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Hierarchical Hollow Heterostructures for Photocatalytic CO₂ Reduction and H₂O Splitting

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Abstract

Using solar-driven photocatalytic systems based on semiconductor photocatalysts to produce valuable energetic fuels is attracting massive research attention due to the global energy and environmental challenges. Developing highly efficient and stable photocatalysts is of decisive importance to this promising technology. Hierarchical hollow heterostructures with ultrathin two-dimensional (2D) nanosheet subunits hold multiple intrinsic advantages for heterogeneous photocatalysis, in terms of increasing light harvesting, expediting charge separation and transfer, and boosting surface redox reactions. This Review summarizes the recent developments of rationally designed hierarchical hollow heterostructures for photocatalytic CO₂ reduction and water splitting in suspension systems. The advantages and progress of hierarchical hollow heterostructured photocatalysts for the solar-fuel-producing applications are highlighted. The challenges of further developments of hierarchical hollow heterostructures and their use in the photocatalytic applications are discussed. Some outlooks on the potential solutions are also proposed.

Keywords: photocatalysis; CO₂ reduction; water splitting; hollow structures; heterostructures

Introduction

The ever-growing concerns on energy shortage and climate changes have motivated widespread research efforts to explore renewable energy alternatives by sustainable technologies.^[1] Among the proposed solutions for these crises, semiconductor-mediated photocatalysis has attracted enormous research interests, because it can directly use solar irradiation to convert CO₂ into hydrocarbon fuels and split water to produce hydrogen energy under atmospheric conditions.^[2-4] Over the past several decades, a huge number of materials have been developed as photocatalysts, the central part of photocatalytic systems, for CO₂ reduction and water splitting with some remarkable progress achieved.^[5-13] Nevertheless, the state-of-the-art efficiency of solar-to-chemical energy conversion is still behind the requirement for practical applications.^[5, 14] One key reason for the poor solar-energy-conversion performance of semiconductor photocatalysts is the low efficiency of the complex and multistep physicochemical processes (**Figure 1**), including the absorption of sunlight irradiation, generation and separation of electron-hole pairs, migration of photogenerated electrons and holes to the surface, and the surface redox reactions by the photoinduced charges (e.g., the reduction of CO₂ and H₂O by the electrons to produce low-carbon fuels and H₂, and the oxidation of water by the holes to form O₂). Besides, the high recombination rate of the light-excited charge carriers both in the bulk and on the surface of the photocatalysts also seriously restricts the efficiency of the CO₂ reduction and water splitting reactions. For realizing the ultimate objective of photocatalytic systems for solar fuel generation, it remains a significant challenge to develop high-performance photocatalysts.

It is well known that the structures of semiconductor photocatalysts greatly influence their photocatalytic performance,^[15-20] and the engineering of them into appropriate nanostructures is a reliable strategy to improve the catalytic functions.^[21-26] So far, numerous nanomaterials with diverse configurations have been developed as photocatalysts to catalyze CO₂ conversion and water splitting

reactions, such as, two-dimensional (2D) nanosheets,^[27-30] hollow nanostructures,^[31-36] heterostructures (e.g., metal/metal oxide heterostructures),^[37-42] and hierarchical nanostructures.^[43-45] In particular, hierarchical hollow heterostructures with ultrathin 2D nanosheet subunits have several intrinsic advantages for semiconductor photocatalysis.^[46-53] First, the hollow structures possess high surface area and abundant catalytically-active sites to promote reactants adsorption and surface-dependent catalytic reactions.^[31-33] Besides, the thin permeable shell of hollow nanostructures can not only shorten the diffusion path of charges to facilitate separation and transfer of photogenerated electron-hole pairs,^[54-55] but also afford inner and outer surfaces to place the locally incompatible cofactors for oxidative and reductive reactions.^[56-57] Moreover, photoabsorption of hollow structures would be strengthened due to multi-light reflection and scattering in the interior cavity.^[53, 58-60] Second, the ultrathin nanosheet subunits are favorable for enhancing separation of light-induced charges by reducing diffusion length from bulk to surface and disclosing plentiful reactive centers to promote surface redox catalysis.^[61-64] Third, the heterojunction interfaces have high capability to accelerate the separation and directed movement of photoexcited charges due to the built-in electric field,^[65-68] and at the same time, ameliorate photostability of composite photocatalysts.^[40, 48, 69] Therefore, the hierarchical hollow heterostructures are versatile platforms for photocatalytic CO₂ reduction and water splitting from the considerations of enhancing light harvesting, accelerating separation and transfer of photo-triggered charges, and boosting surface redox reactions. In addition, the hierarchical hollow heterostructures have also shown apparent advantages as photocatalysts in environmental applications, such as the photocatalytic degradation of rhodamine B and methyl orange.^[47]

