3D defect-enriched Cu/Cu$_2$O–Al$_2$O$_3$ zigzag nanostructures for efficient degradation of tetracycline antibiotics†

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Researching photocatalysts that make full use of sunlight is of great significance for the efficient and environmentally friendly removal of existing toxic and harmful pollutants. Here, defect-enriched Cu/Cu$_2$O–Al$_2$O$_3$ nanoribbons with zigzag edges were successfully prepared and used to degrade tetracycline antibiotics (TCs). The design of the defect-enriched zigzag structure and the metal–semiconductor composition enable them to promote not only the separation of photogenerated carriers, but also the adsorption of oxygen to generate reactive oxygen species (ROSs). Meanwhile, density functional theory (DFT) calculations validate that the Cu/Cu$_2$O structures with oxygen vacancies (OVs) exhibit the best oxygen adsorption and capture ability. The obtained catalyst exhibits a superior degradation efficiency on TCs (e.g., up to 99.2% degradation of TC in 6 min with 0.556 min$^{-1}$ of kinetic constant $k$) and excellent catalytic degradation stability. In addition, the possible degradation pathways, the main species of ROSs and the synergistic mechanism of the photocatalytic system were systematically studied. This study provides an environmentally friendly way to treat antibiotic pollution directly by visible light.

1. Introduction

Effective degradation of tetracycline antibiotics (TCs) using environmentally friendly and economical photocatalytic technology has been widely studied. Among them, semiconductor photocatalysts can effectively utilize light energy for degradation reactions; thus, providing an efficient green photocatalyst is a proven method for degrading TCs. 1–5 However, the photocatalytic process inevitably has the problems of photon absorption and utilization, which are affected by the energy band gap and the recombination of photogenerated carriers, respectively.

Cuprous oxide (Cu$_2$O) is a p-type semiconductor with a narrow direct band gap (2.0 eV) that can effectively utilize visible light, and its conduction band position higher than the reduction potential of water contributes to the generation of various reactive oxygen species (ROSs) to accelerate the photocatalytic reaction. 6–8 However, its photostability in aqueous solution is poor because its low valence band position makes it easy to be oxidized to copper oxide with low activity under light. The introduction of a zero-valence metal phase to form a metal–semiconductor heterostructure is expected to avoid the oxidation of Cu$_2$O to solve its stability problem, and at the same time, it is conducive to the separation of the photoexcited electrons in the conduction band of the semiconductor into the metal phase, thus reducing the recombination rate of carriers and improving the photocatalytic activity. 9–11 In addition, the existence of oxygen vacancies (OVs) in semiconductor photocatalysts has been proven to have excellent potential to enhance the photocatalytic activity. 12–14 These defects can not only capture photoinduced charges and accelerate the separation of electron–hole pairs to improve the photo-efficiency, but also can promote the adsorption and capture of oxygen to produce more ROSs, which is conducive to the photodegradation reaction of TCs. 13,14 However, for Cu$_2$O, the copper vacancies are the most stable defect states, thus the synthesis of anoxic Cu$_2$O is challenging. 15 It is known that elemental doping, morphology and structure design, and reduction retreatment are the main effective ways to regulate the OV density. 16–18

Sawtooth structures are common in daily life because their sharp zigzag edges can concentrate mechanical stress in a small area and more easily break the material. It is conceivable
that nanocatalytic materials with zigzag edges are more conducive to the destruction of chemical bonds, because they have more coordination in unsaturated sites serving as catalytically active centers.

Two-dimensional (2D) nanostructures (sheet or ribbon) are conducive to the effective migration and transfer of photogenic carriers, due to the advantages of their large optical area, short carrier migration distance, numerous surface active sites and difficult formation of an energy barrier. In particular, three-dimensional (3D) nanostructures composed of nanosheets not only have the characteristic advantage of a 2D structure, but also avoid the agglomeration problem of nanosheets. As a consequence, a 3D self-assembled nanosheet structure with zigzag edges would be a promising candidate structure of a photocatalyst that can maximize photon absorption and utilization.

