REVIEWS

Journal of Semiconductors
(2023) 44, 111701
doi: 10.1088/1674-4926/44/11/111701

Photocatalytic removal of heavy metal ions and antibiotics in agricultural wastewater: A review

Jiaxin Song, Malik Ashtar, Ying Yang†, Yuan Liu, Mingming Chen, and Dawei Cao

School of Physics and Electronic Engineering, Jiangsu University, Zhenjiang 212013, China

Abstract: In recent years, the treatment of agricultural wastewater has been an important aspect of environmental protection. The purpose of photocatalytic technology is to degrade pollutants by utilizing solar light energy to stimulate the migration of photocarriers to the surface of photocatalysts and occur reduction-oxidation reaction with pollutants in agricultural wastewater. Photocatalytic technology has the characteristics of high efficiency, sustainability, low-energy and free secondary pollution. It is an environmental and economical method to recover water quality that only needs sunlight. In this paper, the mechanism and research progress of photocatalytic removal of heavy metal ions and antibiotics from agricultural water pollution were reviewed by combining photocatalytic degradation process with agricultural treatment technology. The mechanism of influencing factors of photocatalytic degradation efficiency was discussed in detail and corresponding strategies were proposed, which has certain reference value for the development of photocatalytic degradation.

Key words: photocatalysis; agricultural pollution; water quality remediation; heavy metals; antibiotics

Citation: J X Song, M Ashtar, Y Yang, Y Liu, M M Chen, and D W Cao, Photocatalytic removal of heavy metal ions and antibiotics in agricultural wastewater: A review[J]. *J. Semicond.*, 2023, 44(11), 111701. https://doi.org/10.1088/1674-4926/44/11/111701

1. Introduction

Agriculture plays a critical role in the economic development of a country, "Ecological Agriculture" is the inevitable procedure for the sustainable development of modern agriculture. The current conundrum is how to purify agricultural sewage with minimal energy expenditure in order to get a superior cycle. Due to improper construction of the sewage system in agricultural production, agricultural pesticides, fertilizers, livestock, and poultry waste will not be treated in time and accumulate in agricultural surface water system, causing serious pollution. It can even lead to biological death and endanger human health. Pollutants in sewage are currently treated using a variety of technologies, including adsorption[1], precipitation[2], reverse osmosis, membrane separation, biological approaches[3], and so on. These treatments have a complex disposal mechanism, which causes secondary water pollution during the transfer of pollutants between complex waste liquids and by-products[4]. Green and sustainable waste treatment technology deserves our attention and implementation, which is also the development concept of current pollution removal technology.

The photocatalytic oxidation and photocatalytic reduction technologies are advanced, and their application to reduce agricultural contaminants is promising. Photocatalysis can react at room temperature and pressure without external energy input except for solar energy, which can react friendly without strong acid and alkali reactions. It has the advantages of sustainability, cleanliness, low energy consumption, and no secondary pollution[5]. Photocatalytic techniques can convert antibiotics enriched in agricultural wastewater into biodegradable chemicals or organic molecules with low toxicity[6]. Meanwhile, it can convert high-priced heavy metal ions that are hazardous to organisms into low-priced metal ions that are harmless[5], which is an emerging high efficiency and energy-saving agricultural pollution control technology. The core of this paper is to review and expand the removal process of antibiotics and heavy metal ions in agricultural wastewater based on photocatalytic degradation mechanism. The influencing factors and promotion mechanism of photocatalytic degradation were summarized by analyzing the mechanism and practical application. The new progress in photocatalytic degradation can be explored from the improved system proposed in this paper.

2. Mechanism of photocatalytic removal of agricultural wastewater pollutants

Photocatalytic water splitting is the foundation of photocatalytic degradation of agricultural wastewater, which involves three steps: optical absorption, carrier transport, and reduction-oxidation reaction on the surface[7]. The energy level correlations between the band structure of various typical semiconductor materials and photocatalytic water splitting are depicted in Fig. 1. The photophysics principle and energy band relation were used to determine the reduction and oxidation reaction conditions of photocatalytic water splitting[8]. The band gap of the semiconductor must be greater than the 1.23 eV required to decompose water. Furthermore, thermodynamics state that the conduction potential be slightly more negative than the hydrogen electrode potential (E_{H_2/H^+}) to produce a hydrogen evolution reduction reaction and that the valence band potential be slightly more positive than the oxygen electrode potential (E_{O_2/H_2O}) in order to produce an oxygen evolution reduction reaction. Here, $SrTiO_3$, TiO_2, and CdS are capable of photocatalysis, which

Correspondence to: Y Yang, yingyang@ujs.edu.cn
Received 8 MAY 2023; Revised 15 JUNE 2023.

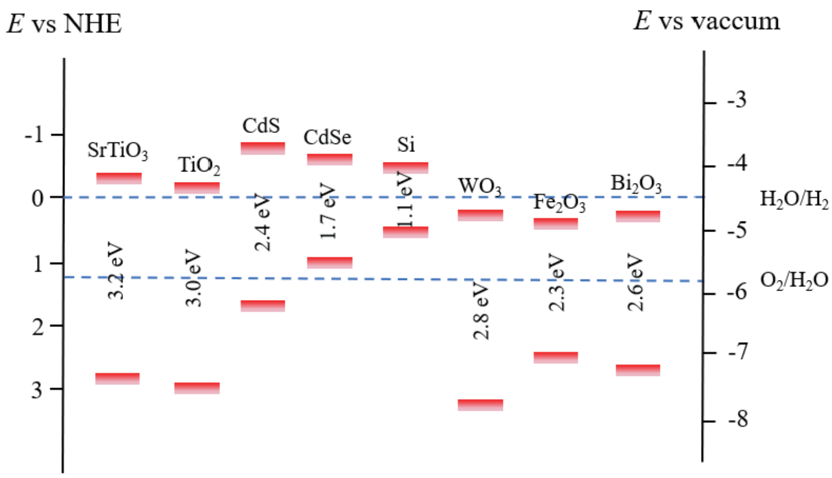


Fig. 1. (Color online) Common semiconductor energy level relationships.

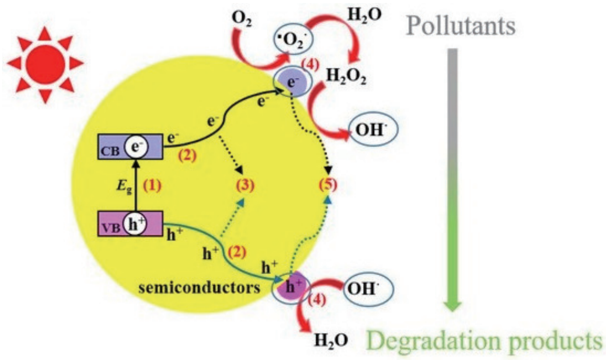


Fig. 2. (Color online) Mechanism of removal of pollutants by photocatalytic reactions[4].

results in the evolutionof hydrogen and oxygen from water. The photocatalytic water hydrogen evolution reaction is possible using CdSe and Si. Similarly, WO_3, Fe_2O_3, and Bi_2O_3 can take place photolysis water oxygen evolution reaction.

Photocatalytic technology, based on the principle of photocatalytic water splitting, can also be used efficiently in the field of agricultural wastewater purification. Fig. 2 depicts the photocatalytic removal of pollutants. First, the photocatalyst semiconductor absorbs more light energy (hv) than its band gap energy (E_g) and excites photogenerated electron–hole pairs (e^-–h^+). Electrons in the valence band (e^-) are photoexcited to transition to the conduction band, which are called photogenerated electrons. A hole (h^+) forms in the valence band where electron is lost, which is called photogenerated hole. Second, due to the diffusion motion of carriers and the effects of electric fields both within and outside the semiconductor, photogenerated electron–hole pairs are separated and migrate to the semiconductor surface. Third, during the migration process, the separated electrons and holes may recombine inside the semiconductor. Fourth, the carriers that migrate to the semiconductor surface during the lifecycle will be captured by the reaction sites and participate in the reduction-oxidation reaction[9, 10]. During the photocatalytic degradation of agricultural wastewater, e^- can interact with O_2 to produce $^{\cdot}OOH$ and O_2^-, while h^+ can interact with OH^- and H_2O adsorbed on the surface of catalyst particles to produce $^{\cdot}OH$. These reactive oxide species will participate in the reduction-oxidation reaction of photocatalytic degradation, $^{\cdot}OH$ is a particularly active oxide among these radicals, capable of oxidizing and mineralizing a wide range of organics[11]. Furthermore, the contaminant in the water is adsorbed on the surface of the catalytic materials, which increases carrier mobility, improves the redox capability of the semiconductors, and facilitates a series of chemical reactions of the active substances produced by the catalyst to degrade agricultural pollutants and purify agricultural wastewater. The photocatalytic degradation equation is Eqs. (1)–(9). Finally, photogenerated electrons and holes recombine on the surface of photocatalysts.

Energy is released as heat or optical energy during the deactivation process, which occurs during steps 3 and 5[12]. Consequently, the recombination of carriers allows the photoinduced excited state to transition back to the ground state in the form of radiation or irradiation, representing the direct composite luminescence and indirect compound energy release of excitons, respectively.

$$hv + \text{Photocatalyst} \rightarrow e^- + h^+, \tag{1}$$

$$e^- + O_2 \rightarrow {}^{\cdot}O_2^-, \tag{2}$$

$${}^{\cdot}O_2^- + H^+ \rightarrow {}^{\cdot}OOH, \tag{3}$$

$$2^{\cdot}OOH \rightarrow O_2 + H_2O_2, \tag{4}$$

$$H_2O_2 + {}^{\cdot}O_2^- \rightarrow {}^{\cdot}OH + OH^- + O_2, \tag{5}$$

$$H_2O_2 + hv \rightarrow 2^{\cdot}OH, \tag{6}$$

$$h^+ + H_2O \rightarrow {}^{\cdot}OH + H^+, \tag{7}$$

$$h^+ + OH^- \rightarrow {}^{\cdot}OH, \tag{8}$$

$$\text{Pollutants} + (OH^-, h^+, e^-, {}^{\cdot}OOH, {}^{\cdot}O_2^-) \rightarrow \text{Degradation products}. \tag{9}$$

2.1. Mechanism of heavy metal ions removal

Due to the accumulation of heavy metal ions produced by the inappropriate use of pesticides and fertilizers, sewage irrigation, livestock manure emissions, and the stacking discharge of wastes, agricultural water pollution threatens the health of organisms and ecological balance. Compared to other contaminants, the toxicity of heavy metal ions exceeds the environment's capacity for self-purification. Heavy metal ions are more difficult for microorganisms to degrade, and they are more likely to be enriched within the organism and then changed into a metallo-organic complex with increased toxicity that endanger the organism's life and health.