In this Review, we summarize the recent advances of rationally designed hierarchical hollow heterostructures for photocatalytic CO₂ reduction and water splitting toward solar fuel generation in suspension systems. We mainly focus on the hierarchical hollow heterostructures with well-developed

architectures and ultrathin 2D nanosheet substructures. The advantages and progress of the hierarchical hollow heterostructured photocatalysts for CO₂ reduction and water splitting are highlighted. The challenges of further developments and some outlooks on the potential solutions of hierarchical hollow heterostructures for the photocatalytic applications are provided. We believe a timely and critical review of this emerging area is highly important and desirable to inspire more innovative works on the design and fabrication of high-performance photocatalytic materials for sustained solar energy conversion. Some excellent previous review papers about hollow nanostructures, heterojunction photocatalysis and hierarchical photocatalysts may supplement some detailed information for this article.^[37-38, 41, 45, 67, 70-75]

Hierarchical hollow heterostructures for photocatalytic CO₂ reduction

As an emerging class of multifunctional photocatalysts,^[46-53] hierarchical hollow heterostructures possessing ultrathin layers as the subunits have the integrated structural and compositional advantages of hollow structures, heterojunctions and 2D nanosheet materials and have thus shown enormous potential for CO₂ photoreduction. This is mainly because the hollow structured configuration and the nanosheet subunits of such types of photocatalysts can provide high surface area and rich active locations to enhance CO₂ adsorption/concentration and promote surface-dependent catalytic reactions.^[33, 46] Besides, their thin-shelled topologies together with the nanoscale sheet-shaped substructures will effectively reduce the bulk-to-surface diffusion length for photogenerated charge carriers to facilitate their separation and migration, prolonging their lifetime to run the redox reactions.^[61, 71] In addition, the heterojunction of these photocatalysts is highly powerful to further accelerate the separation and directed transfer of light-induced electron-hole pairs because of the built-in electric field,^[41, 67] and at the same time, ameliorate stability of the composite photocatalysts.^[40, 48] Moreover, the hierarchical hollow heterostructured photocatalysts can also achieve enhanced utilization of photoabsorption due to the multi-light reflection and scattering in the interior cavity.^[53, 58-60]

The templating method is a classic strategy to produce hollow structures with precise morphologies.^[76-78] With appropriate hollow scaffolds as supports, the surface growth of target 2D nanosheets as subunits is an effective approach to fabricate hierarchical hollow heterostructures.^[76] For instance, Wang et al. have demonstrated the design and synthesis of hierarchical hollow nanostructures constructed by nitrogen-doped carbon (NC) nanoboxes and ultrathin NiCo₂O₄ nanosheets for visible-light-induced reductive conversion of CO₂ to CO.^[46] The multi-step production procedure of the heterostructures is schematically depicted in **Figure 2a**. A Fe₂O₃@PDA core-shell nanocube is first prepared by coating a thin polydopamine (PDA) layer on a Fe₂O₃ nanocube template. Then, the coated PDA layer of Fe₂O₃@PDA is transformed to a NC shell through thermal annealing in N₂, which is followed by an acid etching treatment to selectively remove the oxide core, leading to the formation of a NC nanobox. Afterward, the NC hollow particle is used as a substrate to grow a layer of ultrathin nanosheet subunits of Ni-Co layered double hydroxides (LDH), thus yielding a hierarchical NC@Ni-Co LDH nanobox. After the final annealing treatment in air, the NC@Ni-Co LDH nanoboxes are converted to hierarchical NC@NiCo₂O₄ nanoboxes (Figure 2b-e). Performance of the NC@NiCo₂O₄ hybrid catalyst is tested in a photochemical CO₂ reduction system with [Ru(bpy)₃]Cl₂·6H₂O as a photosensitizer (Fig. 2f-h).^[79-81] The NC@NiCo₂O₄ heterostructures display excellent photocatalytic CO₂ reduction activity and high stability, affording a CO yield rate of 26200 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and an apparent quantum yield (AQY) of 1.07 % under monochromatic photoirradiation ($\lambda = 420 \text{ nm}$). The outstanding CO₂ photoreduction performance of NC@NiCo₂O₄ is attributed to the combined catalytic effects of both the Ni-Co redox active species and the highly conductive NC support that are spatially translated into 3D hierarchical hollow heterostructures with ultrathin 2D substructures on the shell, which is believed to reinforce CO₂ adsorption and expedite charge separation and transfer. Indeed, the NC@NiCo₂O₄ catalyst is efficient and stable for CO₂ photoreduction in the developed system; however, its catalytic function is

