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# Internal electric field boosting visible photocatalytic degradation of antibiotics by flower-like CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> S-scheme heterojunctions†

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An internal electric field can be formed by constructing a heterojunction to achieve effective separation of photogenerated electrons and holes, which is able to solve the problem of easy recombination of photogenerated carriers in a single semiconductor photocatalyst. This research employs a hydrothermal synthesis technique to develop S-scheme heterojunction photocatalysts composed of cerium oxide and bismuth sulfide (CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>) and evaluates their efficacy in degrading TC under visible light. The formation of S-scheme heterojunctions was confirmed by X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations showing that electrons migrate, and the internal electric field of the S-scheme heterojunctions achieves the separation of the electron–hole pairs, retaining the redox capacity of useful electrons and holes, which is responsible for the enhancement of the photocatalytic activity. The synthesized CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 photocatalysts demonstrated a TC degradation rate of 82.43% after a duration of 120 minutes under visible light irradiation. The rate constant of this performance was two times greater than that of CeO<sub>2</sub> alone and 2.75 times greater than that of Bi<sub>2</sub>S<sub>3</sub>. In addition, free radical trapping experiments and electron paramagnetic resonance results confirmed that ·O<sub>2</sub><sup>−</sup> and h<sup>+</sup> are active substances in the photocatalytic reaction process. Liquid chromatography–mass spectrometry (LC–MS) detected possible intermediates and suggested degradation pathways. This study has significant implications for the future development and enhancement of S-scheme heterojunction photocatalysts, contributing to advancements in photocatalytic materials.

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## 1 Introduction

The discovery of antibiotics and their application in disease treatment, alongside the misuse of antibiotics such as tetracycline (TC), have resulted in significant environmental contamination.<sup>1,2</sup> TC is present as a persistent organic pollutant in the environment, leading to the gradual accumulation and the potential development of microbial resistance, which poses risks to both ecological systems and human health.<sup>3,4</sup> Consequently, the remediation of TC residues is critical, which might be achieved using various methods such as physical adsorption,

biodegradation, and chemical techniques.<sup>5</sup> Physical adsorption effectively removes contaminants but necessitates frequent replacement of the adsorbent material. Biodegradation employs microorganisms to degrade TC, offering economic advantages and effective performance; however, it often produces by-products that may be more toxic than TC, rendering it a less attractive choice.<sup>6,7</sup> Chemical methods, such as photocatalytic degradation and precipitation, are also employed. Photocatalytic technology is an advanced oxidation process capable of completely degrading organic pollutants by generating reductive electrons and oxidative holes without producing secondary pollution, garnering significant attention in recent years.<sup>8</sup>

Cerium dioxide (CeO<sub>2</sub>), a widely-used n-type semiconductor, has significant applications in photocatalysis, fuel cells, and industrial catalysis, given its cost-effectiveness, high stability, and low environmental impact.<sup>9,10</sup> However, its relatively broad energy bandgap of approximately 3.2 eV hinders its ability to absorb visible light effectively. As a result, the electrons generated upon photoexcitation are unable to move to the conduction band (CB) and recombine with holes, severely limiting its photocatalytic efficiency.<sup>11,12</sup> Recent studies have addressed these limitations through various strategies, including morphological control,<sup>13,14</sup> metal doping<sup>15–17</sup> and the fabrication

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of heterojunctions.<sup>18–20</sup> For instance, CeO<sub>2</sub> nanoparticles with a precisely controlled size of 2.1 nm demonstrated a glyphosate decomposition rate 20 times greater than that of larger 4.8 nm nanoparticles, highlighting the significant effect of particle size on photocatalytic activity.<sup>21</sup> The photocatalytic degradation of TC was markedly enhanced when using H<sub>2</sub>-reduced Mn-doped CeO<sub>2</sub> compared to pure CeO<sub>2</sub>, with manganese doping facilitating a hierarchical structure and surface atomic arrangement that modifies the electronic properties of the material.<sup>16</sup> Furthermore, Cu–CeO<sub>2</sub>/BiOBr Z-type heterojunction exhibited reduced electron–hole recombination, with copper doping lowering the energy bandgap of CeO<sub>2</sub> and the heterojunction structure expanding the visible light absorption range, achieving a 92.3% degradation of sulfathiazole within 90 min.<sup>15</sup> The construction of heterojunctions has emerged as an effective strategy to enhance photocatalytic performance, with common frameworks including type-II heterojunctions<sup>22</sup> and Z-type heterojunctions.<sup>23,24</sup> However, research indicates that traditional type-II heterojunctions face challenges for effective charge separation, while Z-type heterojunctions encounter issues such as redox pair interactions that reduce the available photogenerated electrons and holes, along with a charge transfer mechanism that undermines their purported benefits.<sup>25</sup>

To address these challenges, the step-structured heterojunction (S-scheme) has been proposed,<sup>26</sup> which integrates an oxidized photocatalyst (OP) with a reduced photocatalyst (RP). This combination creates a catalytic system with enhanced performance, where the CB of the RP is elevated, along with its Fermi level ( $E_f$ ), both of which are superior to those of the OP, establishing a significant driving force for electron transfer.<sup>27,28</sup> Upon contact between the RP and OP, an internal electric field (IEF) is generated, facilitating electron migration and promoting the photocatalytic reaction. This IEF enables the recombination of excess electrons in the CB of the OP with the unwanted holes found in the valence band potential (VB) of the RP. This recombination serves to mitigate the losses associated with excess energy, reducing energy losses.<sup>29,30</sup> Simultaneously, this mechanism ensures the preservation of beneficial electrons and holes, allowing them to maintain their active involvement in the essential redox reactions, thereby enhancing the efficiency of the photocatalytic system. Therefore, there is a need to find a suitable RP semiconductor to construct an S-scheme heterojunction with CeO<sub>2</sub>.

Bi<sub>2</sub>S<sub>3</sub> functions as an n-type semiconductor characterized by a narrow bandgap, which exhibiting significant light absorption within the visible spectrum and allows for tunability in its bandgap energy.<sup>31,32</sup> The Bi<sub>2</sub>S<sub>3</sub> heterojunction, when combined with wide bandgap semiconductors, enhances effective electron transfer. In this heterojunction, electrons migrate from Bi<sub>2</sub>S<sub>3</sub>, which has a comparatively lower CB to a wide bandgap semiconductor with a higher CB. This mechanism not only improves electron mobility but also facilitates the separation of electron–hole pairs generated by light. Such a migration mechanism suggests enhanced visible light absorption when light strikes the heterojunction, ultimately leading to improved efficiency in the separation of photogenerated carriers.<sup>33</sup> Hydrothermal synthesis of g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>S<sub>3</sub> resulted in 95.6% degradation of

Reactive Black 5 and 97.5% degradation of indigo cochineal after 120 min of light exposure.<sup>34</sup> This research underscores the feasibility of the approach and hints that both CeO<sub>2</sub> and Bi<sub>2</sub>S<sub>3</sub> can be used to form highly efficient S-scheme heterojunctions.

In this work, CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> S-scheme heterojunction photocatalysts were synthesized by combining the wide bandgap semiconductor CeO<sub>2</sub> with the narrow bandgap semiconductor Bi<sub>2</sub>S<sub>3</sub> using hydrothermal methods, and were used to degrade TC under light conditions. The assessment of the photodegradation efficiency of the CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> S-scheme heterojunction photocatalysts facilitated an initial exploration of the mechanisms and pathways involved in TC degradation, informed by free radical trapping experiments, energy band structure analysis, and intermediate product characterization. The results showed that the CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> S-scheme heterojunction photocatalyst not only enhanced the charge migration efficiency, but also effectively promoted the directional separation of the photogenerated electron–hole pairs through the establishment of an internal electric field, which significantly enhanced the photocatalytic degradation performance while maintaining the strong redox ability of the dominant carriers. The main text of the article should appear here with headings as appropriate.

## 2 Experimental section

### 2.1 Materials

Cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O), L-ascorbic acid (LA), ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, EG), tetracycline (C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub>, TC) and thiourea (CH<sub>4</sub>N<sub>2</sub>S) were supplied by Shanghai Macklin Reagent Co. Isopropyl alcohol (IPA), sodium hydroxide (NaOH), and sodium ethylenediaminetetraacetic acid (EDTA-2Na) were purchased from Tianjin Kemel Chemical Reagent Co. The water used in the experiment was deionized water. All chemical reagents are directly used without further purification.

