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Hollow micro/nanomaterials as nanoreactors for photocatalysis

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Learning from nature, one of the most prominent goals of photocatalysis is to assemble multifunctional photocatalytic units in an integrated, high performance device that is capable of using solar energy to produce “solar hydrogen” from aqueous media. By analogy with natural systems it is clear that scaffolds with multi-scale structural architectures are necessary. In this perspective, recent progress related to the use of hollow micro/nanomaterials as nanoreactors for photocatalysis is discussed. Organised, multi-scale assemblies of photocatalytic units on hollow scaffolds is an emerging area that shows much promise for the synthesis of high performance photocatalysts. Not only do improved transport and diffusion characteristics play an import role, but increased electron/hole separation lifetimes as well as improved light harvesting characteristics by the hollow structures also do so and are touched upon in this short perspective. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4826155>]

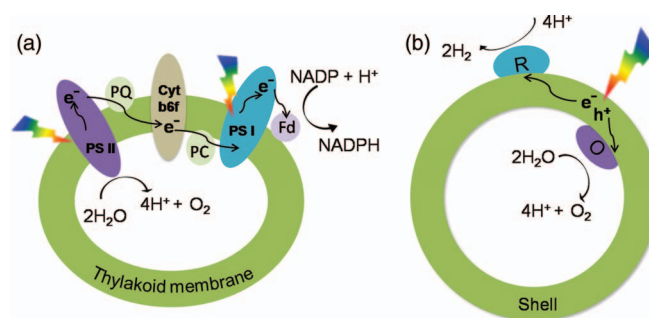
I. INTRODUCTION

Of the renewable energy sources, solar hydrogen obtained from the photocatalytic water-splitting (PWS) reaction is potentially the most abundant and sustainable energy vector as both fuel precursor and combustion product are water. Since the 1970s, the photocatalytic water-splitting reaction has been widely developed and improved.¹⁻³ Nevertheless, the solar energy conversion efficiency is still far from being practical. Maximum apparent quantum yields about 5.1% at 410 nm and 6.3% at 420.5 nm were reported on Rh₂-yCr_yO₃-loaded GaN:ZnO (one-step water splitting system) and a two-step system consisting of Pt/ZrO₂/TaON and Pt/WO₃, respectively.^{4,5} From the practical view, photocatalytic devices with a solar energy conversion efficiency of 10% would be needed.⁵ Improvements are hampered by the insufficient understanding concerning three primary PWS processes: light-harvesting; charge generation and separation; and catalytic reactions.

In contrast, nature has generated efficient photosynthesis systems to convert solar energy into chemical energy after billions of years of evolution. Examining the three PWS processes based on the understanding of natural photosynthesis, it is apparent that the organised assembly and the multi-scale spatial structuring (nano- to macroscopic) of the various photosynthetic units involved (light harvesting, electro-energy transfer, and photoreaction systems) endows the natural systems with unique properties for the light harvesting and energy conversion. Importantly, the two photoreaction systems, photosystem I (PS I) and photosystem II (PS II), are spatially arranged at some distance to avoid/minimise charge recombination (Scheme 1).^{6,7} By analogy similar spatial concepts

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SCHEME 1. (a) A simplified representation of the natural photosynthesis systems I and II, self-assembled on a thylakoid membrane. (b) Photocatalytic water-splitting system assembly on hollow structure scaffolds, analogous to natural photosynthesis system, but in a structural arrangement with a lower complexity.

need to be employed when designing synthetic photocatalytic systems. Photocatalytic units for such complex systems can be mimicked by using both inorganic (e.g., semiconductors, metal or oxide nanoparticles) and organic (e.g., light harvesting complexes, semiconductors, and hydrogenases) components.^{8–10} To incorporate these concepts, the whole system is preferentially built on a structured scaffold similar to natural systems, where the photosynthetic units involved are assembled in and out of a membrane scaffold.

