# Research and Mechanism of Catalytic Degradation of Cefaclor by Platinum Titanium Dioxide Photocatalyst

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**Abstract.** With the global economy and population growth, the misuse of antibiotics in aquaculture has led to a growing problem of water pollution. In this paper, titanium dioxide ($TiO_2$) was used as a catalyst and platinum was added to prepare an efficient photocatalyst for the degradation of the typical antibiotic cefaclor by photocatalysis. $TiO_2$ and Pt-$TiO_2$ nanoparticles were experimentally prepared, characterized by XRD and other means, and the photocatalytic properties were studied. The results showed that the Pt-$TiO_2$ photocatalyst was successfully prepared, with a smaller bandwidth, lower energy photons and higher photocatalytic activity. This study provides a theoretical and practical basis for solving the problem of antibiotic contamination in aquaculture.

**Keywords:** Photocatalysis, cefaclor, antibiotic pollution, XRD, platinum.

## 1. Introduction

With the industrialization and fast development of economy globally, the population growing rapidly since 1960, from 3 billion in the early 1960s, and reach to 8.1 billion in 2025. Therefore, the human requirements for food have increased significantly, which has also promoted the development of aquaculture [1]. One notable area is aquaculture, which put food and drugs containing chemicals directly into the water typically, caused a great deal of water pollution due to accumulation of antibiotics and toxicity to aquatic fauna and flora [2-4]. The resulting environmental contamination using antibiotics in a wide range of human activities has been receiving special attention in recent years [5]. Antibiotics, as antimicrobial agents, have substantially transformed modern medicine, saved countless lives, and prolonged life expectancy [6]. Originally, these pharmaceuticals were used to curve bacterial diseases during aquaculture process [7]. However, the lack of related law caused drug abuse, which makes naturally indecomposable chemical compounds into hydrosphere. If antibiotics persist for a long time, they can lead to toxicity and drug resistance. For example, scientists Dong etal. found that tetracyline exposure induced the breakage of DNA in earthworms, changing enzymatic activity [8].

$TiO_2$ was widely used in photocatalysis industry due to its advantages such as its low cost and stability. While its photogenerated carriers have a high recombination rate and the light response range is narrow, it is necessary to improve catalysis material through adding some specific metal.

Based on the background of the misuse of antibiotics in aquaculture, government and related companies pay more attention to deal with the pollution of antibiotic medications. This article aims to probe into the degradation of a typical antibiotic named Cefaclor, through photocatalysis process using $TiO_2$ and platinum as catalytic agent.

The catalytic mechanism of tubular catalysis will be discussed, explaining the impact of adding metal platinum in this experiment, which will make the related reaction more efficient. We also focused on putting experiment results into real application, exploring which is the best material to use and which is the most efficient and feasible method.

## 2. Methods

### 2.1. Experiment materials

Tetrabutyl titanate (TBOT), ethyl alcohol, titanium dioxide ($TiO_2$), sodium hydroxide (NaOH), Chloroplatinic acid hexahydrate ($H_2PtCl_6·6H_2O$), sodium borohydride ($NaBH_4$), cefaclor solution. All of them were purchased from Sigma-Aldrich. All chemicals and reagents were used as received.

### 2.2. Experimental instruments

Drying oven, xenon lamp, centrifugal machine, UV-Vis spectroscopy absorption spectroscopy (DRS), X-ray diffraction spectroscopy (XRD).

### 2.3. Preparation of silica nanoparticles

Under magnetic stirring, slowly add 25mL of ethanol solution dissolved with 3mL of tetrabutyl titanate (TBOT) to 50mL of ethanol solution. Subsequently, 25mL of ethanol containing 3mL of ammonia was dropped into the mixture. After falling, the resulting solution was stirred at 60℃ for 2 hours, followed by 1.5 hours of reflux. After reflux is complete, place the solution again at 60℃ and stir for 1.5 hours. After agitation, the solution is filtered and the filter residue is washed sequentially with ethanol and deionized water. Finally, the washed filter residue is dried in a vacuum at 60℃ for 10 hours to obtain $TiO_2$ nanoparticles.

