

# Photo-assisted technologies for environmental remediation

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# **Abstract**

Industrial processes can lead to air and water pollution, particularly from organic contaminants such as toluene and antibiotics, posing threats to human health. Photo-assisted chemical oxidation technologies leverage light energy to mineralize these contaminants. In this Review, we discuss the mechanisms and efficiencies of photo-assisted advanced oxidation processes for wastewater treatment and photothermal technologies for air purification. The integration of solar energy enhances degradation efficiency and reduces energy consumption, enabling more efficient remediation methods. We evaluate the technological aspects of photo-assisted technologies, such as photo-Fenton, photo-persulfate activation, photo-ozonation and photoelectrochemical oxidation, emphasizing their potential for practical applications. Finally, we discuss the challenges in scaling up photo-assisted technologies for specific environmental remediation needs. Photo-assisted technologies have demonstrated effectiveness in environmental remediation, although large-scale applications remain constrained by high costs. Future potential applications of photo-assisted technologies will require that technology selection be tailored to specific pollution scenarios and engineering processes optimized to minimize costs.

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### **Key points**

- Photo-assisted advanced oxidation processes efficiently treat wastewater, whereas photothermal technologies are used in air purification.
- The integration of solar energy can enhance efficiency of remediation processes and reduce energy consumption.
- Solar energy interacts with chemical oxidation processes, which results in the formation of reactive oxygen species that accelerate the degradation of pollutants.
- Wastewater treatments, such as the Fenton oxidation process, consume a high quantity of  $\rm H_2O_2$  and are kinetically slow. Integrating solar energy accelerates the process.
- Using compound parabolic collectors and raceway pond reactors optimizes light harvesting and enables remediation at concentrations of milligrams per litre and below.
- Combining different advanced oxidation technologies can help to reduce energy consumption and widen the range of contaminants that can be mineralized.

### Introduction

Environmental pollution of water and air can adversely affect health and ecosystems<sup>1,2</sup>. Remediation technologies, such as chemical oxidation<sup>3-6</sup>, adsorption and filtration<sup>7,8</sup>, have been developed to eliminate organic pollutants. Among these technologies, advanced oxidation processes (AOPs)<sup>9-11</sup> and thermal catalytic oxidation<sup>12-15</sup> are used because of their versatility and ability to achieve complete mineralization of pollutants, avoiding the generation of secondary pollutants<sup>16</sup>. However, these methods can be costly, highlighting the need for more efficient and cost-effective solutions<sup>17</sup>.

Integrating solar energy into remediation technologies can enhance their efficiency and sustainability $^4$ . Solar energy can interact with chemical oxidation processes to promote the generation of reactive oxygen species (ROS) $^{18-20}$ . This accelerates pollutant degradation and reduces reliance on external energy sources $^{19}$ . For example, in photo-Fenton activation, a typical photo-assisted AOP, the integration of light enhances the AOP efficiency by generating more hydroxyl radicals and enabling the complete mineralization of contaminants with minimal energy input $^{21}$ . Other photobased technologies are also used in water and air purification $^{19}$ .

Despite their potential, several challenges hinder the effectiveness and widespread adoption of light-driven remediation technologies in practical environmental applications. The primary challenge lies in the limited light absorption by catalysts and/or oxidants. This limitation arises from two main factors: suboptimal absorption spectra of the materials, which restrict their activity to a narrow portion of the solar spectrum, and interference caused by impurities in the photo-assisted catalytic reaction systems, which reflect or absorb light<sup>22,23</sup>. The stability of catalysts is also a concern<sup>24,25</sup>, with many going through degradation or deactivation over time, which reduces their effectiveness and leads to ion leakage<sup>24</sup>. Furthermore, the presence of competing substances, including heavy metals, and other co-existing pollutants in

polluted media can interfere with the catalytic process, diminishing the availability of the light-induced reactive species needed for effective remediations<sup>26</sup>. This competition often requires higher catalyst dosages or prolonged reaction times, both of which can negatively affect the overall efficiency and practicality of the remediation technology<sup>27</sup>. Another critical yet often overlooked aspect is the economic viability and sustainability of light-driven remediation technologies<sup>28,29</sup>, particularly for large-scale applications where the costs of catalyst production and energy consumption must be carefully balanced to ensure overall efficiency. Addressing these issues is crucial for advancing the use of light-driven technologies in practical environmental remediation.

In this Review, we introduce the applications of photo-assisted technologies to water and air purification (Fig. 1). We outline different photo-assisted advanced oxidation processes, including photo-Fenton, photo-persulfate activation, photo-ozonation and photoelectrochemical oxidation, for water purification, and highlight their mechanisms and efficiencies. Semiconductor-based photocatalysis is excluded from this Review as we aim to present light as an auxiliary method rather than the primary technical approach. Applications and benefits of photo-assisted thermal technologies for air purification, particularly for volatile organic compound (VOC) treatment, are also discussed. Finally, we evaluate the technology development stage and economic costs of these photo-assisted technologies to assess their practical applicability.

## Water purification

For water purification, oxidation processes such as Fenton oxidation involve high chemical consumption of  $H_2O_2$ , contributing to operational costs<sup>30</sup>. These methods, although effective, underscore the necessity for more efficient solutions to reduce the quantity of  $H_2O_2$  oxidants and the overall cost of the system. Strategies aiming at reducing cost by harnessing the power of light have been proposed to address this challenge<sup>31,32</sup> (Fig. 2). By integrating photochemical techniques such as ultraviolet (UV)-assisted catalysis, the efficiency of antibiotics degradation can be enhanced<sup>33</sup>. This approach reduces overall energy requirements and makes use of renewable energy sources<sup>34</sup>. The incorporation of advanced light-harvesting materials and technologies can optimize the use of natural sunlight, thereby minimizing dependency on fossil-fuel based energy sources<sup>35</sup>.

### **Photo-assisted Fenton oxidation**

The Fenton process generates strong oxidizing species (Fig. 2a), 'OH and Fe(IV)=O, through reactions between Fe(II) and  $H_2O_2$  (ref. 36) (equation (1)). However, the inherent slow reduction kinetics of Fe(III) ( $k=0.01-0.001\,M^{-1}s^{-1}$ ) limit the steady and high-efficiency operation of the Fenton process<sup>37</sup> (equation (2)). Introducing external renewable energy into the Fenton process – known as the photo-Fenton process – is a strategy to accelerate the reaction. Under UV light irradiation, the photoactive Fe(OH)<sup>2+</sup> in the Fenton reaction promotes the reduction of Fe(III) and produces additional 'OH (refs. 38,39) (equation (3)). The photolysis of  $H_2O_2$  also contributes to the extra production of 'OH (equation (4)). Thus, with the assistance of light, both the rate of the Fe(II)/Fe(III) redox cycle and the yield of produced active species in the Fenton reaction are improved, promoting pollutant decomposition<sup>39</sup>.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} k \approx 40 - 80 M^{-1} s^{-1}$$
 (1)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^* + H^+ \quad k \approx 0.001 - 0.01 \,\text{M}^{-1} \,\text{s}^{-1}$$
 (2)

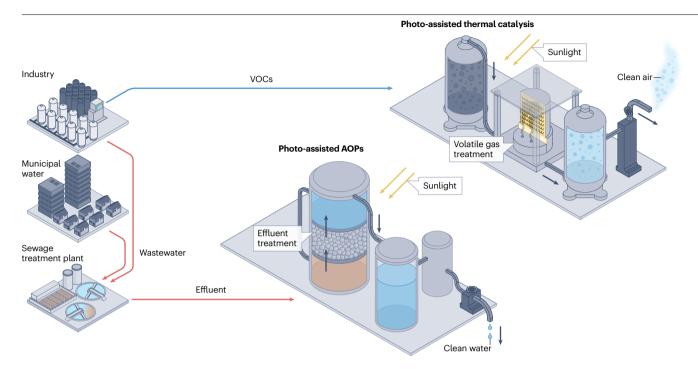


Fig. 1 | Photo-assisted technologies for water and air purification.

