Single-Atom Photocatalysts for Emerging Reactions

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ABSTRACT: Single-atom photocatalysts have demonstrated an enormous potential in producing value-added chemicals and/or fuels using sustainable and clean solar light to replace fossil fuels causing global energy and environmental issues. These photocatalysts not only exhibit outstanding activities, selectivity, and stabilities due to their distinct electronic structures and unsaturated coordination centers but also tremendously reduce the consumption of catalytic metals owing to the atomic dispersion of catalytic species. Besides, the single-atom active sites facilitate the elucidation of reaction mechanisms and understanding of the structure-performance relationships. Presently, apart from the well-known reactions (H₂ production, N₂ fixation, and CO₂ conversion), various novel reactions are successfully catalyzed by single-atom photocatalysts possessing high efficiency, selectivity, and stability. In this contribution, we summarize and discuss the design and fabrication of single-atom photocatalysts for three different kinds of emerging reactions (i.e., reduction reactions, oxidation reactions, as well as redox reactions) to generate desirable chemicals and/or fuels. The relationships between the composition/structure of single-atom photocatalysts and their activity/selectivity/stability are explained in detail. Additionally, the insightful reaction mechanisms of single-atom photocatalysts are also introduced. Finally, we propose the possible opportunities in this area for the design and fabrication of brand-new high-performance single-atom photocatalysts.

1. INTRODUCTION

To resolve the potential global energy and environmental issues, enormous efforts have been made to explore alternative energy resources for fossil fuels. Solar energy has exhibited great potential as a promising alternative to substituting the traditional energy sources because it is clean, renewable, abundant, affordable, and everlasting.1,2 Due to the unpredictable nature of weather, it is challenging to make use of solar light under poor weather conditions and/or at night; therefore, it is necessary to transform solar energy into new forms of energy that are storage-stable. Up to date, solar energy has been extensively utilized to produce storable and transportable fuels with high energy capacity as well as value-added chemicals.3–11 Among various solar energy conversion techniques, photocatalysis is deemed as a promising, environmentally benign, and cost-effective strategy to generate both fuels and high-value chemicals.12–18 During the past decades, numerous studies have been focused on several well-known reactions (e.g., H₂ production,19–26 N₂ fixation27–30 and CO₂ conversion31–34) achieved via photocatalysis. Recently, a range of emerging photocatalytic reactions generating fuels and/or valuable chemicals has been attracting increasing attention.35–37 These emerging reactions can be categorized into three different types, i.e., reduction reactions, oxidation reactions, and redox reactions, based on their specific photocatalytic reaction mechanisms. For instance, several studies demonstrate the production of hydrogen peroxide (H₂O₂) as a value-added chemical and potential energy carrier, using only water (H₂O) and oxygen (O₂) via photocatalytic reduction reaction.38 Moreover, phenol, as a key organic chemical intermediate and precursor, can be achieved via photocatalytic selective oxidation of benzene.41 In another study, low-cost biomass-derived acetone is subject to oxidative C–C coupling to form 2,5-hexanedione (HDN) as an important chemical and redox agent to generate H₂ fuel through a photocatalytic redox reaction.42 Thus, the above three classes of emerging photocatalytic reactions used to produce desirable chemicals and/or fuels are of both great interest and importance.

Recently, single-atom photocatalyst has become one of the most groundbreaking and dynamic research hotspots in heterogeneous photocatalysis.43,44 Single-atom photocatalysts have attracted tremendous attention primarily owing to the following fascinating benefits in comparison to the nano-clusters, nanoparticles, and bulk counterparts: (i) exceptionally high activity and selectivity originating from their distinct electronic structures and unsaturated coordination centers;45,46
H2O2 and aniline, via single-atom photocatalysis, have been reported to catalyze a series of emerging reduction reactions.62−64 The production of fuels and/or value-added chemicals, such as H2, CO, and H2O2, has been investigated utilizing experimental and/or density functional theory (DFT)-based calculations.38,80 Also, it has been reported that the effective activation of O2 for aerobic organic oxidation reactions, a nd (iii) redox reactions. The structure−performance relationships for some specific reactions on single-atom photocatalysts are discussed and summarized. Additionally, we elucidate reaction mechanisms for single-atom photocatalysts, as revealed by the state-of-art characterization techniques and/or theoretical calculations. Moreover, new opportunities in this emerging research area, especially those merging theoretical computations and advanced characterizations are proposed.