### 2.4. Preparation of Pt-$TiO_2$ nanoparticles

Disperse 1.0 g of $TiO_2$ in 100 mL of deionized water and stir well to form a homogeneous suspension. Subsequently, a certain amount of $H_2PtCl_6·6H_2O$ solution was weighed according to the Pt loading of 0.5wt% and slowly added to the suspension. The pH of the mixture was then adjusted to the range of 9.0-10.0 using a NaOH solution at a concentration of 0.25 M, and stirring continuously for 2 hours during the process to ensure that the reaction was fully performed. After stirring is complete, quickly add 20 mL of $NaBH_4$ solution at a concentration of 0.2 M to the beaker and continue stirring for 2 hours to complete the reaction. At the end of the reaction, the solution is filtered, the precipitate is collected, and the pellet is washed several times with deionized water until residual $Na^+$ and $Cl^-$ are completely removed. After annealing at 180 degrees Celsius, one hour. Finally, the annealed solution was centrifuged to obtain a precipitate, placed in an oven at 60℃ for 24 hours, and removed after drying to obtain Pt-$TiO_2$.

### 2.5. Evaluation of photocatalytic performance

The photocatalytic activity of the prepared nanocomposite photocatalyst was studied using cefixime as a model antibiotic. Prepare a 0.03 mM concentration of cefixime solution (80 mL), add 80 mg of Pt-$TiO_2$ photocatalyst, and stir the mixture under light. After every 30 min, 5mL of solution was taken, centrifuged and the spectra of cefixime at λmax=286 nm were studied using a UV-Vis spectrophotometer to analyze its degradation. In contrast, photolysis was also studied under the same conditions under light in the absence of a catalyst. The percentage of degradation is calculated using equation (1):

$$\%D = \frac{A_0 - A_t}{A_t} \times 100 \tag{1}$$

Where $A_0$ is the absorbance at 0 min and $A_t$ is the absorbance after t min.

## 3. Results and discussions

### 3.1. Characterization results of photocatalysts

XRD determines the structure and composition of crystals by measuring the diffraction intensity of X-rays at different angles.

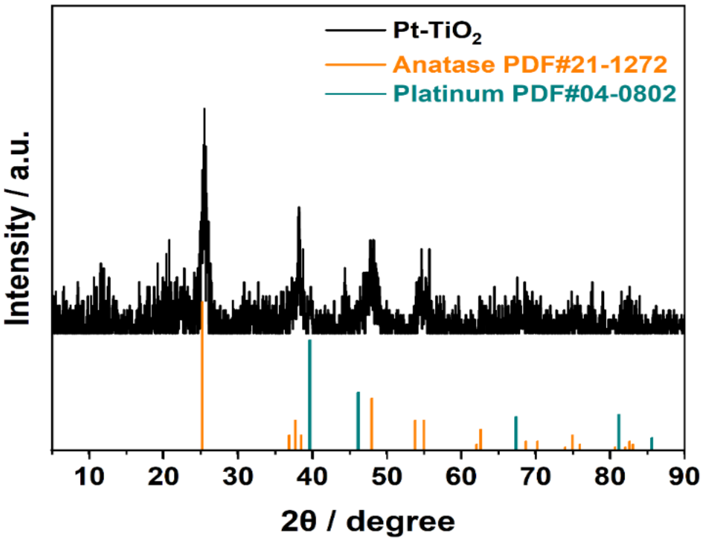

**Fig 1.** The XRD spectrum of Pt-TiO$_2$.

As illustrated in Fig. 1, the orange line represents the Anatase phase, a well - known crystalline form of titanium dioxide, while the green line corresponds to the diffraction pattern of Platinum. The black curve labeled as TiO$_2$ in the X - ray diffraction (XRD) spectrum exhibits a sharp and prominent diffraction peak precisely at the 2θ value that aligns with the characteristic diffraction peak of Anatase. This specific peak position and intensity are indicative of the presence of titanium dioxide in the sample, as the diffraction pattern is a direct result of the periodic arrangement of atoms within the Anatase crystal lattice. According to the principles of XRD, when X - rays interact with the ordered atomic structure of Anatase, constructive interference occurs at specific angles, leading to the formation of these characteristic peaks.