Various scaffolds based on structured micro/nanomaterials are currently being studied for the organised assembly of photocatalytic units.^{11–19} Among them are hollow micro/nanomaterials, mimicking vesicles and cells with “inner” and “outer” space being separated by the shell. These have attracted considerable attention due to their unique structures and design opportunities.^{20–22} Photocatalytic systems based on hollow micro/nanomaterials conceptually allow the organisation of the different photocatalytic units in a defined arrangement, where the assembled photocatalytic units are separated by the shell, analogous to the role of a thylakoid membrane (Scheme 1). Hence, the investigation of photocatalytic reactions in confined hollow spaces can provide insight into photosynthesis process as occurs in nature.^{17,18} Recently, the design and fabrication of photocatalytic systems based on hollow scaffolds with photocatalytic units (light harvesting or photoreaction centre) have been reported. These show very good potential for use in the assembly of more complex systems that are more similar to natural systems.^{23–25} The additional advantage of hollow micro/nanomaterials for the photocatalytic assemblies stems from the interior void space, which provides extra free space for the propagation of light associated with multiple reflection, scattering, and re-adsorption, leading to improved light harvesting.²⁶ Furthermore, the high surface areas and interior void spaces endow such photocatalytic systems with tremendous load capacity for the photocatalytic units.

In this perspective, recent reports of progress in photocatalytic systems based on hollow micro/nanomaterials are divided into two parts. One deals with improved light harvesting and the other with the organised assembly of photocatalytic units using hollow scaffolds. It will become apparent that spatial structuring of the different functional photocatalytic units is necessary to arrive at highly efficient artificial photosynthesis systems. The spatial multi-scale arrangement concept needs to be built into the design phase. Among the available scaffold candidates, hollow micro/nanomaterials (including those obtained from coordination polymer particles (CPP)/metal–organic frameworks, MOFs) provide an excellent point of departure for the design of organised and multi-structured photocatalytic units.

II. HOLLOW STRUCTURE: IMPROVED LIGHT HARVESTING

One of the challenges to be overcome in the development of efficient photocatalytic systems is their low light harvesting efficiency. In addition to band engineering and dye sensitisation, increasing the path length that the light traverses is another efficiency approach to improve the light harvesting. In dye-sensitised solar cells, a typical light scattering layer, which is composed of relatively large TiO_2 particles, can be organised to efficiently scatter and trap the incoming light.²⁷ By using hollow

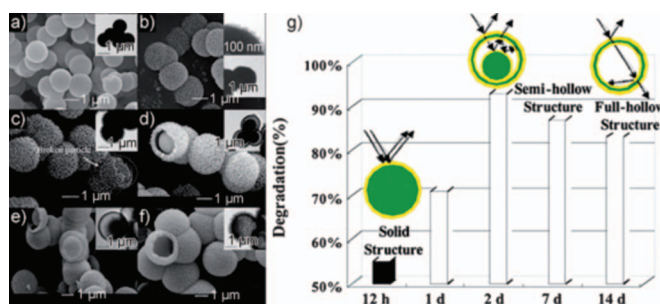


FIG. 1. SEM and TEM images (insets) of titania spheres that were synthesised for (a) 1 h, (b) 12 h, (c) 1 day, (d) 2 days, (e) 7 days, and (f) 14 days, which show a transitioning interior structure from dense, to yolk-shell, to a hollow structure and a surface morphology that transitions from smooth to prickly; (g) comparison of the photocatalytic activities of the titania spheres with solid, yolk-shell, and hollow structures. (Inset) Illustration of multi-reflections within the yolk-shell structure. Reprinted with permission from H. X. Li, Z. F. Bian, J. Zhu, D. Q. Zhang, G. S. Li, Y. N. Huo, H. Li, and Y. F. Lu, *J. Am. Chem. Soc.* **129**, 8406 (2007). Copyright 2007 American Chemical Society.

photocatalysts light traps could also be realised. When the light penetrates the shell of the hollow structure, some of the light gets trapped inside the hollow interior, due to a series of multiple reflection, scattering, and adsorption processes, leading to an overall improved level of light harvesting. Hollow TiO_2 photocatalysts have been widely reported to show such enhanced photoactivity when compared to their solid counterparts. This has been ascribed to the scattering and trapping phenomena described above. Importantly, this enhancement can be further improved upon via the fabrication of multi-level structures within the interiors such as multi-shell, and yolk-shell type structures.^{28–31} These ideas have been exemplified by Li *et al.*,²⁶ who show that light harvesting was much improved when using yolk-shell TiO_2 microspheres, as compared to simple hollow TiO_2 structures (Figure 1).