### 2.2 Preparation of CeO<sub>2</sub>

60.00 g NaOH in 87.5 mL of water was heated and stirred at 70 °C for 30 min to accelerate the dissolution, and 5.42 g Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O in 12.5 mL of deionised water was stirred until it was completely dissolved, and then, the two solutions were mixed slowly and stirred magnetically for 30 min, and the mixture was transferred to 100 mL of a polytetrafluoroethylene-lined stainless steel autoclave, hydrothermal treatment at 100 °C for 24 h, and cooled to room temperature. The mixture was transferred to 100 mL PTFE-lined stainless steel autoclave, hydrothermally treated at 100 °C for 24 h, cooled to room temperature, and the resultant was centrifuged (9000 rpm, 5 min) and washed with water several times until the pH was 7. After drying at 100 °C for 4 h, the product was heated to 500 °C at an elevated rate of 5 °C min<sup>-1</sup> and calcined in air for 5 h. The CeO<sub>2</sub> nanorods were obtained by grinding into powder.



### 2.3 Preparation of CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>

A total of 0.97 g of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was combined with 25 mL of EG and stirred for 30 min, resulting in what is referred to as solution A. Solution B was also prepared by incorporating 0.34 g of CeO<sub>2</sub> and 0.23 g of CH<sub>4</sub>N<sub>2</sub>S was also stirred in 25 mL of EG. Once solution B was successfully prepared, it was gradually combined with solution A and stirred for 30 min to guarantee proper mixing of the two solutions. The ultimate product is subsequently moved to a stainless steel autoclave that has a lining made of polytetrafluoroethylene, and subjected to hydrothermal treatment at 160 °C for 14 h. The resultant products were washed multiple times with water through centrifugation (9000 rpm for 5 min) and then dried at 80 °C for 12 h in a vacuum oven. The CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> composites were ground into powders, and the specific procedure of the experiment is shown in Scheme 1. Based on the different applied molar ratios of CeO<sub>2</sub> to Bi<sub>2</sub>S<sub>3</sub> in the composite photocatalysts were of 3 : 1, 2 : 1, 1 : 1 and 1 : 2, the obtained photocatalysts were named CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-1, CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2, CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-3, and CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-4, respectively. The Bi<sub>2</sub>S<sub>3</sub> photocatalysts were also prepared without doping CeO<sub>2</sub>, *via* same procedure as described above.

### 2.4 Characterization

A D/max-2500PC (Rigaku) instrument was used to perform powder X-ray diffraction to evaluate the physical phases and crystal structure of the photocatalysts. Concurrently, the morphology of the photocatalysts was assessed using a cold field emission scanning electron microscope (SEM, Hitachi S-4800), enabling the observation of the samples' morphological features at the microscopic scale. Additionally, a high-resolution transmission electron microscope (TEM, JEM-2100F), complemented by an energy dispersive spectrometer (EDS), was utilized to provide further insights into the internal structures and compositions of the photocatalysts. Moreover, to thoroughly explore the chemical composition of the samples and their respective oxidation states, an X-ray photoelectron spectrometer (XPS, Shimadzu AXIS Supra<sup>+</sup>) was employed to characterize the oxidation states. The photocatalysts' light absorption characteristics were evaluated using a UV-Vis Diffuse Reflectance Spectrometer (UV-Vis DRS, V-750 (JASCO)), which provide a quantitative information of their light absorption capabilities. Finally, the investigation of the photo-generated carrier complexation in the photocatalysts was carried out using photoluminescence spectroscopy (PL), with a fluorescence photometer (FLS-1000) excited at 365 nm.

Determination of degraded TC intermediates by liquid chromatography-mass spectrometry (Bruker ESI-Q-TOF).

### 2.5 Photoelectrochemical analysis

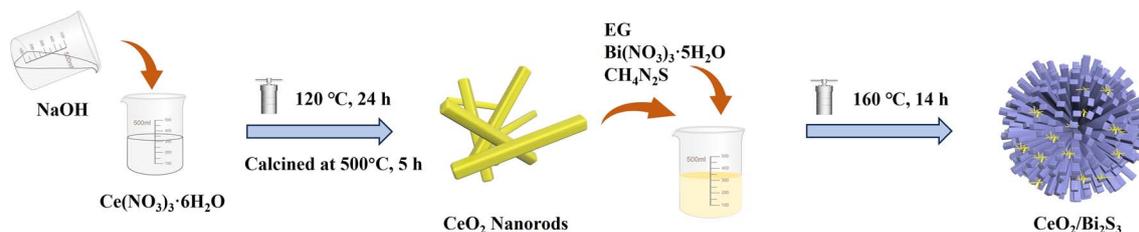
The transient photocurrent response and electrochemical impedance were assessed with a conventional three-electrode setup utilizing the CHI660E electrochemical workstation. The counter electrode was represented by a Pt electrode, whereas the reference electrode was Ag|AgCl (3 M KCl). A mixture of 10 mg of photocatalysts, 800 μL of ethanol, and 200 μL of Nafion was sonicated for 10 min and applied to a 1 × 1 cm<sup>2</sup> FTO glass, which was dried and then the FTO glass electrode was clamped to a copper-violet electrode holder as the working electrode. It was submerged in 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution and placed under the radiation of a 300 W xenon lamp.

### 2.6 Evaluation of photocatalytic performance

The photocatalytic degradation of TC was examined using a 300 W xenon light source (CEL-PF300-T6) equipped with a 420 nm filter to simulate solar light irradiation. A 100 mL solution of TC, with an initial concentration  $C_0 = 10 \text{ mg L}^{-1}$  was transferred into a 200 mL jacketed beaker, into which 20 mg of photocatalyst was introduced. The temperature of the beaker was maintained at 25 °C throughout the experiment using a circulating cooling water system, and the solution was homogenized *via* magnetic stirring. Adsorption equilibrium was established by stirring the solution in the dark for 40 min. Following this, the light source was activated for the photoreaction. After every 20-min intervals, approximately 4 mL of the solution was abstracted with a syringe and filtered through a 0.45 μm water filter to remove the photocatalysts. The reactive radicals produced during photocatalysis were investigated using electron paramagnetic resonance (EPR, Bruker A300, USA). The TC concentration was measured with a UV-visible spectrophotometer (YOKE T3202S) at a designated wavelength of 357 nm, and the degradation rate of TC was assessed in accordance with Beer-Lambert law by utilizing the absorbance measured at that wavelength. The degradation rate of TC ( $D$ ) is computed using eqn (1).

$$D(\%) = \frac{C_t - C_0}{C_0} \times 100 \quad (1)$$

where  $C_t$  denotes the concentration at time  $t$ , while  $C_0$  signifies the initial concentration.



Scheme 1 Schematic illustration of the synthesis of CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> photocatalysts.



## 2.7 Theoretical calculations

The Vienna *Ab initio* Simulation Package (VASP) was employed to perform all the density functional theory (DFT) calculations employing the projector-augmented wave method (PAW).<sup>35,36</sup> To enhance the precision and dependability of our calculations, we utilized the Perdew–Burke–Ernzerhof (PBE) exchange–correlation function.<sup>37</sup> This combination effectively represents electron behavior and associated forces, providing a solid theoretical

foundation for our research. Additionally, we employed a plane-wave basis set with a kinetic energy cut-off of 400 eV to ensure the adequacy of our computational approach. We adopted the lattice parameters  $a = 11.771 \text{ \AA}$ ,  $b = 11.324 \text{ \AA}$  and  $c = 32.670 \text{ \AA}$  for the  $\text{CeO}_2/\text{Bi}_2\text{S}_3$  heterostructure, which consists of a single layer of  $\text{Bi}_2\text{S}_3$  on the  $\text{CeO}_2$  (111) substrate. In this research, a vacuum layer thickness of 20  $\text{\AA}$  is established. To accurately characterize the energetic behavior of the system, a cut-off energy of 520 eV was employed for the plane-wave basis set. Brillouin zone integration was conducted using Monkhorst–Pack  $k$ -point sampling.<sup>38</sup> Throughout the self-consistent calculations, a convergence energy threshold of  $10^{-5}$  eV was maintained, minimizing the potential influence of numerical instability on the results. Additionally, the maximum allowable stress on each atom was constrained to  $0.05 \text{ eV \AA}^{-1}$ .