In this work, we prepared a 3D defect-enriched Cu/Cu2O–Al2O3 photocatalyst assembled from zigzag nanoribbons (ZNR). A CuAl bimetallic hydroxide (CuAl–OH) consisting of CuAl(OH)2(CO3)2 and AlOOH, prepared in a hydrothermal reaction system, was etched with Fe3+ to obtain a 3D CuAl–OH ZNR precursor, and then reduced in situ with H2 to generate Cu/Cu2O–Al2O3 nanocatalysts. The as-prepared photocatalysts have the following advantages: (1) the large surface area of 3D ribbon structures with zigzag edges provides sufficient adsorption reaction sites; (2) the zigzag structure obtained after etching and reduction has a large number of structural defects, such as OVs, which can not only promote the separation of photogenerated carriers, but also promote the adsorption of oxygen to generate ROSs; (3) Cu2O, as an excellent photocatalytic material, can effectively utilize light energy; (4) the designed metal–semiconductor heterostructure can avoid the oxidation of Cu2O to solve its stability problem; meanwhile, it is beneficial for the transfer of photogenerated electrons to reduce the electron–hole pair recombination and improve the photocatalytic activity. Based on the above advantages, the obtained catalyst exhibits a superior degradation efficiency on antibiotics (e.g., up to 99.2% degradation of TC in 6 min with 0.556 min−1 of kinetic constant k), and excellent catalytic degradation stability. The kinetic properties, reusability, degradation path and mechanism of the photocatalytic reaction system were studied by means of different characterization tools, photochemical analysis and catalytic tests.

2. Experimental

2.1. Preparation of the catalyst

3D Cu/Cu2O–Al2O3 photocatalysts assembled from zigzag nanoribbons were synthesized by hydrothermal co-precipitation, etching reaction and H2 reduction. The specific experimental process is as follows:

The aqueous solutions of Cu(NO3)2 (12 mL, 10 mM), Al(NO3)3 (8 mL, 10 mM) and 0.02 g urea were placed in a 25 mL Teflon-lined autoclave, stirred well and heated in an oven at 140 °C for 10 h. Then the precipitate was extracted by centrifugation, washed with deionized water and anhydrous ethanol alternately, dried at 60 °C for 24 h, and then 3D CuAl–OH NR can be obtained. 30 mg of the above products were added to 30 mL of 1 mM Fe(NO3)3 aqueous solution, sonicated for 60 min, mixed and placed in an oil bath at 80 °C for 2 h. The powder was collected by low speed centrifugation, washed and dried, and then reduced under a 5% H2 atmosphere (95% Ar protection) in a tube furnace at 400 °C for 2 h to obtain the product 3D defect-enriched Cu/Cu2O–Al2O3 ZNR. The contrast sample Cu/Cu2O–Al2O3 NR was prepared by directly reducing the CuAl–OH NR precursor without etching. In addition, the synthesis method of Cu/Cu2O contrast sample is similar to the above, only Al(NO3)3 was removed.

2.2. Computational methods

All the structure optimizations were performed using the plane-wave density function as implemented by Quantum Espresso. The generalized gradient approximation in conjunction with the Perdew–Burke–Ernzerhof functional (PBE-GGA) was used to describe the electron exchange–correlation interaction. The DFT-D3 method of Grimme was used to describe the electrostatic properties between the van der Waals (vdW) interactions. In structural relaxation, the energy cutoff for the plane-wave basis expansion and convergence threshold for the force on each relaxed atom was set to 60 Ry and 0.01 eV Å−1, respectively. The binding energy (E_b) was calculated to evaluate the binding strength between the Cu2O (111) surface and O2, which is defined as follows:

\[ E_b = E_{\text{Cu}_2\text{O}(111)-\text{O}_2} - E_{\text{Cu}_2\text{O}} - E_{\text{O}_2} \]

