

Article

Bi(C₆N₇O₃) Nanospheres: A Novel Homogenous Photocatalyst for Efficient Treatment of Antibiotic in Water

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Abstract

The development of photocatalyst material is vital for the practical application of environmental purification, solar energy conversion, and chemical production. In this work, a spherical Bi(C₆N₇O₃) photocatalyst is successfully prepared by replacing K⁺ of rod-shaped K₃[C₆N₇O₃] with Bi³⁺ ions through the ion exchange method, which demonstrates an improved homogeneous photodegradation efficiency over antibiotics in water compared to pristine K₃[C₆N₇O₃]. Under visible light irradiation, Bi(C₆N₇O₃) degraded 81% of tetracycline hydrochloride within 60 min, and the rate constant was 1.8 and 79.1 times greater than K₃[C₆N₇O₃] and bulk g-C₃N₄, respectively. Scavenger experiments revealed that superoxide radicals and holes are the primary active species in the photocatalytic process. This study presents a promising route for designing high-performance visible-light photocatalysts by a simple ion-exchange approach for environmental applications.

Keywords: antibiotic degradation; Bi(C₆N₇O₃) sphere; visible-light photocatalysis; homogeneous photocatalysis



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1. Introduction

Environmental pollution caused by antibiotic misuse directly threatens human life and health [1], which is one of the key problems around the world and needs to be addressed urgently [2–6]. The traditional methods dealing with antibiotic pollution are mainly physical adsorption and microbiological treatment [7]. However, these methods have been labeled as insufficient due to the unconquerable drawbacks such as limited choice of adsorbents, potential for secondary contamination, high cost, long treatment time, and ineffective removal. Developing a green approach is vital for the efficient control of antibiotic pollution. Photocatalytic oxidation directly employs solar energy as a light source to drive catalysis [8], which has become a green and ideal approach to monitor the antibiotic pollutants [9–13].

Graphitic phase carbon nitride (g-C₃N₄) is a prospective polymer photocatalyst with the advantages of strong visible-light response, ease of preparation, and chemical stability, which has been intensively studied and broadly applied in visible-light photocatalysis, such as hydrogen production via water splitting and degradation of the emerging pollutant [14]. However, the practical application is severely restricted due to the drawbacks, such as a lack of active sites and a faint visible-light response. Great efforts have been made to overcome these defects, and strategies such as constructing hollow or porous structures

have been developed to enlarge the specific area recently [15]. Nevertheless, most of the currently reported g-C₃N₄ photocatalysts are heterogeneous phases. They are still suffering from the main insufficiencies such as limited specific surface area and active sites, which hinder the practical applications of g-C₃N₄-type photocatalyst [14,16].

On the contrary, homogeneous photocatalysis deals with a photocatalytic reaction where the catalyst and reactants exist in the same phase, facilitating the complete access of reactants toward the active sites, which may be an alternative approach to optimize the photocatalytic performance. The construction of homogeneous photocatalysts has thrived in recent years. In 2018, Huang et al. successfully synthesized a homogeneous CN-based photocatalyst, which demonstrated an improved photocatalytic activity in comparison with that of the heterogeneous counterpart [17]. However, the prepared photocatalyst is solely soluble in certain corrosive solvents, including CH₃SO₂OH and H₂SO₄, which limits its wide application in water. Given the urgent demand for water purification and pollutant decomposition, the fabrication of water-soluble photocatalysts remains challenging. Recently, a series of CN derivatives such as basic cyanurate of K₃[C₆N₇(NCN)₃] and C₆N₇O₃H₃ with distinct optical properties have been developed via alkali treatment, which are water-soluble compounds [18,19]. In 2021, Yang et al. successfully prepared rod-shaped K₃[C₆N₇O₃] compounds from top to bottom by reacting melon polymer with a hot strong base and applied it as a homogeneous photocatalyst in removing antibiotic residues in water for the first time [20]. The obtained photocatalyst showed 10-fold higher photocatalytic activity than that of bulk g-C₃N₄. However, a further improvement of activity is necessary for the practical application of homogeneous photocatalysis.

In this study, Bi(C₆N₇O₃) was successfully synthesized by replacing the K⁺ ion in K₃[C₆N₇O₃] with the Bi³⁺ ion from an ion-exchange process under solvothermal conditions, which showed improved photocatalytic activity and excellent stability toward the visible-light degradation of antibiotic residue in aqueous solutions. The substitution of K⁺ with Bi³⁺ may introduce a high-valence metal center, effectively modulating the electronic structure and facilitating charge carrier separation, which promotes the photocatalytic behaviors. The as-prepared Bi(C₆N₇O₃) shows 79.1 and 1.8-fold greater activity than those of g-C₃N₄ and K₃[C₆N₇O₃], respectively. Several techniques have been utilized to explore the factors contributing to the enhanced properties and stability. The active species are identified, and a reaction mechanism is proposed in the end. This work offers an easy strategy of ion exchange to manipulate the photocatalytic properties, which may spur the development and application of homogeneous photocatalysis.

