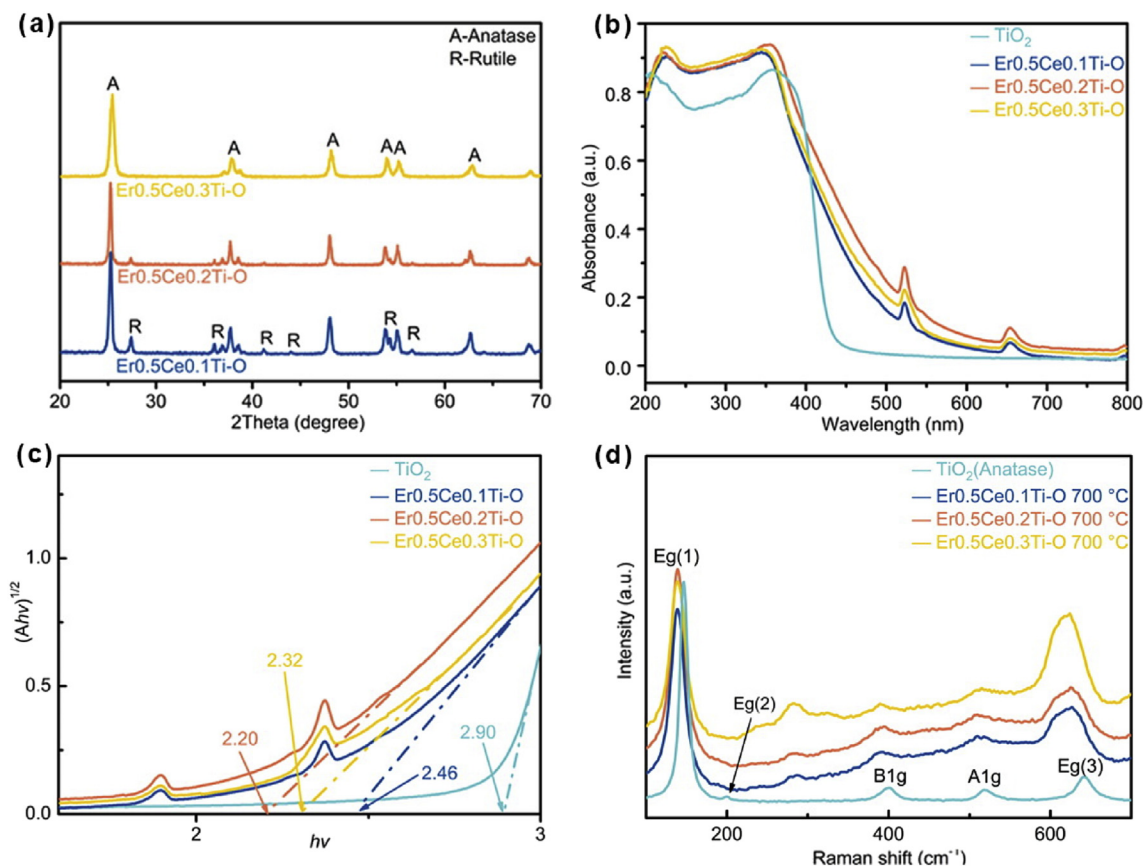


Fig. 3. Characterization of co-doped TiO₂. (a) XRD, (b) UV-vis spectra, (c) band energy gap and (d) Raman spectroscopy.

