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## Feature Article

# Tailoring Assembly, Interfaces, and Porosity of Nanostructures toward Enhanced Catalytic Activity

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The evolutionary nanotechnology has inspired materials scientists to invent nanostructures with achievements in numerous practical applications, particularly in catalysis. The great advancements typically involve flexible control over unique properties of the nanomaterial through tuning their structural geometries and components. In this Feature Article, we present recent progress of our recent researches and other groups in tailoring assembly, interfaces, and porosity of diverse inorganic nanostructures. The enhanced catalytic properties of the engineered nanostructures are discussed in relation to photocatalysis with special emphasis on solar energy conversion including water splitting, CO<sub>2</sub> reduction, and organic photodecomposition. Considering superior catalytic performance and long-term durability aspects, the development of the economical, active nanocatalysts opens practical opportunities for endeavours in sustainable energy conversion and other applied fields. This Review is expected to introduce readers general principles of engineering the nanostructured features of the inorganic nanomaterials capable of improving solar photocatalytic efficiency.

## Introduction

Chemical methods for growing nanocrystals in solution have achieved significant progress in tuning the structural geometry and component of nanomaterials.<sup>[1]</sup> Assembly, interfaces, and porosity engineered in the nanostructure are considered as crucial textures affecting dependent properties of a material.<sup>[2, 3]</sup> Thanks to the evolutionary nanotechnology for devoting synthesis mastery over nanostructured features, exquisitely uniform particles behave like elementary units to build nanoarchitectures for studies on interfacial chemistry.<sup>[4]</sup> An important topic in materials science is the development of nanostructured catalysts with improved activity. Such nanostructures with tailored geometries are crucial components of many industrially relevant heterogeneous catalysts.<sup>[5]</sup>

Nanostructured catalysts play an important role in tackling the environmental and energy issues.<sup>[6]</sup> Since heterocatalytic reactions occur at catalyst's surfaces, tailoring the geometry of catalysts to expose active phases<sup>[2]</sup> and amplify reactant diffusion is a powerful way to improve the catalytic activity.<sup>[3]</sup> There is a general consensus

that the active sites of a catalyst can be arisen from assembly-engineered surfaces and junction-induced interfaces, while the reactant diffusion can be established by porous networks. Elegant examples of these materials include periodic composite (e.g., Au-Fe<sub>2</sub>O<sub>3</sub>) superlattices from particle co-assemblies,<sup>[7]</sup> Au-tipped CdSe rods prepared by photoreduction,<sup>[8]</sup> and porous bilayered CeO<sub>2</sub>/Pt/SiO<sub>2</sub> nanostructures from particle monolayer assemblies.<sup>[9]</sup> The particle colloids can organize into nanoarchitectures that may provide collective properties from interparticle arrangements.<sup>[10]</sup> One of the elegant manners reported by Do group shows the organization of SiO<sub>2</sub> spheres coated with uniform titanate nanodisks (TNDs) to produce photonic Au/TiO<sub>2</sub> hollow nanospheres.<sup>[11]</sup> Further line of this implication focuses on replicating the particles with mesoporous silica templates for reconstructing porous oxide nanostructures.<sup>[12]</sup>

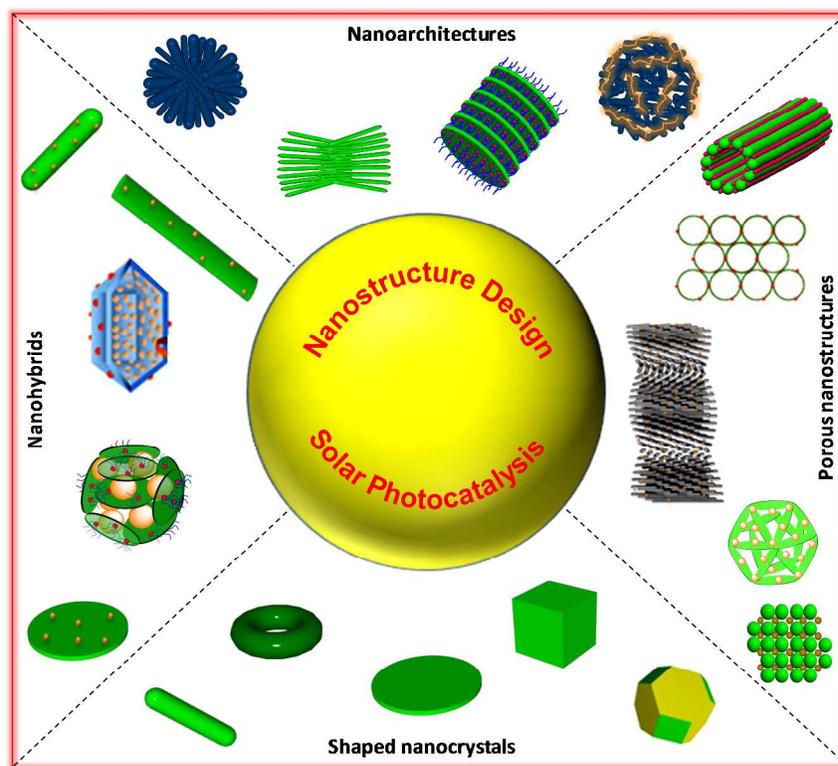
The global pollution and energy crisis originated from the overuse of fossil fuels is a grand challenge facing humanity today. Finding renewable fuels based on widely available energy sources to keep up with the energy demand growth while ensuring the increasing standard of living is the most difficult task in the 21<sup>st</sup> century.<sup>[13,14]</sup> The utilization of semiconductor-based nanomaterials in the field of photocatalysis has become one of the hottest research topics as it facilitates the direct conversion of solar energy, the largest renewable energy source, into chemical energy.<sup>[5, 15, 16]</sup> This solar energy technology remarks a crucial milestone in paving the way for future improvement in producing clean energy alternatives. The solar-to-chemical energy conversion process is also called "artificial photosynthesis", which involves photo-induced water splitting to hydrogen and oxygen and light-driven carbon dioxide

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**Figure 1.** Tailoring hierarchical configurations of diverse inorganic nanostructures for the design of the integrated catalysts.

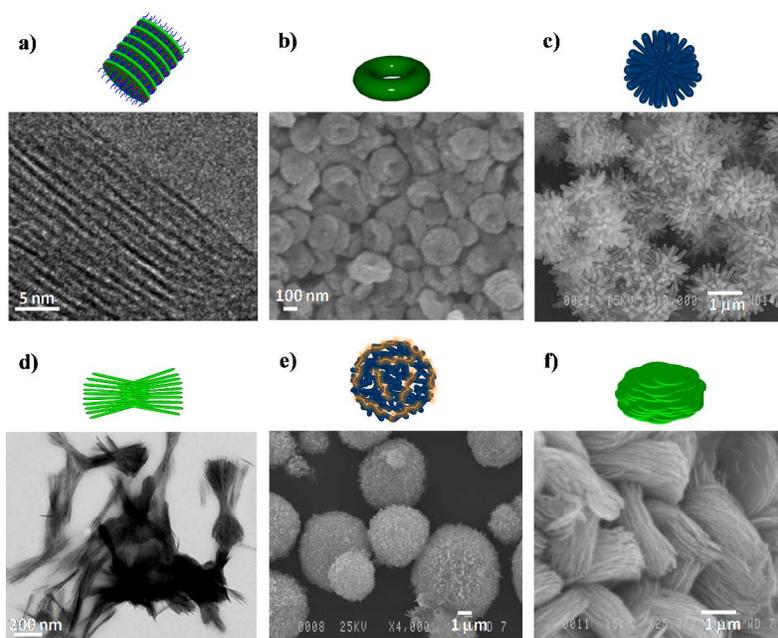
reduction into fuels, replicating natural photosynthesis.<sup>[17, 18]</sup> A key determinant of energy storage in the artificial photosynthesis is the efficiency and cost of the man-made photocatalysts.

Generally, single semiconductor (*e.g.*, TiO<sub>2</sub>) exhibits charge photogeneration much faster than charge separation. This behavior leads to a rapid electron-hole recombination, giving a poor photocatalytic efficiency.<sup>[14]</sup> Learning from nature, materials scientists have developed new heterojunctions by using coupling/assembly techniques to produce integrated catalysts that mimic an electron transfer Z-scheme mechanism of the ideal plant photosynthesis.<sup>[19, 20]</sup> Synergistic interactions can be occurred in the integrated catalysts, enabling a harvesting solar structure with long charge lifetime, thus giving exceptional reaction performance. It is acceptable that photocatalytic efficiency may be still low in case of the absence of suitable active sites on semiconductors even if the semiconductor performs an efficient carrier separation. Proper metal-based cocatalysts that act as active sites are commonly integrated into heterostructures to facilitate surface reactions.<sup>[21]</sup> In this Feature Article, we summarize recent research efforts of our works and other groups, who show tailoring the assembly, interfaces, and porosity of nanostructures for the design of integrated catalysts (Figure 1). Significant progress in superior catalytic performance of heterojunctions through synergistic interactions is followed by discussions of efficient solar energy conversion.