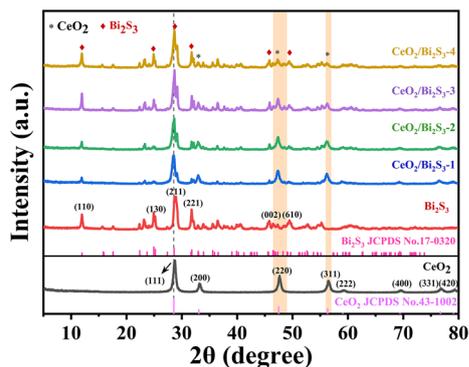


Fig. 1 Powder XRD diffraction patterns of  $\text{CeO}_2$ ,  $\text{Bi}_2\text{S}_3$ , and  $\text{CeO}_2/\text{Bi}_2\text{S}_3$  samples.

## 3 Results and discussion

### 3.1 Structural and morphological analysis

Fig. 1 presents the powder XRD diffraction patterns for the pure  $\text{CeO}_2$ ,  $\text{Bi}_2\text{S}_3$  and  $\text{CeO}_2/\text{Bi}_2\text{S}_3$  photocatalysts at varying molar ratios. The distinctive diffraction peaks of the synthesized  $\text{CeO}_2$  (No. 43-1002) appear at  $2\theta = 28.72^\circ$ ,  $33.16^\circ$ ,  $47.62^\circ$ ,  $56.40^\circ$ ,  $59.34^\circ$ ,  $69.64^\circ$ ,  $76.94^\circ$  and  $79.26^\circ$ , which correlate with the (111),

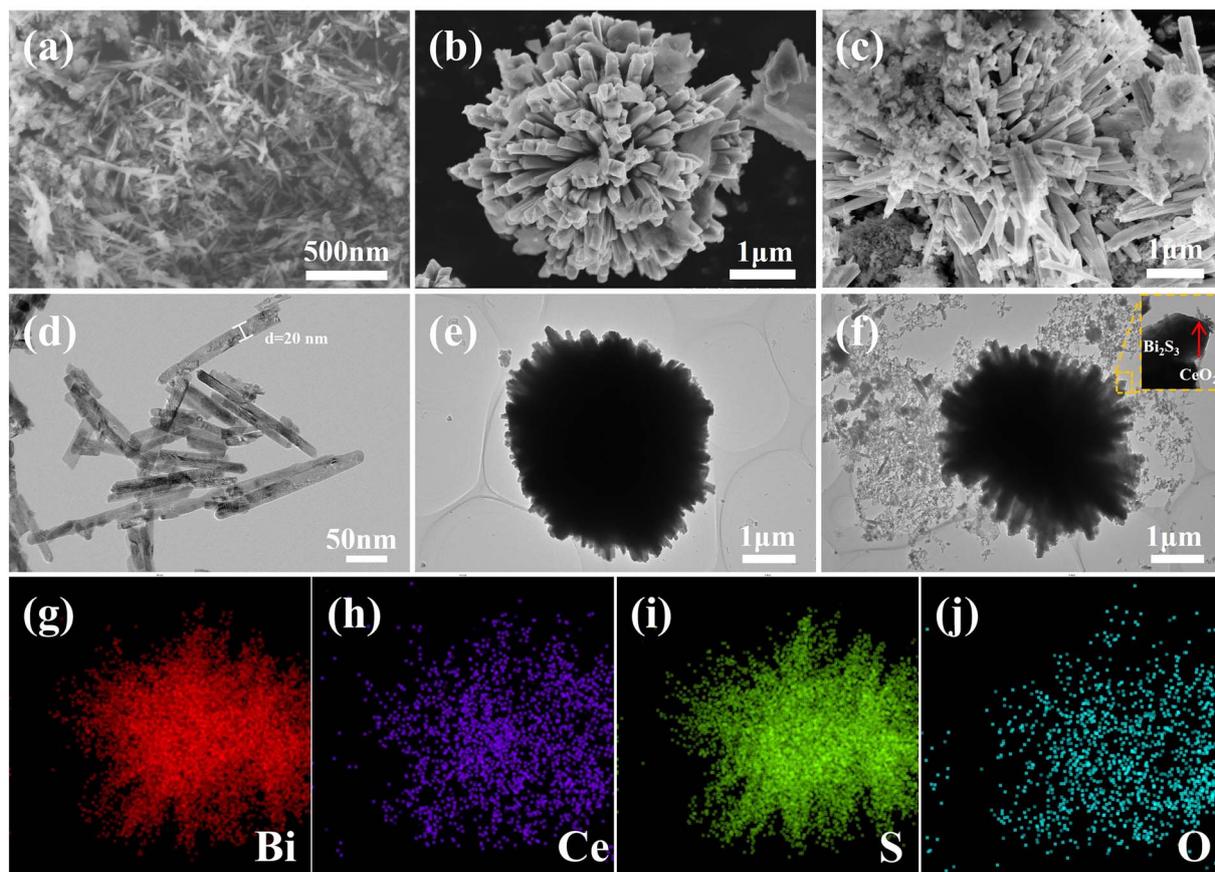


Fig. 2 SEM images of (a)  $\text{CeO}_2$ ; (b)  $\text{Bi}_2\text{S}_3$ ; (c)  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2, TEM images of (d)  $\text{CeO}_2$ ; (e)  $\text{Bi}_2\text{S}_3$ ; (f)  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2; EDS elemental distribution mapping of (g) Bi; (h) Ce; (i) S; (j) O in  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2.





in the binding energies of Ce 3d and O 1s occurs in CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2. The Bi 4f spectrum of Bi<sub>2</sub>S<sub>3</sub> (Fig. 3(d)) has two strong peaks at 158.9 eV and 164.2 eV belonging to Bi 4f<sub>7/2</sub> and Bi 4f<sub>5/2</sub>, which suggests that the Bi exists in the form of Bi<sup>3+</sup>.<sup>43</sup> The binding energy of CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 is enhanced relative to the Bi 4f spectrum of Bi<sub>2</sub>S<sub>3</sub>. When electrons are lost or gained, the binding energy of the constituent elements increases or decreases accordingly.<sup>29</sup> This indicates that electron transfer occurs between the contact surfaces of CeO<sub>2</sub> and Bi<sub>2</sub>S<sub>3</sub>, where the binding energy of Ce and O decreases and electrons are gained, the binding energy of Bi increases and electrons are lost, and electrons are transferred from Bi<sub>2</sub>S<sub>3</sub> to CeO<sub>2</sub>, leading to the creation of heterojunctions.

### 3.3 Photocatalytic performance test

The prepared photocatalysts effectively degraded TC when exposed to light from a 300 W xenon lamp, and it should be noted that the adsorption of TC molecules by the photocatalysts is not negligible, with adsorption equilibrium reached for all samples after 40 min in the dark. In Fig. 4(a), it is evident that the concentration of TC remained almost the same with no addition of photocatalysts. Pure CeO<sub>2</sub> and Bi<sub>2</sub>S<sub>3</sub> achieved photocatalytic degradation rates of 54.85% and 50.78%, respectively, after 120 min. Compared with the pristine materials, the CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> photocatalysts were significantly improved, and the degradation rates of TC by CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-1, CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2, CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-3 and CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-4 were 72.31%, 82.43%, 73.23% and 68.51% within 120 min, respectively. It is evident that the degradation efficiencies of the CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> photocatalysts initially increased and then decreased with higher Bi<sub>2</sub>S<sub>3</sub> content, with CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 exhibiting the highest performance. Quasi-primary kinetic fitting was performed using eqn (2)

$$-\ln(C_t/C_0) = kt \quad (2)$$

where  $k$  represents the apparent reaction rate constant. The kinetic curve indicates that CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 exhibits a  $k$  value of 0.01417 min<sup>-1</sup>, which is higher than all other samples. (Fig. 4(b)). The value observed is significantly greater, demonstrating an increase of two times compared to pure CeO<sub>2</sub>, which has a rate of 0.00709 min<sup>-1</sup>. Additionally, it is 2.75 times higher than the rate for pure Bi<sub>2</sub>S<sub>3</sub>, which is recorded at 0.00516 min<sup>-1</sup>.