Up until now, most reports regarding improved light harvesting by hollowing photocatalysts are limited to TiO_2 systems. The reason might be the lack of general synthetic methodologies for other photocatalysts, such as WO_3 , BiVO_4 , or C_3N_4 . The widely used methodologies for hollow micro/nanomaterials synthesis, such as hard and soft templates, are not always very efficient due to the lack of affinity of metal ions to the templates (e.g., silica spheres, polystyrene spheres, micelles, and vesicles) or the two-dimensional nature of, e.g., carbon nitride. Especially, it remains a big challenge to synthesise these materials with hollow or yolk-shell multi-level structures. An interesting approach to the fabrication of metal oxide hollow structures originates from the use of coordination polymer particles (CCP)/metal–organic frameworks,^{32–35} which are composed of inorganic connectors (metal ions or polynuclear clusters) and organic ligand linkers. After removal of the unstable organic part by thermal treatment, hollow scaffolds are left with the original morphology of the CPP. Through this method, hollow structured $\text{Fe}(\text{OH})_3$,³⁵ ZnS ,³⁶ Fe_2O_3 ,^{37,38} $\text{CuO}/\text{Cu}_2\text{O}$,³⁹ In_2O_3 ,⁴⁰ ZnO ,⁴¹ Co_3O_4 ,⁴¹ and MnO ⁴¹ have been successfully fabricated. In addition, when inorganic connectors are composed of ions from multiple metals, hollow nanostructures with alloy components can be fabricated, which is still a challenge for conventional methods. In addition, the ratio of the constituent metals can be tuned, allowing for the synthesis of multi-component hollow photocatalysts (Figure 2). These are important devices in the maximisation of charge separation and charge migration. For example, heterojunctions formed via coupling two or more semiconductors can improve the charge separation substantially.^{42–44}

When designing the hollow structure, another issue is the construction of the controllable pore size and structure of the shell, this will affect the diffusion length of reactants/products and the efficiency of the encapsulation. In addition, the charge migration might also be affected by the porous structure. More research efforts should be devoted to controllable construction of pore size and structure of the shell. In principle, the ordered arrangement of the mesopore with penetrating channels to the void is highly desirable. In addition, controlling the geometry and complexity of the hollow scaffolds with multiple functionalities will be useful for improving light harvesting. However, synthesis of non-spherical-hollow nanostructures and their interior functionalisation still suffers from several technological difficulties including the deficiency of non-spherical templates

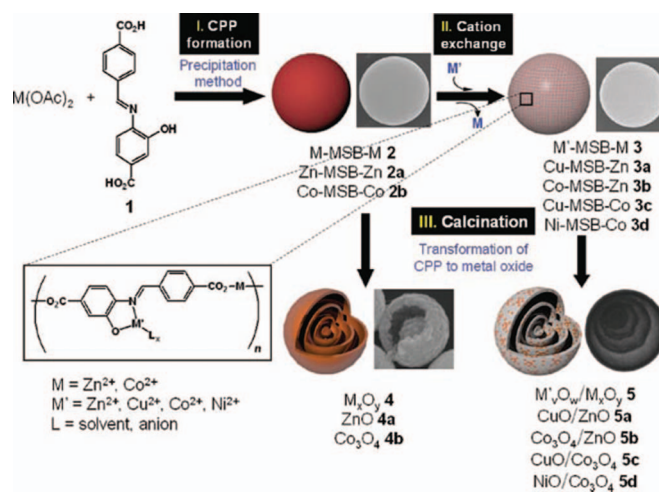


FIG. 2. Typical procedures for the preparation of hollow micro/nanomaterials from CPP. (I) CPP preparation with inorganic connectors and organic ligand linkers; (II) post-cation-exchange that could be applied for the compositional transformation of CPPs with multicomponents; (III) a final calcination processing of pre-prepared CPPs that engenders decomposition of the CPPs and formation of hollow structure metal oxides. Reprinted with permission from W. Cho, Y. H. Lee, H. J. Lee, and M. Oh, *Adv. Mater.* **23**, 1720 (2011). Copyright 2011 Wiley-VCH.

available and poor preservation of the shape. Due to the lack of synthesis method, it is also difficult to obtain non-silica semi-hollow spheres or yolk-shell nanostructures while keeping the uniformity and consistency of the inside sphere sizes and constituents.

