

Metal–Organic Frameworks for Photocatalysis and Photothermal Catalysis

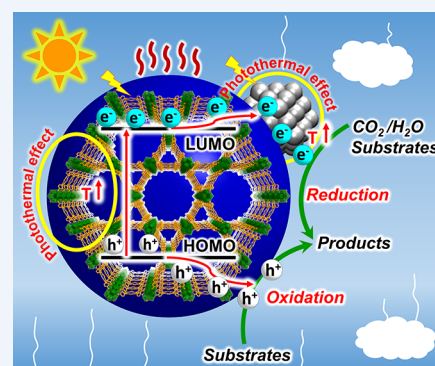
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CONSPECTUS: To meet the ever-increasing global demand for energy, conversion of solar energy to chemical/thermal energy is very promising. Light-mediated catalysis, including photocatalysis (organic transformations, water splitting, CO₂ reduction, etc.) and photothermal catalysis play key roles in solar to chemical/thermal energy conversion via the light–matter interaction. The major challenges in traditional semiconductor photocatalysts include insufficient sunlight utilization, charge carrier recombination, limited exposure of active sites, and particularly the difficulty of understanding the structure–activity relationship. Metal–organic frameworks (MOFs), featuring semiconductor-like behavior, have recently captured broad interest toward photocatalysis and photothermal catalysis because of their well-defined and tailorable porous structures, high surface areas, etc. These advantages are beneficial for rational structural modulation for improved light harvesting and charge separation as well as other effects, greatly helping to address the aforementioned challenges and especially facilitating the establishment of the structure–activity relationship. Therefore, it is increasingly important to summarize this research field and provide in-depth insight into MOF-based photocatalysis and photothermal catalysis to accelerate the future development.

In this Account, we have summarized the recent advances in these two directly relevant applications, photocatalysis and photothermal catalysis, mainly focusing on the results in our lab. Given the unique structural features of MOFs, we have put an emphasis on rational material design to optimize the components and performance and to understand related mechanisms behind the enhanced activity. This Account starts by presenting an overview of solar energy conversion by catalysis. We explain why MOFs can be promising photocatalysts and exemplify the semiconductor-like behavior of MOFs. More importantly, we show that MOFs provide a powerful platform to study photocatalysis, in which the involved three key processes, namely, light harvesting, electron–hole separation, and surface redox reactions, can be rationally improved. Meanwhile, the structure–activity relationship and charge separation dynamics are illustrated in this part. In addition, MOFs for photothermal catalysis have been introduced that are based on the photothermal effect of plasmonic metals and/or MOFs, together with light-driven electronic state optimization of active sites, toward enhanced heterogeneous organic reactions. Finally, our brief outlooks on the current challenges and future development of MOF photocatalysis and photothermal catalysis are provided. It is believed that this Account will afford significant understanding and inspirations toward solar energy conversion over MOF-based catalysis.



1. INTRODUCTION

Solar energy has become a promising alternative to conventional fossil fuels. Despite the abundance and versatility, solar energy utilization and storage present a scientific challenge because of the limited conversion efficiency.¹ Light-mediated catalysis, including photocatalysis and photothermal catalysis, play key roles in the conversion of solar photons to chemicals, fuels, and heat. Based on the light–matter interaction, the exploration of semiconductor photocatalysis has gathered intensive efforts in recent years.^{2,3}

Metal–organic frameworks (MOFs), a class of crystalline porous solids composed of metal ions/clusters and organic linkers, featuring diversified and tailorable structures as well as high surface areas, have captured widespread interest in gas

sorption and separation, sensors, catalysis, etc.^{4–12} Compared with conventional inorganic semiconductors, MOFs have been recently explored toward photocatalysis thanks to their unique advantages in following aspects: (1) the high porosity of MOFs allows the exposure/accessibility of active sites for catalysis and facilitates the transport of substrates/products; (2) the structural tunability of MOFs endows great opportunity to extend the light response over a broad range; (3) the crystalline nature with eliminated structural defects, which are usually centers of electron–hole (e–h) recombination, makes their volume recombination greatly suppressed; (4) the porous

Received: October 17, 2018

Published: December 20, 2018

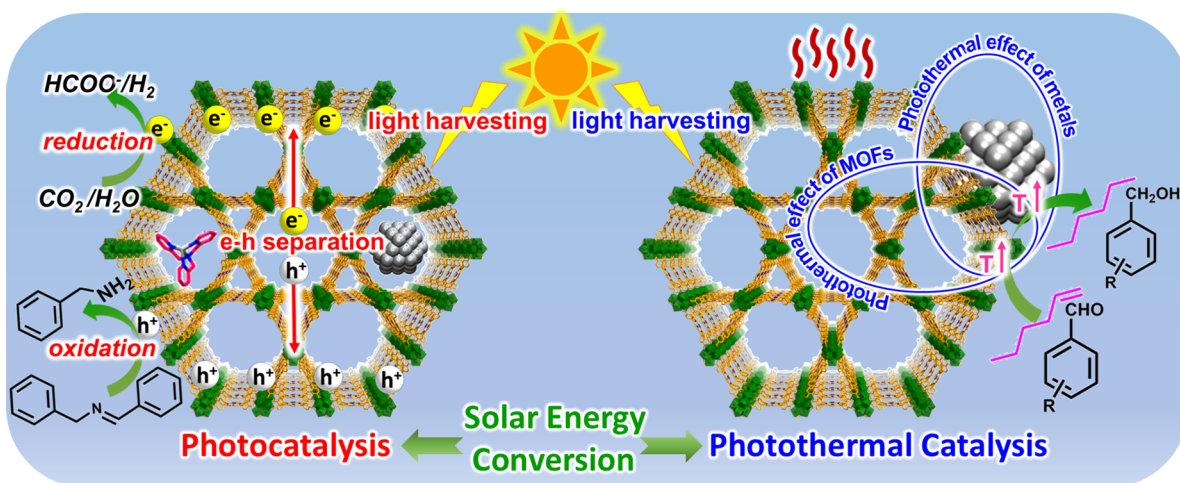


Figure 1. Schematic showing photocatalysis and photothermal catalysis promoted by MOFs.

