

## Recent progress on Sn<sub>3</sub>O<sub>4</sub> nanomaterials for photocatalytic applications

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**Abstract:** Tin(IV) oxide (Sn<sub>3</sub>O<sub>4</sub>) is layered tin and exhibits mixed valence states. It has emerged as a highly promising visible-light photocatalyst, attracting considerable attention. This comprehensive review is aimed at providing a detailed overview of the latest advancements in research, applications, advantages, and challenges associated with Sn<sub>3</sub>O<sub>4</sub> photocatalytic nanomaterials. The fundamental concepts and principles of Sn<sub>3</sub>O<sub>4</sub> are introduced. Sn<sub>3</sub>O<sub>4</sub> possesses a unique crystal structure and optoelectronic properties that allow it to absorb visible light efficiently and generate photoexcited charge carriers that drive photocatalytic reactions. Subsequently, strategies for the control and improved performance of Sn<sub>3</sub>O<sub>4</sub> photocatalytic nanomaterials are discussed. Morphology control, ion doping, and heterostructure construction are widely employed in the optimization of the photocatalytic performance of Sn<sub>3</sub>O<sub>4</sub> materials. The effective implementation of these strategies improves the photocatalytic activity and stability of Sn<sub>3</sub>O<sub>4</sub> nanomaterials. Furthermore, the review explores the diverse applications of Sn<sub>3</sub>O<sub>4</sub> photocatalytic nanomaterials in various fields, such as photocatalytic degradation, photocatalytic hydrogen production, photocatalytic reduction of carbon dioxide, solar cells, photocatalytic sterilization, and optoelectronic sensors. The discussion focuses on the potential of Sn<sub>3</sub>O<sub>4</sub>-based nanomaterials in these applications, highlighting their unique attributes and functionalities. Finally, the review provides an outlook on the future development directions in the field and offers guidance for the exploration and development of novel and efficient Sn<sub>3</sub>O<sub>4</sub>-based nanomaterials. Through the identification of emerging research areas and potential avenues for improvement, this review aims to stimulate further advancements in Sn<sub>3</sub>O<sub>4</sub>-based photocatalysis and facilitate the translation of this promising technology into practical applications.

**Keywords:** photocatalysis; Sn<sub>3</sub>O<sub>4</sub> nanomaterials; building heterostructures; antibacterial therapy; water splitting

### 1. Introduction

Scientific research focuses on solar energy due to environmental and energy challenges. Photocatalysis is pivotal in the conversion of solar light energy to chemical energy, making it an important research field. Compared with traditional semiconductor photocatalysts such as metal oxide [1], metal-organic frameworks (MOFs) [2–3], and covalent organic frameworks (COFs) [4], tin oxides have been extensively investigated due to their abundant availability, nontoxic nature, and remarkable optical and electrical properties [5–7]. The stable stannic oxide (SnO<sub>2</sub>) and the metastable SnO [8] are the most common tin oxide compounds encountered in nature. SnO<sub>2</sub> is an n-type wide-bandgap semiconductor with rutile and cassiterite structures [9]. SnO is a p-type semiconductor with a bandgap ranging from 2.5 to 3.4 eV and naturally exists in three crystallographic forms, including  $\alpha$ -SnO with a cubic crystal structure,  $\beta$ -SnO with a tetragonal crystal structure, and  $\gamma$ -SnO. Over the past decades, SnO<sub>2</sub> and SnO have been extensively applied in areas such as lithium-ion batteries, solar cells, gas sensors, and photocatalysis, owing to their exceptional electrical and optical properties [10–11].

Certain nonstoichiometric tin oxides, including Sn<sub>2</sub>O<sub>3</sub>, Sn<sub>3</sub>O<sub>4</sub>, and Sn<sub>5</sub>O<sub>6</sub>, present unique physicochemical properties, such as magnetism and electrochemical performance [12]. Generally, tin oxides display diverse oxidation states derived from Sn, notably Sn<sup>2+</sup> and Sn<sup>4+</sup>. SnO<sub>2</sub> has been intensively studied due to its low resistance, high optical transparency, multivalence surfaces, and conductivity variations induced by adsorbates. These features have paved the way for the wide application of SnO<sub>2</sub> in transparent conductors, oxide catalysis, and solid-state gas sensors [13]. Moreover, the relatively deep valence band (VB) position of SnO<sub>2</sub> has resulted in its exploration as a photocatalyst for organic compounds such as methylene blue (MB) [14]. SnO is used as a reducing agent in cranberry glass production, and it is used as anode and coating materials in rechargeable lithium-ion batteries (LIBs) [15]. The p-type conductivity exhibited by SnO is a rare characteristic among metal oxide materials [16].

The mixed valence tin oxide, Sn<sub>3</sub>O<sub>4</sub>, has attracted considerable interest in the fields of photocatalysis, electrocatalysis, and photoelectrocatalysis [17–18]. The coexistence of Sn<sup>2+</sup> and Sn<sup>4+</sup> narrows its bandgap, imparting a yellowish hue to the material and enabling it to absorb visible light [19–20].

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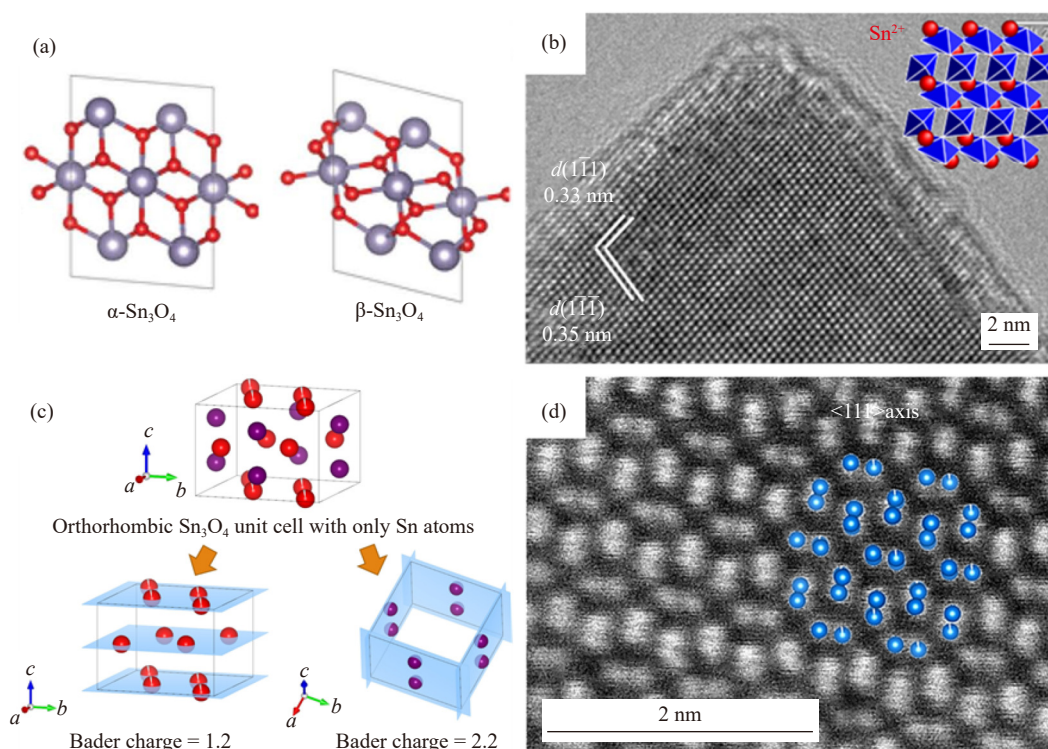
Tanabe *et al.* [21] extensively investigated single-phase  $\text{Sn}_3\text{O}_4$  synthesized via hydrothermal methods, focusing on its application as a photocatalyst for water splitting and  $\text{CO}_2$  reduction. The various types of the tin oxide family feature distinct physical and chemical properties, which render them scientifically intriguing and suitable for a wide range of technological applications [22]. However, the chemical composition of tin oxides extends beyond the two initially described compounds. Besides  $\text{Sn}_3\text{O}_4$ , other forms of  $\text{Sn}_x\text{O}_y$  ( $0.5 < x/y < 1$ ), such as  $\text{Sn}_2\text{O}_3$ ,  $\text{Sn}_4\text{O}_5$ , and  $\text{Sn}_5\text{O}_6$ , have been proposed, but their structures and stability remain debatable [23–24]. Consequently, computational studies have been conducted to predict the structure and property of these tin oxides, and the related calculations have been validated.

This review article presents the latest overview of recent advancements in the field of  $\text{Sn}_3\text{O}_4$  photocatalytic nanomaterials. The article first introduces the crystal structure and property of  $\text{Sn}_3\text{O}_4$ , providing a solid foundation for the comprehension of its photocatalytic behavior. Subsequently, the comprehensive summary of various approaches for the enhancement of the photocatalytic activity of  $\text{Sn}_3\text{O}_4$  are focused such as morphology control, ion doping, and heterostructure construction. Moreover, the diverse applications of  $\text{Sn}_3\text{O}_4$  photocatalytic materials are discussed, with a focus on areas such as photocatalytic degradation, photocatalytic hy-

drogen production, carbon dioxide reduction, antibacterial treatment, and optoelectronic sensing. A thorough discussion centers on the potential of  $\text{Sn}_3\text{O}_4$ -based nanomaterials in these applications, highlighting their unique properties and capabilities. Lastly, the article presents the future development directions in the field, offering valuable insights and guidance for the exploration and advancement of novel and highly efficient  $\text{Sn}_3\text{O}_4$ -based nanomaterials. Key areas of focus and potential research directions are also outlined to stimulate further progress and innovations in the field of  $\text{Sn}_3\text{O}_4$  photocatalysis.

