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Recent advances in wastewater treatment using semiconductor photocatalysts

Jaeyoung Hong[1,2], Ki-Hyun Cho[1], Volker Presser[3,4,5] and Xiao Su[1]

Semiconductor materials demonstrate promising potential for wastewater treatment due to their photocatalytic properties, which can be controlled through the design of the bandgap structure. The photogenerated electron and hole in semiconductor materials provide efficient oxidation/reduction performance for the degradation of pollutants, either directly or indirectly, through the generation of reactive species. Photocatalytic degradation has been utilized to treat contaminants ranging from dyes, chemical precursors, and pharmaceuticals, to diverse organic and inorganic waste. Over the past few years, advances in functional materials have achieved wider light absorption ranges and extended charge carrier lifetime through the doping of heteroatoms or the formation of heterojunctions. Despite these advances, innovative strategies are required to target emerging contaminants with environmental persistence, such as perfluorinated compounds, and improve the efficiency of these nanomaterials in real water matrices in the presence of multicomponent interfering ions. In this review, recent advances on the application of semiconductor catalysts for wastewater treatment and environmental remediation are reviewed, and new approaches that may overcome the current limitations are discussed.

Addresses
[1] Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, IL, 61801, United States
[2] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, IL, 61801, United States
[3] INM – Leibniz Institute for New Materials, 66123, Saarbrücken, Germany
[4] Department of Materials Science and Engineering, Saarland University, 66123, Saarbrücken, Germany
[5] Saarene, Saarland Center for Energy Materials and Sustainability, 66123, Saarbrücken, Germany

Corresponding author: Su, Xiao (x2su@illinois.edu)

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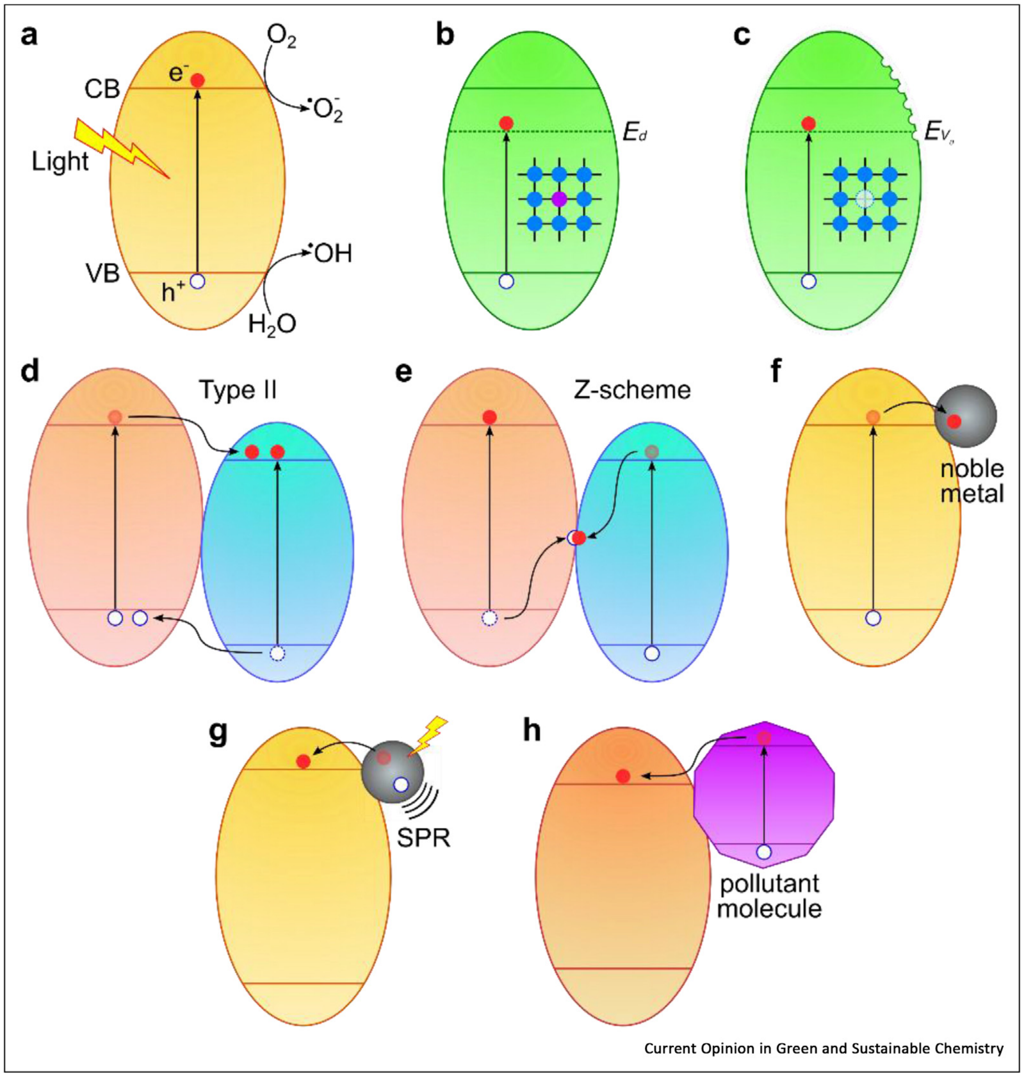
Introduction

Toxic organic molecules and metal ions produced through anthropogenic means are endangering the health of humans and the environment. While great strides have been achieved through electrochemical methods for wastewater treatment, the electrical energy required for the treatment often comes from non-renewable sources, which hampers eco-friendly and sustainable water purification. In this aspect, semiconductor photocatalysts have become a promising emerging approach for water purification and wastewater treatment due to direct sunlight coupling, allowing eco-friendly and mild reaction conditions, coupled with remarkable reactivity for decomposing even trace amounts of pollutants [1]. Our current perspective provides an overview of pollutant degradation in wastewater using semiconductor photocatalysts, focusing on advances from the recent two years. Materials design approaches for photocatalysts have been comprehensively covered by several prior reviews [2–4]. Here, we provide a brief overview of the existing strategies for enhancing light absorption and achieving effective charge separation of semiconductors, and also discuss pathways for system integration of photocatalysts with other separation and reaction approaches towards enabling effective wastewater treatment.