3. Results and discussion

3.1. Mechanism of fabrication

The designed 3D defect-enriched Cu/Cu2O–Al2O3 photocatalyst assembled by ZNR has been successfully prepared by hydrothermal co-precipitation followed by etching and reduction. As shown in Scheme 1A, under the hydrothermal reaction, urea hydrolysis generates an alkaline environment that provides abundant nucleation sites for CuAl–OH. With prolonging hydrothermal time, some organic groups (such as –NH2 and –COOH) originated from urea could be absorbed on the surface of CuAl–OH crystallites, through hydrogen bonding interactions between –OH and –NH2 groups, and the coordination reaction of Al3+ and –COO– to direct the growth of crystallites by cooperative assembly and localized ripening, thus forming the structure of the nanoribbon. Finally, the 3D NR structure was further assembled to reduce the surface energy and stabilize the NR component unit. In addition, it can be seen from Fig. S1 and S2† that the NR structure would gradually disappear with the decrease of Al element. During the etching process shown in Scheme 1B, Fe3+ would hydrolyze to form a Fe(OH)3 colloid, and generate some H+ in the solution, which can etch CuAl(OH)2(CO3)2. Meanwhile, the Fe(OH)3 colloid is mainly suspended in the solution, which can be separated by low speed centrifugation, thus resulting in chemical etching and the formation of the ZNR structure. By observing
**Fig. S3 and S4**, it can be found that with the increase of Fe\(^{3+}\) concentration, the zigzag structure becomes more obvious, meanwhile, the Cu content in energy dispersion X-ray spectrometer (EDS) and the Cu\(_3\)(OH)\(_2\)(CO\(_3\))\(_2\) peaks in powder X-ray diffraction (XRD) decrease gradually. After the reduction of the hydrogen atmosphere, the obtained 3D CuAl\(_2\)-OH ZNR can be converted to Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR nanocomplexes (Fig. S5†).

### 3.2 Morphologies and structures

Fig. 1 exhibits the typical morphology of the synthesized 3D Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Fig. 1A–C show that both Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR and Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) NR (Fig. S6†) have a 3D structure and large surface area. However, the Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR obtained by etching treatment has zigzag edges of its component unit nanoribbons, which enables the designed catalyst to obtain a large number of defects, such as OVs, providing favorable conditions for enhancing the utilization rate of sunlight and the generation of ROSs. In the absence of Al\(_2\)O\(_3\), the Cu/Cu\(_2\)O microsphere formed by the accumulation of large size nanoparticles would be obtained and the gap will increase after etching (Fig. S7†).

The high-resolution TEM (HRTEM) image in Fig. 1D shows clear lattice fringes in addition to the amorphous Al\(_2\)O\(_3\), in which the red line lattice spacing is 0.246 nm, corresponding to the Cu\(_2\)O (111) crystal plane, and the white line lattice spacing is 0.180 nm, corresponding to the (111) crystal planes of Cu, proving the successful preparation of the Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) nanocomposite. And the selective region electron diffraction patterns (SAED) in Fig. 1E show the mixed polycrystalline diffraction rings of the (111) crystalline plane of Cu\(_2\)O, and (111) & (200) planes of Cu in Cu/Cu\(_2\)O–Al\(_2\)O\(_3\). In addition, the composition of the material was further determined by elemental mappings, which confirm the presence of Cu, Al and O elements (Fig. 1F), and these elements were uniformly distributed.

