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Construction of S-scheme heterojunction $CeCuO_3/g-C_3N_4$ photocatalyst for degradation of tetracycline under visible light

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ABSTRACT

Adopting the construction method of S-scheme heterojunction photocatalyst, which exhibits exceptional photo redox performance and efficient charge transfer characteristics, effectively enhances the efficiency of photocatalytic degradation. In this study, an efficient S-scheme CeCuO₃/g-C₃N₄ (CCO/CN) binary heterojunction photocatalyst has been developed through a sol-gel and ultrasound oscillation-assisted hydrothermal method for the degradation of tetracycline (TC) in wastewater. The composite material exhibits optimal photoresponse characteristics, significantly enhancing the separation efficiency of photogenerated carriers. The 40 % CCO/CN binary heterojunction composite not only achieves a TC degradation rate of 92.9 % after 180 min of visible light irradiation at pH 5.0 but also exhibits superior performance compared to pure CCO and CN, with a 1.69 and 2.65 times enhancement, respectively. Advanced characterization techniques, including XRD, XPS, TEM, SEM, FTIR, DRS, and PL were employed to analyze the properties of the catalyst. Moreover, this study corroborates the tCC degradation rate remaining above 90 %. The results of radical trapping experiments indicate that the S-scheme photocatalytic degradation mechanism is responsible for the observed effects. The findings of this research provide new insights into composite photocatalysts for antibiotic wastewater treatment and ecological protection and thus warrant further investigation.

1. Introduction

The acceleration of global economic growth has resulted in a corresponding increase in water demand [1], and the discharge of industrial wastewater, agricultural drainage, and domestic sewage has gradually increased, thereby posing a significant threat to the aquatic environment [2]. Antibiotics represent a significant pollutant, with extensive utilization across diverse industrial sectors, including healthcare, animal husbandry, fisheries, and agriculture [3]. Tetracycline (TC) [4], an antibiotic commonly employed for the treatment of bacterial infections in humans and animals, tends to accumulate in organisms and water bodies due to its incomplete biodegradation and high mobility in wastewater [5]. In light of the pervasiveness of TC in various water bodies and its inherent characteristics concerning degradation and stabilization, the development of efficient and targeted degradation technologies has become a pressing necessity [6].

The high costs associated with existing treatment technologies limit their widespread application, thereby impeding their ability to effectively address the significant challenge of antibiotic pollution [7]. At present, photocatalytic technology is attracting considerable interest as a potential solution for the degradation of pollutants. During the photocatalytic process, highly reactive species such as O_2^- and OH effectively oxidize large organic pollutants into smaller compounds, ultimately leading to their complete mineralization into harmless H₂O and CO₂ [8,9]. Meanwhile, graphitic carbon nitride (g-C₃N₄) [10] has demonstrated considerable potential in the field of photocatalytic degradation of organic pollutants. [11] This is due to several factors, including its non-toxic nature, low cost, environmental friendliness, adjustable morphology, high physicochemical stability, unique electronic configuration, and excellent energy storage capabilities [12–14].

Despite the considerable promise $g-C_3N_4$ displays in photocatalysis, it is not without its limitations. These include high photogenerated carrier recombination rates, weak light absorption capacity, low catalytic activity, and a relatively small specific surface area, which collectively hinder its application in photocatalytic sulfate activation [15–17]. However, researchers have discovered that a series of modification

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techniques—such as ion doping [18], noble metal modification [19], supercritical fluid (SCF) [20,21] treatment, and the formation of heterojunctions with other semiconductor materials [22]—can effectively adjust g-C₃N₄ bandgap, inhibit the recombination of electrons and holes, and enlarge its specific surface area. These modifications result in a reduction in the recombination rate, an expansion of the visible light absorption range, and an enhancement of charge separation efficiency, thereby significantly enhancing g-C₃N₄ photocatalytic degradation capacity for a variety of organic pollutants under sunlight or visible light illumination.

The construction of g-C₃N₄ semiconductor heterostructures typically leads to the generation of an internal electric field, which facilitates the broadening of the light absorption range and enhances the separation efficiency of photogenerated carriers. Consequently, it is concluded that the construction of heterostructures represents an efficacious modification strategy for improving the photocatalytic performance of g-C₃N₄. For instance, heterojunctions formed by combining g-C₃N₄ with semiconductor materials such as g-C₃N₄/BiOCl [23], SbVO₄/g-C₃N₄ [24], Ta₃N₅/BiOCl [25], CdMoO₄/CdO [26], CoO-CuBi₂O₄ [27], and g-C₃N₄/ Ce₂S₃ [28] have exhibited remarkable photocatalytic activity. As a result, researchers have shown a keen interest in developing doped and composite photocatalysts that are responsive to visible light and possess a narrow bandgap energy. Furthermore, the advancement of S-scheme heterojunction photocatalytic degradation technology has emerged as a prominent research area in environmental applications, with significant potential for addressing environmental pollution concerns. In 2019, the Yu [29] team pioneered the concept of the S-scheme heterojunction, ingeniously combining oxidative photocatalysts (OP) with reductive photocatalysts (RP) to achieve effective retention of active electrons and holes. This led to a significant facilitation in the efficient separation of electron-hole pairs [30,31]. It has been demonstrated that the novel Sscheme heterojunction photocatalyst can markedly enhance the efficiency of charge separation. The strong internal electric field endows the material with the capacity to facilitate the transport of charge carriers at the heterojunction interface, thereby markedly enhancing the photocatalytic activity. Moreover, the distinctive "stepwise" charge transfer mechanism of the S-scheme heterojunction guarantees that the two semiconductors retain their redox capabilities following the formation of the heterojunction. When the two semiconductors exhibit interlaced energy band structures and possess appropriate Fermi levels (Ef), the disparity in their Fermi levels results in the formation of a potential gradient at the interface [32]. This gradient induces electrons to flow from higher energy levels to lower ones until an equilibrium state is achieved. This flow process gives rise to the generation of an intrinsic electric field (IEF) at the interface, accompanied by the bending of the energy bands. The IEF accelerates the migration of photogenerated charge carriers, while the curved energy bands serve as "directional channels," precisely controlling the migration paths of photogenerated electrons and holes [33]. This results in effective spatial separation of charge carriers and maintains a robust redox ability. In this regard, rare earth elements have attracted considerable interest due to their distinctive properties. The utilization of rare earth metals as dopants can effectively introduce impurity energy levels into the forbidden band, thereby reducing the band gap of g-C₃N₄. The research conducted by the Bechambi [34] team provides an illustrative example of how the Fermi level can be tuned by doping with the rare earth metal Ce [28], which serves to narrow the band gap of ZnO, thereby significantly enhancing its photocatalytic performance [35]. In recent times, there has been a growing interest in such photocatalytic materials among the scientific research community, including CeO2/g-C3N4 [36], La2Ce2O7/g-C3N4 [37], and Ti-doped Ce-MOF and BiOCl [38].

The perovskite-type metal oxide cerium copper oxide (CeCuO₃) [39] is non-toxic, environmentally friendly, and exhibits exceptional performance in photoelectric sensitivity, with minimal secondary toxicity issues [40,41]. To date, there is no published literature on the use of CeCuO₃/g-C₃N₄ heterojunctions as photocatalysts for the degradation of

tetracycline (TC). This represents an area of research that we are keen to explore further. By simulating the potential Type-II mechanism and S-scheme charge transfer modes on the surface of CeCuO₃/g-C₃N₄, we found that the enhanced photoreactivity during TC decomposition is attributed to the retention of carrier pairs with high redox activity and their faster separation rates. In conclusion, this study not only explores the practical design of stepped CeCuO₃/g-C₃N₄ S-scheme heterojunction photocatalysts but also provides a valuable reference for the advanced treatment of antibiotic wastewater, offering significant scientific and practical insights.

2. Experimental

2.1. Preparation of samples

All reagents employed in the experiment were of analytical purity, including cerium nitrate hexahydrate(Ce(NO₃)₃·6H₂O), copper nitrate hexahydrate(Cu(NO₃)₂·6H₂O), citric acid(C₆H₈O₇), melamine, ethylene glycol, anhydrous ethanol (C₂H₆O), silver nitrate (AgNO₃), benzoquinone (BQ), isopropanol (IPA), and tetracycline (TC). The tetracycline (TC) drugs were procured from Sinopharm Chemical Reagent Co., Ltd. All experiments were conducted using deionized water at room temperature.

