Photothermal Catalytic Degradation of Lomefloxacin with Nano Au/TiO$_2$

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Abstract: With the fast development of intensive poultry and aquaculture, the consumption of antibiotics has ever been increasing. Absorbed or metabolized antibiotics usually enter the water environment in the form of active drugs and metabolites, which can enhance the resistance of pathogenic microorganisms and even cause serious water pollution. Considering the bacteriostatic activity of antibiotics, the main biological method used to treat organic waste water has limited efficiency. Herein, we prepared Au/TiO$_2$ for the efficient photocatalytic degradation of lomefloxacin (LOM) antibiotic wastewater. Based on the characteristics of prepared Au/TiO$_2$, the short-wavelength light can be converted into photogenerated carriers with TiO$_2$ support and the long-wavelength light can be converted into heat, likely due to the localized surface plasmon resonance effect of Au, synergistically promoting the LOM degradation. This study not only demonstrates that Au/TiO$_2$ is an efficient photocatalyst for LOM degradation, but also further indicates the effectiveness of photocatalytic technology in the treatment of antibiotic wastewater.

Keywords: photocatalytic degradation; lomefloxacin; nano Au/TiO$_2$

1. Introduction

Antibiotics, defined as typical pharmaceuticals to treat microbial infections, have been widely used in the therapy and prevention of human and animal diseases, playing an important role in curbing the spread of infectious diseases around the world. Moreover, they have been used as additives to promote animal growth $[1–3]$. The secondary metabolites of antibiotics produced by living organisms in the process of metabolism can selectively inhibit or affect other biological functions $[4–6]$. Until now, the worldwide consumption of antibiotics has been ever increasing. However, studies have confirmed that only a small part of antibiotics used for humans and animals is metabolized or absorbed in the body, and about 40–90% of antibiotics are excreted through urine and feces in the form of original drugs or primary metabolites before entering into the environment $[7,8]$. Recently, various antibiotics have been detected frequently in different environments including water, sediment, and soils $[9–13]$.

China is the highest producer of antibiotics in the world, with about 210,000 tons of antibiotics produced every year $[3]$. Because of the huge consumption and the lack of effective antibiotics management in China, antibiotics have been widely detected in aquatic environments such as the Haihe, Yellow, Huangpu, and East Rivers, as well as...
along the Hong Kong and Bohai Bay coasts [12,14,15]. The concentration of residual antibiotics in aquatic environments is usually low; however, such residual antibiotics pose a long-term and serious threat to organisms due to their potential hazards, toxicity, and persistence [4,16]. Therefore, the problems caused by antibiotics in natural water have been an increasing concern for researchers around the world.

The use of quinolones, a category of powerful antibiotics which can kill bacteria by penetrating their tissues, has increased greatly in recent years due to their characteristics of high bioavailability, broad antibacterial spectrum, long half-life period, and low side effects [8,17–20]. Among quinolones, ciprofloxacin, norfloxacin, ofloxacin, and enrofloxacin account for 98% of the total production of quinolones in China [21–23]. The accumulation of quinolones in the environment brings a direct or potential threat to ecosystem diversity and stability and to human health [24,25]. Therefore, there is an urgency to degrade antibiotics in the aquatic environment.

Currently, advanced oxidation processes have been developed to remove many different classes of antibiotics [26,27]. Semiconductor photocatalysis technology, as a type of advanced oxidation, has received intensive attention because of its mild reaction conditions, no secondary pollution, low energy consumption, and high efficiency. Among many traditional photocatalysts [28–31], TiO\(_2\) has been widely used due to its wide source of raw materials, low cost, simple preparation method, high thermal and chemical stability, and unique electronic band structure [32,33]. However, its low response to visible light limits its practical application [34–36]. Therefore, the development of modified TiO\(_2\) to expand its spectral response range to visible light has become urgent. Among the various methods of catalyst modification, the use of metal nanoparticles with a localized surface plasmon resonance (LSPR) effect (such as Au) has received extensive attention [37–39] and has been applied to efficiently remove pollutants such as Hg [40], organic dye [41], and fungicide [42].

In this study, the sunlight–driven photocatalyst Au/TiO\(_2\) was prepared using a precipitation–reduction method and was further applied to the photocatalytic degradation of lomefloxacin (LOM) by simulating sunlight irradiation in antibiotic wastewater. XRD, SEM, and TEM were applied to characterize Au/TiO\(_2\) morphology and composition. Experimental conditions, such as pH, initial LOM concentration, photocatalyst doses, and salinity, were optimized to improve LOM degradation efficiency.