Semiconductor photocatalysts convert clean, renewable solar energy into electrochemical energy. When light irradiates a semiconductor with a bandgap (E_G) close to or smaller than the energy of the light, electrons (e^-) initially in the valence band of the semiconductor are excited to the conduction band which generates free holes (h^+) in the valence band. Depending on the energy level of the band edges, the excited electrons and holes can react with water or oxygen molecules to form reactive chemicals named reactive oxygen species (ROS) such as hydroxyl radical (•OH) and superoxide radical ($\bullet O_2^-$), that can in turn degrade contaminant molecules. At the same time, the charge carriers can directly reduce or oxidize the target chemical species as well (Figure 1a) [5]. Thus, through different chemical pathways, semiconductors can facilitate eco-friendly wastewater treatment.

Semiconductor photocatalysts have been shown to enable the degradation of organic and inorganic pollutants. Dyes have received intense attention as model contaminants for photodegradation, including methylene

Figure 1



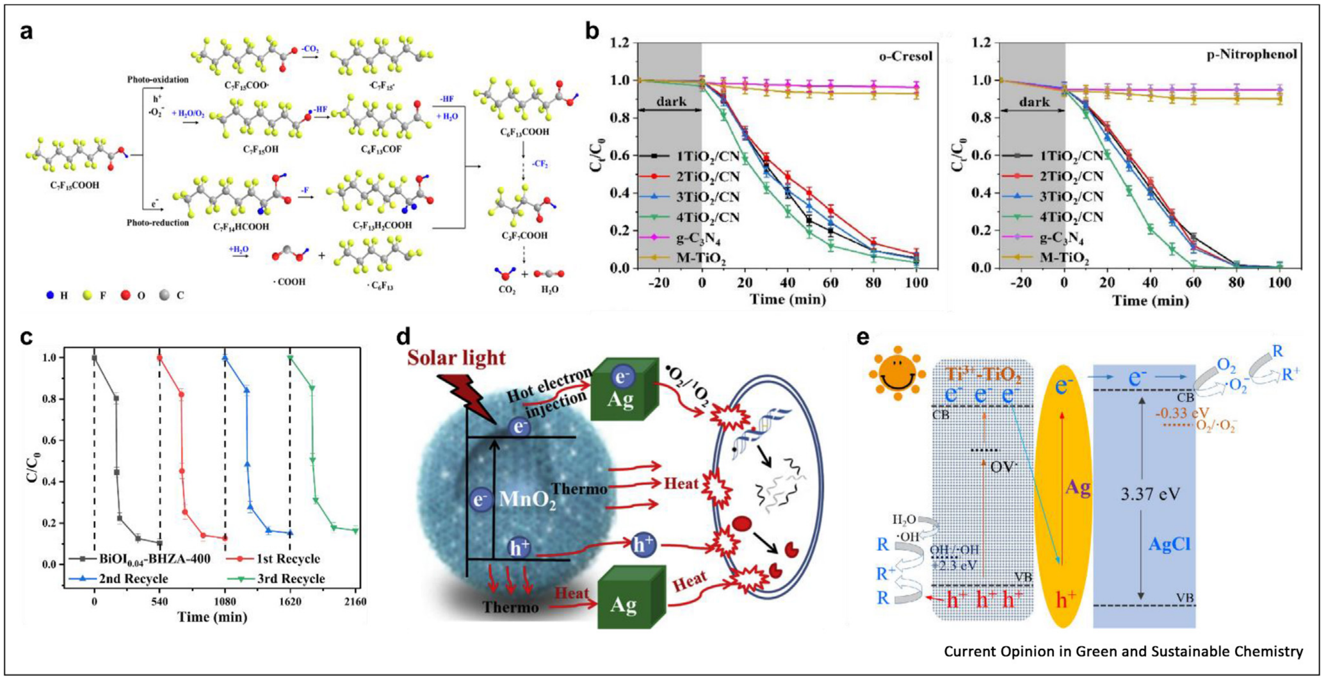
Schematic diagram of the bandgap structure of various photocatalysts. (**a**), Generation of electron (red dot)-hole (blue outlined white dot) pair and following formation of two reactive oxygen species, superoxide radical and hydroxyl radical, upon light irradiation on a semiconductor. (**b–c**), Narrowed band gap due to introduction of defect level by (**b**) heteroatom doping, E_d, and (**c**) vacancy formation, E_{Vo}. Oxygen vacancies on the surface show target adsorption property of it in (**c**). (**d**), Type II heterojunction where both electrons and holes move to more energetically stable CB and VB, respectively. (**e**), Z-scheme heterojunction where electrons in a semiconductor with more positive CB combine with holes in its counterpart with more negative VB. (**f**), Noble metal deposited on the surface of semiconductor working as an electron sink. (**g**), Surface plasmon resonance induced hot electron in noble metal NP flowing into a semiconductor. (**h**), Light-induced electron–hole pair in the surface complex of pollutant on a semiconductor.

blue (MB), methyl orange (MO), and rhodamine B (RhB). Photodegradation has also addressed antibiotics of growing concern such as tetracycline (TC), enrofloxacin (ENR), and other pharmaceuticals including diclofenac. In addition, other toxic chemicals such as phenol and cyanide, heavy metal ions including Cr(VI), and bacteria like *E. coli* have been the subject of the photocatalytic water treatment [6]. Remarkably, even exceptionally stable molecules such as per- and polyfluoroalkyl substances (PFAS) were revealed to be degradable with photocatalysts (Figure 2a), as described in detail in several reviews [7,8]. Finally, more recently, photocatalysts have even been shown to be capable of dissolving and recovering precious metals from e-waste [9]. This noteworthy reactivity towards various toxic substances makes semiconductor photocatalysts a promising approach for sustainable environmental remediation and even resource recovery.