To examine how the initial concentration influences the photodegradation of TC, experiments were conducted using varying initial concentrations of TC solutions, with 20 mg of CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 employed for each trial. The results are illustrated in Fig. 4(c) and (d). Clearly, an increase in the starting concentration of TC leads to an overall decrease in degradation efficiency, which declines from 82.43% to 73.19%. Additionally, the primary kinetic constant decreased from 0.01417 min<sup>-1</sup> to 0.01145 min<sup>-1</sup>. At higher initial concentrations, a greater number of TC molecules compete with one another, resulting in fewer molecules being captured and adsorbed by the photocatalysts.<sup>44,45</sup> In contrast, lower initial concentrations reduce this competitive effect, allowing a greater number of TC molecules to adhere to the photocatalyst's surface.

The quantity of photocatalysts is a significant element that influences the effectiveness of photocatalytic degradation. An investigation was conducted to assess the degradation impact of varying amounts of CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 on TC at a concentration of 10 mg L<sup>-1</sup>. Fig. 4(e) reveals that the efficiency of TC degradation increases and subsequently declines as the catalyst amount rises from 10 mg to 50 mg. During the dark reaction phase, an increase in catalyst dosage provides more adsorption sites, thereby enhancing the adsorption capacity. However, the

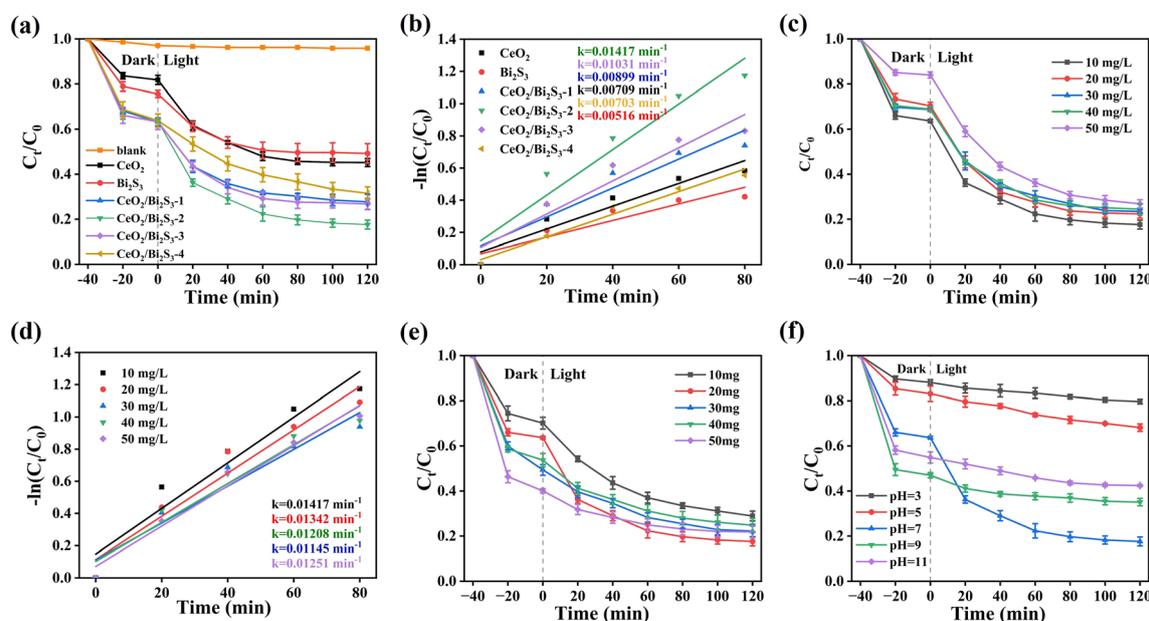


Fig. 4 (a) Photocatalytic degradation of TC by as-prepared photocatalysts under simulated solar illumination and (b) its kinetic fitting curves; 20 mg CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 degradation of (c) different initial concentrations of TC solution and (d) its kinetic fitting curves; photocatalytic degradation of tetracycline solution by CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 at (e) different catalyst dosage (f) different initial pHs.



degradation rate of TC exhibits a pattern of initial increase followed by a decrease during the light reaction phase. The peak degradation of TC was observed at an optimized catalyst dosage of 20 mg. This decline in degradation rate at higher catalyst concentrations may be attributed to increased turbidity in the solution, which impairs the catalyst's ability to absorb light, thus reducing the degradation rate of the photoreactive component.<sup>46,47</sup> Therefore, a dosage of 20 mg is selected as the optimum for subsequent studies.

The pH of the solution is a critical factor influencing the photocatalytic degradation of TC. Variations in pH can significantly alter the interactions between the photocatalyst and the pollutant throughout the reaction process. Consequently, it is essential to optimize the solution's pH by selecting appropriate concentrations of acids and bases, such as 0.1 M HCl and NaOH. In Fig. 4(f), the degradation rates of TC at pH of 3, 5, 7, 9 and 11, the final degradation rate of TC was recorded at 20.31%, 31.86%, 82.43%, 64.96% and 57.60%, respectively. The degradation rate increases as the pH rises from 3 to 7 but declines when the pH exceeds 7. At lower pH levels,  $\cdot\text{O}_2^-$  reacts with  $\text{H}^+$  to form  $\text{H}_2\text{O}_2$  and  $\cdot\text{O}_2^-$  is consumed in large quantities, resulting in a much lower degradation rate.<sup>48</sup> At pH 7, photo-generated electrons react more readily with dissolved oxygen to form  $\cdot\text{O}_2^-$ , resulting in easier separation of carriers, higher electron transfer efficiency and enhanced photocatalytic degradation rates.<sup>49</sup> In alkaline conditions, the adsorption of TC by the catalyst increases, and the excess TC adsorption blocks

the visible light from reaching the catalyst surface, which reduces the light absorption rate of the catalyst, which in turn leads to a lower degradation rate.<sup>50</sup> Furthermore, in alkaline conditions,  $\text{h}^+$  reacts with  $\text{OH}^-$  to form  $\cdot\text{OH}$ , and the  $\text{h}^+$  content decreases, resulting in a lower rate of TC degradation.<sup>51</sup> In the subsequent free radical trapping experiments, it was demonstrated that the contribution of  $\text{h}^+$  to TC degradation was greater than that of  $\cdot\text{OH}$ . Therefore, the degradation rate of TC was reduced under alkaline conditions. The performance of photocatalytic degradation of TC by  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2 photocatalytic material was compared with previous studies, and as shown in Table 1, the degradation performance of the prepared  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2 photocatalytic material was superior to that of most of the other reported photocatalytic materials.

### 3.4 Photoelectrochemical analysis

This research examined the effectiveness of separating photo-generated carriers through photoluminescence spectroscopy. The PL spectra for  $\text{CeO}_2$ ,  $\text{Bi}_2\text{S}_3$ , and  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2 were recorded with an excitation wavelength of 368 nm. An inverse relationship was identified between PL intensity and the efficiency of photogenerated electron-hole pair separation; specifically, lower PL intensity correlates with a reduced likelihood of electron-hole complex formation, thereby enhancing separation.<sup>52</sup> The PL intensity of the  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2 photocatalyst, as shown in Fig. 5(a), is significantly lower when compared to that of both pure  $\text{CeO}_2$  and pure  $\text{Bi}_2\text{S}_3$ , indicating effective suppression of

Table 1 Comparison of TC degradation rate of  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2 with other photocatalysts

Sample	TC ( $\text{mg L}^{-1}$ )	Irradiation time (minutes)	Degradation (%)	Ref.
$\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2	10	120	82.43	This work
$\text{CeO}_2/\text{Bi}_2\text{O}_2\text{CO}_3$	20	90	79.50	12
$\beta\text{-Bi}_2\text{O}_3@/\text{CeO}_2$	10	180	100	19
$\text{CeO}_2/\text{CNNS}$	10	120	79.6	42
$\text{Bi}_2\text{O}_2\text{CO}_3/\text{Ti}_3\text{C}_2$	20	120	81.00	54
$g\text{-C}_3\text{N}_4/\text{CeO}_2$	10	160	77.95	55
$\text{Bi}_2\text{WO}_6$	30	180	79.68	56
2% Au/ $\text{CeO}_2$	20	90	86.40	57
$\text{CeO}_2/\text{Co}_3\text{O}_4$	20	30	85.35	58
$\text{CeO}_2/\text{Co}_3\text{O}_4$	20	60	90	59
PDI/C, N, S- $\text{CeO}_2$	20	30	80.10	60