2. Materials and Methods

2.1. Materials and Method

LOM (99.87%) was purchased from Shanghai Macklin Biochemical Co., LTD, Shanghai, China. Hydrochloric acid was purchased from Sichuan Xilong Chemical Co., Ltd., Chengdu, China.) Sodium chloride (99.5%) and sodium hydroxide (96.0%) were purchased from Shengao Chemical Reagent Co., Ltd., Tianjin, China. Sodium borohydride (98.0%) was purchased from Tianjin Guangfu Fine Chemical Research Institute.

The microstructure of catalyst materials was characterized by SEM (Zeiss SUPRA 55 VP, Oberkochen, Germany), TEM (JEM-2100F, Tokyo, Japan), and ICP-MS (Agilent 8800, Sacramento, CA, USA). The temperature map of TiO\(_2\) and Au/TiO\(_2\) was obtained by dispersing the solid catalysts on a quartz cloth and measuring the temperature under light using an IR camera. Photocatalytic degradation reaction was carried out in a programmable xenon lamp aging testing machine (WJ-XD-500, Hangzhou Wujia Machinery Co., Ltd., Hangzhou, China). The xenon lamp on top of the machine was sealed with a quartz glass window and placed 50 cm away from the samples. It irradiated the samples as the light source during the degradation reaction. The irradiance intensity used in this study was 2500 W/m\(^2\). The degradation efficiency of antibiotics was determined by changes in absorbance before and after the reaction and was measured by spectrophotometry (UV-1800, Shimadzu, Kyoto, Japan).
2.2. Catalyst Preparation

Firstly, 1 g of nano TiO\(_2\) and 300 µL of 0.2 mol/L chlorauric acid solution were added into 200 mL of deionized water to prepare the Au/TiO\(_2\) solution. The Au/TiO\(_2\) solution was agitated overnight on a magnetic stirrer at room temperature. The pH of the solution was adjusted to 10 by using 1.0 mol/L NaOH solution. Next, 2 mL of 1.0 mol/L sodium borohydride solution was continually dropped into the solution under a stirring condition. Then, the mixed Au-TiO\(_2\) solution was filtered by a 0.22 µm membrane and washed to neutral with deionized water. Finally, Au/TiO\(_2\) visible light catalysts were obtained by centrifuging and drying the solid particles in a vacuum condition for 48 h.

2.3. Photodegradation Test

In the photocatalytic degradation experiment, Au/TiO\(_2\) catalysts were added to 100 mL of LOM solution before putting the mixed solution into a programmable xenon lamp aging testing machine. At first, the reaction was carried out under dark conditions for 30 min to ensure adsorption and analytical balance between the catalyst and LOM. Then, the xenon light was turned on to carry out the photocatalytic degradation. After the reaction, the supernatant was collected by a centrifuge and the absorbance was detected by UV-1800. The concentration of LOM was calculated by the standard curve of LOM to ultraviolet-visible spectrophotometer absorbance. The degradation efficiency of the LOM was calculated by the following formula:

\[ y = \frac{(x_0 - x_t)}{x_0} \]  

where \(x_0\) is the initial concentration of LOM; \(x_t\) is the concentration of LOM at a certain reaction time; and \(y\) is the degradation efficiency of LOM.

3. Results and Discussion

3.1. Characterization of Prepared Catalysts

Firstly, the prepared catalyst Au/TiO\(_2\) and pure TiO\(_2\) were characterized by XRD. As displayed in Figure 1a, there is no significant difference between Au/TiO\(_2\) and pure TiO\(_2\). The peaks at 25.3\(^\circ\), 36.9\(^\circ\), 37.8\(^\circ\), 38.6\(^\circ\), 48.1\(^\circ\), 53.9\(^\circ\), 55.1\(^\circ\), 62.7\(^\circ\), 68.8\(^\circ\), 70.3\(^\circ\), 75.1\(^\circ\), and 76.1\(^\circ\) are attributed to the (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), and (215) for the anatase phase TiO\(_2\), and the peaks at around 27.7\(^\circ\), 36.2\(^\circ\), 41.5\(^\circ\), 54.3\(^\circ\), 62.8\(^\circ\), and 76.2\(^\circ\) are attributed to the (110), (101), (111), and (220) for the rutile phase TiO\(_2\) [39]. No special peaks of Au were observed in Au/TiO\(_2\) XRD patterns, possibly due to the small loading amount of Au and small dispersion particle size. Generally, the property of catalysts is mainly estimated based on the optical absorption capacity. The UV–vis spectra of TiO\(_2\) and Au/TiO\(_2\) composite are exhibited in Figure 1b. It was obvious that the absorption edge of TiO\(_2\) is about 410 nm, which could be ascribed to an intrinsic band gap of TiO\(_2\) (3.0 eV) [40]. After loading of Au, the Au/TiO\(_2\) composite showed stronger visible light absorption compared with TiO\(_2\), revealing that Au/TiO\(_2\) might possess a higher activity for the degradation of pollutants. The enhanced absorption peak between 400 and 800 nm could be ascribed to the LSPR effect of Au NPs(nanoparticles). Based on previous studies, the LSPR effect could efficiently expand the spectrum response range and improve photothermal conversion of the material, enhancing the light utilization efficiency [41–43].