## 2. Structure and characteristics of $\text{Sn}_3\text{O}_4$

$\text{Sn}_3\text{O}_4$  is a thermodynamically stable intermediate compound within the Sn–O phase diagram, and it exists in two distinct phases, the stable  $\alpha$  phase and the unstable  $\beta$  phase (Fig. 1(a)) [23].  $\text{Sn}_3\text{O}_4$  has a crystal structure of layered arrangement, with alternating stacked layers of symmetric  $\text{SnO}_6$  octahedra and distorted  $\text{SnO}$ -like units at the interfaces between layers. According to theoretical calculations, the coexistence of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  in  $\text{Sn}_3\text{O}_4$  leads to an optimal band structure for photocatalytic hydrogen evolution, which is characterized by a bandgap that aligns correspondingly with the energy of visible-light photons.



**Fig. 1.** (a) Crystal structure of  $\alpha\text{-Sn}_3\text{O}_4$  and  $\beta\text{-Sn}_3\text{O}_4$ . J.J. Wang, N. Umezawa, and H. Hosono, *Adv. Energy Mater.*, 6, 1501190 (2016) [23]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission; (b) high-resolution transmission electron microscopy (HRTEM) image of  $\text{Sn}_3\text{O}_4$ . Reprinted with permission from M. Manikandan, T. Tanabe, P. Li, *et al.*, *ACS Appl. Mater. Interfaces*, 6, 3790 [24]. Copyright 2014 American Chemical Society; (c) schematic of Bader charge analysis (blue planes added for better visualization): unit cell of orthorhombic  $\text{Sn}_3\text{O}_4$  with tin atoms only, tin atoms with a Bader charge around 1.2 (red) at the 4g and 4h Wyckoff positions and 2.2 (purple) at the 4f Wyckoff positions; (d) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of orthorhombic  $\text{Sn}_3\text{O}_4$ . Y.S. Liu, A. Yamaguchi, Y. Yang, *et al.*, *Angew. Chem. Int. Ed.*, 62, e202300640 (2023) [25]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Manikandan *et al.* [24] fabricated nanoscale structures comprising Sn<sub>3</sub>O<sub>4</sub> nanosheets (Fig. 1(b)). In conjunction with Pt as a cocatalyst, the Sn<sub>3</sub>O<sub>4</sub> material displayed a notable catalytic performance in the visible-light-driven decomposition of water within aqueous solutions. To optimize the synthesis of monoclinic phase Sn<sub>3</sub>O<sub>4</sub>, Liu *et al.* [25] systematically investigated various parameters, including heating time, pH, solution composition, and washing methods. Furthermore, the synthesis was controlled with precision through the modulation of the filling level of the precursor solution and tailoring of the gas composition within the hydrothermal reactor. Their study successfully unveiled a novel phase of Sn<sub>3</sub>O<sub>4</sub> possessing a structure similar to the orthorhombic SnPb<sub>2</sub>O<sub>4</sub> (Fig. 1(c)–(d)). Notably, a narrower bandgap was observed in the orthorhombic Sn<sub>3</sub>O<sub>4</sub> polymorph compared with the conventional monoclinic Sn<sub>3</sub>O<sub>4</sub> phase, which implies the enhanced absorption and utilization of visible light in photocatalytic devices.

### 3. Synthesis of Sn<sub>3</sub>O<sub>4</sub>

The synthesis strategies for Sn<sub>3</sub>O<sub>4</sub> can be broadly classified into two main categories. Solid-phase methods encompass annealing and carbothermal approaches, and liquid-phase methods include hydrothermal and solvothermal techniques [26–28]. Annealing is the earliest successfully applied method, and it entails heating of SnO to influence the transformation of unstable divalent tin to its tetravalent form, yielding a mixed-valence tin oxide. On the other hand, the carbothermal method employs carbon powder as a reducing agent to reduce SnO<sub>2</sub> at elevated temperature, which leads to the formation of Sn<sub>3</sub>O<sub>4</sub>. Meanwhile, solid-phase approaches are used to synthesize Sn<sub>3</sub>O<sub>4</sub> with diverse morphologies, and they often necessitate stringent and time-consuming experimental conditions, resulting in suboptimal sample purity. Conversely, liquid-phase methods, such as hydrothermal or solvothermal routes, offer a comparatively simple, safe, and controllable means of fabricating Sn<sub>3</sub>O<sub>4</sub> nanomaterials [29–30]. For these methods, at specific temperature and pressure conditions, a precursor reactant undergoes a reaction within a reaction vessel lined with polytetrafluoroethylene in a sealed system with either water or organic solvent as the solution, allowing for the precise control of nucleation and growth processes for the production of Sn<sub>3</sub>O<sub>4</sub> nanomaterials with diverse morphologies. The synthesized products exhibit excellent crystallinity, a relatively uniform grain distribution, and notable advantages, including the absence of agglomeration and the elimination of the need for calcination.

## 4. Strategies for improving photocatalytic performance

### 4.1. Mechanisms of photocatalytic enhancement

Semiconductor photocatalysis relies on the principles of solid-state band structures [31–32]. Sn<sub>3</sub>O<sub>4</sub> is an exemplary n-type semiconductor with a band structure comprising an un-

occupied high-energy conduction band (CB), a filled VB with electrons, and a bandgap separating the two [33]. Sn<sub>3</sub>O<sub>4</sub> is an indirect bandgap semiconductor, which means that the excitation of electrons from the VB to the CB occurs when the energy of incident light matches or surpasses the bandgap energy of Sn<sub>3</sub>O<sub>4</sub>. This process initiates the generation of highly active electron–hole pairs within the VB. However, the photogenerated electrons and holes are susceptible to recombination, dissipating stored light energy as heat in the absence of suitable electron or hole capture agents or driving forces. The appropriate acceptors or defects present on the catalyst's surface can suppress the recombination of photogenerated charge carriers, which facilitates their efficient separation and transfer to distinct sites on the surface. Photogenerated holes possess outstanding oxidation capabilities, whereas electrons are known for their strong reduction capacities. Consequently, photogenerated holes can oxidize water on the surface of Sn<sub>3</sub>O<sub>4</sub>, forming hydroxyl radicals ( $\cdot\text{OH}$ ). Meanwhile, electrons engage in reactions involving the dissolved oxygen adsorbed on the surface, yielding superoxide radicals ( $\cdot\text{O}_2^-$ ). These active species exhibit potent oxidation capabilities, which enable the complete mineralization of various organic pollutants into uncontaminated water and carbon dioxide [34]. In addition, highly active photogenerated electrons and holes can interact with water and liberating hydrogen and oxygen [35].

### 4.2. Strategies for photocatalytic enhancement

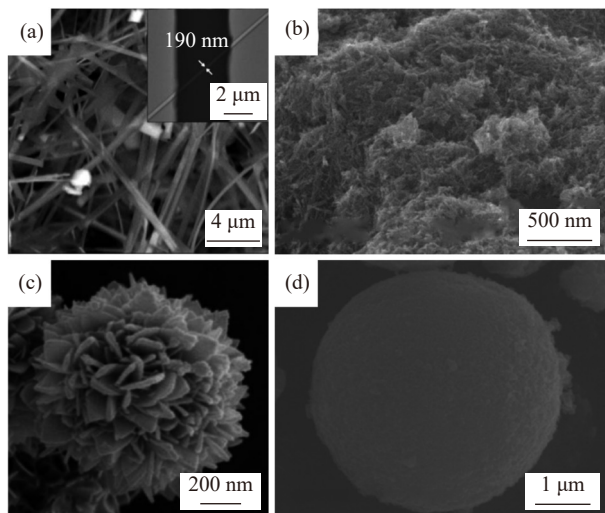
Certain challenges have been associated with single-phase Sn<sub>3</sub>O<sub>4</sub> photocatalytic materials: (1) Conventional synthesis methods typically yield single-phase Sn<sub>3</sub>O<sub>4</sub> materials, leading to elevated recombination rates of photogenerated charge carriers that detrimentally affect the photocatalytic performance. (2) Solar energy utilization remains suboptimal. Visible light energy constitutes approximately 44% of the solar spectrum, with near-infrared light accounting for roughly 50% [36]. Sn<sub>3</sub>O<sub>4</sub> can only absorb a small portion of visible light (<500 nm) [30]. Consequently, recent extensive research has concentrated on the expansion of the light absorption range of photocatalytic materials, which facilitated the efficient separation of photogenerated charge carriers and further enhanced their photocatalytic capabilities. These research endeavors primarily involved morphology control, ion doping, and the construction of heterostructures using Sn<sub>3</sub>O<sub>4</sub> materials.

#### 4.2.1. Morphological control

Semiconductor materials with different morphologies and particle sizes exhibit distinct physicochemical properties, which often influence their photocatalytic performance through variations in the specific surface area and crystal facet exposure [11,37]. In general, small particles possess large specific surface areas and follow short migration paths for photoinduced charges, thereby favoring improved photocatalytic activity. Furthermore, when the particle size approaches the radius of the first exciton (i.e., 1–10 nm), quantum size effects can be observed. These effects result in a widened



bandgap and enhance the catalytic capability of photoinduced electrons and holes and photocatalytic performance. Similar trends have been observed in  $\text{Sn}_3\text{O}_4$  photocatalytic materials. Stable structures of  $\text{Sn}_3\text{O}_4$  nanostructures, such as nanobelts [38], nanowires (NWs) [39], nanoflowers [40], and microball [41], have been prepared successfully through the selection of appropriate precursors and precise control of reaction conditions (Fig. 2).