2. Experimental

2.1. Chemicals and Materials

Melamine (C₃N₃(NH₂)₃, 99%) was bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Potassium hydroxide (KOH, 85%) was obtained from Aladdin Industrial Corporation. (Shanghai, China). N,N-dimethylformamide (HCON(CH₃)₂, 99.5%) and bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 99%) were obtained from Hangzhou Mick Chemical Reagent Co., Ltd. (Hangzhou, China). Methanol (CH₃OH, 99.7%) was obtained from Hangzhou Gaojing Fine Chemical Industry Co., Ltd. (Hangzhou, China). All the reagents were directly used after purchase.

2.2. Preparation

Preparation of rod-shaped K₃[C₆N₇O₃]. The preparation of K₃[C₆N₇O₃] is followed by the previous report [20]. Typically, 14.0 g of KOH and 5.0 g of melon powder were added to 50.0 mL of aqueous solution, mixed thoroughly, and transferred to a 150 mL round-bottom flask. Subsequently, the flask was positioned in an oil bath and refluxed at

130 °C for 2 h under magnetic stirring until the yellow-colored solution turned transparent. The hot solution was filtered, and the filtrate was stored in a refrigerator for 12 h. Finally, the precipitated solid was separated via vacuum filtration and washed repeatedly with absolute ethanol, and then dried under vacuum at 70 °C for 6 h to yield the product of potassium cyanurate $K_3[C_6N_7O_3]$.

Preparation of $Bi(C_6N_7O_3)$ nanospheres. 1.455 g $Bi(NO_3)_3 \cdot 5H_2O$ and 1.005 g gas-prepared $K_3[C_6N_7O_3]$ were dispersed in 50 mL of mixed solution ($DMF:CH_3OH = 3:1$) and stirred for 30 min to form a homogeneous solution. Subsequently, the solution was sealed in an autoclave equipped with polytetrafluoroethylene and heated at 120 °C for 16 h at a rate of 1 °C per minute. After that, the synthesized $Bi(C_6N_7O_3)$ was washed with absolute ethyl alcohol multiple times and dried at 70 °C for 12 h under vacuum.

2.3. Characterization

X-ray diffraction (XRD) pattern was detected on the a Panalytical X'Pert'3 Powder instrument (Malvern Panalytical, Almelo, The Netherlands) applying Cu $K\alpha$ ($\lambda = 1.5406 \text{ \AA}$) as the source. Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Tensor 27 spectrometer (Bruker Corporation, Billerica, MA, USA). Scanning electron microscopy (SEM) pictures and energy dispersive X-ray (EDX) patterns were carried out on a ZEISS Sigma 300 microscope (Carl Zeiss AG, Oberkochen, Germany). X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific K-Alpha instrument (Thermo Fisher Scientific, Waltham, MA, USA). UV-visible diffuse spectrum (UV-vis DRS) was performed on a Shimadzu UV-3600 UV-visible spectrophotometer (Shimadzu Corporation, Kyoto, Japan). Full-wavelength UV-visible absorption spectra were recorded on the UV-2600 UV-visible spectrophotometer (Shanghai Sunny Hengping Scientific Instrument Co., Ltd., Shanghai, China).

2.4. Photocatalytic Degradation Measurements

TC-HCl was employed as the typical antibiotic residue to evaluate the photocatalytic activities of the prepared samples. For simulated visible light, a 300 W Xenon lamp equipped with a 420-nm cut-off filter was employed, with a spectral irradiance of 272.0 mW/cm^2 . Moreover, a circulating cooling system was applied to maintain the reaction temperature at around 20 °C. Briefly, 20.0 mg of the prepared photocatalyst was dispersed in 100 mL of TC-HCl solution (10, 20, and 50 mg/L) using a 150 mL beaker as the reactor. The solution was stirred in the dark for 30 min to reach adsorption–desorption equilibrium. Then, the solution was positioned under the simulated light source, with the bottom of the reactor positioned at a vertical distance of 13 cm from the lamp, and the lamp was turned on for illumination with constant magnetic stirring (550 rpm). The initial pH of the solution before the photocatalytic reaction was measured to be 6.76. 5.0 mL of solution was collected every 10 min, and the supernatant after centrifugation was taken for measurement on a UV-2600 spectrophotometer. All experiments were repeated at least three times to ensure reproducibility.

3. Results and Discussion

The crystal structure of $Bi(C_6N_7O_3)$ was analyzed using XRD, as shown in Figure 1a. The diffraction pattern was compared to that of $K_3[C_6N_7O_3]$, considering the absence of a reference XRD pattern for $Bi(C_6N_7O_3)$. The prominent peak at 28.12° corresponded to the interlayer stacking of aromatic units, while the diffraction peak at approximately 14.02° was characteristic of the melon structure, which was ascribed to the cohesive and ordered arrangement of cyanuric acid units [21]. A notable rightward shift in the diffraction peak positions for $Bi(C_6N_7O_3)$ was observed when compared to the JCPDS pattern of

$\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$. This shift is attributed to the substitution of Bi^{3+} ions, which have a smaller ionic radius than K^+ ions. The introduction of smaller dopant atoms into the lattice leads to a reduction in the unit cell parameters, thereby causing the rightward shift of the XRD peaks.