Subsequently, the morphology of Au/TiO\(_2\) was further investigated through SEM and TEM analysis. As seen from Figures 2 and 3, the morphology of Au/TiO\(_2\) consists of a particle–shaped structure. The average particle size of Au/TiO\(_2\) nanoparticles is about 20 nm and is aggregated due to the high surface energy. Au NPs were loaded on the surface of TiO\(_2\). EDS analysis was conducted to investigate the elemental distribution of the prepared Au/TiO\(_2\). From Figure 2 it can be observed that Au NPs were evenly distributed on the surface of TiO\(_2\). The ICP–MS test confirmed that the loaded Au content on TiO\(_2\) was 1.98%, which is close to the theoretical loading values.
Figure 1. (a) XRD patterns; (b) UV-vis DRS spectrum of TiO₂ and Au/TiO₂.

Figure 2. (a) Secondary electron (SE) emission image and (b-d) EDS elemental mapping (Ti, O, and Au elements) of Au/TiO₂.

Figure 3. (a) SEM images and (b) TEM images of Au/TiO₂.
3.2. Photocatalytic Degradation of LOM with Au/TiO₂

Firstly, a series of experiments was carried out to confirm the photocatalytic degradation performance of prepared catalysts in simulated antibiotic wastewater (LOM, 10 mg/L) with a catalyst dosage of 0.15 g. The initial pH of antibiotic wastewater was adjusted to 5. As shown in Figure 4a, the degradation curve of LOM did not change significantly under the dark condition within 180 min. In contrast, the degradation efficiency of LOM increased gradually over time when the light was introduced into the reaction system and reached 71.8% within 180 min. The photo-induced instability of LOM indicated that the application of photocatalysis might be a desirable choice for LOM removal in wastewater treatment. Meanwhile, as shown in Figure 4b, a significant decrease in the absorption spectrum of LOM was observed before and after the photodegradation, indicating that Au/TiO₂ material is a desirable catalyst and that photocatalytic degradation of LOM in wastewater treatment is a feasible method.

![Figure 4. (a) The degradation efficiency of LOM under different conditions and (b) The UV-Vis absorption spectrum of LOM before and after the degradation reaction (LOM concentration = 10 mg/L, pH = 5, at room temperature).](image_url)

3.3. The Effect of pH on the Photocatalytic Degradation of LOM

Subsequently, the LOM photodegradation experiments with different pH were investigated. As displayed in Figure 5a, the variation of pH led to a significant change in the removal efficiency of LOM and the highest degradation efficiency (90.5%) was obtained at pH = 5. The degradation efficiency dropped to 76.8% within 60 min when the pH decreased to 3. Under acidic conditions, the active components leach easily and hydrogen ions might scavenge sulfate radicals and hydroxyl radicals, inhibiting the activity of the catalysts [28]. In addition, LOM can react with H⁺ and OH⁻ in the solution to form LOMH⁺ (cation), LOM⁻ (neutral), and LOM²⁻ (anion), due to the >NH (the functional group on the molecule of LOM) and carboxyl functional groups in the molecular structure of LOM (Figure 6). LOMH⁺ dominates when the pH is lower than 6, while the neutral LOM dominates in the pH range of 6–8. On the contrary, LOM⁻ is the main species when the pH is >8 [44]. Coincidentally, the isoelectric point of TiO₂ is in the pH range of 5–7. This means that when pH is very high or very low, electrostatic repulsion might inhibit the adsorption of LOM on the surface of Au/TiO₂, leading to low LOM degradation levels, which was confirmed by our experimental results.
Figure 5. (a) Effect of pH on the degradation of LOM (LOM concentration = 10 mg/L, Au/TiO$_2$ = 0.15 g, at room temperature); (b) effect of Cl$^-$ concentration on the photocatalytic degradation of LOM (LOM concentration = 10 mg/L, Au/TiO$_2$ = 0.15 g, pH = 5); (c) effect of catalyst usage on the photocatalytic degradation of LOM (pH = 5, LOM concentration = 10 mg/L); (d) effect of initial LOM concentration on the photocatalytic degradation of LOM (Au/TiO$_2$ = 0.15 g, pH = 5).