2.1.1. Preparation of $g-C_3N_4$

The g-C₃N₄ precursor should be prepared at 80 °C for 24 h. It should be gradually heated to 550 °C at a rate of 2 °C per min, maintaining this temperature for 4 h [42]. Subsequently, the material should be washed thrice with deionized water and dried in a vacuum environment at 80 °C for 24 h to obtain g-C₃N₄ powders and named as CN.

2.1.2. Preparation of CeCuO₃ Powder (CCO)

The requisite quantities of Ce(NO₃)₃·6H₂O and Cu(NO₃)₂·6H₂O were weighed according to a molar ratio of 1:1 and dissolved in an appropriate amount of deionized water. The solution was then stirred thoroughly to obtain a mixed solution, designated as Solution A. A proper quantity of C₆H₈O₇ was subsequently added to the abovementioned solution and stirred until complete dissolution occurred. Typically, the amount of acid citric employed was 1.5 to 2 times the total molar number of metal ions. As mentioned earlier, ethylene glycol was added dropwise to the solution, with stirring maintained throughout. The quantity of ethylene glycol employed was typically equivalent to the molar number of C₆H₈O₇. Subsequently, the solution was heated and stirred at 80-90 °C until a uniform solution was formed. The sol was then permitted to stand at room temperature, allowing for the gradual gelification process to occur. The duration of this process may vary considerably, depending on the soil concentration and the prevailing environmental conditions. The gel is dried at temperatures between 80 and 100 °C to remove residual moisture and solvents. This results in the formation of a dried gel. The dried gel is subsequently subjected to a calcining process at temperatures between 500 and 800 °C for a duration of between 4 h. This step is essential for forming CeCuO₃ powder, which is designated CCO.

2.1.3. Preparation of the Photocatalyst CeCuO₃/g-C₃N₄

2.0 g of g-C₃N₄ was added to a beaker containing 20 mL of C₂H₆O to prepare the photocatalyst. Subsequently, the mixture was subjected to sonication for 30 min, to ensure homogeneous dispersion. Subsequently, 0.2 g of CeCuO₃ (CCO) powder was introduced, and the mixture was continuously stirred for 2 h using a magnetic stirrer to facilitate the thorough mixing of the two materials. Subsequently, the mixture was subjected to a 10 h drying process at 80 °C in a blast drying oven to remove the solvent. Once the sample had been dried, it was transferred to a crucible and preheated at 250 °C for 1 h before being allowed to cool naturally to room temperature. Subsequently, the sample was ground to obtain the 10 % CCO/CN composite catalyst, designated 10CCO/CN.

The steps mentioned earlier were repeated to prepare composite catalysts with varying proportions, with the only alteration being the ratio of $g-C_3N_4$ to CCO. The preparation of composite catalysts with different proportions of CeCuO₃ and $g-C_3N_4$ was completed, resulting in the formation of 20 %, 30 %, 40 %, and 50 % CeCuO₃/ $g-C_3N_4$ (CCO/CN) composite catalysts, designated as 20CCO/CN, 30CCO/CN, 40CCO/CN, and 50CCO/CN, respectively.

2.2. Characterization of samples

In this study, X-ray diffraction patterns of each photocatalyst were recorded using a Lal-6000 X-ray diffractometer with Cu K α target (XRD, Shimadzu Corporation, Japan). The molecular structure and solid surface were determined using TENSOR 27 Fourier Transform Infrared Spectrometer (FT-IR, Bruker AG, Germany) and ESCALAB₂50 X-Ray Photoelectron Spectrometer (XPS, Bruker AG, Germany). S₄800 Scanning Electron Microscope (SEM) and H-600 Transmission Electron Microscope (TEM) are both from the Hitachi Group in Japan, which exploited to observe morphologies and conditions of the samples. UV–Vis absorption spectra of as-obtained photocatalysts were measured by Lamb-da₃5 UV–Visible spectrophotometer (UV–Vis DRS, PerkinElmer, USA) in the tested range of 300–900 nm. Photoluminescence spectra were detected by the RF-540 British spectrophotometer (PL, Shimadzu Corporation, Kyoto, Japan).

2.3. Photocatalytic activity experiments

The present study aims to assess the photocatalytic performance of the synthesized composite photocatalytic material through a systematic simulation of the degradation process of tetracycline (TC) aqueous solutions under conditions of simulated sunlight exposure. The photocatalytic activity tests for all samples comprise two distinct phases: a dark reaction phase and a photoreaction phase. Previous studies have indicated that the mean concentration of antibiotics in wastewater emanating from the field site is roughly 20 mg/L [43]. Accordingly, the 1 L deionized aqueous solution containing 20 mg of tetracycline (TC) was prepared with precision to emulate sewage samples encountered in the field. In each photocatalytic degradation experiment targeting TC, a Xenon lamp light source with a constant light intensity of 20 mW/cm² was employed, focusing on the effect of its visible light component on the reaction. The specific procedure entailed the suspension of 0.02 g of the prepared photocatalyst in 100 mL of tetracycline (TC) aqueous solution with a 20 mg/L concentration. Initially, the suspension was stirred without light for 30 min to achieve equilibrium between tetracycline (TC) and the photocatalyst concerning adsorption and desorption. Subsequently, the suspension was exposed to the Xenon lamp while continuing to be stirred. Throughout the reaction, 5 mL of the reaction suspension was collected at 30 min intervals and subjected to centrifugation at 5000 rpm with a centrifuge radius of 10 cm for 3 min. This was done to separate the supernatant for subsequent analysis. The absorbance was determined using a UV-1800PC spectrophotometer at the absorbed wavelength line of 356 nm, and the data were subjected to analysis to investigate the photocatalytic activity of the catalyst [44].

To comprehensively evaluate the performance differences of composite photocatalytic materials with various composition ratios, an experimental group was explicitly set up in which the original CCO material was gradually replaced with an equivalent amount of CCO/CN composite material at gradients ranging from 10 % to 50 % (a total of five gradients). This approach facilitated a comprehensive evaluation of the performance differences of the materials in question. The aforementioned experimental procedures were repeated to collect the corresponding absorbance data. To ensure the reliability of the experimental results, all degradation experiments were conducted in quintuplicate to measure the absorbance of the solutions. All experiments were performed at room temperature to minimize errors in the photocatalytic effect, with optimal laboratory ventilation and a uniform stirring speed provided by the magnetic stirrer. Furthermore, we ensured that the specifications of the light source used in all experimental groups were consistent to minimize the potential for error during the experimental process.

2.4. Detection of reactive radicals

To evaluate the role of reactive radicals in the photocatalytic reaction, anhydrous ethanol (C₂H₆O), silver nitrate (AgNO₃), benzoquinone (BQ), and isopropanol (IPA) were successively introduced into the system. Specifically, benzoquinone (BQ) was employed to quench superoxide radicals (\cdot O₂--), while isopropanol (IPA) was utilized to quench hydroxyl radicals (\cdot OH). Furthermore, silver nitrate (AgNO₃) was employed to capture e⁻, while anhydrous ethanol (C₂H₆O) was used to capture h⁺. These manipulations were conducted to ensure the accurate detection and analysis of the contributions of the various radicals present during the reaction [45].

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction (XRD) pattern of the prepared catalyst is shown in Fig. 1. This analysis is used to characterize the crystal structure of the prepared photocatalyst. The crystalline phases of the samples were investigated through XRD, and the pure CCO pattern exhibits a series of clear and prominent characteristic peaks. The pattern for pure CCO displays a sequence of distinct and prominent characteristic peaks corresponding to lattice diffraction of (110), (111), (200), (211), (220), (221), and (222). The 20 values were found to be 29.63°, 36.50°, 42.40°, $52.58^\circ,\,61.52^\circ,\,65.70^\circ,\,and\,77.57^\circ,\,respectively.$ These peaks are under the standard pattern of CeCuO₃ (JCPDS NO.75-1531). It is noteworthy that two high-intensity characteristic peaks are observed at 12.89° and 27.69°, which correspond to the (100) and (002) planes of $g-C_3N_4$ (JCPDS NO.87-1526), respectively. Moreover, the XRD patterns of the 10-50CCO/CN nanocomposites exhibit all the diffraction peaks of CN and CCO, with no evidence of impurity peaks. This provides compelling evidence that the CCO/CN composites have been successfully synthesized and are high purity [46-48].