Conventional strategies to improve photocatalytic activity

Two major parameters dictate the photocatalytic activity of semiconductors and thereby their capability to decompose contaminants: bandgap and charge carrier

Figure 2



Schematic diagram of the bandgap structure of various photocatalysts. (**a**), Proposed photocatalytic degradation mechanism of PFOA with BiOF nanosheets. Reproduced with permission from Wang et al. [16], Copyright 2021 Elsevier. (**b**), Degradation of *o*-cresol and *p*-nitrophenol over time upon visible light irradiation in the presence of TiO_2/g-C_3N_4 photocatalysts. Reproduced with permission from Qu et al. [21], Copyright 2021 Elsevier. (**c**), Recyclability of Bi_5O_7I/ZnO photocatalysts toward PFOA degradation. Reproduced with permission from Yang et al. [22], Copyright 2021 Elsevier. (**d**), Schematic diagram showing photothermal catalytic removal of antibiotics. Reproduced with permission from Xia et al. [32], Copyright 2018 Elsevier. (**e**), Proposed pollutant removal mechanism of intricately structured photocatalysts. Reproduced with permission from Yu et al. [37], Copyright 2020 Elsevier.

lifetime. Given that more than half of sunlight is composed of visible light, materials possessing a narrower bandgap can utilize a more significant portion of sunlight, which can improve photocatalytic efficiency. Secondly, photogenerated electrons and holes are likely to interact when spatially close and this recombination leads to their annihilation before reaching the semiconductor's surface where photocatalytic reactions occur, thereby losing photocatalytic activity. In addition to these two parameters, the stability of semiconductors is one factor that should be considered for efficient use in wastewater treatment. Some semiconductors suffer from the photocorrosion, in which excited electrons or holes reduce or oxidize a semiconductor itself under illumination, leading to the decomposition of the semiconductors and subsequent contamination of water. To avoid this detrimental process, oxide semiconductors are often favored due to their high electrical and physical stability.

To achieve higher light absorption and longer charge carrier lifetime, the materials design strategies often can be categorized along two paths: introducing point defects in semiconductors, or forming heterostructures with multiple semiconductors and other materials [4]. Defects can introduce additional energy levels between the valence and conduction band, enhancing light absorption by lowering the effective bandgap. Meanwhile, the formation of heterojunction between two different materials can facilitate effective charge separation and thereby induce a longer charge carrier lifetime [10]. The specific strategies will be discussed below with a concentration of photocatalysts and target contaminants labeled next to each substance in brackets.

Introducing point defects

The introduction of point defects adds extra energy levels to a semiconductor, in which electrons can be excited from defect levels to the conduction band or from the valence band to defect levels depending on its position, thereby allowing a semiconductor to absorb light with smaller energy than its bandgap. However, the defect site can also act as a recombination site of photogenerated electrons and holes, inhibiting charge carriers from participating in the pollutant degradation reactions [11]. However, there is a limitation in inducing a large concentration of point defects in nanomaterials, which are widely used as photocatalysts, owing to the relatively unstable nature of nanomaterials [12].

Doping heteroatoms

Doping heteroatoms in the semiconductor is a commonly used method to add additional energy levels in the middle of the bandgap, leading to an increase in the absorption range of light (Figure 1b). Doping boron to originally UV active ZnO (B-doped ZnO, B−ZnO) nanoparticles (NP) (1.4 g/L) enabled it to degrade 89% of cyanide (10 mg/L) in 2 h under visible light [13]. Fe doping lowered the bandgap of CeO_2 NP (2 g/L) and facilitated Congo red (CR) dye (25 mg/L) degradation under visible light, resulting in 96% removal in 3 h [14]. While doping could enhance the light absorption efficiency, there needs to be consideration that the energy level of the semiconductor is adequate relative to carry out the oxidation/reduction processes that ensure that the reactive species are still formed, to subsequently enable degradation. Bandgap control needs to be performed within the range where the photocatalyst does not lose the capability to decompose the target contaminants.

Oxygen vacancy

Oxygen vacancies can enhance the photocatalytic behavior of semiconductors by inducing defect energy levels, and by serving as adsorption sites for organic molecules (Figure 1c) [15]. Oxygen vacancy induced in (101) faceted BiOF nanosheets (0.7 g/L) narrowed the bandgap to the extent that it could effectively degrade PFOA (15 mg/L) to 100% efficiency in 6 h, under UV [16]. Oxygen vacancy improved light absorption efficiency of $Nb-Bi_2WO_6$ nanosheets (0.5 g/L, 0.3 g/L) by widening the valence band, which facilitated the 100% and 65% degradation of RhB (10 mg/L) and TC (20 mg/L), respectively, under visible light in 2 h [17]. In addition, the capability of oxygen vacancy on the surface of In_2O_3 to adsorb PFOA was critical for MnO_x/In_2O_3 nanorods (0.5 g/L) in degrading PFOA as the hole can directly attack PFOA when the contaminant comes in contact with the surface of the photocatalyst. It removed 99.8% of PFOA (50 mg/L) from the solution under solar light in 3 h, assisted by improved charge separation through heterojunction [18]. However, the controllable formation of oxygen vacancy on the surface remains a challenge and a meticulous approach is required in tuning its concentration as oxygen vacancy can serve as an electron−hole recombination center which deteriorates the activity of photocatalysts [16].

Heterojunction formation

The junction between two different semiconductors changes the electronic band configuration of the system depending on type: type I, II, III, and Z-scheme. Among them, type II or Z-scheme heterojunction are mostly adopted as charge carriers that can be spatially separated to improve the charge carrier lifetime, and enhance light absorption of the photocatalysts [19,20]. A difference in the band structure induces the migration of electrons and holes through the heterojunction interface. However, the interface itself could deteriorate charge transfer between two components of heterojunction or act as a recombination site, both of which are harmful in terms of photocatalytic activity [11].

Type II heterojunction

Type II heterojunction refers to the case where both the conduction band and valence band of one component are more positive than those of the other. Photogenerated electrons accumulate on a more positive conduction band, while holes are collected on a more negative, spatially separated valence band (Figure 1d). More than 95% of phenolic compounds (20 mg/L) such as *o*-cresol, *p*-cresol, *p*-nitrophenol, and phenol were removed by defect-rich $TiO_2/g\text{-}C_3N_4$ (0.75 g/L) under visible light within 100 min (Figure 2b) [21]. Remarkably, 91% of a PFOA solution (1 mg/L) was also successfully degraded with Bi_5O_7I/ZnO microspheres (0.5 g/L) in 6 h under visible light (a few recycling cycles were demonstrated; Figure 2c) [22]. In addition, TC (30 mg/L) was nearly fully degraded with inverse opal TiO_2/CdS nanocomposites (0.3 g/L) in 10 min under visible light [23]. Meanwhile, a ternary heterojunction Co_3O_4/(001)/(101) TiO_2 nanosheet (0.5 g/L) was able to degrade 93% of ENR and about 70% of both ciprofloxacin (CIP) and ibuprofen (IBU) (all 10 mg/L) in 1 h due to enhanced charge separation between two different facet TiO_2 nanosheets [24]. Nevertheless, type II heterojunction inevitably adopts weaker oxidation and reduction power of component semiconductors on account of the nature of it [25].