### Nanoarchitecture assemblies

The oriented assembly of the primary particles into three-dimensional (3-D), hierarchical nanostructures offers access to new materials with unique properties.<sup>[9]</sup> Multi-step templated procedures are commonly applied for fabricating these structures. One notable example was reported by Wang *et al.*<sup>[22]</sup> on a two-step procedure for constructing microstructures by first preparing the nanoparticles (Ag, Ag<sub>2</sub>S, Ag<sub>2</sub>Se) followed by assembling into microspheres in microemulsion. Alternatively, one-pot oriented assembly is highly desirable to these structures from the particles.<sup>[4]</sup> The nanoarchitectures are a variant of the assembled particles with distinction that pores can engineer inside organized networks.

Surfactant-assisted route has emerged as a versatile tool in controlling the uniform particles.<sup>[1]</sup> Do group has investigated the use of different recipes in surfactant-assisted synthesis to prepare the shaped particles that are units for assembling into nanoarchitectures. For example, Dinh *et al.*<sup>[23]</sup> have exploited uniform, ultrathin TNDs with ~22 nm in diameter and ~0.75 nm in thickness prepared from solvolysis of Ti(OBu)<sub>4</sub> in benzyl alcohol/oleylamine/benzyl ether. This is the first preparation of TNDs as elementary units for building nanoarchitectures with plentiful potential uses (presented below). Evidently, the authors observed that TNDs can assemble in ethanol into periodically stacked lamellar structures with spacing between disks of ~2.2 nm (Figure 2a). TNDs were yielded from the growth of TiO<sub>6</sub> octahedra building units generated from the reaction between titanium butoxide (TB) and benzyl alcohol (BA) in the assistance of oleylamine (OM) capping agents for balancing the negative charge of TNDs. The stacked lamellar organization of TNDs upon the



**Figure 2.** (a) TND lamellar structures.<sup>[23]</sup> (b)  $\text{LaCO}_3\text{OH}$  cluster doughnuts.<sup>[24]</sup> (c)  $\text{Er}_2\text{O}_3$  rod microflowers.<sup>[25]</sup> (d) Straw sheaf-shaped  $\text{Er}_2\text{O}_3$  nanowires.<sup>[25]</sup> (e)  $\text{MnWO}_4$  rod microspheres.<sup>[26]</sup> (f)  $\text{MnWO}_4$  sheet microspheres.<sup>[26]</sup> Adapted from references<sup>23,24,25,26</sup> with permission from Wiley-VCH Verlag GmbH & Co, the American Chemical Society, and the Royal Society of Chemistry.

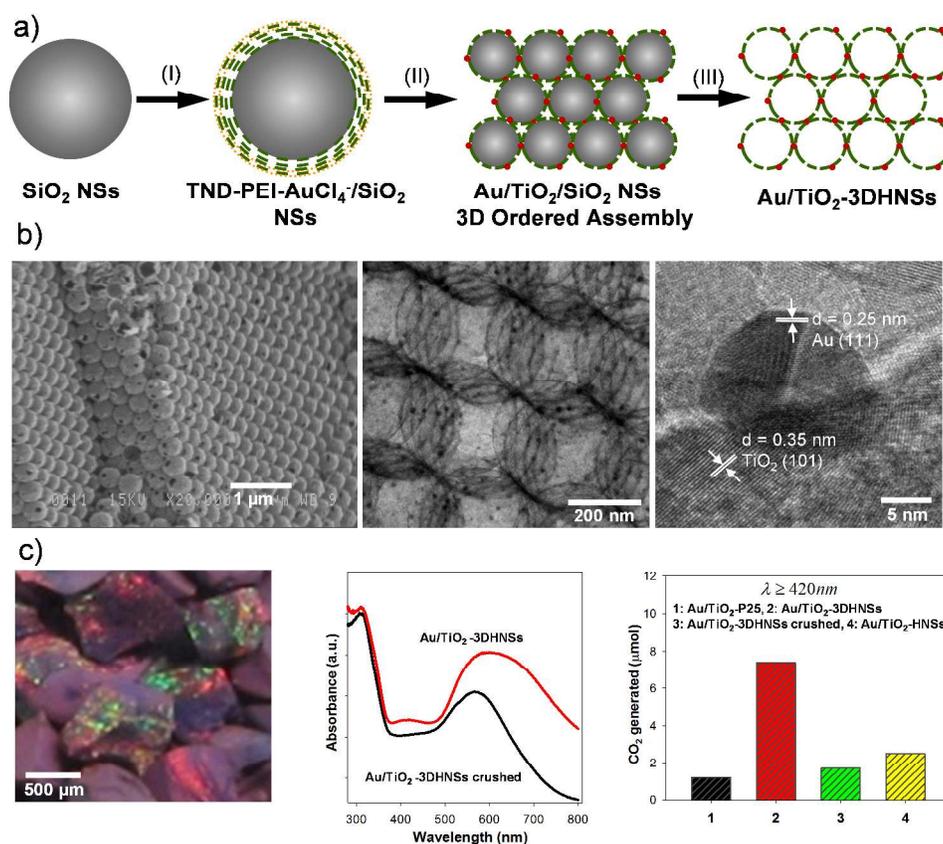
assembling conditions was thought to result from its one-dimensional, ultrathin nanostructure.<sup>[23]</sup> Another report shows a control over slow aggregation of  $\text{LaCO}_3\text{OH}$  clusters, prepared by slow thermolysis of  $\text{La}(\text{oleate})_3$  in water/toluene, into doughnut-shaped mesostructures (Figure 2b).<sup>[24]</sup> Stable  $\text{La}(\text{oleate})_3$  complexes were slowly decomposed in the two-phase water toluene system containing OM capping agents to generate  $\text{LaCO}_3\text{OH}$  nanoclusters. These OM-capped tiny particle colloids are active building units that self-organized into mesoporous nanoarchitectures with annular shapes to minimize interface energy. The  $\text{LaCO}_3\text{OH}$  nanocrystals underwent a metathesis upon calcination to transform into porous  $\text{La}_2\text{O}_3$  doughnuts. These nanodoughnuts resemble  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  nanocages prepared by hydrolyzing  $\text{ZrOCl}_2$  in  $\text{CeO}_2$  spheres/glycol.<sup>[27]</sup> Conversely, the hydrothermal treatment of  $\text{Er}(\text{NO}_3)_3$  in dodecanoic acid/ethanol/water as polar solution media facilitated the evolution of  $\text{Er}_2\text{O}_3$  clusters.<sup>[25]</sup> Upon controlling the cluster growth by the relatively short alkyl capping agents,  $\text{Er}_2\text{O}_3$  nanoarchitectures with tunable intriguing morphologies were obtained from fast aggregation of the primary nanowires (Figures 2c,d), which look similar to those of  $\text{LnVO}_4$  architectures.<sup>[28]</sup>

There is considerable current interest in materials that can control interactions between particles and biomolecules, such as amino acids, peptides, DNA, to assemble into architectures.<sup>[29]</sup> Inspired by our previous work on amino acids, these biomolecules are suitable surfactants to organize the oxide particles into

nanoarchitectures (Figures 2e,f).<sup>[26]</sup> The hydrothermal treatment of a  $\text{Mn}^{2+}/\text{WO}_4^{2-}/\text{aminohexanoic acid (AHA)}/\text{water}$  mixture enabled  $\text{MnWO}_4$  nanorods to be obtained with uniform shapes on significant scales. Once AHA molecules are adsorbed on the particles, the stabilized  $\text{MnWO}_4$  rods become dispersible in water. Free amine and carboxylic acid groups in the capped and residual ligands of the AHA molecules are available in the reaction solution, thus they can coordinate together to form polypeptides through hydrogen bonds. The discrete nanorods can thereby be cross-linked by hydrogen bonds to assemble into  $\text{MnWO}_4$  dendrimer-shaped microspheres. Glycine surfactant, a simplest amino acid, was also used by Ding et al.<sup>[30]</sup> to prepare  $\text{TiO}_2$  hollows. Advances in DNA technological production allow using its supramolecular bundles as hierarchical platforms for assembling the particles.<sup>[31]</sup>