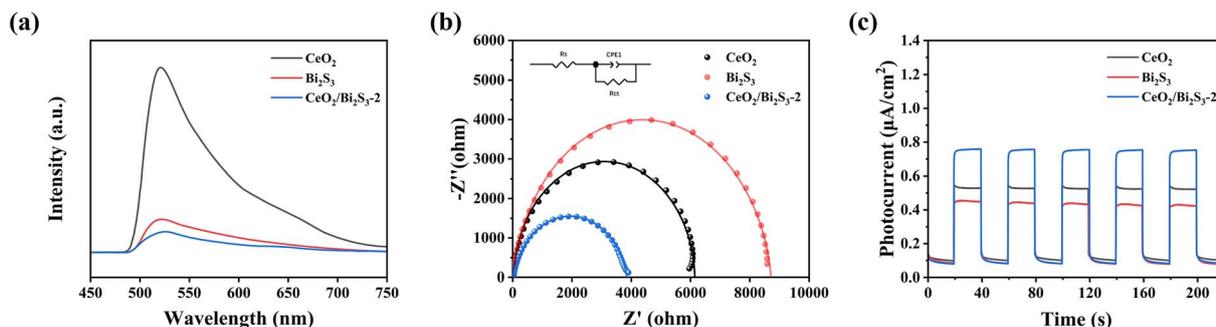


Fig. 5 (a) PL, (b) EIS Nyquist plot, and (c) transient photocurrent response of  $\text{CeO}_2$ ,  $\text{Bi}_2\text{S}_3$  and  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2.



electron-hole complexation. This suppression may be attributed to the development of an IEF within the heterojunction that promotes electron-hole pair separation. The electrochemical impedance spectrum (EIS) presented in Fig. 5(b) shows that a smaller curve radius indicates a reduced level of electrochemical impedance.<sup>53</sup> The impedance curve of CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 exhibits a smaller radius when compared to the curves of the pure CeO<sub>2</sub> and the pure Bi<sub>2</sub>S<sub>3</sub>, suggesting that the heterojunction formed by the composite materials facilitates charge transfer by lowering resistance. Furthermore, findings from the transient photocurrent response of all samples exposed to visible light (Fig. 5(c)) corroborate the EIS results. This evidence underscores the significant advantages of heterojunctions over individual CeO<sub>2</sub> and Bi<sub>2</sub>S<sub>3</sub> in terms of the effectiveness of photogenerated carrier separation, thereby enhancing photocatalytic performance.

### 3.5 Stability and cyclic testing

The stability of the CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 photocatalysts was assessed through cycling experiments. In these experiments, the CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 photocatalysts were collected by filtration after each degradation test, after repeated washing with anhydrous ethanol, and subsequently evaporated excess water in an oven for 12 h at 60 °C before being subjected to cyclic operation again under identical conditions. As depicted in Fig. 6(a), following five cycles of photocatalytic degradation, the rate of photocatalytic degradation dropped from 82.43% to 76.26%, representing a reduction of 6.17%. This decrease is attributed to material loss during the recycling process. Additionally, powder XRD patterns before and after the use of the photocatalyst (Fig. 6(b)) indicated that the structure of CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 remained largely unchanged throughout the reaction process, demonstrating the excellent stability and recyclability of the CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 photocatalyst.

### 3.6 Photocatalytic mechanism analysis

Experiments were conducted to capture and identify free radicals generated during the process as a way to investigate the fundamental mechanisms responsible for the photocatalytic degradation of TC when utilizing CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2. EDTA-2Na, LA,<sup>61</sup> and IPA were utilized as scavengers for various reactive species,

specifically h<sup>+</sup>, ·O<sub>2</sub><sup>-</sup>, and ·OH. The effectiveness of these scavengers in modulating the degradation of TC was evaluated. As depicted in Fig. 7(a), the introduction of IPA resulted into a negligible change in the degradation rate of TC, suggesting that ·OH has a somewhat limited impact on the photo-degradation process of TC. Our observations indicated that the inclusion of LA and EDTA-2Na significantly hindered the photocatalytic degradation process of TC. Specifically, we noted a substantial decline in the degradation rate of TC, which plummeted from 82.43% to 38.96% following the addition of LA. Furthermore, the degradation rate was also impacted by the addition of EDTA-2Na, leading to a decrease to 59.05%. These results suggest that the active species ·O<sub>2</sub><sup>-</sup> and h<sup>+</sup> play a primary role in the degradation process, while ·OH has a minimal impact. To further confirm whether ·O<sub>2</sub><sup>-</sup>, ·OH, and h<sup>+</sup> are indeed present in the photocatalytic process, we performed a qualitative detection of free radicals using EPR. The ·O<sub>2</sub><sup>-</sup> and ·OH radicals were detected using the reagent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), and the presence of h<sup>+</sup> was detected by 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO). As shown in Fig. 7(b), no signal of DMPO-·O<sub>2</sub><sup>-</sup> was detected under dark conditions, while a significant DMPO-·O<sub>2</sub><sup>-</sup> signal was detected after light exposure, which proved that ·O<sub>2</sub><sup>-</sup> was produced during the photocatalytic process. The order of DMPO-·O<sub>2</sub><sup>-</sup> signal intensity is CeO<sub>2</sub> < Bi<sub>2</sub>S<sub>3</sub> < CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2, which indicates that CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 generates more ·O<sub>2</sub><sup>-</sup>. Whereas ·OH had no obvious signal under both dark and light conditions (Fig. 7(c)), indicating that no ·OH was produced during the whole reaction. From Fig. 7(d), it can be seen that the signal peak of TEMPO decreases in intensity after light exposure, which is due to the reaction between h<sup>+</sup> and TEMPO, where h<sup>+</sup> increases and TEMPO consumed by h<sup>+</sup> increases, resulting in a weakening of the TEMPO signal.<sup>46</sup> This proves that h<sup>+</sup> does exist. The intensity of the signal peak for TEMPO-h<sup>+</sup> was weakest for CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2, which generated more h<sup>+</sup>. The above results demonstrate that CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> S-scheme heterojunction generates more ·O<sub>2</sub><sup>-</sup> and h<sup>+</sup> radicals involved in the degradation of TC.

To provide additional insight into the mechanism by which CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 degrades TC, we analysed the light absorption characteristics of the samples that we had prepared using UV-

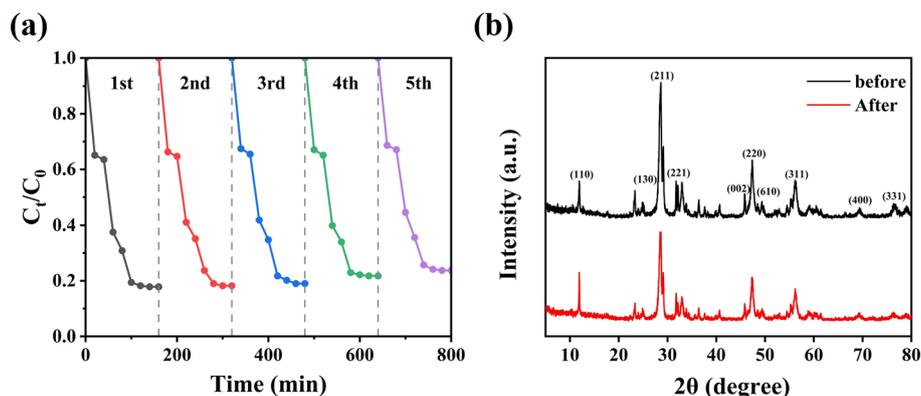


Fig. 6 Powder XRD spectra of CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 catalyst for (a) 5 cycles of TC degradation experiment and (b) before and after the reaction.