Similarly, the black curve denoted as Pt-TiO$_2$ also displays a distinct diffraction peak at the characteristic 2θ value associated with platinum. This peak's appearance suggests the presence of platinum in the sample. The presence of both the characteristic diffraction peaks of titanium dioxide and platinum in the XRD spectrum of the Pt-TiO$_2$ sample provides evidence for the successful synthesis of the Pt-TiO$_2$ photocatalyst. This result not only confirms the incorporation of platinum into the TiO$_2$ matrix but also implies that the synthesis process was able to maintain the characteristic crystal structures of both components, which is crucial for the photocatalytic activity of the Pt-TiO$_2$ material.

### 3.2. Photocatalytic degradation of cefaclor

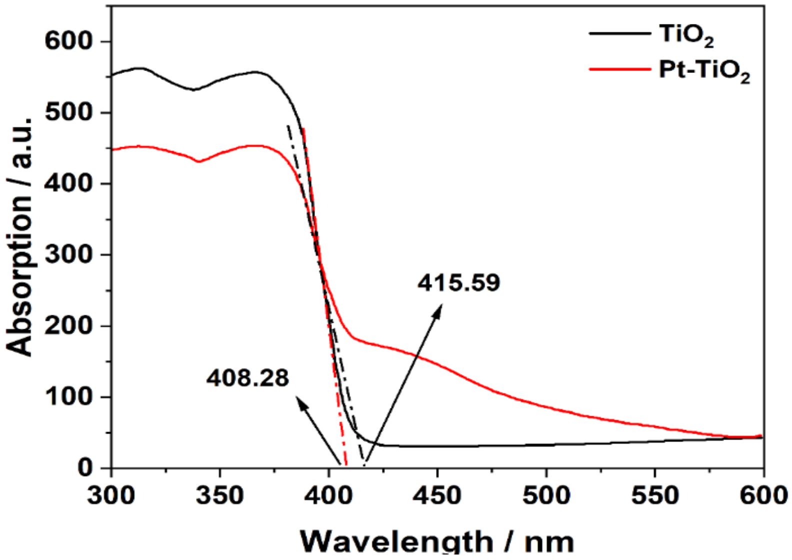

**Fig 2.** DRS spectrum of Pt-TiO$_2$ and TiO$_2$.

As depicted in Fig. 2, the bandwidths of the two materials, namely $TiO_2$ and Pt-$TiO_2$, can be determined through a precise calculation process. The formula $E = 1240/\lambda$, where E represents the energy bandgap (bandwidth) of the material and $\lambda$ denotes the absorption threshold (wavelength at which the material begins to absorb light significantly), is derived from the fundamental relationship between photon energy, Planck's constant, and the speed of light. In the experimental setup, the absorption spectra of the two materials were meticulously measured using a spectrophotometer, which recorded the absorbance of light across a wide range of wavelengths. By identifying the absorption threshold $\lambda$ from the absorption spectra of $TiO_2$ and Pt-$TiO_2$, we were able to substitute the values into the formula for calculation.

After performing the calculations, the obtained results show that the energy bandgap of $TiO_2$, denoted as E($TiO_2$), is 3.04 electron - volts (eV), while that of Pt-$TiO_2$, E(Pt-$TiO_2$), is 2.98 eV. The concept of the energy bandgap is crucial in understanding the optical properties of materials. A smaller energy bandgap implies that the material requires less energy to excite electrons from the valence band to the conduction band. In the context of photon absorption, this means that the material can absorb photons with lower energy levels. Since the energy of a photon is inversely proportional to its wavelength ($E = hc/\lambda$, where h is Planck's constant and c is the speed of light), a material with a smaller bandgap can absorb photons with longer wavelengths, effectively corresponding to a wider absorption range in the electromagnetic spectrum.