### Long-range periodic nanostructures

The uniform particles behave like colloids to assemble long-range order into a periodic structure. Structural coloration arises from 3-D, hierarchical structures as a result of Bragg diffraction of light in a photonic material.<sup>[32]</sup> Another theme for advancing this property is the coupling of the photonic structure with specific additives to produce new materials with amplified optical properties.<sup>[33]</sup> There are therefore efforts in the development of new synthetic methods to these functional materials, which have promise in a variety of areas such as photocatalysis, photovoltaics, and sensors.<sup>[32]</sup>



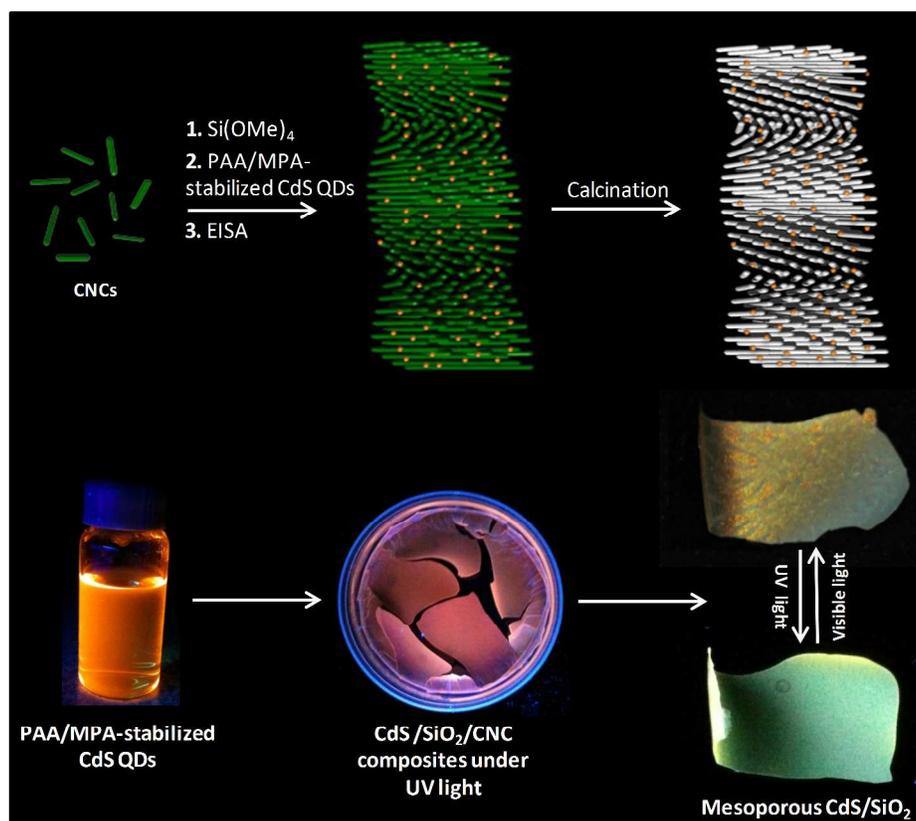
**Figure 3.** (a) Synthetic procedure for the design of Au/TiO<sub>2</sub>-3DHNSs. (b, from left to right) SEM, TEM, HRTEM of Au/TiO<sub>2</sub>-3DHNSs. (c, from left to right) Photograph, UV-vis spectrum, Visible light isopropanol photodecomposition of Au/TiO<sub>2</sub>-3DHNSs in comparison with Au/TiO<sub>2</sub> of different structures.<sup>[11]</sup> Adapted from reference<sup>11</sup> with permission from Wiley-VCH Verlag GmbH & Co.

The original concept of using the external magnetic field to guide the arrangement of the magnetic particles into a photonic nanostructure was pioneered by Yin et al.<sup>[34]</sup> This robust procedure is composed of the preparation of polyacrylate-stabilized Fe<sub>3</sub>O<sub>4</sub> clusters followed by self-organization of these units into periodic NC arrays upon applying the external magnetic field. The magnetic attractive force brings the magnetic particles into ordered linear chains aligned with an external magnetic direction, which results from a balance of the magnetic force and interparticle repulsive force. Iridescent colors of these arrays are observed when the periodicity of the magnetic arrays closely matches the wavelength of the incident light and can appear across the entire visible spectrum under the influence of the external magnetic fields. The authors demonstrated these periodic nanoarrays as responsive photonic materials for transferring into polymer hosts for the design of electronic papers, photonic patterns, and switchable color display sensors.<sup>[35,36]</sup>

Coupling plasmonic metals with photonic semiconductor crystals is an interesting strategy for constructing efficient photocatalysts.<sup>[33]</sup> Photonic structures exhibit slow photon effect by prohibiting propagation of light in the material with extremely low group velocities. When the slow photon wavelength overlaps with the light absorbed of incorporated plasmonic metal particles, an

enhanced light absorption can be obtained. Thus far, metal-semiconductor photonic hybrids, which are primarily based on ordered macrostructures (or inverse opal), have substantially lower surface areas than either their nanoparticles or mesoporous counterparts, preventing them to be efficient photocatalysts. Recently, Do group designed photonic Au/TiO<sub>2</sub> nanostructures that are constructed from long-range ordered assembly of thin-shell Au/TiO<sub>2</sub> hollow nanospheres (denoted as Au/TiO<sub>2</sub>-3DHNSs) that appear iridescent colors (Figure 3).<sup>[11]</sup> These materials show not only high surface area but also photonic behavior originating from periodic macroscopic voids of the thin-shell hollow nanospheres. This architecture evolves multiple light scattering and slow photon effects to enhance the surface plasmon resonance of Au particles, thus giving visible light-responsive Au/TiO<sub>2</sub>-3DHNSs. As a result, these new structures exhibit several-fold higher photocatalytic activity compared to Au/TiO<sub>2</sub> nanopowders, as illustrated by an example of visible-light driven photodecomposition of isopropanol into CO<sub>2</sub>.

The incorporation of quantum dots (QDs) into photonic crystals affords attractive semiconducting photonic materials useful for optoelectronic technology.<sup>[38]</sup> QDs-infiltrated photonic crystals can be commonly fabricated by multi-loading QDs into inverse opals.<sup>[38]</sup> This procedure involves time-consuming steps and uses the cost-



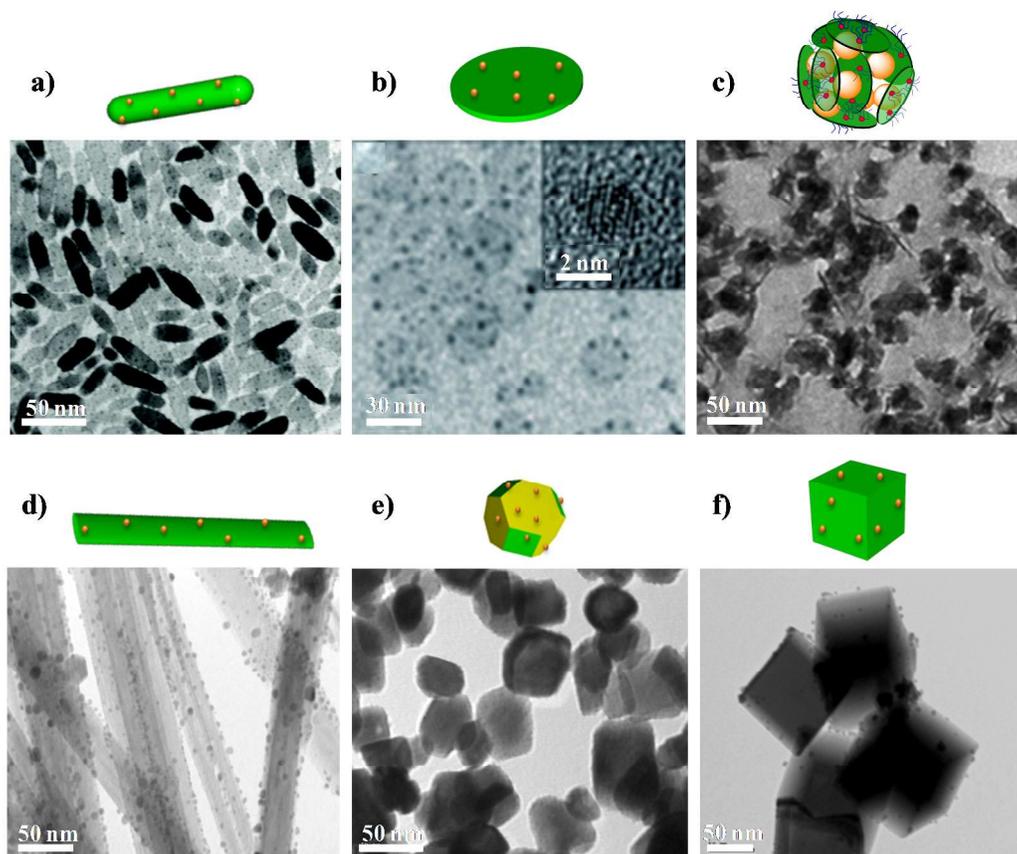
**Figure 4.** Co-assembly of CdS QDs with  $\text{Si}(\text{OCH}_3)_4$  and cellulose LCs for producing chiral mesoporous CdS/SiO<sub>2</sub> films. The films photographed under visible light and UV light.<sup>[37]</sup> Adapted from reference<sup>37</sup> with permission from Wiley-VCH Verlag GmbH & Co.