**Fig. 2.** Scanning electron microscopy (SEM) images of  $\text{Sn}_3\text{O}_4$  with different morphologies: (a) nanobelts. Reprinted with permission from O.M. Berengue, R.A. Simon, A.J. Chiquito, *et al.*, *J. Appl. Phys.*, 107, 033717 (2010) [38]. Copyright 2010 AIP Publishing LLC; (b) NWs. Reprinted from *Nano Struct. Nano Objects*, 24, P. Mone, S. Mardikar, and S. Balgude, Morphology-controlled synthesis of  $\text{Sn}_3\text{O}_4$  nanowires for enhanced solar-light driven photocatalytic  $\text{H}_2$  production, 100615, Copyright 2020, with permission from Elsevier; (c) nanoflower. Republished with permission of Royal Society of Chemistry, from  $\text{Sn}_3\text{O}_4$ : A novel heterovalent-tin photocatalyst with hierarchical 3D nanostructures under visible light, Y.H. He, D.Z. Li, J. Chen, *et al.*, 4, 2013; permission conveyed through Copyright Clearance Center, Inc; (d) microball. Reprinted from *Mater. Chem. Phys.*, 221, S. Balgude, Y. Sethi, B. Kale, D. Amalnerkar, and P. Adhyapak,  $\text{Sn}_3\text{O}_4$  microballs as highly efficient photocatalyst for hydrogen generation and degradation of phenol under solar light irradiation, 493, Copyright 2019, with permission from Elsevier.

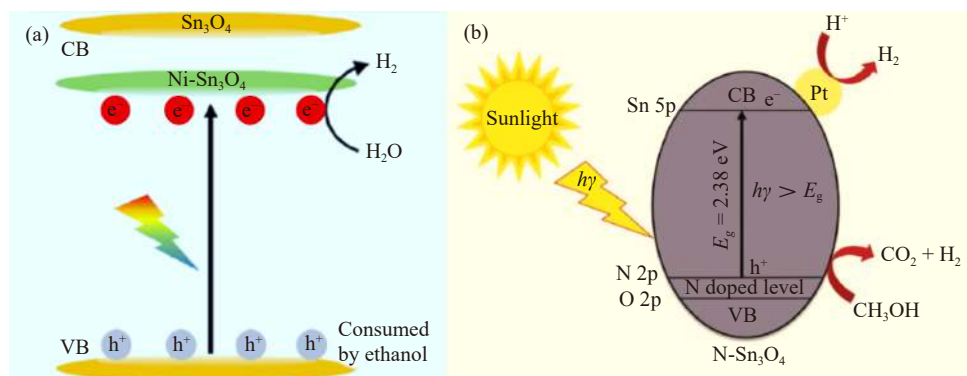
He *et al.* [40] synthesized a three-dimensional (3D) hierarchical nanostructured  $\text{Sn}_3\text{O}_4$  photocatalyst using a template-free solvothermal method.  $\text{SnO}_2$ ,  $\text{Sn}_3\text{O}_4$ , and  $\text{SnO}$  were obtained by adjusting the pH of the suspension. Specifically, white  $\text{SnO}_2$  nanoparticles were prepared at pH = 1, pure  $\text{Sn}_3\text{O}_4$  with a yellow color formed at pH = 3, and black  $\text{SnO}$  was synthesized under alkaline conditions with a pH of 13. Damaschio *et al.* [26] synthesized single-crystalline  $\text{Sn}_3\text{O}_4$  nanobelts, which grew via a gas–solid mechanism through a carbon thermal reduction process. Electrical measurements of individual  $\text{Sn}_3\text{O}_4$  nanobelts at different temperatures revealed the characteristics of undoped semiconductors. Balgude *et al.* [41] used an amber salt-driven hydrothermal

method to synthesize  $\text{Sn}_3\text{O}_4$  microspheres. These microspheres displayed an irregular contour nanostructure with thicknesses ranging from approximately 40 to 80 nm and excellent photocatalytic hydrogen production and phenol degradation activity under solar light irradiation. Mone *et al.* [39] applied a simple apple acid-induced hydrothermal process to synthesize  $\text{Sn}_3\text{O}_4$  NWs with an exceptional hydrogen evolution activity using tin oxalate as the starting material. The NWs exhibited a higher photocatalytic activity than their nanosheets counterparts, which could be attributed to the layered morphology and high crystallinity of  $\text{Sn}_3\text{O}_4$  NWs. Through precise control of the morphology,  $\text{Sn}_3\text{O}_4$  nanostructures with large specific surface areas were prepared, along with the exposure of more active sites and promoted photocatalytic activity.

#### 4.2.2. Ion doping

Ionic doping is an early proposed strategy for catalyst modification. In this method, metallic or nonmetallic ions are introduced into the lattice structure of the catalyst [42–46]. This doping approach broadens a material's absorption spectrum and creates charge separation centers that suppress the recombination of photogenerated charge carriers. Metallic ion doping introduces new charges, induces defects, alters lattice type, affects the movement and distribution of photo-generated electrons and holes, and modifies the band structure of  $\text{Sn}_3\text{O}_4$ , ultimately leading to changes in photocatalytic activity. Yang *et al.* [47] synthesized nickel-doped  $\text{Sn}_3\text{O}_4$  ( $\text{Ni-Sn}_3\text{O}_4$ ) using a one-pot synthesis method, which enabled the successful incorporation of metallic Ni into the lattice of  $\text{Sn}_3\text{O}_4$ . The doped Ni acted as a crystallinity inducer and enhanced the crystal quality of  $\text{Sn}_3\text{O}_4$ . Remarkably, under visible-light illumination,  $\text{Ni-Sn}_3\text{O}_4$  exhibited considerably improved photocatalytic hydrogen evolution performance, which is approximately 3.4 times higher than that of pure-phase  $\text{Sn}_3\text{O}_4$ . This enhanced activity was primarily attributed to the improved crystallinity of  $\text{Ni-Sn}_3\text{O}_4$ . Ni doping effectively reduced the bandgap width, enhancing light absorption, and increasing the susceptibility of the material to visible-light excitation (Fig. 3(a)).

Nonmetal ion doping effectively extends the light absorption range of  $\text{Sn}_3\text{O}_4$  materials and enables the direct utilization of a substantial portion of solar energy, including visible and near-infrared light. The nonmetal elements nitrogen (N), sulfur, carbon, and halogens are commonly used in doping. Balgude *et al.* [43] synthesized N-doped  $\text{Sn}_3\text{O}_4$  ( $\text{N-Sn}_3\text{O}_4$ ) using urea as the N precursor. The introduction of N led to the formation of new N 2p band on the O 2p VB, resulting in bandgap narrowing and the expansion of the light absorption edge to a wider range in the visible-light region (Fig. 3(b)). Furthermore, Zeng *et al.* [44] reported the effect of novel fluorine-doped  $\text{Sn}_3\text{O}_4$  ( $\text{F-Sn}_3\text{O}_4$ ) on the removal of pollutants in water, particularly the reduction of Cr(VI) and the degradation of organic pollutants. They demonstrated that F doping in  $\text{Sn}_3\text{O}_4$  enhanced the redox potential, which led to the generation of more electron–hole pairs and facilitated the separation of photoinduced electron–hole pairs. As a result, more reactive oxygen species (ROS) were produced.



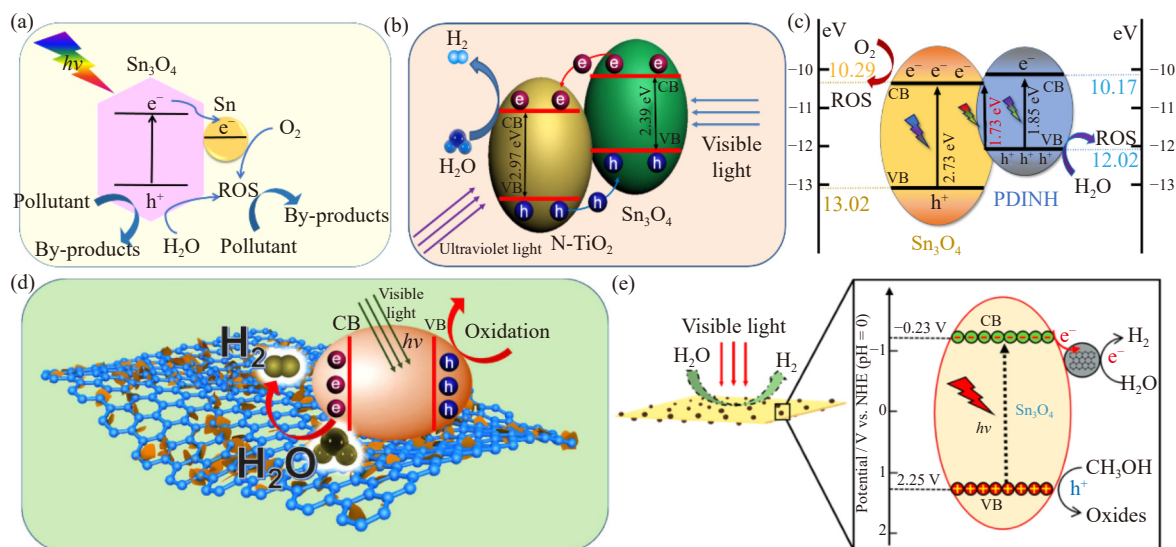
**Fig. 3.** (a) Band alignment of Sn<sub>3</sub>O<sub>4</sub> and Ni-Sn<sub>3</sub>O<sub>4</sub>. Reprinted with permission from R.Q. Yang, Y.C. Ji, L.W. Wang, *et al.*, *ACS Appl. Nano Mater.*, 3, 9268 [47]. Copyright 2020 American Chemical Society; (b) possible mechanism for photocatalytic hydrogen production by N-Sn<sub>3</sub>O<sub>4</sub> under sunlight irradiation. Republished with permission of Royal Society of Chemistry, from Unique N doped Sn<sub>3</sub>O<sub>4</sub> nanosheets as an efficient and stable photocatalyst for hydrogen generation under sunlight, S. Balgude, Y. Sethi, A. Gaikwad, B. Kale, D. Amalnerkar, and P. Adhyapak, 12, 2020; permission conveyed through Copyright Clearance Center.