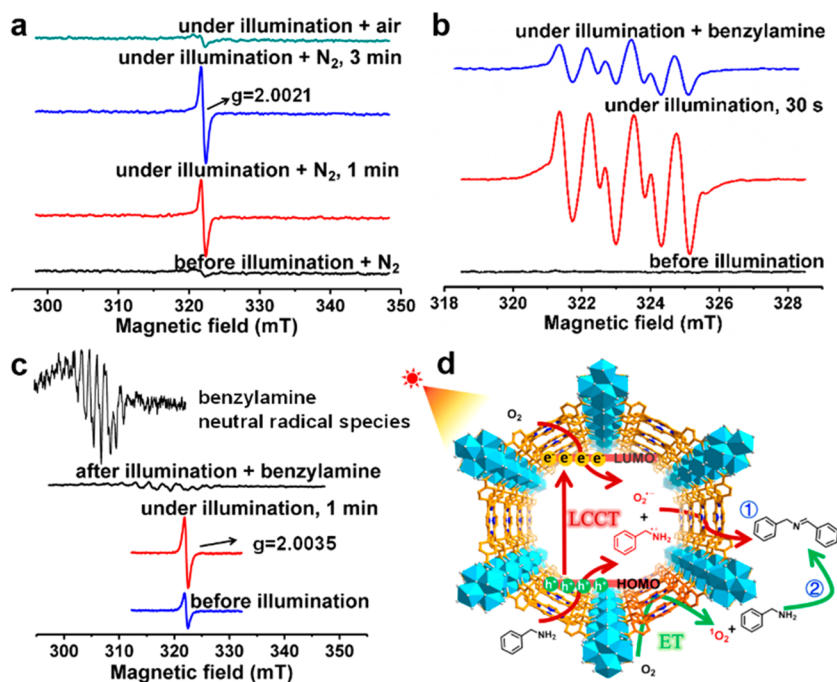


Figure 2. (a–c) ESR detection of (a) the electron transfer process, (b) electron-involved, and (c) hole-involved intermediates in PCN-222. (d) Schematic showing the charge and energy transfer processes in PCN-222. Adapted with permission from ref 20. Copyright 2018 Royal Society of Chemistry.

structure creates short migration paths for charge carriers prior to their reaction with substrates, thus improving the e–h separation; (5) the photosensitizer or the cocatalyst can be flexibly positioned on the framework or in the pore space, favoring the spatial separation of e–h pairs; and (6) the well-defined and tailorable MOF structures hold great advantages in the understanding of the structure–activity relationship. Because of these merits, great efforts have been devoted to developing MOF-based materials toward photocatalysis in recent years.^{13–17} However, in-depth understanding of the related photocatalytic mechanisms remains limited to date. In addition, photothermal catalysis over MOFs is at a nascent stage but exhibits significant promoting effects toward heterogeneous organic reactions.

Toward the future development of photoassisted heterogeneous catalysis, this Account presents an overview of recent

advances in two directly relevant applications, photocatalysis and photothermal catalysis, over MOFs with unique structure advantages, placing the emphasis on the related mechanisms behind the enhanced activity (Figure 1). Starting with direct evidence of MOF charge separation, we exemplify the semiconductor-like behavior and explain why MOFs can be promising photocatalysts. Next, given that photocatalysis involves three crucial processes, namely, light harvesting, e–h separation, and surface redox reactions, we present how these key processes can be improved by MOF-based photocatalysts. The subsequent part introduces MOFs for photothermal catalysis via the photothermal effect and/or light-induced electronic state optimization of active sites toward heterogeneous organic reactions. Finally, our perspectives on current challenges and future development of MOF photocatalysis and photothermal catalysis are briefly discussed.

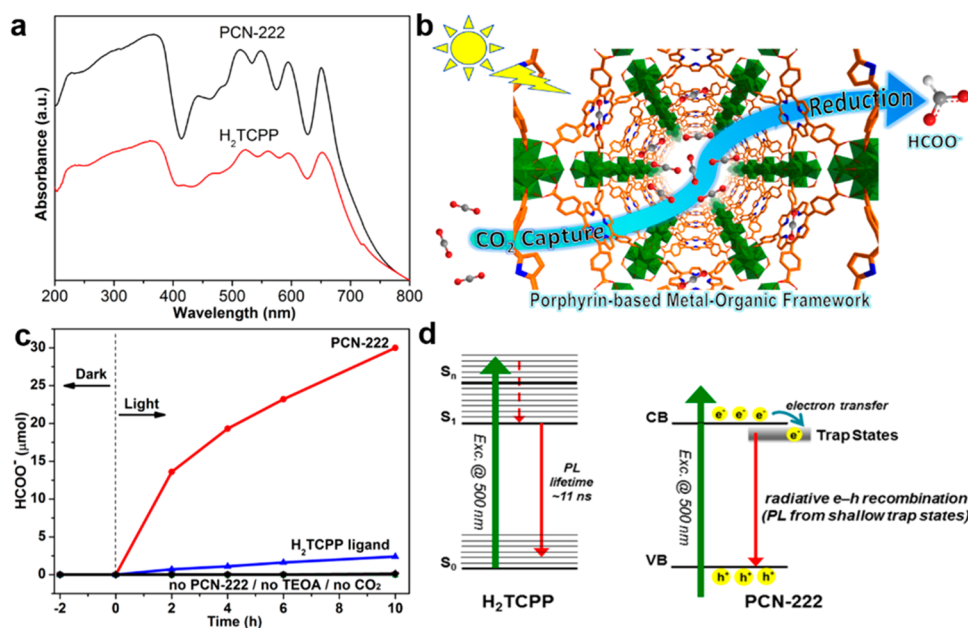


Figure 3. (a) UV-vis spectra of H₂TCPP and PCN-222. (b) Schematic showing photocatalytic CO₂ reduction over PCN-222. (c) Photocatalytic activity in the presence of PCN-222 or the H₂TCPP ligand or in the absence of PCN-222/TEOA/CO₂ molecules. (d) Mechanisms involved in H₂TCPP and PCN-222 based on TA and PL results. Adapted from ref 25. Copyright 2015 American Chemical Society.

2. CHARGE SEPARATION AND SEMICONDUCTOR-LIKE BEHAVIOR OF MOFs

Generally, a complete photocatalytic cycle includes light harvesting, e-h separation, and redox reactions. Typically, MOFs are able to harness sunlight with energy equal to or greater than their band edge. It is assumed that upon light irradiation, electrons are excited to the lowest unoccupied molecular orbital (LUMO) of MOFs, leaving holes in the highest occupied molecular orbital (HOMO) and generating e-h pairs. Then redox reactions take place once the charge carriers migrate to the MOF surface and meet the substrates.

Though the studies of semiconductor-like behavior of MOFs have lasted for ~10 years,¹⁸ unfortunately only electron-mediated metal ions/clusters were detected. The corresponding radical cations, such as excited organic linkers, have not been directly recognized. Direct evidence of both electron- and hole-mediated species in MOF photocatalysts is important to unveil charge separation and semiconductor-like behavior of MOFs.

Following the goal to understand the charge separation process in MOFs, a representative zirconium porphyrin MOF, PCN-222,¹⁹ has been investigated for visible-light photocatalytic aerobic oxidative coupling of amines.²⁰ Electron transfer from the porphyrin ligand to Zr-oxo clusters occurs under visible-light irradiation, giving oxygen-centered active sites with electron spin resonance (ESR) signal of $g = 2.0021$ (Figure 2a). Subsequently, electrons migrate from Zr-oxo clusters to O₂, producing O₂^{•-} (Figure 2b). Additionally, the hole-involved porphyrin π cation radicals were also detected at an ESR signal of $g = 2.0035$, which were quenched immediately once benzylamine was injected, suggesting hole transfer (Figure 2c). The ligand-to-cluster charge transfer (LCCT) process, where O₂^{•-} and benzylamine radicals are produced to promote the oxidative coupling of benzylamine, can be clearly elucidated by the ESR results. In addition, the ¹O₂ species generated by energy transfer (ET) directly reacts with benzylamine to achieve this conversion (Figure 2d).