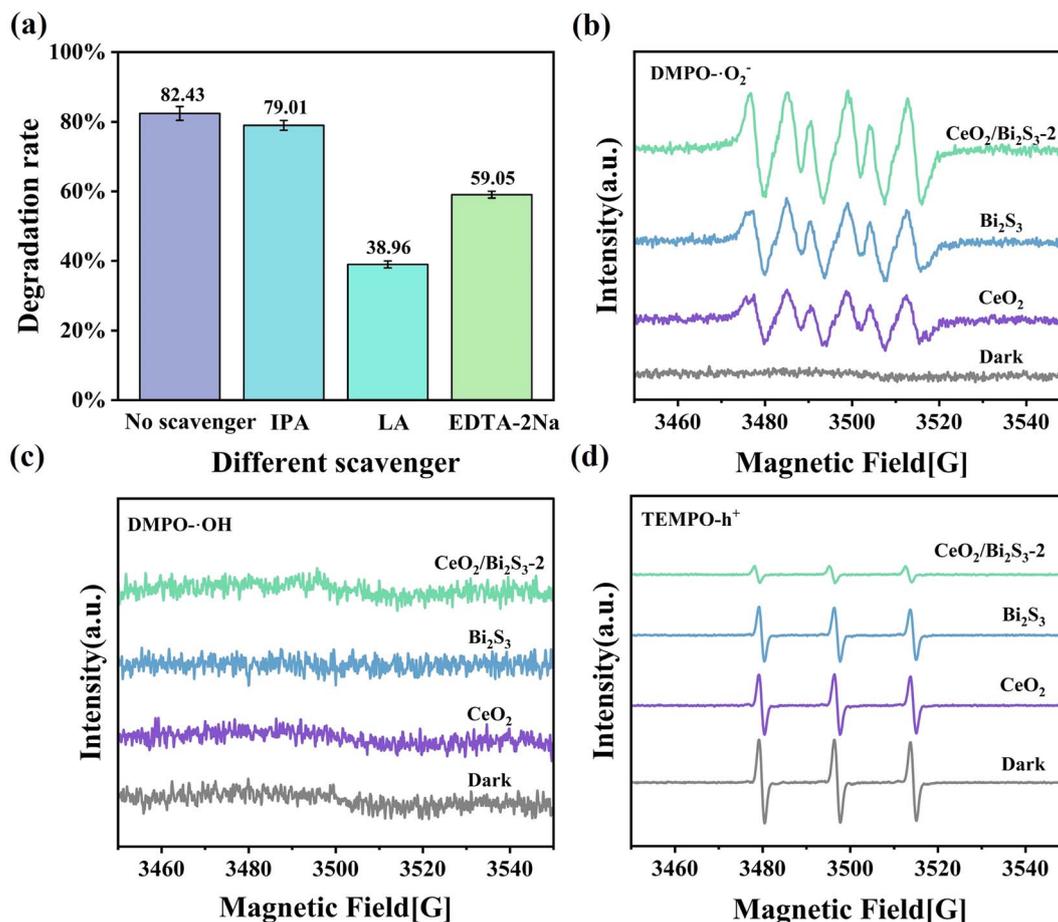


Fig. 7 (a) Effect of different scavengers on the photocatalytic degradation of TC by  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2; EPR signals of (b)  $\text{DMPO}-\cdot\text{O}_2^-$ ; (c)  $\text{TEMPO}-\text{h}^+$ ; (d)  $\text{DMPO}-\cdot\text{OH}$ .

Vis DRS. The findings presented in Fig. 8(a) indicate that the pure  $\text{CeO}_2$  demonstrates significant light absorption capabilities in the ultraviolet spectrum, whereas it shows minimal absorption in the visible region. Additionally, pure  $\text{Bi}_2\text{S}_3$  shows a robust ability to absorb light within the visible region. The formation of a heterojunction that combines  $\text{CeO}_2$  with  $\text{Bi}_2\text{S}_3$  has led to significant improvements in light absorption properties for  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2. When comparing its performance to that of pure  $\text{CeO}_2$  and pure  $\text{Bi}_2\text{S}_3$ ,  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ -2 exhibits superior capability to absorb light within the visible spectrum, attributable to the light-absorbing of  $\text{Bi}_2\text{S}_3$  within the heterojunction. The flat band potentials ( $E_{\text{fb}}$ ) of  $\text{Bi}_2\text{S}_3$  and  $\text{CeO}_2$  were assessed using the Mott-Schottky test. The slopes of the Mott-Schottky curves for both are positive, which proves that both  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$  are n-type semiconductors.<sup>39,44</sup> The results in Fig. 8(b) and (c) reveal that the  $E_{\text{fb}}$  values for  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$  were  $-0.21$  eV and  $-0.59$  eV, respectively, when measured against the  $\text{Ag}/\text{AgCl}$  reference electrode at a pH 7. The energy levels of  $E_{\text{fb}}$  for both  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$  were evaluated from eqn (3) to be  $-0.01$  eV for  $\text{CeO}_2$  and  $-0.39$  eV (vs. NHE) for  $\text{Bi}_2\text{S}_3$ .<sup>62</sup>

$$E_{\text{NHE}} = E_{\text{Ag}/\text{AgCl}} + 0.197 \quad (3)$$

The  $E_{\text{fb}}$  of n-type semiconductors is near the  $E_{\text{f}}$ ,<sup>63</sup> and is situated about 0.1 V more positive than the CB.<sup>64,65</sup> Consequently, the CB levels of  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$  are measured to be  $-0.11$  eV and  $-0.49$  eV (vs. NHE), respectively. The bandwidth of the sample is calculated from eqn (4).

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (4)$$

$$E_{\text{VB}} = E_{\text{CB}} + E_g \quad (5)$$

where the absorption coefficient, Planck's constant, optical frequency and absorbance are represented by  $\alpha$ ,  $h$ ,  $\nu$ , and  $A$ , respectively. As direct bandgap semiconductors,  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$  have an  $n$  value of 2. From Fig. 8(d), the forbidden bandwidths for  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$  are 3.11 eV and 1.97 eV, respectively. Additionally, the VB for  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$  are identified as 2.99 eV and 1.48 eV, respectively, as indicated by eqn (5) (vs. NHE).

The difference in charge density of photocatalysts was calculated using DFT. Fig. 9(a) and (c) show the electron cloud densities of  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$  before contact, respectively. Fig. 9(c) reveals the charge density difference of  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ . The yellow areas indicate regions of electron accumulation, while the green areas signify electron depletion. It is clear that electrons accumulated on the  $\text{CeO}_2$  surface, while the  $\text{Bi}_2\text{S}_3$  surface exhibited



