Photocatalytic degradation performance of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ loading on nickel foam

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Abstract. The band structure of TiO$_2$ nanoparticles doped with La$^{3+}$, Y$^{3+}$ and Eu$^{3+}$ rare earth ions, respectively, was calculated by CASTEP in Materials Studio software. La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ nano powder was prepared by sol-gel method and loaded on nickel foam by dropping method. Photocatalytic degradation performances of methyl orange under ultraviolet light and visible light were studied. The result indicates that La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ is constituted by anatase phase which is single and stable, and its average grain size is 8 nm. The metallic ion doping changes the forbidden bandwidth of TiO$_2$ nanoparticles. Its absorption coefficient is enhancement compared with pure TiO$_2$ under visible light and the red shift phenomenon appears. The photocatalytic degradation of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ loading on nickel foam for methyl orange solution is 49% after 60 mins under visible light, which increases 345% compared with pure TiO$_2$.

1. Introduction
Nano-TiO$_2$ has the advantages of non-toxicity, low cost, stable chemical property and high photocatalytic activity. It can catalyze the decomposition of various organic pollutants into small molecules such as H$_2$O and CO$_2$, and has great potential for application in environmental protection. Therefore, nano-TiO$_2$ as an important photocatalyst has become a new hot spot in recent years [1-4]. However, the forbidden bandwidth of anatase TiO$_2$ is relatively large (about 3.2 eV). In principle, it can only absorb UV light with a wavelength of less than 390 nm. The light response range is narrow, the recombination of photogeneration electron and hole is easy, and the photon efficiency is low. These defects limit the practical application and development of nano-TiO$_2$ photocatalytic materials.

Doping is one of the main methods to improve its photocatalytic activity. Because rare earth elements have incomplete 4f orbitals and 5d orbitals, and have good absorption capacity for both ultraviolet light and visible light, many researchers have used rare earth ions doped TiO$_2$ in recent years in order to expand its light response range and improve its photocatalysis activity [5-7]. AnaMuuiz et al [8] prepared La$^{3+}$ doped TiO$_2$ thin films by sol-gel method and found that the addition of La$^{3+}$ inhibited grain growth and slowed down the transformation of TiO$_2$ from anatase to rutile. XuDapeng et al [9] prepared Y$^{3+}$ doped TiO$_2$ nano-powders. The results show that the addition of Y$^{3+}$ significantly improves the photocatalytic activity of TiO$_2$ on methyl orange solution, compared with the pre-doped TiO$_2$ nano-powder increased by 33%.Wang Rufen et al [10] prepared Y$^{3+}$/Eu$^{3+}$ doped nano-TiO$_2$ photocatalyst by sol-gel method. The results show that both Y$^{3+}$ and Eu$^{3+}$ doping inhibit the growth of crystal size and the transition from anatase to rutile phase, while reducing the aggregation of particles. In visible light 2h, the sample degradation rate of phenol reached 53%. At present, the research of
modification of TiO\textsubscript{2} mainly uses single rare-earth ion doping. However, few rare-earth ions co-doped TiO\textsubscript{2} to further improve photocatalytic performance are rarely reported.

Another drawback of the nano-TiO\textsubscript{2} powder used in the catalytic process is that it is easy to be lost during the catalytic process, and is difficult to be recovered. It is not conducive to regeneration and reuse. The loading on-type nano-TiO\textsubscript{2} photocatalyst can solve the problem of separation and recovery. Now the supports are stainless steel, porous ceramics, quartz tube, carbon fiber, glass fiber and so on. However, the combination of these supports and nano-TiO\textsubscript{2} is not good enough. In practical applications, nano-TiO\textsubscript{2} is easy to fall off, which leads to the deterioration of the catalytic effect and limits their practical application. Nickel foam [11-12] is a uniform and firm, large specific surface area, high porosity, low density, high ductility, high thermal conductivity, good light transmittance, easy processing. It is suitable as a carrier for TiO\textsubscript{2}.

Therefore, this article selected nickel foam as support, La\textsuperscript{3+}/Y\textsuperscript{3+}/Eu\textsuperscript{3+} co-doped TiO\textsubscript{2} powders were loaded on it to study the photocatalytic degradation of methyl orange under ultraviolet and visible light.