3.2. Material surface analysis

To gain a deeper understanding of the surface elemental composition and valence state distribution of CN, CCO, and CCO/CN samples, XPS measurements were conducted. Fig. 2(a-f) presents the prepared samples' XPS spectra. Fig. 2(a) depicts the XPS survey spectrum of the composite catalyst, which unambiguously corroborates the presence of C, N, O, Ce, and Cu elements. This serves as a prerequisite for subsequent elemental composition and valence state analysis. Further analysis of Fig. 2(b) reveals that the C 1 s peaks at 284.6 eV and 288.1 eV correspond to C-C bonds and N-C=C bonds, respectively [49]. These are attributed to impurity carbon and sp² hybridized carbon in g-C₃N₄. The N 1 s peak at 398.7 eV in Fig. 2(c) is attributed to C-N=C and N-(C)₃ bonds [50,51]. In the fitted spectrum of Fig. 2(d), the O 1 s peaks at 532.2 eV and 530.3 eV indicate $\cdot O_2^-$ and hydroxyl oxygen (O-H) [52], respectively. The presence of O-H bonds suggests the presence of adsorbed water molecules on the sample surface. Fig. 2(e) reveals the valence state of copper, with peaks at 952.9 eV and 933.2 eV corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. This indicates the presence of Cu in the +2 valence state [53,54]. Fig. 2(f) illustrates the binding energies of the characteristic peaks of the Ce 3d orbitals, with 882.9, 885.5, and 898.4 eV corresponding to Ce $3d_{5/2}$, and 901.2 eV, 907.9 eV, and 917.3 eV about Ce 3d_{3/2}. The binding energy peaks at 885.5 eV and 901.2 eV can be attributed to the Ce³⁺valence state, while the remaining peaks are attributed to the Ce⁴⁺valence state. This indicates that Ce atoms exist simultaneously in both the +3 and +4



Fig. 1. XRD patterns of CCO, CN, and CCO/CN.

valence states within the material [55]. This suggests that Ce may be partially oxidized to CeO_2 and partially doped into carbon nitride, which facilitates the migration of photogenerated carriers. [56,57]. Notably, XPS spectral analysis also indicates that the CCO/CN sample contains only C, N, O, Cu, and Ce elements, with no other impurity elements detected. The XPS results offer strong evidence for successfully forming the heterojunction structure between CCO and CN. However, they also corroborate the findings of the XRD analysis, thereby providing a deeper comprehension of the material's structure.

3.3. Infrared spectra analysis

As shown in Fig. 3, the Fourier Transform Infrared (FT-IR) spectra of the CN, CCO, and CCO/CN samples were presented. Initially, it is observed that the photocatalysts, comprising CN, CCO, and CCO/CN in proportions ranging from 10 % to 50 %, exhibit broad and overlapping spectral bands within the range of $3600-3000 \text{ cm}^{-1}$ [58]. In the case of the pure CN sample, a series of sharp and intense vibrational peaks within the interval of 1641–1100 cm⁻¹ are attributed to the C=N and C-N bonds in heterocyclic compounds [59]. In particular, the distinctive peak at 808 $\rm cm^{-1}$ corresponds to the vibrational mode of the striazine ring. Moreover, as documented in the literature, the CCO sample displays a distinct Raman band at 454 cm⁻¹. It is worthy of note that copper oxide has a primary Raman band at 628 cm⁻¹, which is derived from the wagging and bending vibrations of Ce–O and Cu–O [60,61]. In contrast, the band at 460 cm⁻¹ indicates the stretching and vibrating of Ce-O and Cu-O [62-64]. Notably, the characteristic peak value at 808 cm⁻¹ (as illustrated in Fig. 1b) corresponds to the breathing mode of the S-thiazine ring unit in g-C₃N₄. The XRD and XPS measurements provide strong proof. The heterojunction photocatalyst CCO/CN has been prepared successfully.

3.4. Morphology and microstructure analysis

The morphologies of the photocatalysts were characterized using SEM and TEM, and their loading states were investigated in great detail.

Fig. 4 presents high-resolution images of the CCO, CN, and CO/CN samples obtained in this study. Fig. 4(a) illustrates the ordered arrangement of CCO nanoparticles with an approximate diameter of 25 nm. Fig. 4(b) illustrates the irregular layered structure of the pure CN, which is characterized by a multitude of nanosized sheet aggregations with a relatively flat surface. Fig. 4(c) illustrates the formation of the CCO/CN nanomaterial through a composite process stimulated by hydrothermal action. From a morphological perspective, the material under examination features the interweaving and stacking of CCO nanoparticles with CN sheets. In the CCO/CN pattern, the CCO particles are uniformly distributed on the CN sheets, resulting in the formation of a heterostructured interface. [39]. Fig. 4(d) depicts the TEM image of the CCO/CN composite, where the bright regions correspond to CN and the dark regions to CCO. The CCO particles are distributed within the CN and exhibit a certain degree of aggregation. This observation corroborates the SEM results, thereby confirming the successful doping of CCO into CN. It is noteworthy that the interface between CCO and CN facilitates continuous interfacial e⁻ transfer, thereby enhancing charge transfer and photocatalytic efficiency [65].

3.5. Optical properties analysis

To further verify their optical properties, UV–Vis DRS spectra were measured for CCO, CN, and CCO/CN samples, to document the light absorption range and optical properties of the prepared photocatalysts. As illustrated in Fig. 5, UV–Vis DRS is also a useful analytical method for studying the bandgap energy of photocatalysts. The absorption edges of the CCO, CN, and CCO/CN samples are observed to be at approximately 633, 516, and 574 nm [64], respectively (Fig. 5a),. In comparison to the pristine CN, the CCO/CN sample exhibits a notable redshift, thereby confirming that the photoactivity of the prepared samples can be effectively excited by visible light, thus enhancing their light absorption efficiency. The estimated bandgaps of CCO, CN, and CCO/CN were calculated using the formula $[eh\nu = C(h\nu - Eg)^p]$ (Fig. 5b) [66], resulting in values of approximately 1.96, 2.40, and 2.16 eV, respectively. These findings indicate that the photocatalysts exhibit photoactivity in the



Fig. 2. XPS survey spectrum of CCO/CN (a); high-resolution XPS spectra of C 1 s (b), N 1 s(c), O 1 s (d), Cu 2p (e), and Ce 3d (f).

visible region. This also corroborates the hypothesis that the photoactivity of the obtained samples can be excited by visible light, in accordance with the observed alterations in the absorption edges. Upon contact between CCO and CN, the bandgap width of CCO/CN is observed to narrow unintentionally. This variation is primarily attributed to the synergistic effect of CCO nanoparticles within the CCO/CN heterojunction system, which exhibits a cooperative interaction between its intrinsic absorption characteristics and staggered layered



Fig. 3. FT-IR spectra of CCO, CN, and CCO/CN.



Fig. 4. SEM images of CCO (a), CN (b), and CCO/CN (c); TEM image of CCO/CN (d).



Fig. 5. The UV-Vis patterns (a) and DRS patterns (b) of CCO , CN and CCO/CN.

structure. It can therefore be concluded that an intermediate band gap is required for photocatalysts to achieve maximum photocatalytic activity. The CCO/CN samples demonstrate the most significant photogenerated electron-hole pairs separation efficiency, indicating their superior photocatalytic performance.