Photo-assisted advanced oxidation processes (AOPs) and photo-assisted thermal catalysis can be used for wastewater and air treatment. The wastewater from industries and municipal water usage is collected and transferred into a sewage

treatment plant for treatment. The effluent containing refractory organic pollutants is purified using photo-assisted AOPs. Volatile organic compounds (VOCs) generated from industry can be purified through photo-assisted thermal technologies.

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH$$
 (3)

$$H_2O_2 + h\nu \to 2 \text{ 'OH}$$
 (4)

Another issue in traditional Fenton processes (both homogeneous and heterogeneous) is a narrow pH operating window<sup>40,41</sup>. Fe(III) tends to hydrolyse at pH > 3, reducing the concentration of the active metal in the system<sup>42</sup>. To address this issue, organic chelating ligands can be introduced in homogeneous Fenton systems, or catalysts can be added to heterogeneous Fenton systems 43,44. Regardless of whether it is a homogeneous or heterogeneous system, the introduction of light can enhance the catalytic degradation efficiency of the Fenton process<sup>45</sup>. Light can aid the complete mineralization of organic compounds and the rapid reduction of Fe(III) by decomposing the partially oxidized by-products, such as iron complexes (for example, oxalates), through a ligand-to-metal charge transfer mechanism<sup>46</sup>. Organic chelate ligands containing several carboxyl groups (for example, nitrilotriacetic acid and ethylene diamine tetra-acetic acid) have been added to the photo-Fenton reaction to ensure operational stability at near-neutral pH44-48. Diversifying the chemical structure, functional groups and steric configuration of organic ligands (for example, nitrogen-containing groups, phosphonic acid groups, cyclic tetradentate ligands) can further functionalize the photo-Fenton reaction by selectively producing active species and extending the photoresponse wavelength to the visible or near-infrared range 49,50.

Heterogeneous Fenton systems show enhanced contaminant removal performance under light. The removal efficiency can increase by 2 to 13 times, depending on the physicochemical properties of the Fenton photocatalysts<sup>51</sup>. The underlying mechanisms include the semiconducting behaviour of Fe(III) oxides, direct activation of surface hydroxyl species and H<sub>2</sub>O<sub>2</sub>, and the leakage of Fe(II) and Fe(III) cations, combining features of heterogeneous and homogeneous chemistry<sup>52</sup>. In the homogeneous photo-Fenton process, the production of active species is heavily influenced by the photoresponsive properties of Fe<sup>3+</sup> aggregates<sup>53</sup>. Consequently, the structure of hydrolysed Fe<sup>3+</sup> species has been correlated with the generation of active species under varying reaction conditions, such as pH and Fe<sup>3+</sup> concentration<sup>53,54</sup>. Alternatively, manipulating the spin state of active metal atoms in heterogeneous catalysts presents an efficient strategy to direct active species generation in the photo-Fenton reaction. The spin states of metal atoms are strongly influenced by the electronic properties of the support materials 55,56. Furthermore, the design of heterogeneous photocatalysts capable of in situ generation of  $H_2O_2(201 \mu mol g^{-1} h^{-1})$  – known as the photo-self-Fenton reaction - can reduce the need for external H<sub>2</sub>O<sub>2</sub> (ref. 56).

Conventional homogeneous Fenton oxidation is used as a pretreatment process before biochemical treatment or as an advanced treatment following conventional wastewater treatment plants to remove emerging contaminants<sup>57</sup>. Compared with the conventional homogeneous Fenton reaction, the homogeneous photo-Fenton reaction demonstrates a higher yield of active species, which leads to an enhanced mineralization rate relative to the Fenton process<sup>58</sup>.

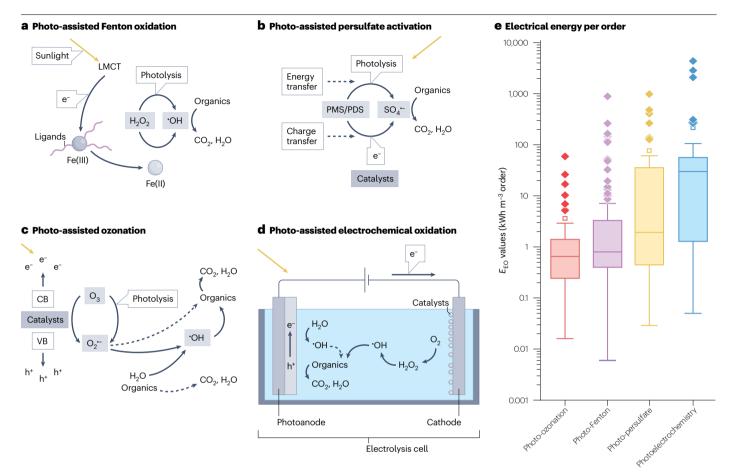


Fig. 2 | Photo-assisted technologies for water purification. Mechanisms of photo-assisted technologies for water purification. **a**, In photo-assisted Fenton oxidation, light can directly photolyse  $H_2O_2$ , or excite catalysts to generate electrons that will decompose  $H_2O_2$  to generate the hydroxyl radical, 'OH. **b**, In photo-assisted persulfate activation, persulfate is activated by light directly or a photogenerated charge carrier to produce  $SO_4$ — and 'OH. **c**, In photo-assisted ozonation, ozone can react with ultraviolet (UV) light or photoexcited electrons to produce 'OH and  $O_2$ — radicals that react with pollutants in water and eliminate them. Full arrows represent the main reaction route, whereas the dashed arrows indicate secondary reaction routes. **d**, In photo-assisted electrochemical oxidation, light can excite either the photoanode or photovoltaic system to produce charge carriers to form reactive oxygen species. **e**, The electrical energy ( $E_{FO}$ ) needed to degrade the concentration of a pollutant by one order

of magnitude in 1 m³ of water varies for different photo-assisted advanced oxidation processes. The  $E_{\rm EO}$  values are based on data from ref. 63 and a defined experimental set-up with controlled conditions, including water quality, target contaminants and other relevant process parameters. When kinetic data are available, compounds that are susceptible to direct oxidation (for example, by ozone or UV photolysis) are excluded from consideration. For ozone-based and UV-based processes, the threshold values for rate constants are set at  $k_{\rm O3} < 10~{\rm M}^{-1}\,{\rm s}^{-1}$  and  $k_{\rm UV} < 10^{-5}\,{\rm m}^2\,{\rm J}^{-1}$ . The box plots show quartiles with the centre line indicating the median and the whiskers extending to 1.5× the interquartile range. CB, catalyst conduction band; LMCT, ligand-to-metal charge transfer; PDS, peroxodisulfate; PMS, peroxymonosulfate; VB, catalyst valence band. Panel **e** adapted with permission from ref. 63, Elsevier.