### 2. SINGLE-ATOM PHOTOCATALYSTS FOR EMERGING REDUCTION REACTIONS

Recently, single-atom photocatalysts have been reported to catalyze a series of emerging reduction reactions.62−64 The production of fuels and/or value-added chemicals, such as H2, CO, and H2O2, has been investigated utilizing experimental and/or density functional theory (DFT)-based calculations.38,80 Also, it has been reported that the effective activation of O2 for aerobic organic conversion was achieved over single-atom photocatalysts. Moreover, the single-atom photocatalysts are applied for the dehalogenation reaction of organic halides, thus achieving detoxification and removal of harmful organic halides. A detailed discussion of the above-mentioned developments (summarized in Table 1) in single-atom photocatalysis is presented below.

| Photocatalyst | Light source | Reactants | Reaction | Main product | Activity | Stability | ref |
|--------------|--------------|-----------|----------|--------------|----------|-----------|-----|
| Co/C3N4     | xenon lamp   | O2, H2O   | H2O2 production | H2O2 | 62 μM h⁻¹ | 8 h | 38 |
| Co Phthalocyanine/g-C3N4 | xenon lamp | Benzyl alcohol | O2 activation | Benzyl aldehyde | 85 |
| Ag/AgF     | 425 nm LED  | 4-idoanisole | Dehalogenation reactions | Biphenyl derivative | 92% conversion | 12 h | 88 |

Table 1. Single-Atom Photocatalysts for Emerging Reduction Reactions

H2O2, a common commodity chemical product, has various industrial and commercial applications, such as an oxidizing agent for chemical production, preventing infections in medical practice, and removing pollutants/contaminants in the environment.81−83 Due to its relatively high oxidation potential (E0 = 1.763 V vs NHE at pH = 0),84 H2O2 is utilized as an environmentally friendly and widely available oxidant with only H2O and O2 produced after usage. Owing to its high energy density, liquid H2O2 shows great potential for storing energy and can be further used in fuel cells. However, the conventional techniques for producing H2O2 on an industrial scale suffer from toxic emissions and/or large energy consumption. Thus, the low-cost generation of H2O2 by using an environmentally friendly photocatalytic process under ambient conditions is highly desirable. Recently, two-dimensional (2D) carbon nitrile (C3N4) loaded with single-atom cobalt (Co) and anthraquinone (AQ) was synthesized for solar-light-driven H2O2 generation.38 Specifically, bulk C3N4 was first exfoliated into C3N4 nanosheets by ultrasonication. Then, single-atom Co was anchored onto the C3N4 surface through Co ion coordination and pyrolysis in the N2 atmosphere followed by phosphorylation. Finally, AQ was linked to the edge of the as-prepared single-atom Co-anchored C3N4 nanosheets (Co1/C3N4) via forming amide bonds between the carboxylic groups in AQ and primary/secondary amine groups on the edge of C3N4, thus yielding Co1/AQ/C3N4 composite photocatalyst. As displayed in Figure 1a, the single-atom Co species on the surface of C3N4 nanosheets serve as the H2O oxidation centers, while AQ at the edge of C3N4 nanosheets acts as the O2 reduction center. The ultra-thin few-layer morphology of C3N4 nanosheets is shown in the TEM image (Figure 1b) of Co1/AQ/C3N4. The dispersion of isolated Co atoms on C3N4 nanosheets is further confirmed by the atomic-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image in Figure 1c. Moreover, the HAADF-STEM image of Co1/AQ/C3N4 (Figure 1d) and the corresponding elemental mapping images (Figure 1e−h) further corroborate the good dispersion of Co across the C3N4 nanosheet surface. Besides, no Co−Co coordination observed in the Fourier transform (FT) extended X-ray absorption fine structure (EXAFS) spectrum of Co1/AQ/C3N4 (Figure 1i) further supports the atomic dispersion of Co. The results in Figure 1i further suggest that P is mainly coordinated with Co in Co1/AQ/C3N4, which supports the complete phosphorylation. Moreover, as displayed in Figure 1j, the absorption edge position and spectral line shape of Co1/AQ/C3N4 and CoO are quite similar, indicating that the valence state of the single-atom Co is near +2. The X-ray absorption near-edge structure (XANES) spectrum of Co1/AQ/C3N4 (Figure 1k) further indicates that the H2O2 production rate was improved by...
7.3 times after coloading single-atom Co species and AQ simultaneously. Besides, Co₁/AQ/C₃N₄ exhibits a high selectivity of over 60%, much higher than other samples, such as bulk C₃N₄, ultrathin C₃N₄, and Co₁/C₃N₄ (Figure 1l). The greatly enhanced photocatalytic H₂O₂ generation activity and selectivity are ascribed to the simultaneous loading of both single-atom Co species as H₂O oxidation centers and AQ as the O₂ reduction center, respectively. Moreover, the DFT-based computations show two distinct and occupied midgap states about 0.5 and 0.9 eV above the valence band edge as the H₂O is absorbed, thus boosting the localization of photo-