Direct evidence of charge separation and the semiconductor-like behavior of MOFs were obtained in this work, as verified by the ESR signals of electron- and hole-involved intermediates. Of course, we call this “semiconductor-like behavior of MOFs” because MOFs have intrinsic differences with genuine semiconductors. The semiconductivity originates from delocalized valence and conduction bands, through which charge transport occurs. Though conductivity in conductive MOFs was recently studied using time-resolved terahertz spectroscopy,²¹ unfortunately the localized nature of electronic states in most MOFs makes them have much lower charge mobility than common semiconductors. However, as demonstrated in the above work, the photoexcitation and charge separation behaviors are crucial, allowing the MOFs behave similarly to a real photocatalyst, which provides important understanding for MOF photocatalysis.

3. MOFs FOR PHOTOCATALYSIS

To gain insight into the relationship between the structural tailorability of MOFs and their photocatalytic performance, a series of MOFs and MOF composites with tailored structures and enhanced photocatalysis have been rationally fabricated. In particular, focusing on the key processes in photocatalysis, different strategies have been developed to improve the light absorption, charge separation, and subsequent utilization.

3.1. Improving Light Harvesting

The solar energy spectrum is constituted by ~5% UV light, 42–45% visible light, and ~50% near-infrared (NIR) light. It is highly desired to extend the light absorption of photocatalysts from the UV to visible and even the NIR region to achieve improved solar energy utilization. The organic linkers with huge diversity in MOFs usually serve as antennas for light harvesting. Therefore, some methodologies have been attempted to improve the light absorption of MOFs by furnishing aromatic carboxylate ligands with -NH₂ or other groups,^{22,23} integrating functional metal complexes,²⁴ etc. While such a strategy has

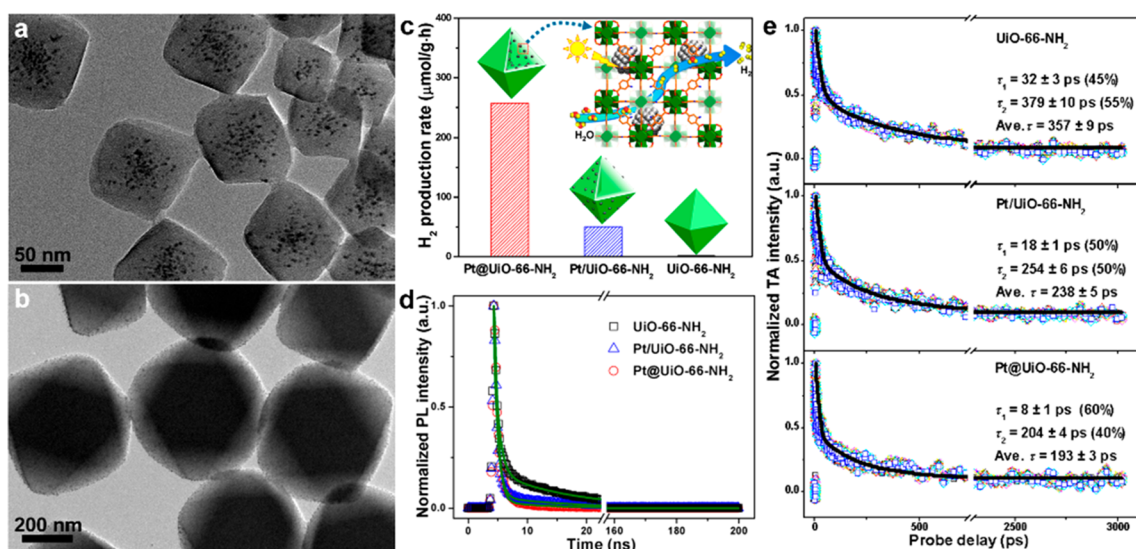


Figure 4. (a, b) Typical TEM images of (a) Pt@UiO-66-NH₂ and (b) Pt/UiO-66-NH₂. (c) Photocatalytic H₂ production rates, (d) PL profiles, and (e) TA kinetics for different photocatalysts. Adapted with permission from ref 26. Copyright 2016 Wiley-VCH.

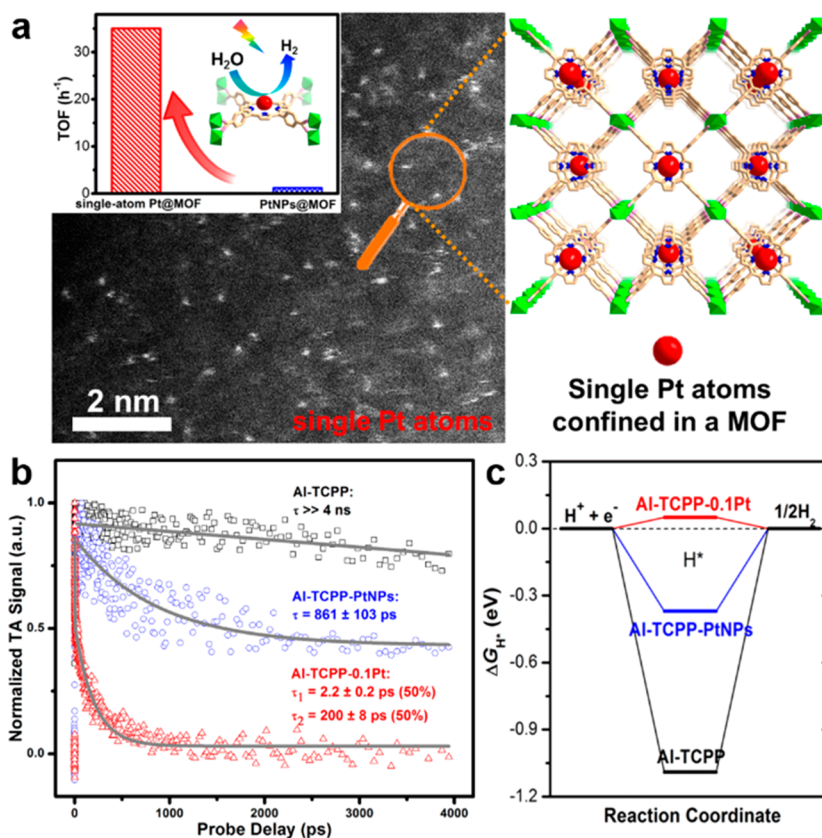


Figure 5. (a) Schematic showing Al-TCPP incorporating single-atom Pt cocatalyst for photocatalytic H₂ production. The inset shows a turnover frequency (TOF) comparison for single-atom Pt@Al-TCPP and PtNPs@Al-TCPP. (b) TA kinetics and (c) DFT calculations for different photocatalysts. Adapted with permission from ref 27. Copyright 2018 Wiley-VCH.

been demonstrated to be effective, the light response can be extended to a limited range (basically up to ~600 nm).