2. Experiment

2.1. First-principles modeling of La\textsuperscript{3+}/Y\textsuperscript{3+}/Eu\textsuperscript{3+} co-doped TiO\textsubscript{2}

The CASTEP module in Materials Studio 8.0 software was used to calculate the first principles of TiO\textsubscript{2} before and after doping. The TiO\textsubscript{2} anatase model used the parameters in the Materials Studio standard library, the exchange correlation function used the generalized gradient approximation (GCA), and the negative potential function used the PBE gradient correction function. The K-point value was 5x5x2, and the plane wave function cut-off energy was 340 eV. The self-consistent field convergence criterion in the model geometric optimization process was as follows: the total energy change of the system was $\leq 5 \times 10^{-7}$ eV/atom, the energy convergence accuracy was $5 \times 10^{-6}$ eV/atom, the maximum atomic force convergence accuracy was $2 \times 10^{-5}$ eV/Å, the maximum strain was $2 \times 10^{-5}$ GPa. By substituting a Ti atom in the lattice for rare earth elements to simulate doping, all calculations were performed in reciprocal space.

2.2. Preparation of La\textsuperscript{3+}/Y\textsuperscript{3+}/Eu\textsuperscript{3+} co-doped TiO\textsubscript{2} Suspension

Butyl titanate and ethyl alcohol were uniformly mixed in a volume ratio of 1: 2, and 5% by mass fraction of acetylacetone was added as a gel inhibitor to prepare liquid A. The liquid B was prepared by dissolving La\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3} and Eu\textsubscript{2}O\textsubscript{3} in a mass percentage of 1% and a molar ratio of 1: 1: 1 in diluted hydrochloric acid. Then, liquid B was slowly added to liquid A to obtain a sol, and the xerogel formed after drying. The xerogel was heat treated at 500 °C for 2 hours to obtain La\textsuperscript{3+}/Y\textsuperscript{3+}/Eu\textsuperscript{3+} co-doped TiO\textsubscript{2} powder. The powder was ground with an appropriate amount of anhydrous ethanol to obtain a solid content of 20% uniformly dispersed La\textsuperscript{3+}/Y\textsuperscript{3+}/Eu\textsuperscript{3+} doped TiO\textsubscript{2} suspension.

With the above method, a group of pure TiO\textsubscript{2} powders without addition of rare earth oxides and a suspension with a solid content of 20% was prepared.

2.3. Preparation of nickel foam coating

The 50 mmx50 mmx1 mm nickel foam was soaked in acetone by ultrasonic pretreatment to remove the surface oil, and then was soaked in dilute HCl concentration of 5% 10mins, washed with deionized water and dried.

A suitable amount of La\textsuperscript{3+}/Y\textsuperscript{3+}/Eu\textsuperscript{3+} co-doped TiO\textsubscript{2} suspension was repeatedly added dropwise to the upper and bottom surfaces of the nickel foam to obtain a La\textsuperscript{3+}/Y\textsuperscript{3+}/Eu\textsuperscript{3+} co-doped TiO\textsubscript{2} sample.

A series of samples of nickel foam loaded with pure TiO\textsubscript{2} were prepared as the control group by the above method, and the loading was the same as that of La\textsuperscript{3+}/Y\textsuperscript{3+}/Eu\textsuperscript{3+} co-doped TiO\textsubscript{2}.

2.4. Photocatalytic degradation performance test

The 50 mmx50 mmx1 mm nickel foam loaded TiO\textsubscript{2} sample prepared above was put into 100 mL, methyl orange solution with a concentration of 10 mg·L\textsuperscript{-1}. The first 30 mins was away from light to
promote the photocatalyst adsorption equilibrium, and after equilibrium taking some of the solution to test its absorbance. The solution was then placed on a 300 W xenon lamp and irradiated with ultraviolet light through a filter simulating ultraviolet light for 1 h, sampled every 10 mins and tested for absorbance. The UV filter was then changed to a UV cut filter to simulate visible light and the experiment was repeated.

3. Experimental results and discussion

3.1. First Principles Calculation of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$

The first-principles calculations of the band structure of anatase TiO$_2$ (Figure 1) were performed using Materials Studio (at the Fermi level of 0). It can be seen from Figure 1 that undoped TiO$_2$ has two forbidden bands with a width of 2.265 eV (experimental value is about 3.2 eV) and 11.293 eV. Among them, only a forbidden bandwidth of 2.265 eV can trigger an electronic transition, so we only discuss the change of the forbidden band for TiO$_2$ before and after doping. There is a certain error between the experimental value and the simulated value, which is due to the fact that the exchange-correlation function under the GGA cannot completely reflect the real multi-electron interaction [13].