Z-scheme heterojunction

Z-scheme heterojunction can overcome the disadvantages of type-II band structure and point defects. Although Z-scheme heterojunction has the same bandgap configuration as type II, electrons and holes transfer in a different way. At the interface, excited electrons generated in a semiconductor with a more positive conduction band recombine with holes generated in the other with a more negative valence band so that this heterostructure can exhibit higher reduction and oxidation power (Figure 1e). For instance, AgI $NP/Zn_3V_2O_8$ nanosheet Z-scheme heterojunction (0.33 g/L) could degrade 91% of TC (20 mg/L) in 140 min under visible light, which would have been impossible if it had been type II [26]. More than 99% of RhB (30 ppm) and MB (10 ppm) also could be destroyed by Ag_3PO_4/WO_3 nanocomposite (1 g/L) in 6 min and $Mn-Bi_2WO_6$/graphene oxide (GO)/MoS_2 ternary nanocomposite (0.5 g/L) in 1 h under visible light [27,28]. Although Z-scheme seems superior to type II, there is also a limitation in the selection of materials to obtain this specific type of heterojunction as the type is determined by the Fermi level of the compound [29], which is an inherent property of a material.

Composite integration with non-semiconductor materials

Noble metal

Noble metal NPs deposited on a semiconductor can act as an electron trap site that assists charge separation (Figure 1f). For example, Ag NPs on CdSe deposited on GO/cellulose acetate support (120 g/L) facilitated degradation of malachite green dye (5 ppm), resulting in 97% removal in 25 min under solar light [30]. Light-induced surface plasmon resonance (SPR) of Au NPs generates hot electrons (Figure 1g), enhancing the photocatalytic dye degradation behavior of Bi_2S_3 (0.5 g/L) under visible light [31]. Besides, Ag-doped MnO_2 porous microsphere (0.2 g/L) could completely inactivate *E. coli* (10^7 cfu/mL) in 10 min through photo-thermocatalytic reaction under sunlight due to Ag atoms deposited on the surface of MnO_2 (Figure 2d) [32]. Still, usage of noble metal may be limited given the scarcity and high-cost of these critical resources.

Surface complex

In some cases, organic molecules could form a complex with a semiconductor, which can be activated by light (Figure 1h). 10 mg/L of TC formed TC-TiO_2 NP complex on the surface of TiO_2 NP (0.2 g/L), and this enabled 25.1% removal of TC even under 700 nm light in 2 h [33]. It showed up to 77% removal depending on wavelength within the visible light range. Meanwhile, 0.05 mM of peroxymonosulfate (PMS) formed a complex with TiO_2 nanotubes and was activated by visible light to generate sulfate radical ($\bullet SO_4^-$) that degraded 94.6% of BPA in solution (1 mg/L) in 30 min [34]. Going forward, a systematic exploration of these surface complex-forming molecules should be carried out, in conjunction with careful surface spectroscopy, to understand the pathways for interfacial interaction of these molecules and even design tailored photocatalysts to take advantage of these effects.

Other heterostructures

Finally, there are several other heterostructure photocatalysts of interest for wastewater treatment. Polypropylene (PP) microplastic was shown to be degradable by ZnO photocatalysts. The volume of PP particles (70 mg/L) decreased by 65% over two weeks under visible light in the solution with ZnO nanorods on glass fibers (60 mg of nanorods on 10 g of fiber) [35]. Carbon QD implanted CdS nanosheet (0.2 g/L) formed heterostructure inducing lowered band gap and suppressed recombination, and this reduced 94% of Cr(IV) (20 mg/L) in 10 min under visible light [36]. Cooperation of several approaches covered above was also tested in the following works. Ag/AgCl@Ti^{3+}-TiO_2 mesocrystals (0.5 g/L) showed 90% removal of TC (50 mg/L) in 24 min and about 55% removal of real industrial paraester wastewater in 2 h under visible light [37]. Defect levels in TiO_2 enabled the formation of electron−hole pairs under visible light, while hot electrons formed in Ag due to light-induced SPR transferred to AgCl to make superoxide radical and holes left in Ag combined with electrons in TiO_2 to form Z-scheme heterojunction, all improving overall degradation efficiency (Figure 2e). Likewise, Bi/$BiOI_{1-x}F_x$ hollow microsphere (0.4 g/L) degraded almost all PFOA (40 mg/L) under visible light in 2 h, due to the lowered band gap of the semiconductor material originating from F doping, the SPR effect of Bi, and large surface area coming from its hollow structure [38].

Conclusions and perspectives

As discussed, there have been significant advances and improvements in the photocatalytic performance of semiconductor materials for wastewater treatment and water purification. To achieve higher degradation efficiencies for contaminants, recent work has been focused on engineering material properties, such as introducing point defects and creating heterojunctions that can lead to improved photocatalytic performance. Adoption of these strategies has improved the effectiveness of these materials for the elimination of both organic and inorganic contaminants, even under solar irradiation. However, critical limitations and challenges remain to be solved before widespread commercialization of these photocatalysts. Important challenges are the scalability and stability of photocatalysts for practical wastewater and groundwater matrices. There is a need to create materials with sufficient longevity, to make the photodegradation process economically feasible on the long-term. Even though certain photocatalysts can achieve close to 100% degradation of pollutants under visible light, the technology remains limited to lab-scale experiments (Table 1). In addition, considering most studied photocatalysts have nanostructures that could be possibly sensitive to degradation or morphology changes, stability checks should be performed in a more rigorous manner beyond just a few cycles. For example, higher number of cycles across different pH solutions [39] could potentially demonstrate the effectiveness of these materials in real wastewater applications.

The study of the effect of interfering species in real wastewater is critical, as many other species present in the solutions may negatively affect photocatalytic properties. Since wastewater has a range of species in excess of the target molecules, the use of real water matrices or synthetic matrices with these interfering species can help de-risk the application of semiconductor photocatalysts for practical wastewater

Table 1

Various photocatalysts modification approaches for enhanced degradation of pollutants.