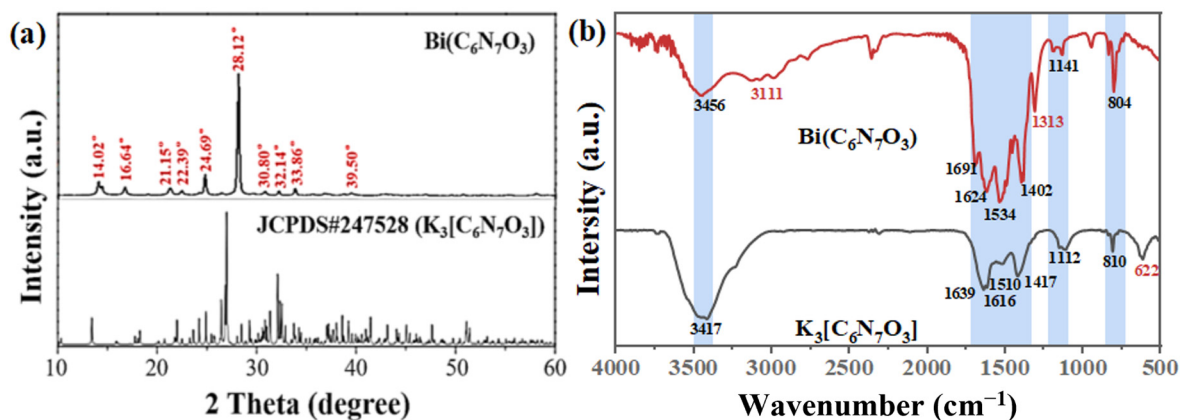


Figure 1. (a) XRD patterns of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ and $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$, (b) Recorded FTIR spectra of $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$ and $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$. The black and red lines correspond to the $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$ and $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ samples, respectively.

As displayed in Figure 1b, the FTIR spectra of $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$ and $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ were consistent with previous studies [18]. The peak at 804 cm^{-1} corresponded to the bending vibration associated with the S-triazine unit. In the range of $1000\text{--}1600\text{ cm}^{-1}$, the observed band was attributed to the stretching vibration of the C-N heterocyclic ring [22]. The peaks at 1624 , 1534 , and 1402 cm^{-1} were associated with the stretching vibration of heptazine-derived repeating units, respectively [23]. Additionally, the broad band between 3111 and 3456 cm^{-1} was attributed to the stretching vibration of N-H bonds and the presence of absorbed water [24]. These characteristic features collectively confirm the identity of the prepared sample as $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$.

The chemical composition and valence states of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ were investigated using XPS measurement. As shown in Figure 2a, the presence of all constituent elements, including carbon (C), nitrogen (N), oxygen (O), and bismuth (Bi), corroborated the above discussion. No peak belonging to potassium (K) was observed, indicating the complete substitution of K by Bi. The fine C 1s spectrum and its deconvoluted peaks, presented in Figure 2b, revealed two principal peaks at 284.8 eV (C-C) and 288.6 eV (N-C=N), corresponding to different carbon environments within $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ [25]. In addition, the peak at 286.5 eV is likely ascribed to the presence of C-O-Bi groups. Figure 2c displayed the N 1s spectrum with a peak at 398.4 eV , characteristic of the sp^2 hybridized N atom in C=N-C bonds [26]. The peaks at 400.0 eV and 401.1 eV are tentatively assigned to N atoms in N-(C)3 and N-H configurations, respectively [27]. The faint peak at 404.8 eV was related to π -excitation [28]. The O 1s (Figure 2d) exhibited a peak at 531.2 eV , which corresponded to C-O-Bi bonds in $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ [29]. Figure 2e revealed two distinct peaks at 159.4 eV ($\text{Bi } 4f_{7/2}$) and 164.7 eV ($\text{Bi } 4f_{5/2}$), which were indicative of the bismuth species present within the compound. These XPS results confirm that the prepared $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ has an aromatic skeleton composed of heptazine units, suggesting the successful synthesis of the target compound.

Figure 3a shows the SEM image of the $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ sample. The prepared $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ had an irregular spherical shape with diameters close to $5\text{ }\mu\text{m}$. As seen in Figure 3b, the chemical composition of Bi was via EDS and peaks at ~ 0.3 , ~ 0.4 , ~ 0.5 , and $\sim 2.4\text{ keV}$ were detected in the EDS spectra, assigned to the elements C, N, O, and Bi, respectively,

indicating that C, N, O, and Bi atoms coexisted in $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ [30]. According to the EDS analysis, the atomic contents of C and N were 31.53% and 36.28%, respectively. The ratio of C to N atoms was 0.87, which is consistent with the structural formula. The EDS elemental mappings of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$, as demonstrated in Figure 3c–f confirmed the uniform distribution of all the elements within $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$. These results further confirm the successful preparation of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$.