These improvements reduce the demand for oxidant chemicals and lower the operational costs of the homogeneous photo-Fenton reaction, highlighting its potential for large-scale applications similar to conventional homogeneous Fenton oxidation  $^{59,60}$ . The technical feasibility of the homogeneous photo-Fenton process has been demonstrated in a  $100 \cdot m^2$  raceway pond reactor with a treatment capacity of  $1.92 \, m^3 \, m^{-2} \, d^{-1}$  (ref. 61). This technology might be used to enhance the biodegradability of wastewater and to remove emerging contaminants, such as microplastics and persistent organic pollutants, in secondary effluents in wastewater treatment plants  $^{62}$ .

Despite the high variability in water quality, process capacity and target substances, the median value of electrical energy per order ( $E_{\rm EO}$ , defined as the electrical energy (kWh) required to degrade a contaminant by one order of magnitude in 1 m³ of water) of the photo-Fenton reaction ( $E_{\rm EO}$  = 2.6 kWh m³ order¹)6³ is at a medium level among AOP technologies (Fig. 2e). The use of compound parabolic collectors and raceway pond reactors can help to further reduce energy consumption of the photo-Fenton process, through the optimization of the light-harvesting capabilities of the reaction6⁴. Typically, when the concentration of pollutants is in the range of milligrams per litre or above, tubular photoreactors with compound parabolic collectors are widely used because they can maximize the usage of irradiation energy (Fig. 3a). To remove contaminants at lower concentrations, raceway pond reactors have emerged as an alternative owing to their

low production cost compared with other reactors, high volume to surface, and flexibility to optimize the liquid depth according to the radiation strength<sup>65</sup> (Fig. 3b).

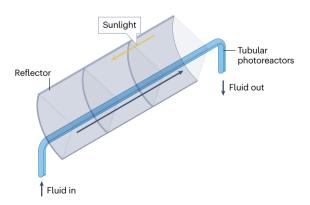
### Photo-assisted persulfate activation

In comparison with hydroxyl radicals ('OH) generated in  $H_2O_2$ -based (or  $O_3$ -based) oxidation processes, sulfate radicals ( $SO_4$ -) offer marked advantages <sup>66,67</sup> (Fig. 2b). These advantages include a longer half-life (30–40  $\mu$ s versus 20 ns for 'OH) and a higher redox potential (2.5–3.1  $V_{\text{NHE}}$  compared with 1.9–2.7  $V_{\text{NHE}}$  for 'OH)<sup>68</sup>. Moreover, the ease of transport and storage of solid persulfate salts (for example, peroxodisulfate and peroxymonosulfate), coupled with their high efficiency in generating radicals ('OH,  $SO_4$ -' and  $O_2$ -') and non-radical species ( $^4O_2$  and high-valent metal-oxo), has made photo-assisted persulfate oxidation technique one of the most relevant AOPs for water decontamination <sup>68</sup>.

Since UV light began being used for peroxodisulfate activation  $^{69}$ , the development of photo-assisted persulfate oxidation has evolved from light-based homogeneous activation processes to photoresponsive catalyst-driven heterogeneous catalysis  $^{70}$ . The catalysts commonly used in a photo-assisted persulfate oxidation include metal-based oxides and their composites (such as  $\text{TiO}_2$ , bismuth oxides, Fe-based and Ti-based metal–organic frameworks, and transition metal dichalcogenides), and non-metal materials (such as graphitic carbon nitride (g-C $_3\text{N}_4$ ), carbon quantum dots and perylene diimide) and their composites  $^{71}$ . In addition to enhancing radical generation, the use of photocatalysts in persulfate activation can also promote the formation of non-radical species  $^{68}$ . These species enable non-radical oxidation of contaminants, which is emerging as a decontamination strategy owing to its strong resistance to complex water matrices and its high persulfate utilization efficiency (up to 90%) with a low stoichiometric ratio  $^{72}$ .

Energy transfer and electron transfer are two accepted mechanisms for photo-assisted persulfate oxidation. External light radiation-mediated energy transfer can directly induce the homolysis of peroxide bonds within peroxymonosulfate and peroxodisulfate, producing SO<sub>4</sub><sup>--</sup> and/or OH in photo-assisted homogeneous persulfate activation<sup>68</sup>. Additionally, peroxymonosulfate and peroxodisulfate

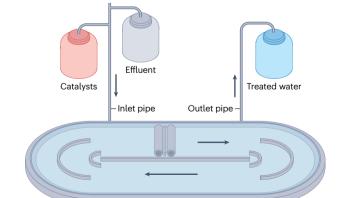
a Composite parabolic collectors



 $\label{lem:fig.3} Power at ion of composite parabolic collectors and raceway pond reactors. Parabolic collectors and raceway pond reactors can improve light harvesting and help reduce the energy consumption of the photo-Fenton process. a, Composite parabolic collectors can concentrate and reflect most of the incident radiation to the absorber, and tubular photoreactors maximize$ 

molecules can act as electron acceptors, capturing electrons generated on the light-irradiated surface of solid photocatalysts  $^{19}$ . The photogenerated electrons can activate peroxodisulfate and peroxymonosulfate via electron transfer processes  $^{68,71}$ . Photoresponsive catalysts, including  $\mathrm{TiO}_2$ , Fe-based and Ti-based metal–organic frameworks, and transition metal dichalcogenides, usually have multiple surface structures and possess different catalytic activities in the persulfate activation, which can lead to the formation of ROS and thus the degradation of pollutants  $^{71,73}$ . The use of photoresponsive materials is advantageous because it extends the light absorption range from UV to visible and near-infrared regions  $^{73}$ . However, the rational design of photocatalysts with near-infrared light-reinforced persulfate activation is still a technological challenge.

The water purification performance of photo-assisted persulfate oxidation relies on the types of ROS and their resistance towards the water matrix (such as pH and inorganic ions)<sup>69,74,75</sup>. Given the broader range of second-order reaction rate constants of SO<sub>4</sub> with organic pollutants  $(10^5 - 10^{11} \, \text{M}^{-1} \, \text{s}^{-1} \, \text{compared with} \, 10^8 - 10^{10} \, \text{M}^{-1} \, \text{s}^{-1} \, \text{for OH})$  and its preferred oxidation pathways<sup>68</sup>, the SO<sub>4</sub> radical is considered a more selective oxidant than 'OH (ref. 76). This selectivity has led to the design of water matrix-specific decontamination processes<sup>77</sup>. For example, UV-mediated persulfate hybrid systems have been used in pilot-scale and industrial-scale tertiary wastewater treatment to remove various micropollutants, bacteria and their associated antibiotic resistant genes<sup>77</sup>. However, the practical implementation of photo-assisted persulfate oxidation techniques in water-related utilities is still in its early stages<sup>74</sup>. For instance, the pilot-scale application of photo-assisted persulfate oxidation is mainly focused on UVA-based homogeneous oxidation processes with a treated wastewater scale of about 50 m<sup>3</sup> d<sup>-1</sup> (ref. 77). Although this pilot-scale application might be suitable for point-of-use water purification systems, it remains largely unknown whether this technology has the capacity to purify real effluents from large sewage treatment plants (>500,000 m<sup>3</sup> per day). Therefore, the technical viability of large-scale wastewater purification with these technologies should be evaluated, as well as their compatibility and potential conflicts with current purification technologies<sup>75</sup>.



**b** Raceway pond reactors

the usage of irradiation energy. **b**, Raceway pond reactors have a high surfacearea-to-volume ratio and the flexibility to optimize the liquid depth. Pretreated effluent and catalysts (for example,  $\rm H_2O_2$  and iron-based catalysts) enter the reactor through a vertical inlet pipe, and treated water is collected through a vertical outlet pipe.