Porphyrins are large conjugated systems that are deeply colored and strongly absorb light in the whole visible region, which is highly desirable. Incorporating porphyrins into MOFs is an effective strategy to obtain MOFs with wide spectral response. PCN-222, featuring light response from 200 to 800 nm inherited from the porphyrin ligand, has been deliberately

employed for selective capture and photoreduction of CO₂, producing HCOO⁻ at a rate much higher than that of the H₂TCPP counterpart (Figure 3a–c).²⁵ Ultrafast transient absorption (TA) and time-resolved photoluminescence (PL) spectroscopy are powerful kinetic measurements to determine the transient species during electron transfer,¹⁶ which were conducted to illustrate the pertinent mechanisms underlying the structure–activity relationship (Figure 3d). In PCN-222, there

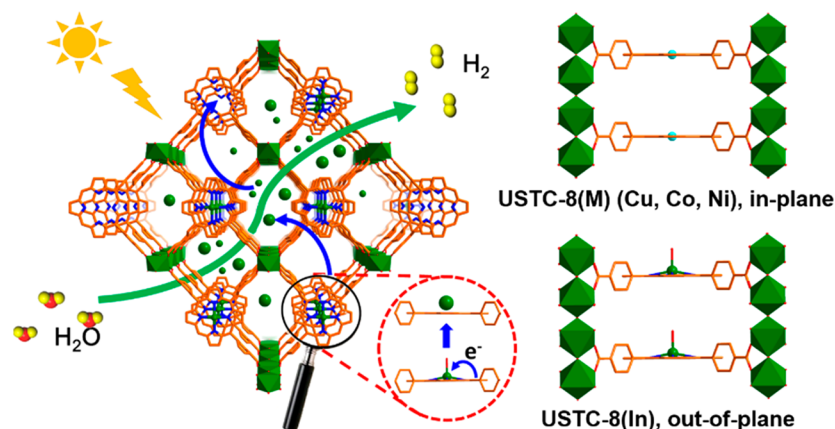


Figure 6. (left) Schematic showing the proposed photocatalytic mechanism in USTC-8(In). (right) Partial structures in USTC-8 highlighting the different locations of the metal centers in the metalloporphyrin. Adapted from ref 29. Copyright 2018 American Chemical Society.

are two common near-band-edge trap states, as nicely reflected by the fitting lifetimes from both TA and PL results. Nevertheless, the third trap state with an extremely long lifetime (typically in the nanosecond domain), which is a unique and rather deep trap state and enables the suppression of e–h recombination and the accumulation of long-lived electrons, is responsible for the high CO₂ reduction activity.

3.2. Boosting Electron–Hole Separation

The e–h separation plays a central role in photocatalysis. Acquiring fundamental information on charge separation and migration in MOFs would be significant to rationalize further design of photocatalysts. Various strategies in MOF-based photocatalyst systems have been developed to boost e–h separation. One of the most successful strategies is to fabricate MOF-based composites by incorporating cocatalysts. However, detailed information disclosing how to promote the e–h separation remains limited.

3.2.1. Influence of the Location and Size of the Pt Cocatalyst in MOF Composites. In conventional semiconductor photocatalysts, metal NPs are usually introduced to promote e–h separation. Similarly, metal NP/MOF composites,¹⁰ where metal NPs act as electron acceptors or cocatalysts, are also effective to boost e–h separation. In addition to the congenital advantage provided by the porosity of MOFs, the location and size of the cocatalyst should play important roles, as these factors will directly affect the migration path length of charge carriers and the utilization efficiency of active centers.

To investigate the influence of the cocatalyst location relative to the MOF particle, we deliberately incorporated Pt NPs (~3 nm) into or onto a typical MOF, UiO-66-NH₂, to afford Pt@UiO-66-NH₂ and Pt/UiO-66-NH₂, respectively (Figure 4a,b).²⁶ With fixed Pt size and content, Pt@UiO-66-NH₂ exhibits a much higher photocatalytic H₂ production rate than Pt/UiO-66-NH₂ and UiO-66-NH₂ (Figure 4c), indicating that the Pt location dominates the photocatalytic efficiency. TA and PL spectroscopy give the involved electron-transfer mechanism (Figure 4d,e), in which the acceleration of the TA decay kinetics in Pt–MOF composites should be attributed to the opening of a new electron-transfer channel from the MOF to Pt; with opening of this additional channel, the PL lifetime in Pt–MOF composites is shortened, further indicating the suppression of the photogenerated e–h recombination (Figure 4d,e). Accordingly, compared with Pt/UiO-66-NH₂, more efficient charge

separation is achieved in Pt@UiO-66-NH₂, leading to significantly higher H₂ production activity.

Considering the significance of the Pt cocatalyst in photocatalysis, the influence of its size on the photocatalytic efficiency was then studied.²⁷ Intuitively, smaller Pt NPs lead to higher atom economy. Therefore, it is necessary to reduce the Pt size as far as possible. Bearing this in mind, we first achieved single-atom Pt (0.1–0.2 nm) confined into a highly stable aluminum porphyrin MOF, Al-TCPP,²⁸ to afford Al-TCPP-0.1Pt, featuring a much higher photocatalytic activity than the Pt NPs (~3 nm) counterpart, Al-TCPP-PtNPs (Figure 5a). The dramatically reduced lifetime of Al-TCPP-0.1Pt in contrast to Al-TCPP-PtNPs and Al-TCPP from TA results suggests the stronger interaction between Al-TCPP and single-atom Pt, providing highly efficient electron transfer channels and suppressing the detrimental e–h recombination (Figure 5b). Furthermore, density functional theory (DFT) calculations showed that Al-TCPP-0.1Pt has a much-improved H binding free energy (Figure 5c), which guarantees both efficient electron–proton acceptance to form H* and fast/favorable hydrogen desorption, accounting for the superior photocatalytic activity.

3.2.2. Influence of Metal Location in the Metalloporphyrin. Not only does the cocatalyst location in the photocatalyst composites affect the activity, but also, the metal location of the metalloporphyrin involved in MOF photocatalysts also plays a special role in e–h separation.²⁹ An indium-based porphyrinic MOF, USTC-8(In), with additional In³⁺ ions located out of plane (OOP) with respect to the porphyrin plane, displays a much higher photocatalytic H₂ production rate than other USTC-8(M) MOFs (M = Cu, Co, Ni) with identical structures except that the metal ions are located in the plane of the porphyrin (Figure 6). The results suggest that the metal location in the metalloporphyrin matters. It is proposed that the In³⁺ at the OOP porphyrin is reduced and detached from the porphyrin ring under light excitation, which induces spatial e–h separation and inhibits the electron back-transfer and e–h recombination, thus resulting in more efficient photocatalysis.

3.2.3. Spatial Charge Separation in MOF Composites. The classical noble metals (particularly Pt) used as electron acceptors are effective for improving charge separation. However, expensive Pt has limited reserves. Therefore, other cost-effective cocatalysts, for example, transition metal complexes, metal phosphides/sulfides, etc., would be more preferred.

