Host/Guest Nanostructured Photoanodes Integrated with Targeted Enhancement Strategies for Photoelectrochemical Water Splitting

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Photoelectrochemical (PEC) hydrogen production from water splitting is a green technology that can solve the environmental and energy problems through converting solar energy into renewable hydrogen fuel. The construction of host/guest architecture in semiconductor photoanodes has proven to be an effective strategy to improve solar-to-fuel conversion efficiency dramatically. In host/guest photoanodes, the absorber layer is deposited onto a high-surface-area electron collector, resulting in a significant enhancements in light-harvesting as well as charge collection and separation efficiency. The present review aims to summarize and highlight recent state-of-the-art progresses in the architecture designing of host/guest photoanodes with integrated enhancement strategies, including i) light trapping effect; ii) optimization of conductive host scaffolds; iii) hierarchical structure engineering. The challenges and prospects for the future development of host/guest nanostructured photoanodes are also presented.

1. Introduction

The renewable solar energy received by the land per year ($3.6 \times 10^5$ Terawatts) far exceeds the predicted global energy consumption by humankind in 2050 (36 Terawatts).[1–4] Converting solar energy into renewable chemical fuels has been considered a promising solution to tackle both energy crises and environmental pollutions.[5–8] Hydrogen fuel is a clean, renewable and carbon-free fuel, which will play a vital role in a clean, secure, and affordable energy future.[9–11] Photoelectrochemical (PEC) water splitting provides a green pathway for hydrogen fuel production through the direct conversion of solar energy.[12–14] In 1972, Fujishima and Honda first conducted the pioneering work for PEC water splitting via TiO$_2$ films as the photoanode.[15] Following that, numerous research efforts have been made to realize a high solar-to-hydrogen (STH) conversion efficiency.[11–14]

The STH conversion efficiency of semiconductor photoanodes for practical application is primarily determined by several critical factors in the PEC process, including efficient visible light absorption, high separation and collection of charge carriers, and good long-term chemical stability.[16–18] Much effort has been made to develop advanced techniques for fabricating novel nanostructures as semiconductor photoanodes.[19–21] Nanostructures can usually enhance solar energy harvesting, reduce diffusion length of the charge carriers, and increase the contact area with the electrolyte, thus improving the STH conversion efficiency of one PEC cell. Various nanostructures such as 1D nanorods (NRs)[22,23] and nanowires (NWs)[24] 2D nanosheets (NSs),[25,26] 3D inverse opals (IOs),[27,28] 2D nanosheets (NSs),[25,26] 3D inverse opals (IOs),[27,28] and 3D inverse opals (IOs)[27,28] have been reported for efficient PEC applications. Although these single semiconductors demonstrate high PEC performance, it is difficult to satisfy these critical factors simultaneously on a single semiconductor photoanode.[29–31] Constructing multicomponent heterostructures photoanodes is one of the most effective strategies to balance the harsh elements and achieve superior properties than individual components.[32–34]

Inspired by the synergistic effects of a tree trunk for mass transport and leaves for light absorption in natural photosynthesis, host/guest multicomponent architectures are proposed...
for PEC water splitting, in which a highly dispersed light absorber acting as the guest material is deposited onto nanostructured host scaffolds.[35–38] Metal oxides such as Fe₂O₃[39] and BiVO₄[40] are usually used as guest materials to absorb visible solar light due to the narrow bandgap and good chemical stability at the highly oxidizing condition required for water oxidation. The wide bandgap materials such as SnO₂,[41] ZnO,[42] and WO₃[43] can act as host scaffolds to allow rapid electron extraction at the contact, owing to their excellent electron transport properties and suitable conduction band alignment to the guest absorber. Thus, the construction of host/guest architecture in photoanodes can simultaneously enhance visible light absorption as well as separation and collection of charge carriers, dramatically improving the solar-to-fuel conversion efficiency of PEC photoanodes.[44–45] Typically, the configuration of PEC devices can be also divided into three types, namely nonintegrated/modular, fully integrated/wireless, and partially integrated/wired PEC devices. In the nonintegrated/modular PEC devices, water splitting and light absorption are achieved by electrodes and photovoltaic cells, respectively. Conversely, for fully integrated/wireless and partially integrated/wired PEC devices, water splitting and light absorption are combined into one electrode. The anode and cathode are in physical contact in fully integrated/wireless PEC devices, while they are connected through external wiring in partially integrated/wired PEC devices.[46] Mostly host/guest photoanodes are designed as nonintegrated/modular PEC devices. After decades of development, numerous host/guest photoanodes have been reported for PEC applications. Therefore, it is essential to give a timely review on the architecture progress of host/guest nanostructured photoanodes.

The present review aims to summarize and highlight recent state-of-the-art progresses in the architectural design of host/guest nanostructured photoanodes with integrated enhancement strategies (Figure 1), including i) light trapping effect; ii) optimization of conductive host scaffolds; iii) hierarchical structure engineering. First, the principle and evaluation factors of PEC water splitting are discussed. Second, the properties of typical host or guest materials are briefly summarized. Third, the architectural progresses of host/guest photoanodes is overviewed based on the integrated enhancement strategies. Finally, the challenges and prospects for the future development of host/guest nanostructured photoanodes are also presented.