Heavy metal elements such as copper (Cu), plumbum (Pb), nickel (Ni), mercury (Hg), cadmium (Cd), chromium (Cr) and arsenic (As) have special physical and chemical properties. The estimated density is 3.5–7 $g\cdot cm^{-3}$, which is distributed in different valence states in nature[13]. However, the photocatalysis technology can transform the high state harmful heavy metal ions into the low state non-toxic heavy metal ions[14]. Three mechanisms mainly contribute to the photocatalytic removal of heavy metal ions. First, direct reduction of metal ions by photogeneration e^- from conduction band. Second, indirect reduction by intermediates formed by photogeneration removal heavy metal ions such as Pb^{2+} by hole oxidation since these heavy metal ions are more stable when the energy level is negative and in high oxidation state[15]. For the direct photocatalytic reduction of metal M, the E^- energy of the conduction band must be negative relative to the M^{n+}/M energy level. Eqs. (10)–(13) specifically describe the reaction process of photocatalytic heavy metal ion removal in agriculture. Manmeet Kaur[16] synthesized calcium ferrite/nitrogen-doped graphene oxide magnetic nanocomposites ($CaFe_2O_4$-NGO), in which $^{\cdot}O_2^-$ and $^{\cdot}OH$ were the primary photocatalytically active components. Within 120 min, the removal rate of Pb(II) ions reached 84.7% at a pH of 6.0. In addition, Yao Chen[17] investigated a technique for selective recovery of expensive metals utilizing photocatalytic technology, which required only sunlight and photocatalyst TiO_2. Within 16 h, the experiment selectively reduced copper (Cu), silver (Ag), gold (Au), and platinum (Pt) ions with a 98% reduction rate, and the photocatalyst could be reused more than 100 times. Recovering heavy metals helps increase economic benefits.

$$hv + \text{Photocatalyst} \rightarrow e^- + h^+, \tag{10}$$

$$M + e^- \rightarrow M(s), \tag{11}$$

$$H_2O + 2h^+ \rightarrow 1/2O_2 + 2H^+, \tag{12}$$

$$M + H_2O + hv \rightarrow M(s) + 1/2O_2 + 2H^+. \tag{13}$$

2.2. Mechanism of antibiotics degradation

Antibiotics are organic substances with anti-pathogen or other activities that are metabolites produced by microorganisms or premier flora and fauna in order to sterilize or prevent bacterial growth[18]. Certain antibiotics may be utilized in anti-tumor or immunological mechanisms[19]. Agricultural antibiotics exhibit unique pharmacological effects at low concentrations that inhibit the secondary metabolites of pathogenic organisms and have the characteristic of easy degradation. The five principal antibiotic classes utilized in agricultural water are tetracycline, sulfonamides, macrolides, chloramphenicol, and fluoroquinolones[18].

Excessive antibiotics are enriched in soil and water along with surface water when untreated contaminated water is used for breeding and agricultural irrigation, which causes pollution and forms a vicious cycle, even endangering the health of organisms and affecting the ecological stability of agriculture. The liquid phase photocatalytic reaction is a degradation process based on the mechanisms of free radical oxidation and hole oxidation. $^{\cdot}OH$, which is produced when electron-hole pairs form on the surface of a semiconductor, has strong chemical activity and may effectively degrade many types of pollutants. The substrate has nearly no selectivity and can be applied directly to the semiconductor's surface. In addition, pollutants can be oxidized directly by holes, and the oxidation of free radicals and holes can facilitate the oxidative degradation of pesticides and antibiotics into small molecular inorganic compounds, such as H_2O, CO_2, and PO_4^-[18]. To degrade fluoroquinolone antibiotics, Zeynab Khazaee[20] synthesized Cu and Bi bimetallic alloy nanosheets coated with surface-functionalized multi-walled carbon nanotubes. Large amounts of $^{\cdot}O_2^-$ and $^{\cdot}OH$ were generated in the photocatalytic process to contribute to the degradation process at pH 7, and the final degradation rates of ciprofloxacin and norfloxacin were 88.7% and 86%, respectively. Eqs. (14)–(18) indicate the photocatalytic degradation of antibiotics.

$$hv + \text{Photocatalyst} \rightarrow e^- + h^+, \tag{14}$$

$$e^- + O_2 \rightarrow {}^{\cdot}O_2^-, \tag{15}$$

$$2{}^{\cdot}O_2^- + H_2O \rightarrow 2OH^- + H_2O_2 + O_2, \tag{16}$$

$$H_2O_2 + e^- \rightarrow {}^{\cdot}OH + OH^-, \tag{17}$$

$$\text{Antibiotics} + ({}^{\cdot}OH, {}^{\cdot}O_2^-, h^+) \rightarrow \text{Degradation Products}. \tag{18}$$

3. Application of photocatalytic degradation of agricultural wastewater

With the continuous development of agricultural technology, drugs to prevent crop diseases are gradually widely used, but improper treatment also leads to the emergence of pollution sources. Effective control of environmental pollution has become a worldwide challenge, and relevant studies have been widely carried out. In the 1990s, researchers published numerous lectures about photocatalysts that could decompose harmful substances in the environment into harmless. This report indicates that the photocatalytic degradation process can react sufficiently at room temperature, remove inorganic heavy metal ions and organic pollutants then mineralize organic matter completely at the same time. At present, the application fields of dealing with photocat-

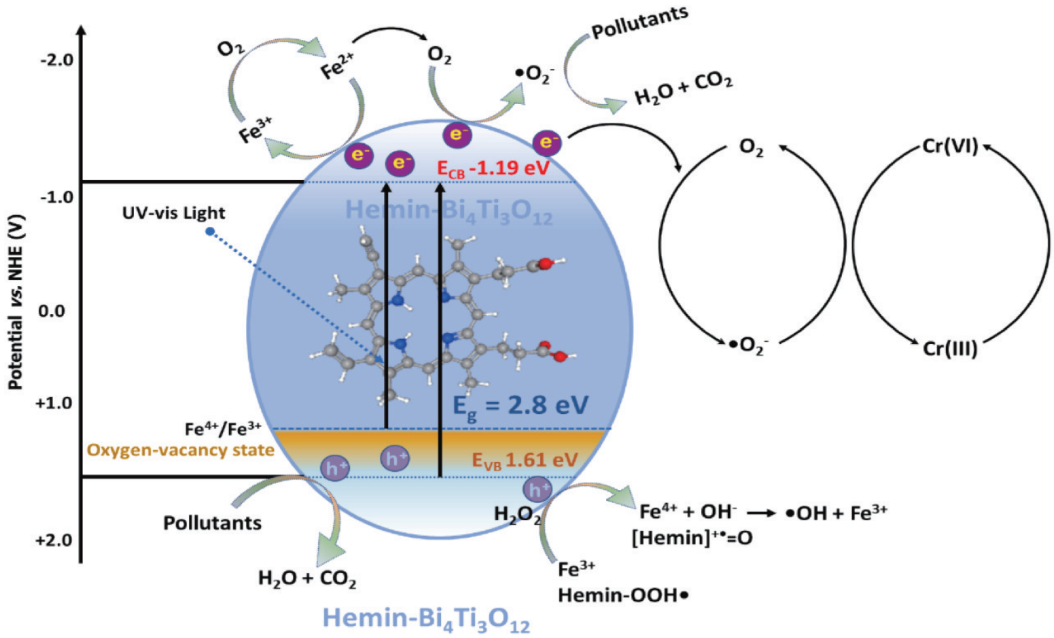


Fig. 3. (Color online) Schematic illustration of charge transfer and charge separation mechanism in the hemin-$Bi_4Ti_3O_{12}$ biomimetic nanocomposite photocatalyst under visible light irradiation[21].

alytic degradation technology include municipal wastewater waste gas, industrial wastewater waste gas, marine pollution and so on. With the development of photocatalytic degradation technology, simple photocatalytic conditions and alkaline photocatalysts are no longer limited. In order to degrade pollutants more effectively, researchers continue to explore this field. This chapter will discuss the application of photocatalytic degradation technology in the purification treatment of agricultural wastewater.

3.1. Photocatalytic removal of agricultural heavy metal ions

Heavy metal salts used in agriculture are often used in herbicides and insecticides, which can prolong the life of crops and improve the quality of crops. However, heavy metal ions cannot self-degrade, which leads to their enrichment in surface water system. The use of untreated wastewater will lead to a variety of irreversible diseases in human body. This section will analyze and summarize the removal methods of heavy metal ions in agricultural wastewater in recent five years.

3.1.1. Biocins

Bionics has been applied to the field of photocatalysis gradually. Inspired by biological states, scientists explore the surface morphology and survival characteristics of photocatalysts, and develop more efficient and novel photocatalysts inspired by biological states to achieve green degradation system. Muhammad Arif[21] synthesized a biomimetic photocatalyst hemin-$Bi_4Ti_3O_{12}$ (HBTO) by immobilizing artificial enzymes on the surface of semiconductor photocatalyst $Bi_4Ti_3O_{12}$. It was found that heme modified HBTO samples could not only improve the light absorption of HBTO, but also be used as electron conduction bridge and surface oxygen absorption site to remove heavy metal ions. The efficiency of heme modified HBTO was 3.7 times higher than that of the original photocatalyst (Fig. 3). Jiafu Qu[22] synthesized the porous coralline shape nanocomposite (SPNH-MOSF@SnS_2), which can selectively chelate soluble Cr(Ⅲ) under UV irradiation. This unique nanocomposite can efficiently reduce and remove hexavalent chromium from wastewater with a degradation rate of 99.5% within 90 min.

