Preparation and properties of ice cream flowers Ce/TiO\textsubscript{2} photocatalyst

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Abstract TiO\textsubscript{2} composite photocatalysts with doping amounts of Ce (0.5\%Ce/ TiO\textsubscript{2}, 1\%Ce/ TiO\textsubscript{2}, 2\%Ce/ TiO\textsubscript{2}, 3\%Ce/ TiO\textsubscript{2} and 5\%Ce/ TiO\textsubscript{2}) were synthesized via a sol-gel method. The structure and morphology of the prepared composites were characterized by XRD, SEM, DRS, XPS. At the same time, the photocatalytic effect of the composite on rhodamine B (RhB) solution under simulated visible light irradiation was explored. The results indicated that the crystal of powder catalyst was anatase type TiO\textsubscript{2}, and the directional aggregation of Ce/TiO\textsubscript{2} composite photocatalyst showed ice cream flowers-shaped structure. The photocatalysis activity was the best when Ce doping amounts were 3\%. The degradation rate of RhB was 96\% in 120 min, which was 50\% higher than pure TiO\textsubscript{2}. Hydroxyl radical (\textbullet OH) played a leading role in the whole photodegradation reaction system, and its contribution rate was about 66.4\%.

1. Introduction
With the rapid development of industry, environmental pollutants are increasing, and the treatment of dye wastewater has become the main problem\cite{1}. At present, the more practical dye wastewater treatment methods mainly include photocatalysis, electrolysis, chemical oxidation and so on\cite{2}. Among them, photocatalysis has attracted more and more attention because of its good catalytic efficiency, non-toxic, cheap and strong stability. Among most semiconductor catalysts, TiO\textsubscript{2} is considered as a promising green environmental protection photocatalyst.

TiO\textsubscript{2} has three crystal forms such as anatase, brookite and rutile, among which anatase TiO\textsubscript{2} has the best photocatalytic performance\cite{4}. Grabowska et al have found that when metal ions are doped, the sites of Ti\textsuperscript{4+} in the TiO\textsubscript{2} crystal lattice will be occupied by the doped ions, which effectively reduces the band gap width of TiO\textsubscript{2} and prevents the recombination of photogenerated electron hole pairs\cite{5-6}. Therefore, metal doping is a very useful TiO\textsubscript{2} modification method for improving the overall performance of the catalyst.

In the present work, anatase TiO\textsubscript{2} and Ce with good oxygen storage capacity were prepared by a sol-gel method, and Ce/TiO\textsubscript{2} composite photocatalysts with different doping amounts were prepared. Meanwhile RhB was used as the target degradation product to test the catalytic performance of the composite photo-catalysts. SEM, XRD, XPS and DRS were used to characterize the structure and properties of the composites, so as to explore the application potential of photocatalysis in dye degradation and provide reference for the research of dye degradation.

2. Experiment section

2.1 Materials
Tetraisopropyl titanate, glacial acetic acid, cerium nitrate hexahydrate, RhB, isopropanol (IPA), potassium dichromate, disodium ethylenediaminetetraacetic acid (EDTA-2Na) were collected from

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Shanghai Jingchun Biochemical Technology Co, Ltd. All the above reagents were analytically pure, it can be used directly without further purification.

2.2 Synthesis of photocatalyst
In the experiment, Ce/TiO$_2$ with different mass fraction was prepared by sol-gel [7]. Taking 1% preparation method as an example, 2.5ml TIPT was added into 4.3ml glacial acetic acid and stirred vigorously in ice bath for 30min to form sol. After that, 170 mg cerium nitrate hexahydrate solution (15ml) was slowly added to the sol system under sufficient stirring conditions. Then the mixture was treated with ultrasound at 0°C for 20 min and stirred for 2h. The mixture was placed at room temperature and dark for 24h. The mixture was placed in the oven and gelatinized at 76°Cfor 12h. The gel was placed in the oven and dried at 120°C for 3h. The dry gel was ground into a fine powder with mortar, and calcined at 550°C for 3h. The initial samples were washed five times with distilled water and absolute alcohol, centrifugated and dried. Finally, it was calcined at 120°C for 5h at the oven, then 1% Ce doped TiO$_2$ was obtained. The catalysts with different Ce doping amounts (0, 0.5%, 1%, 3%, 5%) were prepared by the above method.