intensive templates. Chiral nematic cellulose nanocrystals (CNCs) with structural colors can be used as an alternative liquid-crystalline (LC) template to reinforce photonic porous nanomaterials. This primary concept was recently reported by Nguyen et al.<sup>[37]</sup> through a one-step co-assembly of water-dispersible polyacrylic acid (PAA)/mercaptopropionic acid (MPA)-stabilized CdS QDs with  $\text{Si}(\text{OCH}_3)_4$  and CNC aqueous dispersion to generate chiral nematic CdS/SiO<sub>2</sub>/CNC composites. The subsequent removal of the CNC template by controlled calcination of the composites generated freestanding luminescent, iridescent chiral mesoporous CdS/SiO<sub>2</sub> films (Figure 4). The semiconducting properties of the photonic films were remained intact as they underwent luminescence quenching by trinitrotoluene vapor. These materials, which are available films prepared using renewable CNCs, may be potentially used as a host to embed TiO<sub>2</sub> particles within their pores for producing CdS-contacted TiO<sub>2</sub> structures amenable to photocatalysis. There is a previous attempt to incorporate hydrophobic CdSe/ZnS QDs into a cellulose triacetate matrix, but the resulting composites showed neither photonic chirality nor porosity.<sup>[39]</sup> Pursuits of using other biopolymers, such as lipids and peptides, as soft templates are implemented to make TiO<sub>2</sub>,<sup>[40]</sup> Co<sub>3</sub>O<sub>4</sub> and ZnO<sup>[41]</sup> hierarchical replicas.

### Particle coupling-induced interfaces

Interparticle interfaces in a nanostructure have favorable effects on the catalytic performance.<sup>[2]</sup> It is desirable to introduce the interfaces into nanostructures by applying appropriate combination of constituents. Busbee et al.<sup>[42]</sup> early proposed the surface growth of HAuCl<sub>4</sub> on Au spherical seeds to evolve nanorods. Later, modified surface selective growth routes, such as photoreduction, cation exchange, and surface modification, have been studied extensively by different groups and our recent researches for the design of the nanohybrids.

UV light-induced growth was first reported by Pacholski et al.<sup>[43]</sup> for the synthesis of Ag/ZnO nanorods. The authors proposed that electrons generated on semiconductor surfaces under UV excitation can reduce Ag<sup>+</sup> in the ZnO particle dispersion into deposited Ag clusters. The successful invention of this photodeposition without the aid from organic molecular bridges is the great breakthrough for extending to other semiconductor-based composites. Later, Mokari et al.<sup>[8]</sup> made selective photodeposition of Au clusters at tips of CdSe rods. Recently, Do group represented the photoreduction synthesis of metal/semiconductor nanomaterials. Evidently, UV irradiating an ethanol/toluene dispersion of oleic acid (OA)-capped TiO<sub>2</sub> nanorods and AgNO<sub>3</sub> was carried out to obtain Ag/TiO<sub>2</sub> hybrids (Figure 5a) that show enhanced photodegradation of methylene blue.<sup>[44]</sup> This photodeposition was used by Lu et al.<sup>[45]</sup> to synthesize Ag/TiO<sub>2</sub> nanorods for the design of photovoltaic devices. This route offers



**Figure 5.** (a) Ag/TiO<sub>2</sub> nanorods prepared using photoreduction.<sup>[44]</sup> (b) Ag/TND composites prepared using cation exchange.<sup>[23]</sup> (c) Ni-TND-CdS composites prepared using sequential cation exchange and photoreduction.<sup>[46]</sup> Ag/TiO<sub>2</sub> belts (d), Au/CoWO<sub>4</sub> octahedra (e), Cu/CeO<sub>2</sub> cubes (f) all prepared using amino acid- or diamine-surfaced modification.<sup>[47, 48]</sup> Adapted from references <sup>23,44,46,47,48</sup> with permission from the American Chemical Society, Wiley-VCH Verlag GmbH & Co, the Royal Society of Chemistry, the American Chemical Society, and Elsevier.

feasibility of a precise control over the population of the uniform metal clusters on the individual TiO<sub>2</sub> particles.

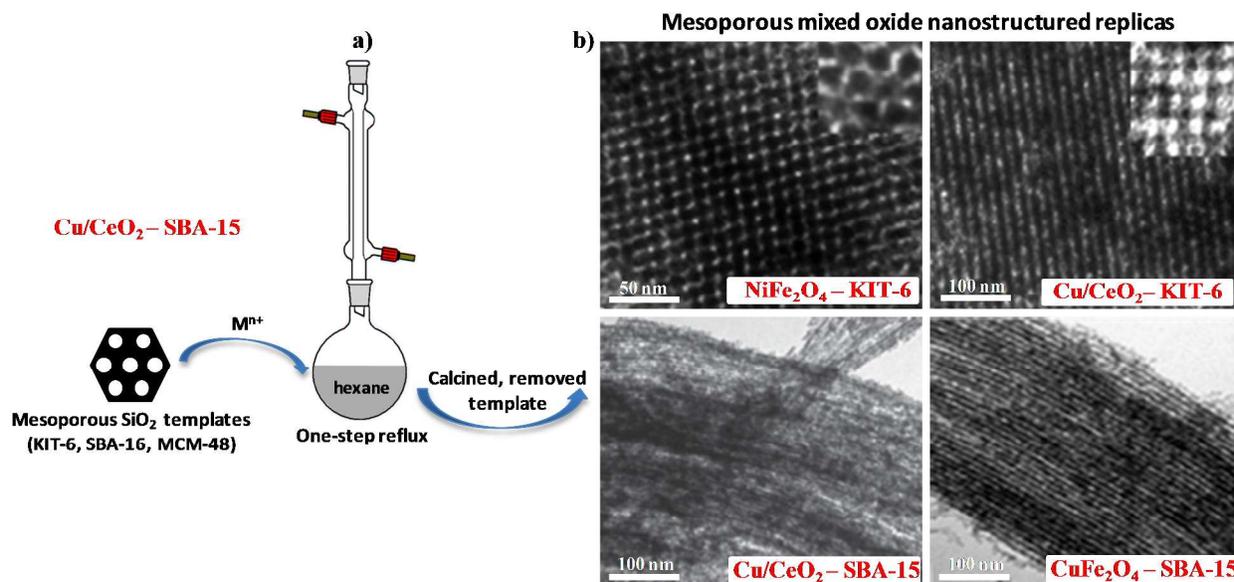
The ion-exchange process was recently used by Do group for selective substitution of the cations ligated on the particles with target ligands in the aqueous solution for controlled deposition of the clusters on TNDs (Figures 5b,c).<sup>[23, 46, 49]</sup> The authors performed the cation exchange of oleylamine-capped TNDs with tetraethylammonium (TEA) ligands in water. The water-dispersible TEA-stabilized TNDs obtained can be solely used as ideal islands for constructing nanohybrids in water. Clusters (metal, metal sulfide)-exchanged TND heterostructures can be obtained by partial replacement of TEA molecules on TNDs by metal cations. The metal cations were strongly attached to the TND's surfaces through electrostatic interaction and then grew up to 2-4 nm deposited metal clusters without any aggregation. The water-dispersible TND-based nanohybrids with a synergistic configuration show enhanced photodegradation of methylene blue. The cation exchange was also applied by Luo et al.<sup>[50]</sup> to selectively deposit CdSe on polystyrene-templated TiO<sub>2</sub> opals for H<sub>2</sub> generation.