#### 4.2.3. Heterostructures

The construction of heterostructures expands light absorption properties and enhances the charge carrier separation capabilities of materials [35–36,48–50]. Interface band engineering enables the formation of heterostructures between Sn<sub>3</sub>O<sub>4</sub> and various components, such as metal particles, inorganic semiconductors, organic semiconductors, carbon materials, and others [51–52]. Yang *et al.* [53] achieved an *in-situ* reduction of Sn<sub>3</sub>O<sub>4</sub> under a H<sub>2</sub> atmosphere and precisely controlled the reduction temperature and duration to create oxygen vacancies in Sn<sub>3</sub>O<sub>4-x</sub>. In addition, a portion of Sn<sub>3</sub>O<sub>4</sub> was reduced to Sn nanoparticles, which led to the formation of

semiconductor–metal contact in the Sn<sub>3</sub>O<sub>4-x</sub>/Sn Schottky junction. The Schottky junction was also established between Sn<sub>3</sub>O<sub>4-x</sub> and Sn, and it effectively enhanced the separation of photogenerated charge carriers. Meanwhile, the Schottky junction at the interface reduced the recombination of photogenerated charge carriers, and the excellent conductivity of Sn metal facilitated electron transfer. This synergistic effect considerably improved the utilization of light energy, resulting in the outstanding photocatalytic performance of the Sn<sub>3</sub>O<sub>4-x</sub>/Sn composite photocatalytic material (Fig. 4(a)).

Furthermore, Yu *et al.* [33] successfully fabricated a 3D semiconductor–semiconductor Janus-type heterostructure



**Fig. 4.** Schematic of the band structure and photoinduced charge transfer and separation at the interface: (a) Sn<sub>3</sub>O<sub>4</sub>/Sn. Reprinted by permission from Springer Nature: *Int. J. Miner. Metall. Mater.*, Sn/Sn<sub>3</sub>O<sub>4-x</sub> heterostructure rich in oxygen vacancies with enhanced visible light photocatalytic oxidation performance, R.Q. Yang, N. Liang, X.Y. Chen, *et al.*, Copyright 2021; (b) Sn<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub>. Republished with permission of Royal Society of Chemistry, from Hierarchical hybrid nanostructures of Sn<sub>3</sub>O<sub>4</sub> on N doped TiO<sub>2</sub> nanotubes with enhanced photocatalytic performance, X. Yu, L.F. Wang, J. Zhang, *et al.*, 3, 2015; permission conveyed through Copyright Clearance Center; (c) Sn<sub>3</sub>O<sub>4</sub>/PDINH. R.Q. Yang, G.X. Song, L.W. Wang, *Small*, 17, e2102744 (2021) [29]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission; (d) Sn<sub>3</sub>O<sub>4</sub>/rGO. Reprinted from *Appl. Catal. B Environ.*, 227, X. Yu, Z.H. Zhao, D.H. Sun, *et al.*, Microwave-assisted hydrothermal synthesis of Sn<sub>3</sub>O<sub>4</sub> nanosheet/rGO planar heterostructure for efficient photocatalytic hydrogen generation, 470, Copyright 2018, with permission from Elsevier; (e) Sn<sub>3</sub>O<sub>4</sub>/GQDs heterostructure. Reprinted with permission from X. Yu, Z.H. Zhao, N. Ren, *et al.*, *ACS Sustainable Chem. Eng.*, 6, 11775 [56]. Copyright 2018 American Chemical Society.

photocatalyst of  $\text{Sn}_3\text{O}_4/\text{N-TiO}_2$  by electrospinning and hydrothermal methods. The contact made by  $\text{Sn}_3\text{O}_4$  with the outer shell of  $\text{N-TiO}_2$  nanotubes led to the formation of a heterostructure. Photogenerated holes and electrons emerged in the VB and CB of  $\text{N-TiO}_2$  and  $\text{Sn}_3\text{O}_4$ , respectively. Given the distinct band positions of  $\text{N-TiO}_2$  and  $\text{Sn}_3\text{O}_4$ , photogenerated electrons in the CB of  $\text{Sn}_3\text{O}_4$  were readily injected into the CB of  $\text{TiO}_2$ , and the holes in the VB of  $\text{TiO}_2$  were injected into the VB of  $\text{Sn}_3\text{O}_4$ . In addition, the unique Janus morphology of  $\text{Sn}_3\text{O}_4/\text{N-TiO}_2$  contributed to the synergistic effect between the band structure and morphology, facilitating the effective separation of photogenerated electron-hole pairs (Fig. 4(b)).

Organic semiconductors refer to a class of organic materials possessing semiconductor properties and exhibiting favorable characteristics, such as good conductivity, nontoxicity, ease of fabrication, high stability, and unique electrochemical and physical properties. Polyaniline (PANI) and perylene diimide (PDI) are commonly used organic semiconductors. Yang *et al.* [29] successfully prepared a  $\text{Sn}_3\text{O}_4$ /pyromellitic diimide (PDINH) heterostructure by depositing a 5 nm-thick PDINH layer onto the surface of  $\text{Sn}_3\text{O}_4$  through recrystallization (Fig. 4(c)). Under illumination, three key processes occurred: (I)  $\text{Sn}_3\text{O}_4$  absorbed light below 450 nm, generating electron-hole pairs; (II) PDINH absorbed light below 670 nm, which also generated electron-hole pairs; (III)  $\text{Sn}_3\text{O}_4$  and PDINH formed a heterostructure via interfacial interaction, and given their favorable band alignment, electrons transitioned from the VB of PDINH to the CB of  $\text{Sn}_3\text{O}_4$ . This heterostructure exhibited a bandgap of 1.73 eV, extending the light absorption range to approximately 720 nm and notably enhancing the utilization of solar energy.

Moreover,  $\text{Sn}_3\text{O}_4$  can form heterostructures with carbon materials such as reduced graphene oxide (rGO). rGO, known for its high surface area and excellent conductivity, is widely used in combination with various semiconductor photocatalysts [54–55]. A microwave-assisted hydrothermal method enables the synthesis of a planar heterostructure consisting of  $\text{Sn}_3\text{O}_4$  nanosheets and rGO [30]. The adoption of the microwave-assisted hydrothermal method considerably reduces the reaction time, allowing the uniform growth of  $\text{Sn}_3\text{O}_4$  nanosheets on rGO. Under visible-light illumination, photogenerated holes and electrons appeared in the VB and CB of  $\text{Sn}_3\text{O}_4$ , respectively. Typically, these charge carriers recombined rapidly, leading to a low photocatalytic hydrogen evolution rate of  $\text{Sn}_3\text{O}_4$  alone. However, when  $\text{Sn}_3\text{O}_4$  nanoparticles were anchored onto the surface of rGO, the photogenerated electrons in the CB of  $\text{Sn}_3\text{O}_4$  transferred to rGO, facilitating hole-electron separation. rGO acted as an electron collector and transporter, effectively prolonging the lifetime of charge carriers and thereby enhancing charge separation and photocatalytic activity (Fig. 4(d)).

Furthermore, graphene can be reduced in size to form graphene quantum dots (GQDs), which exhibit unique capabilities, such as photoinduced electron transfer, photoluminescence, and electron storage, while maintaining a 2D struc-

ture. Under visible-light irradiation, electrons in the  $\text{Sn}_3\text{O}_4/\text{GQD}$  heterostructure can be excited from the VB to the CB of  $\text{Sn}_3\text{O}_4$  [56]. Subsequently, these electrons can transfer to GQDs, facilitating the effective separation of electron-hole pairs and enhancing photocatalytic activity. In addition, the  $\pi$ -conjugated GQDs function as sensitizers akin to organic dyes, sensitizing  $\text{Sn}_3\text{O}_4$  to a broader range of visible-light absorption and providing electrons to the CB of  $\text{Sn}_3\text{O}_4$ , which leads to a more efficient visible-light-driven photocatalytic hydrogen production (Fig. 4(e)). Overall, these findings highlight the potential of  $\text{Sn}_3\text{O}_4$ -based heterostructures for the enhancement of photocatalytic activity and expansion of visible-light absorption range, paving the way for advanced applications in solar energy conversion.

## 5. Application of $\text{Sn}_3\text{O}_4$ -based materials

### 5.1. Degradation of pollutants

The rapid development of industries has resulted in the crucial problem of water pollution for humans [20,44,57–58]. Yang *et al.* [59] successfully prepared a novel full-spectrum photocatalyst,  $\text{Sn}_3\text{O}_4/\text{Ni}$  foam heterostructure, via the *in situ* growth of  $\text{Sn}_3\text{O}_4$  nanosheets on the surface of Ni foam. The porous structure of the Ni foam and the heterostructure that formed between Ni and  $\text{Sn}_3\text{O}_4$  considerably enhanced the light absorption capacity of the photocatalyst.

Han *et al.* [60] introduced  $\text{AgCl}@\text{Ag}$  quantum dots to 2D  $\text{Sn}_3\text{O}_4$  nanosheets at the oil-water interface to create a unique 3D flower-like structure of  $\text{Sn}_3\text{O}_4/\text{AgCl}@\text{Ag}$  composite photocatalyst. The synergistic combination of  $\text{Sn}_3\text{O}_4$  with  $\text{AgCl}@\text{Ag}$  quantum dots enhanced the utilization of solar energy, and the heterostructure facilitated efficient photoinduced charge carrier transfer through the reduction of the energy barrier. The light-harvesting capacity of the material was further enhanced through surface plasmon resonance of Ag nanoparticles. Under visible-light irradiation, the photocatalytic activity of the  $\text{Sn}_3\text{O}_4/\text{AgCl}@\text{Ag}$  composite photocatalyst for the degradation of tetracycline hydrochloride and MB were 9.6 and 7.88 times, respectively, compared with that of pure  $\text{Sn}_3\text{O}_4$  nanosheets. These findings demonstrate the potential of  $\text{Sn}_3\text{O}_4/\text{AgCl}@\text{Ag}$  composite photocatalysts for the efficient degradation of organic pollutants under visible light, paving the way for advanced water treatment technologies.