3.1.2. Removal of heavy metal ions by adsorption and reduction dual channels

Because of the coexistence of inorganic heavy metal ions and organic pollutants antibiotics in the agricultural sewage, the synergistic removal of adsorption and photocatalysis reflects the efficient removal property. The adsorption process provides more surface binding sites for photocatalytic removal reaction to accelerate it partly by making metal ions and surface functional groups create an interaction between surface complexation and static electricity. Adsorption and photocatalysis can synergistically degrade heavy metal ions[23].

Love Kumar Dhandole[24] synthesized Rhodium/antimony co-doped TiO_2 nanorods and titanate nanotubes (RS-TONR/TNT) composite material. This material has the dual functions of adsorption and reduction of heavy metal ions. 80% of Cu^{2+} is reduced to Cu^{+} within 5 h in sewage under neutral condition of pH 7. Shouchao Zhong[25] constructed a composite structure successfully combined covalent organic framework (COF) and graphene-phase carbon nitride nanosheets (CNNS) in situ. This original two-dimensional material stands out in the removal field on account of its high π-conjugated structure and broad optical absorption performance. The photocatalytic removed 99% of Cr(Ⅵ) to Cr(Ⅲ) within 30 min and was applied in the actual factory as the removal reduction rate of the material wastewater is 80%, showing high efficiency and practical application. Chumin Yan[26] prepared $Cd_3(TMT)_2$/CdS heterojunction composite photocatalyst by means of self-formation of CdS nano-particles, which can completely reduce Cr(Ⅵ) to Cr(Ⅲ) in wastewater within 6 min (Fig. 4). Ni Luo[27] proposed the synergistic effect of photocatalysis and adsorption on the removal of heavy metals. Synthesiz-

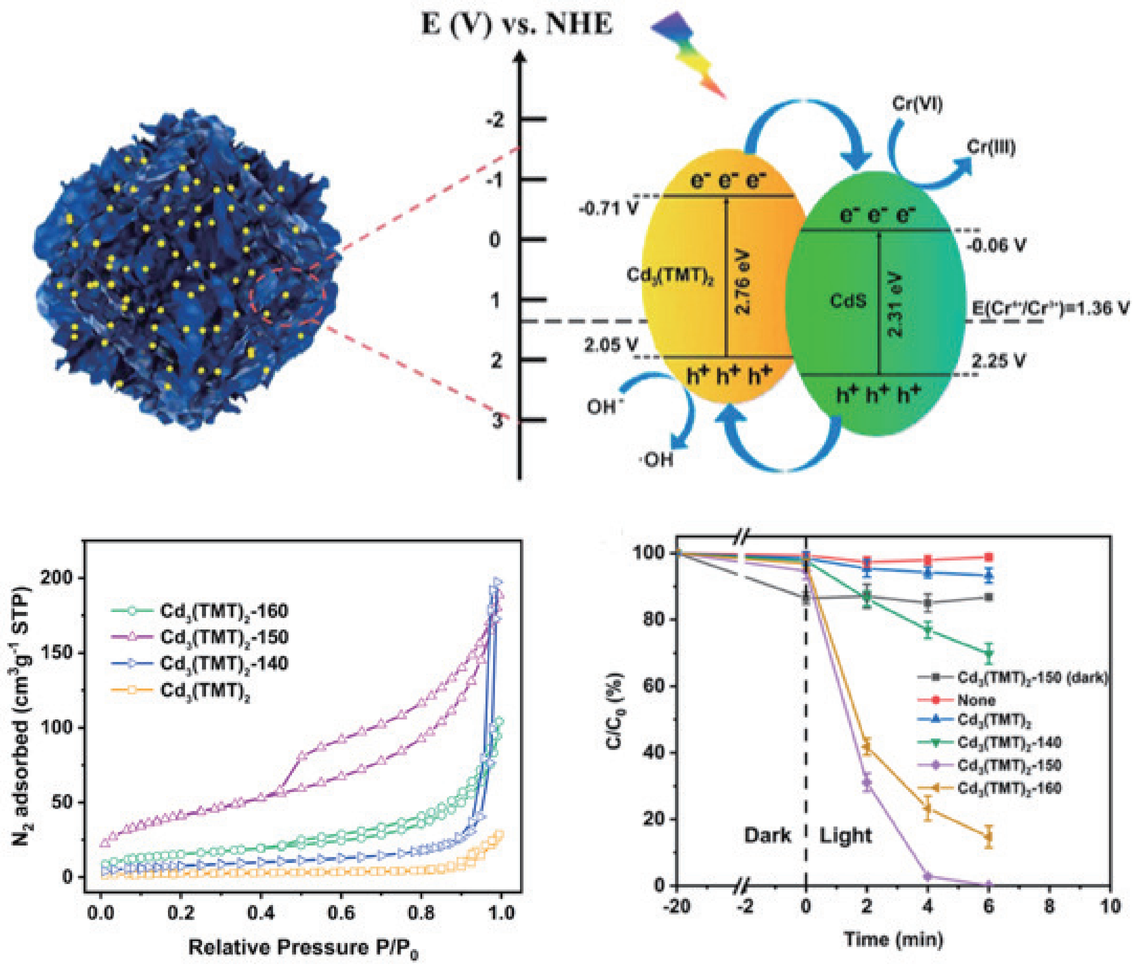


Fig. 4. (Color online) Postulated mechanism, N_2 adsorption/desorption isotherms and photocatalytic activities of visible light-induced photoreduction of Cr(Ⅵ) with the $Cd_3(TMT)_2$/CdS composites[26].

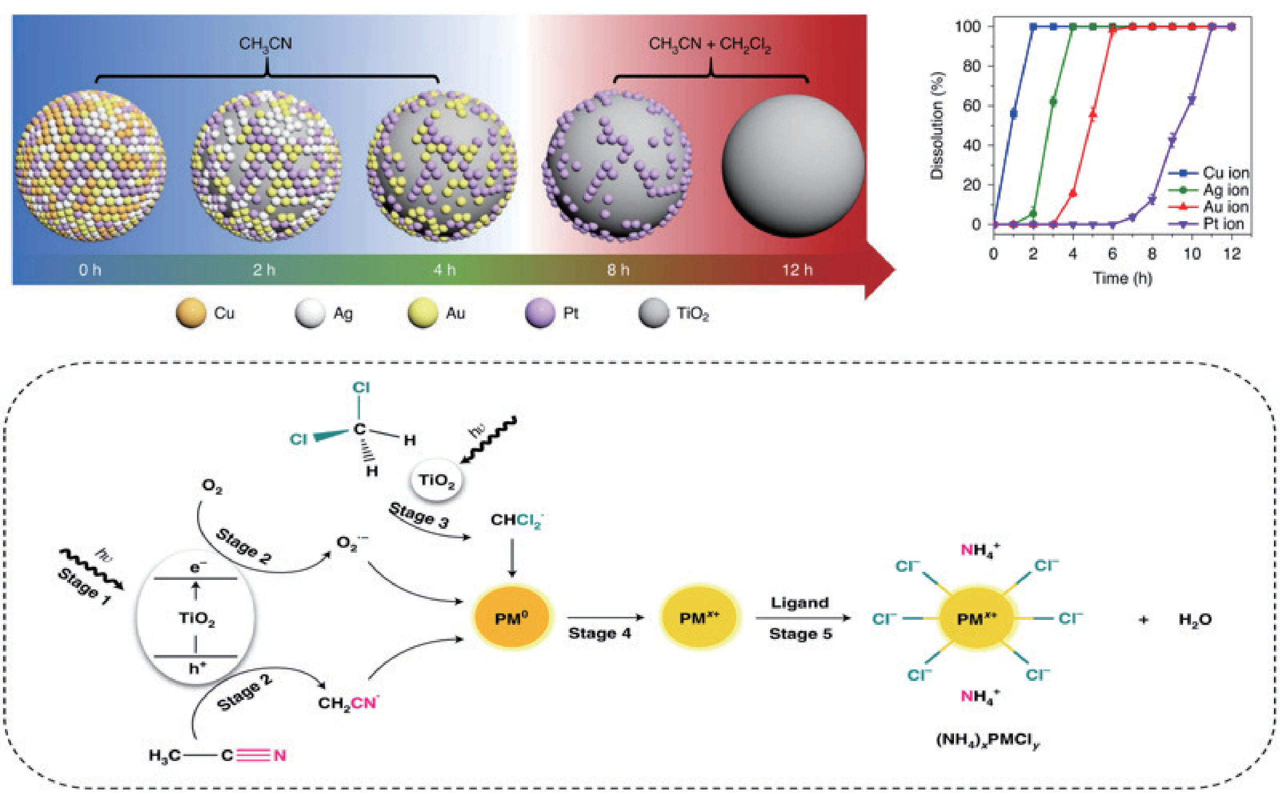


Fig. 5. (Color online) Schematic diagram, the amount of metal obtained and chemical mechanism of selective dissolution of Cu, Ag, Au and Pt by metal catalysts[17].

ing the ultra-thin 2D MoS_2 nanosheets rich in S defects which normalized photoreduction rate is about 15 times higher than that of P-MoS_2, and the Cr(Ⅵ) removal rate can reach 98.9% within 180 min. The photocatalyst can be recycled at least five times.

3.1.3. Selective removal of heavy metal ions

Selective removal of pollutants can be more targeted and orderly to extract a variety of pollutants given the complexity of pollutants in wastewater, which would achieve removal controllability and efficient use of waste.

Yao Chen[17] recycled seven precious metals in sequence selectively used TiO_2 powder from waste circuit boards, ternary autocatalysts and ore, they are silver (Ag), gold (Au), palladium (Pd), platinum (Pt), Rhodium (Rh), ruthenium (Ru), and Iridium (Ir), depending on the affinity of heavy metal ions and photocatalyst, seven noble metals are recovered successively. Complete removal was achieved within 12 h (Fig. 5). Ziyang Lu[28] developed a novel eco-friendly and recyclable magnetically graded porous Cd(Ⅱ) photocatalytic nanoreactor (MHP-CD) using ion imprinting technology. Due to the large number of Cd(Ⅱ) cavities in the imprinted layer and the corresponding high adsorption capacity, the nanocrystalline reactor had well adsorption of Cd(Ⅱ) specifically, and the removal rate of Cd(Ⅱ) reached 80% within 60 min. Xiaofang Song[29] synthesized PVA/PANI/TiO_2 hydrogel with a 3D biomimetic structure, which has high selective adsorption effect on $Cr_2O_{72}^-$ and can effectively reduce Cr(Ⅵ) to Cr(Ⅲ).

