Insights on Carbon Neutrality by Photocatalytic Conversion of Small Molecules into Value-Added Chemicals or Fuels

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1. INTRODUCTION

Facile activation and selective conversion of small molecules such as H₂O, CO₂, N₂, CH₄, and C₂H₆ into value-added chemicals or green fuels is a very promising means for the sustainable development of our society.¹ Nonetheless, one remaining challenge is to break the inert chemical bonds (e.g., C−H, C=O, and N≡N therein) which is an endothermic reaction and energy-intensive process. To achieve this, thermocatalysis and electrocatalysis are proposed. For example, the Haber−Bosch process is used for the industrial NH₃ production, where H₂ and N₂ are involved as reactants over iron- or ruthenium-based catalysts under high temperature (T: 450 °C) and pressure (P: 15 to 30 MPa).² In the electrocatalytic CO₂ reduction system, a much more negative potential compared with the normal hydrogen electrode (NHE) is needed to overcome the high CO₂ reaction barrier and produce CO₂⁻ radicals.³ However, the substantial energy input in the form of heat or electricity in these processes cause a huge amount of energy consumption and expensive capital cost. Therefore, an efficient, environmentally friendly, and economic system for small molecule activation and selective transformation is highly desirable.

Inspired by natural photosynthesis where green plants capture solar energy to convert CO₂ and H₂O into carbohydrates, the artificial photocatalytic process has attracted extensive attention for small molecule activation by a green
Solar light is an abundant and renewable energy source that can be captured and utilized to generate green fuels, thus reducing the dependency on the fossil fuels and avoiding some exhausted gases emissions (e.g., CO$_2$, NO$_x$, SO$_x$, etc.). In addition, this solar-driven process can effectively promote small molecule activation in the presence of catalysts under very moderate conditions. Last, this mild reaction pathway provides a promising strategy for the large-scale application in the future. For instance, a 100 m$^2$ arrayed panel reactor based on Al-SrTiO$_3$ photocatalyst was constructed to achieve photocatalytic H$_2$ production from water with the maximum solar-to-hydrogen (STH) efficiency of 0.76%, which exhibits a great potential for the small molecule activation.

In recent years, various semiconductors such as TiO$_2$, g-C$_3$N$_4$, CdS, ZnO, SrTiO$_3$, and so on have been extensively investigated in small molecule photocatalytic process. However, it still faces a big challenge about the low conversion efficiency and selectivity due to the activation of these very inert molecules. Thus, it is of paramount importance to develop new photocatalysts to boost the conversion efficiency of small molecules into value-added chemicals or fuels. The reaction mechanism for photoinduced small molecule activation and transformation undertaken in our group is depicted in Figure 1 and has been systematically reviewed by our other work.$^{2,3,7,8,10}$

![Figure 1. Schematic illustration of photocatalytic conversion of small molecules into value-added chemicals over semiconductors undertaken in our group.](image)

Then, the ROS participates in a series of oxidation reactions to convert the reactants into oxidation products. In photocatalytic CO$_2$ reduction, the direct reduction of CO$_2$ by photoelectrons to form a CO radical is very difficult and requires a reduction potential of $-1.9$ V vs SHE. Therefore, the first step of CO$_2$ reduction is assisted by one proton, to form a formate radical (Figure 2b). In photocatalytic water splitting, H radicals are first formed from proton reduction by electrons (Figure 2c). Then the coupling reaction of two H radicals results in the formation of one H$_2$ molecule. The methyl radical is the first and the most important intermediate formed in all methane conversion reactions, which results from methane activation by photogenerated holes, with the production of a proton (Figure 2d).

In this critical review, a comprehensive understanding for rational design strategies of highly effective photocatalysts used in our group will be detailed, which will include bandgap engineering for light harvesting, charge separation enhancement, morphology engineering for reactants adsorption/products desorption, and charge separation, as well as operando fundamental observations. Then, the future research direction toward the bottlenecks of photocatalytic conversion of each small molecule will be discussed with an aim to realize carbon neutrality as soon as possible.

### 2. Strategies to Enhance Photocatalytic Efficiency

In general, the criteria for the choice of photocatalysts which either fit for the reduction and/or oxidation reaction can be summarized as follows. First, semiconductors must have appropriate conduction or valence band potentials to proceed the corresponding reduction or oxidation reactions.$^1$ For example, the electrons in the conduction band must have a more negative potential than the reduction potential of H$^+$/H$_2$ (0 eV vs NHE) to proceed the H$_2$ reduction half-reaction. The water oxidation reaction could occur when photoholes exist in the valence band, which has a more positive potential than the oxidation potential of O$_2$/H$_2$O (+1.23 eV vs NHE). Besides, the intrinsic properties of n- or p-type conductors also need to be considered.$^{1,11}$ For instance, when a p-type and a n-type semiconductor are in close and intimate contact to form a p–n heterojunction, the band bending on semiconductor is very significant, which can induce the flow of electrons to the conduction band of the n-type semiconductor and direct the