When light harvesting components (e.g., sensitizers,^{45,46} upconversion nanoparticle/chromophore,^{47,48} and plasmonic metals^{49,50}) are employed they are usually combined with wide gap semiconductors to match the solar spectrum. Their high surface areas, together with the void spaces, make hollow structures intriguing hosts for light-harvesting components, because of the potentially higher loading capacity than that available from conventional particles. By encapsulating, any undesirable leaching and aggregation might also be avoided, leading to enhanced stability. These uniquely confined structures might further enhance the utilisation of the photogenerated charges or of the light from the light-harvesting component as they are completely surrounded by the outer shell. Due to the multi-reflection and scattering effects, a much improved light harvesting efficiency can be expected for such hollow systems. Indeed, this has already been observed by Park *et al.*⁵¹ In addition, by encapsulation it is in-principle possible to transcend the limits the aqueous reaction phases represent for the use of organic/metalloorganic or unstable chromophores, greatly increasing the available choice of organic chromophores with high quantum efficiency. For example, upconversion from 532 nm to 400–500 nm in the aqueous phase has already been reported as facilitated by encapsulating organic-metalloorganic chromophores in microcapsules, in which photochemical production of hydroxyl radical from green (532 nm) light irradiation was demonstrated using WO_3 semiconductor.⁵²

When looking for ways to design solar water-splitting photocatalytic systems, undoubtedly, strategies involving hollow scaffolds are highly promising, in that performance can be tuned, both, through structural and morphological organisation instead of simply by changing chemical compositions.

III. HOLLOW STRUCTURES: SCAFFOLDS FOR ORGANISED MULTI-SCALE ASSEMBLIES

Loading co-catalysts onto photocatalysts can significantly improve the overall photocatalytic performance.^{5,39} In natural photosynthesis, the water oxidation reaction occurs at a manganese calcium oxide cluster at the side of PS II. The reduction of oxidised nicotinamide adenine dinucleotide phosphate (NADP^+) by PS I is facilitated by membrane-bound iron sulfur proteins and soluble ferredoxin. Therefore, it is attractive to employ dual co-catalysts by analogy to provide reaction