3.1.4. Development of heavy metal ion removal

Heavy metal ions in agriculture deposit in surface water, groundwater, and soil, which will enter organisms with water sources, combine with nucleic acids, proteins and small metabolites and destroy organic cells internally, causing irreversible harm to agricultural production and human health. In order to prevent the occurrence of this phenomenon, timely reduction of heavy metal ions in water to low-valence ions or zero-valence metals is a necessary process to degrade agricultural wastewater. Heavy metal ions enriched in agricultural wastewater will have a serious impact on human health and the environment. Take China for example, according to the provisions of *Surface Water Environmental Quality Standard GB3838* of China, class Ⅴ is the limit value of heavy metal elements, which is mainly applicable to agricultural water standards. Table 1 summarizes agricultural sources, agricultural standard concentrations of agricultural water, toxicity hazards caused by enrichment, removal products, and their removal degree. Therefore, the timely disposal of heavy metal pollutants in agricultural water is very important.

3.2. Photocatalytic degradation of agricultural antibiotics

The antibiotics that are used in agriculture can prevent and treat animal and plant diseases, and promote plant and animal growth within the prescribed concentration range. However, excessive usage may lead to antibiotic residues in animals raised for food production, as well as in surface water in agricultural areas and soils, which may cause potential harm to human health and the environment. Overuse can induce bacteria treated with antibiotics to mutate, resulting in drug-resistant bacteria that can pose a threat to human health and the environment. The structural modification of photocatalysts can enhance antibiotic degradation efficiency to a certain extent. In this section, morphologic modification of photocatalysts to promote antibiotic degradation will be discussed.

3.2.1. Construction of heterojunctions to improve photocatalytic degradation performance

The heterogeneous structure forms the energy band structure with barrier, which aims to adjust the work function, Fermi level position, spectral response range, electron migration path, etc., which can finally improve the light capture efficiency of the photocatalytic system, promote the separation and migration of carriers, and expand the specific surface area to accommodate more active sites, promote the diffusion of reactive molecules and high crystallinity to obtain higher photocatalytic activity.

For instance, Chunxu Wu[49] encapsulated spherical $ZnIn_2S_4$ in hollow dodecahedron $K_3PW_{12}O_{40}$ to prepare a flower-shaped hollow dodecahedron core-shell double Z-type superstructure series heterozygous nanoreactor. In the process of degrading tetracycline hydrochloride, the nanoreactor could achieve 99% degradation efficiency. Wei Wang[50] polymerized quantum thick graphitized carbon nitride (G-C_3N_4) onto the surface of anatase titanium dioxide (TiO_2) nanosheets to form TiO_2/G-C_3N_4 (TCN) core-shell quantum heterolinkages to improve the activity of photocatalytic degradation of tetracycline and achieve complete degradation. Yixiao Wu[51] constructed a nano-flower-like $NaBiO_3$ structure of direct z-type heterojunctions with supported by two-dimensional G-C_3N_4. This catalyst has high degradation efficiency and reproducibility, which can degrade 90% of tetracycline within 30 min and can be reused at least 8 times (Fig. 6). Xingyuan Zhang[52] constructed a novel symmetrical double Z-type $BiFeO_3$/$CuBi_2O_4$/$BaTiO_3$ heterojunction structure, which effectively used the solar spectrum to extend the light absorption range to UV–visible light and near-infrared light, and $^{\cdot}OH$ and H^+ played a major role in the degradation process. The photocatalyst could be reused for about five times whose degradation rate was increased to 0.0113 min^{-1} and 93.2% within 60 min.

3.2.2. Construction of surface defects to improve photocatalytic degradation performance

The construction defects can improve the property of the photocatalyst to a certain extent and improve the efficiency of photocatalytic degradation. Among them, oxygen vacancies can provide dangling bonds for the adsorption oligomer. Due to the local electron-rich characteristics, oxygen vacancies can also activate the inert chemical bonds of the adsorbed oligomer and regulate its electronic structure, thus affecting the photocatalytic process greatly[53]. Jian Zheng and Dajun Shu used oxygen vacancy modification to discuss the effect of strain on the surface properties of TiO_2[54].

In addition to the most common oxygen vacancies, surface passivation or the formation of N-vacancy and C-vacancy defect structures can also be performed on the surface of the photocatalyst[55]. Yan Lin[56] first prepared new composite photocatalyst Ag_3PO_4@W_2N_3–NV containing nitrogen vacancies by using molten salt assisted atmosphere calcination, which has high photocatalytic activity and photostability. The presence of nitrogen vacancies can induce the formation of defects and suspended bonds on the surface of W_2N_3–NV,

Table 1. Photocatalytic removal of heavy metal pollutants in agricultural wastewater.

Heavy metal element	Agricultural sources	Agricultural standard (*c*) (mg·kg^{-1})	Toxicity hazards caused by enrichment	Photocatalysts	Cycles index (times)	Reaction condition concentration of removal (*c*) (mg·L^{-1}), pH, illuminator	Removal time (t) (min)	Removal product	Removal degree (%)	References
Arsenic As(Ⅲ)	Arsenic in fertilizer, sewage sludge and fungi	0.1	Produce toxic genes, immunotoxins, etc.	Defect-type $BiVO_4$	3	c = 10 pH = 7 300 W Xenon lamp (λ≥420nm)	180	As(Ⅴ)	95.7	[30]
				ZnO	5	c = 5 pH = 8 ultraviolet irradiation (388nm > λ > 300 nm)	60		98.3	[31]
Cadmium Cd(Ⅱ)	Pesticide production, fertilizer, landfill, fertilizer sewage sludge	0.01	Chronic lung disease, interference with brain and liver function, etc.	RGO/TiO_2	5	c = 100 pH = 5.5	90	Cd(s)	90	[32, 33]
Chromium Cr(Ⅵ)	Fertilizer, landfill, fertilizer sewage sludge	0.1	Respiratory tract cancer, asthma, dermatitis skin diseases, etc.	Bi_5O_7I/ZnAlBi-CLDHs	5	c = 0.1 pH = 6.5 300 W Xenon lamp 100 mW/cm^2 (λ > 420 nm)	60	Cr(Ⅲ)	98	[34, 35]
				In_2S_3/Ti_3C_2	5	c = 0.1 pH = 7 300 W Xenon lamp 100 mW/cm^2 (λ > 420 nm)	6		100	[36]
				PANI/$W_{18}O_{49}$	10	c = 0.1 pH = 2 visible light (λ > 420 nm)	50		100	[37]
Copper Cu(Ⅱ)	Landfill, fertilizer industry, fertilizer sewage sludge	1.0	Toxic plants, reproductive capillary damage, etc.	TiO_2/ZnO-calcium	3	c = 60 pH = 7 UV lamp (λ = 254 nm)	120	Cu(s)	98.9	[38, 39]
				POPD-$CoFe_2O_4$	5	c = 100 pH = 7 300 W Xenon lamp 100 mW/cm^2 (780nm > λ > 380 nm)	60		45.98	[40]

Table 1. (Continued)

Heavy metal element	Agricultural sources	Agricultural standard (c) ($mg{\cdot}kg^{-1}$)	Toxicity hazards caused by enrichment	Photocatalysts	Cycles index (times)	Reaction condition concentration of removal (c) ($mg{\cdot}L^{-1}$), pH, illuminator	Removal time (t) (min)	Removal product	Removal degree (%)	References
Nickel Ni(Ⅱ)	Fertilizer industry, landfill, nickel fuel combustion, fertilizer sewage	0.00248	Skin allergy, gene damage, high toxicity to plants, etc.	TiO_2	3	c = 20 pH = 7 ultraviolet irradiation (388 nm > λ > 300 nm)	540	Ni(s)	36.4	[41]
				$CuCo_2O_4/TiO_2$	4	c = 30 pH = 7 200 W Tungsten lamp × 3	180		65	[42]
				$CrFeO_3/TiO_2$	4	C = 15 pH = 7.2 simulated sunlight 100 mW/cm^2	240		96	[43]
Plumbum Pb(Ⅱ)	Fertilizer, landfill, fertilizer sewage sludge, lead arsenate pesticide	0.1	Kidney damage, metabolic toxicants, reproductive abnormalities, etc.	N-doped TiO_2	4	c = 15 pH = 8 300 W Xenon lamp 100 mW/cm^2 (λ > 420 nm)	30	Pb(s)	81	[44]
				γ-Fe_2O_3	4	c = 1$mg{\cdot}L^{-1}$ pH = 7 visible light (λ > 420 nm)	60		96	[45]
				Bi_2O_3/TiO_2	5	c = 20 pH = 7 300 W Xenon lamp 100 mW/cm^2 (λ > 420 nm)	720		100	[46]
Zinc Zn(Ⅱ)	Fertilizer, landfill, fertilizer sewage sludge	2.0	Skin irritation, agitation, harmful to plants, etc.	His-TiO_2	Many times	c = 20 pH = 7.5 ultraviolet irradiation (388 nm > λ > 300 nm)	160	Zn(s)	98	[47]
				TiO_2/Graphene	3	c = 20 pH = 7 simulated sunlight (650 nm > λ > 300 nm)	90		100	[48]

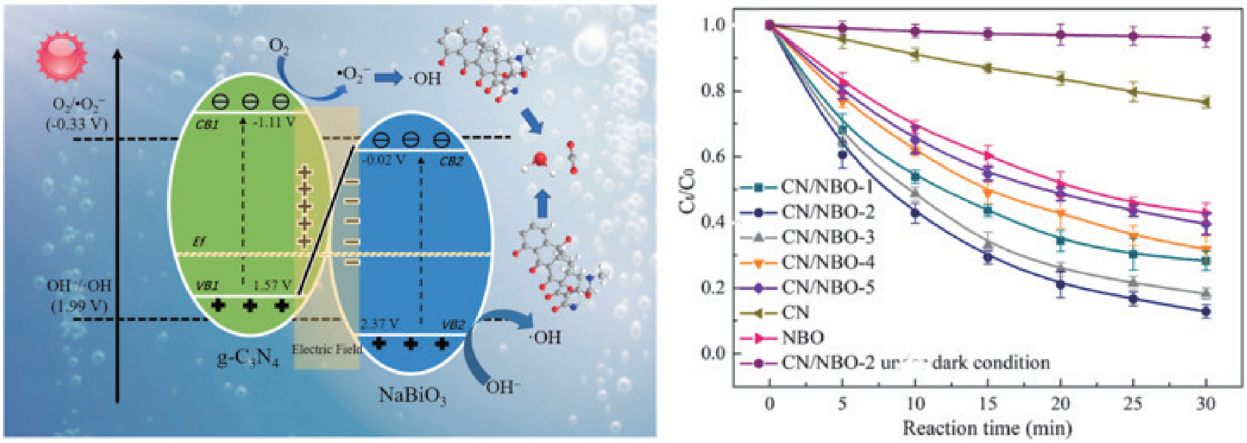


Fig. 6. (Color online) Chemical mechanism and efficiency of TC degradation by CN/NBO photocatalysis[51].