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**Figure 2. Typical radicals including (a) O$_2^-$ and *OH, (b) HCOO*, (c) *H, and (d) *CH$_3$ generated in photocatalytic reactions.**

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flow of holes to the valence band of the p-type semiconductor. This can greatly enhance the charge separation and improve the photocatalytic performance. Furthermore, it is very crucial to choose suitable cocatalyst loading on semiconductors, which can promote the charge separation and control the reaction pathways/product selectivity. Very recently, the single-atom Cu on TiO₂ was proved as an efficient cocatalyst to trap electrons and improve charge transfer. Accordingly, several improvement strategies will be reviewed systematically by us as shown below, aiming at guiding readers to prepare efficient photocatalyst for photocatalytic conversion of small molecules.

2.1. Light Harvesting

Defects. The defect engineering on semiconductors can be used to effectively change the band positions, construct active sites and enhance light harvesting to improve the photocatalytic performance. We recently reported that n-type g-C₃N₄ with introduced N-defects and C—OH terminal groups could work as an efficient photocathode. Combination of open circuit photovoltage decay (OCVD), Mott–Schottky (MS) plot and transit absorption spectroscopy (TAS) analysis proved that the existence of longer-lived shallow-trapped electrons at the microsecond time scale on defective g-C₃N₄ after light irradiation contributed to its superior photocathodic performance, which was also strongly supported by the H₂ evolution.

The introduction of various dopants into semiconductors is another promising strategy to change their electronic structure and surface property in order to boost their photocatalytic performance. In one of our studies, the controlled hydroxyl/oxygen group was doped in CNₓHₓ during the polymerization process to boost its photocatalytic property for H₂ evolution. The DFT results revealed that the heptazine units could be linked by oxygen and nitrogen species, thus leading to a narrow band gap and reduced charge recombination. Besides, the terminal —OH groups on doped CNₓHₓ also increased its surface hydrophilicity, which was beneficial for water adsorption and proton reduction.

Boosted Photocatalytic Hydrogen Production. After introducing bridging-nitrogen defects, the D-CNNS exhibited an enhanced visible light harvesting compared with bulk carbon nitride (BCN) as a result of the improved n → π* optical transition. The theoretical calculations revealed that the bandgap of D-CNNS was greatly decreased to 2.24 eV as compared to that (2.74 eV) on BCN. Further characterizations showed that D-CNNS exhibited an efficient spatial charge separation. As a result, a superior hydrogen yield of 2497.1 μmol g⁻¹ h⁻¹ was reached on the optimized D-CNNS(0.3), which was around 41 times higher than that of BCN.

Doping. The introduction of various dopants into semiconductors is another promising strategy to change their electronic structure and surface property in order to boost their photocatalytic performance. In one of our studies, the controlled hydroxyl/oxygen group was doped in CNₓHₓ during the polymerization process to boost its photocatalytic property for H₂ evolution. The DFT results revealed that the heptazine units could be linked by oxygen and nitrogen species, thus leading to a narrow band gap and reduced charge recombination. Besides, the terminal —OH groups on doped CNₓHₓ also increased its surface hydrophilicity, which was beneficial for water adsorption and proton reduction.

The optimal hydroxyl-doped carbon nitride with the narrowed band gap of 1.55 eV exhibited an excellent H₂ evolution. Further characterizations showed that D-CNNS exhibited a narrow bandgap and reduced charge recombination.
The FAT-1.0 exhibited a stacking layered structure rather than a ribbon-like structure of pristine g-C$_3$N$_4$. Besides, the FAT with different ratio of oxygen linkers exhibited a step-by-step enhanced visible light adsorption (Figure 3b) and the bandgap of the FAT with different amount of oxygen linkers was effectively narrowed (Figure 3c). The DFT calculations proved that the charge efficiency was improved due to the special separation of electrons and holes after the introduction of oxygen-containing linkers (Figure 3d). Therefore, a superior H$_2$ evolution rate (HER) of 772 μmol g$^{-1}$ h$^{-1}$ ($\lambda > 710$ nm) was achieved, which was 18 times higher than that on g-C$_3$N$_4$, resulting in the benchmark AQY of 2.5% at 500 nm. Incorporating oxygen into the covalent triazine-based frameworks (CTF) was again proved to be an effective strategy in tuning its photocatalytic performance. Both water reduction and oxidation activities were improved after the modification. In particular, the oxygenated CTF was very active for boosting photocatalytic hydrogen production.