2.3 Photocatalytic activity study
50 ml RhB (10 mg/L) and 25 mg composite catalysts were added into the beaker. The catalyst was evenly distributed in RhB solution by ultrasound for 10 min. The solution was stirred for 30 min to establish the adsorption desorption equilibrium, and then the light experiment was carried out. A 300 W xenon lamp(λ>420 nm) was used as the visible light source. The distance between the light source and the liquid level was about 14 cm. Under the condition of magnetic stirring, samples were taken every 20 min. After filtration by microporous filter membrane, the absorbance was determined by ultraviolet visible spectrophotometer (λ$_{max}$=554 nm). And the removal rate of RhB was calculated as η.

$$\text{Removal rate } \eta\% = \frac{(A_0-A_t)\times100\%}{A_0}$$

In formula (1), $A_0$ is the initial absorbance and $A_t$ is the absorbance of the supernatant for t minutes.

2.4 Characterization techniques
The phase of the sample was analyzed using a X-ray powder diffractometer (XRD-600, Shimadzu, Japan), irradiated with a Cu-Kα target (λ=1.5418 Å) at a scanning speed of 4° min$^{-1}$ and a scan range of 10°–80°. SEM was used to analyze the microstructure of the samples (s-4800). DRS was used to test the light response characteristics of the catalyst(HITACHIF-7000 fluorescent spectrophotometer of Hitachi Type, Japan). XPS was used to measure the energy of photoelectron. The energy spectrum, photoelectron kinetic energy and relative intensity of each element were obtained, and the valence of each element was analyzed (Axis Ultra DLD multifunctional X-ray photoelectron spectrometer).

3. Results and discussion

3.1 XRD study
The crystal structure of Ce/TiO$_2$ with different doping amounts was analyzed by XRD and the results are shown in Fig.1. From the spectrum of pure TiO$_2$, it is observed that the characteristic peaks at 25.4°, 37.9°, 48.0°, 53.9°, 55.2°, 62.7° of 2θ correspond to the anatase phase of TiO$_2$ (JCPDS No.21-1272). It indicates that the structure of the sample is consistent with anatase TiO$_2$, which confirms anatase TiO$_2$ is successfully prepared [8]. Among the three crystal forms of TiO$_2$, anatase has the best photocatalytic activity. Compared with the characteristic spectra of different Ce doping amounts, the significant absorption peaks are basically the same (The characteristic peak of Ti is in the horizontal coordinate 25°). The diffraction peaks of some positions in the composite spectrum disappear, the reason may be the metal is incorporated into the TiO$_2$ lattice by filling, or the metal replaces Ti atom in the lattice for doping [7]. However, the radius of Ce$^{3+}$ is larger than that of Ti$^{2+}$, most of Ce$^{3+}$ cannot enter into the lattice of TiO$_2$, so there is no change in the lattice. CeO$_2$ is dispersed on TiO$_2$ surface instead, but no crystal diffraction peak of CeO$_2$ is found in the Fig.1, indicating that active components are highly
dispersed on TiO$_2$ carriers or distributed in amorphous form, which is conducive to maintaining a larger specific surface area and more active sites [9].

![XRD patterns of different doping samples](image)

**Fig.1.** XRD patterns of different doping samples

### 3.2 SEM study

The morphology and crystal characteristics of pure TiO$_2$ and 3% Ce/TiO$_2$ were observed by SEM and the results are shown in Fig. 2. From the comparison of Fig. 2(a) and (b), it is observed that the surface structure of pure TiO$_2$ sample is compact and smooth, but it presents irregular shape and uneven size, most of which are tiny blocks, and the particle size is about 1.25μm. A small part of TiO$_2$ is agglomerated, and the shape of TiO$_2$ is spherical nano clusters, and it has the wrinkled, concave and convex surface[10]. From Fig. 2(d), it is observed that Ce/TiO$_2$ structure is more uniform after incorporating into Ce element, and the overall distribution is ice cream flower type. The main reason for the formation of this morphological feature is the high viscosity sol during sample preparation[11]. At the same time, CeO$_2$ is highly dispersed on the surface, which increases the specific surface area of the composite and helps to improve the photocatalytic effect [12]. This characteristic further verifies the conclusion of XRD pattern.