limited by the necessity of an extra ruthenium-based photosensitizer, which is expensive and only stable within limited catalytic turnovers.^[79-81] As such, NC@NiCo₂O₄ can also be regarded as a high-efficiency cocatalyst for CO₂ conversion photocatalysis.^[82] To establish affordable and robust systems for CO₂ photoreduction without noble metals, anchoring appropriate semiconductor nanoparticles with matched band structures as light transducers on the heterostructure may be a possible solution.^[83-85] On the other hand, the grafting of metal complex photosensitizers on suitable semiconductor substrates may also enhance the efficiency and stability of the photocatalytic CO₂ reduction system.^[86]

Considering the case of NC@NiCo₂O₄, it is more favorable to develop the hierarchical hollow heterostructures that can harvest solar energy themselves to generate electron-hole pairs for photocatalytic CO₂ reduction. Towards this direction, Lou and coworkers have successfully synthesized hierarchical In₂S₃-CdIn₂S₄ heterostructured nanotubes as a visible-light photocatalyst for CO₂ reduction.^[48] The overall synthetic process of the In₂S₃-CdIn₂S₄ nanotubes is schematically shown in **Figure 3a**. Initially, uniform In-MIL-68 (MIL = Material of Institute Lavoisier) nanoprisms are used as a self-template to prepare hierarchical In₂S₃ nanotubes via a solvothermal sulfidation treatment. Next, hierarchical In₂S₃-CdIn₂S₄ heterostructured nanotubes are prepared through a facile hydrothermal cation exchange reaction between the as-prepared In₂S₃ nanotubes and Cd²⁺ ions (Figure 3b-e). In a typical photocatalytic CO₂ reduction system without using any noble-metal cocatalysts,^[87] the In₂S₃-CdIn₂S₄ photocatalyst with the optimized composition shows considerable activity and high stability for deoxygenative CO₂ reduction, supplying a CO generation rate of 825 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (Figure 3f, g), which is evidently higher than the hierarchical In₂S₃ and CdIn₂S₄ nanotubes. The self-templated approach involving successive liquid-phase anion- and cation-exchange reactions can effectively combine the two photoactive metal sulfides into well-defined hierarchical 1D hollow heterostructures assembled by building blocks of ultrathin 2D nanosheets. In particular, the cation-exchange reaction is advantageous

to endow the $\text{In}_2\text{S}_3\text{-CdIn}_2\text{S}_4$ hybrid with homogeneously distributed heterojunction interfaces and controllable compositions, which may rarely be realized by conventional solid-state composite methods. Unlike the cases of some metal sulfides that suffer from the notorious photocorrosion effect,^[88] the $\text{In}_2\text{S}_3\text{-CdIn}_2\text{S}_4$ composite photocatalyst displays excellent stability for CO_2 photoreduction catalysis, which may originate from the construction of a so-called type-II heterojunction with staggered bandgaps (Figure 3g).^[67] Specifically, in the photocatalysts with type-II heterojunction, the conduction band (CB) and valence band (VB) of semiconductor A (S-A, e.g., CdIn_2S_4 in Figure 3g) are higher than the corresponding bands of semiconductor B (S-B, e.g., In_2S_3 in Figure 3g). Therefore, under light irradiation, the photogenerated electrons on S-A will migrate favorably to S-B, while the photogenerated holes will transfer from S-B to S-A, leading to the spatial separation of the electron-hole pairs. However, for this category of heterojunction photocatalysts, their redox ability will be weakened because the reduction reaction and the oxidation reaction occur on S-B with lower reduction potential and on S-A with lower oxidation potential, respectively. In a follow-up study, Yang et al. have synthesized the hierarchical $\text{In}_2\text{S}_3\text{-CuInS}_2$ nanotube heterostructures through a similar two-step (e.g., sulfidation and cation-exchange reaction) strategy with the same metal-organic framework (MOF) as the precursor and Cu^{2+} as the exchanging ion.^[89] As expected, the prepared $\text{In}_2\text{S}_3\text{-CuInS}_2$ heterojunction photocatalyst manifests improved CO_2 reduction performance than single In_2S_3 and CuInS_2 .