However, as an effective approximation method, the relative value of the result is still accurate. As can be seen from the density distribution in Figure 2, the bandgap of TiO$_2$ decreases to 1.99 eV after doping with La$^{3+}$, and the band gap of TiO$_2$ decreases to 2.13 eV after doped with Y$^{3+}$. The band gap of TiO$_2$ after doping with Eu$^{3+}$ is almost completely disappeared. There were only two narrow bandgaps of 0.231 eV and 0.434 eV in the 0-2 eV interval.

![Figure 1. Band structure in Pure TiO$_2$ and RE (La$^{3+}$, Y$^{3+}$, Eu$^{3+}$) doped TiO$_2$](image)

Figure 2 shows the state density of TiO$_2$ before and after doping rare earth elements calculated by the first principle. It can be seen that the energy level splitting occurs in Ti-3d after La$^{3+}$ and Y$^{3+}$ doping, which is the main reason for the decrease of the forbidden width of TiO$_2$. The extra impurity levels (La-5p, La-5d and Y- 4p, Y–4d) do not directly affect the forbidden width. After doped Eu$^{3+}$, it has little effect on the O-2p and Ti-3d energy levels. The extra Eu-4f energy level almost completely covers the band gap of TiO$_2$, which is the main reason for the rapid decrease of the band gap of TiO$_2$ after doping.
3.2. XRD characterization of Nano-TiO$_2$ before and after doping with rare earth elements

Figure 3 shows the XRD patterns of pure TiO$_2$ and La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$. Both TiO$_2$ characteristic peaks are at 2$\theta$ = 25.36 $^\circ$, 30.08 $^\circ$, 48.24 $^\circ$, 54.9 $^\circ$ and 62.78 $^\circ$. Comparing with the standard PDF spectra, the two TiO$_2$ phase structures obtained in this experiment are composed of a single, stable anatase phase with no other phase components. The diffraction peak of TiO$_2$ after La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ doping is obviously broadened, which indicates that after La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ doped, TiO$_2$ crystallites become smaller.
The lattice constants of Pure TiO$_2$ and La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ and the grain sizes calculated by the Scherrer formula are shown in Table 1. It can be seen that the lattice constant of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ slightly increases due to the substitution of Ti ions by the larger radius rare earth ions, and the grain size is obviously reduced from 17 nm to 8 nm, because the addition of rare earth elements inhibits the crystal growth.

### Table 1 Lattice constants and average grain sizes of Pure TiO$_2$ and La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$

| sample                      | Lattice constants /nm | average grain sizes /nm |
|-----------------------------|-----------------------|-------------------------|
| Pure TiO$_2$                | a=3.78117, c=9.50427  | 17                      |
| La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ | a=3.79328, c=9.51758 | 8                       |

3.3. UV-Vis light absorption spectroanalysis of nano-TiO$_2$ before and after rare earth doping

Figure 4 shows the UV-Vis absorption spectra of Pure TiO$_2$ and La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ in a detection range of 200-700 nm. As can be seen from Figure 4, the absorption coefficient of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ is lower than that of pure TiO$_2$ in the ultraviolet region of 200-350 nm, but its absorption coefficient in the ultraviolet region of 350-390 nm and the visible region of 390-700 nm is higher than pure TiO$_2$, red shift phenomenon occurs. This is because the doping rare earth ions change the band structure of TiO$_2$. The impurity level is introduced between the top of TiO$_2$ valence band and the bottom of conduction band, which makes the forbidden band width smaller and electrons have different forms of transition under different wavelength illumination. Under 200-350 nm ultraviolet light, the absorption coefficient of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ doped TiO$_2$ is smaller than pure TiO$_2$, which may be due to the easy recombination of the generated photoelectrons and holes. Under 350-700 nm ultraviolet light, the electron can transition to the lowest level with a higher energy level of conduction band, thereby enhancing the absorption of ultraviolet light. Under the visible light of 390-700 nm, the electrons can first transition to the impurity level with lower energy and then transition to the conduction band to improve the absorption of visible light.
3.4. TEM and SEM characterization of rare earth elements co-doped TiO$_2$

