Nanocrystalline ZnO doped lanthanide oxide: An efficient photocatalyst for the degradation of diesel pollutant in seawater under visible light irradiation

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Abstract. In this study, a ZnO doped Er2O3 photocatalyst is employed to degrade diesel pollutant in seawater under visible light irradiation. The photocatalyst was prepared by a precipitation method and was characterized by SEM and XRD analysis. The experimental results proved that the nanocrystalline photocatalysts were highly active in the visible region. The photocatalytic degradation efficiency of diesel was analysed by various experimental parameters namely dosage, doping ratio, initial concentration of diesel, pH value, concentration of H2O2 and illumination time. The degradation of diesel pollution in seawater was optimized by orthogonal experiment. According to the results, the removal rate of diesel is less than 30 % without any catalysts (only evaporation). The best effect exists when the dose of catalysts was 0.6 g/L, doping ratio of catalysts was 10%, initial concentration of diesel was 0.2 g/L, pH value was 8, concentration of H2O2 was 10 mg/L, illumination time was 1 h. The removal rate of diesel can reach 99.38 %. This study would make ZnO utilize sunlight more efficiently and accelerate the practical application of photocatalytic technology in organic pollutants treatment region.

1. Introduction
The semiconductor photocatalysis has received a great attention in recent years, for the advantages of easy process, no secondary pollutant, less manpower demand, low expense and absolutely mineralization. Ultraviolet light can be absorbed by semiconductor photocatalytic materials rather than infrared light. However, ultraviolet light accounts for a small portion of visible light. Visible light can be converted to ultraviolet light by lanthanide doped photocatalyst and the reaction can carry out in the sunlight with high degradation rate, which can be the novelty of this study. Recent years, a lot of researchers has studied the region of photocatalysis and attempt to find a high active photocatalyst to degrade the pollutants. The upconversion luminescence agent can efficiently transform the infrared light into ultraviolet light by TiO2/Y2O3: Yb3+, Tm3+ composite [1]. Preparation, characterization and photocatalytic performance of Mo-doped ZnO photocatalysts were studied, which was found that ZnO with 2 wt.% Mo-doping showed higher activity and stability than pure ZnO [2]. The photocatalytic activity of the PANI-ZnO composites was confirmed superior to that of PANI nanotubes [3]. A research has demonstrated that europium-, praseodymium- and ytterbium- oxide-doped TiO2 exhibit higher photocatalytic activities for degradation of organic pollutants [4]. The degradation of malachite green was above 99 % employing photocatalyst Dy2O3 doped ZnO [5]. The enhanced photocatalytic activity was due to the presence of f shells in the lanthanide oxide crystal lattice which traps the excited electrons further delaying the process of recombination of electron-hole pair [6]. Comparative
study of lanthanide oxide doped titanium dioxide photocatalysts prepared by co-precipitation and sol-gel process shows that the catalysts prepared by co-precipitation exhibited a higher photocatalytic activity than those prepared by the sol-gel process [7]. Complete mineralization has been achieved in the case of lanthanide oxide doped TiO$_2$ photocatalysts in total contrast to the formation of intermediates in case of non-modified TiO$_2$[8]. Ce and Er-doped ZrO$_2$ resulted photoactive in methylene blue removal in aqueous solution promoted by white LEDs lights [9]. In this study, a ZnO doped Er$_2$O$_3$ photocatalyst is employed to degrade diesel pollutant in seawater under visible light irradiation.

2. Materials and methods

2.1. Materials
The main experimental chemicals included Zn(NO$_3$)$_2$·6H$_2$O, Er(NO$_3$)$_3$·5H$_2$O, CTMAB, NaOH solution and absolute ethanol. The apparatus consisted of an ultrasonic cleaner, a drying oven, a UV-visible spectrophotometer, an X-ray diffraction, a muffle furnace, some magnetic stirrers and some fluorescent lamps.

2.2. Preparation of the doped photocatalyst
A series of Er$^{3+}$-ZnO samples were prepared by a co-precipitation method according to the following procedure: First, a certain amount of aqueous Zn(NO$_3$)$_2$ and Er(NO$_3$)$_3$ was prepared. A prescribed amount of lanthanide nitrate (Er(NO$_3$)$_3$·5H$_2$O) was dissolved in the aqueous Zn(NO$_3$)$_2$ solution to form a transparent mixed ion solution. A small amount of CTAB was added to the transparent solution and mixed by ultrasonic dispersion for about 2 h. Then, a NaOH solution was added to the mixed solution slowly under vigorous stirring until the precipitation generated completely. After this, the reaction system was continuously stirred for 1 h at temperature to get a homogeneous precipitate in composition, and then washed by centrifuge with absolute ethanol and deionized water three times respectively. The precipitation was then dried at 105 °C for more than 12 h and ground to powder; next the powder was calcinated at an optimum temperature of 550 °C for 2 h. After the muffle furnace cooled down to room temperature, the samples were taken out and ground to form Er$^{3+}$-ZnO photocatalysts. The molar ratios of Er$^{3+}$ to ZnO are 0, 10%, 20%, 30%, 40% and 50%, which is marked as E0, E10, E20, E30, E40 and E50. The Er$^{3+}$-ZnO photocatalysts appear pink colors and as the increasing doping ratios of Er$^{3+}$, the colors become deeper.