2. Principle and Critical Parameters of PEC Water Splitting

The configuration of one typical n-type semiconductor-based PEC cell is shown in Figure 2, consisting of a working photoelectrode for oxygen evolution reaction (OER) and a counter electrode (such as Pt) for hydrogen evolution reaction (HER). The electrodes are immersed in an electrolyte, such as neutral, acid, alkaline aqueous solutions, or sacrificial reagents. The PEC water splitting process involves three main steps. First, electron-hole pairs are generated through the absorption of incident photons with energy more prominent than the bandgap of the semiconductors. The light absorption efficiency (η₁) reflects the percentage of incident photons that are absorbed by the photoanode. Second, due to the band bending induced space-charge field, the photogenerated electrons are transported toward the semiconductor/electrolyte interface simultaneously. Here, the separation efficiency (η₂) describes the percentage of photogenerated carriers that are successfully transported to the electrode surface. Third, the electrons or holes that transferred to the metal/electrolyte or semiconductor/electrolyte junction take part in HER or OER, respectively. The charge transfer efficiency (η₃) indicates the percentage of surface-reaching photogenerated carriers that finally participate in the desired reactions.[47–50]

Thermodynamically, water splitting is an uphill reaction with a minimum energy requirement of 1.23 eV.[51] Thus, the energy of photons absorbed by a photoanode should be larger than 1.23 eV, corresponding to ≈1100 nm wavelength of light. However, the minimum practical energy required for PEC water splitting is around 1.8–2.0 eV, owing to the energy losses and the overpotential requirement for acceptable surface reaction kinetics.[52,53]

The measured photocurrent density (J_{pec}) at 1.23 V versus RHE is frequently selected to compare the PEC performance of different photoanodes.[54,56] J_{pec} is determined by the theoretical maxi-
but inevitably enlarges the carrier transfer path, resulting in low photocurrent, resulting in the overestimation of PEC performance. The \( \eta_{\text{abs}} \) and \( \eta_{\text{sep}} \) can be experimentally measured by using a hole scavenge, such as \( \text{Na}_2\text{SO}_3 \), with a \( \eta_{\text{trans}} \) of 100%.\(^{[67,68]} \)

When measuring photocurrent, side reactions or photocorrosion of semiconductors may also contribute to the total value of the photocurrent, resulting in the overestimation of PEC performance.\(^{[69]} \) Thus, Faradaic efficiency, incident photon-to-current conversion efficiency (IPCE), and STH efficiency are frequently used as evaluation parameters. Faradaic efficiency can reveal the percentage of the charge carriers that are genuinely used for \( \text{O}_2 \) or \( \text{H}_2 \) production. It can be derived by dividing the electric charge calculated from the measured amount of evolved gas by the total electric charge.\(^{[70]} \) IPCE calculates the efficiency in the form of “electrons out per photons in” and takes the influences of spectral change of incident photons into consideration. IPCE describes the upper limit of efficiency to produce hydrogen or oxygen from water on the condition that all electrons and holes are used.\(^{[71]} \) STH efficiency, which is defined as the ratio of the generated chemical energy divided by the solar energy input, reports the efficiency of a PEC system under zero bias without any addition of sacrificial reagents.\(^{[72]} \) PEC system with a STH efficiency greater than 10% can be used for practical application, hence this parameter is commonly used in the ranking of a PEC device.\(^{[72]} \)

\[ J_{\text{max}} = \frac{e}{\Delta \lambda} \int I(\lambda) \times \text{LHE} \, d\lambda \]

\[ \eta_{\text{abs}} = \frac{e}{J_{\text{max}}} \int I(\lambda) \times \text{LHE} \, d\lambda \]

\[ \text{LHE} = 100\% - \text{Reflectance}% - \text{Transmittance}% \]

Where \( e \) is the charge of a single electron, \( E_g \) is the bandgap energy of a semiconductor, and \( I(\lambda) \) represents the photon flux at a different wavelength. LHE is the light-harvesting efficiency, which can be experimentally measured using a spectrometer equipped with an integrating sphere.\(^{[59]} \)

\( J_{\text{max}} \) describes the maximum photocurrent that can be achieved by a semiconductor under the assumption that all incident photons and photogenerated electrons are utilized for current formation. Bandgap energy determines the achievable \( J_{\text{max}} \), which is the upper limit of \( J_{\text{PEC}} \).\(^{[60,61]} \) The bandgap positions of typical semiconductors and the distribution of solar energy and \( J_{\text{max}} \) over the wavelength are shown in Figure 3. Semiconductors with smaller bandgap energy, such as \( \text{WO}_3 \) (2.7 eV, 3.9 mA cm\(^{-2} \)), \( \text{BiVO}_4 \) (2.4 eV, 7.4 mA cm\(^{-2} \)), and \( \text{Fe}_2\text{O}_3 \) (2.2 eV, 10.5 mA cm\(^{-2} \)) can achieve larger \( J_{\text{max}} \) than semiconductors with wider bandgaps, such as anatase \( \text{TiO}_2 \) (3.2 eV, 1.1 mA cm\(^{-2} \)).\(^{[41]} \)

In the practical PEC process, the measured \( J_{\text{PEC}} \) is much lower than the theoretical \( J_{\text{max}} \) due to poor \( \eta_{\text{abs}} \), \( \eta_{\text{sep}} \), and \( \eta_{\text{trans}} \). Surface coating of efficient OER catalysts is a well-established technique to improve \( \eta_{\text{trans}} \).\(^{[63-65]} \) However, the enhancement of \( \eta_{\text{abs}} \) and \( \eta_{\text{sep}} \) still remains a challenge due to their complex interaction. For example, the direct increase of film thickness is beneficial to \( \eta_{\text{abs}} \), but inevitably enlarges the carrier transfer path, resulting in low \( \eta_{\text{sep}} \).\(^{[66]} \) Therefore, the overall photocurrent of a photoanode is mainly determined by the equilibrium of \( \eta_{\text{abs}} \) and \( \eta_{\text{sep}} \). Developing rationally designed host/guest architectures with the targeted improvement strategies is a promising pathway to optimize \( \eta_{\text{abs}} \) and \( \eta_{\text{sep}} \).\(^{[58]} \) The \( \eta_{\text{abs}} \) and \( \eta_{\text{sep}} \) can be experimentally measured by using a hole scavenge, such as \( \text{Na}_2\text{SO}_3 \), with a \( \eta_{\text{trans}} \) of 100%\(^{[67,68]} \)