Fig. 1G shows the XRD patterns and the EDS analysis of 3D Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR. As can be seen from Fig. 1G, in addition to the 43.5°, 50.5° and 74.0° peaks corresponding to the (111), (200) and (220) planes of Cu (JCPDS no.01-1241), there is a weak peak at 36.5° which can be indexed to the (111) plane of Cu\(_2\)O (JCPDS no. 03-0892). Moreover, due to the amorphous structure of Al\(_2\)O\(_3\), no obvious peak is observed, which is in good agreement with the results of the HRTEM image and SAED pattern. Combined with the characteristic peaks of O, Al and Cu elements in EDS analysis, it is confirmed that the synthesized material is the Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) nanocomposite. X-ray photoelectron spectroscopy (XPS) was also performed to confirm and compare the chemical bonding information of Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR and Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) NR. As shown in Fig. S8† wide spectra of both of them present four photo-emission peaks of Cu 2p, Al 2p, O 1s and C 1s. In addition, the detailed Cu 2p and O 1s spectra were further analyzed using XPSPEAK41 software; it can be clearly observed that the Cu 2p...
spectra for the two Cu/Cu$_2$O–Al$_2$O$_3$ nanocomposites have two strong peaks, 2p$_{3/2}$ at 933.2 eV and 2p$_{1/2}$ at 953.1 eV, which can be deconvoluted into two pairs of peaks, 933.1 & 952.9 eV and 934.2 & 954 eV, corresponding to Cu(0) and Cu(I), respectively (Fig. 1H). And the characteristic peak with the binding energy located at 944 eV is the satellite peak. For the O 1s spectra, both catalysts can be divided into three peaks, namely lattice oxygen at 530 eV, defective oxygen at 531.2 eV, and hydroxyl groups at 532.3 eV, respectively (Fig. 1I).\cite{30,31} However, it was found that the content of defect oxygen for serrated Cu/Cu$_2$O–Al$_2$O$_3$ ZNR was higher than that of the other, which plays an important role in improving the photocatalytic activity.

The optical properties of the Cu/Cu$_2$O–Al$_2$O$_3$ ZNR catalyst and contrast sample Cu/Cu$_2$O–Al$_2$O$_3$ NR were tested by UV-visible diffuse spectroscopy (UV-vis DRS). As shown in Fig. 2A, Cu/Cu$_2$O–Al$_2$O$_3$ ZNR exhibited a wide absorption range due to the amount of defects, indicating its feasibility in a wide range of optical regions. Moreover, the corresponding energy band gaps ($E_g$) of Cu/Cu$_2$O–Al$_2$O$_3$ ZNR and Cu/Cu$_2$O–Al$_2$O$_3$ NR are 1.84 eV and 2.03 eV, respectively, according to the tangent of $(ahv)^2$ versus energy (hv) (Fig. 2B).\cite{32,33} These values are consistent with the calculation of the equation $E_g$ (eV) = 1240/$\lambda$ $^2$, where $\lambda$ is the maximum absorption wavelength. In addition, we analyzed the electronic band structure by XPS valence band spectroscopy. As shown in Fig. 2C, the valence band potentials ($E_{VB}$) of Cu/Cu$_2$O–Al$_2$O$_3$ ZNR and Cu/Cu$_2$O–Al$_2$O$_3$ NR are 0.81 eV and 1.38 eV, respectively. Based on the equation $E_{CB} = E_{VB} - E_g$,\cite{34,35} their corresponding conduction band edge potentials ($E_{CB}$) are calculated as −1.03 and −0.65 eV, respectively. Since $E_{CB}$ value is more negative than the O$_2$/O$_2^-$ potential (−0.33 eV vs. NHE), O$_2$ dissolved in solution can be converted to O$_2^-$ by reacting with electrons. The Cu/Cu$_2$O–Al$_2$O$_3$ ZNR shows a more negative $E_{CB}$ compared to the Cu/Cu$_2$O–Al$_2$O$_3$ NR, and thus the etched Cu/Cu$_2$O–Al$_2$O$_3$ ZNR exhibits a better catalytic activity.