2.3. Methods

2.3.1. Characterization techniques. Scanning electron microscopy (SEM) can be employed to study the crystallization of nanomaterials, observe the morphology and dispersion of nanoparticles and measure or evaluate the particle size of nanoparticles. The qualitative analysis of the phase can be obtained by comparing the diffraction peak with the JCPDS card to obtain the corresponding lattice constant and related parameters according to the X-ray diffraction (XRD). The composition of the sample can be determined by multiphase analysis. Finally, the grain size of the material is calculated by Scherrer equation:

$$\beta = k\lambda / D \cos \theta$$

where, $D$ is the average size of the cristallite; $\beta$ is the full width at half maximum; $\theta$ is Bragg angle (taking radian calculation); $\lambda$ represents the wavelength of X-ray (Å); $K$ is taken as a constant related to the degree of broadening.

2.3.2. Photocatalytic reaction. The photocatalytic degradation efficiency of diesel was analysed by various experimental parameters namely dosage, doping ratio, initial concentration of diesel, pH value, concentration of H$_2$O$_2$ and illumination time. The content of residual diesel could be estimated by spectrophotometer (the wavelength at 225 nm) after reaction. The degradation of diesel pollution in
seawater was optimized by orthogonal experiment. The residual amount of diesel can be calculated by the following formula:

\[
\text{Degradation Rate} = \frac{C_0 - C_i}{C_0} \times 100\% 
\]

where, \(C_0\) is the initial concentration of diesel (g/L); \(C_i\) represents the concentration of residual diesel in simulated seawater (g/L).

3. Results and discussion

3.1. SEM and XRD analysis of the photocatalyst

3.1.1. Characterization by SEM. The Fig.1 shows the SEM (Quanta 200 FEG field emission environmental scanning electron microscopy) images of pure ZnO, 30% Er\(^{3+}\) doped ZnO and 50% Er\(^{3+}\) doped ZnO. The SEM images of prepared photocatalysts proved that the pure ZnO particles to be uniformly distributed, the average particle size of which is about 30-40 nm. The Er\(^{3+}\)-ZnO photocatalysts exhibit spherical morphology with a particle size of approximately 40-50 nm. In E30 and E50 catalysts, it is observed that there are two morphologies existing respectively, ZnO is coated on Er\(_2\)O\(_3\). The Er\(^{3+}\)-ZnO sample shows an aggregation morphology which looks denser than pure ZnO sample, indicating that there may be some mesopores in the particles.

![ZnO, E30(30%), E50(50%)](image)

Figure 1. The SEM images of prepared ZnO, E30 and E50

3.1.2. Characterization of the photocatalyst by X-ray diffraction technique. X’Pert High-Score software was used for data handling. The results are shown in the fig.2. ZnO sample has obvious peaks at 20 of 31.7348°, 34.3994°, 36.2102°, 56.5351°, 61.7981° or 47.4826°; E30 photocatalyst has obvious peaks when 2θ is 36.2429°, 29.2834°, 31.7572°, 34.4099°, or 56.5498°; E50 catalyst has obvious peaks at 2θ of 29.3066, 48.7971, 33.9726, 36.2300, or 57.9491. The diffraction peaks of pristine ZnO and Er\(_2\)O\(_3\) are similar to the standard patterns (ZnO - JCPDS No. 36-1451 and Er\(_2\)O\(_3\) - JCPDS 01-077-0459). The lattice constants of a, b, and c of ZnO are 3.2539Å, 3.2539Å, and 5.2098Å; the lattice constants of a, b, and c of Er\(_2\)O\(_3\) are 10.5500 Å, 10.5500 Å, and 10.5500 Å. The average crystallite sizes of ZnO and Er\(_2\)O\(_3\) are 34.14 nm and 40.94 nm respectively which are calculated by Scherrer equation (1) according to the diffraction peaks (111). Thus, the prepared photocatalysts are pure ZnO and Er\(^{3+}\)-ZnO.
3.2. Photocatalytic degradation of a model pollutant

The ‘control variable method’ is a way of determining the effect of single factor. In this study, dosage, doping ratio, initial concentration of diesel, pH value of solution, concentration of H$_2$O$_2$ and illumination time are employed as single variables. The dosage was 0.6 g/L, doping ratio was E30, initial concentration of diesel was 0.2 g/L, pH value was 8, concentration of H$_2$O$_2$ was 6 mg/L and the illumination time was 2 h. The range of the variable was changed to examine the effect of a variable on the photocatalytic reaction.