3. Review of Host and Guest Materials

The host/guest photoanodes reported in recent years are summarized in Table 1. \( \text{SnO}_2 \), \( \text{WO}_3 \), and \( \text{ZnO} \) are primary host scaffold materials, while narrow bandgap semiconductors, such as \( \text{Fe}_2\text{O}_3 \) and \( \text{BiVO}_4 \), are typical guest materials. The architectures of nanostructured host/guest photoanodes can be divided into 1D core/shell nanostructures and hierarchical nanostructures, such as 1D/1D nanodendrite arrays,\(^{[68]} \) 1D/2D screw-like nanostructures,\(^{[41]} \) and 3D/2D nanospheres/NSs.\(^{[35]} \) Although various architectures have been reported as host/guest photoanodes, their fabrication process can be divided into two indepen-
Table 1. Representative host/guest photoanodes for PEC water splitting.

| Host materials | Architecture | Host/guest photoanodes | Electrolytes | Photocurrent density [mA cm\(^{-2}\)] at 1.23 V versus RHE under AM 1.5 [100 mW cm\(^{-2}\)] | Refs. |
|----------------|--------------|------------------------|--------------|-----------------------------------------------|-------|
| SnO\(_2\)      | 1D/0D        | Sb: SnO\(_2\)/BiVO\(_4\) core/shell nanorods | 1 m Na\(_2\)SO\(_4\) | 5.3                                           | [58]  |
|                |              | Sb: SnO\(_2\) nanotubes/BiVO\(_4\) shell | 1 m Na\(_2\)SO\(_4\) | 5.2                                           | [75]  |
|                | 1D/1D        | SnO\(_2\) nanodendrite arrays/BiVO\(_4\) films | 0.3 m Na\(_2\)SO\(_4\) | 0.6                                           | [74]  |
|                | 1D/2D        | Screw-like SnO\(_2\) nanostructures/CdS QDs | 0.25 m Na\(_2\)S + 0.35 m Na\(_2\)SO\(_4\) | 9.9 [0 V vs SCE] | [61]  |
|                | 3D/0D        | F: SnO\(_2\)/TiO\(_2\)/BiVO\(_4\) composite inverse opals | 0.5 m Na\(_2\)SO\(_4\) | 4.11                                          | [57]  |
|                | 3D/1D        | Sb: SnO\(_2\) macropore/Fe\(_2\)O\(_3\) nanorods | 1 m NaOH | 1.1                                           | [75]  |
|                |              | SnO\(_2\) nanobowl arrays/CdS nanorods | 0.25 m Na\(_2\)S + 0.35 m Na\(_2\)SO\(_4\) | 3                                             | [76]  |
|                |              | F: SnO\(_2\) inverse opals/CdS NRs/CdSe clusters | 0.25 m Na\(_2\)S + 0.35 m Na\(_2\)SO\(_4\) | 9.2                                           | [77]  |
|                | 3D/2D        | SnO\(_2\) microspheres/nanosheets/TiO\(_2\)/BiVO\(_4\) | 0.5 m Na\(_2\)SO\(_4\) + 0.1 m Na\(_2\)SO\(_4\) | 5.03                                          | [55]  |
| WO\(_3\)       | 1D/0D        | WO\(_3\)/BiVO\(_4\) core/shell nanorods | 1 m Na\(_2\)SO\(_4\) | 4.15                                          | [78]  |
|                |              | WO\(_3\)/Fe\(_2\)O\(_3\) core/shell needles | 0.1 m phosphate | 1.75                                          | [79]  |
|                | 2D/0D        | WO\(_3\) nanosheets/barium bismuth niobate films | 0.5 m Na\(_2\)SO\(_4\) | 2.23                                          | [43]  |
|                |              | WO\(_3\)/BiVO\(_4\) core/shell nanosheets | 0.5 m Na\(_2\)SO\(_4\) | 1.62                                          | [80]  |
|                | 2D/1D        | WO\(_3\) nanoplates/Bi\(_2\)S\(_3\) nanorods | 0.1 m Na\(_2\)S + 0.1 m Na\(_2\)SO\(_4\) | 10.2                                         | [81]  |
|                | 3D/0D        | WO\(_3\) nanoplates/Fe\(_2\)O\(_3\) nanorods | 1 m NaOH | 0.25                                          | [59]  |
|                |              | WO\(_3\)/BiVO\(_4\) composite inverse opals | 0.5 m Na\(_2\)SO\(_4\) | 0.8                                           | [40]  |
|                |              | Brochosome-like WO\(_3\)/BiVO\(_4\) arrays | 0.5 m Na\(_2\)SO\(_4\) | 3.13                                          | [36]  |
| ZnO            | 1D/0D        | ZnO/Fe\(_2\)O\(_3\) core/shell nanowires | 1 m NaOH | 1.3                                           | [82]  |
|                |              | ZnO nanorods/BiVO\(_4\) nanoparticles | 0.2 m Na\(_2\)SO\(_4\) | 1.9                                           | [83]  |
|                |              | N: ZnO/Mo-doped BiVO\(_4\) bunched nanorods | 0.5 m Na\(_2\)SO\(_4\) | 3.62                                          | [84]  |
|                | 1D/1D        | ZnO nanorods/CdS/ZnFe\(_2\)O\(_4\) nanoparticles | 0.1 m Na\(_2\)S + 0.2 m Na\(_2\)SO\(_4\) | 9.16 [0.4 V vs SCE] | [42]  |
|                |              | ZnO nanorods/CdS layer | 0.25 m Na\(_2\)S + 0.35 m Na\(_2\)SO\(_4\) | 11.5                                          | [85]  |
|                | 1D/2D        | Al: ZnO nanowires/ZnFe\(_2\)O\(_4\) shell | 0.1 m Na\(_2\)SO\(_4\) | 1.72                                          | [68]  |
|                |              | ZnO nanodendrite arrays/BiVO\(_4\) films | 0.3 m Na\(_2\)SO\(_4\) | 2.45                                          | [68]  |
|                |              | Branched ZnO nanowire arrays/CdS nanoparticles | 0.3 m Na\(_2\)S | 3.58                                          | [87]  |
|                | 2D/1D        | ZnO nanorod-nanosheet/CdS quantum dots | 0.5 m Na\(_2\)SO\(_4\) | 4.25 [0.4 V vs Ag/AgCl] | [88]  |
|                | 3D/0D        | ZnO inverse opals/BiVO\(_4\) films | 0.2 m Na\(_2\)SO\(_4\) | 4.2                                           | [89]  |
|                |              | Al: ZnO inverse opals/BiVO\(_4\) films | Phosphate buffer | 1.5                                           | [90]  |