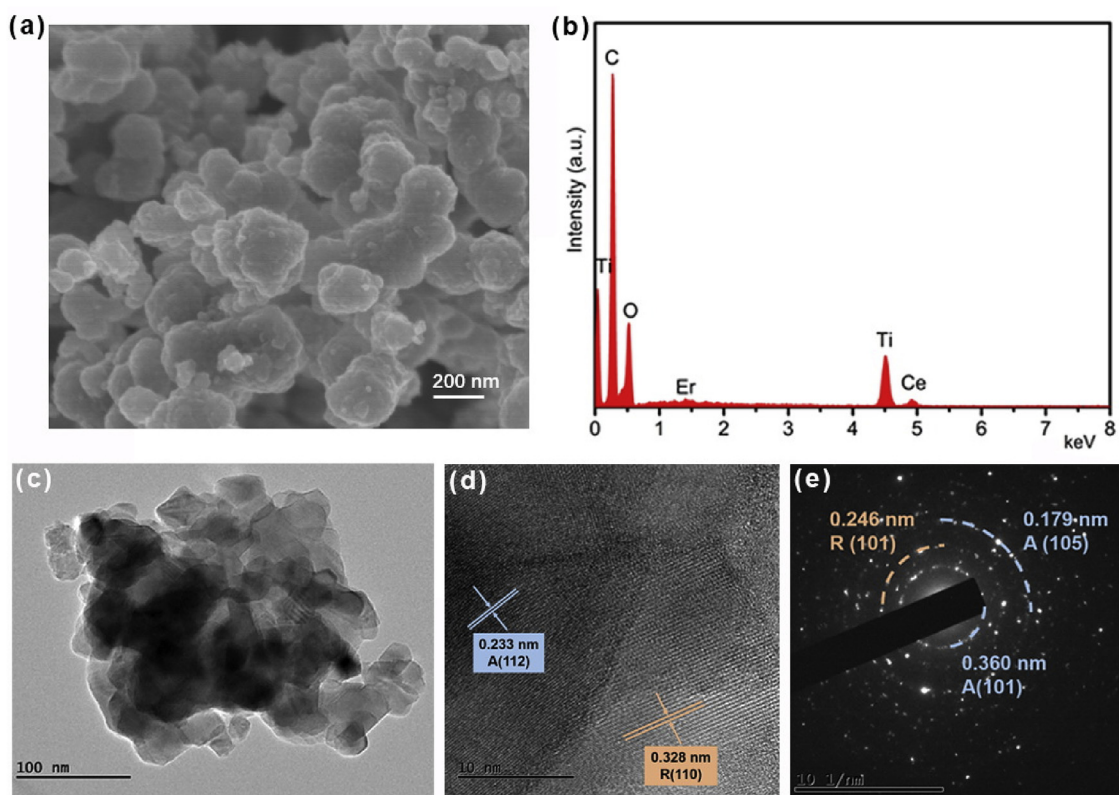


Fig. 4. Characterizations of the Er_{0.5}Ce_{0.2}Ti-O. (a) SEM image, (b) EDS spectrum, (c) TEM image, (d) High-resolution TEM image and (e) selected area electron diffraction (SAED) pattern.