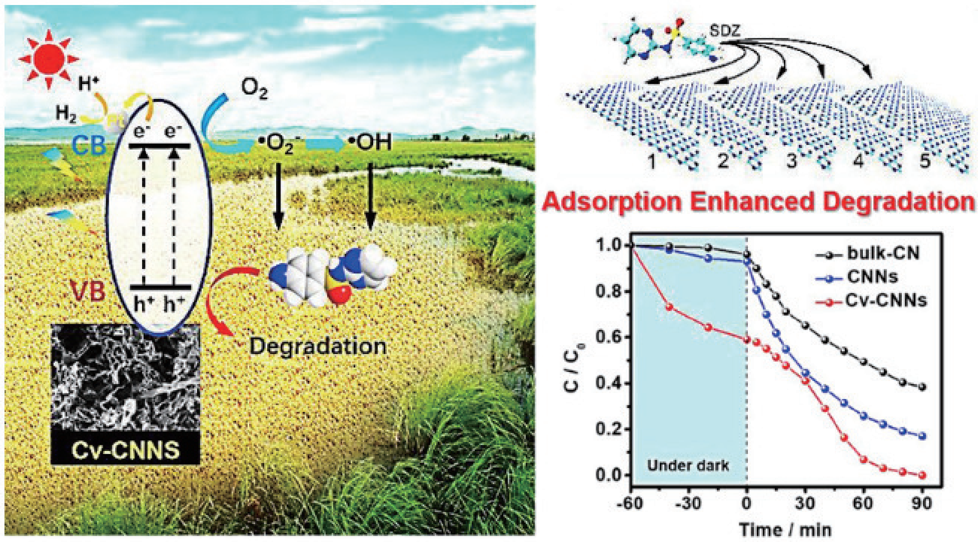


Fig. 7. (Color online) Mechanism and efficiency of Cv-CNNs degradation of sulfadiazine under visible light irradiation[58].

making it easy to integrate with Ag_3PO_4, forming a new chemical bond at the interface and providing a fast transfer channel for carrier transport and separation. The catalyst can achieve 100% complete degradation of amoxicillin and penicillin within 1 and 8 min respectively, and can be recycled at least 5 times. Xiangyang Li[57] took dicyandiamide (DCD) and trimeric acid (CA) as raw materials, obtained intermediates through solvent heat treatment, and calcined them to successfully prepare nitrogen-rich porous polymer carbon nitride (DCCN-S), which achieved 93.5% degradation of levofloxacin within 60 min. Meijun Liu[58] prepared a single/multi-layer carbon nitride nanosheet (CV-CNNs) photocatalyst with carbon vacancies. The induction of carbon vacancies improved the oxidation-reduction capacity of the photocatalyst, which could completely degrade sulfadiazine within 20 min (Fig. 7). Reshalaiti Hailili[59] adjusted the oxygen vacancy morphology in $CaCu_3Ti_4O_{12}$ structure of double perovskite to achieve complete degradation of tetracycline within 50 min and the photocatalyst can be recycled for at least 6 times. Jie Ding[60] synthesized a Z-type $BiO_{1-x}Br/Bi_2O_2CO_3$ photocatalyst with abundant oxygen vacancies. The photocatalytic based on oxygen vacancy formation, using oxygen vacancy as the electron mediator, can significantly promote the separation of photoinduced carriers and mineralize tetracycline to CO_2 and H_2O completely within 3 h.

3.2.3. Doping enhances photocatalytic degradation performance

Doping can change the intrinsic properties of a material by influencing the band structure and composition of materials to control the generation and separation of electrons and holes. It can reduce the band gap width of the material to improve the full utilization of sunlight and increase the transport efficiency of photogenerated electrons and holes, which promote more photogenerated charge carriers migrate to the surface of the semiconductor material and participate in photocatalytic reactions before annihilation.

For example, Lin Chen[61] assembled a new tubular carbon nitride (D-TCN_{450}) with nitrogen defects/boron dopants using the supramolecular reactions and $NaBH_4$ thermal reduction methods, the introduction of boron dopant is conducive to the absorption of oxygen, forming superoxide radical, deepening the position of VB to increase the light capture performance and accelerate the charge migration ability. The tubular structure of the photocatalyst synergies to promote light capture and accelerate charge transfer, and finally achieve 96% degradation of tetracycline hydrochloride within 80 min (Fig. 8). Zeynab Khazaee[20] successfully synthesized carboxylic multi-walled carbon nanotubes loaded with Cu/Bi bimetallic alloy nanosheets to degrade fluoroquinolone antibiotics, achieving 93% degradation within 90 min. Chitiphon

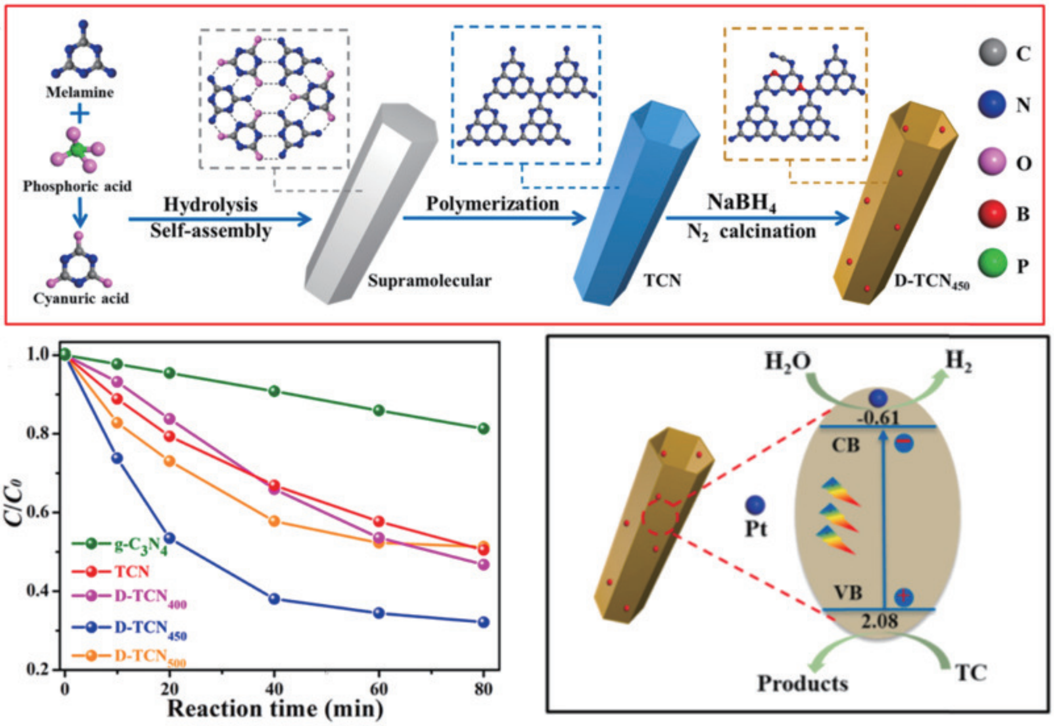


Fig. 8. (Color online) Synthesis process, degradation efficiency and principle of D-TCN450[61].

Chuaicham[62] synthesized oxygen-doped surface porous graphite carbon nitride (OCN), which was three times more efficient than the original C_3N_4 photocatalytic degradation, and could degrade 95% of ciprofloxacin within 20 min. Yang Jin[63] synthesized the sulfur-doped layered s-biobr structure by hydrothermal method. The interlayer complexes can degrade 90% of ciprofloxacin simultaneously within 20 min by intercalation, adsorption, and photocatalysis, the degradation rate was 0.2303 min^{-1}. The photocatalyst can be recycled at least five times.

3.2.4. Development of heavy metal ion degradation

There are large amounts of antibiotics in agricultural wastewater due to the non-standard disposal of water for animal husbandry and irrigation industry, and the enrichment of antibiotics will have a huge impact on the environment and human health. Take the great agricultural country of China as an example. According to the *Agricultural Industry Standard of the People's Republic of China*, the limited amount of agricultural antibiotics is strictly observed. Table 2 provides a comprehensive summary of the most commonly used antibiotics in agriculture, their respective functions, recommended dosages, potential hazards resulting from overuse, and the effectiveness of various photocatalysts in degrading these pollutants. It is important to recognize that ensuring the quality of agricultural water goes beyond simply relying on the quality of the water source. It requires a proactive approach that includes timely treatment of potential antibiotic pollutants in agricultural water. Therefore, implementing effective solutions to treat antibiotic pollutants in agricultural water is crucial in obtaining high quality agricultural water that is safe and sustainable.

4. Factors affecting photocatalytic degradation

Photocatalytic degradation system is a multiplex process involving the interaction of many factors. The system has the advantages of friendly reaction conditions, no secondary pollution and high treatment efficiency. However, there are still some problems in the process of industrialization, such as complex preparation process, high cost, low optimization efficiency and insufficient reaction. It is found that the type of catalyst, light source, pH value and temperature of reaction system all have certain influence on the degradation efficiency. Faced with these challenges, the application potential of photocatalysts and photocatalytic systems, such as full application of photocatalysts and full utilization of sunlight, needs to be further enhanced in future studies to improve the efficiency and stability of degradation processes. The factors affecting the photocatalytic degradation efficiency will be explored from three aspects: photocatalyst, pollution source and degradation process.