dent parts: the growth of nanostructured host scaffolds and the following surface coating of guest semiconductor films. Thus, the benefits of one host scaffold can be applied to different guest materials. The host semiconductors usually exhibit little visible light absorption, owing to their wide bandgap. The bandgap energies of SnO\(_2\) and ZnO are 3.5 and 3.2 eV, respectively, making little contribution to visible light absorption in the host/guest photoanodes. WO\(_3\) has a bandgap of 2.7 eV that can harvest 12% of solar spectrum absorption. [91] Compared to host scaffolds, guest semiconductors with narrow bandgaps have stronger visible light absorption. However, many guest semiconductors suffer from poor electron mobility. For example, Fe\(_2\)O\(_3\) has low electron mobility ($\approx 10^{-2}$ cm\(^2\) V\(^{-1}\) s\(^{-1}\)) and a short hole diffusion length of 2–4 nm. [92–94] Although BiVO\(_4\) has a moderate hole diffusion length of 100–200 nm, it is restricted by poor electron mobility ($\approx 0.02$–0.044 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). [95,96] Under frontside light illumination, the photoexcited electrons are generated near the photoanode/electrolyte interface and have to cross the entire film thick-
ness for chemical reaction. Thus, the low electron mobility inevitably restricts the transport of photogenerated electrons to the electron collector. On the contrary, host semiconductors exhibit a lower visible light absorption but much higher electrons mobility than guest materials, such as SnO$_2$ ($\approx$ 240 cm$^2$ V$^{-1}$ s$^{-1}$), ZnO ($\approx$ 200 cm$^2$ V$^{-1}$ s$^{-1}$), WO$_3$ ($\approx$ 12 cm$^2$ V$^{-1}$ s$^{-1}$). The improvement of host scaffolds on the charge collection of guest materials will be detailed in Section 4.2.

In host/guest photoanodes, the contact between host and guest semiconductors favors the formation of type-II heterojunctions due to the more positive band edges of host materials than that of guest materials. In type-II heterojunctions, photogenerated electrons transfer from the conduction band (CB) of guest materials to the more conductive host materials and finally reach the counter electrode, while holes facilely move in the opposite direction, thus resulting in a spatial separation of electron–hole pairs and a depressed charge recombination. Lee et al. investigated the construction of heterojunction films consisting of guest BiVO$_4$ with a series of host materials, such as Fe$_2$O$_3$, TiO$_2$, SnO$_2$, and WO$_3$. As shown in Figure 4a, SnO$_2$/BiVO$_4$ and WO$_3$/BiVO$_4$ host/guest films can form a type-II heterojunction due to the matched band alignment. Host/guest photoanodes showed an increased photocurrent at 1.23 V versus RHE compared to pristine BiVO$_4$ films. However, the direct combination of Fe$_2$O$_3$/BiVO$_4$ and TiO$_2$/BiVO$_4$ are not beneficial to the charge transfer in the heterojunction due to the unmatched band alignment, resulting in a decreased photocurrent. The band alignment between host materials and guest materials can be further judged with experimental techniques. The Mott–Schottky plots technique is frequently adopted to acquire the flat band potential, which is close to the CB edge.

Figure 4. a) The band alignment of different heterojunction based on BiVO$_4$ composite films. Reproduced with permission.[104] Copyright 2016, Elsevier Ltd. b,c) Mott–Schottky plots of ZnO NWs and Fe$_2$O$_3$ thin film. d) Schematic of the band alignment between ZnO NWs and Fe$_2$O$_3$ thin film. Reproduced with permission.[82] Copyright 2015, American Chemical Society.

4. Targeted Enhancement Strategies for Host/Guest Photoanodes

The emergence of host/guest architectures in photoanodes can enhance visible light absorption as well as the separation and collection of charge carriers, thus dramatically improving photocurrent and STH efficiency of photoanodes. Based on the construction feature of host/guest architectures in photoanodes, three targeted enhancement strategies including i) light trapping effect for enhanced light absorption; ii) optimization of conductive host
scaffolds for improved charge separation; iii) hierarchical structure engineering for simultaneous enhancement of light absorption and charge separation were studied. This section aims to summarize and highlight recent state-of-the-art progress in the architectural design of host/guest photoanodes with these enhancement strategies.