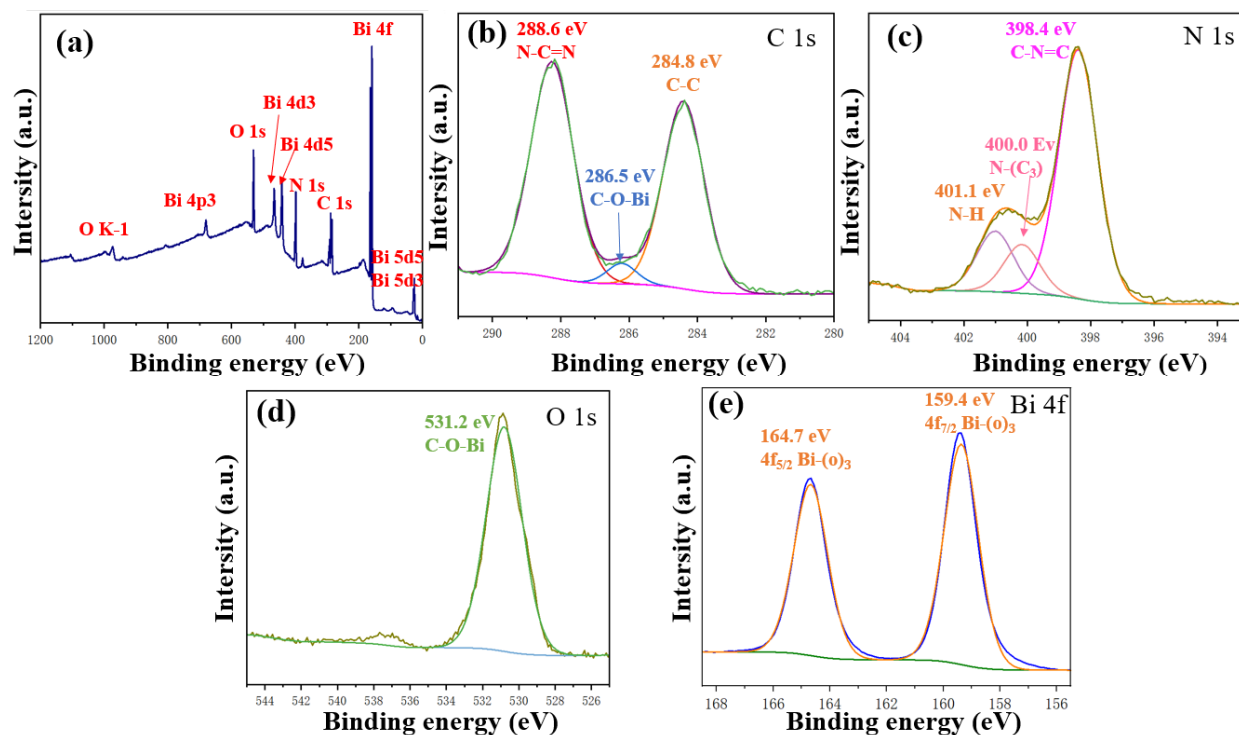


Figure 2. XPS spectra of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$: (a) survey spectrum, (b) C 1s spectrum, (c) N 1s spectrum, (d) O 1s spectrum, and (e) Bi 4f spectrum.

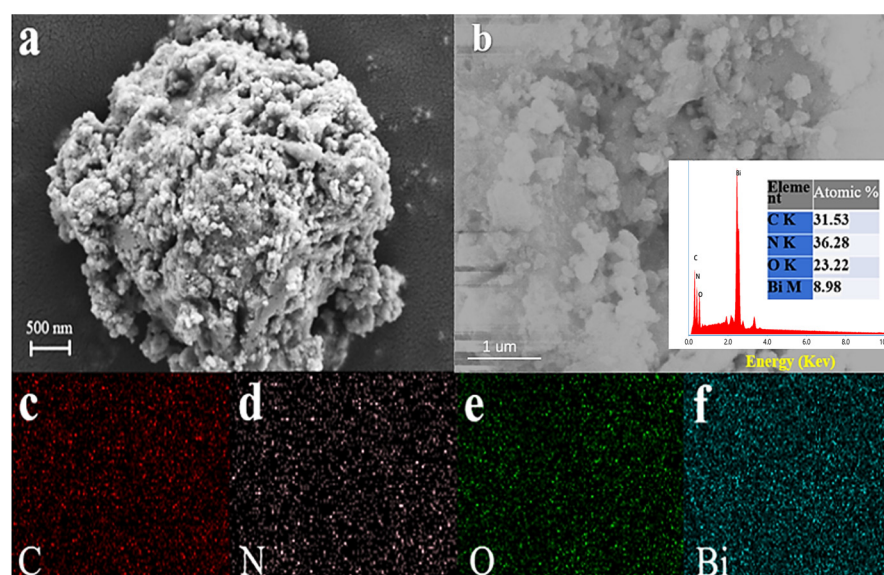


Figure 3. (a) SEM image of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$, (b–f) EDS elemental mappings of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$.

Figure 4 presents the homogeneous degradation profiles of tetracycline hydrochloride (TC-HCl) in aqueous solution under visible-light irradiation using different dosages of photocatalysts. As depicted in Figure 4a, $\text{g-C}_3\text{N}_4$ exhibited minimal degradation of

TC-HCl under visible light, with only a 2.4% reduction observed. In contrast, significant degradation was achieved with $K_3[C_6N_7O_3]$ and $Bi(C_6N_7O_3)$ as photocatalysts, resulting in efficiencies of 63% and 81%, respectively, within 60 min. Further investigation into the photocatalytic degradation efficiency of $Bi(C_6N_7O_3)$ on TC-HCl solutions with different concentrations was shown in Figure 4b. Photocatalytic degradation efficiencies of TC-HCl solutions with initial concentrations of 20, 30, and 50 mg/L were 81%, 75%, and 55%, respectively. These results confirm that the synthesized $Bi(C_6N_7O_3)$ is an effective photocatalyst for homogeneous processes, demonstrating its potential for practical applications in water treatment.

