

Nanostructured Ternary Metal Tungstate-Based Photocatalysts for Environmental Purification and Solar Water Splitting: A Review

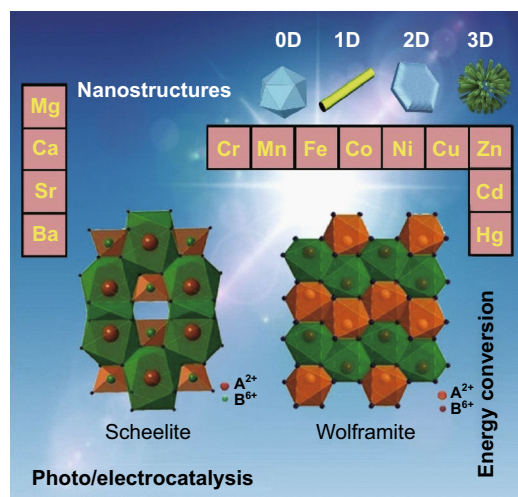
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Highlights

- A series of ternary tungstate-based photocatalysts and their applications in solar energy conversion and environmental purification are systematically introduced.
- The relationship between intrinsic structures and unique properties of ternary tungstate-based photocatalysts is discussed and summarized in detail.
- Various new concepts and innovative strategies are employed to enhance the photocatalytic performance of ternary tungstate-based photocatalysts

Abstract Visible-light-responsive ternary metal tungstate (MWO_4) photocatalysts are being increasingly investigated for energy conversion and environmental purification applications owing to their striking features, including low cost, eco-friendliness, and high stability under acidic and oxidative conditions. However, rapid recombination of photoinduced electron–hole pairs and a narrow light response range to the solar spectrum lead to low photocatalytic activity of MWO_4 -



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based materials, thus significantly hampering their wide usage in practice. To enable their widespread practical usage, significant efforts have been devoted, by developing new concepts and innovative strategies. In this review, we aim to provide an integrated overview of the fundamentals and recent progress of MWO_4 -based photocatalysts. Furthermore, different strategies, including morphological control, surface modification, heteroatom doping, and heterojunction fabrication, which are employed to promote the photocatalytic

activities of MWO_4 -based materials, are systematically summarized and discussed. Finally, existing challenges and a future perspective are also provided to shed light on the development of highly efficient MWO_4 -based photocatalysts.

Keywords Ternary metal tungstates · Micro- and nanostructures · Photocatalysis · Environmental purification · Water splitting

1 Introduction

Since Fujishima and Honda in 1972 demonstrated that titanium dioxide (TiO_2) can be used as photoanode to split water excited by ultraviolet light, photocatalysis technology has been viewed as among the most promising approaches to solve the global energy crisis and environmental problems [1–3]. In general, a complete semiconductor photocatalytic cycle involves light-harvesting, photogenerated charge carrier excitation, charge separation and transfer, and surface redox reactions [4–6] that allow for the formation of reactive oxygen species (ROSs), such as free electrons (e^-), hydrogen peroxide (H_2O_2), hydroxyl ($\cdot OH$), and superoxide radicals ($\cdot O_2^-$) [7, 8]. The aforementioned ROSs play crucial roles in various important applications, including photocatalysis [9–12], photoelectrocatalysis [13–17], plasma photocatalysis [18, 19], and photothermocatalysis [20–22]. Until now, TiO_2 has been among the most extensively studied semiconductor photocatalysts because of its strong oxidative ability, chemical stability, long durability, and nontoxicity [23–25]. However, the TiO_2 photocatalyst possesses a wide band gap of ~ 3.2 eV that can only absorb ultraviolet (UV) light, which is a small fraction ($\sim 5\%$) of solar light, thereby hardly harvesting the remaining solar energy [26, 27]. To efficiently utilize the majority of the solar spectrum, Fe_2O_3 - [28], WO_3 - [29, 30], Bi_2WO_6 - [31], ZnO - [32], Bi_2O_3 - [33], and NiO -based semiconductors [34] have been widely developed as photocatalysts for environmental treatment and solar water splitting (Fig. 1). Nevertheless, low sunlight utilization efficiency and quantum yield, rapid reverse reactions, and poor stability still hinder practical applications of these photocatalytic materials [35–39].

Desired photocatalysts should have a suitable band gap to achieve a high harvesting efficiency of sunlight, sufficient quantum yield, and an appropriate position of the band edge to trigger redox reactions [40–42]. For an ideal photocatalyst, the conduction band (CB) edge should be sufficiently negative to drive the photo-reduction reaction. In contrast, the valence band (VB) edge should be

sufficiently positive to trigger the photo-oxidation reaction [43]. For example, in photocatalytic water splitting, when the VB edge position of the semiconductor photocatalyst is more positive than the potential of H_2O/O_2 (1.23 V vs. NHE) and the CB position is more negative than the potential of H_2/H_2O (0 V vs. NHE), the water splitting reaction can occur [44–47].

Recently, ternary tungstate-based complex oxides have been developed as potential candidates for efficient photocatalytic applications [48–50]. Tungstates are described by the general formula MWO_4 (M denotes a bivalent cation) [51] and are widely used in the luminescence, microwave ceramics, and catalytic fields, given their self-activating fluorescence effect, microwave, and optical properties [52–55]. Owing to the variety of bivalent cations, the crystal structure of MWO_4 is dependent on the size of cationic radii. According to the literature [56], MWO_4 typically has a monoclinic wolframite structure for small M^{2+} cations (M = Fe, Co, Sn, and Ni) and a tetragonal scheelite structure for large M^{2+} cations (M = Ca, Ba, Pb, and Sr), as shown in Fig. 2 [57]. During the past few decades, MWO_4 with large radii cations, including $CaWO_4$ [58, 59], $BaWO_4$ [60, 61], $PbWO_4$ [62], and $SrWO_4$ [63], has been prepared using different synthesis approaches. However, the band gaps of these MWO_4 photocatalysts are much larger than that of TiO_2 and are not suitable for practical photocatalytic applications. In contrast, the band gaps of MWO_4 with small-radii cations are considerably smaller than that of TiO_2 and could be a promising choice for the efficient utilization of solar energy [64–72]. The band-gap energies of representative MWO_4 are summarized in Fig. 3 and Table 1. In addition, the band-gap energies of various MWO_4 and the radii of the metal cations are plotted in Fig. 4. It can be seen that a flock of MWO_4 is in the yellow area, in which each MWO_4 has a smaller metal cation radius (< 0.73 Å) and narrower band-gap energy (< 3.2 eV) than those of the others. In contrast, MWO_4 with a larger cation radius have larger band-gap energy. Notably, for specific MWO_4 , the band gaps presented in Table 1 are not the only ones, because the absorption light range of the semiconductors can be affected and controlled by various factors, including morphology, size, doping, and defects, thus resulting in one semiconductor material possessing several band-gap energies. By comparing the requirements of novel photocatalysts, MWO_4 with small-radius cations is more advantageous and can be further developed as highly efficient photocatalysts. In addition, it is clearly observed that ternary MWO_4 systems with a narrow band gap have transition metals as the cation component, which is earth-abundant, cost effective, and low-toxicity, benefiting wide usage in the future. However, for these visible-light-responsive pristine MWO_4 , photocatalytic activities remain

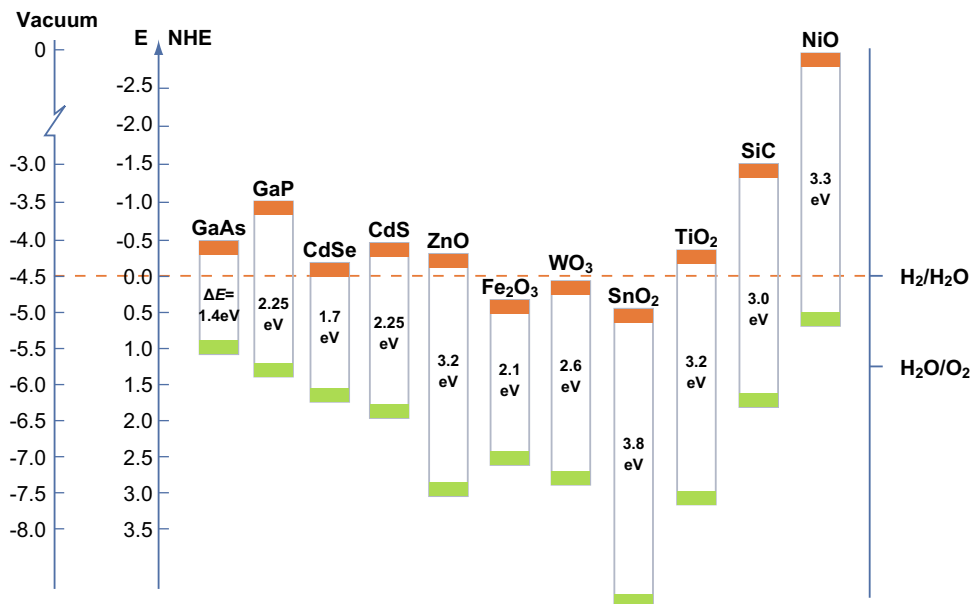


Fig. 1 Schematic overview of the band positions of representative semiconductors

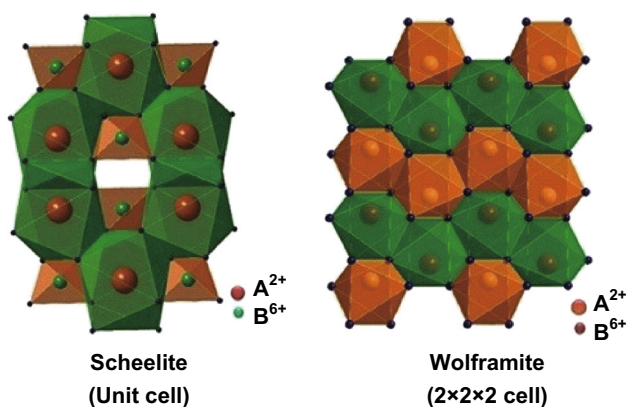


Fig. 2 Illustration of unit cells of scheelite and wolframite. Reproduced with permission from Ref. [57]. Copyright 2014 Elsevier

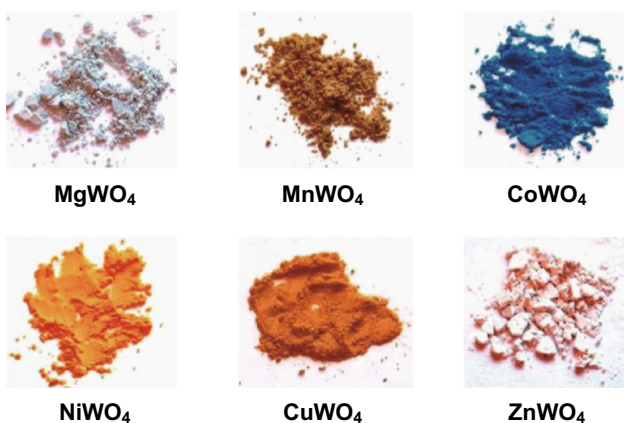


Fig. 3 Colors of different MWO_4 materials. Reproduced with permission from Ref. [51]. Copyright 2014 American Chemical Society

inadequate for practical applications because of the rapid recombination of photogenerated holes and electrons.

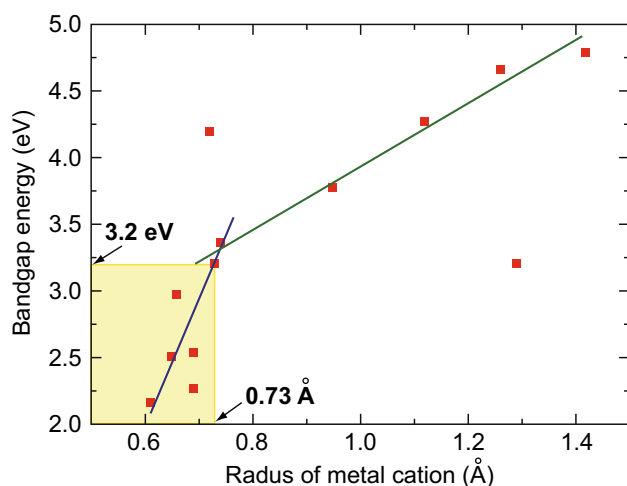
Herein, we provide a comprehensive review of the evolution and current state of the development and application of ternary MWO_4 -based photocatalysts in environmental purification and solar water splitting. First, we discuss the fundamentals of ternary MWO_4 systems, including the crystal composition, electronic structure, and relationship between the intrinsic structures and properties. Subsequently, versatile reported strategies to improve the photocatalytic activities of pristine MWO_4 are systematically summarized. Finally, challenges and future developments of ternary MWO_4 -based photocatalysts are discussed. We believe that this review provides information on recent progress in ternary MWO_4 -based photocatalysts for environmental and energy applications and insight into future perspectives, which will aid the design of highly efficient semiconductor-based photocatalysts.

2 Ternary MWO_4 Photocatalysts (M = bivalent metal cations)

The photocatalytic activity of semiconductor photocatalysts is known to be closely related to their crystal and electronic structures [82]. In this section, an overview of the crystal and electronic structures of ternary MWO_4 is presented and the factors influencing their photocatalytic performance is explored.