**Figure 2.** The XRD images of prepared ZnO, E30 and E50

- (a) Dosage (g/L)
- (b) Doping ratio (%)
- (c) Initial concentration of diesel (g/L)
- (d) pH
Figure 3. Effects of dosage (a), doping ratio (b), initial concentration of diesel (c), pH value (d), concentration of H$_2$O$_2$ (e) and illumination time (f) on photocatalytic degradation

3.2.1. The effect of dosage on photocatalytic efficiency. To determine the optimum amount of composite photocatalyst required to degrade a known concentration of diesel, the initial concentrations of catalysts’ dosages were varied from 0 to 1.2 g/L.

The results shown in Fig.3(a) suggested that as the dosage increases degradation first increases and then decreases and the degradation rate reaches maximum (84.58 %) when the concentration of dosage is 0.6 g/L. It prove that the photocatalyst Er$^{3+}$-ZnO has the capability of degrading diesel pollutant under visible light. At the beginning, the degradation rate increases with the increase of dosage, because of the increasing amount of the active electrons or hole pairs, which can decompose diesel pollutant. Whereas, when the dosage is more than 0.6 g/L, the degradation rate decreases, because it come up with light barrier and light reflection, which leads to the reduction of light irradiation directly. A solution without catalyst (only by evaporation) was also tested. However, without catalyst it showed 26.95 % degradation which suggests the high efficiency of degradation is due to catalytic action.

3.2.2. The effect of doping ratio on photocatalytic efficiency. Studies were conducted to compare the photocatalytic efficiencies of different doping ratio (E0, E10, E20, E30, E40 and E50) under visible light irradiation.

The results shown in Fig.3(b) suggest that as the doping ratio decreases, the degradation rate first increases then decreases and the maximum degradation rate is 91.59 % when the doping ratio is 30 %. The photocatalyst without Er$_2$O$_3$ (only ZnO) was also tested, which is obvious that photocatalyst Er$^{3+}$-ZnO has higher activity than pure ZnO. Moderate doping ratio can increase the degradation rate but excess doping ratio could cover the surface of ZnO and hinder the absorption of visible light.

3.2.3. The effect of initial concentration of diesel on photocatalytic efficiency. To investigate the ability of the photocatalyst to degrade different initial concentrations of diesel pollutant solutions, studies on the variation of initial concentration of diesel from 0.05 g/L to 0.30 g/L were conducted.

The results are shown in Fig.3(c). It is clear that when the initial concentration of diesel is among 0.2 g/L to 0.25 g/L, the degradation rate can reach more than 80 %. The low initial concentration of diesel has influence on the reaction of the photocatalytic process due to it reduces the amount of photo-generated electron-hole pairs, which leads to the effects on diesel degradation directly. In addition, a large number of diesel-coated photocatalysts cannot convert visible light into ultraviolet light. Hence, too low or too high concentration of diesel may lead to the low degradation rate of diesel.

3.2.4. The effect of pH value on photocatalytic efficiency. Diesel degradation studies at pH values between pH 5 and pH 10 were performed and the results are shown in Fig.3(d).
The result confirms that the photocatalytic efficiency is good when the environmental condition is neutral or weakly alkaline. The best degradation rate can reach 83.80%. Under acidic conditions, the H\(^+\) in water could have an effect on the amount of hydroxyl, which can affect the catalytic oxidation efficiency. In addition, the adsorption properties of the catalyst’s reactants are different under different pH values. The photocatalyst has a great effect when pH value equals 8, which illustrates that the Er\(^{3+}\)-ZnO is suitable for the diesel pollution in seawater (the pH of seawater is about 8).

3.2.5. The effect of concentration of H\(_2\)O\(_2\) on photocatalytic efficiency. A certain amount of oxidant can promote the photocatalytic reaction. Different concentration of H\(_2\)O\(_2\) from 2 mg/L to 12 mg/L are studied in order to find a best result.