The organic molecule linkers can function as bridges to assist the coupling of discrete particles into nanocomposites. Bao et al.<sup>[51]</sup> used cysteine to modify the Fe<sub>3</sub>O<sub>4</sub> particle surfaces and then decorated

with Au particles through its amine groups. Do group showed that aminohexanoic acid and hexamethylenediamine are bifunctional linkers for the design of water-dispersible nanohybrids (Figures 5d,e,f).<sup>[47, 48]</sup> Once these linkers stabilized on the particle surfaces, the carboxylic and amine groups not only provide growth sites for the particle deposition but also inhibit any agglomeration. The selective deposition was performed by attaching metal ions on the functional groups of amino acid or diamine molecules stabilized on the nanoparticles and subsequently reducing them to metallic clusters by a reducing agent. This route was spread to different nanocomposites such as Au/MnWO<sub>4</sub> rods, Au/CoWO<sub>4</sub> octahedra, Ag/La<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> sheets, Ag/TiO<sub>2</sub> belts, and Cu/CeO<sub>2</sub> cubes. The synergistic interactions in CeO<sub>2</sub> nanocubes coupled with 2.9-10.0 wt% Cu clusters result in CO oxidation activity substantially higher than bare CeO<sub>2</sub> nanocubes.<sup>[48]</sup>

### Engineering porosity into nanostructures

Opening pores within the nanostructures can amplify the access of the reactants to the surface reactions, in principle, improving the catalytic performance.<sup>[3]</sup> There are several ways to engineer the porosity: one can reconstruct nanohybrid colloids to open pores and the former can be porous nanocomposites obtained from casting.



**Figure 6.** One-step replication of mesoporous mixed oxide nanostructures with silica hard templates.<sup>[53]</sup> Adapted from reference<sup>53</sup> with permission from the Royal Society of Chemistry.

Notably, porous non-siliceous nanomaterials can be prepared by either assembling the discrete particles into an organized porous system or infiltrating porous hard template with a precursor followed by calcination and template removal.<sup>[12]</sup> Another route can be achieved by assembling the polymeric template with a precursor in process to prepare porous nanostructures.<sup>[12]</sup>

The assembled organization was proposed by Shevchenko et al.<sup>[7]</sup> to produce composite superlattices from the particle colloids by ordering interparticle interfaces. Yamada et al.<sup>[9]</sup> modified this protocol to design bilayered catalysts with enhanced interfaces by sequentially assembling Pt and CeO<sub>2</sub> nanocube monolayers on the substrates. Do group extended this theme to construct mesoporous metal/oxide nanostructures. For example, co-assembly of OA-capped metal (Au, Cu) with OA-capped oxide (TiO<sub>2</sub>, ZrO<sub>2</sub>) particles was accomplished to make metal/oxide nanocomposites.<sup>[52]</sup> The removal of the capping agents stabilized on the composites by calcination generated mesoporous structures connected between metal and oxide nanoarrays and ensured the retention of the sizes of the pristine particles. These porous nanocomposites show enhanced CO catalytic activity compared to the single components, probably due to the presence of the porosity and the metal-oxide interfaces in the material.

Once again, Dinh et al.<sup>[23]</sup> used the TEA-exchanged TNDs as brick units for constructing mesoporous supports. The TEA-stabilized TNDs were sequentially exchanged with metal cations (e.g., Ag<sup>+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>) to form precipitates of metal clusters-exchanged TNDs nanohybrids in water. In basic media, the clusters-deposited TND colloids can organize into mesoporous hybrids with large voids formed from good connectivity between edges of the nanodisks. Engineering porous materials with TNDs can be achieved with the surface areas of 250-320 m<sup>2</sup> g<sup>-1</sup> and the pore sizes of 4.9-9.3 nm depending on the sizes of TNDs employed in the preparation.

Hard templating techniques are proven to be successful for preparing porous oxide nanostructures. These porous nanomaterials can be obtained by repeatedly infiltrating the mesoporous silica with a metal salt precursor followed by calcination and template removal. The apparent obstacle of this impregnation is a time-consuming procedure. Hoang et al.<sup>[53, 54]</sup> recently developed a one-step hard templating route to producing mesoporous nanocomposites (Figure 6). The procedure is composed of refluxing a hexane mixture containing binary metal nitrates and mesoporous silica to melt the metal salts in hexane and then infiltrating into the porous silica in exclusive one step. Mesoporous mixed oxide nanostructures can be obtained by calcinating the metal ions/silica composites followed by etching the silica away. This convenient pathway was addressed to truly replicate high-surface-area mesoporous oxide nanoarrays of different composites including NiFe<sub>2</sub>O<sub>4</sub>, CuFe<sub>2</sub>O<sub>4</sub>, Cu/CeO<sub>2</sub>, and Cu/NiO. With the combination of the mesoporosity and multicomponents, the mesoporous 30 wt% Cu/CeO<sub>2</sub> nanostructures showed complete CO oxidation at ~40 °C.<sup>[54]</sup>

## Integrated photocatalysts for solar energy conversion

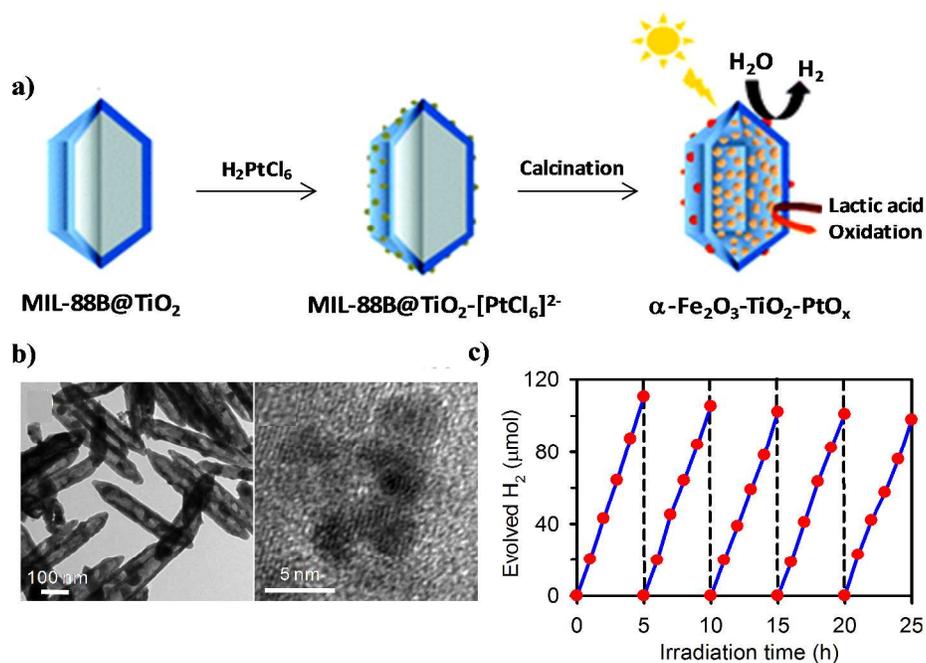
Semiconductor-based nanocatalysts are potentially used for solar energy conversion, which offer a way to alleviate emerging energy and environmental issues. The most significant achievements of this alternative technology are engineering semiconductors with narrow bandgap energy and interfacial contacts that are pivotal to produce the integrated photocatalysts with enhanced power-conversion efficiency. Carbon-free production of H<sub>2</sub> through solar water splitting is widely recognized as the most green and economic method to produce valuable fuels. CO<sub>2</sub> photoreduction may not only alleviate the problem of CO<sub>2</sub> emissions but also convert CO<sub>2</sub> and sunlight into energy in principle. Despite they are simple reactions, these solar energy conversions are slow multielectronic processes

that need to be catalyzed. The original concept and reaction mechanism of using  $\text{TiO}_2$  for photo-induced water splitting and  $\text{CO}_2$  reduction were easily demonstrated in the 1970s.<sup>[55, 56]</sup> Considering electronic states and high-density atomic arrangements at the nanocrystal surfaces, the photocatalytic activity of  $\text{TiO}_2$  nanostructures primarily determined by high-energy surfaces.<sup>[57]</sup> Studies on the shape-dependent photocatalytic activity over  $\text{TiO}_2$  nanocrystals revealed that exposed, chemically active  $\{001\}$  facets are much greater reactivity than lower energy facets.<sup>[58, 59]</sup> Photocatalytic  $\text{H}_2$ -production activity greatly improved by doping nitrogen into exposed  $\{001\}$ -faceted  $\text{TiO}_2$  nanosheets.<sup>[60]</sup> Yu et al.<sup>[61]</sup> demonstrated that engineering co-exposure of the  $\{101\}$  and  $\{001\}$  facets with an optimal ratio of 45:55 in anatase  $\text{TiO}_2$  nanocrystals with a surface heterojunction affords active photocatalysts that show an great enhancement in selective reduction of  $\text{CO}_2$  into  $\text{CH}_4$ . These interesting findings have already to the  $\text{TiO}_2$  materials to be an industrial important semiconductor and are a major creative breakthrough for extending the solar energy conversion to other semiconductors.<sup>[62]</sup>

Since the development of solar fuels requires using natural sunlight, however the pure  $\text{TiO}_2$  materials exhibit the low adsorption ( $\leq 5\%$ ) in the solar spectrum, thus giving a poor energy conversion efficiency. In terms of geometry-dependent catalytic properties, seeking out affordable approaches to producing the integrated catalysts with engineered nanostructures is a key goal for tackling this obstacle. In nature, the plants can perform directly sunlight-to-chemical energy conversion under ambient conditions, which is known as a "Z-scheme" driven by the absorption of two photons on two different reaction centers.<sup>[14]</sup> Materials scientists are trying to

mimic heterojunction semiconductors for efficient energy production that exhibit a similar electron transfer mechanism between components in the ideal plant photosynthesis. The heterojunctions can function as the integrated photocatalysts with exceptionally optoelectronic properties: sunlight harvesting, prolonged electron-hole separation, and photoexcited electrons shuttle on cocatalysts.<sup>[14, 20]</sup> The artificial mechanism was clearly reported by Tada et al.<sup>[63]</sup> on a  $\text{CdS-Au-TiO}_2$  Z-scheme system that contains a vectorial electron-transfer path and a consequent superior  $\text{H}_2$  evolution.