Figure 6. Chemical structure of LOM.

3.4. The Effect of Cl$^-$ on the Photocatalytic Degradation of LOM

It is worth noting that high salinity in the natural waters of the Xinjiang arid region has been a big concern, and Cl$^-$ is the main factor. Therefore, the influence of Cl$^-$ content on the degradation efficiency of LOM was investigated. As shown in Figure 5b, the removal rate steadily increased to around 90% within 60 min when the Cl$^-$ concentrations were lower than 1.5 g/L, without significant differences in the degradation efficiency. The LOM degradation efficiency was inhibited significantly when Cl$^-$ concentration increased to 2.5 g/L. Our results indicate that efficient LOM degradation obtained with Au/TiO$_2$ even under high Cl$^-$ concentrations inspires its application in the treatment of antibiotic-polluted waters in arid regions.
3.5. The Effect of Catalyst Amount on the Photocatalytic Degradation of LOM

Additionally, in order to investigate the influence of the catalyst amount towards LOM degradation, experiments were carried out with different Au/TiO$_2$ catalyst amounts varying from 0 to 0.18 g. According to Figure 5c, the LOM degradation efficiency improved with the increase in the catalyst amount. The LOM degradation efficiency was only 12.4% without adding Au/TiO$_2$ within 60 min. The degradation efficiency dramatically increased to 92.1% when the Au/TiO$_2$ dosage increased up to 0.15 g due to the increased activation sites following the introduction of catalysts, accelerating the formation of active radicals [40]. However, the LOM degradation efficiency was much weaker when the Au/TiO$_2$ amount increased to 0.18 g, indicating that the Au/TiO$_2$ dosage at this level or higher is not beneficial to LOM degradation.

3.6. The Effect of LOM Initial Concentrations on the Photocatalytic Degradation of LOM

To investigate the LOM degradation of LOM initial concentrations, the photocatalytic degradation of LOM with different initial concentrations was also investigated; the results are displayed in Figure 5d. As shown in Figure 5d, the LOM removal rate increases were inversely proportional to the initial LOM concentrations. The final LOM removal rate increased to 99.1% when the initial concentration was 1 g/L within 60 min, implying that higher concentrations could inhibit the mass transfer and contacting efficiency of LOM with active species [44].

3.7. The LOM Photocatalytic Degradation Mechanism

Subsequently, the LOM photocatalytic degradation mechanism was further explored. The intrinsic wide band gap of TiO$_2$ is 3.0–3.2 eV. Therefore, only the light with a short wavelength can offer sufficient energy to excite the electrons in the valence band, forming photogenerated carriers. Some researchers have reported the formation of heat due to the localized surface plasmon resonance effect of Au [45–48]. In order to further investigate the effect of LOM photocatalytic degradation in this study, experiments at different temperatures were also conducted. As illustrated in Figure 7a, a significant increase in LOM degradation efficiency was achieved with the rise in the reaction temperature. The Au nanoparticles could perform LSPR under irradiation, improving the photothermal conversion efficiency of the supported catalyst, and the in-situ generated heat could help to promote the LOM degradation [45,49]. Further, the surface temperature of the catalysts was directly observed using an IR camera in order to compare the photothermal conversion performance of the Au/TiO$_2$ catalyst. It was clearly observed that the prepared catalyst Au/TiO$_2$ had better photothermal effects than TiO$_2$. The surface temperature of Au/TiO$_2$ increased to 76.5 °C within 5 min while that of TiO$_2$ was only 28.1 °C.

![Figure 7](image-url)
4. Conclusions

In summary, a simple catalyst Au/TiO$_2$ with a wide–wavelength response capacity was constructed for the photothermal catalytic degradation of LOM, achieving rather high removal rates even under high Cl$^-$ concentrations, which is a big concern in waste water treatment in the Xinjiang arid regions. TiO$_2$ supported LOM degradation while the introduction of Au NPs could bring in situ generated heat under irradiation, synergistically improving LOM degradation.

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