Besides oxygen doping, modification of carbon nitride with other inorganic elements, such as C and S also plays important roles in manipulation of its photocatalytic activity. We found that an ultrathin sulfur-doped porous carbon nitride (S-CN) nanosheet was very active for boosting photocatalytic hydrogen production. Further investigations revealed that the surface area of S-CN was enlarged and the corresponding conduction band was lifted up with the decreasing doping amount of sulfur. Accordingly, an optimal S-CN prepared with 0.1 g of thiocyanuric acid as a precursor showed a remarkable H$_2$ yield of 6225.4 μmol g$^{-1}$ h$^{-1}$ ($\lambda > 420$ nm), which was around 45 times higher than that on bulk g-C$_3$N$_4$ with the AQY of 10% at 420 nm.

In parallel, many reports have mentioned the use of metal-doped TiO$_2$ in photocatalytic nitrogen reduction, compared with it, a few studies focused on using non-metal-component-doped TiO$_2$ in this field. Recently, we synthesized carbon-doped TiO$_2$ nanosheets with enriched Ti$^{3+}$ by H$_2$O$_2$-assisted thermal-oxidation etching (TOE) treatment of Ti$_3$SiC$_2$ MXenes and a subsequent heat treatment (Figure 4a). The carbon doping over TiO$_2$ was proved to effectively induce the formation of Ti$^{3+}$ active sites and dramatically enhance its...
visible light adsorption (Figure 4b). The elemental mapping spectra of the samples displayed the homogeneous dispersion of C element in the sample, indicating a successful doping of C into the framework of TiO$_2$ (Figure 4c). With the synergetic effects of Ru and RuO$_2$ for enhanced charge separation, a remarkable NH$_3$ yield of 109.3 μmol g$^{-1}$ h$^{-1}$ with the AQE of 1.1% at 400 nm was achieved over 5 wt % Ru/C$_x$-TiO$_2$ under visible light illumination (Figure 4d). Meanwhile, it was discovered that the photocatalytic NH$_3$ production performance was in correlation with the concentration of Ti$^{3+}$, rather than the carbon content (Figure 4e). Besides, direct calcination of Ti$_x$C$_2$ MXenes in air resulted in the formation of carbon-doped TiO$_2$ enriched with oxygen vacancies. The formed oxygen vacancies not only extended the absorption of light but also improved the adsorption of N$_2$.

Apart from the aforementioned two strategies, constructing the heterojunction structure is also an effective way to enhance the light harvesting and several works have been reported by our group. For example, the metal-free heterojunction composed of hollow carbon nanospheres (NCS) and graphic carbon nitride (CN) was successfully prepared and used for efficient photocatalytic H$_2$ evolution. Due to the formation of special coupling interface between NCS and CN, the light absorption on CN/NCS was extended to the visible light region, thus leading to improved catalytic performance of CN. Moreover, the formation of the heterojunction structure is also beneficial for the photoinduced charge separation on semiconductors. Thus, more details about the advantages of the heterojunction structure will be discussed in the subsequent charge separation section.

### 2.2. Charge Separation by Cocatalysts Loading and Junction Structure

In this subsection, the major strategies contributing to the improved charge separation including cocatalyst loading and junction structure are emphasized. The other improvement methods with side contribution on charge separation will be briefed in the next sections.

**Cocatalyst Loading.** Cocatalysts loading has been extensively investigated as an efficient strategy to lower the activation energy and equally important to retard the electrons and holes recombination during photocatalysis, thus leading to enhanced photocatalytic activity. Very recently, we reported a ternary Ru/RuO$_2$/g-C$_3$N$_4$ heterostructure for N$_2$ photoreduction. Benefiting from the improved charge separation by loading Ru and RuO$_2$ and enhanced N$_2$ adsorption and activation on Ru species, the optimal Ru/RuO$_2$/g-C$_3$N$_4$ exhibited an NH$_3$ yield of 13.3 μmol g$^{-1}$ h$^{-1}$ under full spectrum irradiation, while almost no NH$_3$ were detected on pristine g-C$_3$N$_4$.

In one of our recent studies, Pt and CuO$_x$ were coloaded on TiO$_2$ and used in a flow system for photocatalytic oxidative coupling of methane (Figure 5a,b). Pt, a widely used electron-acceptor, and CuO$_x$, which was assumed to be a hole acceptor, ensured maximum separation of photocarriers generated by TiO$_2$. Photoholes on CuO$_x$ with lowered oxidation capability activated methane to generate methyl radicals and protons, avoiding overoxidation. Meanwhile, O$_2$ was reduced by electrons on the surface of Pt to produce the O$_2^-$ radical, which cleaned the surface of TiO$_2$ from the accumulation of H$. As a result, an unprecedentedly high C$_2$H$_6$ production rate of 68 μmol g$^{-1}$ h$^{-1}$ was achieved.
However, the scarcity and high price of noble metal-based cocatalysts in part limit the large-scale application. Iron species were then decorated on TiO$_2$ as a low cost cocatalyst for selective (90% selectivity) methanol production from methane activation with the assistance of H$_2$O$_2$ (Figure 5d). First, electrons generated from TiO$_2$ transferred toward FeO$_x$, where decomposition of H$_2$O$_2$ was accelerated, forming oxidative *OH radicals. In parallel, methane could be activated either by the photoholes or *OH radicals and then by reacting with *OH to generate methanol.