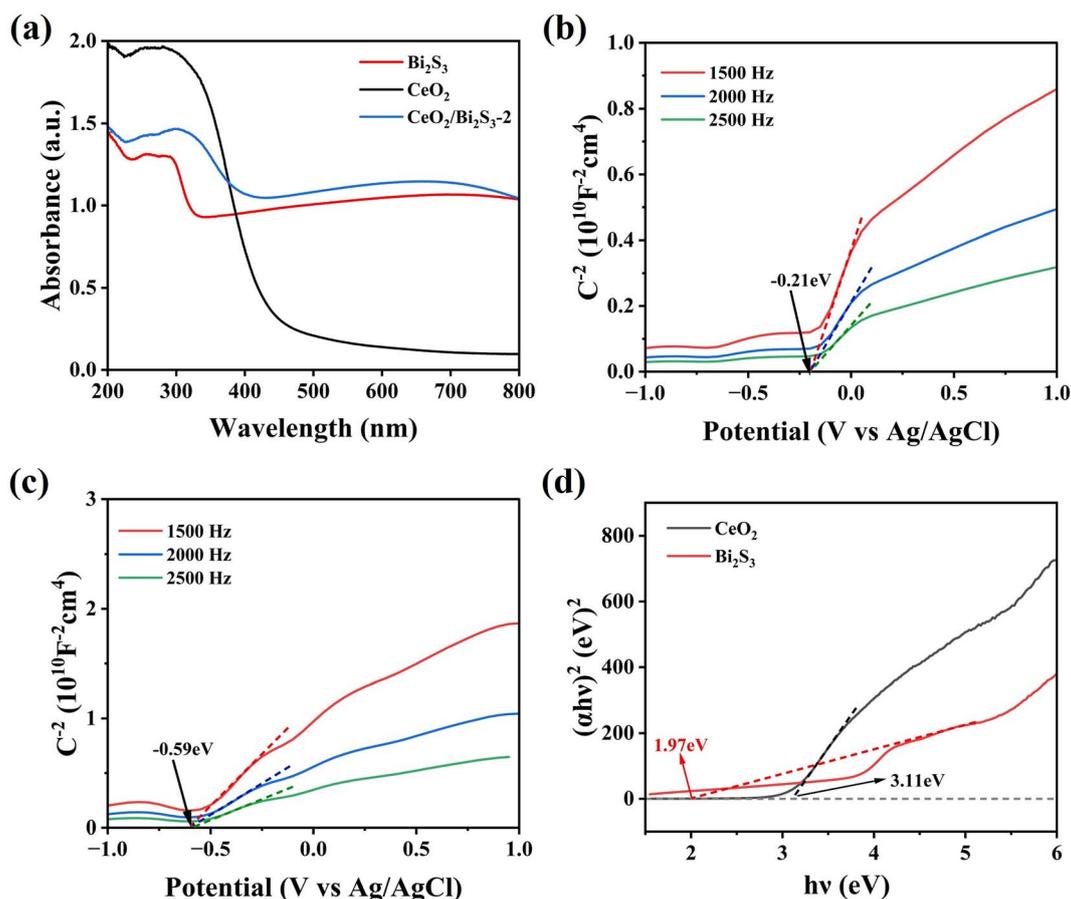


Fig. 8 (a) DRS spectra. Mott–Schottky spectra of (b)  $\text{CeO}_2$  and (c)  $\text{Bi}_2\text{S}_3$ . (d) Tauc plot of  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$ .

charge loss. This charge loss is due to the migration of electrons from  $\text{Bi}_2\text{S}_3$  to  $\text{CeO}_2$  following contact, indicating the formation of an IEF between the two surfaces, with the electric field directed from  $\text{Bi}_2\text{S}_3$  towards  $\text{CeO}_2$ .

Based on the experimental results presented in this study, we propose the energy band configurations and charge transfer mechanisms for  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$ , both before and after their interaction, as well as the processes related to the photocatalytic breakdown of TC (Fig. 10). Prior to contact, the energy bands of  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$  are interleaved, and the reduced semiconductor  $\text{Bi}_2\text{S}_3$  has a higher  $E_f$  than the oxidized semiconductor  $\text{CeO}_2$ . Thus, when the two materials come into contact, the variation in Fermi levels causes the natural movement of electrons from  $\text{Bi}_2\text{S}_3$  to  $\text{CeO}_2$ . This process continues until the Fermi levels

equalize, resulting in the creation of an IEF at the interface directed from  $\text{Bi}_2\text{S}_3$  towards  $\text{CeO}_2$ . Simultaneously, the energy band at the  $\text{Bi}_2\text{S}_3$  interface loses electrons, causing it to curve upwards, while the  $\text{CeO}_2$  interface acquires electrons, which leads to a downward bend. This modification hinders the transfer of electrons between the CB of  $\text{Bi}_2\text{S}_3$  and that of  $\text{CeO}_2$ . Additionally, this alteration also restricts the flow of holes, preventing them from moving from the VB of  $\text{CeO}_2$  to the VB of  $\text{Bi}_2\text{S}_3$ .<sup>29,66</sup> Upon solar illumination, the holes and electrons generated by the excitation of  $\text{CeO}_2$  and  $\text{Bi}_2\text{S}_3$ , in the presence of IEF, the electrons in the CB of  $\text{CeO}_2$  are moved to the interface and recombine with the holes from the VB of  $\text{Bi}_2\text{S}_3$ , which are also transferred to the interface. By eliminating unwanted electrons and holes through recombination, holes on  $\text{CeO}_2$  VB

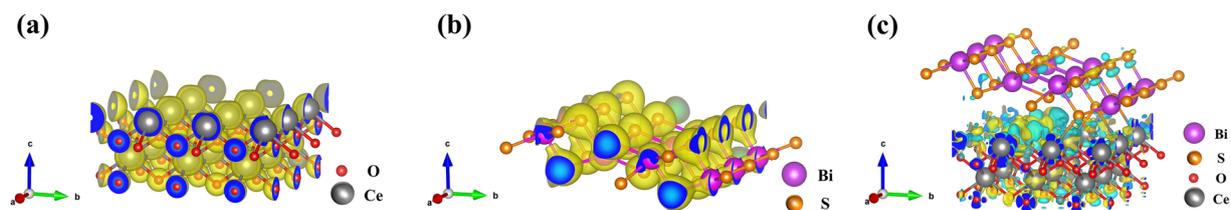


Fig. 9 Charge distribution of (a)  $\text{CeO}_2$  and (b)  $\text{Bi}_2\text{S}_3$  before contacting (c) difference in charge density of  $\text{CeO}_2/\text{Bi}_2\text{S}_3$ .



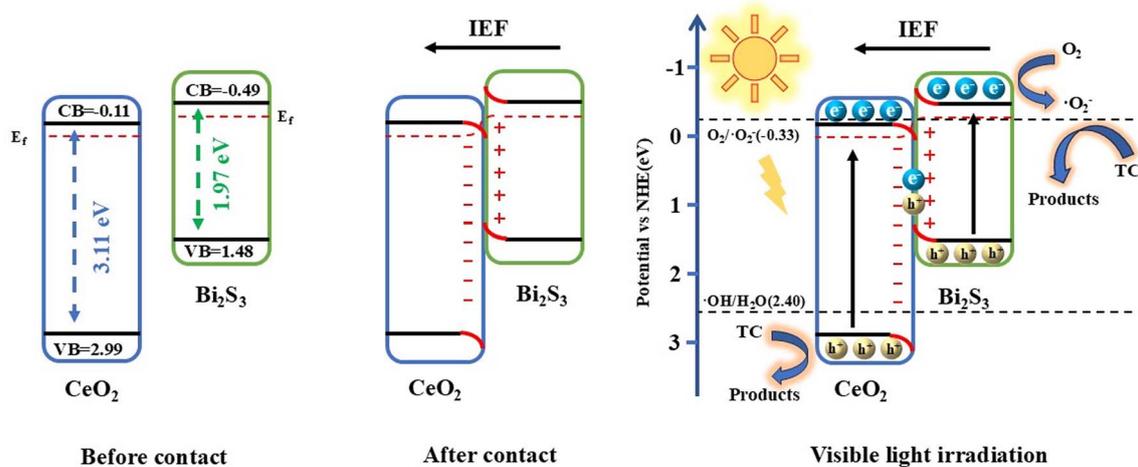


Fig. 10 Schematic energy band structure and photocatalytic mechanism of CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 photocatalysts.