Table 1 Band gaps, crystal sizes, and effective ionic radii of different MWO_4 materials

Compounds	Ionic radius of cation M (\AA)	Band gap E_g (eV)	Crystalline sizes (nm) via Scherrer equation	References
BaWO ₄	1.42	4.79	55	[56]
PbWO ₄	1.29	3.2	11	[73]
SrWO ₄	1.26	4.66	33	[56]
CaWO ₄	1.12	4.27	32	[56]
CdWO ₄	0.95	3.77	21	[74]
ZnWO ₄	0.74	3.37	32	[75]
CuWO ₄	0.73	3.2	36	[76]
MgWO ₄	0.72	4.19	70	[77]
SnWO ₄	0.69	2.27	36	[78]
NiWO ₄	0.69	2.54	31	[71]
MnWO ₄	0.66	2.97	29	[79]
CoWO ₄	0.65	2.5	35	[80]
FeWO ₄	0.61	2.16	50	[81]

**Fig. 4** Relationship between band-gap energy of MWO_4 and the radii of metal cations

2.1 Crystal Structure

As ABO_4 -type compounds, ternary MWO_4 complex materials possess a typical wolframite-type monoclinic crystal structure and scheelite-type tetragonal structure. In the scheelite crystal structure, one W atom coordinates with four O atoms to form the WO_4 tetrahedral unit. In contrast, in the wolframite crystal structure, one W atom is encircled by six oxygen atoms to form the WO_6 octahedral unit. For example, Yan et al. [83] reported a tetragonal structure in $CdWO_4$ material, in which the W atom is situated in the center of the tetrahedra, forming four W–O bonds of the same bond length of 1.758 Å, with the coordination number of the Cd atom being eight. However, the monoclinic structure of $CdWO_4$ is similar to that of previously reported $MnWO_4$ [84]. Both W(VI) and Cd(II)

have octahedral O coordination, in which each octahedron shares two corners with its neighbors. However, the configuration of the WO_6 octahedron leads to severe distortion in which two W–O bonds are much shorter than the other four W–O bonds. The two crystal phases of $CdWO_4$ are shown in Fig. 5. An investigation of methyl orange (MO) degradation showed that the photocatalytic performance of monoclinic $CdWO_4$ was much higher than that of tetragonal $CdWO_4$ and commercial TiO_2 under UV light irradiation, which can be ascribed to the lower lattice symmetry of the monoclinic $CdWO_4$. Furthermore, the electronic structures of the wolframite- and scheelite-type $CdWO_4$ were investigated by theoretical computations and simulations based on density functional theory (DFT). As shown in Fig. 5b–d, both monoclinic and tetragonal $CdWO_4$ are indirect-type semiconductors because the calculated bottom of the CB is not situated in the same line as the top of the VB. The calculated band gap of monoclinic $CdWO_4$ was larger than that of tetragonal $CdWO_4$, which was not consistent with the photocatalytic results. Actually, the monoclinic $CdWO_4$ consisted of distorted WO_6 octahedra, leading to the generation of dipole moments in the WO_6 octahedral units, while the tetragonal $CdWO_4$ comprised normal WO_4 tetrahedra, forming a highly symmetric lattice in the absence of dipole moments. Based on its crystal and geometric structures, the monoclinic structure of $CdWO_4$ is considered a highly efficient photocatalyst, and its catalytic performance has been extensively explored [74, 85, 86].

In addition, it has also been reported that $SnWO_4$ has two crystal structures: α - $SnWO_4$ and β - $SnWO_4$ [87]. The orthorhombic α - $SnWO_4$ is comparatively stable in the structure below 670 °C, whereas the cubic β - $SnWO_4$ is a steady structure above 670 °C. In the crystal unit of

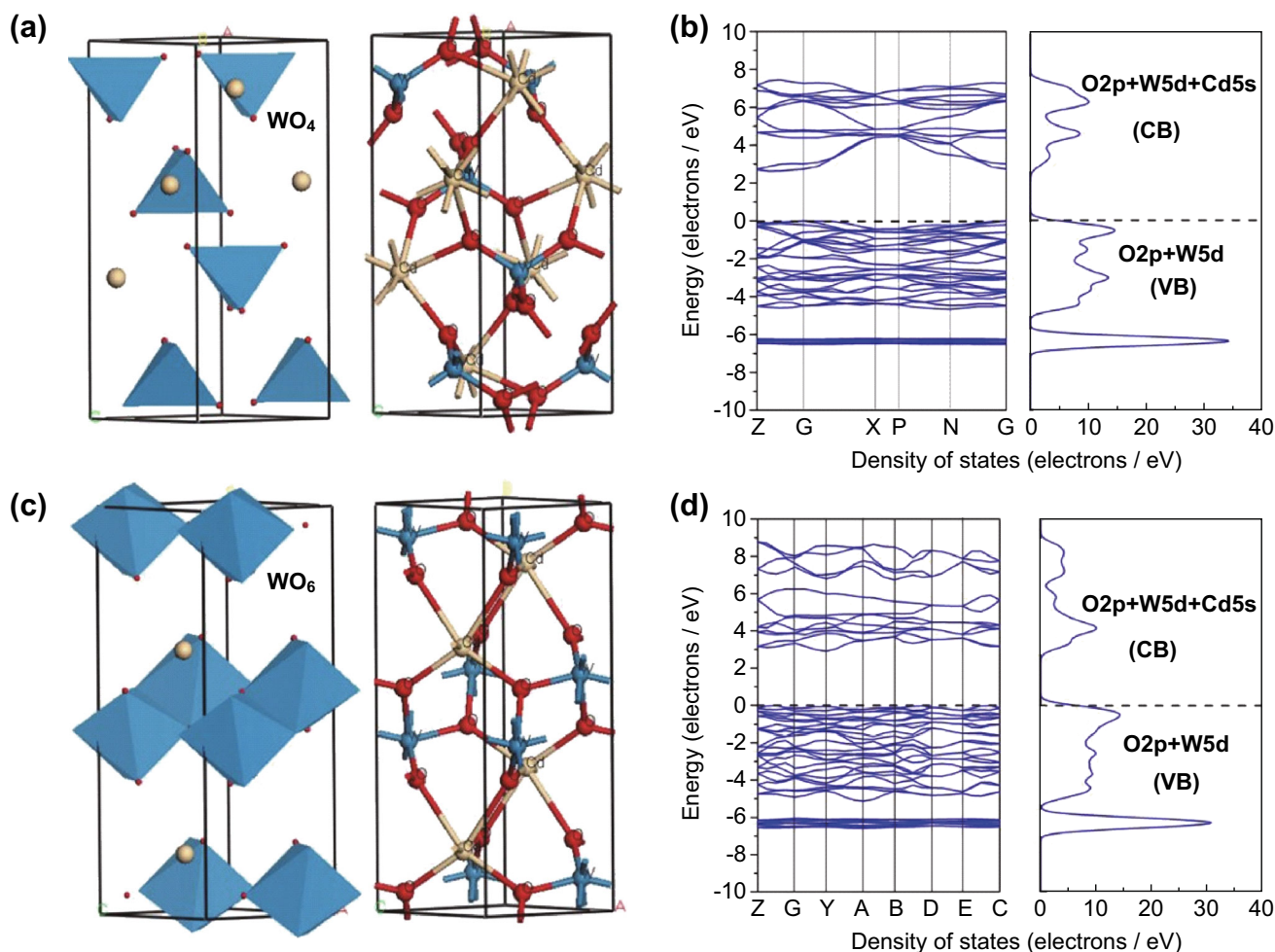


Fig. 5 Models of band structures and calculated density of states for tetragonal (**a, b**) and monoclinic (**c, d**) CdWO_4 . Reproduced with permission from Ref. [83]. Copyright 2011 Elsevier

orthorhombic $\alpha\text{-SnWO}_4$, a single W atom is bonded with six O atoms to constitute typical corner-shared WO_6 octahedra, while the unshared WO_4 tetrahedra are composed of a crystal unit of $\beta\text{-SnWO}_4$. Owing to the lone-pair effects on the Sn(II) ion, distorted SnO_6 octahedra are formed in both polymorphs. Cho et al. [88] prepared the aforementioned SnWO_4 materials with different types of crystal structures and investigated the relationship of the crystal structure with the optical and catalytic properties of SnWO_4 (Fig. 6). It was demonstrated that a difference in atom arrangement could result in an apparent difference in electronic distribution. The VB of SnWO_4 is constituted through high hybridization between the Sn 5 s orbital and O 2p orbital, resulting from the strong interaction between the atomic orbitals with closer energy. Meanwhile, the Sn 5 s orbitals contribute to the lower and upper energy levels of the VB, while the O 2p orbitals are dedicated to the middle energy levels of the VB. Therefore, the VB and CB electronic structures of SnWO_4 are totally different from those of the pristine WO_3 , in which the VB and CB

comprise filled O 2p orbitals and empty W 5d orbitals, respectively. The band gap of $\alpha\text{-SnWO}_4$ was calculated to be 1.65 eV, which was lower than that of WO_3 (1.77 eV), thereby accounting for the broadening effect of the VB, which can be attributed to the contribution of the Sn 5 s orbitals. In contrast, the calculated band gap of 3.45 eV for $\beta\text{-SnWO}_4$ was apparently much larger than that of $\alpha\text{-SnWO}_4$ and WO_3 . Although the Sn 5 s orbitals also contribute to the VB of $\beta\text{-SnWO}_4$ (Fig. 6b), the increase in the band gap stems from the decreased length of the W–O bonds and enhanced crystal field splits, thus resulting in the upshifting of the CB position. Furthermore, the experimental results showed that both $\alpha\text{-SnWO}_4$ and $\beta\text{-SnWO}_4$ exhibited higher photocatalytic performance for the degradation of Rhodamine B (RhB), as compared to other visible-light-response photocatalysts, such as bulk- or nano WO_3 and nano TiON_x (Fig. 6d). Moreover, the $\beta\text{-SnWO}_4$ showed a higher photocatalytic activity for H_2 evolution in the presence of methanol, accompanying Pt as a co-catalyst under visible-light irradiation (Fig. 6e), which

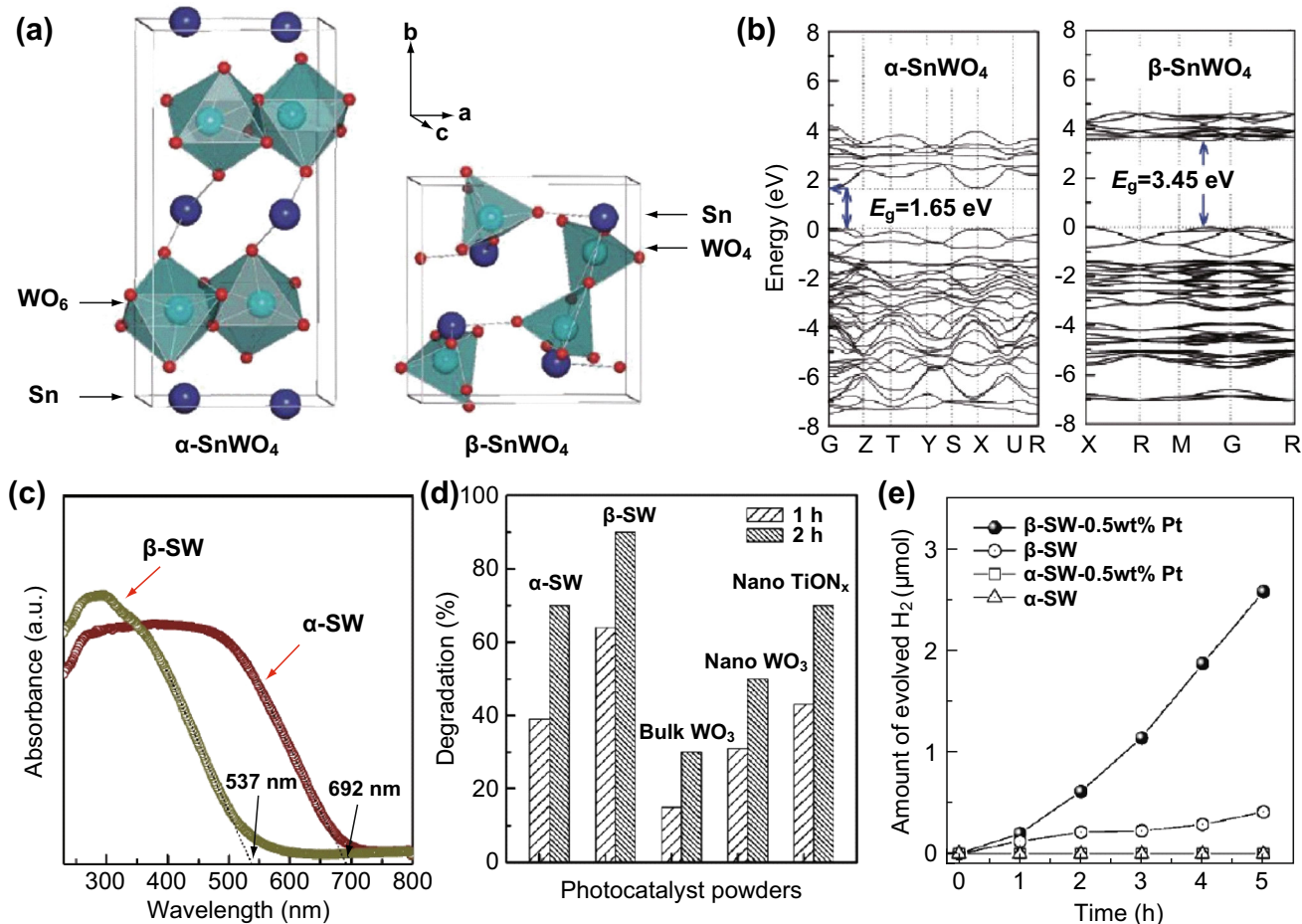


Fig. 6 **a** Crystal structures, **b** density of states, and **c** UV-Vis absorption spectra of α -SnWO₄ and β -SnWO₄. **d** Photocatalytic activity of α -SnWO₄ and β -SnWO₄ in RhB degradation. **e** H₂ evolution. Reproduced with permission from Ref. [88]. Copyright 2009 American Chemical Society

can be mainly ascribed to the higher CB edge of β -SnWO₄ compared to that of α -SnWO₄. Based on the aforementioned analysis, one can conclude that the MWO₄ photocatalysts usually possess more than two types of crystal structure, thus leading to a difference in geometries and local lattice distortions. The non-bonded electrons in the metal ion should be considered an important factor in analyzing the crystal field, particularly in an MWO₄-based asymmetric coordination environment. The distortion of the local crystal structure influences the electronic structure and band distribution, thus affecting the catalytic performances of MWO₄-based photocatalysts.