Comparing the calculated results of the two materials, it is evident that Pt-$TiO_2$ has a smaller energy bandgap than $TiO_2$. This indicates that Pt-$TiO_2$ is capable of absorbing photons with lower energy, extending its absorption range further into the visible and near - infrared regions of the spectrum compared to pure $TiO_2$. In the realm of photocatalytic reactions, the absorption of photons is the initial and crucial step. When a photon with sufficient energy is absorbed by the photocatalyst, it can excite an electron from the valence band to the conduction band, creating electron - hole pairs. These electron - hole pairs are the active species that drive the photocatalytic reactions, such as the degradation of organic pollutants or the production of hydrogen through water splitting. With its ability to absorb a wider range of photons, Pt-$TiO_2$ can generate more electron - hole pairs under the same light illumination conditions, thereby utilizing more light energy. This enhanced generation of electron - hole pairs significantly promote the progress of photocatalytic reactions, making Pt-$TiO_2$ exhibit superior photocatalytic performance compared to $TiO_2$.

### 3.3. Photocatalytic degradation kinetics

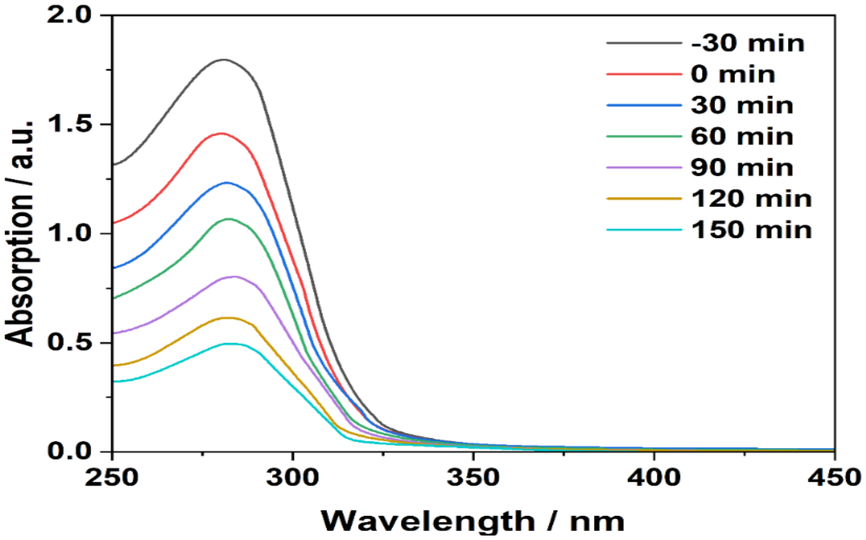

**Fig 3.** Photocatalytic Degradation Curve Diagram.

The experimental results are shown in Fig. 3, during the dark reaction stage, which was carried out under strictly controlled conditions with no external light illumination to eliminate the influence of photonic energy, a portion of the cefaclor solution underwent catalytic degradation. This initial catalytic process can be attributed to the inherent chemical reactivity between the catalyst (Pt-$TiO_2$) and the cefaclor molecules in the solution. The active sites on the surface of the Pt-$TiO_2$ catalyst interacted with cefaclor through various chemical forces, such as electrostatic interactions and hydrogen bonding, initiating a series of chemical reactions that led to the partial decomposition of cefaclor.

Subsequently, when transitioning to the photocatalytic stage, the system was exposed to a specific light source with carefully regulated intensity and wavelength range to mimic realistic environmental conditions as closely as possible. As time elapsed, the concentration of cefaclor in the solution gradually decreased in a continuous and observable manner. This decline in concentration was directly monitored by measuring the absorbance of the solution at specific wavelengths within the range of 250 nm to 350 nm.

As the photocatalytic reaction progressed, the absorbance values of the solution within the 250 - 350 nm range exhibited a consistent downward trend, clearly reflecting the reduction in cefaclor concentration. However, it was also observed that the catalytic rate, which is defined as the rate of change of cefaclor concentration with respect to time, gradually decreased over time. This decrease in the catalytic rate can be attributed to several factors. Firstly, as the reaction proceeded, the number of available cefaclor molecules near the catalyst surface decreased, reducing the frequency of effective collisions between the reactant molecules and the active sites on the Pt-$TiO_2$ catalyst. Secondly, the accumulation of reaction by - products on the catalyst surface may have partially blocked the active sites, inhibiting the further adsorption of cefaclor molecules and thus impeding the progress of the photocatalytic reaction. Additionally, possible changes in the electronic structure of the catalyst over time due to continuous photo-excitation could also have affected its catalytic activity, leading to a decline in the overall catalytic rate.