Photoluminescence spectroscopy (PL) is commonly used to study the efficiency of photogenerated charge transfer and separation. In general, low PL intensity usually indicates high separation efficiency of electron–hole pairs for materials with transport layers.\cite{36,37} Fig. 2D shows the emission spectra of Cu/Cu$_2$O–Al$_2$O$_3$ ZNR, Cu/Cu$_2$O–Al$_2$O$_3$ NR and Cu/Cu$_2$O catalysts at the excitation wavelength of 380 nm. A strong emission peak was observed at 410 nm, and the intensity of the emission peak showed that the Cu/Cu$_2$O > Cu/Cu$_2$O–Al$_2$O$_3$ NR > Cu/Cu$_2$O–Al$_2$O$_3$ ZNR, and since the Cu/Cu$_2$O–Al$_2$O$_3$ ZNR had the weakest emission peak, it showed the best photogenerated charge carrier separation efficiency and the best photocatalytic activity. Additionally, time-resolved photoluminescence (TRPL) was employed to detect the photoelectron lifetime.\cite{38} As shown in Fig. S9,† the photoluminescence decay time of Cu/Cu$_2$O–
Al₂O₃ ZNR (1.634 ns) is significantly shorter than that of Cu/Cu₂O-Al₂O₃ NR (1.965 ns) and Cu/Cu₂O (2.402 ns) samples, which is because the metal Cu and 2D defect structure can effectively promote the separation of charge carriers. We also further analyzed the separation and transfer efficiency of the photogenerated electron–hole pairs by transient photocurrent response and impedance tests. In Fig. 2E, it can be clearly seen that Cu/Cu₂O–Al₂O₃ ZNR has the highest photocurrent. Meanwhile, the electrochemical impedance spectroscopy (EIS) Nyquist curve in Fig. 2F shows that the Cu/Cu₂O–Al₂O₃ ZNR has the lowest current impedance, indicating that the photogenerated electrons can be transferred out quickly, thus reducing the probability of photogenerated electron–hole recombination and enhancing the photocatalytic activity.

### 3.3 Catalytic Performance

The catalytic activities of the as-prepared Cu/Cu₂O–Al₂O₃ nanocatalysts and other comparative catalysts for the degradation of TC have been evaluated by UV-vis spectroscopy after the catalytic samples were placed in darkness for 30 min to achieve adsorption–desorption equilibrium, and the results are shown in Fig. 3. The degradation process of TC molecules can be analyzed by observing the intensity of two characteristic absorption peaks representing benzene and naphthalene rings at 370 nm and 245 nm. As shown in Fig. S10-13, the intensity of the two peaks decreased significantly during the catalytic reaction, indicating the successful ring-opening decomposition of TC molecules. It was clear in Fig. 3A that the etched Cu/Cu₂O–Al₂O₃ ZNR nanocatalyst presents much higher catalytic activity than non-etched Cu/Cu₂O–Al₂O₃ NR and etched Cu/Cu₂O nanocatalysts, which can degrade 99.2% TC within 6 min, and the reaction rate constant K reaches 0.556 min⁻¹ (Fig. S14†), and the total organic carbon (TOC) value becomes 80.73% (Fig. S15†). However, the degradation rate of the other two catalysts can only reach 97.0% and 72.6% in 20 min, with the corresponding K values of 0.185 and 0.093 min⁻¹, respectively. This is because Cu/Cu₂O–Al₂O₃ ZNR is more likely to produce oxygen defects to promote the generation of ROSs, and the presence of Al₂O₃ can effectively maintain the ribbon-like morphology with a high specific surface area to expose a large number of active sites, thus promoting the degradation performance of the catalyst. In order to further explain the effect of etching, the properties of catalysts etched by different concentrations of Fe³⁺ have been studied. It can be observed from Fig. 3B that Cu/Cu₂O–Al₂O₃ ZNR etched by 1 mM Fe³⁺ has the best catalytic performance. In contrast, the degradation rates of 0.5 mM, 1.5 mM and 2 mM Fe³⁺ etched samples reached 77.3%, 84.8% and 67.8% within 15 min, with the corresponding K values are 0.119, 0.144 and 0.088 min⁻¹, respectively (Fig. S14†). This can be explained that the Cu/Cu₂O–Al₂O₃ prepared using a low concentration Fe³⁺ etching agent has fewer defects. However, when Fe³⁺ concentration is too high, the active component Cu in the catalyst would be etched in large quantities, resulting in a decline of catalyst performance.