In parallel, a covalent nickel bis-aminothiophenol catalyst as a new noble metal-free cocatalyst was successfully grafted on 2D carbon nitrides (C$_x$N$_y$H$_z$) for efficient charge separation and photocatalytic H$_2$ production. Time-resolved spectroscopy indicated that the rate of submicrosecond electron transfer in Ni(abt)$_2$ covalently bonded photocatalysts was 6 orders of magnitude higher than that (>2 s) in the nongrafted photocatalysts. Besides, the half-lifetime of photoelectrons (7 ms) in the Ni(abt)$_2$ grafted C$_x$N$_y$H$_z$ was 700 times longer than that (10 μs) in the pristine C$_x$N$_y$H$_z$. Therefore, a remarkable performance on CN$_{area}$—Ni(abt)$_2$ was achieved with the H$_2$ yield and turnover frequency of 92 μmol g$^{-1}$ h$^{-1}$ and 9.2 h$^{-1}$ respectively, which were comparable with those (155 μmol g$^{-1}$ h$^{-1}$ and 6.9 h$^{-1}$) on Pt-loaded CN$_{area}$ under the same experimental conditions. Besides, CN$_{area}$—Ni(abt)$_2$ also exhibited superior durability over 192 h, which was 3 times longer than that on most reported molecular catalyst-based carbon nitrides.

**Junction Construction.** Compared to the photocatalytic system using only one semiconductor, constructing a heterojunction system with two or more photocatalysts such as Z-scheme or type II structure can effectively promote spatial charge separation and enhance the photocatalytic activity. In one of our studies, one metal-free nanojunction (s-BCN) made of boron-doped carbon nitride and bulk carbon nitride was synthesized successfully as a highly efficient photoanode for water oxidation. Boron-doped carbon nitride could shift the valence band of bulk g-C$_3$N$_4$ (G-CN) upward from +1.42 V to +1.35 V vs Ag/AgCl (pH 6.5). The driving force between two different valence bands in the junction structure promoted the hole transfer from G-CN to the surface to participate in the following photooxidation reaction. Besides, s-BCN exhibited a 3-fold higher photocurrent intensity than that on G-CN. As a result, the optimal s-BCN (4%) showed an excellent photocurrent density of 103.2 μA cm$^{-2}$ at 1.23 V vs RHE under one sun illumination and a remarkable high incident photon-to-electron conversion efficiency (IPEC) of 10% at 400 nm, which was 10 times higher than that on bulk carbon nitride.

In parallel, to reduce CO$_2$ into useful chemicals or fuels, heterostructures based on Cu$_2$O were studied as photocatalysts. For instance, the reduced graphene oxide (RGO)/ Cu$_2$O heterojunction was synthesized in one step via a microwave-assisted chemical method. Not only was a 6 times higher CO formation rate compared with bare Cu$_2$O obtained, but also the catalyst stability was significantly prolonged. The Cu leaching was as low as 96 ppm in RGO/Cu$_2$O, compared to the high leaching of 2670 ppm in Cu$_2$O after a 3 h reaction time. Most recently, a cascade Z-scheme system of (001)-TiO$_2$—g-C$_3$N$_4$/BiVO$_4$ (T-CN/BVNS) was successfully constructed to enhance CO$_2$ photocatalytic reduction. The DFT results revealed that the introduced TiO$_2$ as the electron-energy platform could effectively promote the charge transfer and prolong the lifetime of charge carriers. Accordingly, as compared to BVNS, the optimal 5T-15CN/BVNS exhibited
around 19 times better performance for CO₂ photoreduction to CO without any cocatalysts and sacrificial agents under visible light irradiation.

2.3. Reactant Adsorption or Charge Separation by Morphology Engineering

Facets. To date, effort has been made on the facets control over semiconductors because of their distinct impacts on the band edge location, charge separation, and important reactants’ adsorption. The photocatalytic oxidation of water using Ag₃PO₄ was studied by theoretical modeling and experimental analysis. First, it was predicted that the {111} facet of Ag₃PO₄ displayed the higher surface energy of 1.65 J/m² compared with energies of the {110} and {100} planes. Therefore, a series of Ag₃PO₄ nanocrystals with exposed {111}, {100}, and {110} were synthesized. The tetrahedral Ag₃PO₄ mainly composed of the {111} facet, showed an oxygen evolution rate of 6 mmol g⁻¹ h⁻¹, which was 10 times higher than that of cubic Ag₃PO₄ with the exposed {100} facet or rhombic dodecahedron Ag₃PO₄ with the exposed {110} facet. Furthermore, an internal quantum yield of almost unity for water oxidation was realized at 420 nm, which was the highest performance achieved in photocatalytic water oxidation by visible light. We also found that the selectivity of photocatalytic CO₂ reduction could be controlled by facet engineering of Cu₂O nanocrystals. The octahedral Cu₂O with the exposed {111} facet was proved to be beneficial for hydrogen evolution, while the Cu₂O particles consisting of cuboid aggregates could selectively reduce CO₂ to produce CO. A similar effect was also observed using KTaO₃. The charge separation process could be boosted by the facet control on a heterojunction photocatalyst. It was proved experimentally that the {010} facet of BiVO₄ and the {002} facet of ZnO were the electron-rich facets, while the {110} plane of BiVO₄ and the {110} facet of ZnO were the hole-rich planes. Therefore, the delicate growth of ZnO nanorods on BiVO₄ nanocrystals formed a Z-scheme heterojunction, which produced O₂ at a rate of 1.36 mmol g⁻¹ h⁻¹ under visible light irradiation.