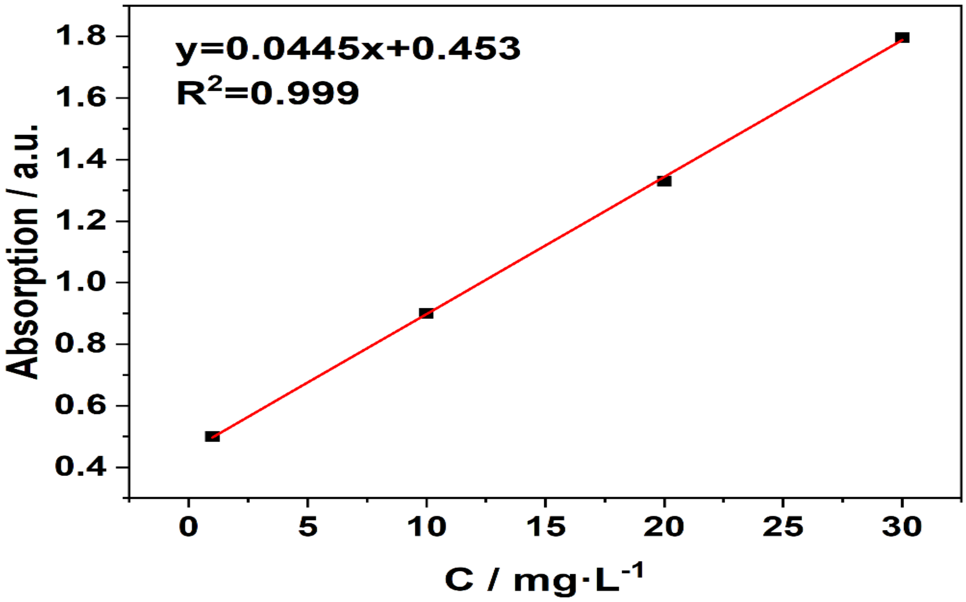

**Fig 4.** The standard relation curve between the absorbance of Cefaclor concentration C.

To thoroughly explore the relationship between concentration and absorbance of cefaclor, we prepared multiple standard cefaclor solutions with distinct concentrations. These solutions were formulated to cover a range of concentrations, providing a comprehensive dataset for analysis.

Subsequently, the UV-Vis spectroscopic absorption spectra of each solution were experimentally measured. The absorbance values of these solutions were accurately obtained, and the collected data were then fitted into curves, as illustrated in Fig. 4. Through in-depth analysis of the fitted curves, a clear conclusion emerged: the absorbance of standard cefaclor solutions is positively correlated with their respective concentrations. This finding lays a crucial groundwork for the application of UV-Vis spectroscopy in quantitatively determining cefaclor in diverse samples, offering valuable insights for future research and practical applications in relevant fields.