The stability of the composite materials, product selectivity, cocatalysis, and the relationship between the structural geometry features and bandgap energy are worth consideration for the design of solar nanostructured catalysts. There is a growing demand for new paradigms to prepare coupled semiconductors with long-lived electron-hole separation and slow charge recombination rate to advance toward more efficient solar energy conversion. Amirav et al.<sup>[64]</sup> proposed the enhanced  $\text{H}_2$  generation by introducing the interfaces into Pt-tipped  $\text{CdS/CdSe}$  nanorods. Coupling narrow-bandgap semiconductors with Pt particles built bridges of interfacial contacts to transfer charges across junctions, resulting in harvesting the visible light and enhancing  $\text{H}_2$  evolution. Silicon (Si) nanowires junctioned with additives are an attractive materials choice for constructing artificial leaves for future photosynthesis.<sup>[6]</sup> Yang et al.<sup>[65]</sup> performed coupling Si nanowires with  $\text{TiO}_2$  nanobranches to produce a dual light-absorber approach that can be imagined as artificial forest trees capable of releasing  $\text{H}_2$  on visible light-responsive Si photocathode and  $\text{O}_2$  on UV-responsive  $\text{TiO}_2$  photoanode. Xiang et al.<sup>[66]</sup> proposed positive synergetic effects between  $\text{MoS}_2$  and graphene in  $\text{TiO}_2$  nanoparticles-decorated



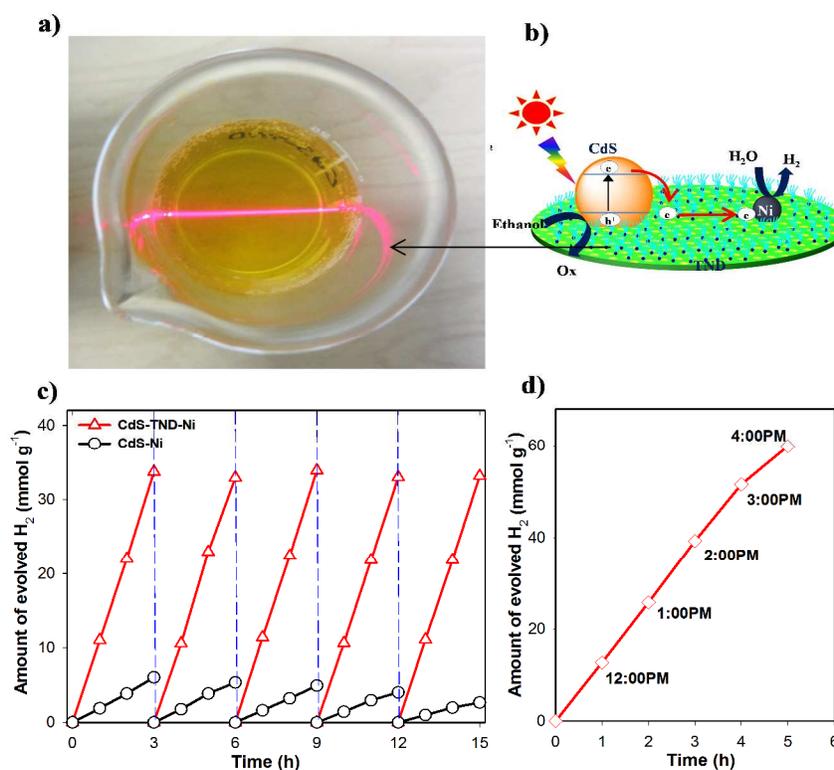
**Figure 7.** (a) Formation of  $\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-PtO}_x$  nanohollows using MOF hard templates. (b) Different-magnification TEM images of the  $\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-PtO}_x$  hollows. (c) Visible-light driven  $\text{H}_2$  evolution of the  $\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-PtO}_x$  photocatalysts.<sup>[72]</sup> Adapted from reference <sup>72</sup> with permission from the Royal Society of Chemistry.

supports, which give access to high-performance integrated photocatalysts for highly efficient H<sub>2</sub> evolution. Recent attempts in visible-light driven CO<sub>2</sub> photoreduction show that the enhanced activity and selectivity can be obtained by introducing the interfaces into the heterojunction catalysts. Ola et al.<sup>[67]</sup> found compounds of H<sub>2</sub>, CH<sub>3</sub>OH, CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>OH derived from CO<sub>2</sub> photoreduction over Cu/TiO<sub>2</sub> heterojunctions threaded with optical fibres. Wang et al.<sup>[68]</sup> proposed active Pt/TiO<sub>2</sub> nano hybrid films for high CO<sub>2</sub> photoreduction efficiency with selective formation of CH<sub>4</sub>. These reports reveal that the presence of the interfaces in the integrated nanocatalysts leads to the enhanced photocatalytic performance.

The introduction of metal-based species as reductive and oxidative cocatalysts into semiconductors results in the enhancement in the photoactivity and selectivity.<sup>[69]</sup> Cocatalysts, such as metal clusters and metal-organic complexes, integrated into photocatalysts provide electron traps for shuttling photoexcited electrons into reagents to perform reaction processes.<sup>[21]</sup> Han et al.<sup>[70]</sup> proposed the role of Ni<sup>2+</sup>-dihydrolipoic acid cocatalysts as solar light absorbers adsorbed on CdSe particles for proton reduction with ascorbic acid to produce H<sub>2</sub>. Ong et al.<sup>[71]</sup> reported decoration of Ni cocatalysts and TiO<sub>2</sub> semiconductors on carbon nanotubes to obtain visible light-responsive active photocatalysts for photoreaction of CO<sub>2</sub> to CH<sub>4</sub>. Do group proposed a new type of hollow PtO<sub>x</sub>-TiO<sub>2</sub> hybrid nanostructures with thin wall thickness (~15-30 nm) templated by metal organic frameworks (MOF) (Figure 7).<sup>[72]</sup> Subsequent deposition of the PtO<sub>x</sub> cocatalysts was performed on two opposite

sides of the calcined hollow structures to produce hollow nano hybrids. These novel materials showed highly visible-light-driven H<sub>2</sub> evolution, which could result from improving charge separation, likely due to its thin wall, porosity, and the isolated location of the two different cocatalysts on the hollow frameworks. Zhou et al.<sup>[73]</sup> performed replicating 3-D hierarchical porous perovskite titanate ATiO<sub>3</sub> (A = Sr, Ca, Pb) architectures with natural leaves as a hard template. Upon removal of template in the composites by calcination, the authors obtained biomimetic materials as artificial leaves that work efficiently as full-sunlight-driven photocatalysts with highly hierarchical porous structures for photoreduction of CO<sub>2</sub> to CO and CH<sub>4</sub> with an enhanced power-conversion efficiency.