![SEM of pure TiO$_2$ and 3% Ce/TiO$_2$](image)

**Fig.2.** SEM of pure TiO$_2$ and 3% Ce/TiO$_2$

### 3.3 DRS study

The optical absorption properties of Ce/TiO$_2$ with different doping amounts are measured by DRS and the results are shown in Fig 3. From Fig. 3 (a), it is observed that there is no obvious difference between the absorption property of pure TiO$_2$ and Ce doped composites in the ultraviolet region of 260-350nm. In the visible region of 400~700nm, the absorption range of Ce/TiO$_2$ is greatly improved. This means that when metal doping photocatalyst, it will be more easily excited, and more electron hole pairs will be generated, thus improving the photocatalytic activity of the catalyst itself [13]. The absorption edge
of pure TiO$_2$ is found at 430 nm. When the doping amount is 3%, the visible light absorption threshold of the composite catalyst is widened to the maximum extent. The band gap width of Ce/TiO$_2$ can be calculated according to the optical absorption band equation. The calculation method is shown in equation (2).

$$a(hv)=A(hv-E_g)^n$$  \hspace{1cm} (2)

In formula (2), $a$ is the absorption coefficient, $h$ is the Planck constant, $v$ is the absorption frequency, $E_g$ is the value of band gap, $A$ is a constant.

When the catalyst is a direct semiconductor, $n = 2$. When it is an indirect semiconductor, $n = 0.5$. For a direct band gap semiconductor, $n$ is equal to 2.$^{[14]}$. By converting the DRS curves of different samples, the corresponding relationship curves between the $(a(hv))^2$ and $(hv)$ are shown in Fig.3 (b). When Ce doping amount is 0%, 0.5%, 1%, 3% and 5%, the band gaps of the samples are respectively 2.87 eV, 2.84 eV, 3.2 eV, 2.4 eV and 2.7 eV. The photocatalytic activity is largely determined by the band gap of semiconductor photocatalyst. The narrower the band gap is, the higher the photocatalytic activity is.

From the data, it is intuitively observed that the band gap width of 3% Ce/TiO$_2$ is 2.4 eV, which is significantly narrower than pure TiO$_2$ (3.2 eV). Among different doping amounts, 3% Ce/TiO$_2$ has higher utilization efficiency of visible light and stronger response to visible spectrum. The significant decrease of band gap width further proves that the formation of Ti-O-Ce covalent bond is due to the site of Ti$^{4+}$ in TiO$_2$ lattice is occupied by doped Ce ion.$^{[15]}$.

![Fig.3. UV-VIS plots of Ce/TiO$_2$ powders prepared with different Ce doping amounts](image)