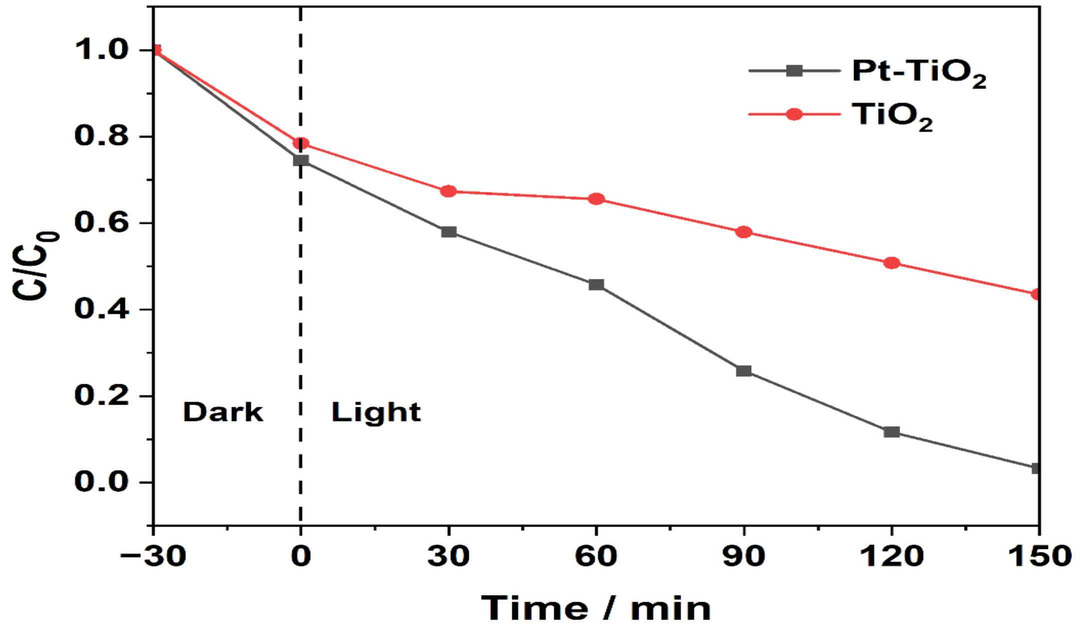

**Fig 5.** The relationship between degradation rate curve over time of Pt-$TiO_2$ and $TiO_2$.

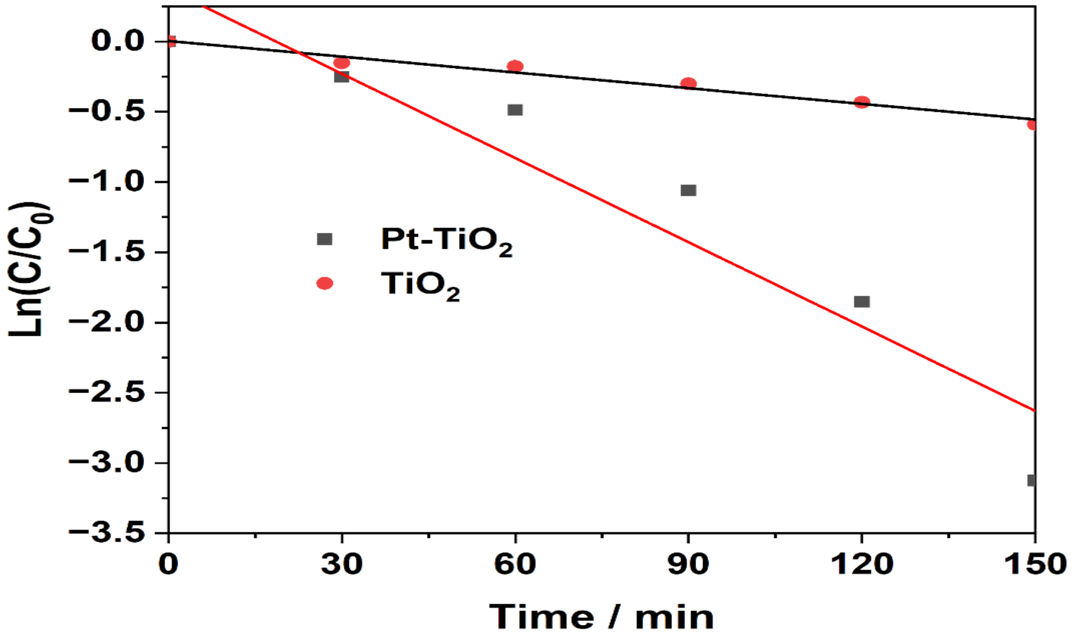

**Fig 6.** The relationship between ln($C/C_0$) over time of Pt-$TiO_2$ and $TiO_2$.

Taking $TiO_2$ as the research object, the effect of adding metal platinum on its catalytic performance was explored, and the degradation ratio of the concentration was used to visually represent the explanation rate, as shown in Fig.5, after 180 minutes of catalytic reaction, the concentration of cefaclor was significantly reduced. Catalyzed by $TiO_2$, the concentration of cefaclor solution decreased to 43.48% of the original solution after 180 minutes. At the same time, in order to explore whether the Pt-$TiO_2$ photocatalyst has better catalytic ability, we catalyzed the same concentration of cephalosporin solution, as shown in the figure, under the photocatalysis of Pt-$TiO_2$, the concentration of the original solution decreased to 3.33% after 180 minutes, which was much smaller than the concentration after no platinum photocatalysis. Then we logarithmic the data to get Fig.6, it can be seen that the curve of the Pt-$TiO_2$ catalytic solution has a larger slope, representing its higher catalytic activity. In the dark reaction, the reaction speed of the two is similar, and in the light reaction, platinum significantly improves the catalytic efficiency. After comparison, it was concluded that the Pt-$TiO_2$ photocatalyst had higher catalytic activity.

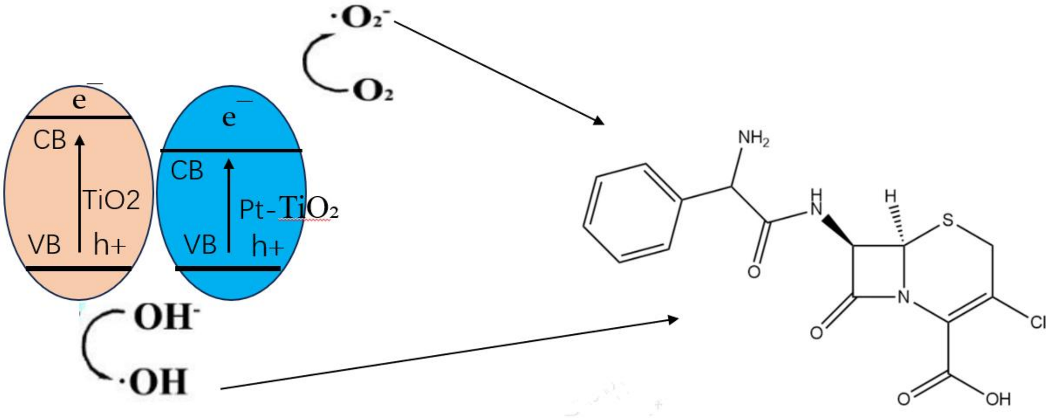