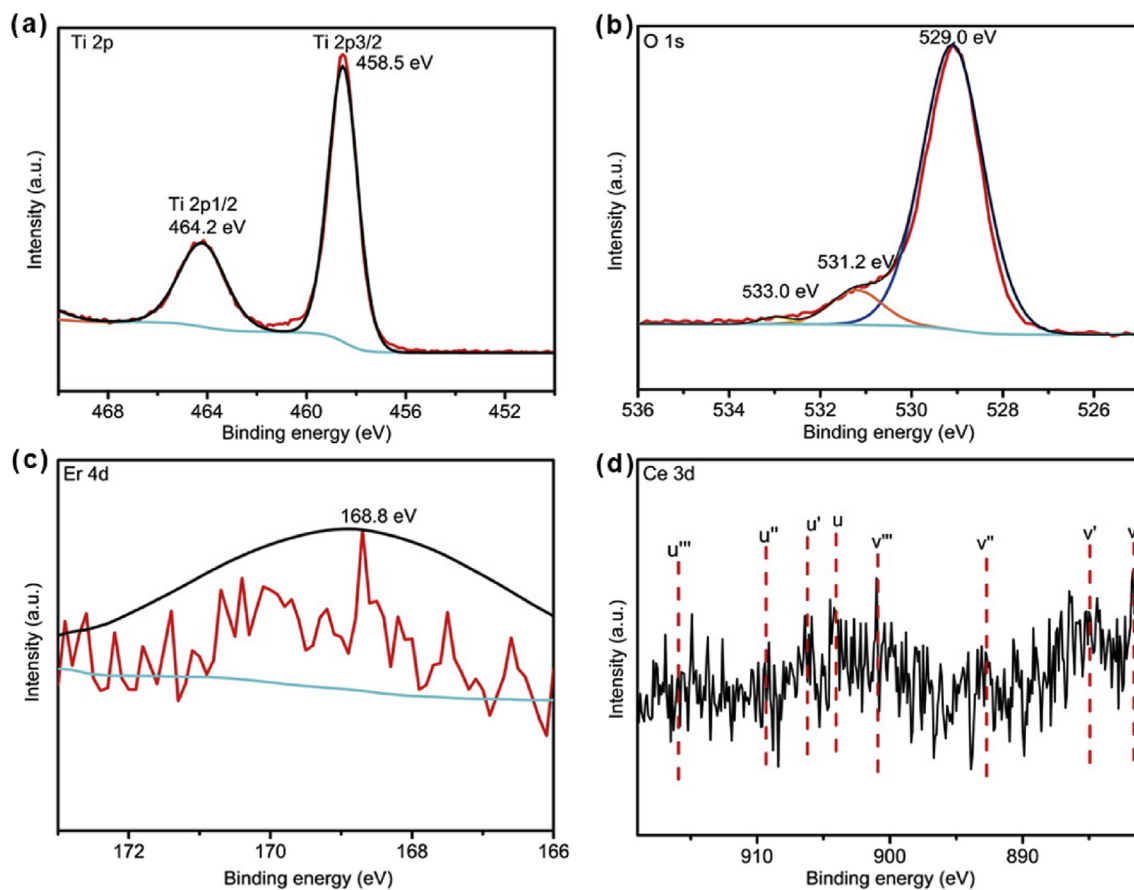


Fig. 5. High-resolution spectra of Ti 2p (a), O 1s (b), Er 4d (c) and Ce 3d (d) for Er_{0.5}Ce_{0.2}Ti-O.

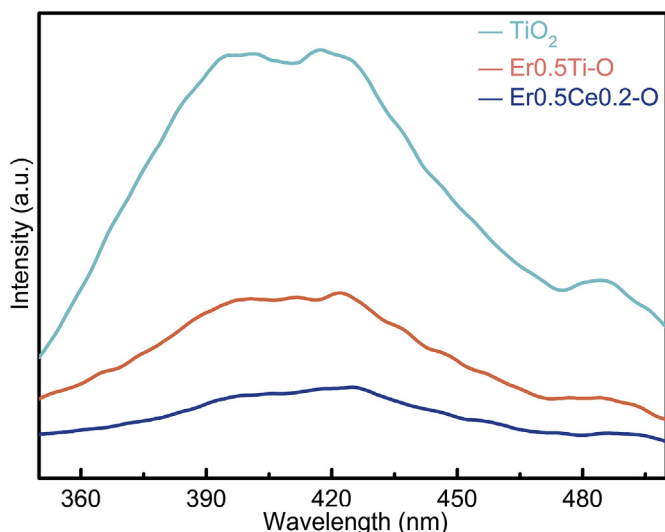


Fig. 6. PL spectra of pure TiO_2 , $\text{Er}_0.5\text{Ti-O}$ and $\text{Er}_0.5\text{Ce}_0.2\text{Ti-O}$.

peaks located at 168.8 eV corresponds to the Er 4d, which is attributed to Er^{3+} [52]. The XPS peak of cerium is affected by the orbital hybridization of Ce 4f and O 2p, presenting four pairs of spin-orbit splitting bands. The v , v' and v'' marked in Fig. 5(d) all correspond to Ce IV, confirming the existence of Ce^{4+} state, and u , u' and u'' owe to O 2p orbital. Meanwhile, the v' and u' denote the existence of Ce^{3+} [42,48,53]. The existence of $\text{Ce}^{3+}/\text{Ce}^{4+}$ mixture on the surface of photocatalysts can interact with photogenerated holes and electrons, preventing their recombination, leading to a higher catalysis efficiency [48].

It's accepted that the PL intensity is connected with the combination of electrons and holes directly. To be specific, lower PL intensity indicates slower combination rate and longer lifespan of photogenerated carriers [33,49]. As shown in Fig. 6, pure TiO_2 exhibits a strong emission peak between 390 nm and 420 nm, caused by the recombination of electron-hole pairs. The intensity of PL spectra decreases obviously after doping Er, which represents a better separation of photogenerated electron-hole. Some researchers have point out that electrons on the valence band (VB) can be excited to some intermediate energy levels by up-conversion emission of Er^{3+} , and then transferred to the conduction band (CB) [46]. Hence, more photogenerated electrons and holes are obtained. And after the presence of Ce ions, the PL intensity continues to become lower, indicating that the electron-hole recombination is inhibited further. We ascribe it to the existence of $\text{Ce}^{3+}/\text{Ce}^{4+}$ on the

