



Article Photocatalytic Bacterial Inactivation of Acinetobacter baumannli on Cu/TiO₂/Diatomite

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Abstract: $Cu_4Ti_2O/TiO_2/diatomite with double interface <math>Cu_4Ti_2O/TiO_2$ and rutile/anatase heterojunction were fabricated, which demonstrated good antibacterial activity (100%) against *Acinetobacter baumannii*. $Cu/TiO_2/diatomite$ prepared under optimum preparation conditions (added diatomite, 0.005 g; Cu, 0.005 g; reaction temperature, 180 °C; reaction time, 8 h) exhibited high antibacterial activity (100%) against A. *baumannii*. For the Cu/TiO₂/diatomite powders, their structural, compositional, optical and morphological traits were characterized by XRD, SEM, TEM, XPS, BET, FTIR, Mapping, and DRS. It was shown that Cu/TiO₂/diatomite under optimum conditions consisted of the double interface Cu_4Ti_2O/TiO_2 and rutile/anatase heterojunction with the narrowest band gap and largest BET surface area, pore size, and pore volume. Then, it could exhibit the best photocatalytic activity.

Keywords: photocatalytic; Cu/TiO2/diatomite; baumannii



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1. Introduction

Given the fast worldwide spread of multidrug-resistant lineages of A. baumannii (Acinetobacter baumannii), a high-risk Gram-negative pathogen, it has become one of the bacteria with strongest antibiotic resistance on a global scale [1,2]. Infection with A. baumannii manifests itself as varying diseases, including nosocomial and community-acquired pneumonia, wound and burn infections, bloodstream infections, infections of skin and soft tissue, urinary tract infections, meningitis, as well as endocarditis. Management of nosocomial meningitis is especially utterly challenging, which is an unpopular neurosurgical complication induced by A. baumannii that possesses broad drug resistance [3,4]. Due to the significant increase in the antimicrobial resistance of Acinetobacter baumannii, many new technologies to block the progression of infection were strongly needed. With "Dual Carbon" targets becoming catchphrases, the photocatalytic antibacterial technology has been widely studied for its simple operation, no secondary pollution as well as the ability to convert solar energy into chemical energy for the mineralization of organic matter and bacteria. AgVO₃/AgI graphene microtube displayed excellent sterilization against E. coli (Escherichia *coli*), with a bacteriostatic efficiency of 100% [5]. Inactivation activity of an all-organic composite PDINH (photocatalytic nanomaterial C₃N₄/perylene-3,4,9,10-tetracarboxylic diimide) heterostructure was outstanding against the Gram-positive and -negative bacteria [6]. Compared with the properties of many photocatalytic antibacterial agents, TiO₂ has more excellent properties. Researchers have been modifying the energy levels by organic and inorganic compounds, various cations and anions, etc., causing the narrowing of TiO_2 band gap or photoinduced charge transfer to achieve high antibacterial performance.

The photocatalytic sterilization behavior of Cu-TiO₂ nanofibers was carried out in viral/bacterial systems and viruses under visible light [7]. During the degradation of

pollutants and inactivation of bacteria in aqueous phase, a photocatalytic reaction appeared in the TiO_2/Cu_xO_y nanotube arrays [8]. It was discovered that the toxicity of films containing Cu ions was much higher than that of Ag, Zn, Co, Al and Hg ions, and copper and copper alloys have a considerable cost advantage over precious metals such as silver. Therefore, TiO_2 has been modified by Cu ion to improve its absorption of visible light and inhibit the photoelectron-hole recombination, which was an active research direction in order to prepare new, stable antibacterial materials [9]. The photocatalytic bactericidal action was strengthened against A. baumannii by the hybrid Cu₂O/TiO₂ nanocomposites [10]. Although a series of copper compounds/TiO₂ catalysts with visible light response have been prepared, the antibacterial efficiency could be significantly improved. The above-mentioned improvements were limited by changing the energy level structure and shape control of the photocatalyst, etc. To enhance the bactericidal action of copper compound/TiO₂ photocatalyst in practical application, the effects of the photocatalyst's morphology, composition, dispersion and combination form on its antibacterial activity should be explored more in-depth, which could be crucially conducive to the development and control of copper compound/ TiO_2 photocatalyst [11,12]. Recently, we have adjusted the shape of the porous catalyst and the construction of a novel heterostructure to improve its photocatalytic activity. A novel hydrophilic copper/titanium dioxide composite composed of $Cu_2Cl(OH)_3$, $Cu_{2+1}O$ and anatase TiO_2 was successfully prepared, and the relationship between the surface micromorphology, crystalline phase and the antibacterial activity of E. coli was investigated [13].