Nanostructure. Carbon dots, due to their attractive electrical, optical, and chemical properties, are drawing increasing attention in photocatalysis. The properties of carbon dots can be easily adjusted by tuning their size, composition, and preparation method. Recently, we reported the special hole-accepting carbon dots prepared by the
microwave method (\textsuperscript{10}CD), which was combined with graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) to drive photocatalytic carbon dioxide reduction to methanol (Figure 6a–c).\textsuperscript{42} The decoration of \textsuperscript{10}CD on g-C\textsubscript{3}N\textsubscript{4} promoted the charge separation, water adsorption and methanol desorption processes in photocatalytic CO\textsubscript{2} reduction. Therefore, a 6-fold enhancement in methanol production rate with nearly 100% selectivity was achieved over the \textsuperscript{10}CD/CN photocatalyst. Combining \textsuperscript{10}CD with another polymeric photocatalyst, FAT (oxygen-doped CN), which displayed a lower methanol oxidation capability, further promoted the CO\textsubscript{2} reduction process, resulting in a quantum efficiency of 6% at 420 nm (Figure 6d–f).\textsuperscript{43}

**Reactant Adsorption.** Loading a reactant adsorbent on the photocatalyst is an effective method to achieve the improved adsorption of reactant molecules. A Cu\textsubscript{3}O\textsubscript{}@Cu\textsubscript{3}(BTC)\textsubscript{2} core–shell structure was fabricated for the photocatalytic CO\textsubscript{2} reduction (Figure 7a,b).\textsuperscript{44} Cu\textsubscript{3}(BTC)\textsubscript{2} on the surface of Cu\textsubscript{3}O could significantly improve the adsorption of CO\textsubscript{2} due to its special porous structure (Figure 7c). Therefore, abundant CO\textsubscript{2} molecules were confined near the surface of Cu\textsubscript{3}O photocatalyst. As a result, a ca. 2 time improvement on the photocatalytic CO\textsubscript{2} reduction into CH\textsubscript{4} was observed (Figure 7d,e). More importantly, the stability of photocatalyst was improved after loading the Cu\textsubscript{3}(BTC)\textsubscript{2} metal organic framework onto Cu\textsubscript{3}O (Figure 6e). Recently, we also found that the Ti\textsubscript{3}C\textsubscript{2} MXenes could act as a N\textsubscript{2} adsorbent on the surface of TiO\textsubscript{2} and improve the photocatalytic N\textsubscript{2} reduction activity.\textsuperscript{35} The DFT calculations suggested that N\textsubscript{2} has a much higher adsorption energy on MXenes (2.7 eV) than on TiO\textsubscript{2} (0.2 eV). With the assistance of CH\textsubscript{3}OH as an electron donor, an NH\textsubscript{3} production rate of 44 \textmu mol g\textsuperscript{−1} h\textsuperscript{−1} was achieved on the optimized 6% Ti\textsubscript{3}C\textsubscript{2} MXenes-P25 under full spectrum light illumination, which was almost 4 times higher than that of pure P25 TiO\textsubscript{2}.

Structure engineering of semiconductor photocatalysts can also improve the absorbance of reactants. In one of our work, among three types of carbon nitride synthesized from urea, dicyandiamide, and thiourea, urea-derived carbon nitride with the lowest protonation showed the highest photocatalytic hydrogen evolution performance.\textsuperscript{46} Protonation at the linkers or terminals of the photocatalysts resulted in the decreased interaction with the protons, which was the source of produced H\textsubscript{2}. Combined with the high surface area, an extraordinary hydrogen evolution rate of 20000 \textmu mol g\textsuperscript{−1} h\textsuperscript{−1} was obtained over urea-derived carbon nitride. Surface engineering also can alter the intrinsic properties of the catalyst surface and vary its adsorption capabilities. Surface-fluorinate TiO\textsubscript{2} (F-TiO\textsubscript{2}) showed a special photoinduced hydrophilicity,\textsuperscript{47} as the adsorption of H\textsubscript{2}O molecules on F-TiO\textsubscript{2} was improved compared with that on bare TiO\textsubscript{2}. As a result, photocatalytic hydrogen evolution from water, aldehyde decomposition and methylene bule degradation were all improved. In particular, the photocatalytic hydrogen evolution rate was improved by more than 2 times over F-TiO\textsubscript{2} compared with that on bare TiO\textsubscript{2}.