3.4 X-ray photoelectron spectroscopy (XPS)
In order to analyze and study the structural composition and specific chemical valence of various main chemical elements of the composite photocatalyst, XPS experimental characterization was shows the XPS spectra of pure TiO$_2$ and 3% Ce / TiO$_2$. The C1s peak at the binding energy of 284.81 eV is derived from the standard determination method of the instrument, which is used for correction. Compared with TiO$_2$, a new characteristic peak of 3% Ce/TiO$_2$ appears at 884.01 eV, which is attributed to Ce element, indicating that Ce is successfully incorporated into TiO$_2$.$^{[16]}$. Fig.4(b–c) respectively shows the high resolution XPS spectra of Ti$_2$p, C1s and Ce3d. However, due to the
different environment of elements, there will be subtle differences in binding energy, which is called chemical shift [17]. Fig. 4 (b) shows the high-resolution XPS spectra of Ti2p of TiO2 and 3% Ce / TiO2. Two photoelectron peaks of Ti2p1/2 and Ti2p3/2 appear near 464.2 and 458.6eV in both samples [18]. Compared with pure TiO2, Ti2p3/2 and Ti2p1/2 of 3% Ce/TiO2 shift to the direction of higher binding energy by 0.4eV and 0.34eV respectively, indicating the decrease of electron cloud density around Ti atom. The characteristic peak of Ce3d in Fig. 4(c) is composed of two sub energy levels of 884.43eV and 903.92eV in the low binding energy region. The corresponding ion final respectively states in this group of binding energy are Ce4+ 3d3/2 and Ce4+ 3d5/2, indicating that Ce in the composite exists in the valence state of Ce4+ [19].

3.5 Photocatalytic activity study
The photocatalytic activity of Ce/TiO2 is verified by degradation of RhB solution. Fig.5 shows the photocatalytic degradation curves of RhB by a series of samples with different Ce doping amounts. Compared with pure TiO2, the degradation effect of RhB solution is obviously enhanced after doping Ce. Under the irradiation of xenon lamp, the degradation efficiency of RhB by pure TiO2 is 46%. TiO2 has a certain photocatalytic effect. When the doping amount of Ce increases, the degradation efficiency increases in varying degrees. When the doping amounts are 0.5%, 1%, 3% and 5%, the degradation efficiency are 69%, 88%, 96% and 89% respectively. When the Ce doping amount is 3%, the composite catalyst has the best degradation effect on RhB solution. When the doping amount continues to increase, the degradation rate will slightly decrease, which may be due to the excess CeO2 covering the active sites on the catalyst surface, thus reducing the activity of the catalyst.
3.6 Photocatalytic degradation mechanism

In the experiment, IPA (1mmol/L), EDTA-2Na (1mmol/L) and K$_2$Cr$_2$O$_7$ (1mmol/L) are added to selectively capture hydroxyl radical (·OH), photogenerated hole (h$^+$) and electron (e$^-$) generated in the reaction system respectively to study the reaction mechanism of Ce/TiO$_2$ photocatalysis of RhB.

As shown in Fig.6(a), when EDTA-2Na, K$_2$Cr$_2$O$_7$ and IPA are added to the reaction system, the degradation rate of RhB is affected to varying degrees, and decreases to 93%, 75% and 52% respectively. Fig.6(b) shows the pseudo-first-order kinetic curve of RhB degradation by 3% Ce/TiO$_2$ with different capture agents. The reaction rate constant k of 3% Ce/TiO$_2$ + EDTA-2Na is the highest, which is 0.03152min$^{-1}$, and the reaction rate constant k of 3% Ce/TiO$_2$ + IPA is the lowest, which is about 0.01246min$^{-1}$. The k value is in the order of 3% Ce/TiO$_2$ + EDTA-2Na > 3% Ce/TiO$_2$ + K$_2$Cr$_2$O$_7$ > 3% Ce/TiO$_2$ + IPA, which is consistent with the experimental results of free radical capture.

In order to further understand the influence of active species on the reaction system, we explore the contribution of active species involved in the reaction. Considering the possible reaction of the system, the reaction equation of the total degradation rate is set as follows.

\[
(dC_{RhB}/dt)_{total} = (r_{h^+} + r_{e^-} + r_{OH} + r_{other}) = k_{h^+}C_{RhB} + k_eC_{RhB} + k_{OH}C_{RhB} + k_{other}C_{RhB} = k_{total}C_{RhB} \tag{3}
\]