4.1. Light Trapping Effect

\( \eta_{\text{abs}} \) is determined by the light-harvesting efficiency. Sufficient light-harvesting is a prerequisite to enhancing PEC performance of host/guest photoanodes. The absorption of more incident photons generates more electron–hole pairs for the chemical reaction in a PEC cell. Light trapping induced by multiple light scattering or slow-photon effect can prolong the optical path to increase the \( \eta_{\text{abs}} \). Concurrently, the short hole diffusion path can be well maintained to avoid the adverse impact on \( \eta_{\text{sep}} \). [106–108] Light trapping effects are usually achieved in well-designed porous or periodic host/guest nanostructured photoanodes.

Multiple light scattering occurs at the void areas of nanostructures, effectively prolonging the optical path at a fixed film thickness, which enhances the light-harvesting capability. Zhou et al. investigated the light-matter interaction in BiVO\(_4\) flat films and nanosphere arrays with relative film thickness ([Figure 5]).[66] The incident light penetrates the film directly without scattering in the flat films, as reflected by the evenly distributed electric field ([Figure 5a]). When the distance between adjacent nanospheres approaches the wavelength of the incident light, the incident light is scattered and trapped in the nanosphere arrays, resulting in an intensified electric field in the void areas (Figure 5b) as observed through finite difference time domain (FDTD) simulation. WO\(_4\)/BiVO\(_4\) nanosphere arrays with sufficient voids were confirmed by scanning electron microscope (SEM) (Figure 5c).

The UV–vis diffuse reflectance spectra shows that WO\(_4\)/BiVO\(_4\) nanosphere arrays could adsorb more incident photons than flat WO\(_4\)/BiVO\(_4\) films (Figure 5d).

3D IOs are periodic porous structures that can provide plenty of controllable void areas, which enhances the light trapping capability.[109,110] 3D host IOs are usually fabricated by the template-assisted method. In a typical synthesis process, the precursors of the host semiconductor are first infiltrated into self-assembled 3D periodic opal templates. 3D host IOs can be obtained through the removal of the opals template by a post-annealing or chemical corrosion. The photoactive guest semiconductors are then coated onto the 3D host IOs by spin-coating or electrodeposition technique to create the host/guest photoanodes with periodic porous structures.[44] Kim et al. reported the coating of guest BiVO\(_4\) thin layer on host 3D ZnO IOs to form typical periodic porous structures for improved PEC application.[89] As shown in [Figure 6a], the periodic and porous structure of ZnO IOs is well retained even after the coating of BiVO\(_4\) films. 3D ZnO IOs/BiVO\(_4\) films exhibited a 50% higher light-harvesting efficiency than ZnO/BiVO\(_4\) bilayer films in the wavelength range of 450–500 nm ([Figure 6b]). The enhanced light absorption can be ascribed to the multiple light-scattering effects within the IOs. Such multiple light scattering can also be achieved in other host/guest IOs, such as SnO\(_2\) IOs/BiVO\(_4\),[111] and ZnO IOs/Zn\(_{33}\)Cd\(_{67}\)Se.[112] 3D IOs can also achieve an additional slow photon effect, further contributing to the light trapping capability.[113] Due to the periodic variation of the refractive index, 3D IOs as a photonic crystal can present an apparent photonic stopband. The wavelength of incident light within the photonic stopband cannot transmit through the 3D IOs, forming a sharp reflection peak. At the edges of the photonic stopband, photons propagating through the material exhibit a strongly reduced group velocity, called slow pho-
tons, which can significantly increase the probability of absorption.[114] Zhang et al. investigated the photonic stopband of WO₃/BiVO₄ core/shell IOs.[40] When compared to disordered WO₃/BiVO₄/Co-Pi, and unpatterned WO₃/BiVO₄/Co-Pi, only ordered WO₃ IOs/BiVO₄/Co-Pi presented a Bragg reflection peak at 675 nm due to the stopband reflection effect (Figure 6c). The slow photon effect could thus enhance the light-harvesting efficiency of ordered WO₃ IOs/BiVO₄/Co-Pi near the stopband edge.

Apart from 3D IOs, other periodic porous host scaffolds can also be used for light trapping. Zhang et al. reported 3D brochosomes like WO₃ arrays as the host scaffolds (Figure 6d) for guest BiVO₄ films.[36] A hollow spherical core with plenty of periodic pits makes up one brochosomes like unit, and these units self-assemble to form the final brochosomes like architectures. Such ordered, hollow and porous structures not only provide a high specific surface area but also induce multiple light scattering effects. Hence, brochosomes like WO₃ arrays/BiVO₄ films show a lower reflectance intensity in the range of 300–500 nm (Figure 6e) and lower transmittance (Figure 6f) in a broad-band wavelength than flat WO₃/BiVO₄ films. This suggests that brochosomes-like architectures have superior light-harvesting abilities.

Therefore, the multiple light scattering and slow photon effect in the periodic and porous architectures are beneficial to light trapping, resulting in an improvement in the light-harvesting efficiency and $\eta_{abs}$. The improved light-harvesting efficiency of host/guest photoanodes can be verified by diffuse reflectance spectra and FDTD simulations.