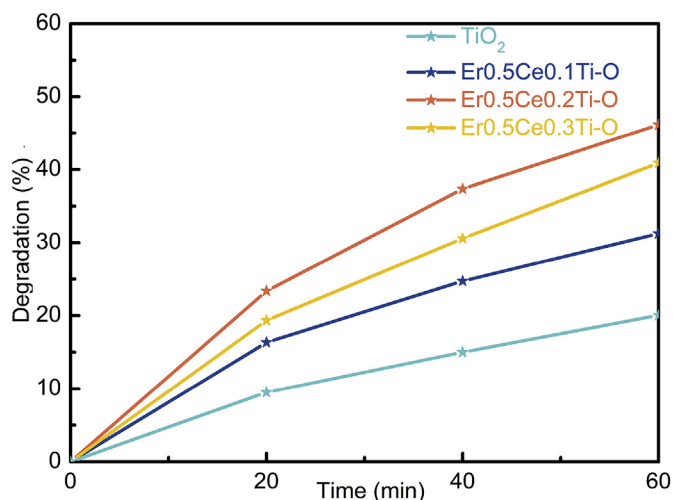


Fig. 8. The degradation rates of MO in the presence of co-doped TiO_2 .

surface of TiO_2 . To forcefully prove that Ce alone can inhibit the recombination of electron-hole pairs, we processed Ce single-doped sample with 0.2 mol% Ce and measured its PL intensity, which is supplied in Fig. S3. Through the comparison of TiO_2 and $\text{Ce}_0.2\text{Ti-O}$, we can draw a conclusion that the addition of Ce can suppress the combination of generated carriers.

3.3. Photo-electrochemistry tests

Both EIS and photocurrent response are relatively powerful methods for characterizing photo-electrical properties of photocatalysts. It can be clearly seen from Fig. 7(a) that the diameter of Nyquist semicircle of TiO_2 is significantly narrowed after doping, suggesting that the carriers transfer resistance is effectively bring and the surface reaction is boosted. It is widely accepted that the photocurrent intensity is decided by the separation efficiency of photogenerated carriers. As shown in Fig. 7 (b), the composite has weak current response in the dark and exhibits a steady current when exposed to Xenon lamp light. Moreover, the photo current is enhanced after doping, indicating that the separation and transition efficiency of carriers can be enhanced visibly along with doping modification.

3.4. Photocatalytic performance

As shown in Fig. 8, pure TiO_2 photocatalysts can degrade 20.04% of MB in 60 min. The degrading rate is improved when using co-doped

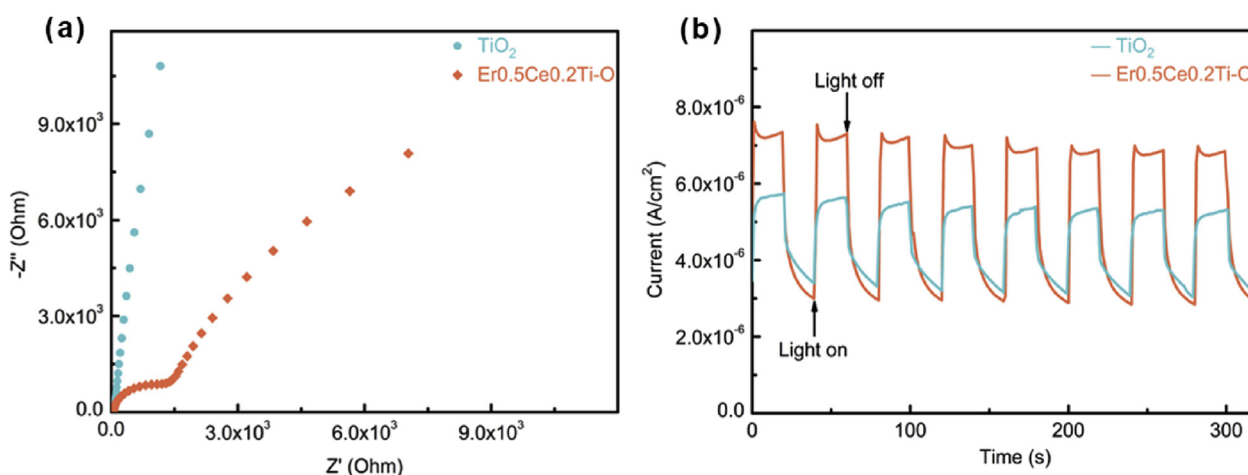


Fig. 7. EIS plots (a) and the photocurrent spectra (b) of pure TiO_2 and modified TiO_2 .