CapType	Materials	Dose (g/L)	Target pollutant	Concentration	Degradation (in %)/time (in h)	Activation source	References
Doping	B−ZnO	1.4	Cyanide	10 mg/L	89%/2	Solar light	[13]
	Fe−CeO_2	2	CR	25 mg/L	96%/3	Visible light	[14]
Oxygen vacancy	(101) BiOF nanosheet	0.7	PFOA	15 mg/L	100%/6	UV	[16]
	MnO_x/In_2O_3	0.5	PFOA	50 mg/L	99.8%/3	Solar light	[18]
	Nb−Bi_2WO_6	0.5, 0.3	RhB, TC	10, 20 mg/L	100, 65%/2	Visible light	[17]
Type II hetero-junction	Bi_5O_7I/ZnO	0.5	PFOA	1 mg/L	91%/6	Visible light	[22]
	Defect-rich TiO_2/g-C_3N_4	0.75	*o*-cresol, *p*-cresol, *p*-nitrophenol, phenol	20 mg/L	>95%/1.67	Visible light	[21]
	inverse opal TiO_2/CdS	0.3	TC, RhB	30 mg/L	99, 60%/0.33	Visible light	[23]
	Co_3O_4 NP/(001)/(101) TiO_2 nanosheet	0.5	ENR, CIP, IBU	10 mg/L	93, 75, 70%/1	Visible light	[24]
Z-scheme hetero-junction	Mn−Bi_2WO_6/GO/MoS_2	0.5	MB	10 ppm	99%/1	Solar light	[28]
	AgI NP/$Zn_3V_2O_8$ nanosheet	0.33	TC	20 mg/L	91%/2.33	Visible light	[26]
	Ag_3PO_4/WO_3	1	RhB	30 ppm	99.9%/0.1	Visible light	[27]
With noble metal	Ag atom/MnO_2	0.2	*E. coli*	10^7 cfu/mL	100%/0.17	Solar light	[32]
	Au NP/Bi_2S_3	0.5	RhB, MO	17.2, 92.7 μM	95%, 97%/1.5	Solar light	[31]
	Ag NP/CdSe/GO/cellulose acetate	120	Malachite green	5 ppm	97%/0.42	Visible light	[30]
Surface complex	TC-TiO_2	0.2	TC	10 mg/L	25−77%/2	Visible light	[33]
	PMS-TiO_2 nanotube electrode	PMS 50 μM	BPA	1 mg/L	94.6%/0.5	Visible light	[34]
Other hetero-structures	ZnO nanorod/glass fiber	6 mg/g	PP microplastic	70 mg/L	65%/2 weeks	Visible light	[35]
	Carbon QD/CdS nanosheet	0.2	Cr(IV)	20 mg/L	94%/0.17	Visible light	[36]
	Ag/AgCl@Ti^{3+}-TiO_2	0.5	TC para-ester wastewater	50 mg/L –	90%/0.4 55%/2	Visible light	[37]
	Bi/$BiOI_{1-x}F_x$ hollow microsphere	0.4	PFOA	40 mg/L	100%/2	Visible light	[38]

applications. For instance, solutions with inorganic ions such as CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, Cl^-, and Cu^{2+} can have a detrimental effect on performance, and confirming photocatalytic activity in the presence of these ions is critical for translation to real world applications in groundwater and industrial wastewater [24,39]. Moreover, the presence of other photocatalytic-active pollutants may affect the degradation behavior of the target molecules [40], so performing studies in the presence of other photodegradable species can be important as well.

In this context, integration with electrochemically-driven advanced separations could be a promising pathway in overcoming challenges from interfering species during the wastewater treatment. For example, the selectivity of photocatalysts can be enhanced through the separation and concentration of the target molecules from competing molecules [41−44]. Several redox-active materials, including organic conducting polymers and metallopolymers, were reported and utilized to selectively adsorb ionic species depending on the redox state of functional groups in the polymers [44]. TEMPO-based copolymers were able to selectively separate PFOA from water through a combination of electrostatics and affinity interactions [42]. Characteristic affinity properties depending on the type of polymer can even achieve selectivity between structurally close anions [45]. Coupling intrinsically non-selective photocatalysts with selective redox-electrodes can achieve more specific contaminant degradation. Other electrode materials for electrosorption can also potentially be coupled with photocatalysts to enhance overall performance of the systems for contaminant remediation [43]. Among them, MXene, layer structured metal carbides, nitrides, or carbonitrides, could improve overall efficiency of water treatment system by virtue of its hydrophilic nature and intercalation-based pseudocapacitive nature [46−

48]. It can also serve as a large surface area support for photocatalysts or components of heterojunction photocatalysts [49], thereby consolidating separation and degradation of target molecules.

Moreover, electrochemistry-based separation systems could potentially couple with the photoelectrochemical (PEC) degradation of pollutants, to enable sustainable process intensification. Electrochemistry can amplify charge separation, dragging photogenerated electrons from the photocatalyst to the electrical circuit under anodic potentials [15,50–53], while the electrode itself can contribute to the formation of reactive radicals. In addition, PEC can potentially advance the efficient degradation of stable fluorine-containing pharmaceuticals and PFAS, which are often challenging compounds to decompose. Provided that a number of widely studied photocatalysts carry toxic elements by themselves, further development of PEC technologies can explore the tradeoff between the utilization of environmentally-benign materials and degradation efficiency [54]. Thus, moving forward, the integration of photocatalyst with electrochemical systems presents a unique opportunity to bring innovation and green chemistry concepts into wastewater treatment.

Declaration of competing interest

The authors declare the following financial interests/personal relationships that may be considered as potential competing interests: Xiao Su reports financial support was provided by National Science Foundation.

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References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

1. Villaseñor MJ, Ríos Á: **Nanomaterials for water cleaning and desalination, energy production, disinfection, agriculture and green chemistry**. *Environ Chem Lett* 2017, **16**:11–34. https://doi.org/10.1007/s10311-017-0656-9.

2. Dong S, Feng J, Fan M, Pi Y, Hu L, Han X, Liu M, Sun J, Sun J: **Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: a review**. *RSC Adv* 2015, **5**:14610–14630. https://doi.org/10.1039/C4RA13734E.