### 5.2. $\text{H}_2$ generation

$\text{H}_2$ , as a clean and renewable energy source, plays a vital role in addressing the problems of environmental pollution and energy scarcity. Photocatalytic water splitting for hydrogen production is a crucial pathway [61–62]. Zou *et al.* [63] developed a  $\text{Sn}_3\text{O}_4/\text{PPy}$  heterostructure photocatalyst by employing a two-step process, which involved chemical oxidative polymerization and hydrothermal treatment for the *in-situ* immobilization of porous  $\text{Sn}_3\text{O}_4$  nanosheets onto the hollow nanorods of polypyrrole (PPy) (Fig. 5(a)). The conductive PPy polymer modification facilitated the transfer of photo-



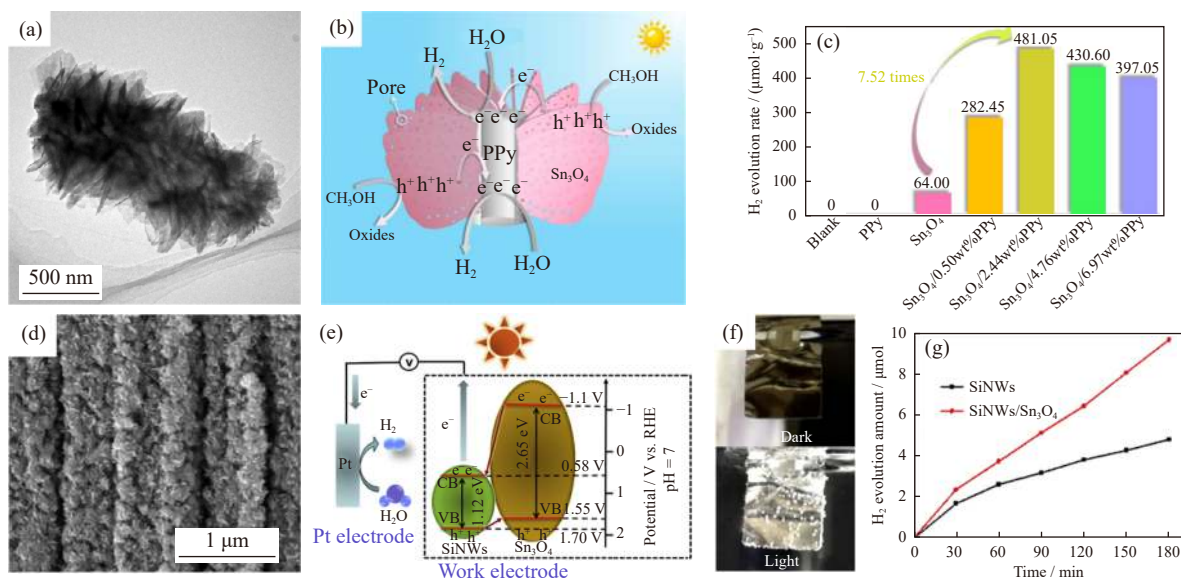
generated electrons from the CB of Sn<sub>3</sub>O<sub>4</sub> to PPy for water reduction and hydrogen production, and the holes were consumed by a methanol sacrificial agent at the VB of Sn<sub>3</sub>O<sub>4</sub>. In this system, PPy acted as an electron acceptor, initiating light-induced electron migration and promoting the separation of photogenerated electrons and holes, which improved the hydrogen generation performance of the Sn<sub>3</sub>O<sub>4</sub>/PPy heterostructure (Fig. 5(b)). In addition, the 3D structure formed by the uniform dispersion of porous Sn<sub>3</sub>O<sub>4</sub> nanosheets on hollow PPy nanorods contributed to the improved performance. A remarkable photocatalyst hydrogen production rate of 481.05  $\mu\text{mol}\cdot\text{g}^{-1}$  was obtained within 5 h, and such value was 7.52 times higher than that of pure Sn<sub>3</sub>O<sub>4</sub> (Fig. 5(c)).

Yang *et al.* [64] synthesized ultrafine Si NW arrays and *in-situ* grew Sn<sub>3</sub>O<sub>4</sub> nanosheets on their surfaces (Fig. 5(d)). Combined with the light confinement effect of Sn<sub>3</sub>O<sub>4</sub> nanosheets, the ultrafine NWs structure enhanced spectrum absorption. The formed heterostructure facilitated the direct transport of charge carriers, and the *in-situ* growth of Sn<sub>3</sub>O<sub>4</sub> reduced the interface resistance during the efficient charge carrier transfer (Fig. 5(e)). Photocatalytic water splitting experiments were conducted to evaluate H<sub>2</sub> production under illumination, and the results revealed a remarkable increase in the generation of H<sub>2</sub> gas bubbles (Fig. 5(f)). Notably, the Si NW/Sn<sub>3</sub>O<sub>4</sub> photoanodes, owing to the formation of a 3D heterostructure, exhibited significantly improved H<sub>2</sub> generation capability compared with the Si NWs (Fig. 5(g)). These findings underscore the potential of Si NW/Sn<sub>3</sub>O<sub>4</sub> heterostructures as candidate photoanodes for enhanced H<sub>2</sub> production via photocatalytic water splitting.

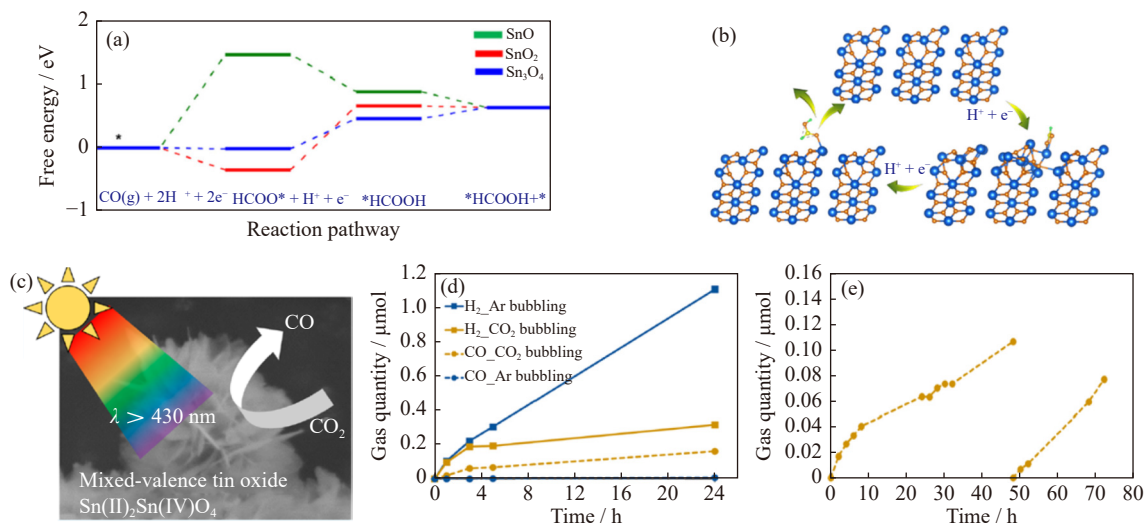
### 5.3. Reduction of CO<sub>2</sub>

The conversion of CO<sub>2</sub> to fuel with the use of solar light presents a promising solution for simultaneously addressing global warming and energy supply challenges. Chen *et al.* [65] conducted density functional theory calculations and experimental investigations and revealed Sn<sub>3</sub>O<sub>4</sub> as the most effective electrocatalyst among SnO<sub>x</sub> materials for the reduction of carbon-containing products under CO<sub>2</sub>. The distinctive electronic structure of Sn<sub>3</sub>O<sub>4</sub> enables synergistic effects between Sn<sup>2+</sup> and Sn<sup>4+</sup>, optimizing the adsorption strength of intermediates (Fig. 6(a)). Moreover, the upshifted band structure of Sn<sub>3</sub>O<sub>4</sub> provides moderate adsorption energies for H and HCOO intermediates, suppresses hydrogen evolution reaction, and enhances the intrinsic catalytic efficiency of CO<sub>2</sub> reduction (Fig. 6(b)). The synthesized Sn<sub>3</sub>O<sub>4</sub> electrocatalyst displayed a partial current density of 16.6 mA·cm<sup>-2</sup> at -0.9 V vs. RHE and carbon-based Faradaic efficiency of approximately 97.7%. Notably, the overpotential (190 mV) is lower than that of most reported SnO<sub>x</sub>-based electrocatalysts.