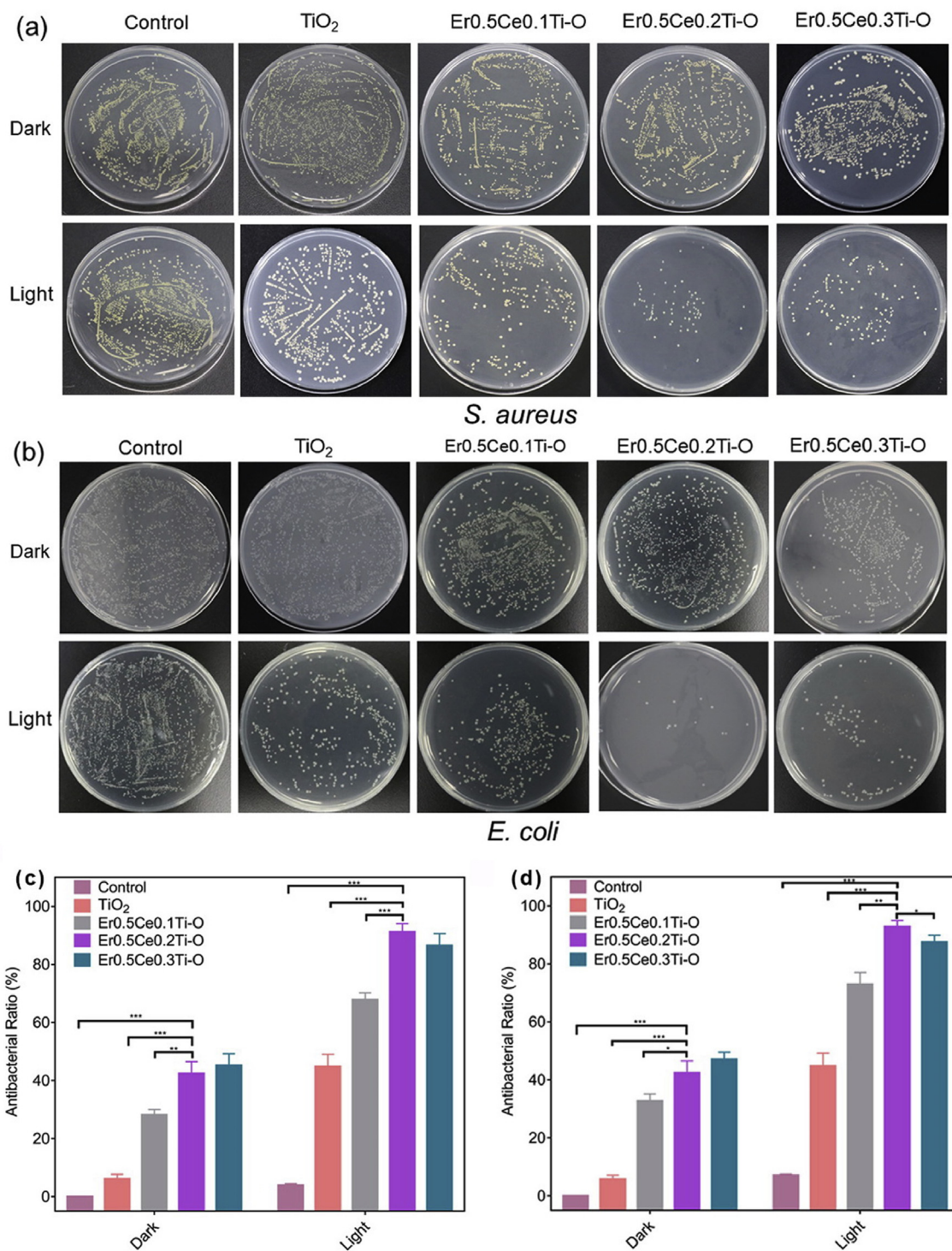


Fig. 9. The formed viable colony units of *S. aureus* (a) and *E. coli* (b) after treated with samples in the dark for 20 min or under simulated sunlight for 20 min and the corresponding abilities of the samples in killing *S. aureus* (c) and *E. coli* (d). The experiment was performed in triplicate and independently. (n = 3, mean ± SD).

TiO₂, and the Er0.5Ce0.2Ti-O composite exhibits the best photo-degradation activity, which could degrade 46.13% MO within 60 min. The addition of Er element successfully turns the near-infrared radiation of the sunlight into visible light and Ce ions can effectively extend the range of spectral response. Meanwhile, both RE ions can improve the separation efficiency and migration rate of the interface carriers, restraining the recombination of electrons and holes. Thus, the photocatalytic activity of co-doped TiO₂ is enhanced obviously.