Among other indicators, the energy consumption volume ( $E_{\rm FO}$  value associated with the production of oxidants and catalysts and the degradation of contaminants) is an environmental and economical assessment parameter<sup>63</sup>. Available  $E_{FO}$  values for typical photo-assisted persulfate oxidation processes range from  $3.8 \times 10^{-4}$ to  $4.8 \times 10^2$  kWh m<sup>-3</sup> order<sup>-1</sup> (ref. 75). Differences in the  $E_{EQ}$  values arise from many factors, such as the types of contaminant, water matrix conditions, catalyst synthesis procedures and the quality objective of water purification  $^{63}$ . Given the wide range of  $E_{FQ}$  values, the introduction of photocatalysts might not necessarily contribute to a lower  $E_{EO}$  value or to environmentally friendly water purification in some cases<sup>75</sup>. Compared with the photo-assisted homogeneous persulfate oxidation process, accurately calculating the  $E_{\rm FO}$  values for photocatalyst-mediated heterogeneous processes is more complex<sup>68</sup>. This challenge arises primarily from the lack of data and uncertainties surrounding energy consumption associated with the recyclability and reusability of catalysts in real wastewater purification scenarios, and makes it difficult to conduct a comprehensive sustainability evaluation. Normalized protocols detailing the preparation of photocatalysts and their recyclability and reusability are encouraged to accurately calculate the energy consumption, and thus assist the development of photo-assisted persulfate oxidation technology with a low carbon footprint.

### Photo-assisted ozonation

Ozone, as a powerful oxidizing reagent, has been used in wastewater purification owing to its strong redox potential  $(2.01 \, V_{NHF})^{78}$ . However, the application of ozone alone faces the disadvantages of high production cost (US\$2.00 kg<sup>-1</sup> of ozone for a concentration of ozone around 10-12 wt%)<sup>79</sup>, slow volumetric mass transfer coefficient (0.5-1.5 min<sup>-1</sup> depending on operating conditions)80 and low mineralization efficiency (20-50%)81,82 due to ozone's relatively poor solubility and stability in water, as well as its selective reactivity with organic compounds at acidic pH<sup>83</sup>. Integrating light with ozone, whether through homogeneous UV-O<sub>3</sub> processes or heterogeneous light-O<sub>3</sub>-semiconductor systems. is advantageous<sup>84</sup>. The ozone consumption, per milligram of total organic carbon (TOC) removal, of a light-O<sub>3</sub>-semiconductor system has been reported to be about 13% of that of a simple ozonation system<sup>84</sup>. In a heterogeneous system (Fig. 2c), light excites the semiconductor to generate electrons that preferably react with ozone rather than with  $O_2$ , owing to the high electrophilicity of ozone, thus generating more ROS, including 'OH, O<sub>2</sub>' and <sup>1</sup>O<sub>2</sub>, to enhance the degradation of pollutants<sup>85</sup>. The interaction between ozone and electrons also aids the separation of electron-hole pairs. The abundant active sites on the surface of photocatalysts, such as g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>, promote the interaction between ROS and pollutants, overcoming mass transfer in the ozonation reaction  $^{86-88}$ . Furthermore, when  $O_3$  is directly exposed to UV light, it dissociates to generate atomic oxygen, which can further react with water to produce 'OH (ref. 84).

Photocatalytic ozonation exhibits synergistically enhanced oxidation efficiencies (pseudo-zeroth-order rate of  $4.79 \times 10^{-2}$  mM min<sup>-1</sup>) compared with the photocatalysis ( $5.00 \times 10^{-4}$  mM min<sup>-1</sup>) and ozonation (0 mM min<sup>-1</sup>) systems operating separately<sup>86</sup>. The synergistic effect of photocatalytic ozonation is evident in the increasing degradation and/or mineralization efficiencies or oxidation rate constants of organic compounds<sup>83</sup>. The apparent rate constant of photocatalytic ozonation is 9.5 and 1.6 times higher than that of photocatalysis and ozonation, respectively, for mineralizing aromatic compounds<sup>89</sup>. This efficiency is attributed to the generation of more reactive but

non-selective 'OH that reacts with almost all organic molecules at rates of  $10^6$ – $10^9$  M<sup>-1</sup> s<sup>-1</sup> during the photocatalytic ozonation process<sup>90</sup>.

Despite the synergistic effects of photocatalytic ozonation on pollutant decomposition in water, its economic viability must also be considered to assess sustainability. Photocatalytic ozonation, which requires additional electrical energy for ozone generation, at first glance seems to be more expensive than simple photocatalysis, which only consumes electricity for light irradiation sources. When comparing the costs of these oxidation techniques for water treatment, the specific energy consumption for each system should consider the decomposed pollutants<sup>83</sup>. Taking a TiO<sub>2</sub>/O<sub>3</sub>/UVA system as an example, the energy consumption primarily arises from the electrical energy necessary to generate O<sub>3</sub> and radiation, which is the main operation cost for those different processes 91. The energy requirement for photocatalytic ozonation is 7.3-22.0 kWh m<sup>-3</sup> order<sup>-1</sup>, which is lower than the energy consumption of photocatalysis (38.9-47.1 kWh m<sup>-3</sup> order<sup>-1</sup>) and O<sub>3</sub> alone (26.2 kWh m<sup>-3</sup> order<sup>-1</sup>)<sup>91</sup>. Accordingly, the operating cost of different systems can be calculated based on local electricity prices. Similar results have been reported in the literature 83,91-93, demonstrating the cost-effectiveness of photocatalytic ozonation.

### Photo-assisted electrochemical oxidation

Although electrochemical advanced oxidation technology shows promise for industrial applications, the high electricity requirements increase operational costs<sup>94</sup>. Integrating solar energy into electrochemical advanced oxidation processes is regarded as an effective strategy to enhance efficiency and reduce energy demands<sup>95</sup> (Fig. 2d).

There are two general routes to achieve photo-assisted electrochemical oxidation processes. The first type consists of coupling external energy input (UV light or photovoltaic (PV) cells) with an electrolyser (UV-EC or PV-EC, Fig. 4a). An electrolyser includes a cathode, anode and electrolyte, in which the anode and cathode are responsible for removing pollutants through direct redox reactions or indirect production of active free-radical species<sup>4</sup>. The efficiency and lifespan of an electrolyser are primarily determined by the electrode substrate, electrocatalysts in the cathode and anode, and the fabrication processes<sup>96</sup>. Additionally, the pretreatment of influent water and the addition of strong oxidants to accelerate the generation of active free-radical species can substantially enhance the production of high-quality effluent water<sup>2</sup>. In a PV-EC system, an electrolyser containing electrocatalytic anodes, such as dimensionally stable anodes and boron-doped diamond electrodes<sup>97</sup>, is powered by commercialized silicon-based PV cells. In a UV-EC system, the UV light can activate the electrolyte to produce free-radical species, thus promoting the degradation of pollutants<sup>98</sup>. The PV-EC system has been proven to be practical for small-scale rural water supply, yet restricted by the high costs (around US\$26,000) associated with equipment and maintenance<sup>99</sup>. For economic reasons, the application of this system could be more suitable in regions with more sunlight throughout the year and concentrated influent streams99.