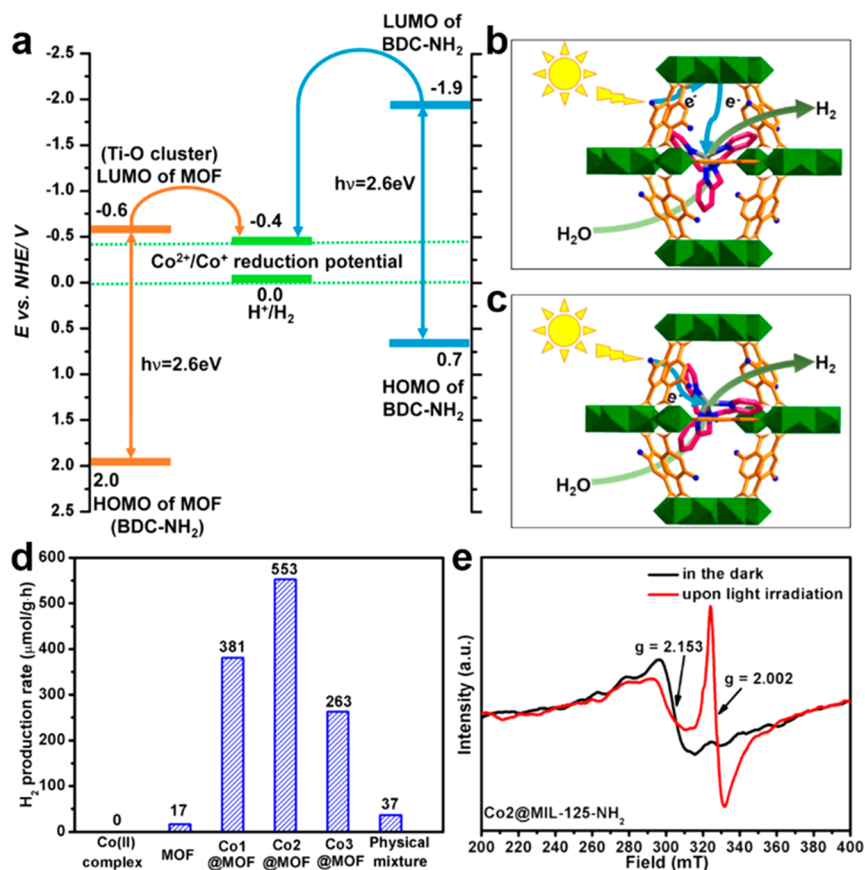


Figure 7. (a) Redox potentials of different species. (b, c) Proposed electron transfer between the Co(II) complex and (b) MIL-125-NH₂ or (c) BDC-NH₂. (d) Photocatalytic activities over different photocatalysts. (e) ESR spectra of Co₂@MIL-125-NH₂. Adapted from ref 31. Copyright 2016 American Chemical Society.

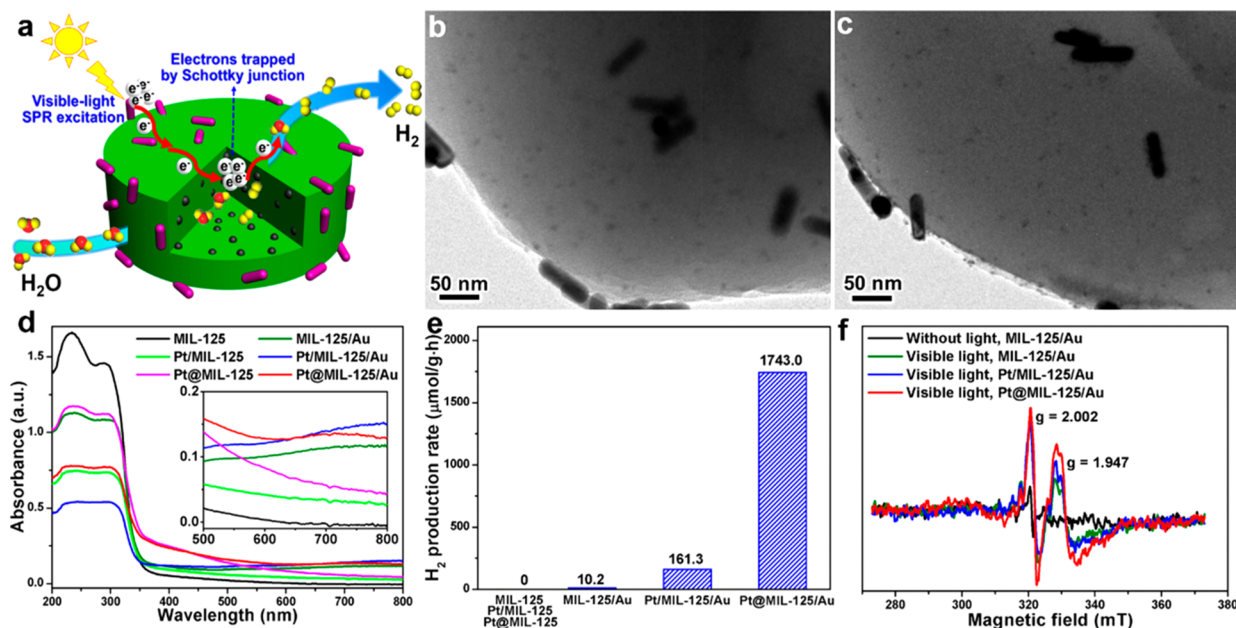


Figure 8. (a) Schematic showing the electron migration path and photocatalytic H₂ production over Pt@MIL-125/Au. (b, c) Typical TEM images of (b) Pt@MIL-125/Au and (c) Pt/MIL-125/Au. (d) UV/vis spectra, (e) photocatalytic H₂ production rates, and (f) ESR spectra of different photocatalysts. Adapted with permission from ref 33. Copyright 2018 Wiley-VCH.

Transition metal complexes exhibit good photocatalytic performance but suffer from the drawback of their homogeneous nature, and expensive photosensitizers are usually required

during the photocatalysis.³⁰ By selecting a Co(II) complex with a larger size than the MOF pore opening but a smaller size than the MOF pore diameter, we rationally fabricated a MOF