TiO₂ exists in the following 3 polymorphs: anatase, brookite (orthorhombic system), as well as rutile (tetragonal system). Most research concerning the synthesis of TiO_2 -supported Cu compounds for photocatalysis discovered the formation of a mere anatase phase [14], whose photocatalytic potential was best compared to the remaining TiO_2 crystalline phase. Recently, some studies demonstrated the better photocatalytic potential of hybrid phases (anatase/brookite, rutile/anatase) compared to the pure rutile or anatase phase because of the interface heterojunction of rutile/anatase, ultimately leading to the electron (e^{-}) hole(h⁺) recombination reduction [15–17]. Under the same concept, diatomite was selected as a porous and natural mineral support for the compound of porous TiO_2 and copper compounds, not only because the diatomaceous was composed of a porous diatomite framework with a Si-O tetrahedral network that was high in specific surface area and porosity and low in density [18], but also because the diatomite could control the rutile/anatase phase ratio in TiO₂. In the present study, the "super bacteria" Acinetobacter baumannii was used as the probe target. The different composites materials $Cu/TiO_2/diatomite$ comprising varying amounts of diatomite, Cu compound and anatase/rutile TiO₂ were fabricated, so that the photocatalytic potential for the removal of Acinetobacter baumannii was optimizable.

2. Results and Discussion

2.1. XRD Analysis

The wide angle XRD spectra for pure diatomite, $TiO_2/diatomite$, Cu/TiO_2 and $Cu/TiO_2/diatomite$ were shown in Figure 1a. The diatomite was amorphous, and the broad peak of its diffraction pattern centered at $2\theta = 17-28^{\circ}$ was assigned to amorphous SiO_2 [3]. In the Cu/TiO₂ diffraction pattern, the peaks at 25.3° and 48.0° corresponded to the (101) and (200) anatase facets of TiO₂ (JCPDS No. 21-1272) and the peak at 27.4° was consistence with the (110) facet of rutile TiO₂ (JCPDS No. 21-1276). In the TiO₂/diatomite diffraction pattern, the peaks at 25.3°, 37.8°, 48.0°, 53.8°, and 55.1° corresponded to the (101), (004), (200), (105) and (211) facets of anatase TiO₂ (JCPDS No. 21-1272) and the peak at 27.4°, 62.9°, 69.0°, and 74.4° corresponded to the (110), (002), (301), and (320) facet of rutile TiO₂/diatomite (JCPDS No. 21-1276). For Cu/TiO₂/diatomite, five strong diffraction peaks were noted at 25.3°, 37.8°, 48.0°, 53.8° and 55.1°, which corresponded to the (101), (004), (200), (105) and (211) planes for the TiO₂ anatase phase (JCPDS No. 21-1272), while the rutile phase evidenced by only two peaks with veer low intensity at 62.9° and 74.4°. For

 $Cu/TiO_2/diatomite$ and $TiO_2/diatomite$, it was not shown that the broad amorphous peak of amorphous SiO_2 due to little diatomite. According to the above result, TiO_2 were the mixed phases (rutile/anatase) in TiO₂/diatomite, Cu/TiO₂, and Cu/TiO₂/diatomite, and these catalysts could exhibit higher photocatalytic potential compared to the pure rutile or anatase phase because of the interface heterojunction of rutile/anatase, ultimately leading to the electron (e^{-}) -hole (h^{+}) recombination reduction [16]. No characteristic peaks of Cu metal or oxide phases were found in the Cu/TiO_2 and Cu/TiO_2 /diatomite diffraction patterns, which indicated that the primary crystalline phase in the composite samples was TiO₂. Therefore, in line with the prior observational report [19], Cu was highly dispersed on the TiO_2 surface or existed in an amorphous phase. Compared with the other three samples, the $Cu/TiO_2/diatomite$ sample had high intensity and its diffraction peaks were narrower than those of the other samples, indicating the formation of larger TiO_2 crystallites and a higher degree of crystallinity. These were important factors that can affect photocatalytic efficiency [20]. On the other hand, the crystallite size for $Cu/TiO_2/diatomite$ sample was about 0.48 µm, which were calculated via Scherrer equation based on (1 0 1) principal diffraction peak at $2\theta = 25.3^{\circ}$.