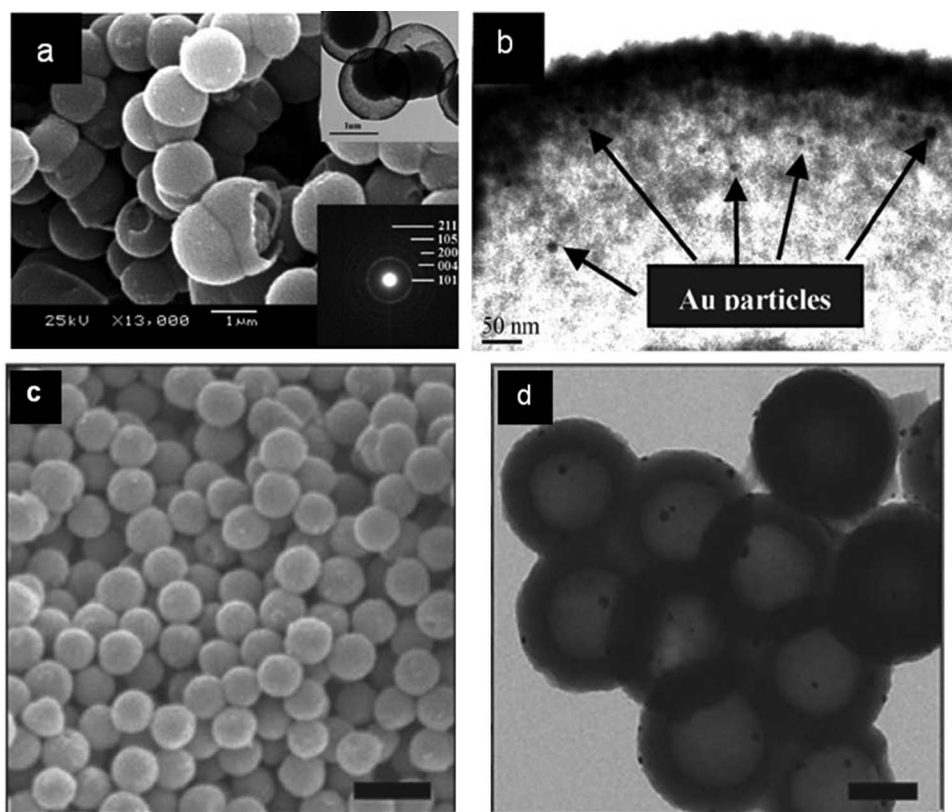


FIG. 3. (a) SEM and (b) TEM images of the Au/TiO₂. The insets are the TEM and SAED images. Reproduced by permission from Z. F. Bian, J. Zhu, F. L. Cao, Y. F. Lu, and H. X. Li, *Chem. Commun.* **2009**, 3789. Copyright 2009 The Royal Society of Chemistry. (c) SEM and (d) TEM images of hollow g-C₃N₄ photocatalysts. The scale bars in (c) and (d) are 500 and 200 nm, respectively. Reprinted with permission from J. H. Sun, J. S. Zhang, M. W. Zhang, M. Antonietti, X. Z. Fu, and X. C. Wang, *Nat. Commun.* **3**, 1139 (2012). Copyright 2012 Nature Publishing Group.

sites for the H₂ and O₂ evolution reactions, in the expectation that two different co-catalysts would lead to synergies in the H₂ and O₂ evolution reactions. However, thus far in practice, only a very few successful examples have been reported.⁵³ This is most likely due to the circumstance that H₂ evolution co-catalysts are mostly composed of noble metals and, therefore, also catalyse the backward reaction, forming water (the thermodynamically much more stable molecule) from H₂ and O₂. Using core-shell co-catalysts was reported to aid this problem. However, that approach is so far limited to the Rh/Cr₂O₃ and Ni/NiO system and still does not give the efficiencies necessary (*vide supra*).^{53,54} In the natural system, the PS I and PS II reaction centres are spatially arranged inside and outside, respectively, of the supporting thylakoid membrane to avoid charge recombination and the backward reaction. When designing a solar water splitting photocatalytic system, a spatial separation of two incompatible photoreaction centre (H₂ and O₂ evolution co-catalysts) in an integrated system, analogous to natural photosynthesis, needs to be designed such as to develop a local environment gradient to prevent the backward reaction and facilitate charge separation. Hollow structure scaffolds with spatial “inner” and “outer” spaces conceptually allows for such organisation to take place, i.e., for the two incompatible photoreaction centres to sit on opposing sides of the shell (analogous to the role of the thylakoid membrane). This would then generate a local environment gradient between the two sides of the shell, preventing the backward reaction.

This represents a research challenge as the proof-of-concept using hollow structure scaffolds to spatially load dual cocatalysts acquires well-designed scheme and sophisticated operation. Nevertheless, successful attempts to control the organisation of single co-catalysts onto either the exterior or the interior of hollow semiconductors have been reported. For example, Au@TiO₂ microsphere photocatalysts with the Au nanoparticles evenly encapsulated were successfully fabricated via the