According to Liu *et al.* [66], under visible-light irradiation ( $\lambda > 430$  nm), the synthesized Sn<sub>3</sub>O<sub>4</sub> can catalyze the reduction of CO<sub>2</sub> to CO in aqueous solutions (Fig. 6(c)). Two different bubbling conditions were compared, and the findings revealed an increased CO production when CO<sub>2</sub> was bubbled, resulting in the generation of 0.16  $\mu\text{mol}$  CO within 24 h (Fig. 6(d)). Furthermore, the rate of CO generation remained stable for 72 h (Fig. 6(e)). CO<sub>2</sub> reduction was environmentally friendly and stable due to the visible-light activity of Sn<sub>3</sub>O<sub>4</sub>, positioning it as a promising photocatalyst that



**Fig. 5.** (a) TEM image of Sn<sub>3</sub>O<sub>4</sub>/PPy heterostructure; (b) schematic of the plausible mechanism for the hydrogen photoevolution reaction catalyzed by Sn<sub>3</sub>O<sub>4</sub>/PPy heterostructure; (c) H<sub>2</sub> photoevolution of Sn<sub>3</sub>O<sub>4</sub>/PPy heterostructures. Reprinted from *Appl. Catal. B Environ.*, 279, L.Q. Yang, M.F. Lv, Y. Song, *et al.*, Porous Sn<sub>3</sub>O<sub>4</sub> nanosheets on PPy hollow rod with photo-induced electrons oriented migration for enhanced visible-light hydrogen production, 119341, Copyright 2020, with permission from Elsevier; (d) SEM image of Sn<sub>3</sub>O<sub>4</sub>/Si heterostructure; (e) schematic of electron transfer in the Sn<sub>3</sub>O<sub>4</sub>/Si heterostructure; (f) photographs of H<sub>2</sub> generation on the Pt counter electrode: off-light and on-light conditions; (g) photoelectrocatalytic (PEC) H<sub>2</sub> generation of Sn<sub>3</sub>O<sub>4</sub>/Si heterostructure. Reprinted from *Appl. Catal. B Environ.*, 256, L.Q. Yang, Y.C. Ji, Q. Li, *et al.*, Ultrafine Si nanowires/Sn<sub>3</sub>O<sub>4</sub> nanosheets 3D hierarchical heterostructured array as a photoanode with high-efficient photoelectrocatalytic performance, 117798, Copyright 2019, with permission from Elsevier.



**Fig. 6.** (a) Free energy diagram of the CO<sub>2</sub> reduction reaction pathway to HCOOH on SnO, SnO<sub>2</sub>, and Sn<sub>3</sub>O<sub>4</sub>; (b) schematic of the CO<sub>2</sub> reduction reaction process on Sn<sub>3</sub>O<sub>4</sub>. Color code: orange for oxygen, yellow for carbon, blue for tin, and green for hydrogen. Faraday efficiency of the target product (for interpretation of the references to color in the figure, the reader is referred to the web version of this article). Reprinted from *Appl. Catal. B Environ.*, 277, Z. Chen, M.R. Gao, N.Q. Duan, *et al.*, Tuning adsorption strength of CO<sub>2</sub> and its intermediates on tin oxide-based electrocatalyst for efficient CO<sub>2</sub> reduction towards carbonaceous products, 119252, Copyright 2020, with permission from Elsevier; (c) schematic of photocatalytic reduction of CO<sub>2</sub> using Sn<sub>3</sub>O<sub>4</sub>; (d) photocatalytic CO<sub>2</sub> reduction properties under visible-light irradiation, with CO<sub>2</sub> (brown) and Ar (blue) bubbling; (e) CO evolution induced by Sn<sub>3</sub>O<sub>4</sub> under visible-light irradiation during 72 h of irradiation. Reprinted with permission from Y.S. Liu, A. Yamaguchi, Y. Yang, *et al.*, *ACS Appl. Energy Mater.*, 4, 13415 [66]. Copyright 2021 American Chemical Society.

warrants further exploration. These findings participate in the advancement of CO<sub>2</sub> reduction research and offer valuable insights into potential applications of Sn<sub>3</sub>O<sub>4</sub> as an efficient electrocatalyst and photocatalyst for CO<sub>2</sub> conversion.

#### 5.4. Antibacterial therapy

Bacterial infections pose an important global public health challenge, affecting millions of individuals annually. This problem is exacerbated by the emergence of multidrug-resistant “superbugs” due to antibiotic misuse, necessitating the development of novel reagents and approaches for the treatment of bacterial infections [67]. Antibacterial photocatalytic therapy (APCT) is a promising treatment modality for drug-resistant bacterial infections, leveraging advances in optical technology and the development of photocatalytic materials [68–70]. However, the efficacy of PDT in *in vivo* antibacterial treatment is often compromised by the limited tissue penetration depth of the light source and low-oxygen microenvironment at the infection site.

Wang *et al.* [71] successfully prepared porous Sn<sub>3</sub>O<sub>x</sub> nanosheets *in-situ* with surface amorphous oxygen-rich vacancies on Ni foam through a simple hydrothermal method. These nanosheets demonstrated an enhanced photoelectrochemical sterilization performance. The porous structure of Sn<sub>3</sub>O<sub>x</sub> enriched the O vacancies on its surface and extended the absorption spectrum from visible light to the near-infrared region. Moreover, the oxygen vacancies boosted the effective separation of electron–hole pairs. Notably, the sheet-like porous structure increased the surface active sites and the contact area between the bacteria and the electrode. As a result, the ROS generated during the photoelectrochemical sterilization process can directly act on the bacterial sur-

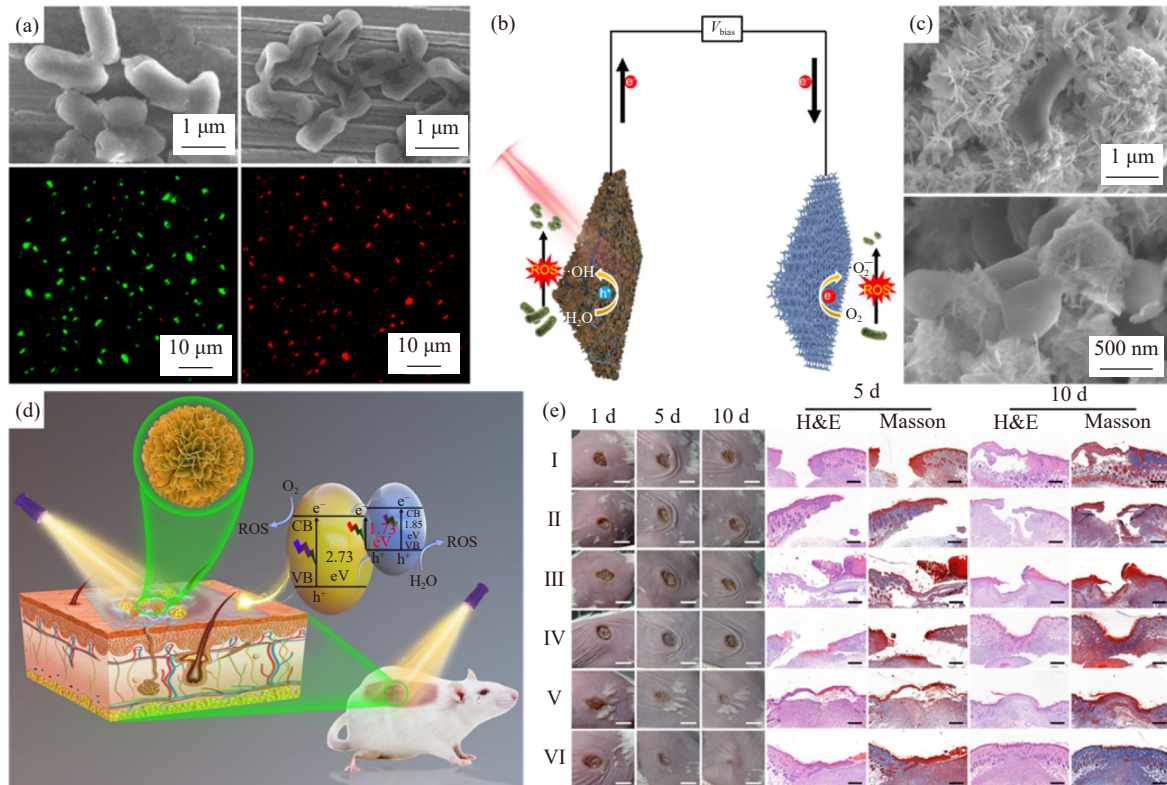
face. Remarkably, drug-resistant bacteria in water were completely eliminated within 30 min, achieving 100% efficiency (Fig. 7(a)–(b)).

Yang *et al.* [29] developed an innovative organic–inorganic hybrid Sn<sub>3</sub>O<sub>4</sub>/PDINH heterostructure for the photocatalytic generation of ROS to combat drug-resistant bacteria (Fig. 7(c)–(e)). The organic semiconductor PDINH was employed to self-assemble on the surface of Sn<sub>3</sub>O<sub>4</sub> nanosheets via abundant hydrogen bonding and π–π stacking interactions. This self-assembly created a unique “hook-loop” adhesive surface that interacted with functional groups on the bacterial surface, resulting in their firm adherence to the bacteria. This hybrid heterostructure also exhibited a remarkably enhanced photocatalytic activity. Moreover, it showed an extended absorption spectrum up to 720 nm in the near-infrared region and effectively reduced the rate of photogenerated charge carrier recombination, thereby generating a high amount of ROS. The hybrid nanostructure was applied as an antibacterial coating on the skin surface for *in vivo* photocatalytic sterilization of a mouse model with *S. aureus*-infected skin wounds, and it considerably promoted the healing of infected skin wounds. This work presented a novel approach for the fabrication of full-spectrum organic–inorganic hybrid adhesive heterostructure photocatalysts with potential applications in wound infection treatment.