3.6. Photoluminescence spectroscopy analysis

In general, the level of photocatalyst activity is dependent on the effective separation of photogenerated e- and h+. Fig. 6 explores the separation rate of photogenerated electron-hole pairs on the surfaces of CCO, CN, and CCO/CN samples, presenting their PL characteristics under an excitation wavelength of 290 nm. By preceding research, a

greater peak intensity in the PL spectrum is indicative of a diminished lifetime of photogenerated carriers, which harms the efficiency and activity of photocatalysis. CN materials display robust PL emission characteristics. However, with an increase in the quantity of CCO incorporated, the photogenerated electron-hole pairs separation efficiency of the CCO/CN composite photocatalyst undergoes notable alterations. It is noteworthy that the emission peak intensity of 40CCO/CN decreases significantly, which directly indicates the effective suppression of the recombination of photogenerated carriers and further highlights the excellent photocatalytic performance of the material. It is noteworthy that the slight variations in the PL emission peaks of the CCO/CN samples indicate the successful establishment of an S-scheme charge transfer mechanism between CCO and CN. Moreover, the



Fig. 6. PL emission spectra of CCO, CN, and CCO/CN.

incorporation of the S-scheme heterojunction system has the additional benefit of further enhancing the photocatalytic performance of the catalyst. In particular, this significantly extends the lifetime of useful photocarriers, enabling them to function at higher redox potentials and effectively driving the recombination of useless photocarriers. [67,68].

3.7. Photocatalytic activity analysis

To ascertain the photocatalytic activity of the CCO, CN, and CCO/CN samples, multiple photocatalytic tetracycline (TC) degradation experiments were conducted under visible light excitation over 180 min. The results of the degradation process are presented in Fig. 7 and Table 1. As illustrated in Fig. 7(a), the absence of a photocatalyst resulted in the TC content remaining unaltered throughout the experimental procedure. However, when pure CCO and CN samples were added separately, the photocatalytic degradation rates of TC reached 55 % and 35 %, respectively, within the 180 min experimental range. This outcome is primarily ascribed to the restricted light absorption capacity inherent in the monomeric materials and the influence exerted by their singlecrystal lattice structures. Nevertheless, establishing a heterojunction system encompassing CCO and CN resulted in a marked improvement in the removal efficiency of tetracycline (TC) by the CCO/CN composite material. Under identical experimental conditions, the removal efficiency of 40CCO/CN reached 92.9 %. Furthermore, the rates of photocatalytic tetracycline (TC) degradation exhibited by the CN, CCO, and CCO/CN samples were found to be in direct correspondence with their PL emission intensity order, thereby reinforcing the crucial role that accelerated separation of photogenerated electron-hole pairs plays in facilitating the efficiency of the photocatalytic process.

Notably, within the optimal doping ratio range, the catalytic performance of the photocatalyst exhibited a positive correlation with the doping amount of CCO. As the concentration of CCO in the CCO/CN samples increased (up to 40 %), the bandgap of CN doped with CCO exhibited a gradual decrease, accompanied by an expansion of the light response range. This was due to an increase in the number of CCO nanoparticles in contact with CN nanosheets, leading to the formation of additional active site S-scheme heterojunction units. The degradation performance was optimized when the CCO content reached 40 % due to the synergistic promotion. However, excess CCO content (>40 %) proved detrimental to the CCO/CN samples. This was because uncontacted CCO nanoparticles could result in light absorption oversaturation, which in turn would lead to a reduction in the utilization rate of visible Table 1

Results of visible-light-driven degradation of TC in CCO,CN and CCO/CN samples.

Sample name	Degradation rate (%)	$Kt (Min^{-1})$	R ₂
CN	35	0.00231	0.92126
CCO	55	0.0038	0.98729
10CCO/CN	63.9	0.00488	0.95781
20CCO/CN	66.9	0.00498	0.95401
30CCO/CN	81.5	0.00787	0.96399
40CCO/CN	92.9	0.01152	0.90281
50CCO/CN	77.9	0.00658	0.95843

light. At this juncture, the recombination rate of electron-hole pairs decelerated, and competition with the S-scheme heterojunction reduced active sites during the photocatalytic reaction. As a result, the bandgap increased gradually, the visible light response range diminished, and the recombination rate of electron-hole pair accelerated, leading to a decline in degradation performance.

It is worth mentioning that the photocatalytic degradation of TC essentially adhered to first-order linear kinetics. Additionally, Fig. 7(b) displays the TC degradation kinetics curves for the CCO, CN, and CCO/CN samples, all falling within the doping ratio range of 10–50 %. The kinetic constants were 0.0038, 0.00231, 0.00488, 0.00498, 0.00787, 0.01152, and 0.00658 min⁻¹. The linear reaction rate of the 40 % CCO/CN sample was 1.69 and 2.65 times that of the CCO and CN samples, respectively. Furthermore, the performance of CCO/CN photocatalysts and other binary heterojunctions for photocatalytic degradation of antibiotics under visible light is compared in (Table 2).

As illustrated in Fig. 8(a), to evaluate the stability and reusability of the prepared heterojunction photocatalyst, we conducted repetitive experiments using the 40CCO/CN sample. Following five photocatalytic cycles, a slight decrease in the degradation efficiency of TC was observed. It is hypothesized that this reduction in efficiency may be attributed to mass loss of the sample during consecutive cycles of use. Nevertheless, despite this slight decline, the photocatalytic removal rate of TC remained around 90 % throughout the five cycles, clearly demonstrating the excellent stability and recyclability of the heterojunction photocatalyst.

Subsequently, the CCO/CN powder samples were meticulously collected and rigorously dried once the reaction had reached completion. Once the catalytic continuous response was complete, the microscopic morphology and XRD and XPS analyses of the photocatalyst were



Fig. 7. Photocatalytic degradation efficiency(a) and first order linear equation fitting graph (b) for CCO,CN, CCO/CN.

Table 2

Performance of other binary heterojunctions for photocatalytic degradation of antibiotics under visible light.

Photocatalyst	Degradation	Time	Target	Ref.
g-C ₃ N ₄ /BiOCl	89.33 %	120 min	Tetracycline	[23]
SbVO ₄ /g-C ₃ N ₄	82.30 %	150 min	Tetracycline	[24]
Ta ₃ N ₅ /BiOCl	89.60 %	60 min	Tetracycline	[25]
CdMoO ₄ /CdO	88.48 %	90 min	Norfloxacin	[26]
CoO-CuBi ₂ O ₄	89.50 %	90 min	Tetracycline	[27]
g-C ₃ N ₄ /Ce ₂ S ₃	98.00 %	90 min	Tetracycline	[28]
CeCuO ₃ /g-C ₃ N ₄	92.9 %	180 min	Tetracycline	This work

conducted. These formed the basis for evaluating its stability and recovery potential. As illustrated in Fig. 8(b) and 8(c), the nanoscale CCO particles are securely embedded in the CN layer, exhibiting no indications of fracture or deformation. This evidence substantiates the assertion that the continuous catalytic reaction has not compromised the microstructure of CCO/CN. Additionally, the XRD spectrum depicted in Fig. 8(d) of the CCO/CN heterojunction demonstrates that the diffraction peaks of its crystal lattice align precisely with those of the individual CCO and CN crystals, indicating that the crystal structure of the CCO/CN remained unaltered throughout the continuous reaction process. Moreover, the XPS analysis presented in Fig. 8(e) corroborates the stability of the elemental composition on the sample surface, with no significant alterations observed. These findings further corroborate the structural stability and exceptional catalytic activity of the CCO/CN heterojunction throughout the continuous reaction process.

We conducted an exhaustive investigation into the pivotal role of active substances in the TC decomposition process within suspensions, with particular attention paid to the influence of pH on the TC adsorption process. To this end, the requisite experiments were conducted, wherein alterations were observed by adjusting the pH of the pollutant solution. As illustrated in Fig. 9, the experimental conditions were established with pH values of 3, 5, 7, 9, and 11 (with a permitted



Fig. 8. Degradation results (a) of five photocatalytic cycle experiments of 40CCO/CN, (b) TEM images, (c) SEM images, (d) XRD pattern, and (e) XPS spectra of CCO/CN after continuous photocatalytic reaction.

deviation of ± 0.2). The experimental results demonstrated that the photocatalytic activity was relatively low and significantly inhibited in solutions with pH values of 3, 7, 9, and 11. Fig. 9 also clearly illustrates the TC decomposition results of CCO/CN under different pH environments, among which the most significant degradation efficiency was obtained at a pH of 5 [69]. Further analysis indicated that, in a neutral pH environment of the TC suspension, the adsorption of TC onto CCO/CN was more efficient. Consequently, the degradation effect of the material on pollutants was also the most significant. Additionally, there was a more adequate correspondence between active sites and TC. Given the aforementioned experimental outcomes, we optimized and controlled the TC solution's pH to 5.0 throughout the photocatalytic process, intending to attain the most efficacious degradation effect.