The second type of photo-assisted electrochemical oxidation process involves using semiconductor materials to prepare photoelectrodes for photoelectrochemical advanced oxidation (PECAO, Fig. 4b). In PECAO, the use of photoelectrodes simplifies the equipment set-up and enables more convenient connections with other multifunctional tandem components compared with a PV-EC system<sup>100</sup>. Moreover, a higher charge separation efficiency and easier recovery of the catalyst could be achieved compared with a photocatalytic system<sup>100</sup>. In the PECAO system, the solar energy used by the

# a UV- and PV-electrolyser system **b** Photoelectrochemical advanced oxidation system Sunlight ROS Anode Cathode Photoanode Cathode C Electrochemical advanced oxidation systems Low ohmic loss Mechanical durability Pretreatment Thin Continuous flow layer Value-added by-products Additives Photoanode Cathode

Fig. 4 | Photo-assisted electrochemical oxidation processes.

 $\label{eq:continuous} \textbf{a}, Ultraviolet (UV)-electrolyser and photovoltaic (PV)-electrolyser system. \\ \textbf{b}, Photoelectrochemical advanced oxidation (PECAO) system. \\ \textbf{c}, Key properties of electrochemical advanced oxidation systems for practical wastewater treatment applications. The pretreatment reduces the interference of the influent water, whereas the continuous-flow mode enhances throughput capacity and operational stability. Under sunlight, the photoanode absorbs light energy to generate holes and electrons. A thin layer on the photoanode improves light utilization efficiency. The cathode catalyses oxygen reduction to$ 

produce reactive oxygen species (ROS), with electrolyte additives accelerating their generation. The mechanical durability of the electrodes determines their lifespan, directly influencing the overall device longevity. Low ohmic loss in the system minimizes unnecessary electrical consumption and improves operational stability. By coupling the photoanode and cathode, organic pollutants are efficiently removed. Furthermore, tuning catalytic properties and operating parameters can yield targeted value-added by-products, enhancing the economic viability of the process. D, degradation products; P, pollutants.

photoelectrode lowers the voltage required to drive the reactions, whereas the applied bias accelerates the charge separation process under an electric field<sup>101</sup>. The PECAO system includes photoelectrocatalysis, photoelectrochemical oxidation, photo-electrocoagulation and photoelectrochemical Fenton processes<sup>102</sup>. The photoelectrodes in the PECAO system undergo similar processes for solar light utilization. Upon absorbing solar light, the photoelectrodes generate electrons and holes in the conduction and valence bands, respectively<sup>103</sup>. The electrons are transferred to the counterelectrode, while the holes drive various reactions 103. In photoelectrocatalysis, the holes aid the formation of ROS upon reaching the surface of the photoelectrocatalysts 104. In photoelectrochemical oxidation, the holes directly oxidize pollutants 105. In photo-electrocoagulation, the holes accelerate the electrochemical dissolution of the anode, resulting in the formation of coagulant agents<sup>102</sup>. In photoelectrochemical Fenton processes, the holes enhance the Fenton reaction 106. Considering that different ROS (for example, O<sub>2</sub><sup>-</sup>, H<sub>2</sub>O<sub>2</sub>, OH, and O<sub>2</sub>) have distinct standard potential values, reaction tendencies and complex interconversion pathways, photo-assisted electrochemical oxidation demonstrates potential by offering a convenient method

to control ROS generation with specific compositions for targeted was tewater treatment  $^{\rm 107}.$ 

Photoelectrodes in PECAO are generally composed of inorganic semiconductors, such as TiO<sub>2</sub> and BiVO<sub>4</sub>, which have limited solid-liquid interface for both bulk and dense nanostructure photoelectrodes, resulting in low efficiencies 108. Porous materials, such as metal-organic frameworks and covalent organic frameworks, which possess highly ordered structures, large porosities and diversified pore surfaces, are expected to lead to efficient wastewater treatment due to their fast mass transfer pathways and abundant exposed active sites 109. As most ROS are generated at the anodic side by photogenerated holes, the cathode can accept photogenerated electrons to catalyse oxygen's reduction to generate H<sub>2</sub>O<sub>2</sub> in an O<sub>2</sub>-saturated solution using carbonaceous materials 110,111. Although carbonaceous materials are cheap and readily available compared with metal materials, they are short lived and unstable in electrolytes, which motivates the development of inexpensive materials with high stability<sup>110,111</sup>. Alternatively, an electron-ion acceptor cathode can enhance the separation of electrons and holes, producing strong oxidant free radicals at the photoanode<sup>112</sup>. Based on mechanistic studies of charge transfer, separation kinetics and redox

reactions on photoelectrodes, further research is recommended to explore the structure–activity relationship between ROS generation and their interactions with pollutants. This knowledge would help to advance the development of PECAO for practical applications in wastewater treatment.

Although substantial efforts have been made to improve the properties of the PECAO system under simplified simulated conditions in the laboratory, challenges remain for its practical application, Real-world wastewater treatment imposes higher demands on the design of the PECAO system and electrodes because of complex interferences, variable water quality and large-scale water volumes 113 (Fig. 4c). To reduce the interferences, membrane filtration<sup>52</sup> has been a common pretreatment process used to remove suspended solid and colloidal particles in wastewater. Moreover, to improve the throughput capacity of a PECAO system, rationally designing continuous-flow reactors and larger photoelectrodes of higher specific surface area can enhance the mass transfer and treatment efficiency<sup>114</sup>. To further increase the light utilization efficiency, reducing the thickness of semiconductors and electrolytes between the photoelectrodes and light source could be a cost-effective strategy<sup>114</sup>. Additionally, designing photoanodes that respond to near-infrared light could be an effective approach to increase sunlight utilization115,116.

The lifetime of a PECAO system is another important aspect that is heavily affected by the properties of wastewater and the abovementioned improvement strategies <sup>117</sup>. However, current research on the PECAO system is mainly focused on its feasibility, and its practical application is still very limited. The mechanical stability of catalyst immobilization on photoelectrodes primarily determines the lifetime, especially in continuous-flow systems <sup>117</sup>. Advanced preparation methods of photoelectrodes, such as sputtering and atomic layer deposition, have been developed to improve the mechanical stability of catalysts. The sputtering method focuses on depositing thin films on the surface of the silicon and/or wafer glass, and the atomic layer deposition method can create planar or nanostructured electrodes <sup>118,119</sup>.

Finally, the cost of electrical energy consumption limits the present output-to-input ratio of the PECAO system and other photo-assisted electrochemical oxidation technologies  $^{113}$ . Simultaneously reducing the unnecessary electrical cost and increasing the added revenue would promote the practical application of PECAO  $^{113}$ . Electrical cost can be reduced by lowering the ohmic loss of every component in devices and developing photoelectrodes for using solar energy  $^{113}$ . The added revenue could be increased by coupling the photo-assisted electrochemical oxidation processes with value-added production processes, such as  $\rm CO_2$  reduction or  $\rm H_2$  evolution, when the concentration of pollutants is low and the produced  $\rm H_2$  can be used as an electron donor for anaerobic fermentation  $^{120}$ . Although photo-assisted electrochemical oxidation technologies are currently challenged by cost and lifetime, they have shown potential for sustainable water treatment.