3. Lee KM, Lai CW, Ngai KS, Juan JC: **Recent developments of zinc oxide based photocatalyst in water treatment technology: a review**. *Water Res* 2016, **88**:428–448. https://doi.org/10.1016/j.watres.2015.09.045.

4. Ge J, Zhang Y, Heo Y-J, Park S-J: **Advanced design and synthesis of composite photocatalysts for the remediation of wastewater: a review**. *Catalysts* 2019, **9**:122. https://doi.org/10.3390/catal9020122.

5. Li Y, Jiang H, Wang X, Hong X, Liang B: **Recent advances in bismuth oxyhalide photocatalysts for degradation of organic pollutants in wastewater**. *RSC Adv* 2021, **11**:26855–26875. https://doi.org/10.1039/d1ra05796k.

6. Ren G, Han H, Wang Y, Liu S, Zhao J, Meng X, Li Z: **Recent advances of photocatalytic application in water treatment: a review**. *Nanomaterials* 2021, **11**:1804. https://doi.org/10.3390/nano11071804.

7. * Leonello D, Fendrich MA, Parrino F, Patel N, Orlandi M, Miotello A: **Light-induced advanced oxidation processes as PFAS remediation methods: a review**. *Appl Sci* 2021, **11**:8458. https://doi.org/10.3390/app11188458.

This review provides health issue that PFAS may cause and summarizes several approaches in utilization of light in degradation of PFAS and underlying mechanism.

8. Olatunde OC, Kuvarega AT, Onwudiwe DC: **Photo enhanced degradation of polyfluoroalkyl and perfluoroalkyl substances**. *Heliyon* 2020, **6**, e05614. https://doi.org/10.1016/j.heliyon.2020.e05614.

9. Chen Y, Xu M, Wen J, Wan Y, Zhao Q, Cao X, Ding Y, Wang ZL, Li H, Bian Z: **Selective recovery of precious metals through photocatalysis**. *Nat Sustain* 2021, **4**:618–626. https://doi.org/10.1038/s41893-021-00697-4.

10. Cai H, Wang B, Xiong L, Bi J, Yuan L, Yang G, Yang S: **Orienting the charge transfer path of type-II heterojunction for photocatalytic hydrogen evolution**. *Appl Catal B Environ* 2019, **256**, 117853. https://doi.org/10.1016/j.apcatb.2019.117853.

11. Kudo A, Miseki Y: **Heterogeneous photocatalyst materials for water splitting**. *Chem Soc Rev* 2009, **38**:253–278. https://doi.org/10.1039/B800489G.

12. NatureErwin SC, Zu L, Haftel MI, Efros AL, Kennedy TA, Norris DJ: **Doping semiconductor nanocrystals**. *Nature* 2005, **436**:91–94. https://doi.org/10.1038/nature03832.

13. Núñez-Salas RE, Hernández-Ramírez A, Hinojosa-Reyes L, Guzmán-Mar JL, Villanueva-Rodríguez M, Maya-Treviño MdL: **Cyanide degradation in aqueous solution by heterogeneous photocatalysis using boron-doped zinc oxide**. *Catal Today* 2019, **328**:202–209. https://doi.org/10.1016/j.cattod.2018.11.061.

14. Aboutaleb WA, El-Salamony RA: **Effect of Fe2O3-CeO2 nanocomposite synthesis method on the Congo red dye photodegradation under visible light irradiation**. *Mater Chem Phys* 2019, **236**, 121724. https://doi.org/10.1016/j.matchemphys.2019.121724.

15. Di Y, Liu L, Ma H, Ma C, Dong X, Fu Y: **Bi doping into Ti/Co3O4 NWs (nanowires) for improved photoelectrochemical decolorization of dyeing wastewater (reactive brilliant blue KN-R)**. *J Mater Sci Mater Electron* 2020, **31**:9504–9513. https://doi.org/10.1007/s10854-020-03492-7.

16. * Wang J, Cao C, Zhang Y, Zhang Y, Zhu L: **Underneath mechanisms into the super effective degradation of PFOA by BiOF nanosheets with tunable oxygen vacancies on exposed (101) facets**. *Appl Catal B Environ* 2021, **286**, 119911. https://doi.org/10.1016/j.apcatb.2021.119911.

Degradation pathway of PFOA was studied with DFT calculations and various experiments including liquid chromatography and mass spectroscopy. Both oxidative and reductive mechanism were proposed.

17. Chen H, Zhang C, Pang Y, Shen Q, Yu Y, Su Y, Wang J, Zhang F, Yang H: **Oxygen vacancy regulation in Nb-doped Bi2WO6 for enhanced visible light photocatalytic activity**. *RSC Adv* 2019, **9**:22559–22566. https://doi.org/10.1039/c9ra02862e.

18. Wu Y, Li Y, Fang C, Li C: **Highly efficient degradation of perfluorooctanoic acid over a MnOx-modified oxygen-vacancy-rich In2O3 photocatalyst**. *ChemCatChem* 2019, **11**:2297–2303. https://doi.org/10.1002/cctc.201900273.

19. Low J, Yu J, Jaroniec M, Wageh S, Al-Ghamdi AA: **Heterojunction photocatalysts**. *Adv Mater* 2017, **29**, 1601694. https://doi.org/10.1002/adma.201601694.

20. Khurram R, Wang Z, Ehsan MF: **α-Fe2O3-based nanocomposites: synthesis, characterization, and photocatalytic response towards wastewater treatment**. *Environ Sci Pollut*

Res Int 2021, **28**:17697–17711. https://doi.org/10.1007/s11356-020-11778-w.

21. * Qu X, Chen C, Lin J, Qiang W, Zhang L, Sun D: **Engineered defect-rich TiO2/g-C3N4 heterojunction: a visible light-driven photocatalyst for efficient degradation of phenolic wastewater**. *Chemosphere* 2022, **286**, 131696. https://doi.org/10.1016/j.chemosphere.2021.131696.

Four kinds of phenolic wastewater were degraded by small sized defect-rich TiO_2 nanoparticles anchored on g-C_3N_4 nanosheet under visible light. It was synthesized via pyrolysis of MOF and this enabled large contact area between TiO_2 and g-C_3N_4.