Figure 1. Wide-angle XRD patterns of (**a**) diatomite, Cu/TiO₂, TiO₂/diatomite, and Cu/TiO₂/diatomite, (**b**) Cu/TiO₂/diatomite and Cu/TiO₂/diatomite-30.

To clarify Cu's crystal morphology, we prepared Cu/TiO₂/diatomite-30 catalyst, and the wide-angle XRD patterns of Cu/TiO₂/diatomite and Cu/TiO₂/diatomite-30 were shown in Figure 1b. In the Cu/TiO₂/diatomite-30 diffraction pattern, the peaks at 35.0° and 60.9° corresponded to the (101) and (110) anatase facets of Cu₄Ti₂O (JCPDS No. 21-0199). Additionally, by comparing these two composites, the Cu/TiO₂/diatomite-30's characteristic diffraction peak of TiO₂ is stronger than Cu/TiO₂/diatomite.

2.2. BET Analysis

Figure 2 displays the pore structural parameter and BET-specific surface area statistics for the $Cu/TiO_2/diatomite$ and Cu/TiO_2 composites, as well as the pure diatomite based on the N₂ adsorption–desorption approach. As shown in Figure 2a, the textural analysis revealed that Cu/TiO₂ depicted a type I isotherm (IUPAC) characteristic of a microporous material. The sample of Cu/TiO₂/diatomite and pure diatomite exhibited a typical type IV isotherm with an H_3 hysteresis loop that was characteristic of a mesoporous material in accordance with IUPAC classification. Compare with pure diatomite, the adsorption branch of $Cu/TiO_2/diatomite$ rises slowly when the pressure scope was low within P/P0 < 0.8, while it could exhibit a sharp rise when P/P0 > 0.8. The results showed that $Cu/TiO_2/diatomite$ had more dense mesopores [5]. According to the reference, the reaction system used diatomite as the carrier, and the added TiO₂ also has the effect of creating pores [6], increasing the pore capacity. Figure 2b depicts the distributions of BJH pore sizes for the pure diatomite, Cu/TiO_2 , as well as $Cu/TiO_2/diatomite$. The cumulative pore volume of Cu/TiO_2 as the pore diameter increases, the pore volume hardly changed. The cumulative pore volume of diatomite was based on the pore diameter of 2.5 nm as the watershed, presenting a trend of increasing first and then decreasing. However, the

cumulative pore volume of Cu/TiO₂/diatomite was based on the pore diameter of 15.0 nm as the watershed, showing an initial increase and subsequent decrease trend. The result was consistent with to the reference [6]. The reaction system was used diatomite as the carrier, and the added TiO₂ also has the effect of creating pores, which can increase the pore capacity. The above results were also consistent with the pore structure parameters for the pure diatomite, Cu/TiO₂/diatomite and Cu/TiO₂ detailed in Table 1. Compared to the Cu/TiO₂ and pure diatomite, the BET surface area, pore size and pore volume of Cu/TiO₂/diatomite were larger, which corroborated the remarkable enhancement of porous structure by the TiO₂ nanoparticle loading. Both Cu/TiO₂/diatomite and pure diatomite were mesoporous materials, and Cu/TiO₂ was a microporous material.



Figure 2. (a) Nitrogen adsorption–desorption (b) Pore radius distributions of diatomite, Cu/TiO_2 , $TiO_2/diatomite$, and $Cu/TiO_2/diatomite$.