2.4. Fundamental Understanding by in Situ and Operando Studies

Time/spatial-resolved operando techniques are powerful tools to monitor the charge carrier dynamics and reaction pathway during the photocatalytic process, thus guiding the improvement of the photocatalytic performance.\textsuperscript{48} In 2014, we employed transient absorption spectroscopy (TAS) to monitor the behavior of charge carriers on Cu\textsubscript{3}O/Ru\textsubscript{3}O for CO\textsubscript{2} photoreduction.\textsuperscript{49} The TAS results revealed that the junction of Cu\textsubscript{3}O/Ru\textsubscript{3}O could produce a 2 times higher yield of long-
lived (>100 μs) photoexcited electrons as compared to Cu₂O, indicating less recombination of electrons and holes. Thus, Cu₂O/RuₓO exhibited a 6-fold higher initial CO yield of 0.88 μmol g⁻¹ h⁻¹ than that of 0.16 μmol g⁻¹ h⁻¹ over pure Cu₂O under a 150 W Xe irradiation. Furthermore, we also studied the different charge carrier kinetics among a family of g-C₃N₄ derived from various precursors by TAS and photoemission studies. The TAS results suggested that DCDA and thiourea-derived materials had a higher yield of deep-trapped carriers than that on urea-derived g-C₃N₄, thus leading a decreased photocatalytic activity. Besides, the steady-state emission studies revealed that the enhanced photocatalytic performance on urea-derived g-C₃N₄ was attributed to the increased driving force for electron transfer to the [Co(bpy)]₆²⁺ cocatalyst. Hence, urea–g-C₃N₄ exhibited a superior CO yield of 460 μmol g⁻¹ h⁻¹ (300 nm < λ > 795 nm), which was 20 and 5 times higher than that on thiourea and DCDA-derived g-C₃N₄, respectively.

Lately, time-resolved photoluminescence (tr-PL) and TAS were employed together to study the photophysics of urea-derived carbon nitrides. The TAS spectra revealed that electrons on g-C₃N₄ were excited within 200 fs and then trapped in a pico time scale, followed by a power law decay that indicated a trapping–detrapping process. Additionally, with the assistance of the modeling analysis, it pointed out that the thermal equilibrium between the nonradiative trapped and the emissive states caused the faster decay of tr-PL compared to TAS decay. Further experimental and DFT results demonstrated the inverse correlation between the yield of deep-trapped long-live inactive electrons over g-C₃N₄ and the related H₂ production. Most recently, we constructed an in situ vis–NIR spectroscopy system to elucidate the initial steps of methane photoactivation over anatase TiO₂ (Figure 8a). From the in situ experimental study, under constant light irradiation, the intensity of photogenerated electrons on anatase TiO₂ increased in the NIR region under methane atmosphere as compared to that under argon gas. Combined with the significantly decreased signal intensity of electrons under air condition (Figure 8b), it was strongly evidenced that methane was a hole scavenger in photocatalytic methane conversion (Figure 8c). In addition, the photoinduced absorption results revealed that 90 ± 6% of photogenerated electrons and 61 ± 9% of photogenerated holes were depleted by O₂ (in dry air) and methane (10% in argon), respectively. Meanwhile, there was no obvious difference of the number of photoexcited electrons even if the ratio of O₂ was reduced from 20% to 2%, which indicated that O₂ was a much more easily activated component as compared to methane under light illumination.

TAS was also used to study the charge separation and transformation process of carbon dot modified g-C₃N₄. Recently, a special hole-accepting carbon dot via the microwave method (mCD) was developed in the group. The main features on the TAS spectra indicated the electron signal observed at 700 nm in g-C₃N₄. As shown in Figure 9a–f, compared with pure g-C₃N₄ (CN), mCD modified g-C₃N₄ (mCD/CN) displayed a stronger electron signal, indicating holes were effectively extracted from CN to mCD. In contrast, carbon dots by the traditional ultrasonication method (sCD) decorated g-C₃N₄ (sCD/CN) gave a lower TAS intensity than...
pure g-C₃N₄, suggesting electron transfer from g-C₃N₄ to "CD. The addition of Ag⁺, a strong electron scavenger, resulted in a decrease in the signal of CN and "CD/CN, which was caused by the consumption of electrons on the surface of CN by Ag⁺. However, the spectra of "CD/CN barely changed. All these suggested that electrons were transferred from CN to "CD while holes were transferred from CN to "CD (Figure 9g).