TC exists in water systems with different pH values in the real environment, and the pH value has a significant effect on TC degradation. Thus, it is of great significance to research the degradation reaction in different pH reaction systems. As illustrated in Fig. 3C, when pH is 3, the degradation rate is the worst, only 20.4%, and the kinetic constant K is 0.01 min⁻¹. Except for strong acidic or alkaline environment, the TC removal rates of Cu/Cu₂O–Al₂O₃ ZNR catalyst at pH (4.5–9.5) are all over 80%, and the degradation rate is up to 99.2% at pH 7.2, indicating that the system is suitable for a wide pH range. Particularly, the degradation rate of TC decreases significantly...
when the acidity or basicity of the solution is enhanced, mainly because TC has the highest electron density under neutral conditions, which is conducive to the attack of free radicals.\(^{41,42}\) On the side, \(\cdot O_2^-\) is the main free radical in the reaction system, which plays a key role in maintaining the high degradation efficiency of TC. Under acidic conditions, excessive H\(^+\) will react with \(\cdot O_2^-\), resulting in poor catalytic performance.\(^{43}\) Under alkaline conditions, more \(\cdot O_2^-\) react with H\(_2\)O to form \(\cdot \text{OH}\), and the oxidation ability is weakened.

Furthermore, to understand the universality of the designed photocatalyst, the degradation activity of Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR over other two typical TCs (chlorotetracycline (CTC) and oxytetracycline (OTC)) was studied (Fig. 3D). As anticipated, Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR also shows significant catalytic activity for CTC and OTC oxidation, with removal rates of 97.9% and 98.2% within 30 min, respectively. All the results explain that the synergy of photocatalysis and oxygen vacancy, as well as the combination of metal–semiconductor phase interface make Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR an excellent photocatalyst for the effective degradation of TCs. In order to reveal the reusability and stability of the catalyst, the cycling experiments of Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR were also carried out. As shown in Fig. 3E, the photocatalytic degradation efficiency remains at 87.1% after 5 cycles. The degradation properties of catalysts decrease slightly, mainly due to the attachment of trace pollutants and degradation intermediates to the surface of the catalyst. The morphology, structure and composition of recycled Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR have not changed, which could be proven by the SEM, XRD and EDS analyses, as shown in Fig. S16.\(^{†}\)

To detect the contribution of different ROS for the oxidative degradation of TCs, the radical capture experiments were performed. Herein, tert-butanol (TBA), triethanolamine (TEA), and \(p\)-benzoquinone (BQ) were selected as scavengers to quench \(\cdot \text{OH}\), \(h^+\), and \(\cdot O_2^-\), respectively.\(^{44}\) As depicted in Fig. 3F, the addition of these scavengers inhibits the degradation of TC to different degrees compared with the experiment without scavengers. The results show that after adding TBA, TEA, and BQ, the degradation rate of TC catalyzed by Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR decreases from 99.2% to 90.0%, 19.4% and 11.3%, respectively. It can be seen that \(\cdot O_2^-\) plays the main role in the catalytic reaction, while \(\cdot \text{OH}\) has the least effect, which is mainly indirectly produced by \(\cdot O_2^-\), and H\(_2\)O\(_2\) as the intermediate in the formation process of \(\cdot \text{OH}\) can be proven by catalase tests. As shown in Fig. S17,\(^{†}\) catalase can consume the produced H\(_2\)O\(_2\) during the reaction with 89.1% degradation rate of TC. In order to further verify the contribution of \(\cdot O_2^-\) in the photocatalytic degradation, an anaerobic degradation reaction was carried out, and the highest efficiency of TC degradation was only 6.3%. In addition, compared with unetched Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) NR and etched Cu/Cu\(_2\)O nanocatalysts, Cu/Cu\(_2\)O–Al\(_2\)O\(_3\) ZNR has the highest catalytic degradation efficiency, and it is most obviously affected by the scavengers (especially BQ and TEA), because it can produce the largest number of \(\cdot O_2^-\) and \(h^+\) radicals in the catalytic reaction.
To monitor the analysis of trapping experiments, electron spin resonance (ESR) spectroscopy using DMPO and TEMP as spin-trapping reagents was used to further demonstrate the formation of active species during the photocatalytic degradation process. As shown in Fig. 3G and H, no ESR signal can be observed in the dark, while under simulated sunlight, the signal intensity of O$_2^-$ and OH increases significantly as the reaction time is extended from 0 to 4 min. Besides, EPR is also a powerful tool to explore the relative concentration and distribution of intrinsic defects (such as OVs) in catalysts.$^{45,46}$ It can be seen from Fig. 3I that, compared with the other two catalysts, an EPR signal with a larger line width and stronger intensity at around $g = 2.004-2.006$ can be observed in Cu/Cu$_2$O–Al$_2$O$_3$ ZNR, reflecting the existence of abundant OVs on the catalyst that will not only effectively promote the separation of electron hole pairs, but also facilitate the activation of oxygen molecules.