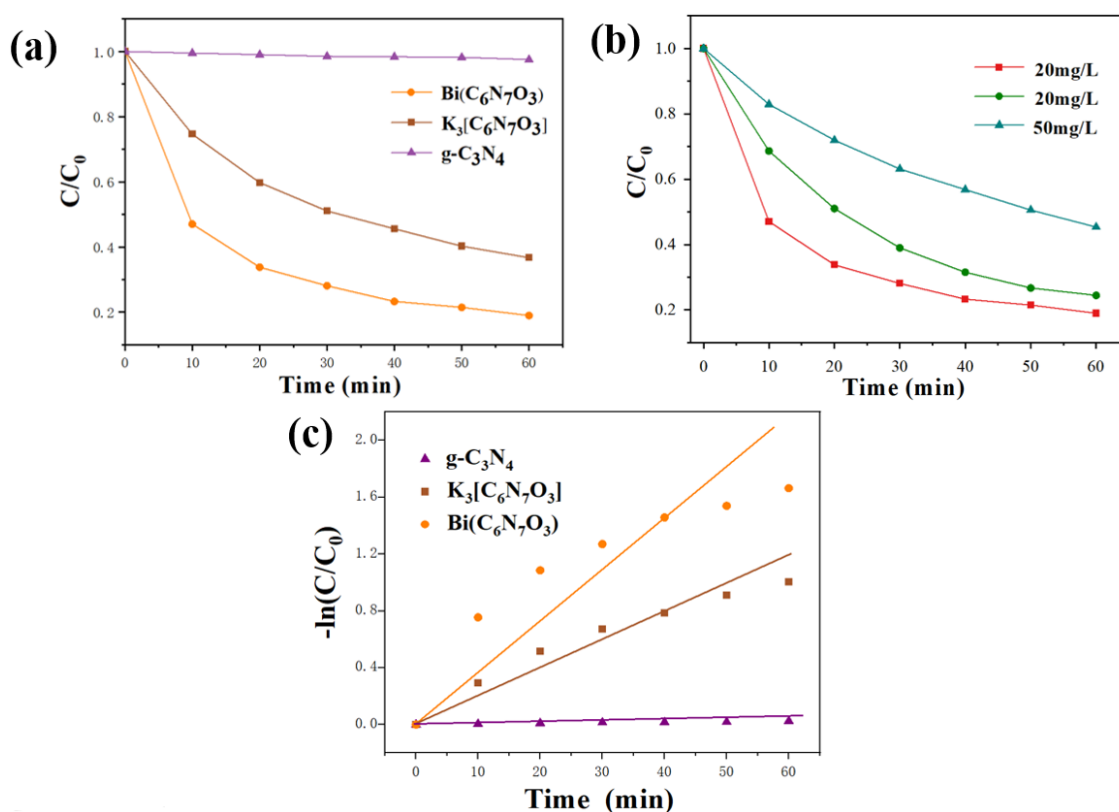


Figure 4. (a) Photocatalytic degradation efficiency of TC-HCl under the visible light irradiation using $g-C_3N_4$, $K_3[C_6N_7O_3]$, and $Bi(C_6N_7O_3)$; (b) Degradation efficiency of TC-HCl solutions with different concentrations (20, 30, and 50 mg/L) using $Bi(C_6N_7O_3)$; (c) Pseudo-first-order kinetic fitting of TC-HCl degradation over the three photocatalysts.

The photocatalytic activity of the obtained samples was quantified using a pseudo-first-order model, Equation (1).

$$k = \frac{-\ln(C_t/C_0)}{t} \quad (1)$$

where C_0 represented the initial TC-HCl concentration, and C_t represented the TC-HCl concentration following t min of irradiation. The optimum slope, corresponding to the apparent rate constant k_{app} , was obtained by the method of least squares [28]. In Figure 4c, the calculated k_{app} values for $g-C_3N_4$, $K_3[C_6N_7O_3]$, and $Bi(C_6N_7O_3)$ photocatalysts were 0.00042 min^{-1} , 0.01873 min^{-1} , and 0.03323 min^{-1} , respectively. Obviously, the k_{app} value of $Bi(C_6N_7O_3)$ is 79.1 and 1.8-fold higher than that of $g-C_3N_4$ and $K_3[C_6N_7O_3]$, demonstrating the superior photocatalytic activity of $Bi(C_6N_7O_3)$.

The photocatalytic performance of $Bi(C_6N_7O_3)$ was compared with that of the recently reported photocatalysts. As summarized in Table 1, the $Bi(C_6N_7O_3)$ catalyst exhibits a

notably higher k_{app} than most of the compared materials, underscoring its superior activity and reinforcing the advancement presented in this study.

Table 1. Comparison of the k_{app} for various photocatalysts reported in recent studies.