Sample	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Size (nm)
Diatomite	42.456	0.069	2.516
Cu/TiO ₂ /Diatomite	207.759	0.305	3.938
Cu/TiO ₂	13.361	0.020	1.356

2.3. Energy Dispersive Spectrometer (EDS) and SEM Mapping

Figure 3 presents an energy dispersive spectrometer (EDS) in the diatomite and $Cu/TiO_2/diatomite$ samples. As shown in Figure 3a, diatomite contains Si, P, C, N and O elements. Compared to the EDS of diatomite, $Cu/TiO_2/diatomite$ had more Cu and Ti. As shown in Figure 3b, the Cu and Ti were very evenly dispersed in the Cu/TiO₂/diatomite sample, demonstrating the effectiveness of diatomite as a carrier.



Figure 3. (a) SEM and (b) EDS-mapping of Cu/TiO₂/diatomite.

2.4. SEM and TEM Analysis

Figure 4 presented the SEM and TEM of Cu/TiO₂/diatomite. Figure 4a showed the SEM images of Cu/TiO₂/diatomite. It could be seen that Cu/TiO₂/diatomite has stacked with nanoparticles (about 0.5 μ m). The TEM of the Cu/TiO₂/diatomite was shown in Figure 4b, and TiO₂'s distinct lattice fringe revealed a 0.36-nm interplanar gap, showing agreement with the (101) plane of anatase TiO₂. In addition, the clear lattice fringes of Cu₄Ti₂O calibrated by TEM showed a 0.24 nm lattice gap, which coincided with the (110) plane, indicating that Cu-Ti bonds might be formed. The obtained results were highly consistent with the XRD analysis results.



Figure 4. (a) SEM and (b) TEM of Cu/TiO₂/diatomite.

2.5. FTIR Analysis

Structural traits about the Cu/TiO₂/diatomite and pure diatomite were further analyzed using FTIR spectra in Figure 5. For both diatomite and Cu/TiO₂/diatomite, the bands at about 3378 and 1642 cm⁻¹ could be attributed to the stretching vibration of hydroxyl and water, respectively [21]. The peaks at 1094 and 801 cm⁻¹ are derived from the stretching vibration of Si-O-Si. The peak in the 466 cm⁻¹ vicinity was ascribed to the antisymmetric flexural vibration of Si–O–Si in [SiO₄] tetrahedron [22]. According to Ref. [23], the absorption bands in the 473–695 cm⁻¹ vicinity corresponded to the [TiO₆] vibrations and the characteristic absorption peaks of TiO₂ for the Cu/TiO₂/diatomite, suggesting the formation of TiO₂. The absorption peak at 956 cm⁻¹ was ascribed to Ti–O–Si's eigen peaks. Summarizing the foregoing analysis, new chemical bonds were established among Ti, O and Si in the composites [24]. The 575 cm⁻¹ bands were ascribed to the Cu–O stretching vibration from Cu₄Ti₂O [25]. These results were highly consistent with the XRD analysis results.



Figure 5. FTIR of Cu/TiO₂/diatomite and diatomite.

2.6. XPS Analysis

Chemical state elucidations based on XPS analysis were presented in Figure 6 for the pure diatomite and $Cu/TiO_2/diatomite$. It can be observed from the XPS analysis that there was only one O1s characteristic peak at the binding energy of 532.25 eV in diatomite in Figure 6a. However, the binding energy of O1s in Cu/TiO₂/diatomite was 528.85 eV, 530.35 eV and 531.60 eV with three characteristic peaks in Figure 6b. The binding energy was the characteristic peak of O1s in diatomite corresponding to the characteristic peak of 531.60 eV, while the peak is shifted to the direction of low binding energy. It demonstrated that diatomite and Cu/TiO_2 are closely combined. The characteristic peaks 528.85 and 530.35 eV in respective binding energies, corresponding to O in Cu_4Ti_2O and TiO_2 in the Cu/TiO_2 /diatomite composite, respectively. This implied the transfer of electrons between the Si and Ti atoms, which was accomplished through the motion of the intermediate O atom, ultimately resulting in the Si-O-Ti bond establishment [26]. As shown in Figure 6c, Cu 2p peaks appeared at 934.15 eV. According to reports [27], the peaks near 934.00 eV and 954.00 eV were assigned to Cu 2p. Therefore, the Cu 2p peak at a high binding energy (about 934.15 eV) indicated that the main valence state of Cu in Cu/TiO₂/diatomite was Cu²⁺.



Figure 6. XPS of (a) O 1s of diatomite and (b) O 1s (c) Cu 2p of Cu/TiO₂/diatomite samples.