### Integrated multiple photo-assisted oxidation processes

Coupling multiple AOP technologies might help achieve more efficient water-treatment outcomes and reduce overall energy consumption, compared with individual advanced oxidation technologies 100,121. By combining different AOPs, a wider variety of ROS and radicals such as hydroxyl, sulfate and ozone-derived radicals can be generated 100. This variety increases the likelihood of targeting and degrading a broader range of contaminants 100. The introduction of light can activate catalysts and/or sensitizers within the system, leading to the generation of additional reactive species. These reactive species

can accelerate the degradation of pollutants and improve the overall energy efficiency of the remediation process <sup>122,123</sup>. For example, the photoelectro-Fenton process combines the advantages of photo-Fenton and electro-Fenton processes <sup>122</sup>, using light to enhance the production of hydroxyl radicals while the electrochemical component regenerates the iron catalyst and hydrogen peroxide, ensuring continuous pollutant degradation.

Additionally, light helps to regenerate  $Fe^{2^+}$  from  $Fe^{3^+}$ , maintaining the catalytic cycle and aiding continuous production of hydroxyl radicals. The stability of catalysts over longer periods can be further improved by integrating light with multiple AOPs, reducing frequent replacement or regeneration of catalysts  $^{121}$ . A coupled solar photoelectro-Fenton and solar photocatalysis system exhibited higher efficiency and stability than electrochemical oxidation and photoelectro-Fenton processes towards salicylic acid degradation  $^{121}$ . The energy consumption of the coupled system at 50 mA cm $^{-2}$  was determined to be 0.249 kWh g $^{-1}$  TOC at 360 min, which is less expensive than solar photoelectro-Fenton (0.286 kWh g $^{-1}$  TOC) and anodic oxidation $^{-1}$ 20 $^{-1}$ 2 solar photocatalysis (0.751 kWh g $^{-1}$  TOC), confirming the viability of the solar photoelectro-Fenton and solar photocatalysis system for the remediation of polluted wastewater  $^{121}$ .

Photo-assisted multi-technologies could improve treatment efficiency, but this has challenges, such as the complexity of reaction mechanisms and the risk of formation of by-products<sup>19</sup>. The interactions between different oxidative species and pollutants can lead to unexpected reaction pathways, potentially generating harmful by-products<sup>82</sup>. Photo-assisted multi-system structures can be rationally optimized to be more efficient<sup>124</sup> through strategic considerations across multiple factors, including the selection of AOP combinations, catalyst development, reaction conditions and reactor design<sup>125</sup>. Different photo-assisted AOPs generate specific reactive species (for example, 'OH, O<sub>2</sub>' and SO<sub>4</sub>' ), enabling broader pollutant degradation<sup>100</sup>. By coupling AOPs that produce complementary radicals, treatment processes can target diverse contaminants more effectively while minimizing by-products and reducing the need for post-treatment<sup>100</sup>.

Catalyst development has a role in enhancing the generation of reactive species and overall degradation efficiency. Designing dual-function photocatalysts that activate multiple oxidants, such as H<sub>2</sub>O<sub>2</sub> and persulfate under light irradiation, can optimize systems such as photo-Fenton-persulfate<sup>126</sup>. Incorporating noble or transition metals with semiconductor catalysts improves light absorption, charge carrier separation, and activation of oxidants such as H<sub>2</sub>O<sub>2</sub> and ozone<sup>85</sup>, enhancing both Fenton and ozonation processes efficiencies in multi-AOPs systems. Reaction conditions also influence the system performance. Parameters such as pH, light intensity, temperature, and the concentrations of oxidants and contaminants must be carefully controlled75. For instance, excessive oxidant concentrations could result in radical scavenging, whereas insufficient levels reduce oxidation efficiency<sup>127</sup>. Acidic conditions favour Fenton reactions, whereas persulfate systems are more effective under neutral to slightly alkaline conditions 128,129. Designing systems that operate efficiently across a pH range enhances their adaptability for diverse wastewater compositions.

Efficient reactor design is critical for maximizing interactions between light, catalysts and pollutants<sup>125</sup>. Reactor configurations that enhance light penetration, such as cylindrical reactors with central light sources or flat-plate reactors, promote even illumination and minimize shadowing effects<sup>130</sup>. Optimized flow configurations

Table 1 | Advantages and disadvantages of photo-assisted advanced oxidation process technologies

Photo-assisted advanced oxidation processes	Advantages	Disadvantages	Environmental scenarios
Photo-Fenton	Formation of strong non-selective 'OH Efficient for a wide range of contaminants Simple implementation	High operational costs <sup>194</sup> (€0.44 to €2.18 m <sup>-3</sup> ) Additional oxidants ( $H_2O_2$ ) required Difficulties in transporting chemicals such as $H_2O_2$	Drinking water treatment system; effluent from municipal wastewater treatment plants; raw oily wastewater
Photo-persulfate	Longer lifetime of $SO_4^-$ (30–40 µs) than 'OH (20 ns) High oxidation potential <sup>68</sup> (2.5–3.1 $V_{NHE}$ ) Rapid reaction rate (10 <sup>5</sup> –10 <sup>11</sup> $M^{-1}$ s <sup>-1</sup> ) Wide work pH range (2.0–8.0)	Increases the salt content and presence of sulfate ions as end products Additional oxidants (persulfate, peroxymonosulfate) required Health and safety concerns	Pharmaceutical wastewater; effluent from municipal wastewater treatment plants
Photo-ozonation	High yield of 'OH radicals (above 13%) <sup>195</sup> Efficient for a wide range of contaminants No pH restrictions No oxidants required	Risks associated with ozone generation Requires high electrical energy to generate reactive species (7–161.8 kWhm <sup>-3</sup> order <sup>-1</sup> ) <sup>91,196</sup> Generation of toxic by-products	Drinking water treatment system; effluent from municipal wastewater treatment plants; pharmaceutical wastewater
Photoelectrochemical oxidation	High controllability No oxidants required Multiple reactive species production Easy to recycle	High cost of electrode materials (such as conductive diamond electrodes <sup>197</sup> , platinum, ruthenium, iridium) Electrode fouling Requires high electrical energy to generate reactive species (39.3–331.8 kWhm <sup>-3</sup> order <sup>-1</sup> ) <sup>198</sup> Generation of secondary pollutants	Petroleum refinery wastewater; effluent from municipal wastewater treatment plants

ensure consistent pollutant–catalyst contact and effective mixing  $^{131}$ . For large-scale applications, continuous-flow reactors equipped with UV lamps or solar collectors can improve throughput while reducing operational costs  $^{130}$ . The degradation efficiency can also be improved using advanced control and monitoring systems, integrating real-time sensors for light intensity and pollutant concentration  $^{132}$ .

For large-scale applications, photo-assisted AOP technologies must consider practical environmental scenarios, as different photo-assisted AOPs offer distinct advantages and limitations (Table 1). The varying conditions of wastewater necessitate the selection of the most appropriate treatment approach (Supplementary Table 1).