22. * Yang Y, Ji W, Li X, Zheng Z, Bi F, Yang M, Xu J, Zhang X: **Insights into the degradation mechanism of perfluorooctanoic acid under visible-light irradiation through fabricating flower-shaped Bi5O7I/ZnO n-n heterojunction microspheres**. *Chem Eng J* 2021, **420**, 129934. https://doi.org/10.1016/j.cej.2021.129934.

Heterojunction between Bi_5O_7I and ZnO enabled successful degradation of PFOA under visible light. Degradation pathway was investigated with liquid and ion chromatography and mass spectrometry to reveal that PFOA becomes shorter chain perfluorocarboxylic acids over time.

23. * Lv C, Lan X, Wang L, Dai X, Zhang M, Cui J, Yuan S, Wang S, Shi J: **Rapidly and highly efficient degradation of tetracycline hydrochloride in wastewater by 3D IO-TiO2-CdS nanocomposite under visible light**. *Environ Technol* 2021, **42**: 377–387. https://doi.org/10.1080/09593330.2019.1629183.

This work reports the effect of novel design on photocatalytic performance of TiO_2/CdS nanocomposite. Honeycomb-like structured inverse opal TiO_2 showed higher tetracycline degradation efficiency under visible light compared to ordinary bulk TiO_2, destroying most of tetracycline within just 20 min.

24. Wu Y, Li Y, Hu H, Zeng G, Li C: **Recovering hydrogen energy from photocatalytic treatment of pharmaceutical-contaminated water using Co3O4 modified {001}/{101}-TiO2 nanosheets**. *ACS EST Engg* 2021, **1**:603–611. https://doi.org/10.1021/acsestengg.1c00003.

25. Low J, Yu J, Jaroniec M, Wageh S, Al-Ghamdi AA: **Heterojunction photocatalysts**. *Adv Mater* 2017, **29**, 1601694. https://doi.org/10.1002/adma.201601694.

26. Luo J, Ning X, Zhan L, Zhou X: **Facile construction of a fascinating Z-scheme AgI/Zn3V2O8 photocatalyst for the photocatalytic degradation of tetracycline under visible light irradiation**. *Separ Purif Technol* 2021, **255**, 117691. https://doi.org/10.1016/j.seppur.2020.117691.

27. You L, Gao M, Li T, Guo L, Chen P, Liu M: **Investigation of the kinetics and mechanism of Z-scheme Ag3PO4/WO3 p–n junction photocatalysts with enhanced removal efficiency for RhB**. *New J Chem* 2019, **43**:17104–17115. https://doi.org/10.1039/c9nj04369a.

28. Tahir N, Zahid M, Bhatti IA, Jamil Y: **Fabrication of visible light active Mn-doped Bi2WO6-GO/MoS2 heterostructure for enhanced photocatalytic degradation of methylene blue**. *Environ Sci Pollut Res Int* 2021. https://doi.org/10.1007/s11356-021-16094-5.

29. Xu Q, Zhang L, Yu J, Wageh S, Al-Ghamdi AA, Jaroniec M: **Direct Z-scheme photocatalysts: principles, synthesis, and applications, Mater**. *Today Off* 2018, **21**:1042–1063. https://doi.org/10.1016/j.mattod.2018.04.008.

30. Ahmed MK, Shalan AE, Afifi M, El-Desoky MM, Lanceros-Mendez S: **Silver-doped cadmium selenide/graphene oxide-filled cellulose acetate nanocomposites for photocatalytic degradation of malachite green toward wastewater treatment**. *ACS Omega* 2021, **6**:23129–23138. https://doi.org/10.1021/acsomega.1c02667.

31. Nwaji N, Akinoglu EM, Giersig M: **Gold nanoparticle-decorated Bi2S3 nanorods and nanoflowers for photocatalytic wastewater treatment**. *Catalysts* 2021, **11**:355. https://doi.org/10.3390/catal11030355.

32. Xia D, Liu H, Xu B, Wang Y, Liao Y, Huang Y, Ye L, He C, Wong PK, Qiu R: **Single Ag atom engineered 3D-MnO2 porous hollow microspheres for rapid photothermocatalytic inactivation of E. coli under solar light**. *Appl Catal B Environ* 2019, **245**:177–189. https://doi.org/10.1016/j.apcatb.2018.12.056.

33. ** Wu S, Hu H, Lin Y, Zhang J, Hu YH: **Visible light photocatalytic degradation of tetracycline over TiO2**. *Chem Eng J* 2020, **382**, 122842. https://doi.org/10.1016/j.cej.2019.122842.

This article reports the photodegradation of tetracycline under visible light with pure TiO_2 photocatalyst for the first time. TiO_2 and tetracycline formed surface complex which could be excited by visible light.

34. Jia J, Liu D, Wang S, Li H, Ni J, Li X, Tian J, Wang Q: **Visible-light-induced activation of peroxymonosulfate by TiO2 nanotubes arrays for enhanced degradation of bisphenol A**. *Separ Purif Technol* 2020, **253**, 117510. https://doi.org/10.1016/j.seppur.2020.117510.

35. ** Uheida A, Mejía HG, Abdel-Rehim M, Hamd W, Dutta J: **Visible light photocatalytic degradation of polypropylene microplastics in a continuous water flow system**. *J Hazard Mater* 2021, **406**, 124299. https://doi.org/10.1016/j.jhazmat.2020.124299.

This article reports degradation of microplastic using ZnO photocatalyst. ZnO nanorods deposited on glass fibers degraded polypropylene microplastics under visible light. plastic volume has decreased more than half over two weeks and the toxicity of degradation byproducts was examined.

36. Zhang Y, Zhao Y, Xu Z, Su H, Bian X, Zhang S, Dong X, Zeng L, Zeng T, Feng M: **Carbon quantum dots implanted CdS nanosheets: efficient visible-light-driven photocatalytic reduction of Cr (VI) under saline conditions**. *Appl Catal B Environ* 2020, **262**, 118306. https://doi.org/10.1016/j.apcatb.2019.118306.

37. ** Yu X, Huang J, Zhao J, Liu S, Xiang D, Tang Y, Li J, Guo Q, Ma X, Zhao J: **Efficient visible light photocatalytic antibiotic elimination performance induced by nanostructured Ag/AgCl@Ti3+-TiO2 mesocrystals**. *Chem Eng J* 2021, **403**, 126359. https://doi.org/10.1016/j.cej.2020.126359.