2.7. DRS Analysis

Figure 7a displays the Uv-vis absorption patterns for $TiO_2/diatomite$, Cu/TiO_2 and $Cu/TiO_2/diatomite$. As we all have known, the energy band structure of semiconductors had an important influence on their optical properties [28]. As shown in Figure 7a, 200–400 nm was the absorption of TiO_2 in the ultraviolet region. Cu/TiO_2 , $Cu/TiO_2/diatomite$ and $TiO_2/diatomite$ had obvious absorption values in the ultraviolet region. Among them, the absorption of pure diatomite was weak within the Vis-light region probably [28]. In comparison with diatomite, Cu/TiO_2 , and $TiO_2/diatomite$, $Cu/TiO_2/diatomite$ showed stronger visible-light absorption, enabling better utilization of solar energy and helping to obtain high photocatalytic activity. Using the Kubelka–Munk function, (Figure 7b) the band gap energies of $Cu/TiO_2/diatomite$, Cu/TiO_2 and $TiO_2/diatomite$ calculated from the Tauc curve were 3.11 eV, 3.51 eV and 3.36 eV. The photocatalyst whose band gap was narrower was universally considered to attain a unit-time acquisition of more visible light and its conversion into more chemical energy [29]. $Cu/TiO_2/diatomite$, whose band gap was the narrowest, could exhibit the best photocatalytic potential.



Figure 7. UV-vis DRS of diatomite, Cu/TiO₂, TiO₂/diatomite, and Cu/TiO₂/diatomite.

2.8. Antibacterial Activity

Acinetobacter baumannii was used as a probe to test the antibacterial properties of the catalyst. The synthesis conditions of the catalyst were optimized for *Acinetobacter baumannii*. Based on Figures 8 and 9a, we adjusted the dosages of CuSO₄, TiCl₄, Dodecanol, reaction time and reaction temperature to explore the best antibacterial effect. Clearly, at a 180 °C temperature of the reaction, the dosage of TiCl₄ was 0.8 mL, the dosage of CuSO₄ was 0.005 g, the amount of Dodecanol was 4.5 mL, and the reaction time was 8 h, the antibacterial rate against *Acinetobacter baumannii* reached the best, and the antibacterial rate was 100%.



Figure 8. The influence of synthesis condition on the activity of *A. baumannii*.



Figure 9. The influence of synthesis temperature on the activity of *A. baumannii* (**a**), bacteriostatic rate of Cu/TiO₂, TiO₂/diatomite and Cu/TiO₂/diatomite (**b**).

Subsequently, based on the above-mentioned optimal conditions, we conducted antibacterial experiments on several other materials (diatomite, $TiO_2/diatomite$ and Cu/TiO_2), and the results revealed that the $Cu/TiO_2/diatomite$ showed the best antibacterial performance from Figure 9b. The good antibacterial performance of diatomite was because of that diatoms that were negatively charged could attract microorganisms and positively charged substances (fungi, molds, bacteria, protozoa, viruses, heavy metals and drug metabolites) [30]. The interface heterojunction between Cu_4Ti_2O/TiO_2 and $TiO_2/diatomite$, respectively. The above result could be attributed to its highest photocatalytic due to the double interface heterojunction between Cu_4Ti_2O/TiO_2 and rutile/anatase, resulting in the electron (e⁻)-hole(h⁺) recombination reduction, highest crystallinity, highest BET surface area, the narrowest band gap of $Cu/TiO_2/diatomite$ microporous material.

3. Materials and Methods

3.1. Materials and Chemicals

Titanium tetrachloride, N-dodecanol, CuSO₄, glycol, sodium chloride, tryptone, and yeast powder were supplied by Aladdin Reagent Co., Ltd. (Shanghai, China). Diatomite was supplied by Yunnan Sea Soul Diatom Mud Technology Co. LTD (Qujing, China).

3.2. Synthesis of Cu/TiO₂/Diatomite

First, 0.005 g of diatomite was introduced separately into a Glycol solution, followed by being ultrasounded continuously at room temperature for 10 min. Subsequently, 0.8 mL titanium tetrachloride and dodecanol were added. With continuous stirring CuSO₄ being added, the prepared solution was reacted in a vacuum oven at a certain temperature (12 h). In order to ensure product purity, the reaction solution was purified by centrifugation and rinsed with anhydrous ethanol three times, which was dried in a vacuum oven (80 °C, 12 h). Finally, the resulting faint yellow color powder was collected and marked as Cu /TiO₂/diatomite.