### 4.2. Optimization of Conductive Host Scaffolds

Host scaffolds with high electron-extraction ability can effectively accelerate the electron transfer from guest photoactive semiconductors to the conductive substrates, reducing the bulk recombination of photogenerated electron–hole pairs.[115–117] 1D nanostructures with a reduced quantity of dead ends and fewer grain boundaries could provide direct and ordered channels for charge transport.[118–120] Thus, various 1D host NRs or NWs have been reported as scaffolds. Tao et al. reported the high-aspect-ratio WO₃ nanoneedles, fabricated with a seed-mediated hydrothermal reaction method, as the host scaffolds for Fe₂O₃ NPs.[79] The single crystalline structure with (020) orientation of monoclinic WO₃ can be observed by the high-resolution transmission electron microscopy (HRTEM), as shown in Figure 7a. Due to its single crystallinity, monoclinic WO₃ has inherently remarkable electron transport properties that greatly inhibited electron–hole recombination in Fe₂O₃ NPs.[79] The single crystalline structure with (020) orientation of monoclinic WO₃ can be observed by the high-resolution transmission electron microscopy (HRTEM), as shown in Figure 7a. Due to its single crystallinity, monoclinic WO₃ has inherently remarkable electron transport properties that greatly inhibited electron–hole recombination in Fe₂O₃ NPs.[79] Yu-Kuei et al. reported 1D ZnO/Fe₂O₃ core/shell nanostructures as the host/guest photoanode.[82] Fe₂O₃ films with a thickness of a few nanometers were coated on 1D ZnO NWs that has a thickness of 80 nm (Figure 7b). By optimizing Fe₂O₃ films thickness, 1D ZnO/Fe₂O₃ photoanode achieved a photocurrent density of 1.5 mA cm⁻² at 0.6 V versus AgCl, while Fe₂O₃ films only exhibited a photocurrent density of 0.5 mA cm⁻² (Figure 7c).

Element doping is an effective strategy to improve the electrical conductivity of host scaffolds, which can further enhance its charge collection ability.[121–123] The more efficient collection of the photogenerated carriers in the photoanodes can be indicated
by the higher carrier density. Kim et al. reported nitrogen-doped ZnO (N: ZnO) NRs as the host scaffold.[84] Figure 7d,e shows the O 1s X-ray photoelectron spectroscopy (XPS) spectra of ZnO NRs and N: ZnO NRs, respectively. After introducing N dopants, the oxygen vacancy peak at 531.8 eV is highly intensified, indicating an increase in the oxygen vacancies in N: ZnO NRs. Oxygen vacancies could enhance electron densities, which can be experimentally calculated from the slope of Mott–Schottky plots. The Mott–Schottky plots of ZnO NRs and ZnO: N NRs are shown in Figure 7f. The charge carrier density of ZnO: N NRs (8.58 × 10^{18} \text{cm}^{-3}) is threefold that of undoped ZnO NRs (2.42 × 10^{18} \text{cm}^{-3}), suggesting an improvement in the charge collection in ZnO: N NRs. Similarly, 1D Sb: SnO\textsubscript{2} nanotubes,[73] and Sn: In\textsubscript{2}O\textsubscript{3} NWs[124] were reported as conductive host scaffolds to improve charge collection of the guest films. Suchel et al. further investigated the direct contribution of conductive scaffolds on \( \eta_{\text{sep}} \).[125]

The patterned F: SnO\textsubscript{2} micropillar nanostructures were developed using printing and spray pyrolysis techniques. By adjusting the periods, two types of F: SnO\textsubscript{2} micropillar nanostructures were obtained, denoted as MP1 and MP2. MP1 and MP2 have the same height of 1.9 \text{μm} and diameter of 500 nm, but different periods of 2 and 4 \text{μm}, respectively (Figure 7h,g). The \( \eta_{\text{sep}} \) of both MP1/BiVO\textsubscript{4} (88.8%) and MP2/BiVO\textsubscript{4} (74.2%) host/guest photoanodes at 1.23 V versus RHE are higher than that of flat BiVO\textsubscript{4} films (49.2%) (Figure 7i), suggesting that conductive scaffolds can significantly improve \( \eta_{\text{sep}} \).

More techniques have been applied to investigate the influence of conductive scaffolds. The terahertz time-domain spectroscopy (THz-TDS) spectra is a contact-free technique to investigate the carrier dynamics over nanometer length scales and the intrinsic conductivity within individual host scaffolds.[126,127] Zhou et al. prepared thin layers of guest BiVO\textsubscript{4} coated onto host Sb: SnO\textsubscript{2}...
Figure 8. a) Schematic of the structure and energy band diagram of Sb: SnO₂/BiVO₄ NRA on FTO substrate. b) The cross-section and inset top-view SEM images of Sb: SnO₂/BiVO₄ NRA thin films. THz-TDS spectra of c) Sb: SnO₂ NRA and d) undoped SnO₂ NRA. e,f) LSV plots and ηsep of Sb: SnO₂/BiVO₄ NRA thin films and undoped SnO₂/BiVO₄ NRA thin films with sacrificial reagents. Reproduced with permission. [58] Copyright 2016, American Chemical Society.

nanorod arrays (NRA) (Figure 8a,b). [58] As shown in the THz conductivity spectra (Figure 8c,d), the electrical conductivity values of Sb: SnO₂ and undoped SnO₂ NRA were calculated as 33.2 ± 6.4 S cm⁻¹ and 7.4 ± 1.8 S cm⁻¹, respectively. The greater electrical conductivity of Sb: SnO₂ NRA scaffold enhanced ηsep from 58% to 71% at 0.6 V versus RHE for Sb: SnO₂/BiVO₄ host/guest photoanodes under backside illumination (Figure 8e). This resulted in a higher photocurrent performance, compared to undoped SnO₂/BiVO₄ NRA host/guest photoanodes (Figure 8f).