3.8. Photocatalytic mechanism

It is apparent that to attain a comprehensive understanding of the photocatalytic degradation of tetracycline (TC), it is fundamentally essential to elucidate the contributions and mechanisms of action of each active species, which include h^+ , e^- , and $\cdot O_2^-$, and $\cdot OH$. To this end, we introduced active species scavengers into the photocatalytic system to conduct quenching experiments. Specifically, as illustrated in Fig. 10, we employed AgNO3 to scavenge e⁻, BQ to scavenge ·O₂⁻, IPA to scavenge ·OH, and C₂H₆O to scavenge h⁺. Fig. 10 depicts the outcomes of the active species quenching experiments conducted with the CCO/CN composite catalyst. The experiments demonstrated that the quenching of any of these active species resulted in a notable decline in the photocatalytic degradation efficiency of TC, thereby substantiating their indispensable roles in the photocatalytic process [70]. Further analysis revealed that the photocatalytic degradation of pollutants involved the participation of e⁻, h⁺, ·O₂⁻, and ·OH. Notably, O₂⁻ can generate ·OH species through a series of reactions, which directly participate in the oxidative catalytic degradation of pollutants and attack TC contaminants. However, from the perspective of TC degradation pathways, while ·OH species play an auxiliary role, they are not the primary contributors.

To determine the locations of the valence band (VB) and conduction band (CB) for the CCO and CN photocatalysts, we employed the following empirical equation [71]:

 $E_{VB} = X - Ee + 0.5Eg$

 $E_{CB}=E_{VB}-Eg\,$

Specifically, the X values for CCO and CN, calculated according to the formula, are approximately 5.05 eV and 4.72 eV [72]. In this



context, Ee means the energy of free electrons on the hydrogen scale (~4.5 eV) [73]. Based on the information mentioned above, it is possible to estimate the CB_{CCO} edge values and VB_{CCO} edge to be -0.43 eV and 1.53 eV, respectively. Similarly, the estimated values for the CB_{CN} and the VB_{CN} are -0.98 eV and 1.42 eV.

In light of the experimental findings, we propose two potential mechanisms for the photocatalytic degradation or charge transfer process involving CCO/CN. The first mechanism is the traditional Type-II heterojunction mode on CCO/CN, as illustrated in Fig. 11(a). In a traditional Type-II heterojunction [74], the separation of electron-hole pairs results in the transfer of photoinduced e^- from the CN_{CB} to the $\text{CCO}_{\text{CB}},$ while photoinduced h^+ migrate in the opposite direction, from the CCO_{VB} to the CN_{VB} . However, an analysis of the results of radical quenching experiments revealed that the migration of photogenerated carriers in CCO/CN does not conform to the traditional mechanism. The experimental results indicate that $\cdot O_{2}$ - are the primary active species responsible for the photocatalytic degradation of TC. However, the generation of $\cdot O_2$ - is not conducive during the electron-hole pairs separation process of a traditional Type-II heterojunction [75], in contrast to our experimental results. Hence, the photoinduced carrier transfer mechanism of the Type-II heterojunction is not applicable in this case, as the dominant role of active sites (e^{-}/h^{+}) is not reflected. From the perspective of heterojunction dynamics, this transfer scheme of CCO/CN exhibits significant deficiencies, including electrostatic repulsion and carrier consumption, which clearly contravene the original design intention for the CCO/CN heterojunction. Therefore, a novel S-scheme is proposed for the CCO/CN heterostructure (Fig. 11b). Despite its energy band structure bearing resemblance to that of the Type-II scheme, the migration pattern of carriers is wholly distinct.

As illustrated in Fig. 11b, in the absence of light, the CCO/CN composite material demonstrated the ability to adsorb pollutants. When the light energy exceeded the bandgap width (Eg) of the material, the internal electric field (IEF) of the S-scheme heterojunction activated the photogenerated electron and hole pairs. Upon contact between the two semiconductors, due to differences in their Fermi levels, e⁻ from CN spontaneously flowed towards CCO until equilibrium was reached, thereby forming an internal electric field directed from CN to CCO. The strong charge transfer capability of the electric field facilitated the transfer of photogenerated electrons from CCO to CN, leading to the recombination of some e⁻ and h⁺ at the interface. Concurrently, the combined action of the internal electric field (IEF), Coulomb attraction (CA) [64], and the driving force generated by band edge bending resulted in an upward bending of the CN interface band due to electron loss, while the CCO interface band exhibited a downward bending due to electron accumulation. This bending of the interface bands effectively regulated the unidirectional flow of photogenerated e⁻ and h⁺, facilitating the transfer of e⁻ from CCO to CN while impeding the reverse transfer of h⁺. This maintained the charge separation between the CN_{CB} and the CCO_{VB}, ensuring the retention of reducing e⁻ on the CN_{CB} and oxidizing h^+ on the CCO_{VB} [76,77]. As a result, the S-scheme heterojunction formed by combining CCO and CN effectively promoted the separation of electron-hole pairs, thereby enhancing the photocatalytic efficiency. Concurrently, the oxygen present in the solution reacted with the electron to produce the $\cdot O_2\text{-},$ which rapidly attacked the pollutant molecules and subsequently generated the ·OH, thus directly participating in the oxidative degradation process [78]. The reactive species reacted with pollutants to produce CO2 and H2O, as well as other harmless products. In conclusion, in comparison to the conventional type-II heterojunctions, the S-scheme heterojunctions demonstrated a superior separation efficiency of the photogenerated electron-hole pairs and enhanced redox capabilities [79]. The formation of the S-scheme heterojunction system facilitated the generation of ·O2- and other reactive species during photocatalytic reactions, thereby enabling the efficient degradation of various pollutants [80].





Fig. 10. Results of active substance quenching experiments.



Fig. 11. The possible mechanism of TC degradation by CCO/CN photocatalyst.

4. Conclusion

The objective of this study was to successfully synthesize S-scheme heterojunction composites of CeCuO₃/g-C₃N₄ (CCO/CN) with varying weight ratios through a sol-gel and ultrasound-assisted hydrothermal method and to evaluate their photocatalytic activity for the degradation of tetracycline (TC) under simulated visible light. The photocatalytic degradation rates of these composites were compared with those of pure CeCuO₃ and g-C₃N₄. In comparison to the pure CN, pure CCO, and other CCO/CN composites, the 40CCO/CN catalyst demonstrated superior stability and efficiency in its photocatalytic activity. In particular, under 20 mW/cm² xenon lamp irradiation at pH 5.0, the catalyst degraded 92.9 % of TC after 180 min and demonstrated excellent recyclability after five cycles of use. Radical trapping experiments provided further evidence that e^- and h^+ are essential for the photocatalytic process. The improvement in the photocatalytic activity of the CCO/CN photocatalyst can be attributed to the successful construction of a heterogeneous interface scheme, which offers the following advantages: 1) The S-scheme structure expanded the light-harvesting range of the heterojunction photocatalyst, thereby enabling a synergistic effect in photocatalysis. 2) The formation of the S-scheme heterojunction structure in the CCO/CN binary photocatalyst inhibited the recombination of electron-hole pairs on the surfaces of CCO and CN, thereby creating a novel pathway for the effective separation of e^- and h^+ . In conclusion, this research not only provides novel ideas and methods for constructing high-efficiency composite photocatalysts but also makes significant contributions to the effective treatment of antibiotic wastewater and ecological environmental protection. Further in-depth research and promotion of this work are warranted.

CRediT authorship contribution statement

Zhengru Zhu: Visualization, Validation, Supervision. **Yu Ban:** Writing – review & editing, Writing – original draft. **Longjun Tang:** Investigation. Hong Li: Investigation.

Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

Data availability

The data that has been used is confidential.