In 2018, Wang et al. have further designed and assembled sandwich-like $\text{ZnIn}_2\text{S}_4\text{-In}_2\text{O}_3$ hierarchical tubular heterostructures as an efficient CO_2 reduction photocatalyst.^[49] The schematic diagram for making the $\text{ZnIn}_2\text{S}_4\text{-In}_2\text{O}_3$ heterostructures is presented in **Figure 4a**. In step I, hexagonal In_2O_3 microtubes with two open ends are synthesized by thermally treating In-MIL-68 micropillars in air. In the next step, both the inner and outer surfaces of the In_2O_3 microtubes are simultaneously coated with one layer of ZnIn_2S_4 nanosheets through a low-temperature hydrothermal reaction to form the three-

layered ZnIn₂S₄-In₂O₃ hierarchical hollow heterostructures (Figure 4b-d). In a non-noble-metal visible-light reaction system, the optimal ZnIn₂S₄-In₂O₃ photocatalyst exhibits an impressive CO₂-to-CO conversion rate of 3075 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (Figure 4e, f), which is substantially higher than the reference samples of bare In₂O₃ microtubes, nanosheet-assembled ZnIn₂S₄ particles, and free-standing ZnIn₂S₄ nanosheets. The superior photocatalytic CO₂ conversion performance of ZnIn₂S₄-In₂O₃ should be related with the desirable structural and compositional virtues, such as an open hollow configuration, ultrathin layered subunits and dual lengthwise interfacial junctions. This work demonstrates the first production of a three-layered sulfide/oxide composite photocatalyst, which possesses double type-II heterojunction interfaces and precisely controlled nanodomains of components, through a one-pot *in situ* self-assembly of a layered metal sulfide on a tubular oxide semiconductor. In addition, the two-step preparation strategy may offer more chances to modify the structures and components of the heterostructures for improved photoredox catalysis. However, the use of sacrificial electron donor (e.g., triethanolamine, TEOA) in the catalytic system disfavors the practical application of the ZnIn₂S₄-In₂O₃ photocatalyst, and continuous efforts are needed to build more sustainable photosynthetic systems for CO₂ reduction to generate carbon fuels.^[40, 90]

Hierarchical hollow heterostructures for photocatalytic water splitting

Photocatalytic water splitting to produce H₂ and O₂ gases is another encouraging application of hierarchical hollow heterostructured photocatalysts for solar-to-chemical energy conversion.^[14] The overall water splitting reaction comprises two half-reactions, that is, H₂O oxidation to release O₂ and H₂O reduction to liberate H₂. Up to date, both of the two H₂O conversion reactions have been achieved by photocatalysts with hierarchical hollow heterostructures.^[50-51, 53] For example, Duan and coworkers have reported the preparation of hierarchical TiO₂@CoAl-LDH hollow nanospheres as a photocatalyst for O₂ evolution from water oxidation.^[50] A two-step synthetic process, including the first synthesis of

TiO₂ hollow nanospheres and the subsequent surface growth of CoAl-LDH nanosheets, is developed to fabricate the hierarchical TiO₂@CoAl-LDH hollow heterostructures (**Figure 5a-c**). Using AgNO₃ as a sacrificial electron scavenger, the TiO₂@CoAl-LDH photocatalyst delivers an outstanding O₂-releasing rate of 2.34 mmol h⁻¹ g⁻¹ under UV-visible light irradiation ($\lambda \geq 200$ nm, Figure 5d, e). In comparison, both individual counterparts of TiO₂ hollow nanospheres and CoAl-LDH nanosheets display much inferior O₂ evolution rates of 0.27 and 0.98 mmol h⁻¹ g⁻¹, respectively. The formation of strong donor-acceptor coupling between the TiO₂ inner shell and LDH outer shell with desired band matching is considered mainly responsible for the excellent H₂O photosplitting performance. This work demonstrates the advantages of hierarchical hollow heterostructured photocatalysts for oxidative H₂O splitting catalysis toward solar energy conversion. However, in view of that the TiO₂ inner shell can only be activated by UV-light, the exploitation of suitable visible-light-responsive alternatives with preferred hollow nanostructures to couple with the LDH nanosheets may be more attractive from the viewpoint of better harvesting the solar resource.^[33, 57]