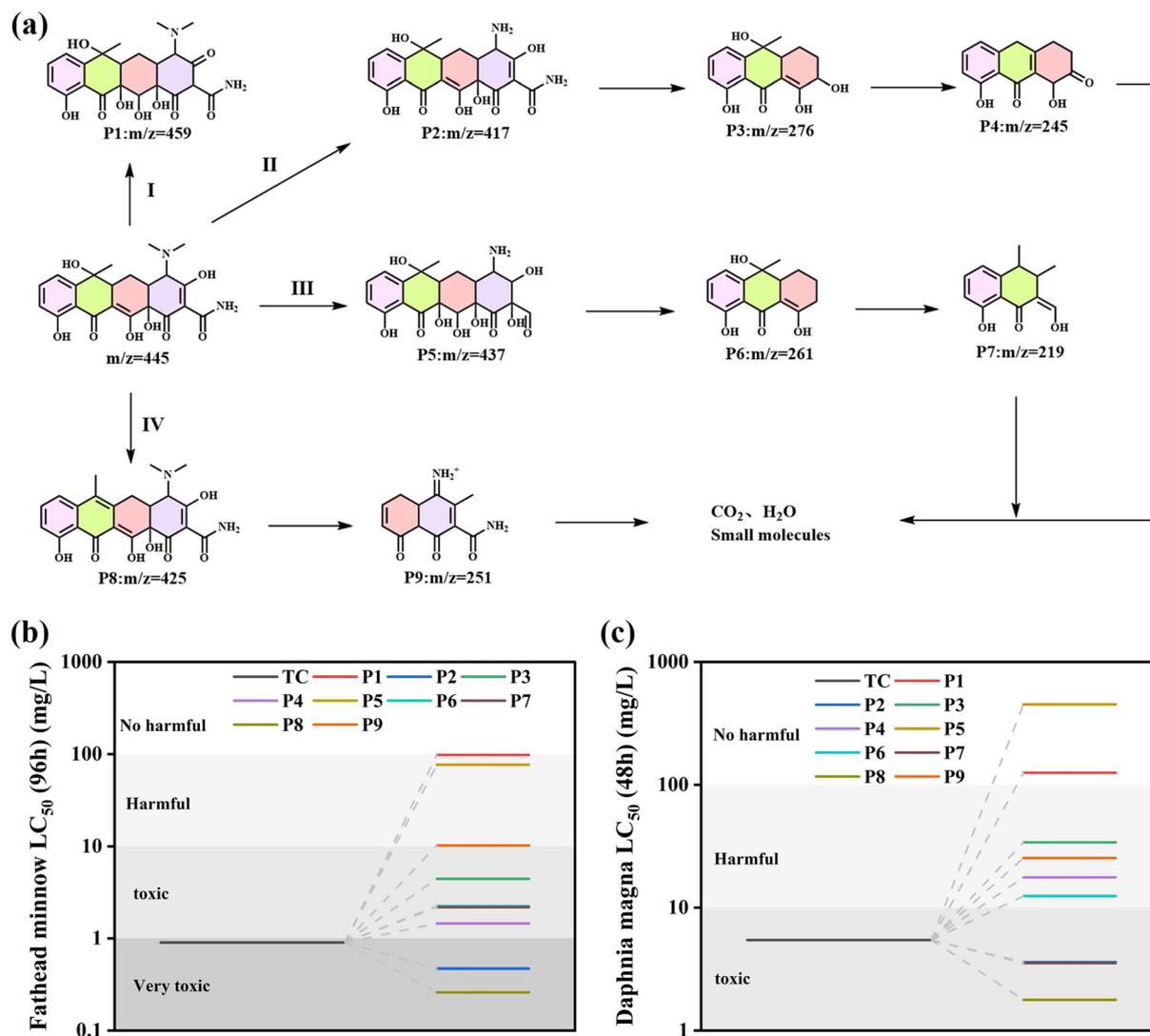
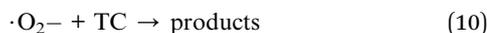
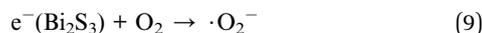
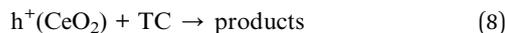
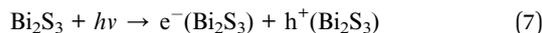
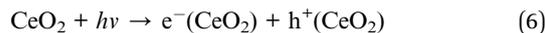


Fig. 11 (a) Possible intermediates and pathways for TC degradation by CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 photocatalysts; (b) fathead minnow LC<sub>50</sub> (96 h); (c) *Daphnia magna* LC<sub>50</sub> (48 h).



and electrons on Bi<sub>2</sub>S<sub>3</sub> CB are retained and accumulated, which are strongly oxidizing and reducing, respectively.<sup>25</sup> And a more direct degradation of TC by holes on CeO<sub>2</sub> VB. The CB of Bi<sub>2</sub>S<sub>3</sub>, measured at -0.49 eV, which is higher compared to the -0.33 eV of O<sub>2</sub>/ $\cdot$ O<sub>2</sub><sup>-</sup> (vs. NHE). In this process, the electrons in the CB facilitate the reduction of dissolved O<sub>2</sub> in water to produce  $\cdot$ O<sub>2</sub><sup>-</sup>, which subsequently reacts with TC to contribute to its degradation. Specific reactions are represented by eqn (6)–(10).



The intermediates of TC degradation by CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 at different light durations were explored by mass spectrometry (MS). The peak that was recorded at an  $m/z$  value of 445 was linked to the original molecule TC. As the duration of light exposure increased, the intensity at  $m/z = 445$  significantly diminished. In addition, peaks at  $m/z$  values of 459, 437, 425, 417, 276, 261, 251, 245 and 219 were identified, with the related MS spectra displayed in Fig. S1(a)–(f).† Based on the detected intermediates and available literature, a pathway for TC degradation was raised (Fig. 11(a)). In pathway I, the TC molecule undergoes a process known as hydroxylation, which results in the formation of a new compound designated as **P1** ( $m/z = 459$ ). In pathway II, the N–C bond's low binding energy makes it susceptible to destruction, leading to demethylation that produces **P2** ( $m/z = 417$ ). Subsequently, **P2** experiences a ring-opening reaction, yielding **P3** ( $m/z = 276$ ), which further experiences dehydroxylation and dehydration to form **P4** ( $m/z = 245$ ). In pathway III, the TC molecule experiences several hydroxylation and demethylation processes to produce **P5** ( $m/z = 437$ ). This process subsequently entails a ring-opening reaction followed by dehydroxylation, resulting in the generation of a product designated as **P6** ( $m/z = 261$ ). Subsequently, **P6** also undergoes ring-opening and dehydroxylation, resulting in the formation of **P7** ( $m/z = 219$ ). For pathway IV, the TC molecule dehydroxylates one hydroxyl group to produce **P8** ( $m/z = 425$ ), which in turn generates **P9** ( $m/z = 251$ ) by ring opening and demethylation and dehydroxylation. TC is broken down into intermediates with smaller molecular weights, which are further oxidized to small molecular compounds or even to CO<sub>2</sub> and H<sub>2</sub>O.

In addition, the toxicity of TC and intermediates was evaluated using the Toxicity Estimation Software (T.E.S.T), and the specific values are shown in Table S2.† TC was evaluated to be highly toxic to fathead minnow (LC<sub>50</sub> = 0.9 mg L<sup>-1</sup>) and toxic to *Daphnia magna* (LC<sub>50</sub> = 5.44 mg L<sup>-1</sup>). The LC<sub>50</sub> of all products except **P8** was higher than that of TC (Fig. 11(b)), and the LC<sub>50</sub> of most products was higher than that of TC for *Daphnia magna*

(Fig. 11(c)), which indicated that CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-2 degraded TC into a low toxicity compound.

## 4 Conclusions

In this study, flower-shaped CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> composite photocatalysts were synthesized using hydrothermal methods. Characterization using SEM, TEM and XRD confirmed that the CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> is a heterojunction. Through XPS analysis, DRS analysis, DFT calculation and Mott–Schottky tests, the CeO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> heterojunction was found to function according to a charge transfer mechanism of the S-scheme type, which enhances charge mobility and generates an internal electric field that effectively separates electron–hole pairs. This process maintains the redox capacity of the resultant beneficial electrons and holes, thereby improving photocatalytic degradation efficiency. Under optimal reaction conditions, a significant degradation of TC was observed following 120 min of exposure to light. The results indicated that the degradation rate reached an impressive 82.43%. Free radical trapping experiments and LC-MS analysis of degradation products revealed that TC degradation primarily involves  $\cdot$ O<sub>2</sub><sup>-</sup> and h<sup>+</sup> radicals, leading to the formation of CO<sub>2</sub>, H<sub>2</sub>O, and other small molecules through a series of ring-opening, demethylation, and dehydroxylation reactions. This research provides robust evidence for the photocatalytic breakdown of antibiotics through S-scheme heterojunctions and presents a viable approach for developing heterojunctions that integrate wide bandgap and narrow bandgap semiconductors.

## Data availability

The data that has been used is confidential.

## Author contributions

Shanlin He: writing – original draft, investigation, writing – review & editing, formal analysis, data curation. Yawei Du: formal analysis, visualization. Chen Li: resources, supervision. Claudia Li: writing – review & editing, supervision. Jingde Li: writing – review & editing, supervision. Jaka Sunarso: writing – review & editing, supervision. Sibudjing Kawi: writing – review & editing, supervision. Yinhui Li: writing – review & editing, supervision, project administration, funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

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