3.5. Antimicrobial performance

In vitro *E. coli* and *S. aureus* antibacterial activities of different samples are given in Fig. 9. It can be seen from Fig. 9 that bacterial colonies on TiO₂ are slightly less than that on the control group after visible light irradiation of 20 min with an intensity of double solar light, and the bacterial colonies on doped TiO₂ decrease massively. Among all co-doped groups, the Er0.5Ce0.2Ti-O shows the best antibacterial efficacy, whose antibacterial ratios toward *E. coli* and *S. aureus* are 92.8%

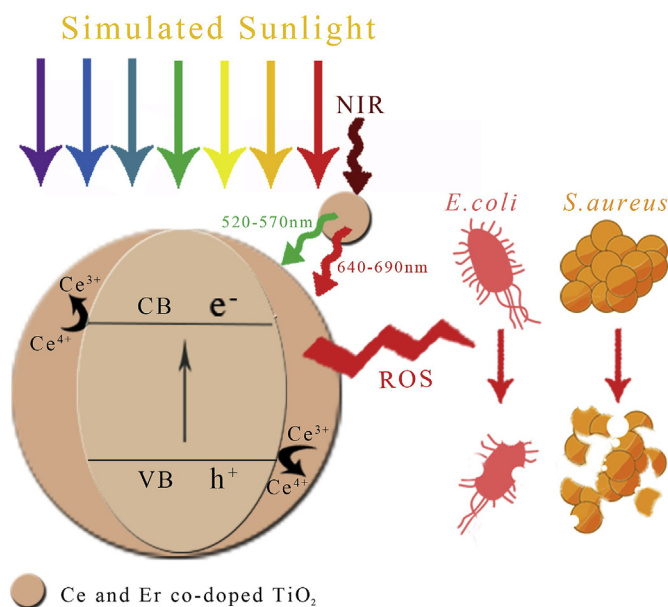


Fig. 10. Schematic illustration of the mechanism of enhanced photocatalytic disinfection of Ce and Er co-doped TiO_2 .

and 91.23%, respectively, compared to 44.79% and 44.85% of undoped TiO_2 . The results of antibacterial activities mainly agree with photocatalytic results. That is to say that the better photocatalytic performance means more ROS generated during visible light irradiation, thus providing better antibacterial property [54]. Obviously, the co-doped nanoparticles exhibit antibacterial effects without external activation as well and the antibacterial performance is intensified with the increase of Ce. Therefore, we consider that the antibacterial performance in the absence of irradiation arises from Ce ions. In fact, previous studies have put forward that Ce ions have antibacterial effects based on the reaction with cell walls and interference with bacterial cellular respiration [55].

The mechanism of the enhanced photocatalytic disinfection is schematically illustrated in Fig. 10. After doping modification by Ce, the energy gap of TiO_2 is decreased, which means that it can harvest not only pure UV but also visible light and generate more ROS when exposing to solar sunlight. Meanwhile, the addition of Er can turn the near-infrared region into visible range, which is easier to be absorbed by synthesized TiO_2 . What's more, both Ce and Er ions can inhibit the recombination of photogenerated charge carriers thanks to the incompletely occupied 4f and 5d electron orbitals, thus enhancing the photocatalytic activity effectively. In conclusion, the dual elements doped TiO_2 can be driven by solar sunlight to display outstanding visible light photocatalytic performance for rapid sterilization eco-friendly.

4. Conclusions

In this work, the dual elements doped TiO_2 NPs were synthesized using sol-gel method, which displayed superior visible light photocatalytic performance than the untreated ones. The doped Er can convert the near-infrared radiation of the solar spectrum into visible region, improving the visible light absorption of synthesized TiO_2 NPs while the addition of Ce can broaden absorption spectra of TiO_2 NPs and decrease their energy gap. In addition, the two kinds of RE ions can hinder the recombination of electrons and holes, which can enhance the photocatalytic properties effectively. The optimum dosage of Er and Ce may approximate to 0.5 mol% and 0.2 mol%, respectively, which can endow the doped TiO_2 calcined at 800 °C with higher antibacterial efficacy of 91.23% and 92.8% against *S. aureus* and *E. coli*, respectively

under the visible light irradiation.

CRediT authorship contribution statement

Yawei Ren: Conceptualization, Methodology, Data curation, Writing - original draft. **Yajing Han:** Conceptualization, Methodology, Data curation. **Zhaoyang Li:** Methodology. **Xiangmei Liu:** Conceptualization, Writing - review & editing, Supervision, Project administration. **Shengli Zhu:** Methodology. **Yanqin Liang:** Methodology. **Kelvin Wai Kwok Yeung:** Methodology. **Shuilin Wu:** Conceptualization, Writing - review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.bioactmat.2020.02.005>.

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