At the same time, we used the same method to prepare the Cu/TiO_2 , $TiO_2/diatomite$.

3.3. Synthesis of Cu/TiO₂/Diatomite-30

 $Cu/TiO_2/diatomite-30$ is synthesized by increasing the amount of TiCl₄ and CuSO₄ to 30 times, and other synthesis steps are the same on the basis of preparing Cu/TiO₂/diatomite.

3.4. Antibacterial Study

Acinetobacter baumannii were cultured on LB solid medium at 37 °C for 48 h. After further culturing and subsequent dilution, a bacterial suspension of ~10⁸ CFU/mL (corresponding to the MacFarland scale) in sterile physiological saline (10 mL) was obtained. These bacterial suspensions were then used for bactericidal experiments. The bacterial suspension was added aseptically with Cu/TiO₂/diatomite photocatalysts for a 10 min assessment of bactericidal action under visible light irradiation ($\lambda > 420$ nm) at ambient temperature using a xenon lamp. Here was the spectra of the xenon lamp (Figure 10). The bacterial suspension was then diluted 10-fold with a physiological saline solution. Then, a nutrient agar plate was spread with 1 mL of bacterial suspension for 37 °C incubation in the dark. After 24 h incubation, the surviving bacterial colonies were evaluated by the plate count method. To calculate the antibacterial rate, the number of colonies obtained under control conditions was also counted. Finally, the antibacterial rate was marked as P, and the number of colonies with a catalyst and the number of colonies without a catalyst was marked as X and X_o. The reproducibility of the results was checked by repeating the experiments at least three times and was found to be within acceptable limits ($\pm 2\%$).



Figure 10. The spectra of the xenon lamp.

The experiments were all triplicated, and averaged values were used in the calculation. The antibacterial rate was calculated as follows:

$$P = \frac{X_o - X}{X_o} 100\%$$

3.5. Characterization

The catalysts were structurally elucidated by XRD assessment with a Rigaku Dmax-3C (Cu K α radiation). A NOVA 4000 was utilized to acquire the N₂ adsorption–desorption isotherms at 77 K, based on which the BJH computation of SBET (specific surface area), VP (pore volume) and average DP (pore diameter) was accomplished. FESEM (field-emission scanning electron microscopy; Hitachi S-4800) combined with TEM (transmission electron microscopy; JEM2100) were adopted for monitoring and examining the material morphologies. A Perkin-Elmer PHI 5000C was utilized to make the XPS (X-ray photoelectron spectroscopy) analysis. Binding energies were all calibrated against the contaminant reference carbon (C 1S, 284.6 eV). The FT-IR spectra were obtained on a Fourier transform infrared spectrometer (Bruker Equinox55). Varian Cary-Eclipse 500 and MC-2530 were separately utilized to perform the UV-vis DRS (UV-vis diffuse reflectance spectroscopy). In every measurement, an identical sample amount was confirmed for comparison purposes.

4. Conclusions

Here, we successfully prepared Cu/TiO₂/diatomite that consisted of the double interface Cu₄Ti₂O/TiO₂ and rutile/anatase heterojunction. Cu/TiO₂/diatomite prepared under optimum preparation conditions (reaction temperature:180 °C, the amount of TiCl₄: 0.8 mL, the dosage of CuSO₄: 0.005 g, the amount of dodecanol: 4.5 mL, and the reaction time: 8 h) exhibited high antibacterial activity (100%) when used as a catalyst for the inhibition of *Acinetobacter baumannii* growth. The investigation indicates that the Cu/TiO₂/diatomite could exhibit higher photocatalytic activity because of the double interface heterojunction of rutile/anatase, ultimately resulting in the electron (e⁻)–hole (h⁺) recombination reduction. Additionally, the composite whose pore size and specific surface area were large offers substantial active sites. Moreover, the Cu/TiO₂/diatomite whose band gap was narrowest enabled more visible light acquisition per unit time and more chemical energy conversion therefrom.

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