3.4. Catalytic mechanism

Due to the relatively high electron density, functional groups (such as amine groups, phenolic groups and double bonds) in TC would be attacked by O$_2^-$ and OH free radicals, resulting in dehydroxylation, demethylation, hydroxylation, amide bond cleavage and other reactions, thus achieving the degradation of TC. In order to clarify the degradation mechanism of TC by the Cu/CuO-Al$_2$O$_3$ photocatalyst, the reaction solutions at different reaction times have been analyzed by liquid chromatography-mass spectrometry (LC-MS) technology, which clearly shows the intermediates of TC degradation. The LC-MS spectra are shown in Fig. S18,† and the mass/charge ratio (m/z), molecular formula and molecular structure of the main intermediates are summarized in Table S1,† According to the intermediates listed in Table S1, three possible TC degradation pathways catalyzed by the Cu/Cu$_2$O–Al$_2$O$_3$ ZNR catalyst were proposed and shown in Fig. 4. For pathway I, the formation of TC1 (m/z = 417) was caused by the demethylation of N at the C2 position, after that TC4 (m/z = 374) was formed by the deamination reaction at the C18 position. The hydroxyl group at the C6 position was then removed to form TC7 (m/z = 362). Subsequently, the double bond at C1 was cleaved and ring-opening, hydroxylation and ketonization occurred to form TC10 (m/z = 318). For pathway II, the amide bond of TC was first hydrogenated and produced TC2 (m/z = 447). Then the carbon double bond was cleaved and the ring opening oxidation reaction occurred to form TC5 (m/z = 279). Subsequently, by dehydroxylation, TC5 was converted to TC8 (m/z = 242). In pathway III, TC3 (m/z = 405) was first formed by deamination at the C18 position of TC, followed by TC3 transformation into TC6 (m/z = 306) by ring-opening cleavage, and then TC9 (m/z = 274) was formed by removing the aldehyde group at C16 of TC6. Finally, the ROSs formed in the reaction system mineralized these intermediates into H$_2$O and CO$_2$.

To better understand the catalytic effects of OVs and Cu/Cu$_2$O metal–semiconductor heterostructures, DFT calculations were carried out to simulate the activation process based on the theoretical models (Cu/Cu$_2$O, Cu$_2$O–OVs and Cu/Cu$_2$O–OVs) shown in Fig. S19,† According to the above test and analysis results, O$_2^-$ as the most dominant ROS plays a major role in the catalytic process. Therefore, the most stable adsorption models of oxygen have been constructed, and the adsorption energy of oxygen was calculated. As shown in Fig. 5A, compared with Cu/Cu$_2$O and Cu$_2$O–OVs, Cu/Cu$_2$O–OVs show the best oxygen adsorption and capture ability.