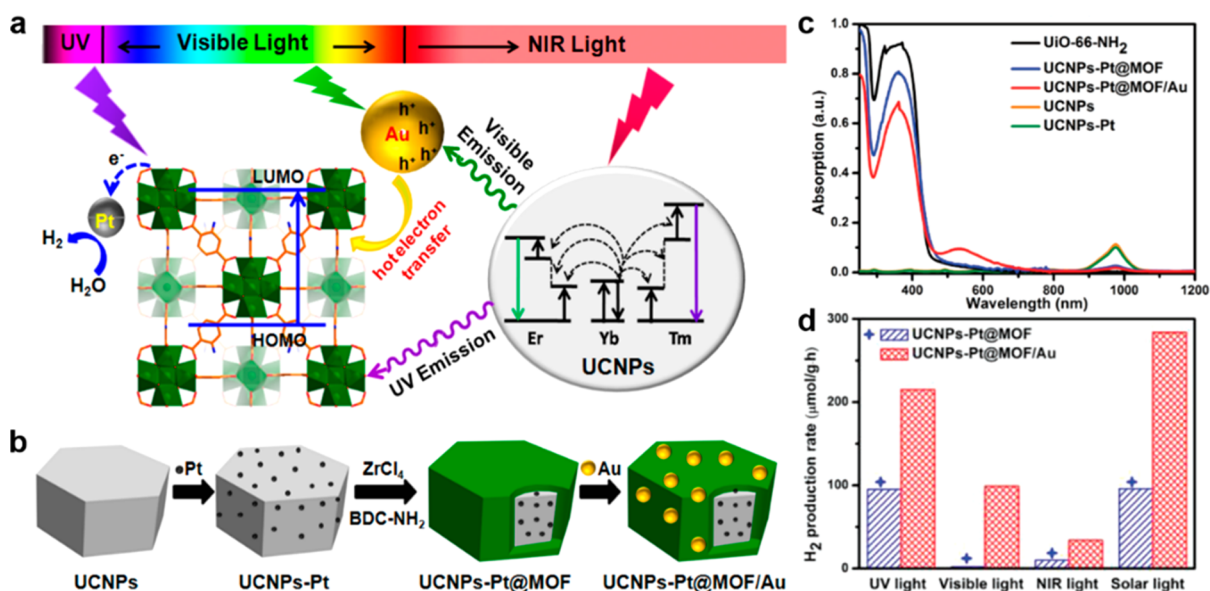


Figure 9. (a, b) Schematics showing (a) the mechanism involved in photocatalytic H₂ production and (b) the synthetic process for UCNP-Pt@MOF/Au. (c) UV–vis–NIR absorption spectra and (d) photocatalytic activity comparison under UV, visible, NIR (980 nm, emitted by laser), and simulated solar light irradiation. Adapted with permission from ref 36. Copyright 2018 Wiley-VCH.

composite, Co(II) complex@MIL-125-NH₂, via a “ship in a bottle” two-step synthesis.³¹ The redox potential of the Co(II) complex is located between the LUMO of MIL-125-NH₂ (also BDC-NH₂) and the H⁺/H₂ potential, which facilitates acceptance of electrons from the MOF or BDC-NH₂ for photocatalytic H₂ production (Figure 7a–c). In this way, spatial e–h separation is effectively realized. The best performance can be achieved with optimized component ratio (Figure 7d). ESR results (Figure 7e) suggest direct photoinduced electron transfer from BDC-NH₂ to the Co(II) complex for proton reduction (Figure 7c), not or seldom passing through Ti–oxo clusters. The spatial separation between the host MOF and guest Co(II) complex greatly accelerates charge transfer and thus improves the catalytic activity.

3.3. Simultaneously Improving Light Harvesting and Charge Separation

Given the uniqueness of structures, MOFs are able to offer the opportunity to combine both improved light harvesting and charge separation in a single photocatalyst to integrate synergistic functions of multiple components, resulting in enhanced photocatalysis.

3.3.1. Introducing Plasmonic Metals and Schottky Junction into MOFs. Nanostructured plasmonic metals can interact with light through surface plasmon resonance (SPR), which originates from the collective oscillation of electrons confined to the surface of metals. The introduction of plasmonic metals into MOFs is an effective strategy to extend the MOF light absorption.³² We recently integrated the SPR effect of plasmonic Au and Schottky junction into a wide-band-gap MOF, MIL-125, to form Au–MOF and Pt–MOF interfaces.³³ The Au plasmonic effect extending the visible-light absorption and the Pt–MOF Schottky junction promoting e–h separation have been synergistically utilized for enhanced visible-light photocatalysis (Figure 8a).

To unveil the inherent structure–activity relationship behind the synergistic effect, we deliberately fabricated Pt@MIL-125/Au and Pt/MIL-125/Au with similar Pt and Au loadings (Figure 8b,c). The SPR excitation of Au NRs gives extended light

harvesting in the visible region (700 nm) for all of the Au-involved samples (Figure 8d). Remarkably, Pt@MIL-125/Au possesses ca. 170-fold activity enhancement compared with MIL-125/Au and >10 times higher activity than Pt/MIL-125/Au (Figure 8e). The results unambiguously demonstrate the significance of both Au SPR and the location of Pt NPs. Additionally, Pt@MIL-125/Au gives the strongest Ti³⁺ signal at 1.947 among all samples, pointing to the greatly accelerated electron transfer (Figure 8f). It is believed that the spatial separation of Au and Pt by the MOF in Pt@MIL-125/Au is of great importance to form “electron flow” from Au to the MOF and finally to Pt for proton reduction under photoexcitation, which significantly inhibits the e–h recombination and thus leads to the highest activity.

3.3.2. Integrating Upconversion, SPR, and Schottky Junction into MOFs. Not limited to visible light, this approach is able to further extend the light harvesting of MOF composites to the NIR region. Upconversion (UC) is a technology to convert long-wavelength radiation, for example, IR or NIR radiation, to short-wavelength emissions, through materials doped with transition metal, lanthanide, or actinide ions. Among them, lanthanide-doped nanocrystals are the main choice and offer particular opportunities to harness NIR light for photocatalysis,³⁴ though NIR photocatalysis over MOF-based materials remains extremely rare.³⁵

By fabricating core–shell-structured upconversion nanoparticles (UCNPs)–Pt@MOF/Au composites (UCNPs denote NaYF₄: Yb, Tm, Er), we enabled the synergistic utilization of long-wavelength visible/NIR light harvesting and improved e–h separation by the Schottky junction for enhanced photocatalysis (Figure 9a,b).³⁶ The representative MOF, UiO-66-NH₂, is responsive to UV light and a bit to visible light (300–450 nm), and the plasmonic Au NPs accept visible light (500–600 nm), whereas the UCNPs absorb NIR light (980 nm) to emit UV light and visible light that are harvested by the MOF and Au once again (Figure 9c). Consequently, UCNP-Pt@MOF/Au exhibits the highest H₂ production rate (280 μmol g^{−1} h^{−1}) under simulated solar light irradiation (Figure 9d). Generally,

upon NIR irradiation, efficient energy transfer in UCNPs from Yb^{3+} to Tm^{3+} and Er^{3+} ions takes place. The upconverted UV emission from Tm^{3+} is harvested by UiO-66-NH_2 , and the upconverted visible emission from Er^{3+} is absorbed by Au. The photoexcited electrons in UiO-66-NH_2 and hot electrons from Au rapidly migrate to Pt sites for proton reduction, achieving NIR photoactivity. As a result, for the first time, SPR and upconversion effects have been integrated into a MOF photocatalyst to greatly extend light absorption, and the Pt–MOF Schottky junction further boosts the charge separation, conceptually realizing the excellent photocatalysis toward all UV, visible, and NIR regions.

3.4. Promoted Redox Reactions: Coupling H_2 Production with Valuable Organic Oxidation

Presently, almost all reports of photocatalytic water splitting over MOF-based materials are based on a half-reaction, while the other half-reaction is sacrificed by electron/hole donors. As O_2 has limited commercial value and its separation from H_2 is costly, it is possible to replace the sacrificial agent consumption or O_2 evolution with organic oxidation, which further enables the synthesis of value-added organic chemicals. Moreover, coupling of H_2 production with valuable organic oxidation was successful with semiconductor-based photocatalysts, for example, Ni-decorated CdS nanorods and carbon nitride–NiP photocatalyst,^{37,38} which should be possible for MOF photocatalysts.