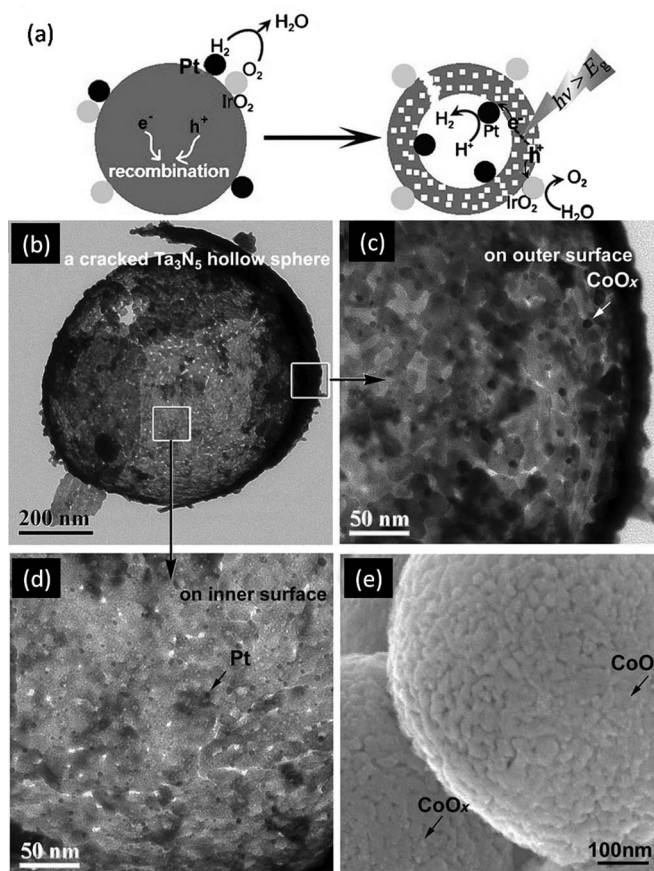


FIG. 4. (a) Design principle, which involves the use of two separated cocatalysts on the hollow Ta_3N_5 photocatalyst as effective charge collectors for water splitting; (b)–(d) TEM images of a cracked Ta_3N_5 hollow sphere with spatially separated CoO_x on the outer shell surface (c) and Pt cocatalysts on the inner Ta_3N_5 shell surface (d); (e) SEM images of hollow Ta_3N_5 photocatalyst with 2 wt.% CoO_x cocatalyst loaded on the outer shell surface. Reprinted with permission from D. Wang, T. Hisatomi, T. Takata, C. Pan, M. Katayama, J. Kubota, and K. Domen, *Angew. Chem. Int. Ed.* (2013) (published online). Copyright 2013 Wiley-VCH.

consecutive solvothermal and hydrothermal treatments (Figures 3(a) and 3(b)).²⁴ The homogenous dispersion of Au nanoparticles allows for the photogenerated electrons to migrate preferentially toward the inner space, a migration which facilitates and promotes charge separation, leading to high photoactivity. Also, recently Wang reported a bio-inspired approach to assemble another type of organised photocatalytic unit using conjugated polymer semiconductor hollow nanospheres (Figures 3(c) and 3(d)).²³ Hollow $\text{g-C}_3\text{N}_4$ nanospheres with tunable shell thicknesses were successfully synthesised using silica nanoparticles as templates. Pt nanoparticles acting as co-catalysts were placed onto the surface of hollow $\text{g-C}_3\text{N}_4$ nanospheres. A promising 7.5% apparent quantum yield was reported for the photocatalytic hydrogenation evolution reaction.

Thrillingly, a latest result reported by Domen⁵⁵ shows a proof-of-concept using hollow scaffold to spatially assemble dual cocatalysts on opposing sides of the shell. Pt on the inner shell as H_2 evolution cocatalysts and IrO_2 or CoO_x on the outer shell as O_2 evolution cocatalysts were loaded on Ta_3N_5 hollow scaffold (Figure 4). The resulting photocatalyst showed significantly enhanced water reduction and oxidation performance under visible light irradiation. The high activity was attributed to the hollow structure and separated cocatalysts that assisted separation and collection of the electrons and holes at the respective cocatalysts.

These examples show the excellent potential of the structured and organised assembly of dual co-catalysts using hollow structures. Overall water splitting can be expected in the future based on our understanding of natural photosynthesis and on the further development of nanotechnology

regarding materials assembly. One of the big, remaining challenges is the development of novel and general methods of hollowing semiconductor with overall water splitting ability, such as GaN:ZnO, and the controllable location of cocatalysts in these hollow structures.

IV. OUTLOOK

The photocatalytic system should integrate three necessary functions, that is, light harvesting, charge generation, and the photoreaction, to accomplish the light-induced charge generation/separation and subsequent water oxidation and reduction reactions. Although a simple proof-of-principle approach is to use a single semiconductor with these three functions, a reasonable anticipation is that combined multicomponent systems with different functions for different components are necessary to fabricate a photocatalytic system with high performance. Thus, the light harvesting component is usually employed to match the solar spectrum; proper cocatalysts are usually loaded serving as the heterogeneous electron transfer reaction sites and accelerating the oxidation–reduction kinetics; heterojunctions are applied to achieve spatial separation of electrons and holes. All of the strategies involve the integration of multiple functional components with topologically defined arrangements in a suitable scaffold. The final goal is the assembly of multifunctional photocatalytic units (e.g., semiconductors, metal or oxide nanoparticles, light harvesting complexes, and hydrogenases or their mimics) in an organised integrated device with tunable photophysical properties capable of converting solar energy to solar hydrogen with high performance. One synthetic strategy that can reasonably be anticipated is to use tailored hollow structures as scaffolds for such complex systems (this concept includes the scaffold itself having a chemical functionality). To realise this, continuous improvements, including the methodologies for the synthesis and assembly of hollow structures and procedures for the organised assembly of the multicomponent devices, are necessary.

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