With respect to photocatalyzing H₂O reduction reaction to release H₂ by hierarchical hollow heterostructures, one successful example is recently demonstrated with hierarchical Co₉S₈@ZnIn₂S₄ heterostructured cages.^[51] The general synthetic process for the Co₉S₈@ZnIn₂S₄ composite is schematically exemplified in **Figure 6a**. At the first step, ZIF-67 (ZIF = zeolitic imidazolate framework) dodecahedral particles are transformed into Co₉S₈ cages through a sulfidation reaction followed by a thermal annealing treatment in Ar. In the second step, a layer of ZnIn₂S₄ nanosheets is grown on the surface of Co₉S₈ hollow particles via a solvothermal method, forming hierarchical Co₉S₈@ZnIn₂S₄ heterostructured cages (Figure 6b-d). The optimal Co₉S₈@ZnIn₂S₄ photocatalyst can exhibit a high H₂-evolving rate of 6250 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and high stability in a cocatalyst-free photocatalytic system using TEOA as an electron donor (Figure 6e). The H₂ generation rate of hierarchical Co₉S₈@ZnIn₂S₄ cages is

much higher than those of Co_9S_8 , ZnIn_2S_4 and solid $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ counterparts. The two-step preparation approach of $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ is effective to strongly couple Co_9S_8 and ZnIn_2S_4 into the 3D hollow heterostructure with a favorable substructure of ultrathin nanosheets on the outer surface. Importantly, the solution-processed growth of ZnIn_2S_4 nanosheets on the Co_9S_8 cage is vital for the creation of close contact between the two metal sulfides. Nonetheless, the $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ composite is revealed to be a type-I heterojunction photocatalyst with straddling bandgaps (Figure 6f).^[67] For these heterojunction photocatalysts, the CB and VB levels of S-A (e.g., ZnIn_2S_4 in Figure 6f) are correspondingly higher and lower than those of S-B (e.g., Co_9S_8 in Figure 6f). As a result, the light-induced electrons and holes will migrate to the CB and VB of S-B under light irradiation, respectively. Since both the electrons and holes will accumulate on the same semiconductor, the photogenerated charges cannot be well separated for the type-I heterojunction photocatalyst. Besides, similar to the type-II heterojunction, the redox reactions take place on the semiconductors possessing the lower redox potentials, thus the reductive and oxidative abilities of such heterojunction photocatalysts will be reduced largely.

In another most recent work, Wang et al. have fabricated the hierarchical $\text{Co}/\text{NGC}@\text{ZIS}$ heterostructured cages by supporting ZnIn_2S_4 NSs on Co/N -doped graphitic carbon (Co/NGC) nanocages, composed of ultrafine Co nanoparticles confined in few-layered NGC shells. The assembly process involves a solution growth of ZnIn_2S_4 NSs on the surface of dual-MOF-derived Co/NGC nanocages (Figure 6g). The overall hollow architectures and the sheet-shaped secondary structures can provide large surface area and abundant disclosed active sites for photoredox reactions (Figure 6h-j). It is revealed that the metallic Co nanoparticles serve as a cocatalyst for photocatalytic H_2 evolution, which is similar to the Pt cocatalyst widely used in the reaction. To be more specific, due to the energy difference between the Fermi levels of Co/NGC and ZnIn_2S_4 , it is thermodynamically favorable for the photogenerated

electrons on the CB of ZnIn₂S₄ to transfer from ZnIn₂S₄ to Co/NGC to induce the H₂ evolution reaction. Of note, the NGC shell possesses the highly porous structure and excellent charge transfer mobility, thereby effectively mediating the electron transfer from ZnIn₂S₄ to the active Co sites. The formation of surface heterojunction in the Co/NGC@ZIS photocatalyst can lower the reaction barrier and accelerate the reaction kinetics, which coupled with structural and commotional virtues render the photocatalyst high-efficiency for water photosplitting with a H₂-evolving rate of 11270 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (Figure 6k).

In order to promote the efficient spatial separation of electron-hole pairs, as well as to maximize the redox potentials of the heterojunction systems, it would be much more promising to develop the direct Z-scheme heterojunction photocatalysts.^[41, 91-92] Generally, the Z-scheme photocatalysts are constructed by directly contacting two different semiconductors (e.g., S-A and S-B) with staggered band structures. After their combination, charge redistribution will take place at their interface because of the different Fermi levels and the Fermi levels will then be aligned.^[47] Under light irradiation, both semiconductors are excited and the electrons on their VB will transfer to their CB. The S-A with low Fermi level (e.g., Co₉S₈ in **Figure 7a**) will accept the electrons from S-B with high Fermi level (e.g., CdS in Figure 7a). In the Z-scheme heterojunction photocatalysts, the photogenerated electrons possessing low reduction potentials on the CB of S-B recombine with the holes holding low oxidation potential on the VB of S-A, while the electrons and holes with high redox potentials will be preserved on the CB of S-A and VB of S-B, respectively. As a result, the formation of direct Z-scheme heterojunction photocatalysts is highly desirable for enhancing the charge carrier separation and maximizing the redox capability for photocatalytic reactions. Given this consideration, Zhang and coworkers have developed the hierarchical CdS/Co₉S₈ nanoboxes as a Z-scheme heterojunction photocatalyst for H₂O reduction to generate H₂.^[53] A template-engaged multistep strategy is developed to prepare the hierarchical hollow heterostructure (Figure 7b). In the first step, a Cu₂O nanocube is used as the template to prepare a hierarchical Co(OH)₂