Figure 5 shows the TEM morphology (a) and electron diffraction pattern (b) of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$. From Figure 5(a), it can be seen that the grain size of the rare earth-doped nano-TiO$_2$ is about 10 nm, which is similar to the XRD calculated average grain size of 8 nm. In addition, there is a small amount of agglomeration. This is because the surface of the nano-scale crystal lacks adjacent coordination atoms, has a higher surface energy, and therefore easily agglomerates with each other. Figure 5(b) shows that the doped nano-TiO$_2$ contains TiO$_2$, La$_2$O$_3$, Y$_2$O$_3$ and Eu$_2$O$_3$ these components. Based on the XRD analysis of the sample, we believe that only some of the La, Y, and Eu ions doping into the TiO$_2$ lattice replace the Ti ions, and the other forms a La$_2$O$_3$/Y$_2$O$_3$/Eu$_2$O$_3$/TiO$_2$ complex.

Figure 6 shows the SEM of TiO$_2$ loading on Nickel foam. Figure 6 (a) shows that nickel foam support presents a 200 μm pore structure with a large specific surface area. The nanometer powders of pure TiO$_2$ in Figure 6 (b) and rare earth doped TiO$_2$ in Figure 6 (c) are distributed on the surface of nickel foam, and the agglomeration is more serious, but the distribution of the latter is more uniform. From table 1, we know that the grain size of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ doped TiO$_2$ is only 8 nm, much smaller than that of 17 nm pure TiO$_2$, and the specific surface area is larger. Therefore, its adhesion with foam nickel is larger, which is beneficial to reduce the loss of catalyst in its use and regeneration process.
3.5. Photocatalytic degradation of nano-TiO$_2$ before and after rare earth doped

Catalytic degradation curves of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ loading on nickel foam under ultra violet light and visible light is shown in Figure 7. It can be seen from Figure 7 that under the visible light, the catalytic activity of pure TiO$_2$ loading on nickel foam is very poor. After 60 minutes, the catalytic degradation rate of methyl orange solution is only 11%. But the catalytic effect of rare earth doped sample has greatly improved compared with single rare earth doped sample, and the catalytic degradation rate for methyl orange solution is 49 % after 60 mins under visible light, which increases 345% compared with pure TiO$_2$.

The main reason is that the doping of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ expands the photoreaction range of TiO$_2$, and the lower energy of visible light can also stimulate the photogenerated electrons, thereby increasing the catalytic degradation rate.

After 60 mins under UV light, pure TiO$_2$ loading on nickel foam has a good catalytic effect, and the catalytic degradation rate of methyl orange solution reaches 77%. After doping rare earth, the catalytic effect of TiO$_2$ in methyl orange solution is slightly lower under ultraviolet light (60 mins degradation rate reaches 58%). The reason for this is that the photogenerated electron-hole pairs generated under the ultraviolet light after the rare earth doping are easy to recombine, so that the overall low absorption coefficient of the ultraviolet light leads to the deterioration of the catalytic effect.

The mass of the pure TiO$_2$ and La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped nano-TiO$_2$ samples before and after catalysis was tested, and the loss of both samples was found to be within 5%, which proved that the combination between the carrier and the catalyst was better. Therefore, TiO$_2$ loading on nickel foam...
can solve the defects caused by the direct use of TiO$_2$ in the photocatalytic process, such as easy loss, difficult recovery, unfavorable for regeneration and reuse.

![Catalytic degradation curves of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ loading on nickel foam under ultra violet light and visible light](image)

**Figure 7.** Catalytic degradation curves of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ loading on nickel foam under ultra violet light and visible light

### 4. Conclusions

- a) Three kinds of rare earth La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ powders are prepared by sol-gel method consist of a single, stable anatase phase with an average grain size of 8 nm.
- b) La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ rare-earth doped TiO$_2$ are produced additional impurity levels, which lead to a decrease in the band gap of TiO$_2$ and increase the absorption coefficient of TiO$_2$ in the visible region, resulting in a redshift phenomenon.
- c) The photocatalytic degradation of La$^{3+}$/Y$^{3+}$/Eu$^{3+}$ co-doped TiO$_2$ loading on nickel foam for methyl orange solution is 49% after 60 mins under visible light, which increases 345% compared with pure TiO$_2$. After 60 mins under UV irradiation, the catalytic degradation rate of methyl orange solution reaches 58%, slightly lower than that before doping.

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