2.2 Electronic Structure

Generally, tungstates are considered derivatives of H₂WO₄ and WO₃ because of their similar elemental constitutions and crystal structures [89–91]. The DFT [92] and ab initio [93] calculations indicate that the CB of MWO₄ consists of W 5d orbitals in tungstates, as in WO₃, while the O 2p

orbitals only comprise the upper part of the VB because the bivalent metal cation in tungstates contributes differently to the VB and CB positions given different outer electronic arrangements [55].

For instance, visible-light-driven CuWO₄ is employed for photoelectrochemical (PEC) water splitting because of its suitable band gap of 2.3 eV [94–96]. For most binary metal oxides, the VB is mainly constituted of O 2p orbitals; thus, the VB energy is usually in the range of 2.5–3.0 eV, indicating that the top of the VB is not significantly shifted in the metal oxides. For ternary metal oxides, however, the mixing atomic orbitals between the O 2p orbitals and metal orbitals could result in an apparent shift in the top position of the VB [97]. Thus, for CuWO₄, the VB shifts upward, in comparison to that of WO₃, accounting for the hybridization between the O 2p orbitals and Cu 3d orbitals (Fig. 7a). The upward movement in the VB position indicates a decrease in the band gap, which results in an increased visible-light absorption range [98]. However, the composition of the CB is still a topic of hot debate. DFT

calculations show that the VB of CuWO_4 is composed of O 2p orbitals with a small portion of Cu 3d, whereas the CB of CuWO_4 is composed of W 5d orbitals [99, 100]. Moreover, the Cu 3d orbitals may contribute to the CB of CuWO_4 except for the top of the VB [101]. Experimental results demonstrate that the CB shift of CuWO_4 relative to that of WO_3 can be ascribed to the incorporation of Cu 3d orbitals into the energy level of the CB [102]. Yet, strong evidence of an accurate contribution proportion of Cu 3d orbitals to the CB of CuWO_4 has not been obtained. Although the CB composition of CuWO_4 is unclear, the CuWO_4 photoanode presented a high photocatalytic activity with a photocurrent density of up to 0.07 mA cm^{-2} at 1.23 V and a high stability under AM 1.5G illumination (Fig. 7b, c), indicating that the CuWO_4 photoanode has a

thermodynamic potential for water oxidation. In this system, a physical model of the photogenerated charge carrier pathways in CuWO_4 is proposed as shown in Fig. 7d. It shows that when the photogenerated electrons are transferred from a solution medium to a mid-gap state, the thermodynamic potential of the mid-gap state can be utilized to determine which elementary reaction is favored to occur and which is the rate-limiting reaction.

Apart from CuWO_4 , the electronic structures of other MWO_4 materials have also been previously studied. For example, Rajagopal and co-workers [103, 104] used X-ray emission spectroscopy and DFT computation to study the electronic structures and related properties of FeWO_4 and CoWO_4 photocatalysts. The theoretical calculation results demonstrated that O 2p orbitals mainly contributed to the

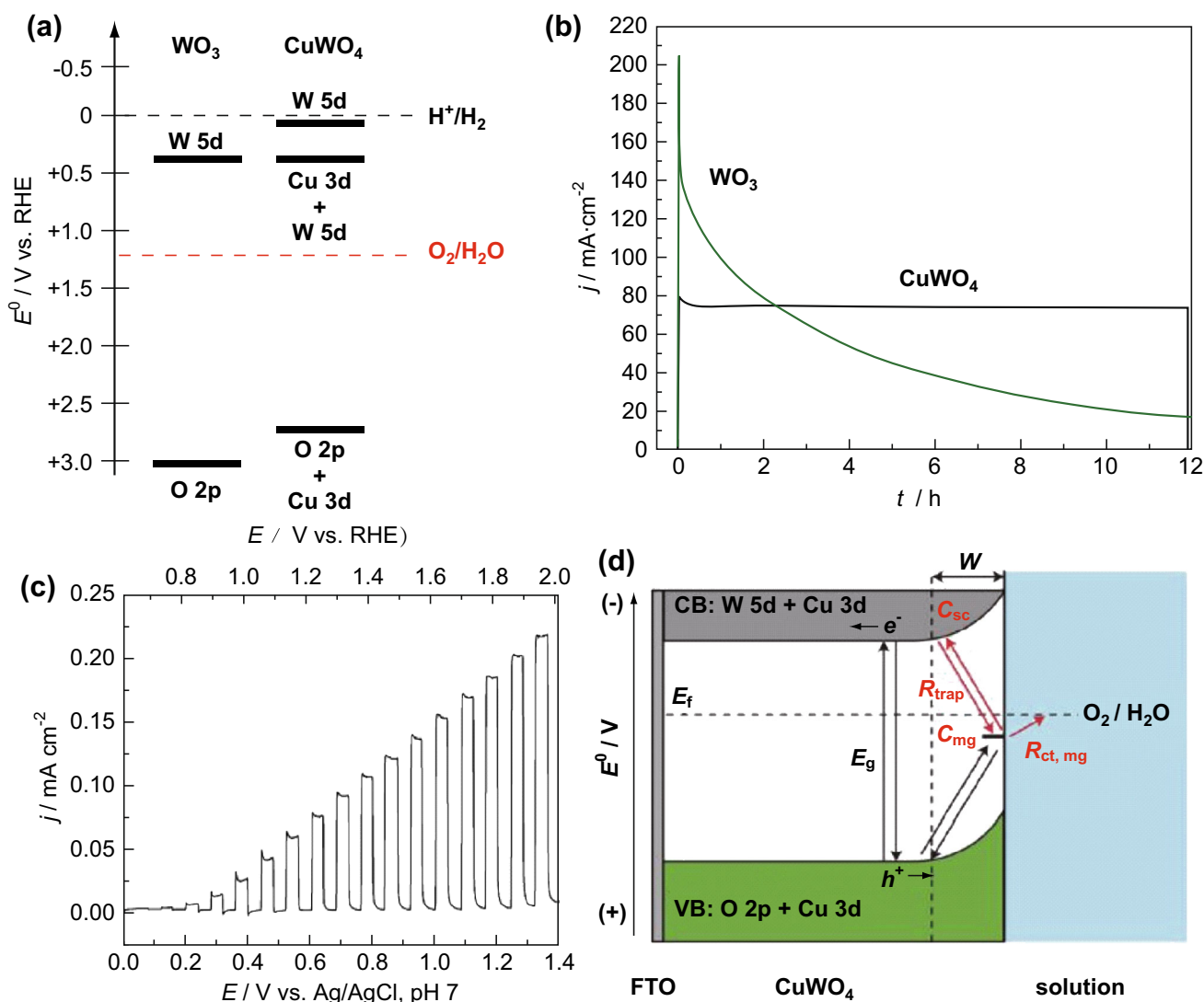


Fig. 7 a Distribution of energy level and b chronoamperometry curves of CuWO_4 and WO_3 . c Polarization curve of CuWO_4 photoanode under AM1.5G irradiation. d Illustration of the physical model of charge carrier transfer in CuWO_4 . Reproduced with permission from Ref. [102]. Copyright 2016 American Chemical Society

VB of tungstates, while the unoccupied Fe 3d orbitals and Co 3d orbitals were dominantly dedicated to the CB of FeWO₄ and CoWO₄, respectively. In addition, the density of states showed that Co 3d and W 5d orbitals also contributed to the VB regions of CoWO₄, similar to that of FeWO₄. Hence, the VBs of FeWO₄ and CoWO₄ are composed of O 2p, W 5d, and Fe/Co 3d orbitals. However, X-ray emission spectroscopy results revealed that the W 5d orbitals and O 2p orbitals are dedicated to the entire VB of the tungstates, in which the O 2p orbitals are dedicated to the upper region of the VB and W 5d orbitals are dedicated to the lower region of the VB. The theoretical results agreed well with the experimental results for FeWO₄ and CoWO₄. In addition, the electronic structure of NiWO₄ was obtained. For NiWO₄, the CB predominantly consists of W 5d orbitals and Ni 3d orbitals, while the VB primarily consists of Ni 3d orbitals and O 2p orbitals [105]. It was found that the VB composition of NiWO₄ is different from those of FeWO₄ and CoWO₄, which is related to the energy level distribution of the orbital electrons around the metal ions. Therefore, based on the aforementioned results, one can conclude that the electronic structures of ternary MWO₄ systems mainly depend on the position of the M²⁺ cation in the periodic table, which affects the outer electronic arrangements and hybridized electrons of the atomic orbital to the M²⁺ cation.

3 Strategies for Enhanced Photocatalytic Activity

As described in Sect. 1, ternary MWO₄ systems can act as highly promising photocatalysts for environmental purification and solar water splitting. However, among the major limiting factors in enhancing their photocatalytic activities is the rapid recombination of photogenerated electron and hole pairs. To overcome this problem and improve the overall catalytic performance of MWO₄ photocatalysts, many research groups have endeavored to develop various techniques to enhance the separation and transfer efficiency of photoexcited charge carriers inside MWO₄ or at the interface between different components. In this section, an overview of the developed strategies is provided to offer insights on their effects for the separation efficiency of photogenerated charge carriers and the corresponding catalytic performance of MWO₄-based photocatalysts.

3.1 Morphological Control

As is known, the morphology, facet exposure, and dimensions of photocatalysts have a significant influence on the photocatalytic performance. For example, nanostructured photocatalysts can exhibit excellent photocatalytic activities because the morphologies and particle sizes

of the photocatalysts have a significant influence on the optical and electronic properties, which in turn affect the photocatalytic activities. For example, Yu et al. [106] prepared FeWO₄ samples with different morphologies, including nanoparticles, flakes, nanorods (NRs), and a mixture of NRs with flakes and tiny granules, by varying pH values during the hydrothermal process, and systematically investigated their optical properties. The results indicated that the band-gap values of FeWO₄ are correlated with specific morphologies. Hosseinpour-Mashkani and co-workers [75] synthesized ZnWO₄ nanoparticles with different sizes through a precipitation route using different polymeric surfactants. The photocatalytic degradation experiments of MO demonstrated that the ZnWO₄ with the smallest size of 27 nm exhibited the highest photoactivity, compared with other ZnWO₄ samples under UV light illumination. It has been demonstrated that particle size can affect the band gap of semiconductors because of quantum size effects. The exposed surface area of nanoparticles increases with a decrease in nanoparticle size, which can provide more active sites for a surface catalytic reaction. In addition to morphologies and particle sizes, size-related crystallinity of MWO₄ has an important influence on the photophysical and photocatalytic properties. For example, Tong et al. [74] reported nanostructured CdWO₄ with controllable particle sizes via a hydrothermal process and studied the effects of the particle sizes on the lattice symmetry and crystallinity. It was found that the decreased size of the CdWO₄ nanoparticles resulted in an expanded lattice, lowered crystallinity, and broadened band gap. Meanwhile, the decrease in particle sizes caused an apparent decrease in the photocatalytic activity of CdWO₄. These results illustrate that size-related properties are closely correlated with the photocatalytic activity of MWO₄. Apart from the effects of the aforementioned factors on photoactivity, the crystal phase of MWO₄ is also regulated by various synthetic routes to obtain the desired physicochemical and optical properties, because different crystal phases can lead to distinct differences in the exposure of crystal facets and reactivities. For instant, different crystal phases of CdWO₄ nanocrystals were prepared by adjusting the used solvents for photocatalytic H₂ evolution (Fig. 8) [86]. The solvent significantly affected the chelation and growth of the CdWO₄ material, thus leading to apparent differences in the crystal phase. m-CdWO₄ nanocrystals with particle sizes ranging from 4.4 to 31 nm can be prepared using short-chain solvents, while t-CdWO₄ nanocrystals can be easily prepared utilizing long-chain solvents. The obtained m-CdWO₄ nanocrystals exhibited much higher H₂ production than the t-CdWO₄ nanocrystals.