nanobox through a Pearson's hard and soft acid-base (HSAB) method.^[93] Then, CdS quantum dots (QDs) are deposited on the Co(OH)₂ nanobox via a solvothermal process to form a hierarchical CdS/Co(OH)₂ intermediate. By prolonging the solvothermal reaction, an ion exchange reaction will occur between Co(OH)₂ and S²⁻ ions and eventually yield the CdS/Co₉S₈ nanobox. The hierarchical hollow heterostructured photocatalyst exhibits significantly enhanced H₂O splitting activity and stability compared to CdS, Co₉S₈ and solid CdS/Co₉S₈ particles, and delivers a H₂-producing rate of 1061 $\mu\text{mol h}^{-1} \text{g}^{-1}$ under simulated sunlight irradiation with Na₂S-Na₂SO₃ as the sacrificial reagents (Figure 7c). The improvements on the H₂ evolution performance is mainly ascribed to the Z-scheme heterojunction (Figure 7a) and the multiple reflections of sunlight within the hollow cavity (Figure 7d). However, the desired hierarchical hollow structure of CdS/Co₉S₈ nanoboxes is not developed very well and the mechanistic understanding of the Z-scheme photocatalyst is not explored in detail, and future efforts may be devoted to such aspects.

As discussed above, the hierarchical hollow heterostructures have demonstrated apparent enhancements on H₂O splitting catalysis. Nevertheless, the use of sacrificial agents (e.g., AgNO₃, TEOA and Na₂S-Na₂SO₃) will surely discourage the practical operation of the photosynthetic systems. Meanwhile, the present studies are still limited to the half-reactions of H₂O splitting. The continuing studies should be concentrated on the optimization and construction of advanced hierarchical hollow heterojunction photocatalysts for overall H₂O splitting.^[14, 94]

Conclusion and Outlook

In summary, we have reviewed the recent developments of rational design and synthesis of hierarchical hollow heterostructures with ultrathin 2D nanosheet subunits for photocatalytic CO₂ reduction and water splitting in suspension systems. This emerging category of functional materials possesses the combined structural and compositional merits of hollow structures, ultrathin 2D nanosheets and heterojunctions,

and has thus shown apparent advantages in improving the performance of semiconductor photocatalysts for solar fuel production via CO₂ conversion and water splitting catalysis (Table 1).

Despite the encouraging progress, we should also recognize that the application of hierarchical hollow heterostructures in such photocatalytic fields is still in the early stage and there exist significant challenges. For example, there are only limited hierarchical hollow heterostructured photocatalysts achieved so far, mainly because of the complex synthetic strategies. Some of the preparation approaches involve more than three steps,^[46, 53] which may introduce many negative factors influencing the performance and also hamper the large-scale production of the photocatalysts. Developing facile and general methods to construct hierarchical hollow heterostructures with excellent crystallinity and high surface area is still urgently desired, yet very challenging. Optimistically, the established strategies for synthesizing MOF-derived hollow nanostructures with tunable structures and compositions may be considered as one potential candidate,^[77, 95-97] when exploring new and advanced preparation methods for the hierarchical hollow heterostructures. Meanwhile, to promote spatial separation and migration of photo-stimulated charges and preserve redox potentials, the formation of Z-scheme heterojunction for hierarchical hollow heterostructures is more preferred than the type-I and type-II alternatives,^[92] but the related studies yet remain to be well conducted, especially for photocatalytic CO₂ fixation. Besides, the current hierarchal hollow heterostructured photocatalysts still necessitate the assistance of sacrificial agents to reduce CO₂ and split water,^[46, 48-51, 53] mainly due to the sluggish kinetics of water oxidation half-reaction. In order to construct more feasible and sustainable photocatalytic systems for solar energy conversion, the coupling of photocatalytic CO₂ and water reduction reactions with value-added organic oxidation transformations is supposed to be the promising strategies.^[90, 98-100] In addition, the present studies lack deep understanding of the working mechanisms of hierarchical hollow heterostructures in the photocatalytic applications. In the future, more research efforts should be devoted to revealing how