Based on the above test and analysis results, the photocatalytic mechanism of high efficiency degradation of TC by the Cu/Cu$_2$O–Al$_2$O$_3$ ZNR catalyst has been proposed, and the reasonable schematic diagram is shown in Fig. 5B. Under visible light irradiation, the photogenerated electrons generated by the VB can easily migrate to the CB with a relatively low potential and leave holes in its VB (eqn (1)). Photoexcited electrons are rapidly transferred to Cu, which forms a Schottky junction with Cu$_2$O and is an excellent electron acceptor, thus facilitating the separation of electron-hole pairs. The accumulated excited electrons are then captured by O$_2$ on the catalyst surface and in solution to generate O$_2^-$ (eqn (2)), because the $E_{CB}$ of the Cu/Cu$_2$O–Al$_2$O$_3$ ZNR catalyst (−1.03 eV) is much higher than the O$_2$ adsorption energy of Cu$_2$O–OVs (−0.68 eV).
lower than the standard reduction potential $O_2 (E^\theta(O_2/O_2^-) = -0.33$ eV vs. NHE), and part of the resulting $O_2^-$ generates $\cdot OH$ by reacting with photogenerated electrons and $H_2O$ (eqn (3)). Meanwhile, the $E_{VB}$ of Cu/Cu$_2$O-Al$_2$O$_3$ ZNR catalyst is 0.81 V, which is insufficient to oxidize $H_2O$ or $OH^-$ to generate $\cdot OH$ ($E^\theta(H_2O/OH) = 2.38$ eV vs. NHE, $E^\theta(OH^-/OH) = 1.99$ eV vs. NHE). Thus, these holes in the VB would directly act as active species to catalyze the oxidation of TCs.

$$\text{Cu/Cu}_2\text{O-Al}_2\text{O}_3 + h\nu \rightarrow h^+ + e^-$$  (1)

$$O_2 + e^- \rightarrow O_2^-$$  (2)

$$O_2^- + H_2O + e^- \rightarrow \cdot OH + OH^-$$  (3)

In addition, for the prepared 2D defect-enriched Cu/Cu$_2$O–Al$_2$O$_3$ nanocomposite, the surface OVs can narrow the bandgap and then increase the conductivity of materials.\(^{12}\) Moreover, the surface OVs can serve as the reactive sites and trap the separated charge carriers for the subsequent quick surface reaction. During the entire photocatalytic degradation process, the OVs can also adsorb $O_2$ and generate $O_2^-$ (eqn (4)). Ultimately, the TC on the surface of the catalyst would be efficiently decomposed into $CO_2$ and $H_2O$ by the ROSs formed in the system (eqn (5)). In conclusion, the zigzag structure with a large specific surface area, metal–semiconductor composition, and abundant OVs are essential factors for the Cu/Cu$_2$O–Al$_2$O$_3$ catalyst to achieve excellent catalytic activity.

$$[2\equiv\equiv\text{Cu}^+,\text{OVs}] + O_2 \rightarrow [\equiv\equiv\text{Cu}^+ + \equiv\equiv\text{Cu}^{2+}] + O_2^-$$  (4)

$$O_2^-/\cdot OH/h^+ + \text{TCs} \rightarrow CO_2 + H_2O + \text{Inorganic ions}$$  (5)

4. Conclusions

In summary, a 3D defect-enriched Cu/Cu$_2$O–Al$_2$O$_3$ ZNR has been prepared in a hydrothermal reaction system, followed by etching and reduction processes. The as-obtained photocatalyst assembled from the zigzag nanoribbon structure has a very high specific surface area and structural defects; combined with the designed metal–semiconductor heterostructure it can prolong the life of photogenerated carriers and promote the activation of molecular oxygen, so as to obtain excellent degradation efficiency for antibiotics. This study sheds new light on the methods of defect introduction and interface construction to design excellent photocatalysts.

Author Contributions


Conflicts of interest

There are no conflicts to declare.
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