Following this idea, we attempted the full use of electrons and holes by coupling the photocatalytic H_2 production half-reaction with value-added benzylamine oxidation over a MOF, PCN-777, involving a conjugated 4,4',4''-(1,3,5-triazine-2,4,6-triyl)-tribenzoic acid (H_3TATB) ligand (Figure 10a).³⁹ In the presence of Pt as a cocatalyst, the electrons rapidly reduce protons to generate H_2 ($332 \mu\text{mol g}^{-1} \text{h}^{-1}$) and the holes promote considerable benzylamine oxidation to *N*-benzylben-

zaldimine ($486 \mu\text{mol g}^{-1} \text{h}^{-1}$) with high selectivity under photoexcitation (Figure 10b). The results suggest that the conjugated ligand TATB in PCN-777 benefits the charge separation, as supported by DFT calculation results showing that the HOMO and LUMO in PCN-777 are spatially spaced, facilitating the e–h separation and thus enhancing the photocatalytic efficiency. This was the first report on employing electrons for H_2 generation and holes for promoting organic transformation over a MOF-based photocatalyst, providing a promising solution for simultaneous utilization of photo-generated electrons and holes.

4. MOF-BASED PHOTOTHERMAL CATALYSIS

The photothermal effect is an alternative approach for efficient solar energy conversion. Upon light irradiation, except for e/h-engaged redox reactions over photocatalysts, thermal energy (heat) can be produced on the basis of the photothermal effect caused by the photoexcitation of semiconducting materials (e.g., plasmonic noble metals, carbon-based materials, etc.) with local heating of the lattice to promote endothermic reactions. Photothermal catalysis over MOF-based materials is a seldom developed yet very promising field.

4.1. Photothermal Effect by Plasmonic Metals in MOF-Based Composites

The porous character endows MOFs with particular advantages to achieve additional functions via pore space engineering. It is convenient to introduce guest species, such as metal NPs, into MOFs for improved catalytic performance by integrating synergistic advantages of MOFs and NPs. We rationally incorporated nonclassical plasmonic Pd nanocubes (NCs) into a representative MOF, ZIF-8, to yield a core–shell-structured Pd NCs@ZIF-8 composite for selective hydrogenation reactions (Figure 11a).⁴⁰ The Pd NCs are well-dispersed inside ZIF-8 particles (Figure 10b), preventing Pd aggregation and guaranteeing the recyclability. Taking advantage of the SPR-driven photothermal effect of Pd NCs better promotes the endothermic reaction at ambient temperature under light irradiation instead of heating (Figure 11c). Meanwhile, the ZIF-8 shell guarantees the transport of substrates/products to access Pd sites and enables H_2 enrichment, leading to a much higher activity of Pd NCs@ZIF-8 compared with Pd NCs (Figure 11d). Moreover, size-selective catalysis can be achieved on the basis of the well-defined pore structure of ZIF-8. This was the first attempt to combine the photothermal effect of metal nanocrystals with the favorable properties of MOFs to accelerate catalytic reactions, opening up an avenue to photothermal solar energy conversion instead of heating to boost catalysis.

4.2. Photothermal Effect by Both Plasmonic Metals and MOFs in MOF-Based Composites

Previous reports showed that the photothermal effect can be induced by not only metals but also some carbon-based polymeric agents.⁴¹ Porphyrin nanoparticles are also promising alternatives.⁴² Therefore, porphyrinic MOFs are believed to possess a photothermal effect. With this idea, we first achieved synergistic photothermal conversion by both metal nanocrystals and MOFs, accelerating selective oxidation of alcohols (Figure 12a).⁴³

To synergistically utilize the photothermal effects from both noble metals and MOFs, we fabricated Pt/PCN-224(M) composites (Figure 12b), in which both PCN-224(M) and Pt nanocrystals exhibit a photothermal effect and are able to

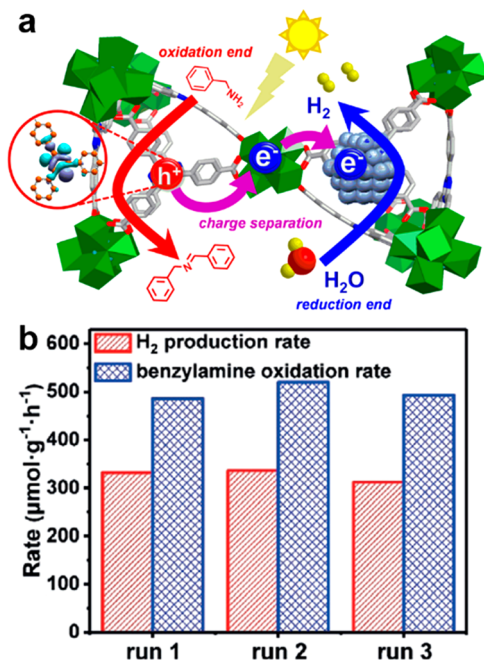


Figure 10. (a) Schematic illustration showing simultaneous photocatalytic H_2 production and benzylamine oxidation over Pt/PCN-777 and (b) the recycling performance. Adapted with permission from ref 39. Copyright 2018 Wiley-VCH.

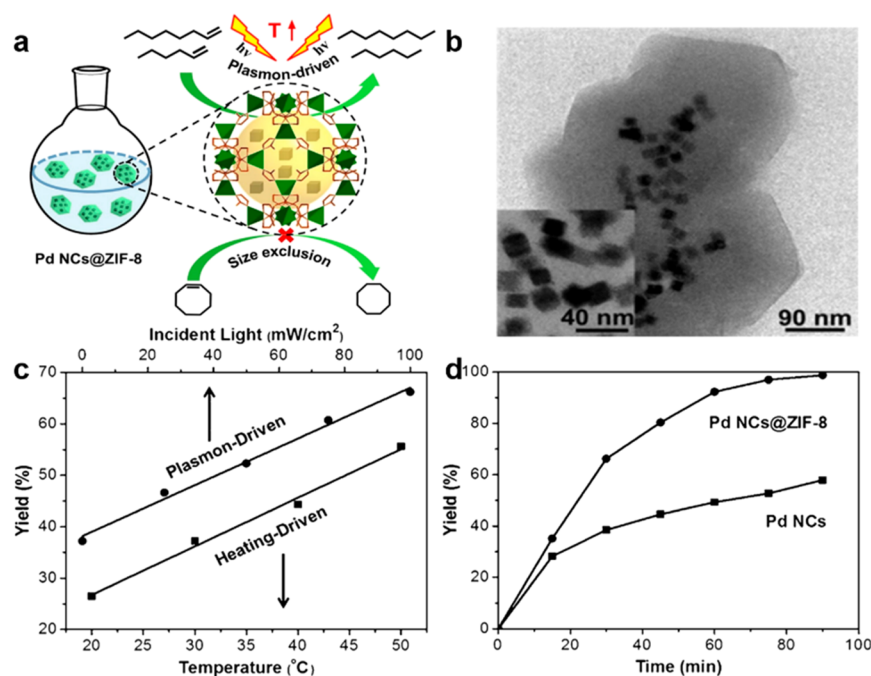


Figure 11. (a) Schematic illustration showing Pd NCs@ZIF-8 for phototherm-accelerated selective hydrogenation of olefins. (b) Typical TEM image (inset: enlarged view) of Pd NCs@ZIF-8. (c) Reaction yields of the hydrogenation of 1-hexene at 1 atm H_2 over Pd NCs@ZIF-8 under full-spectrum irradiation with different light intensities at ambient temperature or under heating at different temperatures. (d) Catalytic kinetic curves of Pd NCs and Pd NCs@ZIF-8. Adapted with permission from ref 40. Copyright 2016 Wiley-VCH.