The visible light photoreduction of CO<sub>2</sub> was performed over three-component CdSe/Pt/TiO<sub>2</sub> photocatalysts reported by Wang et al.<sup>[74]</sup> The roles of the interfaces and Pt cocatalysts in the heterojunctions determined reaction yields of gas-phase products with CH<sub>4</sub> as primary product. Recently, Do group<sup>[46, 49]</sup> reported a water-dispersible noble-metal free photocatalytic system, metal sulfide-TND-Ni, that shows superior reaction activity originating from the introduction of the interfaces and cocatalysts into a three-component heterojunction. This unprecedented junction gave access to active photocatalysts for sunlight-driven H<sub>2</sub> evolution with exceptional longevity, maintaining high activity with no decrease after five recycle experiments (Figure 8). Under visible light illumination over an irradiation area of 125 cm<sup>2</sup>, the CdS-TND-Ni



**Figure 8.** (a) CdS-TND-Ni heterojunction aqueous dispersion. (b) Transfer mechanism of charge carriers in CdS-TND-Ni for solar H<sub>2</sub> evolution. (c) Comparative H<sub>2</sub> evolution from CdS-TND-Ni and CdS-Ni catalysts under visible light. (d) Solar-driven H<sub>2</sub> production from CdS-TND-Ni.<sup>[46]</sup> Adapted from reference <sup>46</sup> with permission from the Royal Society of Chemistry.

nanocatalysts generated H<sub>2</sub> with an average rate of 31.8 mmol g<sup>-1</sup> h<sup>-1</sup> from ethanol-water,<sup>[46]</sup> which are one of the most highly active metal sulfide photocatalysts in the absence of noble metal cocatalysts.<sup>[75]</sup> In the CdS-TiO<sub>2</sub>-Ni system, Ni clusters and CdS particles localized at interlayers between TiO<sub>2</sub> disks, which lead to electrons photogenerated from CB of CdS to be injected into CB of TNDs and are then capped by the Ni cocatalysts for H<sub>2</sub> evolution. The authors speculated that the outstanding features of large-contact-area interfaces, good dispersion of deposited Ni clusters, and water dispersion are important factors of these heterojunctions for contributing to superior H<sub>2</sub> evolution. It is conceptually new to begin with the uniform TNDs to make new nanomaterials, as our works have demonstrated.<sup>[23, 46, 49]</sup> The one-dimensional TiO<sub>2</sub> nanodisks are being studied extensively for developing solar photoelectrochemical hybrid cell films as efficient photoanode electrodes via multilayered assembly on functionalized substrates. In this context, combined with earth-abundant, photostable inert, and synthetic feasibility, these materials provide great chances of applicability for the photocatalytic production of solar fuels.

## Conclusions and Outlook

In this Feature Article, we summarized recent progress reported by our researches and other research groups in tailoring the assembly, interfaces, and porosity of well-defined inorganic nanostructures and demonstrated synergistic effects of the integrated catalysts on the reaction performance. Main criterion for dealing with desirable surfactant-assisted routes is to produce well-defined nanostructures with precise control over surface properties. The controlled growth of surface-functionalized nanoclusters is important for speculating the construction of the hierarchically organized nanostructures. Interparticle interfaces induced from clever coupling of constituents can donate surface sites in heterojunction nanostructures for enhancing catalytic activity. We aim to present selective growth concepts for bringing single particles into heterojunctions such as Ag-photodeposited TiO<sub>2</sub> nanorods, metal sulfide-exchanged TiO<sub>2</sub> nanodisks, and metal (Ag, Au)-amino acid, diamine functionalized oxide (CeO<sub>2</sub>, MnWO<sub>4</sub>, La<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>) nanohybrids. Engineering porosity into the nanostructures was performed by templating capable of amplifying reactant diffusion for reaction performance. We presented significant attempts to exploit self-construction of the particles into mesoporous nanostructures such as metal (Ag, Au)/oxide (CeO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>) nanocomposites, chiral CdS-encapsulated SiO<sub>2</sub> thin films, and silica-templated mixed oxide (*e.g.*, Cu/CeO<sub>2</sub>) nanosized replicas.

Conversion of energy from photons in sunlight to chemicals is the most promising technology for producing renewable fuels in the future. The nanostructured features of the engineered nanomaterials were presented through progress in synergistic interactions to boost the activity and selectivity in solar energy conversion for solar water splitting, CO<sub>2</sub> photoreduction, and organic photodecomposition. We discuss synergistic effects of the assembly-induced interfaces and pores involved in the engineered nanostructures on the enhanced reaction activity via inspiration from the artificial photosynthesis. Along with expressive achievements of the integrated catalysts available from the literatures, our recent works highlighted the

successful development of the integrated catalysts, *e.g.*, CdS-TiO<sub>2</sub>-Ni disks and Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-PtO<sub>x</sub> hollows for superior H<sub>2</sub> evolution and Au/TiO<sub>2</sub> hollow nanocrystals for decomposition of volatile organic compounds (VOCs) under visible light. We demonstrated layer-by-layer assembly of TiO<sub>2</sub> nanodisks with SiO<sub>2</sub> nanospheres to obtain ordered thin-shell Au/TiO<sub>2</sub> hollow nanospheres with enhanced photodecomposition of VOCs. Tailoring the structural geometry of the photocatalysts decorated with metal-based cocatalysts leads to an enhancement in energy conversion efficiency. Our researches showed that Ni cocatalysts incorporated selectively into CdS/TiO<sub>2</sub> hybrid nanodisks yield water-dispersible heterojunctions that are highly active for natural sunlight-driven water splitting. The integration of PtO<sub>x</sub> cocatalysts into Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanohollows afforded new visible light-driven photocatalysts showing high H<sub>2</sub> generation rate.

In terms of superior catalytic performance and long-term durability aspects, the economical, active photocatalysts open up practical opportunities for developing the artificial photosynthesis and other fields such as photodegradation of persistent organic pollutants and solid-processable photovoltaic cells for electrical generation. The great evolution of solar fuel technology is acknowledged over 40 years after the first demonstration of TiO<sub>2</sub> photocatalysts. However, water photosplitting still requires further improvement in order to approach the record efficiencies achieved by semiconductor solar fuel devices to compete with fossil fuels. While the conversion efficiency of CO<sub>2</sub> into valuable energy-bearing hydrocarbons is in an embryonic state, since CO<sub>2</sub> is a highly stable molecule. It means that the component- and structural geometry-dependent photocatalytic properties and the cost of the solar-driven photocatalysts have not yet been satisfactorily investigated and many questions remain unanswered. It is therefore necessary to clarify a link between photocatalytic efficiency and cost-effectiveness of solar junction devices. Continuous researches for developing new nanomaterials will certainly facilitate tackling the unaddressed challenges and translating artificial solar-fuel generation technology into reality in the upcoming decade. Once the efficient solar-driven nanocatalysts are widely available in industrial processing activities, the alternative technology plays an alternative role in reproducing green fuels, reducing CO<sub>2</sub> emission, serving our life, and saving the planet.

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## Notes and references

† The authors declare no competing financial interest.