During recent years, the construction of hierarchical structures to tune the morphologies of MWO₄

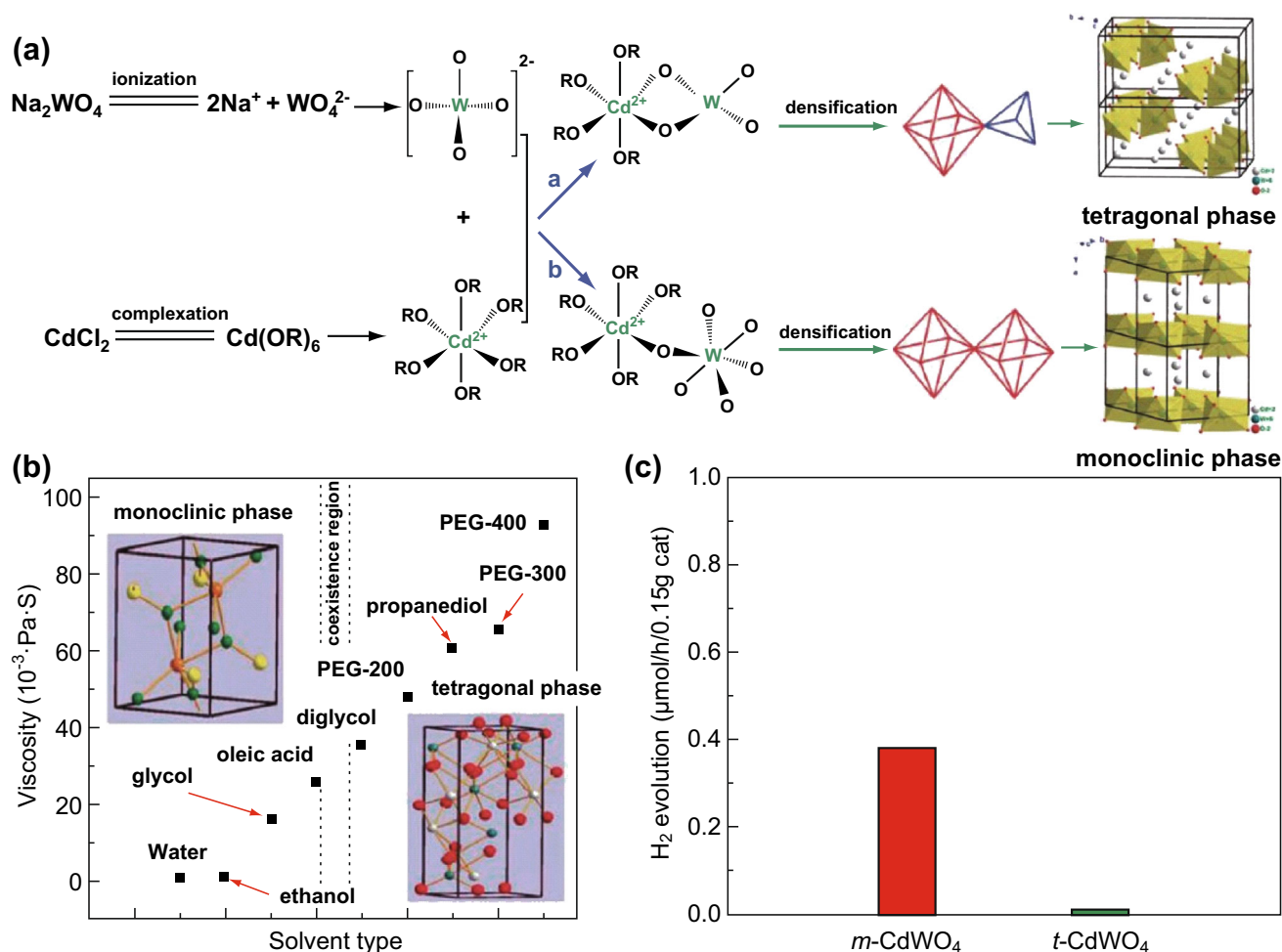


Fig. 8 **a** Formation mechanism of $m\text{-CdWO}_4$ and $t\text{-CdWO}_4$ and the **b** relationship between different crystal phases of CdWO_4 and used solvents. **c** Photocatalytic H_2 evolution of $m\text{-CdWO}_4$ and $t\text{-CdWO}_4$ under visible light irradiation. Reproduced with permission from Ref. [86]. Copyright 2012 Royal Society of Chemistry

photocatalysts has attracted more attention, because hierarchical structures can offer more exposed surfaces and/or active sites. For example, highly efficient hydrophobic CdWO_4 microspheres were synthesized by Hou et al. [107] through a microwave-assisted interfacial hydrothermal strategy. The CdWO_4 microspheres showed enhanced photocatalytic activity for the degradation of MO under mercury lamp irradiation (Fig. 9). The advantages of a hierarchical structure for the enhanced photocatalytic activity of MWO_4 are supported by several research groups [108–111]. Chen et al. [112] prepared FeWO_4 microspheres by using an ethylene glycol-assisted solvothermal approach, in which ionic 1-octyl-3-methylimidazolium tetrachloroferrate was used as one of the starting materials and played an important role as both a reactant and template. The microsphere-like FeWO_4 material consisted of numerous nanosheets and exhibited a much better photo-Fenton activity in water purification (Fig. 10) because of the generation of hydroxyl radicals, which are produced

from the chemical reaction between Fe^{2+} on the surface of FeWO_4 and H_2O_2 . The formed Fe^{3+} was further reduced by the photoinduced electrons to generate Fe^{2+} , which is a virtuous cycle, to maintain high photocatalytic performance. Recently, Zhou et al. [113] synthesized an urchin-like MnWO_4 hierarchical structure through a facile hydrothermal process with the assistance of cetyltrimethylammonium bromide (CTAB) as surfactant. The introduction of CTAB as the surfactant had significant effects on the morphology and magnetic properties of the MnWO_4 nanocrystals. Subsequently, Xing et al. [114] provided a new route for the synthesis of a complex three-dimensional (3D) MnWO_4 nanostructure. In this case, a 3D flower-like MnWO_4 nanocomposite was synthesized using a microemulsion-based solvothermal approach. Moreover, Chen et al. [115] discussed the effect of the morphology of $\beta\text{-SnWO}_4$ on its photocatalytic performance, in which the $\beta\text{-SnWO}_4$ with a multi-armed architecture and hexahedral symmetry displayed much higher photocatalytic activities

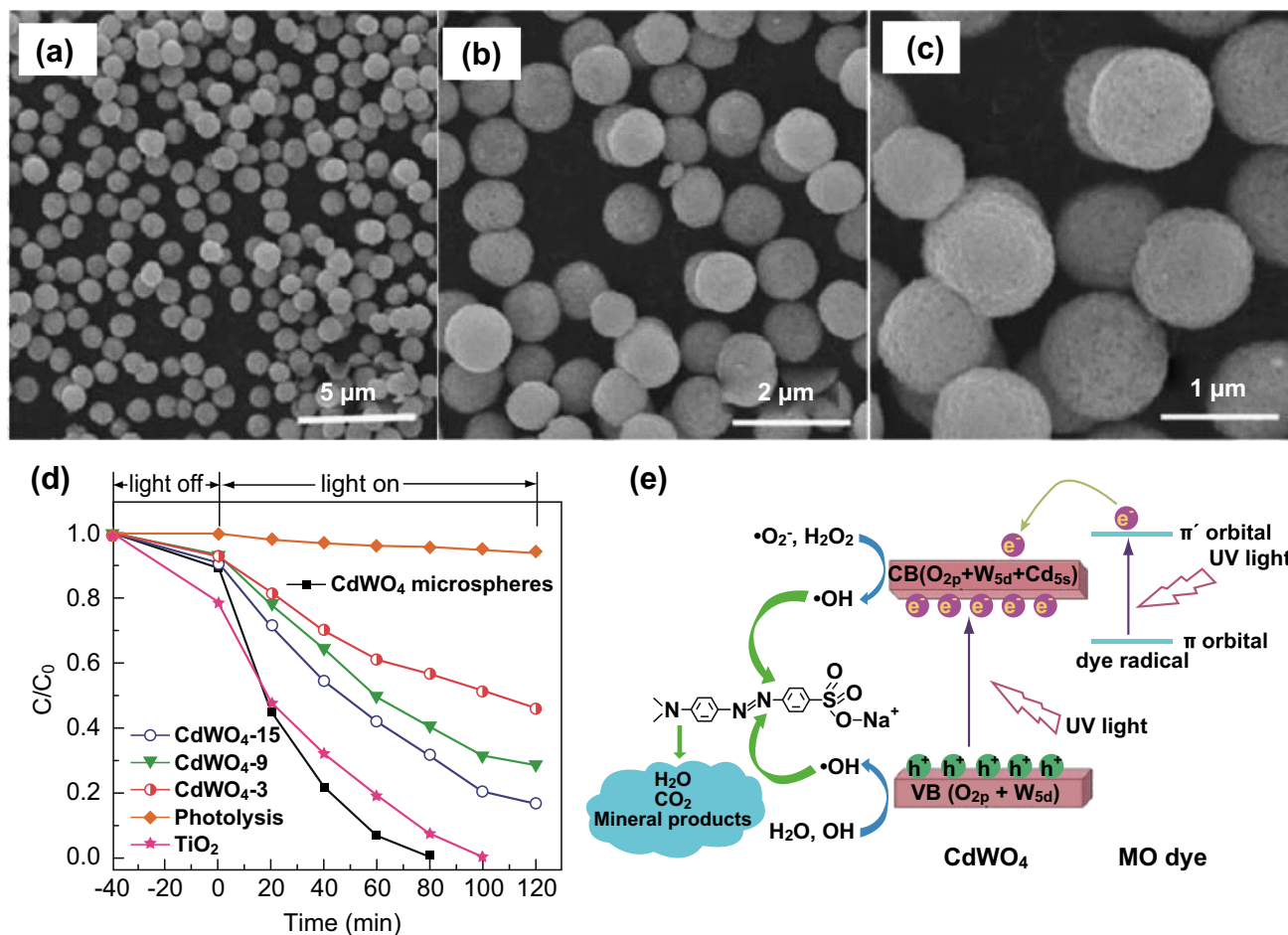


Fig. 9 a–c FESEM images of CdWO₄ microspheres. **d** Photocatalytic degradation efficiencies of MO in the presence of different photocatalysts. **e** Photocatalytic mechanism for CdWO₄ microspheres. Reproduced with permission from Ref. [107]. Copyright 2014 Royal Society of Chemistry

than those of both cubic β -SnWO₄ and commercial WO₃. Hence, more surface reaction sites induced by the hierarchically multi-armed architecture and the band structure reframing caused by incorporation of the Sn atom into WO₃ contributed to the excellent photocatalytic activity.

Previously, crystal facet exposure was viewed as an effective strategy to regulate the surface physicochemical and photophysical properties, thus optimizing the reactivity and selectivity of photocatalysts. In general, a crystal facet with a high percentage of unbonded atoms has superior reactivity in comparison to that with a low ratio of unpaired atoms. In addition, crystal facets possessing high surface energy are usually unstable during preparation. It is desirable to synthesize photocatalysts with a high exposure of high-energy crystal facets to enhance the photocatalytic reactivity and selectivity. Using DFT calculations, Qiu and co-workers [116] reported the atom distributions and electronic properties of MnWO₄ and FeWO₄ with specific facets. The calculated results showed that the {010} and {100} facets have the lowest surface energies in

wolframite-type FeWO₄ and MnWO₄, respectively. Meanwhile, it was observed that the Fe and Mn atoms on the {010} and {001} planes as absorption sites can be used to absorb anions. These results indicated that the exposed {100} facet in MnWO₄ and FeWO₄ can provide a path for improving their photoactivities, while the other exposed facets can offer a certain selectivity to a specific reaction, such as a dichlorination reaction. Recently, Ungelenk et al. [117] synthesized phase-pure β -SnWO₄ with truncated rhombic dodecahedrons using a microemulsion technique with CTAB as a co-surfactant with n-hexanol (Fig. 11). Benefitting from the rapid Na₂WO₄-induced nucleation and slow crystal growth controlled by the CTAB-mediated microemulsion reaction, the as-prepared β -SnWO₄ with truncated rhombic dodecahedrons was encircled with highly exposed {100} and {110} facets. By comparing a series of β -SnWO₄ to other photocatalysts of Ag₃PO₄ and m-BiVO₄, the β -SnWO₄ microcrystals with exposed {100} and {110} facets showed outstanding photocatalytic activity for the degradation of organic pollutants under