the hierarchical hollow heterostructured photocatalysts contribute to the key processes in photocatalysis and disclosing the structure-composition-performance relationships, which can in turn enable the optimization of the photocatalysts for better performance. To support such researches, some *in situ* characterization techniques should be helpful to investigate the photoredox reactions occurred on the surfaces and interfaces, such as scanning electron microscope, transmission electron microscope, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and time-resolved transient absorption spectroscopy. Last but not the least, from the viewpoint of commercial applications, suspension photocatalytic systems are problematic for separation of products and reuse of photocatalysts. As motivated by a recent study from Domen's group,^[5] the anchoring of particulate hierarchical hollow heterostructures on suitable conductive substrates may be a promising approach to manufacture artificial photosynthetic devices for practical solar-to-chemical energy conversion applications.

With continuous studies on the hierarchical hollow heterostructures, more improvements on the solar energy conversion efficiency can be expected, regarding the unique structural and compositional benefits of such photocatalysts. We hope that this Review will highlight the significance of hierarchical hollow heterostructures for photocatalytic CO₂ reduction and water splitting, and inspire further advancements in this area towards the ultimate objective of sustained solar fuel production in practice.

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Figures and Captions

Figure 1. Schematic illustration of the processes of photocatalytic CO_2 reduction and H_2O splitting over semiconductor photocatalysts: I) absorption of sunlight irradiation, II) generation and separation of electrons and holes, III) migration of electrons and holes to the surface and active sites, IV) bulk and surface recombination of the charge carriers, and V) surface redox reactions by the electrons and holes.

Figure 2. (a) Schematic illustration for the formation of hierarchical NC@NiCo₂O₄ heterostructured nanoboxes. (b,c) FESEM images and (d,e) TEM images of hierarchical NC@NiCo₂O₄ nanoboxes. (f-h) CO₂ photoreduction performance of NC@NiCo₂O₄ nanoboxes. Reproduced with permission.^[46] Copyright 2018, Royal Society of Chemistry.

Figure 3. (a) Schematic illustration of the synthetic processes of hierarchical $\text{In}_2\text{S}_3\text{-CdIn}_2\text{S}_4$ heterostructured nanotubes. (b,c) FESEM images, (d) TEM image and (e) elemental mappings of hierarchical $\text{In}_2\text{S}_3\text{-CdIn}_2\text{S}_4$ heterostructured nanotubes. (f) Photocatalytic CO_2 reduction performance $\text{In}_2\text{S}_3\text{-CdIn}_2\text{S}_4$ and the reference samples. (g) Schematic illustration of photocatalytic CO_2 reduction processes over the hierarchical $\text{In}_2\text{S}_3\text{-CdIn}_2\text{S}_4$ nanotubes (e.g., type-II heterojunction). Reproduced with permission.^[48] Copyright 2017, American Chemical Society.

Figure 4. (a) Schematic illustration of the construction of sandwich-like $\text{ZnIn}_2\text{S}_4\text{-In}_2\text{O}_3$ hierarchical tubular heterostructures. (b,c) FESEM images and (d) TEM image of sandwich-like $\text{ZnIn}_2\text{S}_4\text{-In}_2\text{O}_3$ hierarchical tubular heterostructures. (e) Photocatalytic CO_2 reduction activities of bare In_2O_3 microtubes, $\text{ZnIn}_2\text{S}_4\text{-In}_2\text{O}_3$ heterostructures with different compositions, nanosheet-assembled ZnIn_2S_4 particles (ZnIn_2S_4) and free-standing ZnIn_2S_4 nanosheets ($\text{ZnIn}_2\text{S}_4\ \text{NSs}$). (f) Schematic illustration of photocatalytic CO_2 reduction processes over the $\text{ZnIn}_2\text{S}_4\text{-In}_2\text{O}_3$ heterostructure. Reproduced with permission.^[49] Copyright 2018, American Chemical Society.

Figure 5. (a) Schematic illustration of the fabrication of hierarchical TiO₂@CoAl-LDH hollow nanospheres toward oxygen evolution from water splitting. (b) FESEM image and (c) TEM image of hierarchical TiO₂@LDH hollow nanospheres. (f) Photocatalytic O₂ evolution performance of TiO₂ hollow nanospheres, CoAl-LDH nanosheets and TiO₂@LDH hollow nanospheres. (g) Schematic illustration of photocatalytic O₂ evolution processes over TiO₂@CoAl-LDH heterostructures. Reproduced with permission.^[50] Copyright 2015, Wiley-VCH.