- B. L. Cushing, V. L. Kolesnichenko, C. J. O'Connor, *Chem. Rev.* **2004**, *104*, 3893-3946.
- S. Sumev, A. Fortunelli, F. P. Netzer, *Chem. Rev.* **2012**, *113*, 4314-4372.
- Q. Zhang, I. Lee, J. B. Joo, F. Zaera, Y. Yin, *Acc. Chem. Res.* **2012**, *46*, 1816-1824.
- Z. Nie, A. Petukhova, E. Kumacheva, *Nat. Nanotechnol.* **2010**, *5*, 15-25.
- X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.* **2010**, *110*, 6503-6570.
- C. Liu, N. P. Dasgupta, P. Yang, *Chem. Mater.* **2013**, *26*, 415-422.
- E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, C. B. Murray, *Nature* **2006**, *439*, 55-59.
- T. Mokari, C. G. Sztrum, A. Salant, E. Rabani, U. Banin, *Nat. Mater.* **2005**, *4*, 855-863.
- Y. Yamada, C. K. Tsung, W. Huang, Z. Huo, S. E. Habas, T. Soejima, C. E. Aliaga, G. A. Somorjai, P. Yang, *Nat. Chem.* **2011**, *3*, 372-376.
- S. H. Kim, J. M. Lim, S. K. Lee, C. J. Heo, S. M. Yang, *Soft Matter* **2010**, *6*, 1092-1110.
- C. T. Dinh, Y. Hoang, F. Kleitz, T. O. Do, *Angew. Chem. Int. Ed.* **2014**, *53*, 6618-6623.
- D. Gu, F. Schuth, *Chem. Soc. Rev.* **2013**, *43*, 313-344.
- U. Banin, Y. B. Shahar, K. Vinokurov, *Chem. Mater.* **2013**, *26*, 97-110.
- T. Yasuhiro, V. Lionel, R. D. James, *Nat. Photonics* **2012**, *6*, 511-518.
- M. Josef, *Nat. Chem.* **2011**, *3*, 268-269.
- J. Low, S. Cao, J. Yu, S. Wageh, *Chem. Commun.* **2014**, *50*, 10768-10777.
- N. S. Lewis, Nocera, D. G. *Proc. Natl. Acad. Sci.* **2006**, *103*, 15729-15735
- J. Michl, *Nat. Chem.* **2011**, *3*, 268-269.
- R. Costi, A. E. Saunders, U. Banin, *Angew. Chem. Int. Ed.* **2010**, *49*, 4878-4897.
- P. Zhou, J. Yu, M. Jaroniec, *Adv. Mater.* **2014**, *26*, 4920-4935.
- J. Yang, D. Wang, H. Han, C. Li, *Acc. Chem. Res.* **2013**, *46*, 1900-1909.
- D. Wang, T. Xie, Q. Peng, Y. Li, *J. Am. Chem. Soc.* **2008**, *130*, 4016-4022.
- C. T. Dinh, Y. Seo, T. D. Nguyen, F. Kleitz, T. O. Do, *Angew. Chem. Int. Ed.* **2012**, *51*, 6608-6612.
- T. D. Nguyen, C. T. Dinh, T. O. Do, *Inorg. Chem.* **2011**, *50*, 1309-1320.
- T. D. Nguyen, C. T. Dinh, T. O. Do, *ACS Nano* **2010**, *4*, 2263-2273.
- T. D. Nguyen, D. Mrabet, T. T. D. Vu, C. T. Dinh, T. O. Do, *CrystEngComm* **2011**, *13*, 1450-1460.
- X. Liang, X. Wang, Y. Zhuang, B. Xu, S. Kuang, Y. Li, *J. Am. Chem. Soc.* **2008**, *130*, 2736-2737.
- H. Deng, C. Liu, S. Yang, S. Xiao, Z. K. Zhou, Q. Q. Wang, *Cryst. Growth Des.* **2008**, *8*, 4432-4439.
- M. B. Dickerson, K. H. Sandhage, R. R. Naik, *Chem. Rev.* **2008**, *108*, 4935-4978.
- S. Ding, F. Huang, X. Mou, J. Wu, X. Lu, *J. Mater. Chem.* **2011**, *21*, 4888-4892.
- R. J. Macfarlane, B. Lee, M. R. Jones, N. Harris, G. C. Schatz, C. A. Mirkin, *Science* **2011**, *334*, 204-208.
- C. I. Aguirre, E. Reguera, A. Stein, *Adv. Func. Mater.* **2010**, *20*, 2565-2578.
- S. Kim, A. N. Mitropoulos, J. D. Spitzberg, H. Tao, D. L. Kaplan, F. G. Omenetto, *Nature Photon.* **2012**, *6*, 818-823.
- J. Ge, Y. Yin, *Adv. Mater.* **2008**, *20*, 3485-3491.
- H. Kim, J. Ge, J. Kim, S. Choi, H. Lee, H. Lee, W. Park, Y. Yin, S. Kwon, *Nature Photon.* **2009**, *3*, 534-540.
- M.; Wang, L. He, Y. Hu, Y. Yin, *J. Mater. Chem. C* **2013**, *1*, 6151-6156.
- T. D. Nguyen, W. Y. Hamad, M. J. MacLachlan, *Adv. Func. Mater.* **2014**, *24*, 777-783.
- K. Aoki, D. Guimard, M. Nishioka, M. Nomura, S. Iwamoto, Y. Arakawa, *Nature Photon.* **2008**, *2*, 688-692.
- T. Abitbol, D. Gray, *Chem. Mater.* **2007**, *19*, 4270-4276.
- S. Liu, S. Han, Y. Duan, S. Asahina, O. Terasaki, Y. Cao, L. Ben, L. Ma, J. Zhang, S. Che, *Nat. Commun.* **2012**, *3*, 1215-1215.
- H. Ceylan, C. O. Akgun, T. S. Erkal, I. Donmez, R. Garifullin, A. B. Tekinay, H. Usta, N. Biyikli, O. M. Guler, *Sci. Rep.* **2013**, *3*, 2306.
- B. D. Busbee, S. O. Obare, C. J. Murphy, *Adv. Mater.* **2003**, *15*, 414-416.
- C. Pacholski, A. Kornowski, H. Weller, *Angew. Chem.* **2004**, *116*, 4878-4881.
- C. T. Dinh, T. D. Nguyen, F. Kleitz, T. O. Do, *ACS Appl. Mater.* **2011**, *3*, 2228-2234.
- Q. Lu, Z. Lu, Y. Lu, L. Lv, Y. Ning, H. Yu, Y. Hou, Y. Yin, *Nano Lett.* **2013**, *13*, 5698-5702.
- C. T. Dinh, M. H. Pham, F. Kleitz, T. O. Do, *J. Mater. Chem. A* **2013**, *1*, 13308-13313.
- T. D. Nguyen, C. T. Dinh, T. O. Do, *Nanoscale* **2011**, *3*, 1861-1873.
- T. D. Nguyen, C. T. Dinh, D. Mrabet, T. M. N. Tran, T. O. Do, *Colloid Interface Sci.* **2013**, *394*, 100-107.
- C. T. Dinh, M. H. Pham, Y. Seo, F. Kleitz, T. O. Do, *Nanoscale* **2014**, *6*, 4819-4829.
- J. Luo, S. K. Karuturi, L. Liu, L. T. Su, A. L. Y. Tok, H. J. Fan, *Sci. Rep.* **2012**, *2*, 451.

- 51 J. Bao, W. Chen, T. Liu, Y. Zhu, P. Jin, L. Wang, J. Liu, Y. Wei, Y. Li, *ACS Nano* **2007**, *1*, 293-298.
- 52 D. Mrabet, M. H. Zahedi-Niaki, T. O. Do, *J. Phys. Chem. C* **2008**, *112*, 7124-7129.
- 53 H. Yen, Y. Seo, R. G. Nicolas, S. Kaliaguine, F. Kleitz, *Chem. Commun.* **2011**, *47*, 10473-10475.
- 54 H. Yen, Y. Seo, S. Kaliaguine, F. Kleitz, *Angew. Chem. Int. Ed.* **2012**, *51*, 12032-12035.
- 55 A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37-38.
- 56 T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature* **1979**, *277*, 637-638.
- 57 K. Zhou, Y. Li, *Angew. Chem. Int. Ed.* **2012**, *51*, 602-613.
- 58 Q. Xiang, J. Yu, M. Jaroniec, *Chem. Comm.* **2011**, *47*, 4532-4534.
- 59 H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, *Nature* **2008**, *453*, 638-641.
- 60 Q. Xiang, J. Yu, W. Wang, M. Jaroniec, *Chem. Comm.* **2011**, *47*, 6906-6908.
- 61 J. Yu, J. Low, W. Xiao, P. Zhou, M. Jaroniec, *J. Am. Chem. Soc.* **2014**, *136*, 8839-8842.
- 62 L. Hammarstrom, S. H. Schiffer, *Acc. Chem. Res.* **2009**, *42*, 1859-1860.
- 63 H. Tada, T. Mitsui, T. Kiyonaga, T. Akita, K. Tanaka, *Nat. Mater.* **2006**, *5*, 782-786.
- 64 L. Amirav, A. P. Alivisatos, *J. Phys. Chem. Lett.* **2010**, *1*, 1051-1054.
- 65 C. Liu, J. Tang, H. M. Chen, B. Liu, P. Yang, *Nano Lett.* **2013**, *13*, 2989-2992.
- 66 Q. Xiang, J. Yu, M. Jaroniec, *J. Am. Chem. Soc.* **2012**, *134*, 6575-6578.
- 67 O. Ola, M. M. M. Valer, *Catal. Sci. Technol.* **2014**, *4*, 1631-1637.
- 68 W. N. Wang, W. J. An, B. Ramalingam, S. Mukherjee, D. M. Niedzwiedzki, S. Gangopadhyay, P. Biswas, *J. Am. Chem. Soc.* **2012**, *134*, 11276-11281.
- 69 D. Wang, T. Hisatomi, T. Takata, C. Pan, M. Katayama, J. Kubota, K. Domen, *Angew. Chem. Int. Ed.* **2013**, *52*, 11252-11256.
- 70 Z. Han, F. Qui, R. Eisenberg, P. L. Holland, T. D. Krauss, *Science* **2012**, *338*, 1321-1324.
- 71 W. J. Ong, M. M. Gui, S. P. Chai, *RSC Adv.* **2013**, *3*, 4505-4509.
- 72 M. H. Pham, C. T. Dinh, G. T. Vuong, N. D. Ta, T. O. Do, *Phys. Chem. Chem. Phys.* **2014**, *16*, 5937-5941.
- 73 H. Zhou, J. Guo, P. Li, T. Fan, D. Zhang, J. Ye, *Sci. Rep.* **2013**, *3*, 1667.
- 74 C. Wang, R. L. Thompson, J. Baltrus, C. Matranga, *J. Phys. Chem. Lett.* **2009**, *1*, 48-53.
- 75 X. Wang, G. Liu, L. Wang, Z. G. Chen, G. Q. Lu, H. M. Cheng, *Adv. Energy Mater.* **2012**, *2*, 42-46.