References

- J. Georgin, D.S.P. Franco, A. Bonilla-Petriciolet, L. Meili, T.A. Kurniawan, G. Imanova, E. Demir, I. Ali, Environmental remediation of the norfloxacin in water by adsorption: advances, current status and prospects, Adv. Colloid Interface Sci. 324 (2024) 22.
- [2] I.A. Lakhiar, H. Yan, J. Zhang, G. Wang, S. Deng, R. Bao, C. Zhang, T.N. Syed, B. Wang, R. Zhou, X. Wang, Plastic pollution in agriculture as a threat to food security, the ecosystem, and the environment: an overview 14 (2024) 548.
- [3] W.Q. Yang, J. Li, Z.L. Yao, M. Li, A review on the alternatives to antibiotics and the treatment of antibiotic pollution: current development and future prospects, Sci. Total Environ. 926 (2024) 18.
- [4] J.S. Niroumand, S.J. Peighambardoust, R. Mohammadi, Tetracycline decontamination from aqueous media using nanocomposite adsorbent based on starch-containing magnetic montmorillonite modified by ZIF-67, Int. J. Biol. Macromol. 259 (2024) 18.
- [5] Y.N. Zhang, H. Zhang, J.L. Yao, Y.Y. Song, W.M. Li, X.T. Xuan, Coordination tuning of Fe²⁺ ions concentration in Fe-doped black phosphoruscarbonized cotton fiber (Fe-BP-CCF) composites to regulate photocatalysis and peroxymonosulfate (PMS) activation towards highly efficient degradation of organic pollutants, Chem. Eng. J. 483 (2024) 15.
- [6] M.P. Rayaroth, G. Boczkaj, O. Aubry, U.K. Aravind, C.T. Aravindakumar, Advanced oxidation processes for degradation of water pollutants-ambivalent impact of carbonate species: a review, Water 15 (2023) 19.
- [7] X.H. He, T.H. Kai, P. Ding, Heterojunction photocatalysts for degradation of the tetracycline antibiotic: a review, Environ. Chem. Lett. 19 (2021) 4563–4601.
- [8] S.X. Ren, S.Y. Wang, Y.F. Liu, Y.X. Wang, F. Gao, Y.J. Dai, A review on current pollution and removal methods of tetracycline in soil, Sep. Sci. Technol. 58 (2023) 2578–2602.
- [9] D.Q. Tian, H.Y. Zhou, H. Zhang, P. Zhou, J.J. You, G. Yao, Z.C. Pan, Y. Liu, B. Lai, Heterogeneous photocatalyst-driven persulfate activation process under visible light irradiation: from basic catalyst design principles to novel enhancement strategies, Chem. Eng. J. 428 (2022) 15.
- [10] H. Guo, C.G. Niu, C.Y. Feng, C. Liang, L. Zhang, X.J. Wen, Y. Yang, H.Y. Liu, L. Li, L. S. Lin, Steering exciton dissociation and charge migration in green synthetic oxygen-substituted ultrathin porous graphitic carbon nitride for boosted photocatalytic reactive oxygen species generation, Chem. Eng. J. 385 (2020) 15.
- [11] K. Saravanakumar, V. Maheskumar, Y. Yea, Y. Yoon, V. Muthuraj, C.M. Park, 2D/ 2D nitrogen-rich graphitic carbon nitride coupled Bi₂WO₆ S-scheme heterojunction for boosting photodegradation of tetracycline: influencing factors, intermediates, and insights into the mechanism, Composites Part B-Engineering 234 (2022) 13.
- [12] S. Gong, W. Zhang, Z. Liang, Y. Zhang, T. Gan, H. Hu, Z. Huang, Construction of a BaTiO₃/tubular g-C₃N₄ dual piezoelectric photocatalyst with enhanced carrier separation for efficient degradation of tetracycline, Chem. Eng. J. 461 (2023).
- [13] M. Ismael, Environmental remediation and sustainable energy generation via photocatalytic technology using rare earth metals modified g-C₃N₄: A review, J. Alloys Compd. 931 (2023).
- [14] Q. Wen, D. Li, H. Li, M. Long, C. Gao, L. Wu, F. Song, J. Zhou, Synergetic effect of photocatalysis and peroxymonosulfate activated by Co/Mn-MOF-74@g-C₃N₄ Zscheme photocatalyst for removal of tetracycline hydrochloride, Sep. Purif. Technol. 313 (2023).
- [15] G. Tan, R.Q. Jia, X. Zhao, Y.Q. Guo, L.L. Zhang, X.H. Wang, J.G. Wang, X. Feng, B. Li, L.Y. Wang, Fabrication of two isomorphic and hyperstable rare earth-based metal-organic frameworks with efficient ratiometric probe and photocatalytic performances, Inorg. Chem. 61 (2022) 11866–11878.
- [16] B. Palanivel, R.R. Macadangdang, M.S. Hossain, F.A. Alharthi, M. Kumar, J.-H. Chang, S. Gedi, Rare earth (Gd, La) co-doped ZnO nanoflowers for direct sunlight driven photocatalytic activity, J. Rare Earths 41 (2023) 77–84.
- [17] J. Yu, J. Dong, X. Su, J. Yang, D. Zhang, J. Liu, P. Cai, Z. Li, D. Zhang, X.J.J.O.A. Pu, Compounds, Preparation and Characterization of AgVO₃/Ag₄V₂O₇/BiOI double Sscheme Heterojunctions for the Photocatalytic Degradation of Methylene Orange and Tetracycline, 2024, 174187.
- [18] M. Lin, H. Liu, H. Wang, J. Wu, H. Jiang, H. Wei, M. Ou, Z. Guan, Z. Dong, J.J.C.E. J. Qi, Co dopant anchored in the BiOIO₃ nanosheets to induce oxygen vacancies for enhanced photocatalytic activity 484 (2024) 149472.