#### 5.5. Solar cells

In the field of perovskite solar cells (PSCs), 2D mixed-valence tin oxide Sn<sub>3</sub>O<sub>4</sub> has emerged as a promising electron transport layer (ETL) due to its low defect density and suitable band structure. Li *et al.* [72] reported the controllable synthesis of 2D van der Waals mixed-valence tin oxides





**Fig. 7.** (a) SEM images of Chf *E. coli* before and after PEC oxidation for 30 min and the corresponding fluorescence microscopic images; (b) schematic of Sn<sub>3</sub>O<sub>x</sub>/Ni foam photoanode. Reprinted by permission from Springer Nature: *Rare Met.*, Surface amorphization oxygen vacancy-rich porous Sn<sub>3</sub>O<sub>x</sub> nanosheets for boosted photoelectrocatalytic bacterial inactivation, L.W. Wang, L. Liu, Z. You, *et al.*, Copyright 2023; (c) SEM images of bacterial treatment with Sn<sub>3</sub>O<sub>4</sub>/PDINH heterostructure; (d) schematic of Sn<sub>3</sub>O<sub>4</sub>/PDINH APCT; (e) photographs of the infected wound treated on 1, 5, and 10 d and infected wound histologic analyses on days 5 and 10 at different treatments (I: phosphate-buffered saline (control), II: only light, III: Sn<sub>3</sub>O<sub>4</sub>/PDINH, IV: Sn<sub>3</sub>O<sub>4</sub>+light, V: PDINH+light, VI: Sn<sub>3</sub>O<sub>4</sub>/PDINH+light). The scale bar is 0.5 cm in the photographs and 400  $\mu$ m in the histologic picture, respectively. R.Q. Yang, G.X. Song, L.W. Wang, *Small*, 17, e2102744 (2021) [29]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

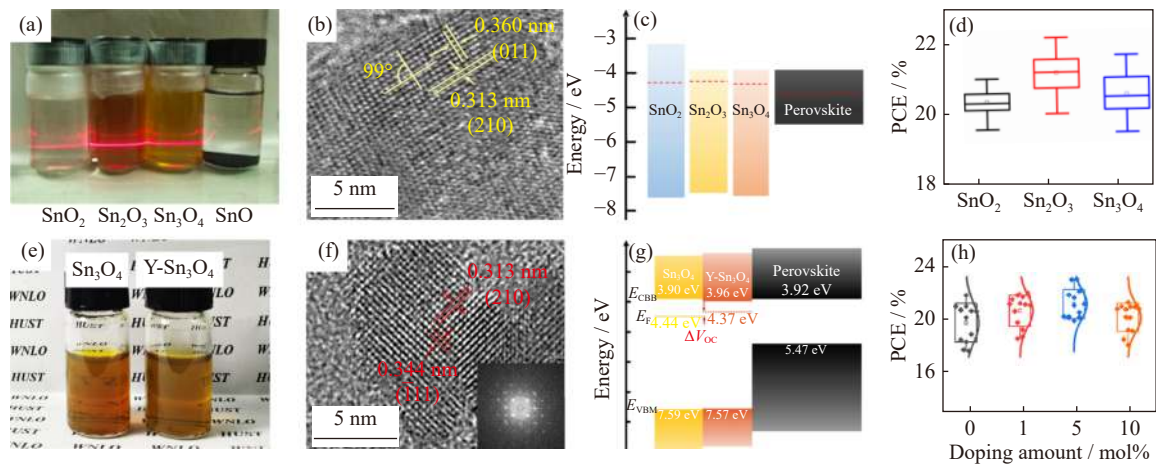
(Sn<sub>2</sub>O<sub>3</sub> and Sn<sub>3</sub>O<sub>4</sub>) and their application as electron transport materials in planar PSCs. The sizes of the synthesized Sn<sub>2</sub>O<sub>3</sub> and Sn<sub>3</sub>O<sub>4</sub> nanoparticles, which can be stably dispersed in water as colloids for several months, ranged from 5 to 20 nm (Fig. 8(a)–(b)). In addition, Sn<sub>2</sub>O<sub>3</sub> and Sn<sub>3</sub>O<sub>4</sub> demonstrated typical n-type semiconductor band structures, low trap densities, and appropriate energy level alignment with halide perovskites (Fig. 8(c)). According to experimental results, the steady-state power conversion efficiencies (PCEs) of Sn<sub>2</sub>O<sub>3</sub>-based and Sn<sub>3</sub>O<sub>4</sub>-based planar PSCs reached 22.36% and 21.83%, respectively (Fig. 8(d)).

Furthermore, the n-doping of Sn<sub>3</sub>O<sub>4</sub> mixed-valence tin oxide through YCl<sub>3</sub> doping was explored to enhance its potential as an ETL in PSCs [73]. For Y doping levels below 10mol% (Y-to-Sn mol ratio), both products appeared as yellow colloids with good dispersibility in water (Fig. 8(e)). The Y-Sn<sub>3</sub>O<sub>4</sub>, with an optimal doping level of 5mol%, exhibited an elliptical shape with a length of approximately 20 nm and a thickness of approximately 5 nm (Fig. 8(f)). The doping level played a crucial role in the performance of Sn<sub>3</sub>O<sub>4</sub> as excessive YCl<sub>3</sub> doping resulted in phase segregation along with the formation of SnO. However, at the 5mol% Y doping level, the electronic properties of Sn<sub>3</sub>O<sub>4</sub> can be successfully optimized by increasing the electron density and conductiv-

ity and shifting the Fermi level upward (Fig. 8(g)). The optimized electronic performance, achieved through enhanced electron extraction and transport capabilities, and optimized energy level alignment in Sn<sub>3</sub>O<sub>4</sub> considerably improved its potential as an ETL in PSCs. Consequently, the PSCs attained a PCE of 23.05% (Fig. 8(h)). These findings further highlight the application prospects of mixed-valence tin oxides in highly efficient PSCs.

## 5.6. Sensors

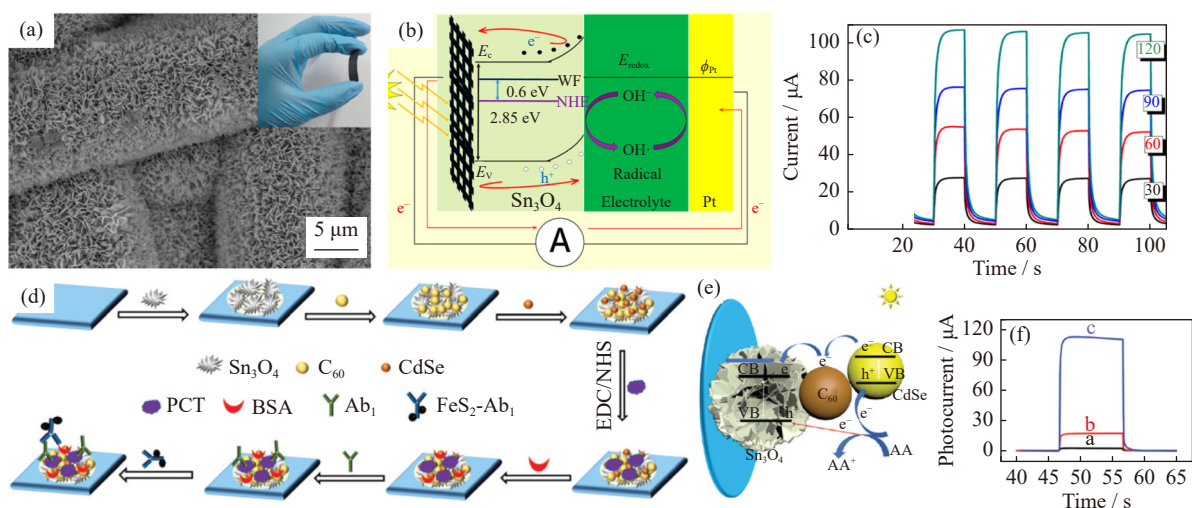
Considerable attention has been paid to photodetectors based on particularly self-powered photodetectors that eliminate the need for external power sources such as batteries. These self-powered devices show remarkable potential for high-sensitivity and high-speed applications. However, the fabrication of visible-light photodetectors remains a challenging task. Wang *et al.* [74] introduced a novel photovoltaic chemical platform based on Sn<sub>3</sub>O<sub>4</sub>, where Sn<sub>3</sub>O<sub>4</sub> served as the active material for visible-light detection. A hydrothermal method was used to *in-situ* modify Sn<sub>3</sub>O<sub>4</sub> nanosheets on the carbon fiber paper (CFP), and a molecularly imprinted polymer (MIP) layer with a specific selectivity for 2,4-dichlorophenoxyacetic acid (2,4-D) was synthesized on Sn<sub>3</sub>O<sub>4</sub>/CFP through the electropolymerization reaction of



**Fig. 8.** (a) Photographs of  $\text{SnO}_2$ ,  $\text{Sn}_2\text{O}_3$ ,  $\text{Sn}_3\text{O}_4$  dispersions, and  $\text{SnO}$  precipitation in water; (b) HRTEM image of  $\text{Sn}_3\text{O}_4$  for phase identification; (c) band alignments with halide perovskites; (d) box plot of efficiency distribution values of PSCs based on  $\text{SnO}_2$ ,  $\text{Sn}_2\text{O}_3$ , and  $\text{Sn}_3\text{O}_4$  ETLs. Error bars represent the standard deviation. Reprinted with permission from S. Li, F. Qin, Q. Peng, *et al.*, *Nano Lett.*, 20, 8178 [72]. Copyright 2020 American Chemical Society; (e) photograph of  $\text{Sn}_3\text{O}_4$  and  $\text{Y-Sn}_3\text{O}_4$  dispersions in water; (f) HRTEM image and crystal labeling of  $\text{Y-Sn}_3\text{O}_4$ . The inset image shows the fast Fourier transform result; (g) band alignment of  $\text{Sn}_3\text{O}_4$  and  $\text{Y-Sn}_3\text{O}_4$  with perovskite; (h) efficiency distribution of devices corresponding to various Y-doping concentrations [73].

pyrrole in the presence of 2,4-D. 2,4-D was selected for the analysis due to its classification as a “potentially carcinogenic compound” for humans. The label-free photodetector leverages the structural advantages of  $\text{Sn}_3\text{O}_4$ /CFP and the selectivity of MIP and demonstrates a linear range of  $5.0 \times 10^{-11}$  to  $1.0 \times 10^{-7}$   $\text{mol} \cdot \text{L}^{-1}$  for 2,4-D and an exceptionally low detection limit of  $1.08 \times 10^{-11}$   $\text{mol} \cdot \text{L}^{-1}$ . This photovoltaic chemical platform exhibited outstanding stability, repeatability, ease of preparation, low cost, and an impressively low detection limit. In addition, the photovoltaic chemical sensor was integrated onto surfaces of various nonplanar shapes and sizes, given the flexibility and bendability of CFP, thereby expanding the application range of this material in sensor construction.