4.1. Characteristics of photocatalysts

Photocatalyst characteristics include semiconductor band structure[75], morphology [76], defect[77], size[78] and so on. The band structure determines the oxidation and reduction capacity of the photocatalyst. Firstly, the band structure includes the semiconductor valence band, the conduction band position and the band gap width. The positions of valence band and conduction band reflect the REDOX capacity of semiconductor. The more negative the conduction band is, the stronger the reducibility of photocatalyst is, and the more positive the valence band is, the weaker the reduction of photocatalyst is[79]. The band gap reflects the photoexcitation characteristics and REDOX capacity of different semiconductors. The energy band structure determines the REDOX capacity of the material and the range of light absorption band, and also determines whether the removal reaction of agricultural water pollution can occur.

Secondly, by adjusting the preparation method of photocatalyst, different material morphology closely related to the specific surface area can be obtained. The large specific

Table 2. Effects and hazards of common agricultural antibiotics.

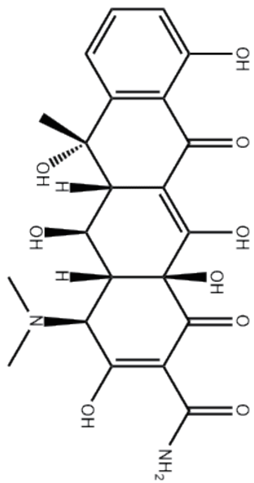
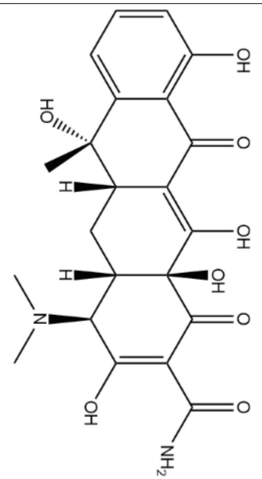
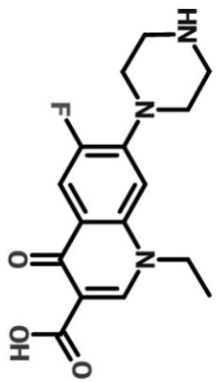
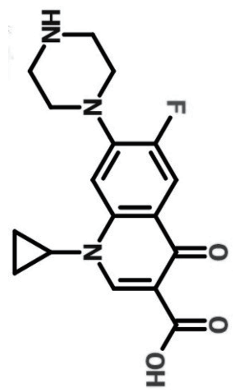
Antibiotics	Structural formula	Effect	Agricultural standard concentration (c) (mg·kg^{-1})	Side effect	Photocatalyst	Cycle index (times)	Reaction condition concentration of degradation (c) (mg·L^{-1}), pH, illuminator	Removal time (t) (min)	Removal degree (%)	References
Oxytetracycline		Insecticide, antibacterial agent	0.5	Abdominal discomfort vomiting, etc.	AgI-$ZnSn(OH)_6$	4	c = 10 mg·L^{-1} pH = 9 visible light (λ > 420 nm)	20	96.57	[64]
					HDMP	4	c = 30 pH = 6.7 300 W Xenon lamp 100 mW/cm^2 (λ > 420 nm)	60	79.3	[65]
					BiOBr/Ag/g-C_3N_4	5	c = 10 pH = 9 visible light (780 nm > λ > 380 nm)	60	91.7	[66]
Tetracycline		Poultry and husbandry antibacterial	0.5	Affect bone growth, vomiting, etc.	N-CQDs/OV-BiOBr	5	c =30 pH = 4.3 visible light (λ ⩾ 400 nm)	60	80	[67]
					BP/BiOBr	4	c = 30 pH = 7 visible light (λ ⩾ 400 nm)	90	85	[68]
					h-BN/Bi_2MoO_6	5	c = 20 pH = 7 visible lLight (λ ⩾ 400 nm)	140	99.19	[69]

Table 2. (Continued)

Antibiotics	Structural formula	Effect	Agricultural standard concentration (*c*) (mg·kg^{-1})	Side effect	Photocatalyst	Cycle index (times)	Reaction condition concentration of degradation (*c*) (mg·L^{-1}), pH, illuminator	Removal time (*t*) (min)	Removal degree (%)	References
Norfloxacin		Poultry and husbandry antibacterial	1.4	Slow bone development, immune deficiency, crystallization urine etc.	CdS/Au/TiO_2	5	$c = 5$ pH = 5 simulated sunlight	60	64.67	[70, 71]
					copper-doped BiOBr	5	$c = 10$ pH = 5–7 200 W Xenon lamp 100 mW/cm^2	90	100	[72]
					$BiFeO_3/CuBi_2O_4/BaTiO_3$	5	$c = 10$ pH = 5 simulated sunlight	60	93.5	[52]
Ciprofloxacin		Poultry and husbandry antibacterial	0.8	Crystallized urine,septicemia, ear, nose, and throat infection	OCN-1	5	$c = 10$ pH = 8 500 W Xenon lamp (λ > 380 nm)	20	95	[63]
					$ZnFe_2O_4$/RGO	4	$c = 20$ pH = 8 125 W Xenon lamp (λ > 400 nm)	60	73.4	[73]
					$ZnFe_2O_4$/BiOBr	4	$c = 15$ pH = 8 visible light (λ > 420 nm)	60	84	[74]

surface area enables the photocatalyst to have good catalytic performance[79], and there are a large number of active sites on its surface[80], so that the electron hole pairs excited from the semiconductor have more reaction sites participating in the reaction on the surface. It is one of the effective methods to increase the reactive sites on the surface to accelerate the catalytic reaction and improve the photocatalytic efficiency.

In terms of size, the quantum size effect exists in nanoscale catalyst. As the size decreases, the width of semiconductor band gap increases, and the REDOX capacity will be enhanced. Correspondingly, as the size decreases and the band gap width increases, the light absorption capacity becomes weaker, which reflects the important role of band structure in photocatalysis.

Defect introduction with appropriate concentration can change the work function value, surface dipole, charge density and surface chemistry of the defective photocatalyst, as well as introduce new energy levels into the band gap, which helps to modulate band structure and improve the performance of the photocatalyst[81].

4.2. Nature of pollutant

The mechanism property of pollutants is mainly reflected in their molecular structure. For the photocatalytic degradation reaction to proceed, the groups involved in the reaction of pollutants first need to be matched with the active free radicals produced by the photocatalyst to be decomposed. In addition, the appropriate photocatalyst should be selected according to the molecular structure of pollutants, which may affect the affinity of the photocatalyst and make it limited. For photocatalysts, large pores and specific surface areas are needed to adsorb pollutants, have appropriate carrier band gaps that can be excited by light and conductance band levels that meet reaction conditions, so as to achieve a wide spectrum response range[82] .

4.3. The effect of reaction conditions

In the photocatalytic degradation process, light source[83], pH value[84], temperature, liquid waste flow rate and other factors have an impact on the system efficiency. In terms of light source, photocatalytic chemical reactions have a high Gibbs free energy. Some photocatalysts can only be excited by ultraviolet light, but the absorption range of ultraviolet light is narrow and the utilization rate of light energy is low. Shortwave ultraviolet light with wavelength less than 170 nm has a higher energy to excite photogenerated electron transition, so shortwave ultraviolet light has a significant photocatalytic effect, but the acquisition of light source in this band is the current obstacle.

In acidic, neutral and alkaline degradation systems, the change of pH value not only affects the output of different free groups of photocatalyst, but also affects the affinity between groups carried by pollutants and free radicals, thus affecting the photocatalytic degradation efficiency. Therefore, the appropriate pH value selection is one of the factors to improve the reaction efficiency of the system.

The influence of temperature change is reflected in molecular thermal motion, photothermal effect of some materials, internal changes of pyroelectric materials, etc. The flow rate of waste liquid affects the contact area between photocatalyst and waste liquid[85] and the internal electric field of piezoelectric materials. Changing the external dynamic factors will also affect the photocatalytic degradation rate.

5. Conclusion and prospects

This paper has reviewed the reaction mechanism of photocatalytic degradation technology, the mechanism of degradation of agricultural wastewater, especially the residual heavy metal ions and antibiotics, the research progress of photocatalytic degradation, and the factors affecting its efficiency. To achieve the benefit of photocatalytic degradation of agricultural wastewater, it is necessary to link various pollutants in wastewater with the photocatalytic degradation mechanism to form a multidisciplinary application system. It is also necessary to design photocatalyst and photocatalytic systems reasonably and attach importance to advanced characterization technology of photocatalytic water treatment to explore its degradation mechanism and degradation efficiency. Finally, the green low-energy photocatalytic degradation system will degrade the residual organic matter in agricultural boiling water into CO_2 and H_2O, and achieve the goal of sustainable agricultural development planning and ecological green agriculture.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (52272213), Natural Science Research of Jiangsu Higher Education Institutions of China (21KJB140005), and Jiangsu Province and Education Ministry Co-Sponsored Synergistic Innovation Center of Modern Agricultural Equipment (XTCX2024).