The complementary in situ and operando experiments such as XAFS (X-ray absorption fine spectroscopy), XPS (X-ray photoelectron spectroscopy), EPR (electron paramagnetic resonance), etc. were also widely studied in the small molecule photoactivation process. Very recently, we employed the in situ XPS and EPR to monitor the real active sites on single-atom-copper-loaded TiO₂ (CuSA-TiO₂) for photocatalytic hydrogen production.13 As seen from the in situ XPS (Figure 10a), after 30 min light irradiation, the fraction of Cu²⁺ in the sample increased dramatically from 29.42% to 61.68% and kept 62–66% after that. Then, the in situ EPR also confirmed the valence states of Cu in the CuSA-TiO₂ (Figure 10b), where the CuSA-TiO₂ exhibited a strong signal of Cu²⁺ before light irradiation. Nevertheless, the Cu²⁺ EPR signal was dramatically decreased after 60 min irradiation and then recovered after exposure to the air. All these results provide strong evidence that Cu²⁺ was the electron acceptor and then Cu⁺ was active sites to reduce proton for H₂ production, while the photoinduced holes could oxidize methanol to produce the value-added chemicals including formaldehyde and formic acid, as shown in Figure 10c. Similarly, we also employed the in situ XPS to reveal the valence state of Au on ZnO for photocatalytic methane oxidation to C1 oxygenates.53 It could be seen that the XPS peak of Au₄⁺ had a significant shift to a high binding energy under light irradiation (Figure 10d), which indicated that Au served as a hole acceptor. As a result, a reaction mechanism for photocatalytic methane oxidation was proposed as shown in Figure 10e, where Au cocatalysts accepted holes to form Au³⁺, which further activated H₂O to produce *OH and H₂.

Besides, the in situ XAFS is also a promising way to monitor the change of catalytic active sites under real reaction conditions.54 Very recently, the extend X-ray absorption fine structure (EXAFS) was employed in our group to prove the existence of a single Pd atom on Pd-loaded defective In₂O₃ with oxygen vacancies.55 Additionally, we also used the EXAFS technique to confirm the existence of the iron in the form of small clusters or even a single atom on the Fe-loaded TiO₂ photocatalyst.56

3. CONCLUSIONS AND PERSPECTIVE

Photocatalytic conversion of small molecules into valued-added chemicals has been critically viewed, mainly taking research results achieved in our group as examples to indicate an efficient, environmentally friendly, and energy-saving strategy to mitigate the current energy and environment issues. The key factors in photoinduced small molecule conversion are to overcome the reaction energy barrier of small molecule activation and promote their adsorption and product desorption. Despite substantial effort in past decades, the conversion efficiency and selectivity to valuable chemicals by photocatalysis are still relatively low and cannot meet the requirements for the large-scale production. Thus, it is still at the infancy stage with a long way to go.

In this Account, we enumerate several strategies used in our group for enhanced photoactivity involving (i) light harvesting by bandgap engineering such as defects and elements doping, (ii) charge separation enhancement by cocatalysts loading and junction construction, (iii) reactants adsorption or product desorption together with charge separation by morphology engineering including facets and nanostructures, and (iv) fundamental understanding by in situ and operando investigations, which have been validated by us over the past two
decades. To further facilitate these research areas, the future key challenges in the photocatalytic small molecule conversion processes are discussed below based on our understandings:

(i) Photocatalytic H$_2$O splitting. Photocatalytic H$_2$ production from water provides an attractive pathway to achieve green H$_2$ production. Until now, much progress has been made in search of effective photocatalysts for H$_2$O splitting. However, the photocatalytic efficiency under real sunlight is still relatively low (~1%). Thus, it is urgent to design effective visible-light response photocatalysts. Besides, there are very few studies about the design of the monolith reactor for photocatalytic H$_2$O splitting. Considering the realization of large-scale H$_2$ production in the future, an effective and inexpensive photocatalytic reactor, together with a H$_2$ and O$_2$ gas separator are expected. Furthermore, in most cases, the sacrificial agents were used to improve the H$_2$ yield in the photocatalytic H$_2$ production system, whereas the real proton source and reaction pathway are still unclear. As a result, the isotope labeling experiments and in situ and/or operando techniques should be applied for mechanistic understanding in order to improve the solar to H$_2$ conversion efficiency of above 10%, which is widely regarded as a threshold for the application of this technology.

(ii) Photocatalytic CO$_2$ reduction. Although massive progress has been achieved in photocatalytic CO$_2$ reduction, the low conversion rate of CO$_2$ and selectivity toward valuable products are the main challenges faced in photocatalytic CO$_2$ reduction. More attention should be paid to the surface reaction, for instance, reactant adsorption and activation, the formation and transformation of intermediates, and product desorption, as most of the current studies paid too much attention to the light harvesting and charge separation steps in photocatalysis. The reaction pathway and mechanism study can definitely promote the development of photocatalytic carbon dioxide reduction, which should be comprehensively investigated by combination of experiments and theoretical modeling.