The author presents heterostructure photocatalysts targeting tetracycline under visible light irradiation. This composite showed 3.52 and 22.43 times higher performance than Ti^{3+}-TiO_2 and commercial TiO_2, respectively. Possible plasmonic activation mechanism was suggested to describe its working mechanism. The photocatalyst was also tested for real industrial wastewater and showed promising results.

38. ** Wang J, Wang Y, Cao C, Zhang Y, Zhang Y, Zhu L: **Decomposition of highly persistent perfluorooctanoic acid by hollow Bi/BiOI1-xFx: synergistic effects of surface plasmon resonance and modified band structures**. *J Hazard Mater* 2021, **402**, 123459. https://doi.org/10.1016/j.jhazmat.2020.123459.

This article presents collaborative effect of band modification, surface plasmon resonance of metal, and hollow structure that empowered bismuth oxyhalide photocatalyst with high photocatalytic degradation efficiency. Mechanism investigation revealed that superoxide radical was effective in PFOA elimination.

39. Hassan M, Zhao Y, Xie B: **Employing TiO 2 photocatalysis to deal with landfill leachate: current status and development**. *Chem Eng J* 2016, **285**:264–275. https://doi.org/10.1016/j.cej.2015.09.093.

40. Pandiyan R, Dharmaraj S, Ayyaru S, Sugumaran A, Somasundaram J, Kazi AS, Samiappan SC, Ashokkumar V, Ngamcharussrivichai C: **Ameliorative photocatalytic dye degradation of hydrothermally synthesized bimetallic Ag-Sn hybrid nanocomposite treated upon domestic wastewater under visible light irradiation**. *J Hazard Mater* 2022, **421**, 126734. https://doi.org/10.1016/j.jhazmat.2021.126734.

41. Su X, Tan K-J, Elbert J, Rüttiger C, Gallei M, Jamison TF, Hatton TA: **Asymmetric Faradaic systems for selective electrochemical separations**. *Energy Environ Sci* 2017, **10**: 1272–1283. https://doi.org/10.1039/c7ee00066a.

42. Kim K, Baldaguez Medina P, Elbert J, Kayiwa E, Cusick RD, Men Y, Su X: **Molecular tuning of redox-copolymers for selective electrochemical remediation**. *Adv Funct Mater* 2020, **30**, 2004635. https://doi.org/10.1002/adfm.202004635.

43. Srimuk P, Su X, Yoon J, Aurbach D, Presser V: **Charge-transfer materials for electrochemical water desalination, ion separation and the recovery of elements**. *Nat Rev Mater* 2020, **5**: 517–538. https://doi.org/10.1038/s41578-020-0193-1.

44. Su X, Hatton TA: **Redox-electrodes for selective electrochemical separations**. *Adv Colloid Interface Sci* 2017, **244**: 6–20. https://doi.org/10.1016/j.cis.2016.09.001.

45. Chen R, Feng J, Jeon J, Sheehan T, Rüttiger C, Gallei M, Shukla D, Su X: **Structure and potential-dependent selectivity in redox-metallopolymers: electrochemically mediated multicomponent metal separations**. *Adv Funct Mater* 2021, **31**: 2009307. https://doi.org/10.1002/adfm.202009307.

46. Wang Y, Niu B, Zhang X, Lei Y, Zhong P, Ma X: **Ti3C2Tx MXene: an emerging two-dimensional layered material in water treatment**. *ECS J Solid State Sci Technol* 2021, 047002. https://doi.org/10.1149/2162-8777/abf2de.

47. Srimuk P, Kaasik F, Kruner B, Tolosa A, Fleischmann S, Jackel N, Tekeli MC, Aslan M, Suss ME, Presser V: **MXene as a novel intercalation-type pseudocapacitive cathode and anode for capacitive deionization**. *J Mater Chem* 2016, **4**:18265–18271. https://doi.org/10.1039/c6ta07833h.

48. Torkamanzadeh M, Wang L, Zhang Y, Budak O, Srimuk P, Presser V: **MXene/activated-Carbon hybrid capacitive deionization for permselective ion removal at low and high salinity**. *ACS Appl Mater Interfaces* 2020, **12**:26013–26025. https://doi.org/10.1021/acsami.0c05975.

49. Huang K, Li C, Li H, Ren G, Wang L, Wang W, Meng X: **Photocatalytic applications of two-dimensional Ti3C2 MXenes: a review**. *ACS Appl Nano Mater* 2020, **3**:9581–9603. https://doi.org/10.1021/acsanm.0c02481.

50. He S, Yan C, Chen X-Z, Wang Z, Ouyang T, Guo M-L, Liu Z-Q: **Construction of core-shell heterojunction regulating α-Fe2O3 layer on CeO2 nanotube arrays enables highly efficient Z-scheme photoelectrocatalysis**. *Appl Catal B Environ* 2020, **276**, 119138. https://doi.org/10.1016/j.apcatb.2020.119138.

51. Du Y, Zheng Z, Chang W, Liu C, Bai Z, Zhao X, Wang C: **Trace amounts of Co3O4 nano-particles modified TiO2 nanorod arrays for boosted photoelectrocatalytic removal of organic pollutants in water**. *Nanomaterials* 2021, **11**:214. https://doi.org/10.3390/nano11010214.

52. Li L, Feng H, Wei X, Jiang K, Xue S, Chu PK: **Ag as cocatalyst and electron-hole medium in CeO2 QDs/Ag/Ag2Se Z-scheme heterojunction enhanced the photo-electrocatalytic properties of the photoelectrode**. *Nanomaterials* 2020, **10**:253. https://doi.org/10.3390/nano10020253.

53. Goulart LA, Alves SA, Mascaro LH: **Photoelectrochemical degradation of bisphenol A using Cu doped WO3 electrodes**. *J Electroanal Chem* 2019, **839**:123–133. https://doi.org/10.1016/j.jelechem.2019.03.027.

54. Xu T, Ji H, Gu Y, Tong T, Xia Y, Zhang L, Zhao D: **Enhanced adsorption and photocatalytic degradation of perfluorooctanoic acid in water using iron (hydr) oxides/carbon sphere composite**. *Chem Eng J* 2020, **388**, 124230. https://doi.org/10.1016/j.cej.2020.124230.