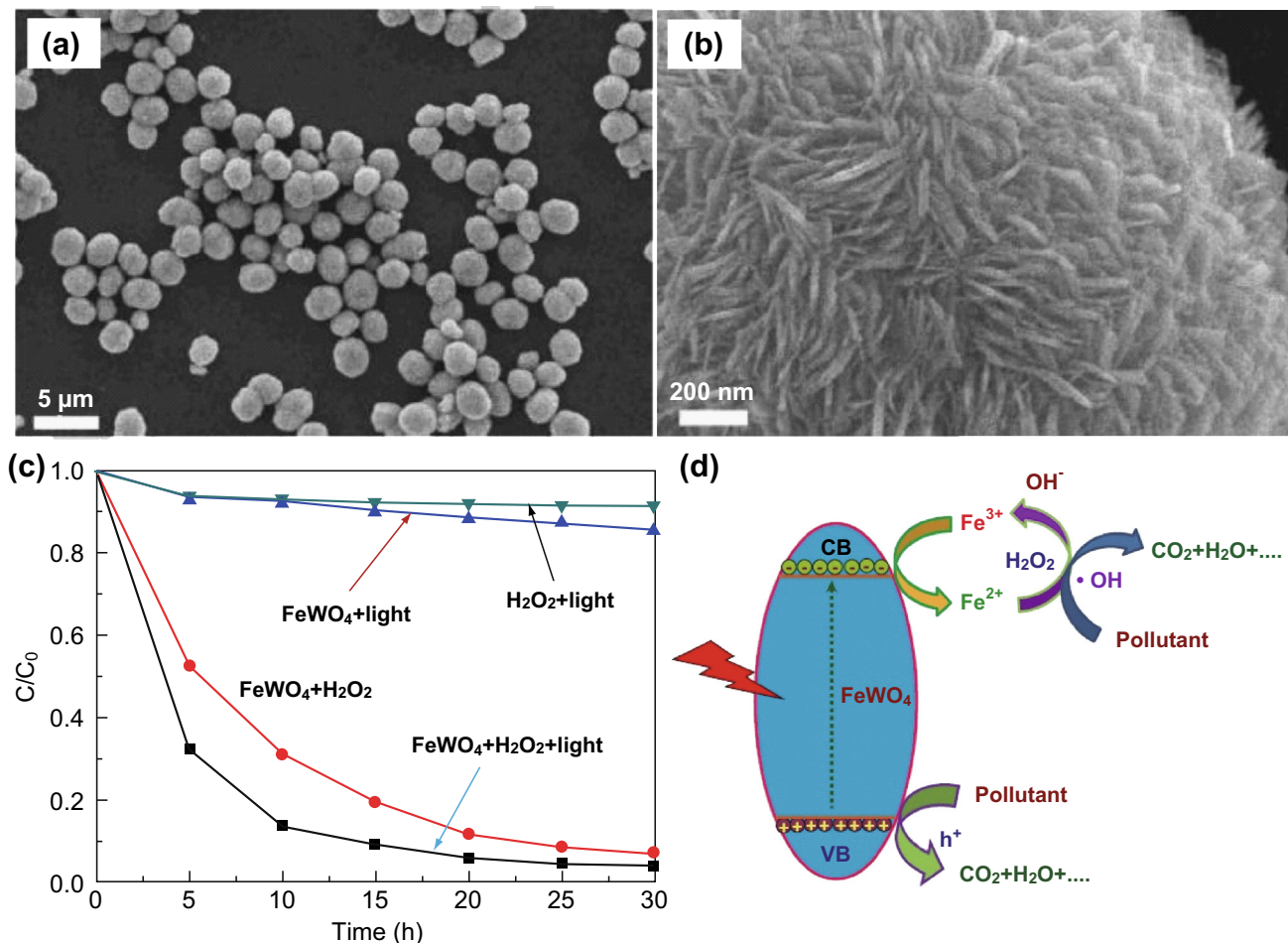


Fig. 10 **a, b** FESEM images of FeWO₄ microspheres. **c** Photocatalytic performance of FeWO₄ microspheres for the degradation of RhB. **d** Schematic illustration of photocatalysis mechanism for FeWO₄ microspheres. Reproduced with permission from Ref. [112]. Copyright 2016 Elsevier

daylight irradiation, which was far better than that of other photocatalysts, including bulk non-faceted β-SnWO₄ and spherical-like β-SnWO₄ nanoparticles. In addition, given the slight difference in specific surface area between the faceted β-SnWO₄ and non-faceted β-SnWO₄, it was concluded that optimized facet exposure was the predominant reason for the distinct photocatalytic activity. In addition, Tian et al. [118] reported a facile solvothermal method for the synthesis of hierarchical FeWO₄ nanosheets with an exposed {100} facet, which exhibited excellent peroxidase-like catalytic activity for oxidizing the peroxidase substrate of 3,3',5,5'-tetramethylbenzidine (TMB) because of the formation of hydroxyl radicals in the presence of H₂O₂. The surface Fe²⁺ in FeWO₄ can activate the H₂O₂ molecule to produce active hydroxyl radicals for the oxidation of TMB. The results clearly indicated that the {100} facet of FeWO₄ had a much higher ratio of Fe atoms than that of the {001} and {010} facets, which explained the enhanced catalytic activity of FeWO₄ with the exposed {100} facet.

Owing to the high surface area and large absorption cross section it provides, a low-dimensional nanostructure can be constructed to manipulate and regulate optical, electrical, and magnetic properties [119, 120]. Low-dimensional nanostructures including those that are one-dimensional (1D) or two-dimensional (2D) cause the growth of a crystal along one or two directions, which can contribute to more exposure of specific surface facets. For example, 1D CdWO₄ NRs were prepared using microwave or hydrothermal approaches and exhibited excellent photocatalytic activity for environmental treatments, as compared to nanoparticles [121–123]. Kovacs and co-workers [111] prepared a series of FeWO₄ with different morphologies, including nanoparticles, NRs, and nanosheets, by varying the Fe precursors. The nanosheet-like FeWO₄ with band-gap energy of ~ 2.2 eV exhibited excellent absorption ability throughout the UV and visible-light range, which was attributed to the formation of a cavity assembled by nanosheets that resulted in enhanced photon harvest. Therefore, the FeWO₄ nanosheets showed higher

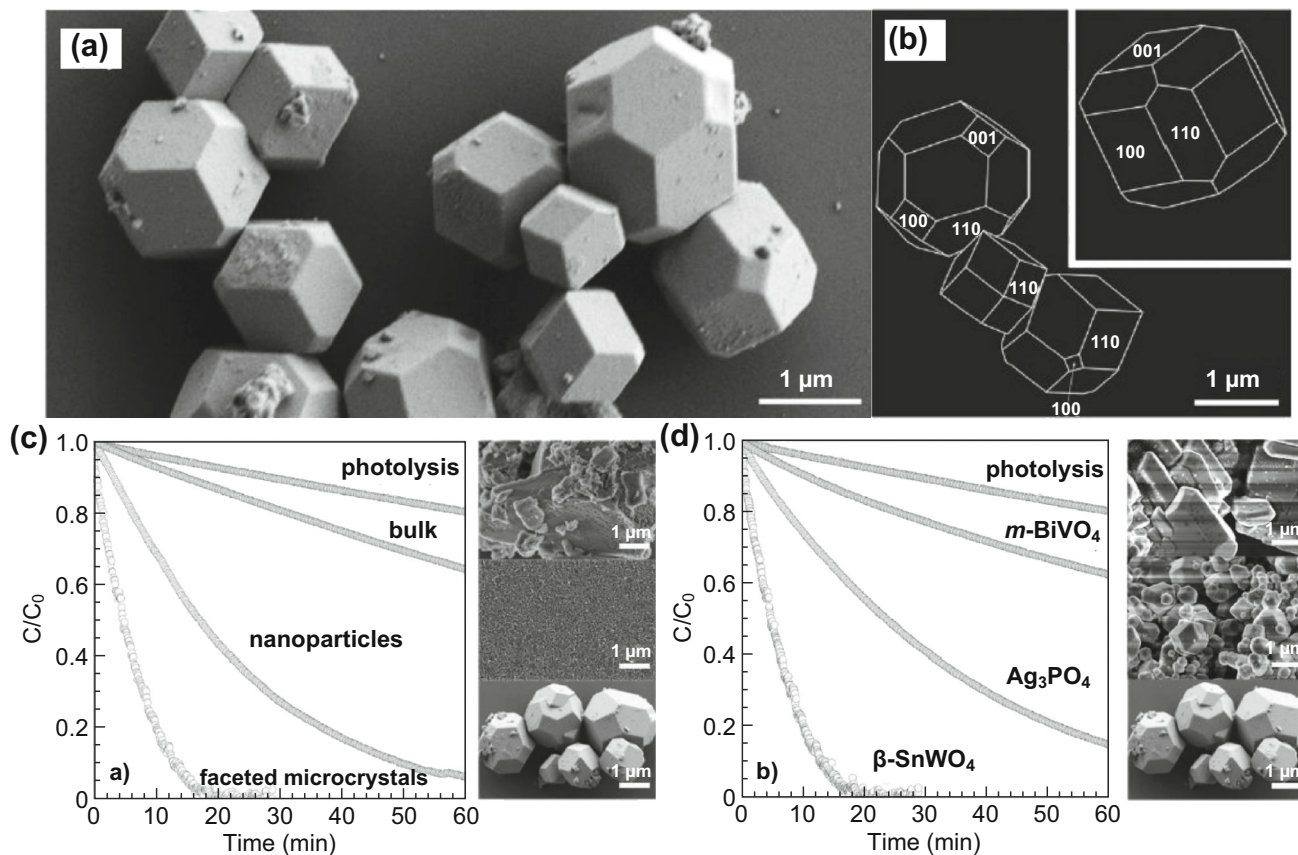


Fig. 11 **a, b** FESEM images of faceted β - SnWO_4 microcrystals. **c, d** FESEM images and photocatalytic activities for the degradation of MB over faceted β - SnWO_4 microcrystals, bulk β - SnWO_4 , and β - SnWO_4 nanoparticles under sunlight irradiation. Reproduced with permission from Ref. [117]. Copyright 2012 Royal Society of Chemistry

photocatalytic activity than other control samples for the degradation of organic dyes under visible-light irradiation.

3.2 Surface Modification

Considering that the photocatalytic reaction proceeds on the surface of semiconductors, the surface physiochemical properties of semiconductor-based photocatalysts are important for improvement of photocatalytic activity. Several strategies, including chemical etching, surface coverage, and co-catalyst attachment, have been developed to tune the surface properties of semiconductor-based photocatalysts.

The purpose of etching techniques, such as chemical etching and laser or electron-beam irradiation, is to form non-stoichiometric or metal/oxygen vacancies on the surface of an inorganic semiconductor. The formation of metal or oxygen vacancies has proven to have an apparent influence on the electronic distribution because of the introduction of a new defect energy level, thus affecting the light absorption range and photocatalytic activity. For example, Aloysius-Sabu et al. [124] investigated the effects of intentional electron-beam irradiation on the crystal

phase, size, and surface properties of CaWO_4 that was prepared through chemical precipitation and heat treatment. The experimental results showed that the high-energy electron beam significantly affected the crystal size and surface structure, but not the crystal phase. When the CaWO_4 photocatalyst was irradiated by an electron beam, the surface atomic layers of CaWO_4 underwent stretching and compressive strain, which resulted in the formation of surface defects and a new energy level in the band gap. Therefore, an apparent absorption tail and narrowed band-gap energy were observed in the irradiated CaWO_4 sample. In addition, Lin et al. [125] prepared a visible-light-driven Ag_2WO_4 photocatalyst through a laser irradiation route in liquid using commercial Ag_2WO_4 as a starting material for organics degradation and H_2 evolution. Because of the laser irradiation, the crystal structure was recrystallized and a lattice defect was introduced in Ag_2WO_4 , leading to the formation of intermediate energy levels with a decrease of 0.44 eV in the band gap. The synthesized Ag_2WO_4 exhibited a photocatalytic H_2 evolution rate as high as $13.73 \mu\text{mol} (\text{hg})^{-1}$ under visible-light illumination, while no H_2 evolution was observed in the unirradiated

commercial Ag_2WO_4 sample, which was ascribed to a large band gap of 3.22 eV for bulk Ag_2WO_4 .

However, to enhance the solar conversion efficiency of tungstates, surface coverage has been adopted to increase the charge transfer efficiency by means of passivating the surface via deposition of a protective layer. For example, Karthiga and co-workers [71] reported the synthesis of NiWO_4 nanoparticles modified by a plant extract, *A. indica*, as a capping agent through a precipitation route for enhanced photocatalytic activity. The introduction of *A. indica*, which possesses rich water-soluble heterocyclic groups, led to the formation of a passivation layer on the surface of the NiWO_4 nanoparticles, which allowed the NiWO_4 nanoparticles to separate well from each other. In comparison to the bare NiWO_4 nanoparticles, the *A. indica*-coated NiWO_4 exhibited a much higher photocatalytic activity for the degradation of organic contaminants under visible-light irradiation because of the formation of the passivation layer of the plant extract, which significantly suppressed the recombination of photoinduced electrons and holes. Meanwhile, modified NiWO_4 presented higher antimicrobial activity as compared with pure NiWO_4 nanoparticles.

Apart from chemical etching and surface coverage strategies, attachment of noble metal co-catalysts (such as, Pt, Au, and Ag) is another effective means to tune the surface photophysical properties of photocatalysts because of the surface plasmon resonance (SPR) effect [126, 127]. The SPR effect not only significantly enhances visible-light absorption, but also produces a localized electromagnetic field, thus improving the separation efficiency of the photogenerated charge carriers at the interfaces between the metal and semiconductor [128, 129]. Furthermore, the metal–semiconductor heterostructure could efficiently suppress the recombination of photogenerated electrons and holes because of the formation of Schottky barriers at the contacted interface, thus enhancing photocatalytic performance [126]. Based on the aforementioned features, the introduction of a noble metal into MWO_4 is a feasible approach to realize enhancement of its photocatalytic performance. Recently, Liu et al. [130] prepared Ag nanoparticles (NPs)/ α - SnWO_4 nanosheets through microwave-assisted anchoring of Ag NPs on SnWO_4 nanosheets. The loading amount of the deposited Ag NPs was well-tuned by adjusting the initial concentration of the Ag^+ precursor and CTAB surfactant (Fig. 12a). The obtained Ag NPs/ α - SnWO_4 hybrid showed enhanced light absorption ability and photocatalytic activity for the degradation of MO, compared to pure α - SnWO_4 , under visible-light irradiation. Moreover, the hybridized Ag NPs/ α - SnWO_4 system exhibited improved transient photocurrent density in comparison to that of pristine α - SnWO_4 (Fig. 12c), indicating that more photoinduced charge carriers could be

produced and further participated in the redox reaction. In addition, Yan et al. [131] synthesized Ag-loaded CdWO_4 NRs using a photo-assisted co-precipitation method with the addition of the PEG-100 surfactant, which exhibited a higher photocatalytic activity than that of pure CdWO_4 NRs because of the SPR effect. In another study, Au NPs were utilized to construct Schottky barriers in an MWO_4 -based system. For instance, Au NRs/ MnWO_4 , with a diameter of 20–40 nm, was reported by Chakraborty et al. [132] to enhance the photocatalytic decomposition of 2-propanol and phenol. The Au NPs as co-catalysts in the Au/ MnWO_4 hybrid were beneficial to multi-electron O_2 reduction and hole oxidation.