Figure 6. (a) Schematic illustration of the production processes of hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ heterostructured cages. (b,c) FESEM images and (d) TEM images of hierarchical $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ cages. (e) Photocatalytic H_2 evolution activities of nanosheet-assembled ZnIn_2S_4 particles (ZnIn_2S_4), $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ cages with different compositions, $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ nanoparticles (NPs) and pristine Co_9S_8 cages. (f) The separation and transfer processes of photogenerated electrons and holes in the $\text{Co}_9\text{S}_8@\text{ZnIn}_2\text{S}_4$ cages (e.g., type-I heterojunction) for H_2 evolution. Reproduced with permission.^[51] Copyright 2018, American Chemical Society. (g) Schematic illustration of the production processes of hierarchical Co/NGC@ZIS cages. (h) FESEM image and (i,j) TEM images of hierarchical Co/NGC@ZIS cages. (k) Photocatalytic H_2 evolution performance of Co/NGC nanocages, ZnIn_2S_4 particles and hierarchical Co/NGC@ZIS cages. Reproduced with permission.^[52] Copyright 2019, Wiley-VCH.

Figure 7. (a) Separation and movement of photogenerated electrons and holes in hierarchical $\text{CdS}/\text{Co}_9\text{S}_8$ nanoboxes (e.g., Z-scheme heterojunction). (b) Preparation process of hierarchical $\text{CdS}/\text{Co}_9\text{S}_8$ nanoboxes and the corresponding TEM images. (c) Time course of H_2 production of Co_9S_8 , CdS , solid $\text{CdS}/\text{Co}_9\text{S}_8$ and $\text{CdS}/\text{Co}_9\text{S}_8$ nanoboxes under simulated sunlight irradiation (AM1.5 air mass filter). (d) Illustration of multiple reflections within $\text{CdS}/\text{Co}_9\text{S}_8$ nanoboxes. Reproduced with permission.^[53] Copyright 2017, Wiley-VCH.

Table 1. Comparison of hierarchical hollow heterostructures for photocatalytic CO₂ reduction and H₂O splitting.

Catalyst	Reaction	Product generation rate	Ref.
NC@NiCo ₂ O ₄ nanoboxes	CO ₂ reduction	CO: 26200 $\mu\text{mol h}^{-1} \text{g}^{-1}$ ($\lambda \geq 420$ nm, sacrificial agent: TEOA)	[46]
In ₂ S ₃ -CdIn ₂ S ₄ nanotubes	CO ₂ reduction	CO: 825 $\mu\text{mol h}^{-1} \text{g}^{-1}$ ($\lambda \geq 400$ nm, sacrificial agent: TEOA)	[48]
In ₂ S ₃ -CuInS ₂ nanotubes	CO ₂ reduction	CO: 19.00 $\mu\text{mol g}^{-1} \text{h}^{-1}$ ($\lambda \geq 420$ nm, sacrificial agent: TEOA)	[89]
In ₂ O ₃ -ZnIn ₂ S ₄ microtubes	CO ₂ reduction	CO: 3075 $\mu\text{mol h}^{-1} \text{g}^{-1}$ ($\lambda \geq 400$ nm, sacrificial agent: TEOA)	[49]
TiO ₂ @CoAl-LDH hollow spheres	H ₂ O oxidation	O ₂ : 2.34 mmol $\text{h}^{-1} \text{g}^{-1}$ ($\lambda \geq 200$ nm, sacrificial agent: AgNO ₃)	[50]
Co ₉ S ₈ @ZnIn ₂ S ₄ cages	H ₂ O reduction	H ₂ : 6250 $\mu\text{mol h}^{-1} \text{g}^{-1}$ ($\lambda \geq 400$ nm, sacrificial agent: TEOA)	[51]
Co/NGC@ZIS cages	H ₂ O reduction	H ₂ : 11270 $\mu\text{mol h}^{-1} \text{g}^{-1}$ ($\lambda \geq 400$ nm, sacrificial agent: TEOA)	[52]
CdS/Co ₉ S ₈ nanoboxes	H ₂ O reduction	H ₂ : 1061 $\mu\text{mol h}^{-1} \text{g}^{-1}$ ($\lambda = \text{AM } 1.5$, sacrificial agent: Na ₂ S/Na ₂ SO ₃)	[53]

For Table of Content Entry

This Review summarizes recent research progress of rationally designed hierarchical hollow heterostructures for photocatalytic CO₂ reduction and water splitting. This unique class of photocatalysts has some important advantages in enhancing light absorption and photo-generated charge separation.