Year	Photocatalyst	k_{app} (min^{-1})
2025	$\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$	0.033
2025	$\text{ZnO}_2/\text{Bi}_2\text{O}_2\text{CO}_3$ [31]	0.012
2025	20SA-CN [32]	0.012
2025	2% Ni-decorated melem hydrate/ $\text{g-C}_3\text{N}_5$ [33]	0.032
2025	EG- BiOCl [34]	0.019
2025	$\text{Fe}_{0.1}\text{Co}_{0.05}\text{Ni}_{0.05}/\text{CdS}$ [35]	0.031

The reusability and sustainability of photocatalysts are crucial for their practical applications. The $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ photocatalyst in ethanol was collected and washed after the initial photocatalytic run and then subjected to an additional three cycles of the same procedure, as illustrated in Figure 5. A decline in photocatalytic activity with each cycle was observed, which could be attributed to the gradual leaching of Bi^{3+} from the $(\text{C}_6\text{N}_7\text{O}_3)^{3-}$ framework as the cycles progress. Additionally, $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ has good solubility, readily soluble in water, leading to noticeable mass loss during the recovery process in ethanol, considering that ethanol contains a small amount of water.

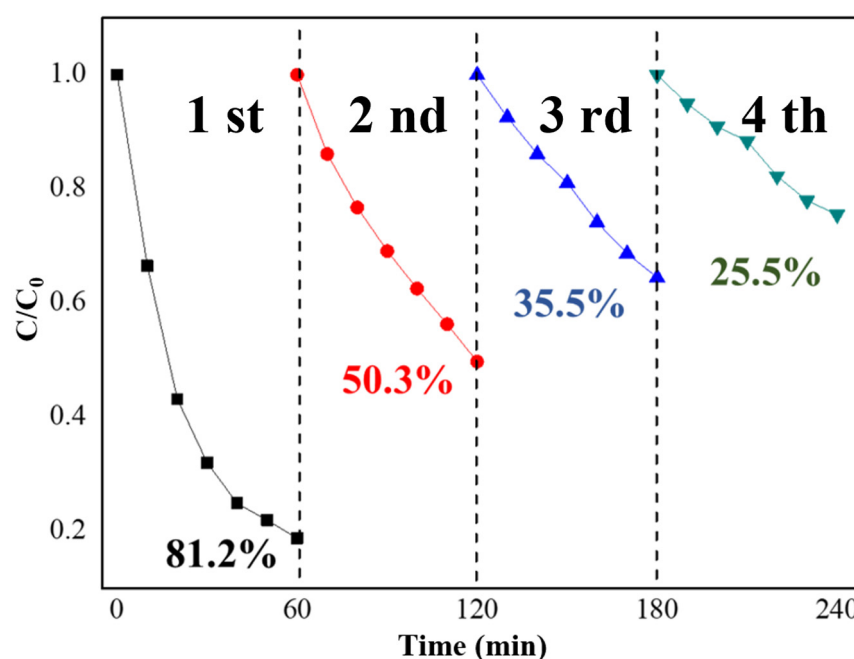


Figure 5. Cyclic stability tests of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ for TC-HCl photodegradation.

The underlying mechanism of the enhanced photocatalytic property of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ was investigated. The UV-Vis diffuse reflection absorption spectra for the synthesized photocatalysts were measured, as depicted in Figure 6a. Both $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$ and $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ demonstrated strong absorption across the UV-visible spectrum, with distinct absorption edges observed at 438 and 486 nm. These edges suggest that the samples can capture a fraction of the visible light. The bandgap of the $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$ and $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ was calculated using the Tauc plot, as shown in Figure 6b, yielding bandgap values of 2.8 eV for $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$ and 2.2 eV for $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$. Compared to $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$, the band gap

of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ was reduced, allowing it to absorb more light energy and generate more electron-hole pairs, increasing its photosensitivity and photovoltaic effect.

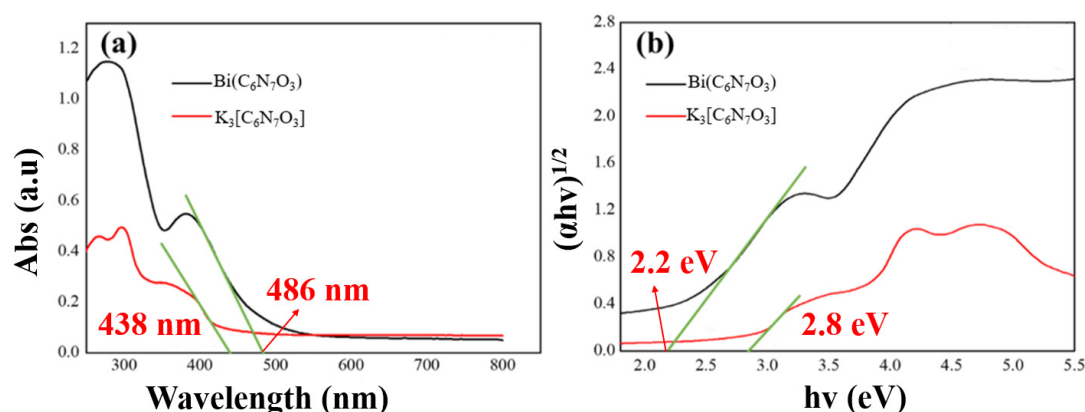


Figure 6. (a) UV-vis absorption spectrum of $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$ and $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$; (b) Tauc plots derived from UV-Vis spectra.