The charge transport capability of the host scaffolds in host/guest photoanodes is also frequently investigated with the photoassisted electrical impedance spectroscopy (EIS), which can reveal the charge transfer at the photoanode surface and in the bulk semiconductor. [128] Nyquist plots from the EIS test can be fitted with two resistance and capacitance (RC) circuit models. In the equivalent circuit, the series resistance (Rₛ), first RC circuit (R₁ and CPE₁), and charge transfer resistance (R₂) can be acquired. R₁ and CPE₁ are determined by the charge transport process, and R₂ is the charge transfer resistance across the semiconductor-liquid junction interface, which corresponds to the biggest arc at the lower frequency. [63, 129] Xu et al. reported the in situ growth of photoactive guest ZnFe₂O₄ on host Al: ZnO NWs as the host/guest photoanode. [86] Al: ZnO NWs/ZnFe₂O₄ films showed a lower Rₛ (158.5 Ω) than pristine ZnO NWs/ZnFe₂O₄ (309.4 Ω), indicating a higher conductivity of Al: ZnO scaffolds for the transport of photogenerated electrons (Figure 9a,b). Zhang et al. reported Sn: In₂O₃ NWs/BiVO₄ films as the host/guest photoanode. The Sn: In₂O₃ NWs/BiVO₄/rGO (2.5 Ω) by EIS measurements could be partly attributed to the conductive Sn: In₂O₃ NWs, compared to pristine In₂O₃ NWs/BiVO₄ (243.3 Ω).

Apart from 1D conductive host scaffolds, 3D conductive host scaffolds have also been reported for improved charge collection. Zhang et al. prepared 3D Al-doped ZnO IOs to be used as efficient electron collectors for BiVO₄ films, and it showed enhanced light-harvesting and electron transport from BiVO₄ to Al: ZnO IOs. [90] The optimization of dopant concentration in host metal oxides is also a critical factor for efficient PEC performance of host/guest photoanodes. Xu et al. investigated the effect of dopant concentration of Sn element in SnO₂ macropores as the host scaffolds (Figure 9c,d). [75] The maximum photocurrent was achieved with 10% of dopant concentration. Further increase of dopant concentration to 15% resulted in a decline in the photocurrent due to the detrimental electron scattering effect. Mott–Schottky plots and EIS were further employed to verify the contribution of optimized scaffolds on charge separation. The introduced conductive host scaffolds may further act as the doping source for guest photovoltaic materials, resulting in significant carrier density improvement of both host and guest semiconductors due to the synergic doping effects (Figure 9e,f). For example, Zhang et al. reported Sn: In₂O₃ NWs/Fe₂O₃ host/guest photoanode for enhanced PEC performance. [124] In the postannealing treatment, Sn atoms diffuse from Sn: In₂O₃ NWs to the Fe₂O₃ nanostructures. The doping of the guest semiconductor resulted in efficient electron transfer from the guest Sn-doped Fe₂O₃ to the Sn: In₂O₃ electron collector, which enhanced the PEC performance.

Therefore, the charge separation efficiency can be promoted by having conductive host scaffolds in host/guest photoanodes. The impact of conductive platforms can be investigated exper-
4.3. Hierarchical Structure Engineering

Hierarchical nanostructures are constructed by the secondary growth of nanostructures on preacquired nanostructures, which would inherently increase the surface areas for mass transfer. Through hierarchical structure engineering, several enhancement strategies can be combined within one host/guest photoanode, making it possible to improve $\eta_{\text{abs}}$ and $\eta_{\text{sep}}$ simultaneously. Typical fabrication techniques for hierarchical host/guest nanostructures are summarized as follows: i) direct growth of 1D guest nanostructures on 1D, 2D, or 3D host scaffolds; ii) coating of guest films on the fabricated hierarchical host scaffolds.

Compared to single-dimensional host/guest nanostructures, hierarchical host/guest nanostructures inherently exhibit an enlarged surface area and volumes of the depletion regions, resulting in more efficient charge separation or light absorption in host/guest photoanodes. Yang et al. investigated the contribution of 1D/1D ZnO nanodendrite arrays to the PEC performance of guest BiVO$_4$ thin films. Hierarchical ZnO nanodendrite host scaffolds were fabricated by the secondary growth of 1D ZnO branches on 1D ZnO NRs (Figure 10a,b). As shown in Figure 10b, both ZnO NRs/BiVO$_4$ and hierarchical ZnO nanodendrite arrays/BiVO$_4$ exhibit more significant light-harvesting efficiency than flat BiVO$_4$ films. Additionally, hierarchical ZnO nanodendrite arrays/BiVO$_4$ films exhibit higher $\eta_{\text{sep}}$ than ZnO NRs/BiVO$_4$ and flat BiVO$_4$ films (Figure 10c), suggesting the extraordinary promotion effect of hierarchical nanostructures on charge separation. Similarly, Zhang et al. reported screw-like SnO$_2$ nanostructures through the growth of 2D SnO$_2$ NSs onto 1D single-crystalline SnO$_2$ NRs. The resultant hierarchical 1D/2D host scaffolds offer a large surface-to-volume ratio for mass transfer. Through adjusting the coverage and the distance between adjacent SnO$_2$ NSs, a significant increase in light absorption by $\approx33\%$ is achieved for 1D/2D SnO$_2$ NRs/SnO$_2$ NSs as compared to 1D SnO$_2$ NRs. Liu et al. reported the 2D/1D ZnO NSs/NRs mixed dimensional architectures as the host scaffolds. The light absorption in the 1D/1D branched ZnO NRs, and 2D/1D ZnO NSs/NRs nanoarchitecture was investigated by FDTD simulation. In such composite photoanodes, 3D SnO$_2$ hollow microsphere arrays coated with 2D SnO$_2$ NSs act as the hierarchical host scaffolds (Figure 10d). TiO$_2$ and BiVO$_4$ take the roles of a hole blocking layer and a visible absorption layer, respectively. Due to a large specific surface area and efficient interface contact, hierarchical SnO$_2$/TiO$_2$/BiVO$_4$ arrays achieved a higher light-harvesting efficiency (Figure 10e) and $\eta_{\text{sep}}$ (Figure 10f) than SnO$_2$ NSs/TiO$_2$/BiVO$_4$ and SnO$_2$ NSs microsphere/TiO$_2$/BiVO$_4$.