3.3 Heteroatom Doping

It has been demonstrated that the introduction of impurities via doping of heteroatoms into a semiconductor can influence the photocatalytic performance [133, 134]. However, heteroatom doping might either have positive or negative impacts for the photocatalytic performance of semiconductors, because there are two different doping levels—the shallow level near the surface and deep level inside the body [135]. Deep-level doping can usually provide a recombination center to intensify the meaningless dissipation of absorbed photons, thus undermining the photocatalytic activity. Therefore, appropriate heteroatom doping is vital to increasing the photocatalytic performance of heteroatom-doped photocatalysts. To overcome shortcomings, such as a narrow wavelength range and rapid recombination of photogenerated electron–hole pairs, a few recent reported types of heteroatom doping to enhance the photocatalytic performances of ternary MWO_4 materials are reviewed and their roles discussed in detail.

In heteroatom doping, the dopants are mainly non-metal elements such as B [136], Cl [137], and various transition metals (Zn, Ni, Fe, Co, etc.) [138, 139], which exhibit enhanced photocatalytic activity for mineralizing organic pollutants. For instance, Chen et al. [140] synthesized F-doped ZnWO_4 nanocrystals (F_i - ZnWO_4 nanocrystals) using a two-step hydrothermal process and investigated its chemical bonds via band structure calculations (Fig. 13). In comparison to undoped ZnWO_4 , the F_i - ZnWO_4 nanocrystals exhibited significant red shifts and improved light absorption in the range of UV–visible light, which resulted in enhancement of photocatalytic activity for the degradation of RhB under mercury lamp irradiation. Additionally, the experimental results showed that the crystallinity and morphology of the prepared F_i - ZnWO_4 was strongly related to the photocatalytic activity. F_i - ZnWO_4 exhibited higher photocatalytic performance for the degradation of organic dyes than F_i - ZnWO_4 NPs. Based on the theoretical calculation results, the enhancement of the photocatalytic

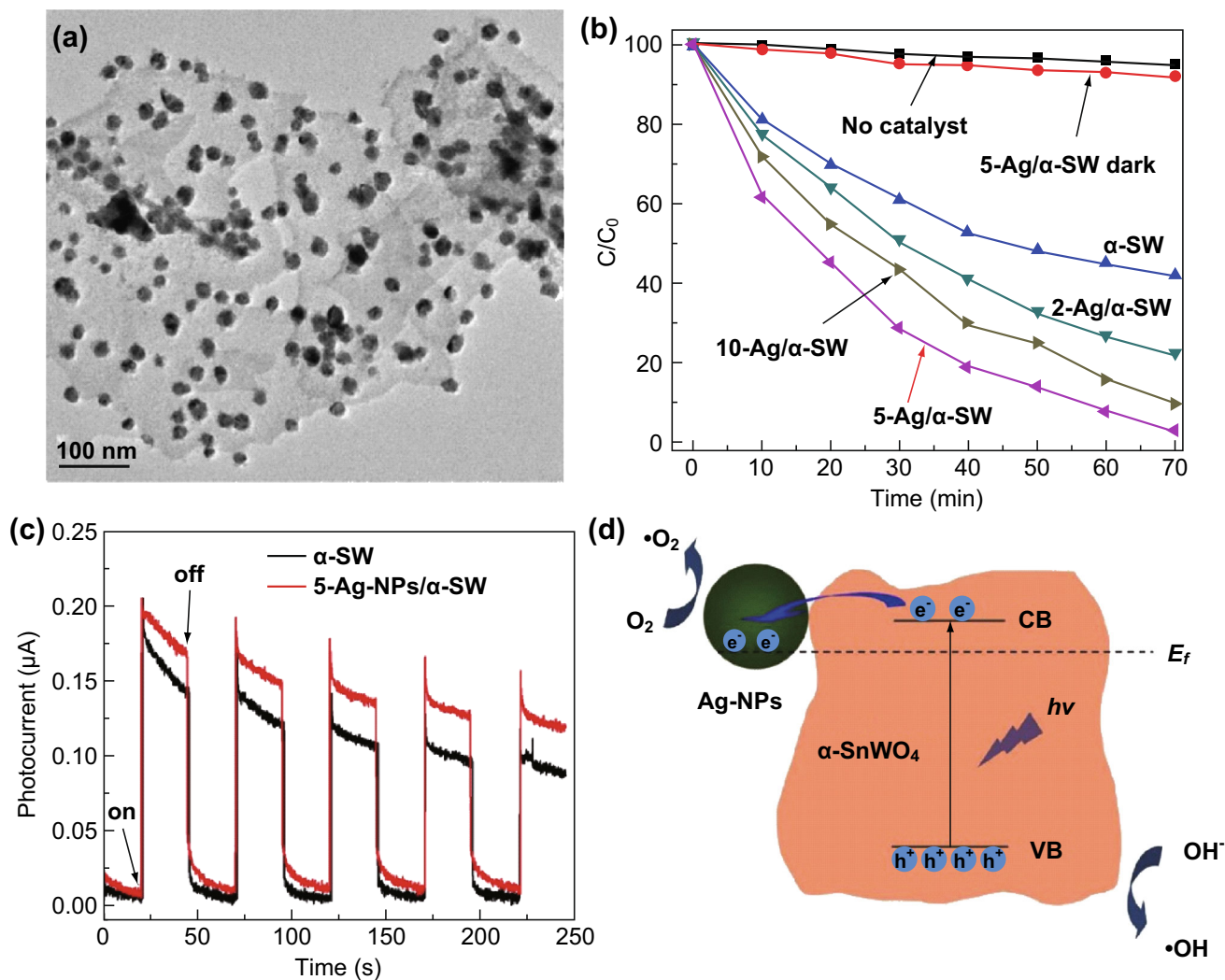


Fig. 12 **a** TEM image and **b** photodegradation efficiency of Ag NPs/α-SnWO₄ under visible-light irradiation. **c** Transient photocurrent response for different samples. **d** Illustration of photocatalytic mechanism of Ag NPs/α-SnWO₄. Reproduced with permission from Ref. [130]. Copyright 2017 Elsevier

activity of F_i-ZnWO₄ might be ascribed to the following reasons. First, F-doping increased the absorptivity of F_i-ZnWO₄, such that it could absorb more reactants to enhance the photocatalytic activity. Second, a new half-filled state was introduced into the original band gap of ZnWO₄ accompanying the F-doping, which could provide more holes to enhance the photocurrent density of F_i-ZnWO₄. Thus, heteroatom doping could efficiently improve the photocatalytic activities of MWO₄ by introducing a new energy level to regulate the original electronic structure.

Apart from the introduction of non-metal elements, transition metal elements can also be a potential dopant. For example, Su et al. [141] prepared Zn²⁺-doped SnWO₄ nanocrystals, and reported that the morphological alteration of SnWO₄ nanocrystals from nanosheets to nanowires can be controlled by Zn²⁺ doping. Consequently, the Zn²⁺-

doped SnWO₄ exhibited a greater Brunauer–Emmett–Teller surface area (54 and 100 m² g⁻¹ for pure SnWO₄ and Zn²⁺-doped SnWO₄, respectively), narrowed band gap (2.68 and 2.64 eV for pure SnWO₄ and Zn²⁺-doped SnWO₄, respectively), and highly enhanced photocatalytic performance for the degradation of MO (95% and 30% for pure SnWO₄ and Zn²⁺-doped SnWO₄, respectively) compared to that of pure SnWO₄. In addition, Song et al. [142] reported the synthesis of Zn-doped CdWO₄ NRs using a hydrothermal process to enhance the photocatalytic conversion efficiency of organic pollutants into low-toxicity small molecules under simulated sunlight irradiation. The influence of the Zn-doping amounts on the crystal phase, morphology, and optoelectronic properties of CdWO₄ NRs was also systematically investigated. Compared to the undoped sample, the Zn-doped CdWO₄ NRs exhibited much higher photocatalytic activity, which was assigned to

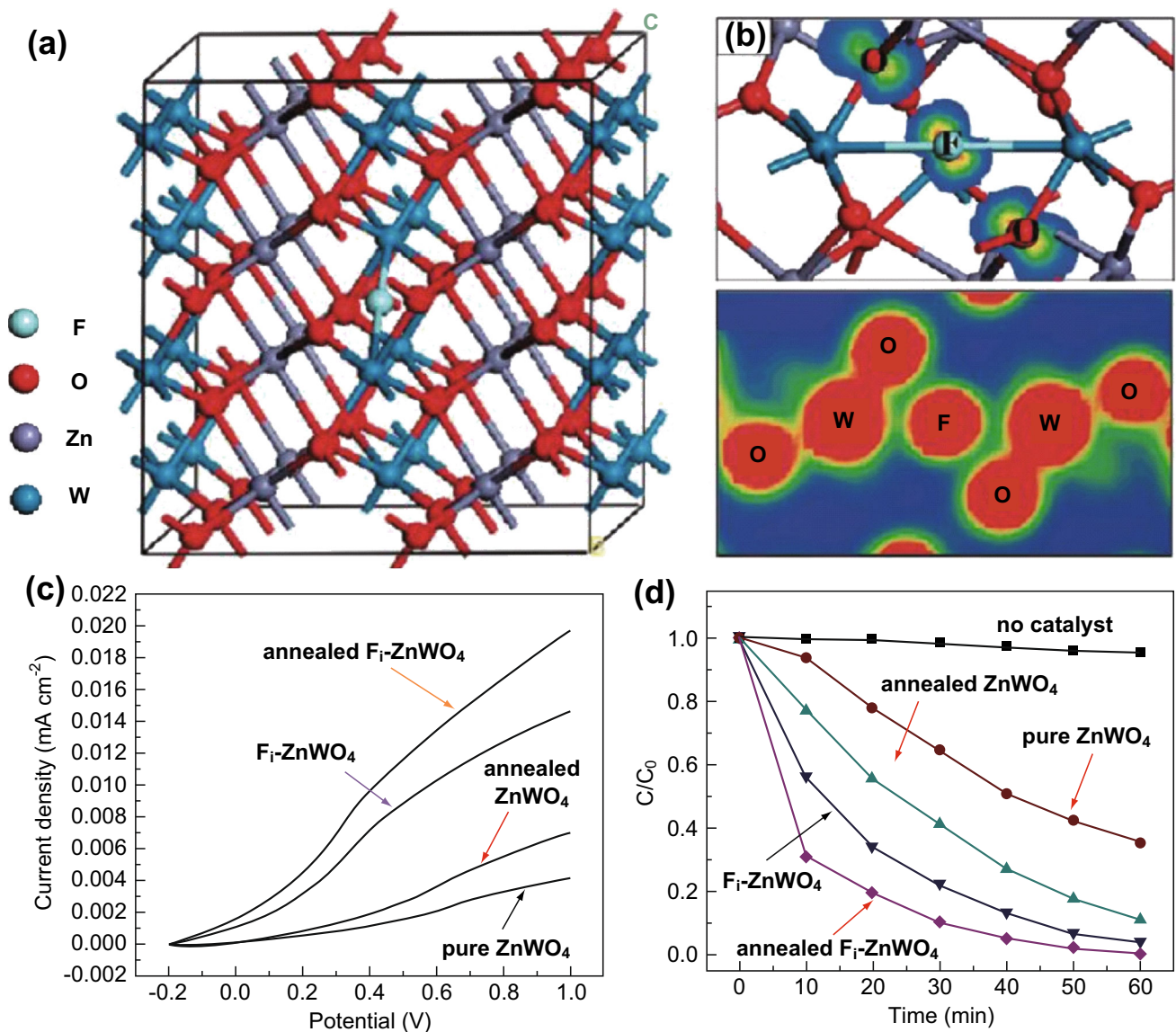


Fig. 13 a Geometric structures for the F_1 - $ZnWO_4$. Spin density (top) and total charge density (bottom) for F_1 - $ZnWO_4$. c Photocurrent density of the synthesized samples under UV-light irradiation. Photocatalytic degradation of RhB over different samples under UV light irradiation. Reprinted with permission from Ref. [140]. Copyright 2010 American Chemical Society

the narrowed band gap due to Zn-doping. Heteroatom doping could be an effective means to tune the distribution of the energy level and further enhance the photocatalytic performance of MWO_4 without consuming excess foreign substances.