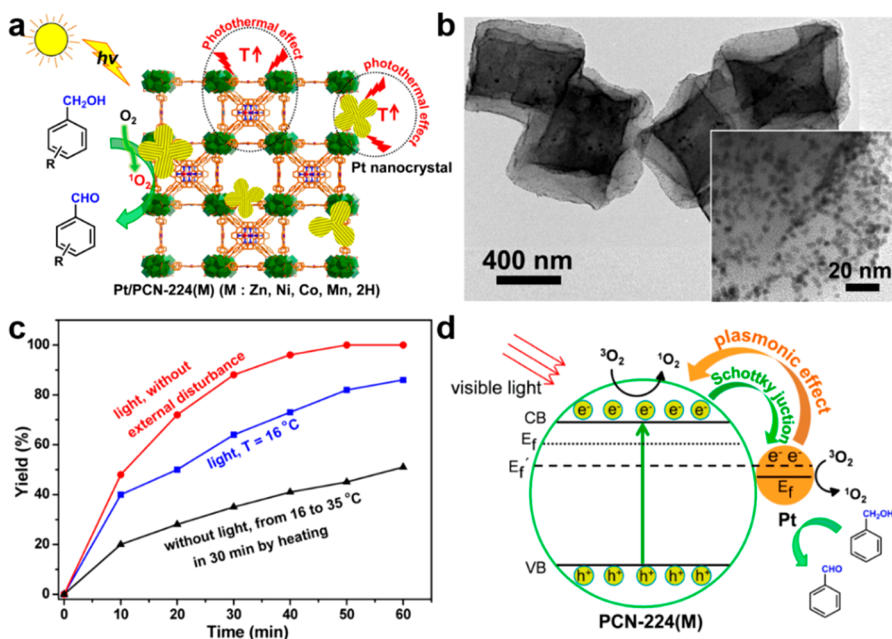


Figure 12. (a) Schematic showing the photothermal effect of both Pt nanocrystals and the MOF as well as $^1\text{O}_2$ -engaged selective oxidation of alcohols over Pt/PCN-224(M). (b) Typical TEM image and (c) catalytic efficiency of Pt/PCN-224(Zn) with or without light irradiation or external heating. (d) Mechanism involved in $^1\text{O}_2$ generation and electron transfer in the photothermal catalysis. Adapted from ref 43. Copyright 2017 American Chemical Society.

activate O_2 to $^1\text{O}_2$ under light irradiation. Apparently, exposure of the reaction system to light irradiation is important, where light not only can be converted to heat but also induces the oxygen activation. In contrast, simple heating or light irradiation with manually controlled low temperature is detrimental to the reaction (Figure 12c). Detailed characterizations show that the Pt electronic state can be flexibly tailored by adjusting the light intensity via the competitive electron transfer between Pt and

PCN-224(Zn), which affects the catalytic performance (Figure 12d). Upon photoexcitation at low intensity ($<100 \text{ mW}/\text{cm}^2$), electrons in the LUMO of PCN-224(Zn) flow to Pt by the Schottky junction, which induces the delivery of more electrons to the Pt surface with higher light intensity and improves the activation of O_2 to $^1\text{O}_2$ and the activity. However, with further increased light intensity ($>100 \text{ mW}/\text{cm}^2$), hot electrons based on Pt SPR, which is more competitive than the Schottky

junction, can be produced and reversely injected into the LUMO of PCN-224(Zn), resulting in electron-deficient Pt surface, unfavorable $^1\text{O}_2$ generation, and decreased activity. The enhanced catalysis by integration of electronic state optimization of the metal surface and the photothermal effect in metal–MOF composites under light irradiation opens a new door toward solar energy utilization.

5. CONCLUSIONS AND PERSPECTIVES

In this Account, we have summarized our recent contributions toward MOF-based photocatalysis and photothermal catalysis. We have presented how the three key processes in photocatalysis can be improved over MOF-based materials: (1) by the introduction of long-wavelength-light-responsive units (e.g., porphyrin units, plasmonic Au nanoparticles, lanthanide-doped UCNPs, etc.) into MOFs, light harvesting can be extended to visible or NIR light; (2) upon the formation of a heterojunction in MOF composites by introducing a Pt cocatalyst with controlled size and location or via spatial separation of the photosensitizer and electron acceptor, the e–h separation can be significantly improved; (3) boosting two useful redox half-reactions by simultaneous consumption of electrons and holes has great potential from a realistic perspective. We have also indicated how the photothermal effect from noble metals and/or MOFs boosts heterogeneous catalysis, especially involving light-induced electronic state optimization of active sites.

Despite the remarkable advances achieved in this field, MOF photocatalysis and particularly MOF photothermal catalysis are still in a very early developmental stage. Therefore much effort should be devoted to their continued development, and some great challenges must be addressed. First, it is highly desired to develop cost-effective and stable MOF photocatalysts with high activity. In addition to the synthesis of new stable MOFs, the polydimethylsiloxane (PDMS) coating approach to improve the moisture/water stability of MOFs without disturbing their inherent crystallinity and porosity^{44,45} is very promising. Second, we are still far from the target to achieve efficient photocatalysis for practical applications. Fortunately, it is possible to achieve synergistic improvement in the three main processes in photocatalysis for enhanced activity over MOF-based composites, even including MOF-derived photocatalysts,⁴⁶ given their structure/composition tailorability. Third, more efforts should be devoted to achieving in-depth insights into the structure–activity relationship and the dynamics of charge carriers, which are of great significance to rationalize future photocatalyst design. It is noteworthy that although the ESR/TA/PL spectra and DFT calculations mentioned above are powerful, Kelvin probe force microscopy-based spatially resolved surface photovoltage technique is also preferred to unveil the photocatalytic mechanism,⁴⁷ which can be introduced into MOF photocatalysis system. Last but not least, the integration of low-cost photothermal agents with high conversion efficiency, instead of the currently used precious metals, into MOF catalysts is much preferred, which would enable the reaction to proceed under moderate conditions. Given the great tunability of MOFs, we strongly believe that solar energy conversion via photocatalysis and photothermal catalysis over MOF-based materials will possess a very bright future ahead.

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ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21725101, 21673213, 21871244, and 21521001).

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