### Air purification

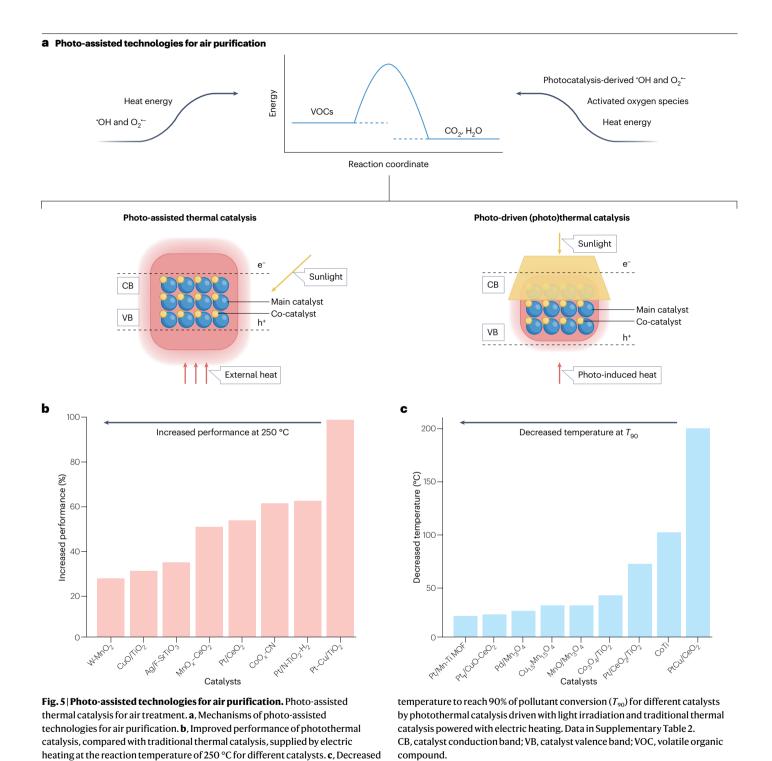
Air purification technologies include both recovery techniques (such as absorption, condensation and membrane separation) and destructive methods (such as thermal incineration and thermal catalytic oxidation)<sup>133–135</sup>. Destructive methods completely degrade organic pollutants (especially VOCs such as toluene and benzene) into small molecules such as CO<sub>2</sub> and water<sup>136</sup>. However, destructive methods generally require the application of external energy and/or catalysts to decompose pollutants into final products<sup>137,138</sup>. A typical process like thermal catalytic oxidation benefits from the introduction of renewable energy sources, such as solar energy, as an auxiliary energy source 135,139. Solar energy can be directly converted into electrical, thermal and chemical energy via photo-assisted thermal (or photothermal) catalysis 140, which enables a more comprehensive exploitation of energy across the solar spectrum, encompassing extended wavelength ranges such as visible and infrared light. Therefore, energy-intensive thermal catalysis methods can benefit from light-induced heating effects or concentrated solar irradiation to attain elevated temperatures, which reduces the energy consumption of the system<sup>141-143</sup>.

Photothermal catalytic processes can be generally classified into two categories <sup>144,145</sup>: photo-assisted thermal catalysis driven by external electric heating and auxiliary light, and photo-driven

(photo)thermal catalysis obtaining energy from the solar spectrum (Fig. 5a). Photo-assisted thermal catalysis uses photochemical processes to enhance thermal reactions by introducing additional light into traditional thermal catalytic systems <sup>146</sup>. Photogenerated charge carriers and their derived oxidizing species boost the primary thermal oxidation process <sup>140</sup>. During photo-assisted thermal catalytic oxidation, light promotes the activation of reactants, improving the overall efficiency <sup>140</sup>. Additionally, the charge separation in the photocatalytic system can be accelerated by the presence of an external heat source <sup>143</sup>. The selection of a photo-assisted thermal catalysis process should consider the volume of pollutant gases (Supplementary Fig. 1).

Photo-induced (photo)thermal catalysis involves light as a heat source without relying on external heat<sup>147</sup>. Taking transition metal oxides as examples, the oxidation mechanism of VOCs follows the Mars-Van Krevelen mechanism<sup>143</sup>. Under light irradiation, the photothermal catalyst layer absorbs photons and converts solar energy into thermal energy through non-radiative relaxation, leading to a rapid increase in the layer temperature <sup>138,148–150</sup>. Then, the lattice oxygen in catalysts reacts with VOC molecules driven by the light-induced heat and is subsequently replenished by adsorbed oxygen species 151,152. Additionally, transition metal oxide semiconductors can be excited by light to generate charge carriers, producing strong oxidative species (photogenerated holes, 'OH and O<sub>2</sub>'-) that enhance VOC oxidation performance<sup>153</sup>. The high temperature of catalysts (generally above 200 °C) also aids the separation and mobility of charge carriers 143. Moreover, light enhances the activation of lattice oxygen in transition metal oxides, thereby accelerating the reaction rate 143. This approach uses the entire solar spectrum (200-2,500 nm) without the need for external electric heat sources, integrating the benefits of both photochemical and thermochemical pathways<sup>145</sup>.

Photo-assisted thermal catalysis for air purification has advanced owing to its harnessing of sunlight and its superior catalytic efficiency compared with conventional thermal catalytic processes  $^{154-156}$ . With the



assistance of light irradiation, the thermal catalytic reaction system performance – VOC conversion efficiency – can increase by at least 30%<sup>146</sup>. This increase is attributed to the enhanced activation of the reactants by photoexcited holes and the generated oxidative radicals<sup>146</sup>. Tailoring the microscopic structure of catalysts can help to enhance

light-harvesting efficiency and catalytic activity  $^{157-159}$ . The design criteria of photothermal catalysts typically aims to achieve comprehensive absorption across the solar spectrum, high photothermal conversion efficiency (>99%) and good reactivity and stability (longer than 100 h) towards targeted reactions  $^{143}$ .

Commonly used photothermal catalysts include supported precious metal catalysts (such as Au, Ag and Pt)<sup>156,160,161</sup>, transition metal oxides (such as  $MnO_x$  and  $CoO_x$ )<sup>147,162</sup>, plasmonic metals<sup>138</sup> and zeolites 163,164, many of which absorb light, making them suitable for photothermal catalytic VOC oxidation (Fig. 5b.c and Supplementary Table 2). Factors such as cost, reaction activity and operational stability are critical for the development and application of these catalysts<sup>156</sup>. For example, precious metal catalysts are efficient and thus appealing in industrial applications, but their high cost limits their widespread use<sup>153</sup>. Enhancing the activity of non-precious metal catalysts while reducing reliance on precious metals is crucial for the economic viability of photothermal catalytic air purification. Addressing stability and resistance to carbon deposition and poisoning by chlorine and sulfur is also essential for practical applications 165-167. In industrial settings, the economic repercussions of catalyst poisoning and instability, which can lead to production halts, are often substantial 165. Therefore, improving the resilience of catalysts to such issues is a key area of ongoing research and development.

Photo-assisted thermal catalysis for air purification remains largely confined to laboratory-scale experimentation and has not achieved large-scale applications 168. However, compared with conventional thermal catalysis, laboratory-scale photothermal catalytic processes using artificial sunlight (xenon lamp) show some cost advantage. In some cases, the costs of photothermal reactions can be reduced by 40% compared with thermal catalysis, even though the use of simulated light sources requires additional energy input<sup>169</sup>. Moreover, the use of renewable solar energy could reduce the carbon emissions and simultaneously produce fuels such as methanol during the reaction process<sup>170-172</sup>. For large-scale applications, optimizing energy supply mechanisms and reactor configurations is important to achieve high temperatures for VOC degradation. One approach uses an electric heating furnace with a light window on its sidewall for light ingress<sup>173</sup>. Another approach uses a cylindrical stainless-steel model mimicking the design of a photocatalytic reactor, with light introduced from above through quartz glass<sup>174</sup>. Owing to the intermittent nature of solar irradiance, electron storage mechanisms within materials need to be investigated to enable reactions to continue in the absence of light.

The practical applications of photothermal catalytic oxidation of VOCs also focus on harnessing outdoor natural sunlight<sup>175</sup>. An all-quartz reactor was used outdoors for gas pollutant degradation under natural sunlight. Complete VOC conversion was achieved using a condenser lens under midday sunlight, although sensitivity to cloud cover was observed<sup>176</sup>. The development of photothermal catalytic systems under natural sunlight decreases the need for thermal sources (electrical energy supply) and thus reduces the overall cost<sup>175</sup>.