Recently, rare earth element-doped photocatalysts have attracted more attention because of their special 4f electron configuration, which could be beneficial for introducing a suitable energy level into the original band gap of MWO_4 [143]. Phuruangrat et al. [144] synthesized Ce-doped $ZnWO_4$ using a hydrothermal process and investigated the influence of Ce doping on the crystal phase, morphology, electronic structure, and photocatalytic activity of $ZnWO_4$. After the introduction of Ce atoms, the photocatalytic

activity of $ZnWO_4$ improved with the increase in Ce content, owing to the following two reasons. First, the introduction of the Ce^{3+} dopant led to the generation of defects on the surface of Ce-doped $ZnWO_4$. Second, the Ce^{4+} ions on the surface of $ZnWO_4$ could efficiently trap electrons at the CB by the reduction of Ce^{4+} into Ce^{3+} ions, thus efficiently suppressing the recombination of photoinduced electrons and holes in the Ce-doped $ZnWO_4$. Therefore, rare earth elements with variable valence, such as Ce, La, and Eu, are promising dopants to improve the photocatalytic activity by trapping photogenerated electrons, consequently limiting the recombination of photogenerated charge carriers.

3.4 Heterojunction Fabrication

3.4.1 Hybridization with Semiconductors

Among the aforementioned approaches, constructing a semiconductor heterostructure is an effective means to obtain highly efficient photocatalysts [145–148]. When heterojunctions are composed of different semiconductors that have matching band potentials to form type-I or type-II heterojunctions through realignment of the energy level, the excited photogenerated holes and electrons can be moved from one semiconductor to another in opposite directions driven by the formed built-in electric fields [149, 150], thus strengthening the separation efficiency of the photoinduced electrons and holes and further enhancing photocatalytic performance.

For constructing MWO₄-based heterojunctions, semiconductors with a narrow band gap were chosen as a counterpart component to form the heterojunction system, which exhibited remarkable advantages for enhancing the photocatalytic performance. Among most semiconductors with a narrow band gap, cadmium sulfide (CdS) has attracted increasing attention for heterojunction fabrication because of its narrow band gap and high CB position, which could be beneficial for photocatalytic H₂ production [151, 152]. Therefore, various CdS/MWO₄ heterojunction photocatalysts have been developed, which exhibit enhanced photocatalytic activities in water purification and energy conversion [153, 154]. For instance, Yan et al. [155] prepared a CdS/MnWO₄ heterojunction using a facile hydrothermal method to mineralize MB and methyl violet (MV) under visible-light irradiation. Owing to the overlapping of energy bands and tightly contacted interfaces between CdS and MnWO₄, the holes at the VB of MnWO₄ could transfer to the VB of CdS, and the excited electrons at the CB of CdS could in turn move into the CB of MnWO₄. This model could efficiently limit the recombination rate of the photogenerated electrons and holes, thus intensifying the separation of the photogenerated charge carriers in the hybrid system (Fig. 14). Nevertheless, it is apparent that the introduced CdS amount was not synchronous with the photocatalytic activities of the heterojunction, while there was an optimal amount of CdS in the hybrid. Excessive CdS amounts caused severe agglomeration of MnWO₄, damaging the heterojunction and worsening the separation efficiency of the photogenerated electrons and holes. This phenomenon was nearly discovered in the heterojunctions by combining two or more components into one system. In addition, Xu et al. [156] prepared a CdS/ZnWO₄ heterojunction consisting of ZnWO₄ NRs and CdS NPs using a hydrothermal method for the photodegradation of ciprofloxacin antibiotics. Compared to the ZnWO₄ NRs and CdS NPs, the CdS/

ZnWO₄ hybrids showed higher photocatalytic activity than bare ZnWO₄ NRs and CdS NPs, which was ascribed to the highly efficient separation of the photogenerated electrons and holes in the hybrid structure.

The CdS/CdWO₄ heterojunction also exhibited enhanced efficiency in the photocatalytic H₂ production. For instance, Jia [157] and Wang et al. [158] deposited CdS on the surface of CdWO₄ via an ion-exchange and in situ growth route, and the fabricated Z-scheme CdS/CdWO₄ hybrid exhibited significantly enhanced photocatalytic performance for H₂ evolution compared to that of the pure CdWO₄ and CdS. As discussed in the previous section, the MWO₄ with a small M²⁺ cation has a narrow band-gap energy, which can be considered an efficient solar energy harvester to connect with wide band-gap semiconductors for constructing MWO₄-based heterojunctions [159–161]. Thus, Jiang et al. [162] fabricated an MnWO₄/TiO₂ heterojunction with excellent mechanical adhesion by the in situ growth of MnWO₄ on a porous TiO₂ film; it presented extremely high photocatalytic performance for degrading MB because of its high crystallinity, large surface area, and strong mechanical properties (Fig. 15). Similarly, Buvaneswari et al. [163] prepared an FeWO₄/ZnO heterojunction via a simple co-precipitation route; the band gap of the prepared FeWO₄/ZnO heterojunction was estimated to be 2.12 eV, which was apparently smaller than that of ZnO (3.01 eV). In comparison to pristine ZnO, the photocatalytic activity of the FeWO₄/ZnO hybrid was substantially enhanced because of the formation of a FeWO₄/ZnO heterojunction structure. Additionally, the CuWO₄/ZnO hybrid consisting of ZnO NRs and CuWO₄ NPs fabricated by Mavric et al. [164] showed enhanced photocatalytic activity compared to that of pure CuWO₄ NPs and ZnO NRs.

Furthermore, a MO_x/MWO₄ hybrid as a smart-built heterojunction was fabricated using a facile one-pot synthetic strategy to enhance the interaction between MO_x and MWO₄, in which M is generally reported to be Fe, Ni, Co, or Cu [165–168]. Cao et al. [169] fabricated a novel p-n heterojunction consisting of Fe₃O₄ NPs and FeWO₄ nanowires. The calculated band gap of the FeWO₄/Fe₃O₄ heterojunction was 2.50 eV, lower than that of pristine FeWO₄ nanowires. The FeWO₄/Fe₃O₄ heterojunction exhibited enhanced photo-Fenton activity compared to that of the bare FeWO₄ nanowires under UV–visible-light irradiation with the addition of H₂O₂. In addition, a α-SnWO₄/SnO₂ heterostructure was synthesized with CTAB as the surfactant [170] and displayed enhanced photocatalytic performance compared to that of pure α-SnWO₄. Considering that WO₃ can be obtained by dehydration from tungstate acid, WO₃ is considered to be simultaneously produced during the synthesis of MWO₄ and is likely to form a MWO₄/WO₃ heterojunction, such as CoWO₄/WO₃

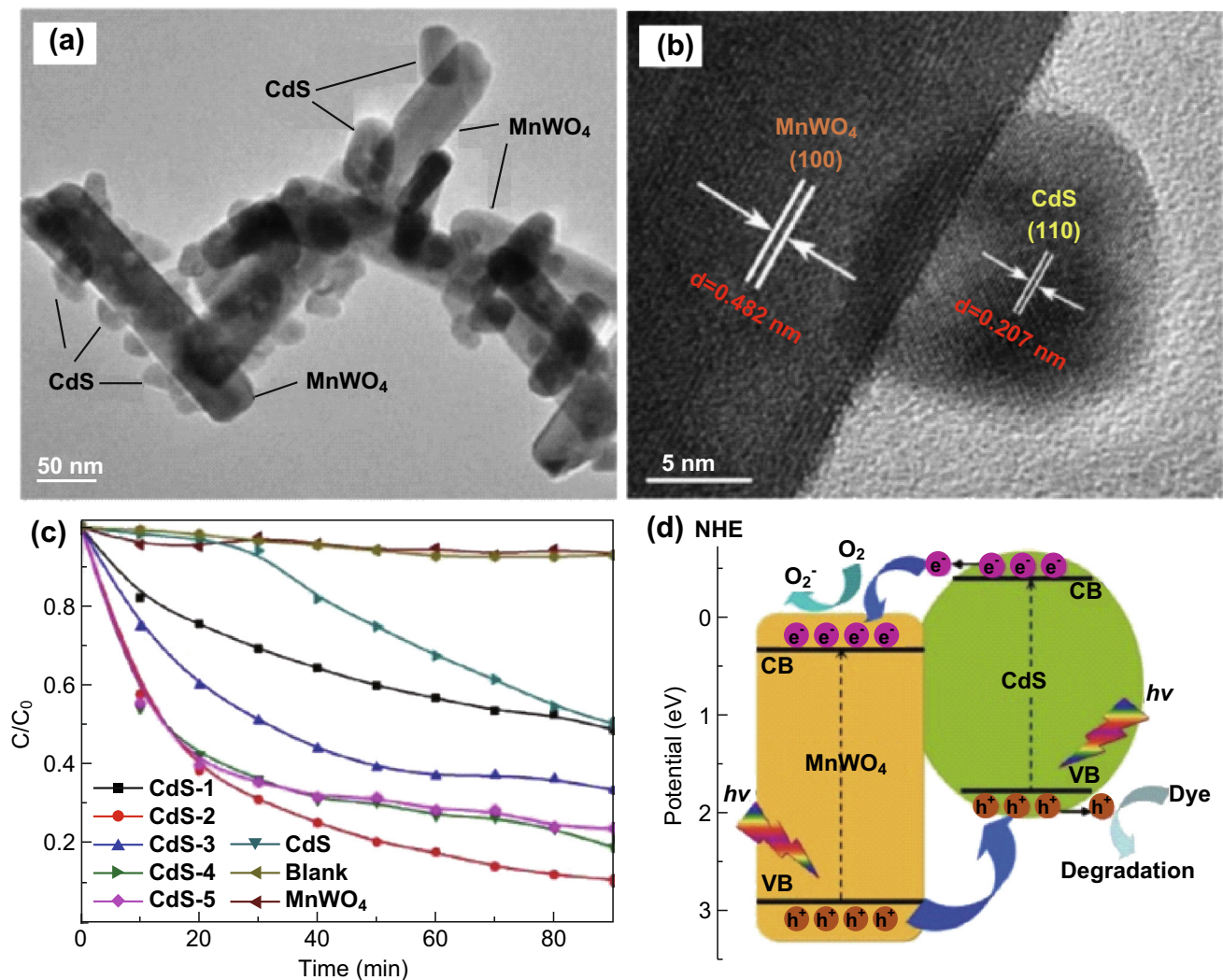


Fig. 14 **a, b** TEM and HRTEM images of a CdS/MnWO₄ heterojunction. **c** Photocatalytic degradation of MB over CdS/MnWO₄ with different CdS contents. **d** Schematic photocatalytic mechanism of CdS/MnWO₄ heterojunction. Reproduced with permission from Ref. [155]. Copyright 2017 Elsevier

[171, 172], NiWO₄/WO₃ [173, 174], or CuWO₄/WO₃ [175, 176]. Aslam et al. [177] prepared a CdWO₄/WO₃ heterojunction using a hydrothermal and chemisorption method, and reported enhanced photocatalytic activities toward the degradation of organic pollutants, compared with pure CdWO₄ and WO₃. This section clearly demonstrates in detail that the construction of MWO₄-based heterojunction systems is an effective and controllable method for enhancing the photocatalytic activities of MWO₄-based semiconductors.

3.4.2 Hybridization with Carbon-Rich Materials

Carbon-rich materials, including carbon nanotubes (CNTs), graphene, and graphitic carbon nitride (g-C₃N₄), possess unique physical and chemical properties such as a large surface area, high absorption co-efficiency, and chemical

stability, ensuring excellent and long-lasting applications in the fields of photochemical and PEC water treatment, photovoltaic devices, and water splitting [178–183]. Carbon-rich materials have a conjugative π structure and unique sp^2/sp^3 hybrid carbon network, which are suitable substrates for constructing hybrid photocatalysts to intensify the separation and transportation of photoinduced charge carriers inside carbon-rich networks, thus improving the photocatalytic performance [184–187]. Based on this strategy, Gaillard et al. [188] synthesized a novel photoelectrode consisting of CuWO₄ and a multi-wall CNT (MWCNT) to tune the photogenerated charge transfer in the nanocomposite film for enhancing the performance of solar-driven PEC water splitting. Compared to the bare CuWO₄ photoelectrode, the resistance and photocurrent density of the CuWO₄/MWCNT composite photoelectrode decreased and increased by 30% and 26%, respectively.