The results are shown in Fig.3(e). It clearly proves that the catalyst shows maximum efficiency at the concentration of H\(_2\)O\(_2\) 4 mg/L, the degradation rate is 92.37%. The H\(_2\)O\(_2\) solution has a strong oxidizing property which acts as an electron acceptor to capture the induced electrons formed on the surface of the catalyst and prevent the recombination of electron-hole pairs (e\(^-\)/h\(^+\)). However, it is also used as a scavenger for the formation of hydroxyl radicals and superoxide. It is clear that superoxide and specific hydroxyl radicals act as mineralized active agents for organic compounds \(^{[10]}\). Thus, moderate H\(_2\)O\(_2\) will increase the removal rate, but excess H\(_2\)O\(_2\) will be detrimental to the photocatalytic process.

3.2.6. The effect of illumination time on photocatalytic efficiency. The photocatalytic reaction conducts from 0.5 h to 3.0 h in order to find the fastest growth rate of degradation.

The results are shown in Fig.3(f). The degradation percentage increases as the illumination time increases. It is obvious that the fastest increase in the rate of degradation is between 1.5 and 2. The reason for this is that the oxygen molecules in the water receive electrons, which results in an increase in hydroxyl radical and high active superoxide anion radical. Hydroxyl has strong oxidizing properties, which can oxidize organic pollutants into inorganic matter to achieve the purpose of degradation. However, as the illumination increases, the rate of removal of diesel increases slowly. The residual amount of diesel decreases as the photocatalytic reaction takes place in the mixed solution. After a period of time, the residual amount of diesel reduces the concentration gradient of the diesel oil, which is consistent with the effect of the initial concentration of diesel on the photocatalytic reaction.

4. The Optimization of Photocatalytic Conditions of Er\(^{3+}\)-ZnO

The experiment is based on the different parameters namely dose of catalyst, doping ratio, initial concentration of diesel, pH value, concentration of H\(_2\)O\(_2\); and illumination time to study the interaction of the factors of photocatalysts. Six factors and five levels table was designed and the orthogonal experimental data is shown in Table 1.

The optimization of photocatalytic conditions of Er\(^{3+}\)-ZnO is the following: when the dose of catalysts was 0.6 g/L, doping ratio of catalysts was 10%, initial concentration of diesel was 0.2 g/L, pH value was 8, concentration of H\(_2\)O\(_2\) was 10 mg/L, illumination time was 1 h, the removal rate can reach 99.38%, which is the optimal efficiency. The order of the effect of factors on removal rate is the following: doping ratio> concentration of H\(_2\)O\(_2\)>illumination time> dosage>initial concentration of diesel> pH value. The orthogonal experimental data is shown in Table 1.

### Table 1. Design matrix and experimental results for orthogonal array

| Experiment | Illumination time (h) | Initial concentration of diesel oil (g/L) | Doping ratio (%) | Dosage (g/L) | Concentration of H\(_2\)O\(_2\) (mg/L) | pH value | Removal rate (%) |
|------------|-----------------------|------------------------------------------|-----------------|--------------|--------------------------------------|----------|------------------|
| 1          | 0.5                   | 0.05                                     | 10              | 0.2          | 2                                    | 6        | 94.39            |
| 2          | 0.5                   | 0.10                                     | 30              | 0.8          | 10                                   | 7        | 92.52            |
| 3          | 0.5                   | 0.15                                     | 50              | 0.4          | 8                                    | 8        | 76.32            |
| 4          | 0.5                   | 0.20                                     | 20              | 1.0          | 6                                    | 9        | 90.81            |
| 5          | 0.5                   | 0.25                                     | 40              | 0.6          | 4                                    | 10       | 95.76            |
5. Summary

The \( \text{Er}^{3+}/\text{ZnO} \) composite photocatalyst was made by a co-precipitation method. This experiment used marine oil pollution as the target pollutants, studied the effects of dose of catalysts, doping ratio of catalysts, initial concentration of diesel, pH value, concentration of \( \text{H}_{2}\text{O}_2 \) and illumination time on degradation efficiency of photocatalyst, and concluded the optimization of photocatalytic conditions. Based on the research and study, we can draw the following conclusions:

1) The SEM and XRD characterization shows that the up-conversion material particles appear as a conglomerate with good dispersibility, the average particle size of which is 40.94 nm.

2) The results show that \( \text{Er}^{3+}/\text{ZnO} \) composite photocatalyst can degrade the diesel pollutants in seawater efficiently under the visible light irradiation.

3) The optimized effect exists when the dose of catalysts was 0.6 g/L, doping ratio of catalysts was 10\%, initial concentration of diesel was 0.2 g/L, pH value was 8, concentration of \( \text{H}_{2}\text{O}_2 \) was 10 mg/L and illumination time was 1 h. Under these conditions, the diesel degradation rate can reach 99.38\%.

4) The order of the effect of factors on degradation rate is: doping ratio > concentration of \( \text{H}_{2}\text{O}_2 \) > illumination time > dosage > initial concentration of diesel > pH value.

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