Xu *et al.* [75] used an improved hydrothermal method to synthesize vertically aligned  $\text{Sn}_3\text{O}_4$  nanosheets on CFP and exploited them as self-powered photovoltaic chemical batteries for visible-light detection. The  $\text{Sn}_3\text{O}_4$  nanosheets grew perpendicularly on the CFP and formed a dense and uniform distribution on its surface. The intersecting nanosheets created numerous mesopores measuring hundreds of nanometers (Fig. 9(a)). The enhanced photoresponse was attributed to the synergistic effect between the vertically grown  $\text{Sn}_3\text{O}_4$  nanosheets and the CFP substrate. The vertically aligned nanosheets provided efficient active sites by exposing more catalytic sites to the electrolyte. Furthermore, the layered structure of  $\text{Sn}_3\text{O}_4$  with mesopores enhanced light absorption as the incident light was scattered between the nanosheets



**Fig. 9.** (a) SEM image of hierarchical  $\text{Sn}_3\text{O}_4$ /carbon fiber heterostructure; (b) bandgap and  $V_O$  positions for  $\text{Sn}_3\text{O}_4$ ; (c) photocurrent response under on/off cycling for 20 s at 0 V vs.  $\text{Ag}/\text{AgCl}$  for incident intensities equal to 30, 60, 90, and 120  $\text{mW} \cdot \text{cm}^{-2}$ . Reprinted with permission from W.W. Xia, H.Y. Qian, X.H. Zeng, J. Dong, J. Wang, and Q. Xu, *J. Phys. Chem. C*, 121, 19036 [75]. Copyright 2017 American Chemical Society; (d) construction process of the PEC sensor for procalcitonin (PCT) detection; (e) feasible mechanism of electron transfer of the PEC assay; (f) photocurrent of different electrodes. Republished with permission of Royal Society of Chemistry, from Antigen down format photoelectrochemical analysis supported by fullerene functionalized  $\text{Sn}_3\text{O}_4$ , R. Xu, Y. Du, D.Q. Leng, *et al.*, 56, 2020; permission conveyed through Copyright Clearance Center.

and captured by the mesopores. Light reflection was reduced in addition to enhanced light absorption. The CFP substrate contributed to the large surface area and facilitated charge and mass transfer (Fig. 9(b)).

The performance of the self-powered photovoltaic chemical batteries was evaluated using continuous visible-light pulses with varying intensities in alternating on/off cycles at specific time intervals. The photocurrent remained high after multiple on/off irradiation switching cycles. Moreover, the photocurrent increased with the increase in incident intensity (Fig. 9(c)). Compared with other self-powered devices that require binders, the in situ grown Sn<sub>3</sub>O<sub>4</sub> electrodes on the CFP eliminated the need for binders, resulting in improved flexibility and performance, long-term stability, and easy recovery. Given its simplicity, cost-effectiveness, and environmentally friendly nature, this self-powered detector is highly promising for various applications in visible-light devices.

Wei et al. [76] proposed a novel competitive photovoltaic chemical sensor based on an Ag-down configuration (Fig. 9(d)). In this setup, a photosensitive material was immobilized on the electrode using a standard Ag method. Subsequently, specific immune reactions were induced for the comodification of the first antibody (Ab1) and the target Ag on the electrode. Finally, the second antibody (Ab2) labeled with a suitable marker was immobilized. Fig. 9(e) depicts the possible mechanism of this configuration. The Sn<sub>3</sub>O<sub>4</sub> material exhibited high photosensitivity, effectively absorbing visible light and displaying a satisfactory photoelectrochemical response. However, its relatively wide bandgap limited its potential for PEC analysis. To overcome this limitation, the researchers introduced C<sub>60</sub>, a carbon nanostructure material known for its excellent photocatalytic performance. With its unique delocalized conjugated structure, C<sub>60</sub> acted as an excellent electron acceptor, which enhanced charge separation and reduced the charge recombination of

Sn<sub>3</sub>O<sub>4</sub>. As a result, the photocatalytic activity was improved. In addition, CdSe, an easily functionalized photosensitizer, was utilized to connect biomolecules. The cosensitization of C<sub>60</sub> and CdSe enhanced the PEC response by more than five-fold compared with the pure material in the presence of ascorbic acid (Fig. 9(f)). This sensor demonstrated excellent sensitivity and stability, providing a powerful platform not only for the sensitive detection of PCT but also for the potential monitoring of other proteins.

## 6. Conclusions and future perspectives

Sn<sub>3</sub>O<sub>4</sub> possesses thermodynamic stability and a bandgap within the visible light spectrum and shows promise as a visible-light-driven photocatalyst. This compound exhibits favorable properties, including suitable band edge positioning, low resistance, abundance, nontoxicity, and excellent photochemical stability in acidic and alkaline environments. Nonetheless, the low charge separation efficiency of pure Sn<sub>3</sub>O<sub>4</sub> restricts its photocatalytic performance. This article presented a comprehensive overview of the latest advancements in the enhanced photocatalytic activity of Sn<sub>3</sub>O<sub>4</sub>. Various strategies, such as morphology control, ion doping, and heterostructure construction, have been employed for the design and fabrication of Sn<sub>3</sub>O<sub>4</sub>-based nanocomposites. The photocatalytic performances of these materials were thoroughly investigated, which led to their utilization in diverse applications, such as photocatalytic degradation, photocatalytic H<sub>2</sub> production, photocatalytic CO<sub>2</sub> reduction, photocatalytic disinfection, photovoltaics, and other related areas. Table 1 summarizes the latest functions and advantages of Sn<sub>3</sub>O<sub>4</sub>-based materials. The potential and research significance of Sn<sub>3</sub>O<sub>4</sub>-based photocatalytic materials extend to various fields. However, some issues remain to be addressed.

First, researchers have achieved considerable progress in

**Table 1. Latest functions and advantages of Sn<sub>3</sub>O<sub>4</sub>-based materials**

Materials	Application	Performance	Advantages	Ref.
Sn <sub>3</sub> O <sub>4</sub> /Sn	Degradation of pollutants	Rh b degradation	Oxygen vacancies; metal–semiconductor heterostructure; lower cytotoxicity	[53]
Sn <sub>3</sub> O <sub>4</sub> /Ni	Degradation of pollutants	PAM degradation	Metal–semiconductor heterostructure; photoelectrocatalysis	[59]
Sn <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub>	Degradation of pollutants H <sub>2</sub> generation	MO degradation Water splitting	Semiconductor–semiconductor heterostructure; Janus heterostructure;	[33]
Ni-Sn <sub>3</sub> O <sub>4</sub>	H <sub>2</sub> generation	Water splitting	Enhanced crystallinity	[47]
Sn <sub>3</sub> O <sub>4</sub> /rGO	H <sub>2</sub> generation	Water splitting	Planar heterostructure; more catalytic active sites	[30]
Sn <sub>3</sub> O <sub>4</sub> /GQDs	H <sub>2</sub> generation	Water splitting	Mott–Schottky plots; GQDs as a photosensitizer	[56]
Sn <sub>3</sub> O <sub>4</sub> nanoflowers	Reduction of CO <sub>2</sub>	Reduction of CO <sub>2</sub> to CO	No cocatalysts	[66]
Sn <sub>3</sub> O <sub>4</sub> /PDINH	Antibacterial therapy	Inactivation of bacteria ( <i>E. coli</i> and <i>S. aureus</i> )	Inorganic–organic heterostructure; capture bacteria	[29]
Sn <sub>3</sub> O <sub>x</sub> /Ni	Antibacterial activity	Inactivation of bacteria ( <i>E. coli</i> and <i>S. aureus</i> )	Oxygen vacancies; photoelectrocatalysis	[71]
Y-Sn <sub>3</sub> O <sub>4</sub>	Solar cells	ETL for PSCs	High electron density; enhanced electron extraction capability	[73]
Sn <sub>3</sub> O <sub>4</sub> /CPF	Sensors	Visible-light detector	Large surface areas; good conductive channel for electron transport	[75]



the development of diverse and scalable approaches for the synthesis of Sn<sub>3</sub>O<sub>4</sub> catalysts. However, the reproducible large-scale synthesis of Sn<sub>3</sub>O<sub>4</sub> with precisely controlled morphology and composition remains a huge challenge. Further investigations must be conducted on the catalytically active surfaces of tin(IV) oxide and the crucial factors influencing its controllable synthesis. Under environmentally friendly conditions, the use of cost-effective and ecofriendly synthetic methods remains necessary.

Second, although the photocatalytic process involving Sn<sub>3</sub>O<sub>4</sub> appears conceptually straightforward, its practical implementation is intricate and incompletely understood. Theoretical studies and *in-situ* surface chemistry research must be performed to gain insights into the intricate reactions of Sn<sub>3</sub>O<sub>4</sub> and pave the way for the refinement and optimization of future catalyst designs.

Third, despite the immense potential of photocatalytic technology, the photovoltaic conversion efficiency of most Sn<sub>3</sub>O<sub>4</sub>-based semiconductor photocatalysts remains relatively low and thus must be improved. The modification of mixed-valence Sn<sub>3</sub>O<sub>4</sub> presents a viable route to further enhance its photocatalytic performance. The use of advanced characterization techniques and computational studies is required for a comprehensive understanding of this aspect.

Last, compared with the studies on other materials, the research on Sn<sub>3</sub>O<sub>4</sub> is relatively nascent, and its functionalities, effects, and applications require further exploration and advancements. Notably, properties resembling those of noble metals, surface plasmon resonance effects, influence of carriers, and organic reactions exhibit remarkable potential and merit extensive investigation. When harnessed effectively, these characteristics will play a pivotal role in photocatalytic applications.

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## Conflict of Interest

The authors declare no competing financial interest.

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