- [19] T. Deka, R.G.J.I.J.O.H.E. Nair, Recent advancements in surface plasmon resonance and Schottky junction assisted photocatalytic water splitting of noble metal decorated titania: a review 59 (2024) 322–342.
- [20] L. Mao, B. Zhai, L. Wen, W. Xiao, J. Shi, X. Kang, Y. Liu, C. Cheng, H. Jin, L. Guo, Simultaneous bulk and surface modifications of g-C₃N₄ via supercritical CO₂assisted post-treatment towards enhanced photocatalytic activity, Applied Catalysis B: Environment and Energy 362 (2025).
- [21] L. Mao, B. Zhai, J. Shi, X. Kang, B. Lu, Y. Liu, C. Cheng, H. Jin, E. Lichtfouse, L. Guo, Supercritical CH(3)OH-triggered isotype heterojunction and groups in g-C (3)N(4) for enhanced photocatalytic H(2) evolution, ACS Nano 18 (2024) 13939–13949.
- [22] G. Wang, S. Lv, Y. Shen, W. Li, L. Lin, Z.J.J.O.M. Li, Advancements in heterojunction, cocatalyst, defect and morphology engineering of semiconductor oxide photocatalysts 10 (2024) 315–338.
- [23] Y. Wei, Y.-B. Liu, C. Liu, X. Li, G.-H. Zhao, R.-H. Liu, H.-Y. Wang, Y.-Y. Jiang, Y.-L. Zhang, Y.-H.J.J.O.E.C.E. Gao, Construction of oxygen-doped g-C₃N₄/BiOCl (S-scheme) heterojunction: efficient degradation of tetracycline in wastewater 12 (2024) 113354.
- [24] L. Wang, X. Zhu, J. Rong, C. Feng, C. Liu, Y. Wang, Z. Li, S.J.S.S.S. Xu, Construction of Z-scheme SbVO₄/g-C₃N₄ heterojunction with efficient photocatalytic degradation performance 155 (2024) 107639.
- [25] S. Li, M. Cai, C. Wang, Y. Liu, N. Li, P. Zhang, X.J.J.O.M.S. Li, Technology, rationally designed Ta₃N₅/BiOCl S-scheme heterojunction with oxygen vacancies for elimination of tetracycline antibiotic and Cr (VI): performance, toxicity evaluation and mechanism insight 123 (2022) 177–190.
- [26] Z. Chen, T. Ma, Z. Li, W. Zhu, L.J.J.O.M.S. Li, Technology, Enhanced photocatalytic performance of S-scheme CdMoO₄/CdO nanosphere photocatalyst 179 (2024) 198–207.
- [27] X. Wang, N. Su, X. Wang, D. Cao, C. Xu, X. Wang, Q. Yan, C. Lu, H. Zhao, Fabrication of 0D/1D S-scheme CoO-CuBi(2)O(4) heterojunction for efficient photocatalytic degradation of tetracycline by activating peroxydisulfate and product risk assessment, J. Colloid Interface Sci. 661 (2024) 943–956.
- [28] P. Hemmati-Eslamlu, A. Habibi-Yangjeh, A. Khataee, S-scheme g-C₃N₄/Ce₂S₃ nanocomposites for visible-light activation of persulfate ions: photocatalytic degradations of antibiotics and dyes, Journal of Photochemistry and Photobiology a-Chemistry 453 (2024) 11.
- [29] Q. Xu, L. Zhang, B. Cheng, J. Fan, J.J.C. Yu, S-scheme heterojunction photocatalyst 6 (2020) 1543–1559.
- [30] Y.N. Zhang, M. Gao, S.T. Chen, H.Q. Wang, P.W. Huo, Fabricating Ag/CN/ZnIn₂S₄ S-scheme heterojunctions with plasmonic effect for enhanced light-driven photocatalytic CO₂ reduction, Acta Phys. -Chim. Sin. 39 (2023) 13.
- [31] A.S. Golda, A.P. Varghese, N. Rabiee, B. Neppolian, S.K. Lakhera, Synergistic hydrogen generation through a 2D-2D NiCuInS₂:In₂S₃g-C₃N₄ dual S-scheme heterojunction nanosheets, Carbon 215 (2023) 10.
- [32] T. Li, N. Tsubaki, Z.J.J.O.M.S. Jin, Technology, S-scheme heterojunction in photocatalytic hydrogen production 169 (2024) 82–104.
- [33] F. Li, G. Zhu, J. Jiang, L. Yang, F. Deng, X.J.J.O.M.S. Li, Technology, A review of updated S-scheme heterojunction photocatalysts 177 (2024) 142–180.
- [34] O. Bechambi, L. Jlaiel, W. Najjar, S. Sayadi, Photocatalytic degradation of bisphenol A in the presence of Ce-ZnO: evolution of kinetics, toxicity and photodegradation mechanism, Mater. Chem. Phys. 173 (2016) 95–105.
- [35] P. Sarkar, S. Neogi, S.R.D. De, Activation of peroxymonosulfate by S-scheme Bi₂S₃/ doped gCN heterostructure photocatalyst for highly efficient visible light driven tetracycline degradation: insights into reaction mechanisms, Sep. Purif. Technol. 308 (2023) 16.
- [36] C. Feng, J. Rong, Y. Zhang, X. Zheng, X. Li, S. Xu, Z. Li, An S-scheme CeO₂/ foveolate g-C₃N₄ composite with horseradish peroxidase activity for photo-enzyme synergistic catalytic degradation of phenanthrene, Appl. Catal. Environ. 337 (2023).
- [37] X. Chen, Z. Li, J. Zhou, S. Chen, Y. Huang, W. Wang, W. Wang, Q. Xu, X. Xi, Constructing 2D/2D La₂Ce₂O₇/g-C₃N₄ S-scheme heterojunction for markedly enhanced interfacial charge separation and photocatalytic activity under visible light irradiation, J. Alloys Compd. 960 (2023).
- [38] D. Zhao, P. Wu, H. Zhu, R. Jiang, J. Chen, C. Qiu, S. Jiang, G. Lu, Construction of Sscheme heterojunctions of a Ti-doped Ce-MOF and BiOCI for efficient photocatalytic selective oxidation of amines, Inorganic Chemistry Frontiers 11 (2024) 1583–1595.
- [39] Q. Hu, B. Yue, H. Shao, F. Yang, J. Wang, Y. Wang, J. Liu, Facile syntheses of cerium-based CeMO₃ (M = Co, Ni, Cu) perovskite nanomaterials for highperformance supercapacitor electrodes, J. Mater. Sci. 55 (2020) 8421–8434.
- [40] S. Soren, S. Chakroborty, R.R. Mahalik, P. Parhi, K. Pal, D. Behera, C.R. Sahoo, R. N. Padhy, M.K. Aulakh, S. Sareen, S.B.N. Krishna, Evaluation of the antimicrobial potential of cerium-based perovskite (CeCuO₃) synthesized by a hydrothermal method, New J. Chem. 46 (2022) 19147–19152.
- [41] F.Q. Cui, X.L. Shi, Z.R. Sun, CuCe-LDHs anchored on CNTs-COOH/copper foam cathode for the electrocatalytic degradation of sulfamethoxazole under nearneutral conditions, Journal of Water Process Engineering 47 (2022) 14.
- [42] Q. Xu, C. Jiang, B. Cheng, J.J.D.T. Yu, Enhanced visible-light photocatalytic H 2generation activity of carbon/gC 3 N 4 nanocomposites prepared by two-step thermal treatment 46 (2017) 10611–10619.
- [43] M. Lee, H. Lee, P.J.A.-A.J.O.A.S. Ryu, Public health risks: chemical and antibiotic residues-review 14 (2001) 402–413.
- [44] J. Durán-Álvarez, M. Méndez-Galván, L. Lartundo-Rojas, M. Rodríguez-Varela, D. Ramírez-Ortega, D. Guerrero-Araque, R.J.T.I.C. Zanella, Synthesis and characterization of the all solid Z-scheme Bi 2 WO 6/Ag/AgBr for the photocatalytic degradation of ciprofloxacin in water 62 (2019) 1011–1025.