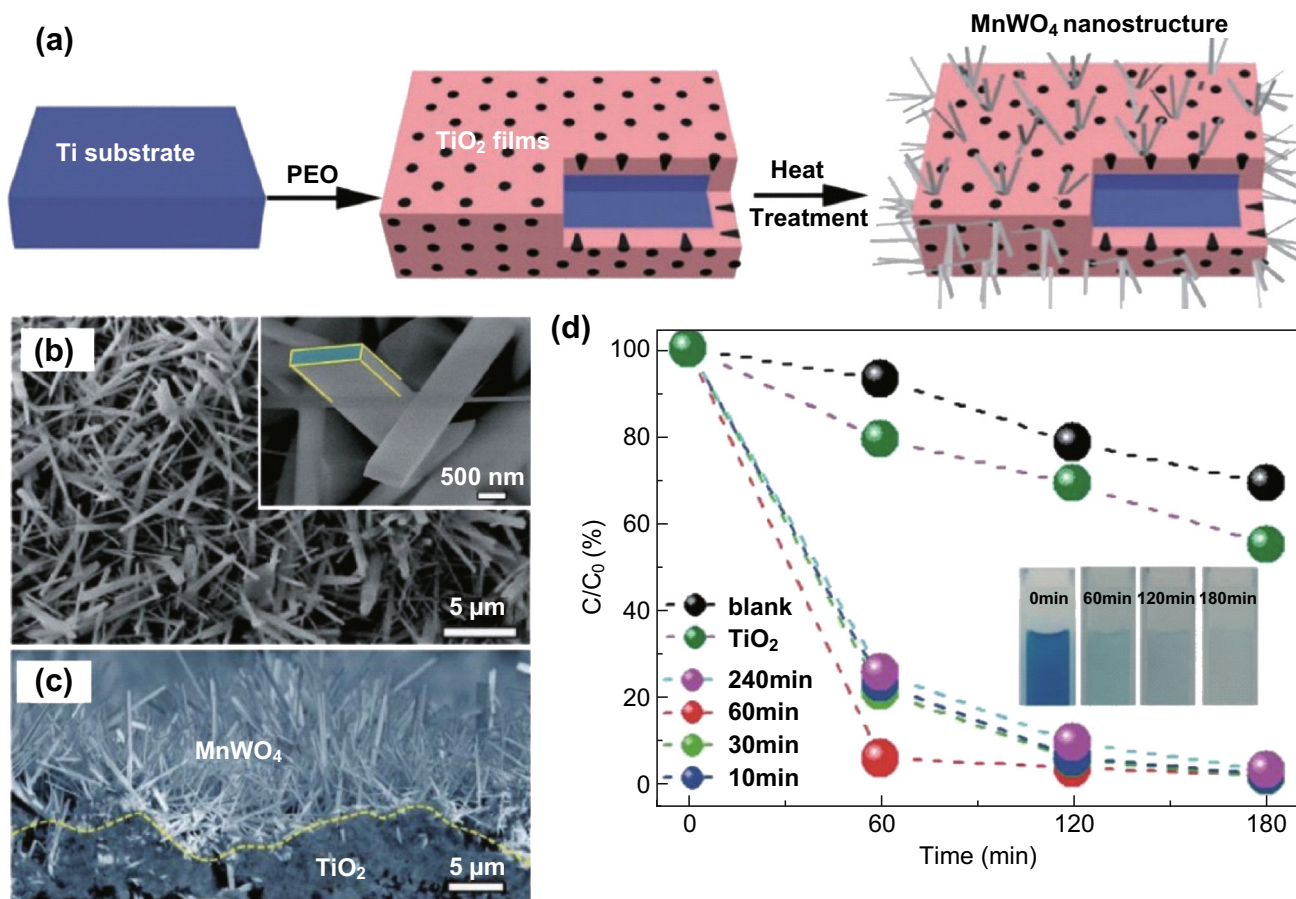


Fig. 15 a Schematic diagram describing the formation of MnWO₄ nanoplates. b–c FESEM images of the MnWO₄ nanoplates and MnWO₄ nanoplates on TiO₂ film. d Photodegradation efficiency of different samples heated at 850 °C for different times. Reproduced with permission from Ref. [162]. Copyright 2016 Royal Society of Chemistry

This was mainly attributed to the complete dispersion of the MWCNT as an electron collector in the entire CuWO₄ layer. Compared to CNTs, graphene nanosheets produced via the chemical oxidation treatment of graphite have more *sp*³ hybridized edge structure because of the destroyed perfect *sp*² structure. It is well-known that a perfect *sp*² carbon structure (CNT) is beneficial for rapid charge mobility, and that an *sp*³-hybridized carbon structure (graphene) can lead to a small band gap in the semiconductor [189, 190]. Meanwhile, layer-structure carbon materials have a richer porosity substructure assembly from graphene stacking and surface defects, which could provide more reactive sites, in comparison to tube-like carbon materials. Recently, Bai et al. [191] designed a ZnWO₄/graphene hybrid, demonstrating that graphene could act as a photo-sensitizer in the hybrid and improve the production of ·OH and ·O₂⁻ radicals. The excited photogenerated electrons at the CB of ZnWO₄ could be easily injected into the lowest unoccupied molecular orbital (LUMO) of graphene, resulting in a beneficial spatial separation between the holes and electrons inside the

ZnWO₄/graphene hybrid, in which more holes and electrons can participate in the production of active species, in comparison to bare ZnWO₄. Xu et al. [192] reported a CdWO₄/graphene hybrid using a hydrothermal process, in which the formed heterojunction showed significantly enhanced photocatalytic activity compared to that of the bare ZnWO₄. However, it was found that excessive graphene could have a negative effect on the photocatalytic performance because of the reduced light absorption efficiency of CdWO₄ with the addition of the superfluous graphene.

Apart from graphene, other carbon-rich materials, such as g-C₃N₄ and mesoporous carbon materials, have been considered as promising candidates to build MWO₄-based heterojunctions. g-C₃N₄, which is regarded as an allotrope of C₃N₄, possesses excellent chemical stability, a suitable band gap of 2.7 eV, and a high specific surface area, which are beneficial for anchoring various other semiconductor materials [193–195]. For instance, Sun et al. [196] synthesized g-C₃N₄/ZnWO₄ NRs via a thermal treatment route, and investigated the microcosmic mechanisms of the

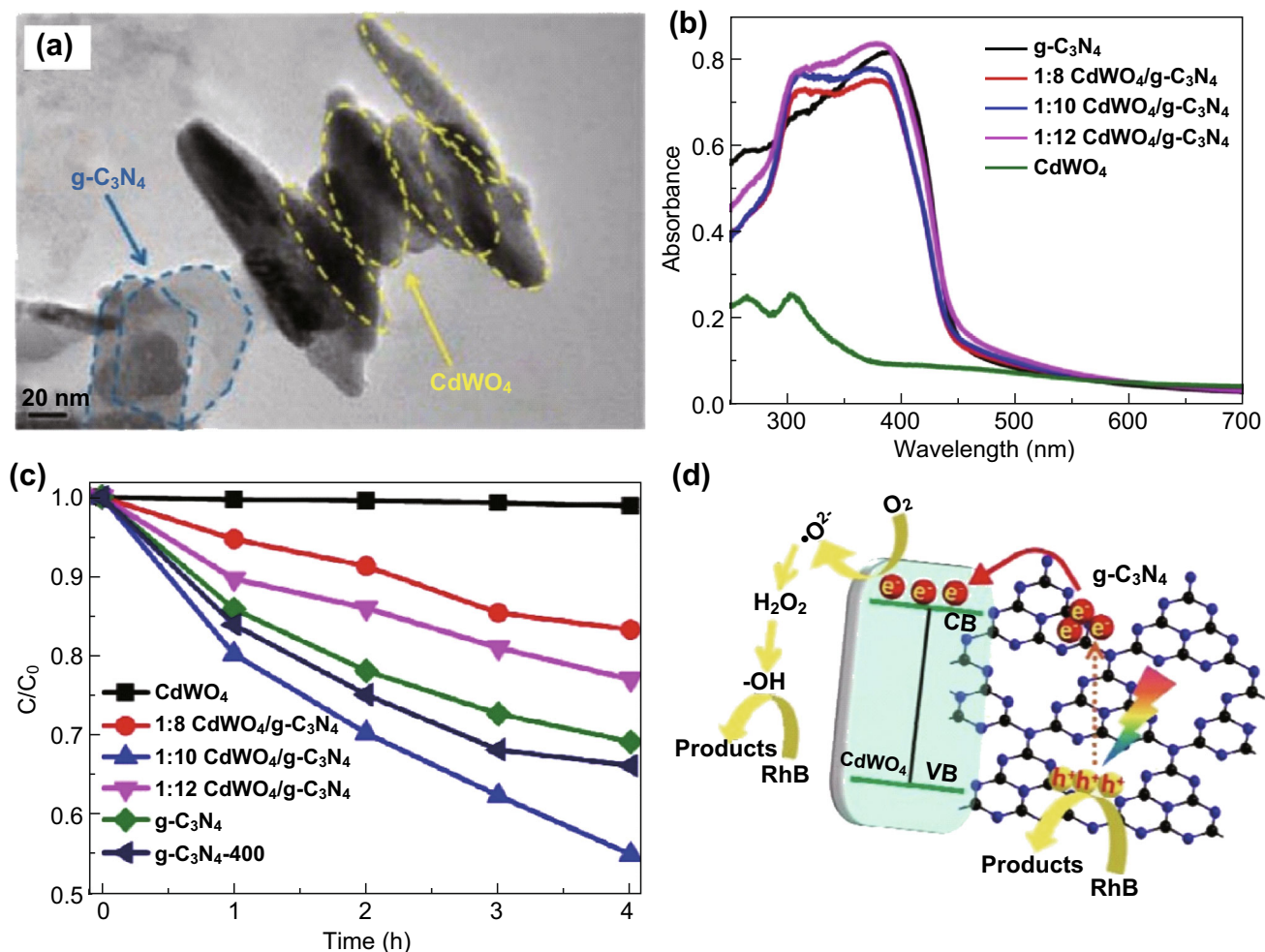


Fig. 16 **a** TEM image, **b** UV-vis diffused reflectance spectra, and **c** photocatalytic degradation curves of CdWO₄/C₃N₄. **d** Mechanism of photocatalytic reaction on the CdWO₄/C₃N₄. Reproduced with permission from Ref. [197]. Copyright 2015 Elsevier

enhanced photocatalytic activity of C₃N₄/ZnWO₄ in comparison to pristine ZnWO₄ NRs and C₃N₄. Together with theoretical calculation results, it was found that the well-matched energy level alignment of the C₃N₄ and ZnWO₄ NRs was the primary reason for the enhancement of the photocatalytic performance, in which the electrons at the VB top edge of the C₃N₄, when excited by the incident light, quickly jumped to the CB bottom edge of C₃N₄ and then transferred to the CB of ZnWO₄ because of the staged alignment, thus enhancing the charge transfer and separation efficiency. In addition, Tian et al. [197] synthesized a CdWO₄/C₃N₄ hybrid using a hydrothermal process, followed by a mixed-calcination treatment. Compared to pure CdWO₄, the CdWO₄/C₃N₄ heterojunction exhibited higher photocatalytic activity (Fig. 16c), the proposed mechanism for which is shown in Fig. 16d. The matched band structures between the two components contributed to the separation and transfer process, in which the excited electrons at the CB of C₃N₄ moved to the CB of CdWO₄ following a

downward staged band, such that the photoinduced electrons and holes were efficiently separated, thus enhancing the overall photocatalytic activity. Considering its appropriate band energy level, g-C₃N₄ is usually used to construct a Z-scheme hybrid system to enhance photocatalytic activities. Instead of a type-II heterojunction, the direct Z-scheme configuration not only forms a built-in electronic field to promote the separation and transfer efficiency of photogenerated electrons and holes, but it also maintains the reductive and oxidative ability of electrons and holes [198, 199]. Recently, Zhu and co-workers [200] reported a direct Z-scheme heterojunction by combining g-C₃N₄ with Ag₂WO₄ through a facile precipitation route. Because of the use of g-C₃N₄ as a support in the precursor solution, Ag₂WO₄ was able to nucleate and grow on the surface of the layered C₃N₄, thus resulting in the Ag₂WO₄ evenly distributing on the surface of the layered g-C₃N₄-nanosheets. In comparison to the bare Ag₂WO₄ and g-C₃N₄, the Z-scheme of the g-C₃N₄/Ag₂WO₄ hybrid system exhibited

a much higher photoactivity for the degradation of MO, owing to the efficient separation between the photoinduced electrons and holes in the direct Z-scheme configuration. Given the aforementioned examples and explanations, it is obvious that carbon-rich materials possess a high charge carrier mobility and large specific surface area, which could efficiently promote the separation efficiency of photoexcited electrons and holes in the MWO₄, ultimately leading to improvement of the photocatalytic activity.

4 Summary and Outlook

This review summarized the development of novel strategies to enhance the photocatalytic performance of MWO₄-based materials with a special emphasis on their applications in environmental purification and solar water splitting. Although significant improvements have been achieved in the construction of highly efficient ternary MWO₄-based oxides, challenges remain that need to be addressed. First, the recombination rate of photogenerated charge carriers for MWO₄-based photocatalysts is still considerably high, accounting for poor reduction ability in the photoexcited electrons at a low potential of the CB edge, which are easily quenched by defects and holes. Second, although morphological engineering could improve the photocatalytic activity of MWO₄-based systems by regulating the crystal structure, particle size, and surface area, the current synthetic methods are inadequate for large-scale preparation, particularly for nanosized materials, which would significantly improve the separation efficiency of the photogenerated charge carriers. Third, the surface effect, particularly the crystal surface effect on the photocatalytic performance of MWO₄-based systems, has not been synergistically and comprehensively investigated. It is thought that the atom configurations and surface defects should be paid more attention, to provide important information for designing highly efficient photocatalysts. Fourth, based on this review, it is clear that the MWO₄ materials consisting of a single valence metal ion, such as Cd, Zn, or Sn, have been well-developed in the past, while those composed of a versatile valence metal, for instance, Co, Fe, or Ni, have been insufficiently explored in surface engineering and theoretical computation.

To overcome these challenges, future research needs to focus on the exploration of novel photocatalytic materials. Although the sunlight-harvesting ability and separation efficiency of photogenerated charge carriers could be strengthened by heteroatom doping or heterojunction fabrication as reported by previous literature, traditional material screening, high-throughput screening, and computational materials design can guide the construction of photocatalysts with a proper band edge position and

suitable band gap, thereby shortening the experimental period, reducing the workload, and saving experimental cost. In other fundamental studies, combining experiment and theory would enable understanding the photocatalytic principles and screen alternative high-performance photocatalysts. Future work also needs to focus on facile synthetic approaches for constructing stable MWO₄ materials with high active crystal surface and/or quantum size, and developing advanced techniques for large-scale production. It is expected that further progress in ternary MWO₄-based photocatalysts for applications in environmental purification and solar water splitting will be made in future studies.

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