References

[1] Zhao X L, Yu X Z, Wang X Y, et al. Recent advances in metal-organic frameworks for the removal of heavy metal oxoanions from water. Chemical Engineering Journal, 2021, 407, 127221

[2] Shrestha R, Ban S, Devkota S, et al. Technological trends in heavy metals removal from industrial wastewater: A review. J Environ Chem Eng, 2021, 9, 105688

[3] Liu M X , Dong F Q , Nie X Q, et al. Reduction of heavy metal Ions mediated by photoelectron-microorganism synergistic effect and electron transfer mechanism. Progress in Chemistry, 2017, 29, 1537

[4] Ren G M, Han H T, Wang Y X, et al. Recent advances of photocatalytic application in water treatment: A review. Nanomaterials, 2021, 11, 1804

[5] Gao X Y, Meng X C. Photocatalysis for heavy metal treatment: A review. Processes, 2021, 9, 1729

[6] Wu S Q, Hu H Y, Lin Y, et al. Visible light photocatalytic degradation of tetracycline over TiO_2. Chem Eng J, 2020, 382, 122842

[7] Lin L H, Hisatomi T, Chen S S, et al. Visible-light-driven photocatalytic water splitting: Recent progress and challenges. Trends Chem, 2020, 2, 813

[8] Ma M M, Wang Z J, Lei Y. An in-depth understanding of photophysics in organic photocatalysts. J Semicond, 2023, 44, 030401

[9] Bai S, Jiang J, Zhang Q, et al. Steering charge kinetics in photocatalysis: Intersection of materials syntheses, characterization techniques and theoretical simulations. Chem Soc Rev, 2015, 44, 2893

[10] Ng B J, Putri L K, Kong X Y, et al. Z-scheme photocatalytic systems for solar water splitting. Adv Sci, 2020, 7, 1903171

[11] Noor S, Ashar A, Taj M B, et al. Advanced oxidation processes for remediation of persistent organic pollutants. Advanced Oxida-

tion Processes for Wastewater Treatment. Boca Raton: CRC Press, 2022
[12] Qian R F, Zong H X, Schneider J, et al. Charge carrier trapping, recombination and transfer during TiO_2 photocatalysis: An overview. Catal Today, 2019, 335, 78
[13] Perea Vélez Y S, Carrillo-González R, del Carmen Angeles González-Chávez M. Interaction of metal nanoparticles–plants–microorganisms in agriculture and soil remediation. J Nanoparticle Res, 2021, 23, 1
[14] Liu Z L, Zhang C, Liu L Z, et al. A conductive network and dipole field for harnessing photogenerated charge kinetics. Adv Mater, 2021, 33, 2104099
[15] Fouda-Mbanga B G, Prabakaran E, Pillay K. Carbohydrate biopolymers, lignin based adsorbents for removal of heavy metals (Cd^{2+}, Pb^{2+}, Zn^{2+}) from wastewater, regeneration and reuse for spent adsorbents including latent fingerprint detection: A review. Biotechnol Rep (Amst), 2021, 30, e00609
[16] Kaur M, Kaur M, Singh D, et al. Synthesis of $CaFe_2O_4$-NGO nanocomposite for effective removal of heavy metal ion and photocatalytic degradation of organic pollutants. Nanomaterials, 2021, 11, 1471
[17] Chen Y, Xu M J, Wen J Y, et al. Selective recovery of precious metals through photocatalysis. Nat Sustain, 2021, 4, 618
[18] Samar S, Thi H P, Mohammed A T. Review on the visible light photocatalysis for the decomposition of ciprofloxacin, norfloxacin, tetracyclines, and sulfonamides antibiotics in wastewater. Catalysts, 2021, 11, 437
[19] Cheng D M, Liu X H, Wang L, et al. Seasonal variation and sediment–water exchange of antibiotics in a shallower large lake in North China. Sci Total Environ, 2014, 476/477, 266
[20] Khazaee Z, Mahjoub A R, Cheshme Khavar A H. One-pot synthesis of CuBi bimetallic alloy nanosheets-supported functionalized multiwalled carbon nanotubes as efficient photocatalyst for oxidation of fluoroquinolones. Appl Catal B Environ, 2021, 297, 120480
[21] Arif M, Muhmood T, Zhang M, et al. Highly visible-light active, eco-friendly artificial enzyme and 3D $Bi_4Ti_3O_{12}$ biomimetic nanocomposite for efficient photocatalytic tetracycline hydrochloride degradation and Cr(VI) reduction. Chem Eng J, 2022, 434, 134491
[22] Qu J F, Chen D Y, Li N J, et al. Coral-inspired nanoscale design of porous SnS_2 for photocatalytic reduction and removal of aqueous Cr (VI). Appl Catal B Environ, 2017, 207, 404
[23] Li Z W, Wang L, Qin L, et al. Recent advances in the application of water-stable metal-organic frameworks: Adsorption and photocatalytic reduction of heavy metal in water. Chemosphere, 2021, 285, 131432
[24] Dhandole L K, Kim S G, Bae H S, et al. Simultaneous and synergistic effect of heavy metal adsorption on the enhanced photocatalytic performance of a visible-light-driven RS-TONR/TNT composite. Environ Res, 2020, 180, 108651
[25] Zhong S C, Wang Y, Li S X, et al. Enhanced photo-reduction of chromium(VI) from aqueous solution by nanosheet hybrids of covalent organic framework and graphene-phase carbon nitride. Sep Purif Technol, 2022, 294, 121204
[26] Yan C M, Dong X L, Wang Y, et al. Porous $Cd_3(C_3N_3S_3)_2$/CdS composites with outstanding Cr(VI) photoreduction performance under visible light irradiation. Sep Purif Technol, 2022, 293, 121077
[27] Luo N, Chen C, Yang D M, et al. S defect-rich ultrathin 2D MoS_2: The role of S point-defects and S stripping-defects in the removal of Cr(VI) via synergistic adsorption and photocatalysis. Appl Catal B Environ, 2021, 299, 120664
[28] Lu Z Y, He F, Hsieh C Y, et al. Magnetic hierarchical photocatalytic nanoreactors: Toward highly selective Cd^{2+} removal with secondary pollution free tetracycline degradation. ACS Appl Nano Mater, 2019, 2, 1664
[29] Song X F, Qin J T, Li T T, et al. Efficient construction and enriched selective adsorption-photocatalytic activity of PVA/PANI/TiO_2 recyclable hydrogel by electron beam radiation. J Appl Polym Sci, 2020, 137, 48516
[30] Yu T, Lv L Y, Wang H M, et al. Enhanced photocatalytic treatment of Cr(VI) and phenol by monoclinic $BiVO_4$ with {010}-orientation growth. Mater Res Bull, 2018, 107, 248
[31] Moafi M H, Ardestani M, Mehrdadi N. Use of zinc oxide nano-photocatalyst as a recyclable catalyst for removal of arsenic and lead ions from polluted water. J Health, 2021, 12, 130
[32] Ren W Q, Wan C L, Li Z W, et al. Functional CdS nanocomposites recovered from biomineralization treatment of sulfate wastewater and its applications in the perspective of photocatalysis and electrochemistry. Sci Total Environ, 2020, 742, 140646
[33] Zhang J Y, Yan M W, Sun G C, et al. Simultaneous removal of Cu(II), Cd(II), Cr(VI), and rhodamine B in wastewater using TiO_2 nanofibers membrane loaded on porous fly ash ceramic support. Sep Purif Technol, 2021, 272, 118888
[34] Zhang J Y, Zhang W T, Yuan F, et al. Effect of Bi_5O_7I/calcined ZnAl-Bi-LDHs composites on Cr(VI) removal via adsorption and photocatalytic reduction. Appl Surf Sci, 2021, 562, 150129
[35] Li Y X, Wang C C, Fu H F, et al. Marigold-flower-like TiO_2/MIL-125 core–shell composite for enhanced photocatalytic Cr(VI) reduction. J Environ Chem Eng, 2021, 9, 105451
[36] Huang H S, Jiang X, Li N J, et al. Noble-metal-free ultrathin MXene coupled with In_2S_3 nanoflakes for ultrafast photocatalytic reduction of hexavalent chromium. Appl Catal B Environ, 2021, 284, 119754
[37] Zhao X S, Huang S B, Liu Y, et al. *In situ* preparation of highly stable polyaniline/$W_{18}O_{49}$ hybrid nanocomposite as efficient visible light photocatalyst for aqueous Cr(VI) reduction. J Hazard Mater, 2018, 353, 466
[38] Bilgic A. Fabrication of monoBODIPY-functionalized Fe_3O_4@SiO_2@TiO_2 nanoparticles for the photocatalytic degradation of rhodamine B under UV irradiation and the detection and removal of Cu(II) ions in aqueous solutions. J Alloys Compd, 2022, 899, 163360
[39] Kanakaraju D, Ravichandar S, Lim Y C. Combined effects of adsorption and photocatalysis by hybrid TiO_2/ZnO-calcium alginate beads for the removal of copper. J Environ Sci, 2017, 55, 214
[40] He F, Lu Z Y, Song M S, et al. Selective reduction of Cu^{2+} with simultaneous degradation of tetracycline by the dual channels ion imprinted POPD-$CoFe_2O_4$ heterojunction photocatalyst. Chem Eng J, 2019, 360, 750
[41] Kabra K, Chaudhary R, Sawhney R L. Solar photocatalytic removal of Cu(II), Ni(II), Zn(II) and Pb(II): Speciation modeling of metal–citric acid complexes. J Hazard Mater, 2008, 155, 424
[42] Bagtache R, Zahra S, Abdi A, et al. Characterization of $CuCo_2O_4$ Prepared by Nitrate Route: Application to Ni^{2+} reduction under visible light. J Photochem Photobiol A Chem, 2020, 400, 112728
[43] Djilali M A, Mellal M, Mekatel H, et al. Synthesis, physical, optical and electrochemical properties of the ilmenite $CrFeO_3$: Application to photo-reduction of Ni^{2+}. Int J Hydrog Energy, 2022, 47, 1589
[44] Xiao R, Tobin J, Zha M Q, et al. A nanoporous graphene analog for superfast heavy metal removal and continuous-flow visible-light photoredox catalysis. J Mater Chem A, 2017, 5, 20180
[45] Miri A, Sedighi A S, Najafidoust A, et al. Study of photodegradation performance and ability of lead removal of green synthesised maghemite nanoparticles. Int J Environ Anal Chem, 2021, 1
[46] You S Z, Hu Y, Liu X C, et al. Synergetic removal of Pb(II) and dibutyl phthalate mixed pollutants on Bi_2O_3-TiO_2 composite photocatalyst under visible light. Appl Catal B Environ, 2018, 232, 288
[47] Hosseini F, Mohebbi S. High efficient photocatalytic reduction of aqueous Zn^{2+}, Pb^{2+} and Cu^{2+} ions using modified titanium dioxide nanoparticles with amino acids. J Ind Eng Chem, 2020, 85, 190