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- [45] F. Wang, P.H. Chen, G.S. Liu, Copper-catalyzed radical relay for asymmetric radical transformations, Acc. Chem. Res. 51 (2018) 2036–2046.
- [46] P. Pandey, A.K.J.J.O.A. Choubey, Green synthesized ZnO@ CuO nanocomposites using Achyranthes aspera leaves extract for dielectric applications, Compounds 970 (2024) 172492.
- [47] J. Yuan, B. Yu, D. Pan, X. Hu, J. Chen, M. Aminua, Y. Liu, L. Sheng, Y. Chen, Y.J.A. F.M. Wu, Universal source-template route to metal selenides implanting on 3D carbon Nanoarchitecture: Cu₂- xSe@ 3D-CN with se, C Bonding for Advanced Na Storage 33 (2023), 2305503.
- [48] M. Isik, S. Delice, N.J.P.E.L.-D.S. Gasanly, Temperature dependence of band gap of CeO₂ nanoparticle photocatalysts, Nanostructures 150 (2023) 115712.
- [49] H. Xie, J. Zeng, G. Zhou, CeCu composite oxide for chlorophenol effective removal by heterogeneous catalytic wet peroxide oxidation, Environ. Sci. Pollut. Res. Int. 27 (2020) 846–860.
- [50] X. Zeng, S. Shu, Y. Meng, H. Wang, Y.J.C.E.J. Wang, Enhanced photocatalytic degradation of sulfamethazine by g-C₃N₄/Cu, N-TiO₂ composites under simulated sunlight irradiation 456 (2023) 141105.
- [51] S. Srinithi, S.-M. Chen, V. Balakumar, R.-H. Li, Fabrication of N-rich graphitic carbon nitride supported CeO₂ for improved photocatalytic charge separation and electrochemical electron transfer properties, Surfaces and Interfaces 39 (2023).
- [52] G. Zhou, B. Dai, H. Xie, G. Zhang, K. Xiong, X. Zheng, CeCu composite catalyst for CO synthesis by reverse water-gas shift reaction: effect of Ce/Cu mole ratio, Journal of CO2 Utilization 21 (2017) 292–301.
- [53] Y. Zhang, J. Zhao, H. Wang, B. Xiao, W. Zhang, X. Zhao, T. Lv, M. Thangamuthu, J. Zhang, Y.J.N.C. Guo, Single-atom Cu anchored catalysts for photocatalytic renewable H₂ production with a quantum efficiency of 56% 13 (2022) 58.
- [54] J. Pan, S. Wang, A. Chen, Y. Chen, M. Wang, Y.J.J.O.A. Chen, Visible-light-active mesoporous ceria (CeO₂) nanospheres for improved photocatalytic performance, Compounds 898 (2022) 162895.
- [55] S. Vignesh, S. Suganthi, B. Palanivel, A.M. Ali, M. Shkir, H. Algarni, G. Sreedevi, Design a novel g-C₃N₄ based Ce₂O₃/CuO ternary photocatalysts for superior photodegradation performance of organic mixed pollutants: insights of Z-scheme charge transfer mechanism, J. Phys. Chem. Solid 162 (2022).
- [56] Z. Chu, J. Li, H.Y. Sohn, C. Chen, X. Huang, Y. Lan, A. Murali, J.J.C.P.B.E. Zhang, CeO₂-g-C₃N₄ S-scheme heterojunctions for enhanced photocatalytic performance: effects of surface C/N ratio on photocatalytic and adsorption properties 257 (2023) 110689.
- [57] G. Zhang, Y. Zhang, X. Zhao, Y. Jiao, Y. Yan, J.J.J.O.R.E. Jiang, Synergistic enhancement of Ce–ZnO/g-C₃N₄ photocatalytic performance using N, O-bisvacancy induction and S-scheme heterojunctions 42 (2024) 817–826.
- [58] O. Iqbal, H. Ali, N. Li, A.I. Al-Sulami, K.F. Alshammari, H.S. Abd-Rabboh, Y. Al-Hadeethi, I.U. Din, A.I. Alharthi, R.J.M.T.P. Altamimi, A review on the synthesis, properties, and characterizations of graphitic carbon nitride (g-C₃N₄) for energy conversion and storage applications 34 (2023) 101080.
- [59] Y.-Y. Li, B.-X. Zhou, H.-W. Zhang, T. Huang, Y.-M. Wang, W.-Q. Huang, W. Hu, A. Pan, X. Fan, G.-F.J.C.E.J. Huang, A host–guest self-assembly strategy to enhance π-electron densities in ultrathin porous carbon nitride nanocages toward highly efficient hydrogen evolution 430 (2022) 132880.
- [60] K.L. Ameta, J. Sharma, V.S. Solanki, Photocatalytic mineralization of brilliant green dye using bimetallic CeCuO₃ nanoparticles in LEDs irradiations: A green and economically viable approach, Results in Chemistry 4 (2022).
- [61] M. Jeyaraj, R. Atchudan, S. Pitchaimuthu, T.N.J.I. Edison, P. Sennu, Photocatalytic degradation of persistent brilliant green dye in water using CeO₂/ZnO nanospheres, Process Saf. Environ. Prot. 156 (2021) 457–464.
- [62] J.A. Onrubia-Calvo, S. López-Rodríguez, I.J. Villar-García, V. Pérez-Dieste, A. Bueno-López, J.R.J.A.C.B.E. González-Velasco, Molecular elucidation of CO₂ methanation over a highly active, selective and stable LaNiO₃/CeO₂-derived catalyst by in situ FTIR and NAP-XPS 342 (2024) 123367.

- [63] F. Khoerunnisa, M. Nurhayati, H. Herlini, Q.A.A. Adzkia, F. Dara, H. Hendrawan, W.-D. Oh, J.J.J.O.W.P.E. Lim, Design and application of chitosan-CuO nanocomposites synthesized via novel hybrid ionic gelation-ultrasonication methods for water disinfection 52 (2023) 103556.
- [64] X. Zhang, C. Zhou, S. Shi, X. Jing, Z. Zheng, W. Yuan, Mechanism insight into double S-scheme heterojunctions and atomic vacancies with tunable band structures for notably enhanced light-driven enrofloxacin decomposition, J. Colloid Interface Sci. 662 (2024) 614–626.
- [65] A. Haroon, K. Anwar, A.S. Ahmed, Visible light-driven photo remediation of hazardous cationic dye via Ce-doped WO₃ nanostructures, Journal of Rare Earths 42 (2024) 869–878.
- [66] V. Ragupathi, M.A. Raja, P. Panigrahi, N.G.J.O. Subramaniam, CuO/g-C₃N₄ nanocomposite as promising photocatalyst for photoelectrochemical water splitting 208 (2020) 164569.
- [67] P. Karthik, T.N. Kumar, B.J.I.J.O.H.E. Neppolian, Redox couple mediated charge carrier separation in g-C₃N₄/CuO photocatalyst for enhanced photocatalytic H₂ production 45 (2020) 7541–7551.
- [68] F.M. Cadan, C. Ribeiro, E.B.J.A.S.S. Azevedo, Improving g-C₃N₄: WO₃ Z-scheme photocatalytic performance under visible light by multivariate optimization of g-C₃N₄ synthesis 537 (2021) 147904.
- [69] Y. Cao, K. Cui, Y. Chen, M. Cui, G. Li, D. Li, X.J.S.S.S. Yang, Efficient degradation of tetracycline by H₂O₂ catalyzed by FeOCI: a wide range of pH values from 3 to 7 113 (2021) 106548.
- [70] N. Madima, K.K. Kefeni, S.B. Mishra, A.K.J.H. Mishra, TiO₂-modified g-C₃N₄ nanocomposite for photocatalytic degradation of organic dyes in aqueous solution 8 (2022).
- [71] P. Yu, X. Zhou, Y. Yan, Z. Li, T.J.C. Zheng, Enhanced visible-light-driven photocatalytic disinfection using AgBr-modified g-C₃N₄ composite and its mechanism, Biointerfaces 179 (2019) 170–179.
- [72] S. Jian, Z. Tian, K. Zhang, G. Duan, W. Yang, S. Jiang, Hydrothermal synthesis of Ce-doped ZnO heterojunction supported on carbon nanofibers with high visible light photocatalytic activity, Chem. Res. Chin. Univ. 37 (2021) 565–570.
- [73] G. Chen, S. Bian, C.-Y. Guo, X.J.M.L. Wu, Insight into the Z-scheme heterostructure WO₃/g-C₃N₄ for enhanced photocatalytic degradation of methyl orange 236 (2019) 596–599.
- [74] K. Qi, C. Imparato, O. Almjasheva, A. Khataee, W.J.J.O.C. Zheng, TiO₂-based photocatalysts from type-II to S-scheme heterojunction and their applications, I. Science 675 (2024) 150–191.
- [75] A. Shabbir, S. Sardar, A.J.J.O.A. Mumtaz, Mechanistic investigations of emerging type-II, Z-scheme and S-scheme heterojunctions for photocatalytic applications-A review, Compounds (2024), 175683.
- [76] Q.L. Xu, S. Wageh, A.A. Al-Ghamdi, X. Li, Design principle of S-scheme heterojunction photocatalyst, Journal of Materials Science & Technology 124 (2022) 171–173.
- [77] X. Yuan, J. Yang, Y. Yao, H. Shen, Y. Meng, B. Xie, Z. Ni, S.J.S. Xia, P. Technology, Preparation, characterization and photodegradation mechanism of 0D/2D Cu₂O/ BiOCl S-scheme heterojunction for efficient photodegradation of tetracycline 291 (2022) 120965.
- [78] Y. Yang, Z.J.S.O.T.T.E. Bian, Oxygen doping through oxidation causes the main active substance in g-C₃N₄ photocatalysis to change from holes to singlet oxygen 753 (2021) 141908.
- [79] K. Zhang, D. Li, Q. Tian, H. Cao, F. Orudzhev, I.A. Zvereva, J. Xu, C.J.C.I. Wang, Recyclable 0D/2D ZnFe₂O₄/Bi₅FeTi₃O₁5 S-scheme heterojunction with bismuth decoration for enhanced visible-light-driven tetracycline photodegradation 47 (2021) 17109–17119.
- [80] Z. Dai, Y. Zhen, Y. Sun, L. Li, D.J.C.E.J. Ding, ZnFe₂O₄/g-C₃N₄ S-scheme photocatalyst with enhanced adsorption and photocatalytic activity for uranium (VI) removal 415 (2021) 129002.