(iii) Photocatalytic N$_2$ reduction. To date, compared with other photocatalytic processes, N$_2$ photoreduction suffers from serious challenges. First, the yield of NH$_3$ is currently too moderate, in the magnitude of a micromole or even below, close to the natural NH$_3$ concentration in air or in river water. Thus, more effort should be paid to new photocatalyst designs such as dual metal photocatalyst and polymer/oxide junction to enhance N$_2$ adsorption and activation. Second, one robust and reliable detection procedure of NH$_3$ yield should be applied to avoid the interference of environmental impurities or detection agents. Besides, the current study for N$_2$ photoreduction occurs in lab-based batch reactors, where the NH$_3$ yield is usually restricted by the mass transfer among N$_2$, H$_2$O, and solid catalysts due to the extremely low solubility of N$_2$ in water. Thus, a novel flow reactor integrating gas reactants and solid photocatalysts is expected, which might show great potential for future large-scale application. Last, the reaction pathways for N$_2$ photoreduction over semiconductors is currently unclear and less investigated. The in situ and/or operando techniques, together with computational modellings should be explored in order to give clear guidance for future effective photocatalysts synthesis and reaction system design.

(iv) Photocatalytic CH$_4$ conversion. Besides photocatalytic activation of inert inorganic molecules discussed above, organic molecule conversion is the other key research subarea in photocatalysis. Methane, the smallest organic molecules, can be converted to methanol, ethane, ethylene, ethanol, and other oxygenates by photocatalysis. Due to the inert nature of methane and the high reactivity of products, the selectivity toward desired products is relatively moderate, although the feasibility has been proved. Therefore, improving the selectivity by controlling overoxidation or coking should be the main task in the study of photocatalytic methane conversion. Furthermore, oxygen or air is a preferable oxidant for partial oxidation of methane, instead of peroxide, carbon monoxide, or nitrogen oxide used in many studies. In addition, only some UV-responsive photocatalysts were used in methane conversion. Photocatalysts with higher visible light efficiency should be developed. Currently, C1 and C2 products have been reported as major products by photocatalytic methane conversion. More valuable products, such as oxygenates and hydrocarbons with longer carbon chains, are encouraged to be selectively produced. The complex radical reactions and intermediates formed during the methane conversion process should be studied using advanced spectroscopies and microscopies. In situ and operando characterizations should be applied to understand the true reaction sites and key intermediates formed at the catalysts surface. These will greatly guide the research directions in photocatalytic methane conversion.

(v) Photocatalytic alcohol and benzene oxidation. The real application of selective photocatalytic oxidation of organics is our last, but not least, subject of interest. It presents some difficulties compared with the degradation of organic pollutants. The primary issues in this subject are the control of the reactive oxygen species (ROS) generation and the understanding of reaction mechanisms. Despite the relatively fast progress in the development of catalysts for photocatalytic oxidation of organic substances in the past few decades, there are still challenges to be overcome in this field. For example, the operando observation of the reaction intermediates, related to the catalytic reaction mechanism is highly desirable. Combining time-resolved IR and Raman spectroscopy with mass spectrometry, one can observe species adsorbed on the photocatalyst surface, species in the gas phase, and subtle surface changes of catalysts under “true” reaction conditions, leading to clarification of the photooxidation mechanisms. Based on these experimental results, theoretical calculation is the next essential step to confirm the reaction mechanism, which can also predict effective strategies for catalyst optimization.

Overall, the core of these photochemical processes is the discovery of effective, stable, and low cost photocatalysts. State-of-the-art methods for modifying the electronic and chemical structures of photocatalysts should be further developed and employed. Specifically, single-atom catalysts (SACs), which can potentially bring exclusively high activity
and selectivity in photocatalytic organic synthesis, are still scarcely employed in this field. Very recently, we have successfully developed several single-atom photocatalysts for the methane oxidation to methanol and water reforming of methanol for hydrogen evolution, both achieving very high photocatalytic activity.\(^{13,56}\) It is therefore of paramount importance to develop new strategies to controllably synthesize SACs with high metal content in an appropriate circumstance. On the other hand, SACs can provide new opportunities to capture reaction intermediates at the atomic scale and further monitor the dynamic behaviors of both the geometric structure and electronic state of the active sites. Furthermore, the operando study on SACs can achieve the atomic-level knowledge of these active sites, leading to deep and comprehensive understanding of the reaction mechanisms. Furthermore, the big data, together with artificial intelligence and machine learning are becoming a very promising research field for novel photocatalyst development, which can effectively optimize experimental process, save experimental time, reduce raw materials consumption, and enhance the experimental safety. Therefore, the combination of the data-related diverse technologies should be paid particular attention for photocatalysis in future studies.

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**Notes**

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