[48] Kumordzi G, Malekshoar G, Yanful E K, et al. Solar photocatalytic degradation of Zn^{2+} using graphene based TiO_2. Sep Purif Technol, 2016, 168, 294

[49] Wu C X, Xing Z P, Fang B, et al. Polyoxometalate-based yolk@shell dual Z-scheme superstructure tandem heterojunction nanoreactors: Encapsulation and confinement effects. J Mater Chem A, 2022, 10, 180

[50] Wang W, Fang J J, Shao S F, et al. Compact and uniform TiO_2@g-C_3N_4 core-shell quantum heterojunction for photocatalytic degradation of tetracycline antibiotics. Appl Catal B Environ, 2017, 217, 57

[51] Wu Y X, Zhao X S, Huang S B, et al. Facile construction of 2D g-C_3N_4 supported nanoflower-like $NaBiO_3$ with direct Z-scheme heterojunctions and insight into its photocatalytic degradation of tetracycline. J Hazard Mater, 2021, 414, 125547

[52] Zhang X Y, Wang X, Chai J N, et al. Construction of novel symmetric double Z-scheme $BiFeO_3/CuBi_2O_4/BaTiO_3$ photocatalyst with enhanced solar-light-driven photocatalytic performance for degradation of norfloxacin. Appl Catal B Environ, 2020, 272, 119017

[53] Zhang J W, Shen B X, Hu Z Z, et al. Uncovering the synergy between Mn substitution and O vacancy in ZnAl-LDH photocatalyst for efficient toluene removal. Appl Catal B Environ, 2021, 296, 120376

[54] Zheng J, Shu D J. Regulation of surface properties of photocatalysis material TiO_2 by strain engineering. J Semicond, 2020, 41, 091703

[55] Babu A, Vasanth A, Nair S, et al. WO_3 passivation layer-coated nanostructured TiO_2: An efficient defect engineered photoelectrode for dye sensitized solar cell. J Semicond, 2021, 42, 052701

[56] Lin Y, Yang C P, Niu Q Y, et al. Interfacial charge transfer between silver phosphate and W_2N_3 induced by nitrogen vacancies enhances removal of β-lactam antibiotics. Adv Funct Materials, 2022, 32, 2108814

[57] Li X Y, Li K Y, Du J, et al. Nitrogen-rich porous polymeric carbon nitride with enhanced photocatalytic activity for synergistic removal of organic and heavy metal pollutants. Environ Sci: Nano, 2022, 9, 2388

[58] Liu M J, Zhang D P, Han J L, et al. Adsorption enhanced photocatalytic degradation sulfadiazine antibiotic using porous carbon nitride nanosheets with carbon vacancies. Chem Eng J, 2020, 382, 123017

[59] Hailili R, Wang Z Q, Li Y X, et al. Oxygen vacancies induced visible-light photocatalytic activities of $CaCu_3Ti_4O_{12}$ with controllable morphologies for antibiotic degradation. Appl Catal B Environ, 2018, 221, 422

[60] Ding J, Dai Z, Qin F, et al. Z-scheme $BiO_{1-x}Br/Bi_2O_2CO_3$ photocatalyst with rich oxygen vacancy as electron mediator for highly efficient degradation of antibiotics. Appl Catal B Environ, 2017, 205, 281

[61] Chen L, Wang Y X, Cheng S, et al. Nitrogen defects/boron dopants engineered tubular carbon nitride for efficient tetracycline hydrochloride photodegradation and hydrogen evolution. Appl Catal B Environ, 2022, 303, 120932

[62] Chuaicham C, Sekar K, Xiong Y H, et al. Single-step synthesis of oxygen-doped hollow porous graphitic carbon nitride for photocatalytic ciprofloxacin decomposition. Chem Eng J, 2021, 425, 130502

[63] Jin Y, Li F, Li T, et al. Enhanced internal electric field in S-doped BiOBr for intercalation, adsorption and degradation of ciprofloxacin by photoinitiation. Appl Catal B Environ, 2022, 302, 120824

[64] Zhang C, He D H, Fu S S, et al. Silver iodide decorated $ZnSn(OH)_6$ hollow cube: Room-temperature preparation and application for highly efficient photocatalytic oxytetracycline degradation. Chem Eng J, 2021, 421, 129810

[65] Yang Y, Zeng G M, Huang D L, et al. Molecular engineering of polymeric carbon nitride for highly efficient photocatalytic oxytetracycline degradation and H_2O_2 production. Appl Catal B Environ, 2020, 272, 118970

[66] Ni J X, Liu D M, Wang W, et al. Hierarchical defect-rich flower-like BiOBr/Ag nanoparticles/ultrathin g-C_3N_4 with transfer channels plasmonic Z-scheme heterojunction photocatalyst for accelerated visible-light-driven photothermal-photocatalytic oxytetracycline degradation. Chem Eng J, 2021, 419, 129969

[67] Yu H B, Huang J H, Jiang L B, et al. Enhanced photocatalytic tetracycline degradation using N-CQDs/OV-BiOBr composites: Unraveling the complementary effects between N-CQDs and oxygen vacancy. Chem Eng J, 2020, 402, 126187

[68] Li X B, Xiong J, Gao X M, et al. Novel BP/BiOBr S-scheme nano-heterojunction for enhanced visible-light photocatalytic tetracycline removal and oxygen evolution activity. J Hazard Mater, 2020, 387, 121690

[69] Du Z, Feng L, Guo Z L, et al. Ultrathin h-BN/Bi_2MoO_6 heterojunction with synergetic effect for visible-light photocatalytic tetracycline degradation. J Colloid Interface Sci, 2021, 589, 545

[70] Kumar A, Sharma G, Kumari A, et al. Construction of dual Z-scheme g-$C_3N_4/Bi_4Ti_3O_{12}/Bi_4O_5I_2$ heterojunction for visible and solar powered coupled photocatalytic antibiotic degradation and hydrogen production: Boosting via I^-/I_3^- and Bi^{3+}/Bi^{5+} redox mediators. Appl Catal B Environ, 2021, 284, 119808

[71] Li J Y, Xia Z, Ma D, et al. Improving photocatalytic activity by construction of immobilized Z-scheme CdS/Au/TiO_2 nanobelt photocatalyst for eliminating norfloxacin from water. J Colloid Interface Sci, 2021, 586, 243

[72] Lv X C, Yan D Y S, Lam F L Y, et al. Solvothermal synthesis of copper-doped BiOBr microflowers with enhanced adsorption and visible-light driven photocatalytic degradation of norfloxacin. Chem Eng J, 2020, 401, 126012

[73] Behera A, Kandi D, Mansingh S, et al. Facile synthesis of $ZnFe_2O_4$@RGO nanocomposites towards photocatalytic ciprofloxacin degradation and H_2 energy production. J Colloid Interface Sci, 2019, 556, 667

[74] Chen M X, Dai Y Z, Guo J, et al. Solvothermal synthesis of biochar@$ZnFe_2O_4$/BiOBr Z-scheme heterojunction for efficient photocatalytic ciprofloxacin degradation under visible light. Appl Surf Sci, 2019, 493, 1361

[75] Xu X F, Chen J, Lai G X, et al. Theoretical study on enhancing the monolayer MoS 2 photocatalytic water splitting with alloying and stress. J Fuel Chem Technol, 2020, 48, 321

[76] Wang G W, Zhang H G, Wang M, et al. Morphology-dependent photocatalytic activity of TiO_2 crystals. Indian J Chem Sect A, 2020, 59, 646

[77] Gupta S K, Tripathi D C, Garg A, et al. Determination of defect states and surface photovoltage in PTB7: PC71BM based bulk heterojunction solar cells. Sol Energy Mater Sol Cells, 2021, 224, 110994

[78] Nam H J, Amemiya T, Murabayashi M, et al. The influence of Na^+ on the crystallite size of TiO_2 and the photocatalytic activity. Res Chem Intermed, 2005, 31, 365

[79] Wang H, Tang Q, Chen Z, et al. Recent advances on silica-based nanostructures in photocatalysis. Sci China Mater, 2020, 63, 2189

[80] Zalfani M, van der Schueren B, Mahdouani M, et al. ZnO quantum dots decorated 3DOM TiO_2 nanocomposites: Symbiose of quantum size effects and photonic structure for highly enhanced photocatalytic degradation of organic pollutants. Appl Catal B Environ, 2016, 199, 187

[81] Maarisetty D, Baral S S. Defect engineering in photocatalysis: Formation, chemistry, optoelectronics, and interface studies. J Mater Chem A, 2020, 8, 18560

[82] Serrà A, Philippe L, Perreault F, et al. Photocatalytic treatment of natural waters. Reality or hype? The case of cyanotoxins remediation. Water Res, 2021, 188, 116543

[83] Kang F W, Sun G H, Boutinaud P, et al. Recent advances and pro-

spects of persistent luminescent materials as inner secondary self-luminous light source for photocatalytic applications. Chem Eng J, 2021, 403, 126099

[84] Patiphatpanya P, Intaphong P, Phuruangrat A, et al. Effect of ph on photocatalytic activities of biobr nanomaterials synthesized by sonochemical method. Dig J Nanomater Biostructures, 2020, 15, 115

[85] Lotfi S, Fischer K, Schulze A, et al. Photocatalytic degradation of steroid hormone micropollutants by TiO_2-coated polyethersulfone membranes in a continuous flow-through process. Nat Nanotechnol, 2022, 17, 417

Jiaxin Song graduated from Northeastern University with a bachelor's degree in 2021 and is now studying for a master's degree in Jiangsu University under the supervision of Professor Cao Dawei. Her main research interest is the regulation of photocatalytic degradation efficiency of ferroelectric materials.

Malik Ashtar received Master's degree from Air University Islamabad in 2015 and PhD from the prestigious Huazhong University of Science and Technology, Wuhan in 2021. At present, he is diligently contributing as a postdoc fellow at Jiangsu University. His research mainly revolves around the intricate domains of frustrated magnetic materials and innovative ferroelectric materials.

Ying Yang received her B.Sc. from Huaiyin Normal University in 2008 and Ph.D. from Nanjing University in 2014. Then she worked at the Ilmenau University of Technology as a postdoc. She joined Jiangsu University in 2017 as an Associate Professor. Her research interest includes oxide materials and nonlinear optics.