**Fig 7.** Photocatalytic mechanism of Pt-$TiO_2$ and $TiO_2$.

As shown in Fig. 7, we used Pt-$TiO_2$ as a photocatalyst to degrade the cefaclor solution. Under the irradiation of sunlight, the valence band electrons in the crystal are excited, forming free electrons and transitioning to the conduction band, the rewinding electrons will react with the oxygen molecules in the solution, decomposing the oxygen into superoxide anions, and the holes in the valence band react with the hydroxyl groups in the solution to form superoxide anions. These two reaction products have high reactivity and will participate in the degradation reaction of cefaclor. As shown in the figure, Pt-$TiO_2$ has a narrower bandwidth, so it can produce more electrons and holes, so the misspeech activity is higher and the catalytic rate is relatively faster.

## 4. Conclusion

In this study, the Pt-$TiO_2$ photocatalyst was successfully prepared, and its structure was confirmed by XRD characterization. By comparing $TiO_2$, it is found that Pt-$TiO_2$ has a smaller bandwidth, lower absorbed photon energy and a wider range. In the photocatalytic degradation of cefaclor experiments, Pt-$TiO_2$ showed higher activity, and the concentration of cefaclor decreased to 3.327% after 180 minutes, which was significantly better than that of $TiO_2$, which provided an effective solution for antibiotic contamination treatment.

This study provides a new way to solve the problem of antibiotic pollution in aquaculture, and is of great significance to ensure the aquatic ecological environment and human health. In the future, the preparation process of Pt-$TiO_2$ can be further optimized to reduce costs, expand its application in the degradation of other antibiotics, and be combined with other technologies to improve the degradation efficiency and promote the wide application of photocatalytic technology in the field of environmental governance.

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