Photocurrent measurement upon light illumination is a robust indicator of the efficiency of photogenerated carrier separation and transport, which are key factors in photocatalytic performance. Figure 7a showed the photocurrent responses of $\text{g-C}_3\text{N}_4$, $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$, and $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ under visible light irradiation in ethanol, considering the water solubility of the latter two compounds. Upon turning on the light source, both $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$ and $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ exhibited significant photocurrent, with $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ exhibiting the highest response. This suggests that $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ might have a more efficient separation and migration of photoexcited carriers compared to $\text{g-C}_3\text{N}_4$ and $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$. Furthermore, EIS was utilized to evaluate the electron transfer characteristics of the prepared samples, as depicted in Figure 7b. $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ had the smallest arc diameter among these samples, indicating the lowest electron transfer resistance. These results show that $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ has a narrow band gap, a high charge separation capability, and a low electron transfer resistance, which collectively improve its photocatalytic performance.

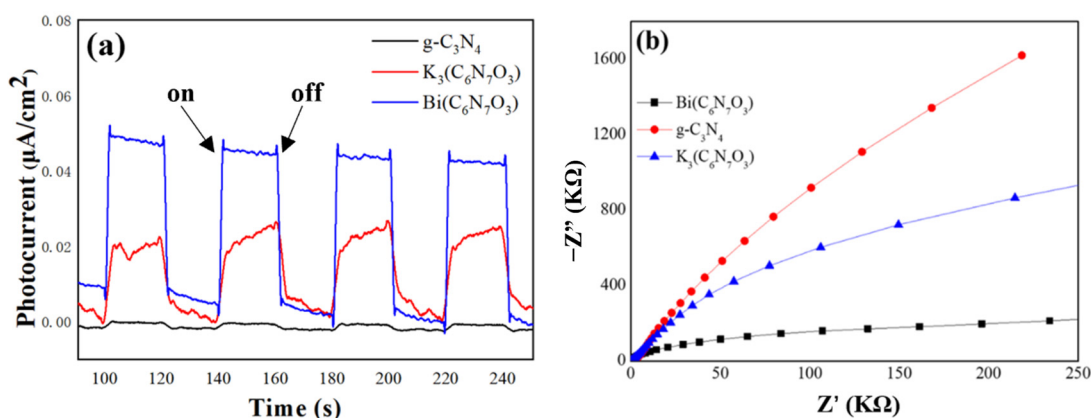


Figure 7. (a) Transient photocurrent response under visible light irradiation and (b) Electrochemical impedance spectroscopy (EIS) Nyquist plots of $\text{g-C}_3\text{N}_4$, $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$, and $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$.

As shown in Figure 8, radical trapping experiments were conducted to identify the active substances involved in the photocatalytic reactions. Ethylenediamine tetraacetic acid (EDTA-2Na), p-benzoquinone (BQ, 0.5 mM), and tert-butanol (TBA, 2 mM) were employed as the scavengers of photogenerated holes (h^+), superoxide radicals ($\cdot\text{O}_2^-$), and hydroxyl radicals ($\cdot\text{OH}$), respectively. The low concentration of BQ used (0.5 mM) is well-established

in the literature to specifically quench $\cdot\text{O}_2^-$ without significant side reactions under standard photocatalytic conditions [36,37]. Similarly, TBA is a highly specific scavenger for $\cdot\text{OH}$, whose steric hindrance makes reactions with $\cdot\text{O}_2^-$ or h^+ unlikely [37]. The addition of BQ and EDTA-2Na resulted in a significant decrease in photocatalytic activity, indicating that both $\cdot\text{O}_2^-$ and h^+ were primary reactive species in the photocatalytic process. In contrast, the introduction of TBA did not affect the degradation efficiency, suggesting that $\cdot\text{OH}$ had an insignificant effect in the photocatalytic process [38].

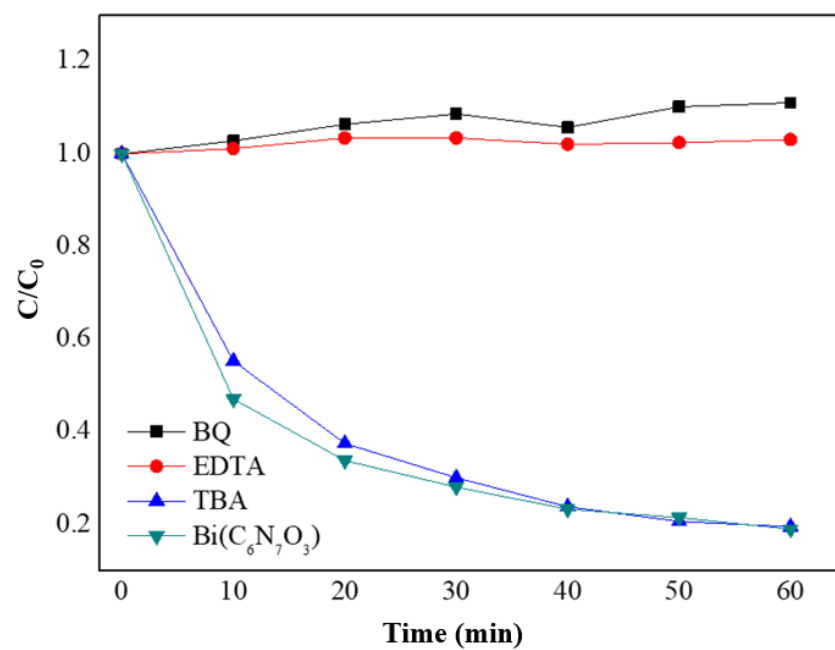


Figure 8. Effects of different radical scavengers (TBA for $\cdot\text{OH}$, EDTA-2Na for h^+ , BQ for $\cdot\text{O}_2^-$) on the photocatalytic degradation of TC-HCl over $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$.