In formula (3), $r_{h^+}$, $r_{e^-}$, and $r_{OH}$ represent the degradation rates of RhB by h$^+$, e$^-$ and ·OH produced by the catalyst under light irradiation respectively, and other represents the degradation rates of RhB by other active substances produced by the system. $k_{h^+}$, $k_e$, $k_{OH}$, and $k_{other}$ represent the corresponding quasi first order reaction rate constants respectively. Then the quasi first order reaction rate constant of ·OH is calculated as $k_{OH} = k_{total} - k_{h^+}$. The quasi first order reaction rate constant of h$^+$ is calculated as $k_{h^+} = k_{total} - k_3$. The quasi first order reaction rate constant of e$^-$ is calculated as $k_e = k_{total} - k_3$. The calculated data according to the experimental results are shown in Table 1.

| min$^{-1}$ | k$_{total}$ | k$_{h^+}$ | k$_e$ | k$_{OH}$ | k$_{other}$ |
|-----------|-------------|-----------|-------|-------|-------------|
| RhB       | 0.03712     | 0.0056    | 0.00669 | 0.02466 | 0.00017     |

Then we draw a pie chart of the contribution rate of each active species in the reaction system according to the calculated data, which makes it more intuitive. As shown in Fig.6(c), the contribution rates of h$^+$, ·OH and e$^-$ in the whole photocatalytic degradation reaction system are 15%, 66.4% and 18% respectively. The contribution rate of other active species was 0.6%. According to the above results, in the 3% Ce/TiO$_2$ photocatalytic degradation of RhB reaction system, active species such as ·OH, e$^-$, h$^+$ will be generated, among which ·OH plays a leading role in the reaction process, and the order of importance of the three species is h$^+$<e$^-$<·OH.

Based on the above experimental results and previous reports, in order to further explore the reaction mechanism of photocatalytic degradation system, the band gap energies of valence band (VB) and conduction band (CB) can be estimated by the following equation,
\[ E_{VB} = X - E_e + \frac{1}{2} E_g \]
\[ E_{CB} = E_{VB} - E_g \]

In formula (4), \( E_{VB} \) is the VB band edge position, \( E_{CB} \) is the CB band edge position, \( X \) is the average electronegativity of the semiconductor (\( X_{TiO_2} = 5.81 \)), \( E_e \) is the free electron energy based on hydrogen (\( E_e = 4.5 \) eV), and \( E_g \) is the band gap energy of the semiconductor. The results of DRS show that the \( E_g \) of TiO\(_2\) is 2.87 eV. According to the above equation, the CB value of TiO\(_2\) is -0.125 eV and the VB value is +2.745 eV. Fig. 7 shows the approximate location of both. When Ce\(^{4+}\) contacts with the surface of TiO\(_2\) catalyst, ·OH is transferred from the semiconductor with higher fermi level to the Ce\(^{4+}\) surface with lower fermi level. More and more ·OH accumulates on the Ce\(^{4+}\) surface and increases its fermi level until it is the same as the fermi level of the semiconductor, thus forming Schottky barrier\([20,21]\). This barrier can be used as an effective trap for capturing ·OH and effectively separating ·OH and \( h^+ \), the activity of photocatalyst is further improved. Then ·OH will move to the surface of TiO\(_2\) and react with the adsorbed O\(_2\) and H\(_2\)O to form OH and ·O\(_2^-\), both of which have high oxidation ability and can react directly with the target pollutants.

![Fig.6. Photocatalytic degradation of RhB by samples after addition of capture agent, quasi first order kinetic curve and contribution of each active species](image)

![Fig.7. Schematic diagram of the reaction mechanism of Ce/TiO\(_2\) photocatalytic degradation of RhB](image)
4. Conclusions
Ce/TiO$_2$ composite photocatalyst doped with different molar amounts of Ce was prepared by sol-gel method. The doping of Ce element introduced new impurity level, promoted the effective separation of photoelectron hole pairs, and further enhanced the photocatalytic activity of the composites. When the doping amount of Ce is 3%, the photocatalytic activity of Ce/TiO$_2$ is the highest. After 120 min, the degradation rate of RhB reaches 96%, which is about 50% higher than pure TiO$_2$. In the whole degradation system, $e^-$, $h^+$ and ·OH are the main active species to participate in the photocatalytic reaction, in which ·OH plays a leading role, and the contribution rate is about 66.4%.

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