The light-trapping effect can also be achieved in periodic hierarchical nanoarchitectures. Bai et al. reported the photoresist template-assisted growth of periodic 1D/1D branched ZnO NWs as the hierarchical host scaffolds (Figure 11a). Due to an increased roughness factor, 1D/1D branched ZnO NWs show a higher UV light absorption than 1D ZnO NWs (Figure 11b). The light-trapping effect was further investigated by the FDTD simulation. 1D/1D branched ZnO NWs show larger electric intensity than 1D ZnO NWs (Figure 11c). After coating with CdS films, vis-

![Figure 9](image_url)
Figure 10. Hierarchical ZnO nanodendrite arrays/BiVO₄ films: a) The cross-section and inset top-view SEM images of ZnO nanodendrite arrays; b) Light-harvesting efficiency at different wavelengths; c) \( \eta_{\text{sep.}} \). a–c) Reproduced with permission. [68] Copyright 2017, Elsevier Ltd. Hierarchical ternary SnO₂/TiO₂/BiVO₄ arrays: d) SEM image of hierarchical SnO₂ arrays; e) Light-harvesting efficiency; f) \( \eta_{\text{sep.}} \). d–f) Reproduced under the terms of the Creative Commons CC-BY license. [35] Copyright 2020, The Authors. Published by Wiley-VCH.

Wang reported the growth of 1D guest CdS NRs on 3D periodic SnO₂ nanobowls as the hierarchical host/guest photoanode. [76] The periodic structure of SnO₂ nanobowls is not disrupted after the growth of CdS NRs (Figure 11d,e), which is essential to the formation of multiple light scattering. SnO₂ nanobowls/CdS NRs show a lower reflectance between 300 and 500 nm but a considerably higher reflectance above 500 nm (Figure 11f). As the absorption edge of CdS is 540 nm, the higher reflectance above 500 nm can be ascribed to the multiple light scattering effect. The lower reflectance between 300 and 500 nm indicates more efficient light absorption and lower surface reflection. The light-trapping effect can be complemented with multiple scattering by constructing hierarchical 3D IOs/1D NRs architectures. Xu et al. reported 3D Sb: SnO₂ macro pores/1D Fe₂O₃ NRs as the hierarchical host/guest photoanodes. [75] 1D Fe₂O₃ NRs were grown on the walls of Sb: SnO₂ macro pores (Figure 11g,h). The sketch of charge transport and separation is shown in Figure 11i. Sb: SnO₂ macro pores take the role of extracting electrons from Fe₂O₃ NRs. The periodic and porous structure of Sb: SnO₂ macro pores is also beneficial to light-harvesting. Similarly, 1D CdS NRs have also been grown on 3D F: SnO₂ IOs for the simultaneous improvement of \( \eta_{\text{abs}} \) and \( \eta_{\text{sep.}} \). [77]

Different enhancement strategies, such as increased specific surface areas, light trapping effect, and introduction of conductive scaffolds, can be combined into one hierarchical host/guest photoanode. Due to the synergic effects, hierarchical host/guest photoanodes usually exhibit an improved PEC performance compared to the corresponding pristine host/guest photoanodes.

### 5. Challenges and Perspectives

Owing to the significant enhancements of light-harvesting as well as the separation and collection of charge carriers, construction of host/guest photoanodes is one of the most effective strategies to improve the PEC performance dramatically. The recent state-of-the-art progress in the architectural design of host/guest photoanodes with integrated enhancement strategies including i) light trapping effect; ii) optimization of conductive host scaffolds; and iii) hierarchical structure engineering are summarized and highlighted.

However, photoactive guest materials may still suffer from slow OER kinetics, and the mere introduction of host scaffolds cannot overcome this problem. Surface modification of photoanodes with active OER catalysts such as Co-Pi NPs[83] and Ni-Fe-OH NSs,[132] is one of the common strategies to accelerate OER kinetics and reduce surface trap states. The detailed contribution of OER catalysts in PEC application can be found in many other reviews, which is not summarized in the scope of this review. Another challenge is in obtaining the uniform coating of photoactive thin films on the host scaffolds, especially for the hierarchical host scaffolds with a high aspect ratio. Traditional coating techniques such as spin-coating, dip-coating, and chemical vapor deposition may not fully infiltrate precursors into the bottom areas of the host scaffolds. Pressure tuned atomic layer deposition (ALD) has been reported for the uniform coating of photoactive films on porous structures.[113] However, only certain photoactive semiconductors, such as TiO₂ and Fe₂O₃,[115,134] can be prepared by the ALD technique. Besides, the precursors for ALD applications are usually expensive.[135–137] Thus, it is necessary to explore
other methods for the uniform coating of photoactive thin films on the host scaffolds at a low cost.

Host/guest architectures are not only applicable for PEC water splitting, but also for electrocatalyst,[138] solar cell,[139] and ion battery.[140,141] Based on the review of various nanostructured host scaffolds, an ideal host scaffold should fulfill the following requirements: low cost, high chemical stability, superior electrical conductivity, and periodic architectures. With the help of host scaffolds, the optical and electrical properties of various guest materials can be improved simply in constructing host/guest structures. However, to date, none of the reported host scaffolds can be scaled up for practical and commercial applications yet. Compared to ZnO, WO₃, and pristine SnO₂, F: SnO₂ shows greatest potential as the candidate material for ideal host scaffolds. Although patterned F: SnO₂ micropillar nanostructures and periodic F: SnO₂ IOs have been reported as the host scaffolds, they still suffer from high cost and complicated fabrication processes. Research into alternative patterned F: SnO₂ host scaffolds, with potential for mass production to replace flat F: SnO₂ glass substrates, could generate substantial technological advances and commercial value in various fields. Moreover, the designing of fully integrated/wireless and partially integrated/wired PEC devices with host/guest structures should be developed for practical application.

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