The photocatalytic performance of the $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ nanospheres was compared with a recently reported $\text{Fe-TiO}_2/\text{biochar}$ composite, similarly identifying $\cdot\text{O}_2^-$ as the predominant reactive species [39]. The k_{app} of our $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ catalyst for TC-HCl degradation was calculated to be 1.99 h^{-1} (from 0.03323 min^{-1}), which is higher than the k_{app} of 0.202 h^{-1} on $\text{Fe-TiO}_2/\text{biochar}$ composite.

The Mott–Schottky plot for $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ displayed a positive slope, as illustrated in Figure 9a, which indicates that the sample is an n-type semiconductor. With respect to the normal hydrogen electrode, the conduction band (CB) energy level of an n-type semiconductor is measured to be -0.62 V . Typically, the conduction band energy level of an n-type semiconductor is approximately 0.1 eV less negative than the conduction band energy level of the flat-band potential [40]. Consequently, the conduction band level of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ is estimated to be -0.72 V with respect to the normal hydrogen electrode (NHE), and the position of the valence band (VB) is obtained according to Equation (2) [41]:

$$E_{\text{VB}} = E_{\text{CB}} + E_{\text{g}} \quad (2)$$

Based on the above results, a plausible mechanism for the photocatalytic degradation is proposed. As illustrated in Figure 9b, upon illumination with visible light, the electrons (e^-) in $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ are excited to a conduction band, leaving behind holes (h^+) in the valence band. This process results in the formation of electron-hole pairs, where the holes possess sufficient positive potential to produce $\cdot\text{OH}$ radicals. However, the radical scavenger test confirms that $\cdot\text{OH}$ radicals have an insignificant role in the photocatalytic process. Rather, it is the holes at the surface of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ that are primarily engaged in the photocatalytic

activity. In conclusion, the active species, including superoxide radicals, photogenerated electron-positive hole pairs, are crucially involved in the photodegradation of TC-HCl.

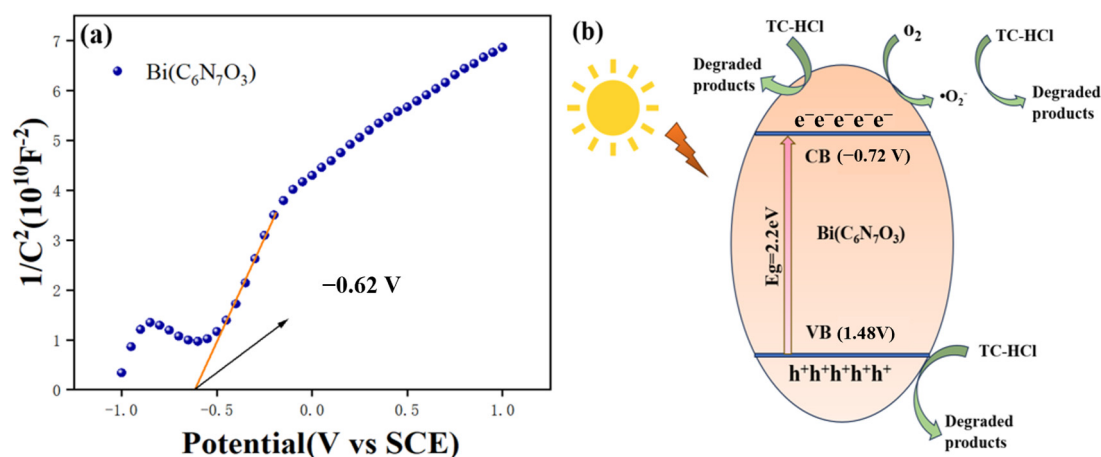


Figure 9. (a) Mott-Schottky curve of $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ and (b) schematic illustration of the proposed mechanism for photocatalytic degradation of TC-HCl over $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ nanospheres under visible light irradiation.

4. Conclusions

$\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ nanospheres are successfully prepared by replacing K^+ of as-synthesized $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$ with Bi^{3+} ions, which are applied as a prominent homogeneous photocatalyst for dealing with the emerging pollutant in water for the first time. The as-prepared compound can combine with three surroundings $(\text{C}_6\text{N}_7\text{O}_3)^{3-}$ ions because Bi^{3+} has three positive charges. Therefore, metal ions and organic ligands can be connected by self-assembly to form a category of crystalline materials with a periodic network structure. Experiments with photocatalysis have shown that $\text{Bi}(\text{C}_6\text{N}_7\text{O}_3)$ demonstrates a greatly improved photocatalytic activity, which is 79.1- and 1.8-fold greater than that of $\text{g-C}_3\text{N}_4$ and $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$, respectively. The enhancement may be attributed to the increased optimized visible-light response and charge separation. This work offers a strategy to build high-performance photocatalysts by simple ion substitution and broadens the application of homogeneous photocatalysis in environmental control and other fields.

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