Furthermore, in practical applications, various VOCs might be present in complex environments, such as high temperature (>250 °C) and high humidity (10–90%) conditions  $^{177,178}$ . The combination of photothermal catalysis with multiple technologies demonstrates an effective way to further improve the efficiency of VOC elimination  $^{179,180}$ . Combining photo-assisted catalytic technology with established adsorption, catalytic oxidation or plasma technologies might improve overall removal efficiencies while mitigating secondary pollution  $^{175}$ .

For real-world application of photo-assisted technologies for air purification, their sustainability should be assessed considering environmental, economic and social dimensions<sup>181</sup>. Traditional thermal catalysis relies on electric heating systems to raise the temperature of the entire system (200–1,200 °C)<sup>182</sup>, leading to energy waste and low efficiency of heat utilization<sup>181</sup>. By contrast, photothermal catalytic

VOC oxidation achieves precise local heating of active sites of catalysts with high heat utilization efficiency at lower reaction temperatures (room temperature to  $400\,^{\circ}\text{C}$ ) $^{168}$ . This method shows a similar or superior pollutant mineralization and is expected to reduce carbon deposition by-products compared with the conventional thermal catalytic oxidation process $^{183}$ .

Like most chemical engineering systems, photo-assisted thermal catalytic oxidation of VOCs involves initial device costs (reactor construction and installation, catalyst preparation and startup expenses), operating costs (running and maintaining) and life-cycle costs <sup>184–186</sup>. The main cost can be attributed to the construction of the catalytic reaction system <sup>185</sup>. For photo-assisted air purification, a critical challenge is selecting catalysts with optimal spectral absorption characteristics and catalytic active components that have good photothermal activity, high stability and low cost <sup>181</sup>. When sunlight is the sole energy source, optimizing its utilization for powering reactions is required. Dependence on solar irradiance reduces electricity consumption, and over time the cost savings from harnessing light energy can offset the initial investment in the device <sup>185</sup>.

Despite the various advantages of photo-assisted thermal technologies, their development faces some challenges. Photo-assisted thermal catalytic reactions involve both photochemical and thermochemical processes, complicating the differentiation between the roles and quantities of photoelectrons and hot electrons<sup>181</sup>. Conventional thermocouple-based temperature measurement methods provide insights only into the overall temperature of the catalytic bed, failing to capture the nuanced local temperature variations of nanoparticles<sup>183</sup>. Additionally, VOC oxidation reactions typically involve exothermic processes, and localized temperature spikes can induce structural alterations in the catalyst, diminishing removal efficiency, promoting undesired reduction reactions, and generating by-products<sup>186</sup>. Catalyst deactivation due to carbon deposition – a common issue in VOC oxidation reactions – also affects photothermal catalytic processes 167,187. Assessments of VOC catalytic reactions often overlook the introduction of contaminants such as sulfur or chlorine, which are prevalent in actual operational environments and typically involve single-component reactants 165,166,188. Consequently, the potential impact of sulfur, chlorine and composite pollutants (such as the mixture of benzene, toluene and chlorobenzene) on photothermal catalyst performance remains uncertain. Furthermore, given the predominantly unidirectional illumination of the catalyst bed, research on designing photothermal catalytic reactors and optimizing the catalyst stacking configuration to enhance light energy absorption is still lacking. Photothermal catalytic air purification remains predominantly at the laboratory scale. Enhancing our understanding of these aspects is vital for the successful implementation of photothermal catalytic technologies in real-world applications.

# **Summary and future perspectives**

Photo-assisted technologies can be used to eliminate organic pollutants in water and air. By harnessing the power of solar energy, pollutant removal efficiency can be enhanced along with reduced energy consumption. Despite progress, there are still challenges to the large-scale application of these photo-assisted technologies for environmental remediation, such as limited efficiency of light utilization.

During wastewater treatment, the impurities in water can absorb or reflect light, which reduces the interaction between light and catalytic materials or oxidants such as  $H_2O_2$  and  $O_3$ , thus diminishing the efficiency of photo-assisted AOPs. To address this challenge, designing

reactors that minimize the need for deep light penetration, such as flat reactors, can enhance the effectiveness of photo-assisted technologies. Additionally, it is important to design advanced catalytic materials with high light absorption efficiency to use low-energy photons, such as visible or infrared light. Enhanced light absorption can be achieved through several strategies: selecting narrow-bandgap catalysts, introducing dopants or defects to create mid-gap states that narrow the bandgap of semiconductors, coating catalysts with substances that show localized surface plasmon resonance effects (such as plasmonic materials or carbon-based materials), using dye-sensitizers or quantum dots, integrating up-conversion materials to convert infrared light into UV or visible light, and creating nanostructured materials (such as nanorods, nanowires, photonic crystal structures and surface texturing). Improving light absorption will benefit the generation of ROS and increase the degradation efficiency. For air purification in office buildings, factories and homes, developing catalysts capable of harnessing indoor light could offer a pathway towards the practical implementation of photo-assisted technology for air purification systems<sup>189</sup>.

The economic analysis of photo-assisted technologies has often been overlooked. Much of the existing research has been focused on operational expenses and energy consumption, such as the light sources, which are generally lower for photo-assisted technologies compared with traditional methods<sup>121</sup>. However, traditional methods benefit from established infrastructure and are easier to scale up<sup>190</sup>, whereas the initial capital costs for implementing light-assisted technologies - including investments in photoreactors, light sources, catalysts and associated infrastructure - are seldom considered. High-quality light sources, effective and stable catalysts, and well-designed photoreactors are essential for achieving high environmental remediation efficiency<sup>191</sup>. Combining photo-assisted technologies with other wastewater treatment systems could reduce system costs. For instance, the total energy consumption associated with a solar photoelectro-Fenton process for the removal of organic pollutants in anaerobic digestion is US\$1.4 per hour at current densities of 10 mA cm<sup>-2</sup>, which is approximately one-tenth of the energy cost for a conventional activated sludge process<sup>192</sup> (US\$10.64 per hour). Similarly, combining photo-Fenton or ozonation with a membrane system could reduce the operating costs of the oxidation process due to the decrease of the total treatment volume<sup>193</sup>. Therefore, integrating these technologies with existing systems shows potential for cost reduction and improved efficiency, potentially making them a viable option for large-scale environmental remediation.

Many of these technologies rely on catalysts made from rare or expensive materials such as noble metals. The extraction, processing and disposal of these materials can have a substantial environmental impact. Catalysts should be both economical and stable in the long term, and able to withstand prolonged exposure to light and contaminants without degrading. To enhance the sustainability of these processes, the development of new reaction systems is also essential. For instance, dual-functional photo(electro)catalytic processes that enable wastewater treatment while simultaneously recovering energy, such as by producing  $\rm H_2$  and  $\rm H_2O_2$ , could be a strategy for the next-generation of photo-assisted water-treatment technologies  $^{120}$ . A comprehensive life-cycle assessment — evaluating the entire process, from raw material extraction to end-of-life disposal — is crucial to verify the sustainability of these technologies. Such assessments are still lacking in the photo-assisted technologies field.

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### **Author contributions**

All authors contributed substantially to discussion of the content, wrote the article and reviewed and/or edited the manuscript before submission.

### **Competing interests**

The authors declare no competing interests.

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