Figure 1. (a) 2D C₃N₄ nanosheets with spatially separated single-atom Co and AQ species as the H₂O oxidation centers and the O₂ reduction centers, respectively. (b) TEM image of Co₁/AQ/C₃N₄. (c) Atomic-resolution HAADF-STEM image of Co₁/AQ/C₃N₄ and the corresponding EDX elemental mapping images of (e) N element, (f) C element, (g) O element, and (h) Co element. (i) Fourier transform (FT) EXAFS spectra of Co K edge for Co₁/AQ/C₃N₄, Co foil, and Co₃O₄. (j) Normalized XANES of Co K edge for C₃N₄, Co₁/AQ/C₃N₄, Co foil, Co₃O₄, and CoO. (k) Time course of H₂O₂ generation utilizing simulated solar light illumination on Co₁/AQ/C₃N₄ and CoNano/AQ/C₃N₄. Dotted lines (Co₁/AQ/C₃N₄ and CoNano/AQ/C₃N₄) are H₂O₂ generation estimated assuming additive improvement of each cocatalyst. Solid line (ultrathin C₃N₄) in Figure 1k is the fitting result of the kinetic model. (l) H₂O₂ generation selectivity of bulk C₃N₄, ultrathin C₃N₄, AQ/C₃N₄, Co₁/AQ/C₃N₄, and Co₁/AQ/C₃N₄. Density of states calculated using the DFT-based theory for (m) ultrathin C₃N₄ and (n) Co₁/C₃N₄. Reproduced with permission from ref 38 (with CC BY-NC-ND License). Copyright 2020 National Academy of Sciences.
induced holes and the dissociation of photoinduced electrons and holes (Figure 1m and n).

Aniline is a significantly widely used raw material in the modern chemical industry and pharmaceutical industry. Due to the lack of efficient and excellent catalysts, He et al. used the DFT calculations to predict the possible highly active photocatalyst for the synthesis of aniline from nitrobenzene under solar light irradiation. Based on their calculation results, a single-atom Pt decorated graphitic carbon nitride (Pt@g-C3N4) showed excellent catalytic performance for the hydrogenation of nitrobenzene and high selectivity for forming aniline. They explored four possible reaction pathways in Figure 2a to find the most suitable one. According to the calculation results of reaction energies and the activation energies required for all the possible intermediates, the preferential thermodynamic route over Pt@g-C3N4 is hydrogenation of nitrobenzene producing aniline. Hence, the activation barrier for each reaction step was computed and the corresponding energy profiles are shown in Figure 2b. The N−O bonds on Pt single atom of Pt@g-C3N4 are cracked by a single hydrogen atom, followed by the Ph-NO → Ph-NOH → Ph-N hydrogenation pathway, while in the conventional dissociation of N−O bonds on the Pt (111) surface, these bonds are attacked by two hydrogen atoms and undergo the Ph-NO2 → Ph-NOOH → Ph-NO → Ph-NOH → Ph-N → Ph-NH → Ph-NH2 hydrogenation pathway. The DFT-based calculations also indicate that the energy barriers for hydrogenations of phenyl, -C≡C, -C≡C, and -CHO substituents on single-atom Pt@g-C3N4 photocatalyst are 1.05, 1.49, 1.29, and 1.53 eV, higher than those for the overall hydrogenation of nitrobenzene. Besides, the incorporation of single Pt atom narrows the bandgap of g-C3N4 from 2.7 to 0.72 eV, suggesting that both visible light and infrared light could be harvested by Pt@g-C3N4 (Figure 2c), thus enhancing the light-capturing ability of the pristine g-C3N4.

The efficient activation of O2 is of great importance for achieving sunlight-driven aerobic organic conversion under atmospheric pressure. Recently, Chu et al. reported the photocatalytic O2 activation by cophtalocyanine/g-C3N4(CoPc-g-C3N4) heterostructure with single Co−N4 (II) sites. Based on theoretical calculations, they utilized melamine and cyanuric acid as the raw materials to fabricate carbon nitride nanosheets, followed by phosphate modification and introduction of CoPc to obtain the CoPc-g-C3N4 heterojunction (shown in Figure 3a). The rough dark shadows in Figure 3b could be assigned to the loaded CoPc, which is confirmed by the HAADF-STEM image (Figure 3c) and the corresponding elemental mapping images (Figure 3d). The UV−vis absorption spectra and FT-IR and Raman spectra indicate that the thinner assemblies and high dispersion of CoPc are induced by phosphates and CoPc could interact with g-C3N4 and P-doped g-C3N4(P-CN) via the H-bonding. The interfacial charge transfer between CoPc and P-doped g-C3N4 was confirmed by the steady-state surface photovoltage spectroscopy and photoluminescence (PL) and fluorescence spectral (FS) data. The electron paramagnetic resonance (EPR) results in Figure 3e indicate that 0.5CoPc/9P-CN is the optimized photocatalyst for O2 activation where O2 is reduced to produce •O0 radicals. As regards the catalytic performance test for O2 activation, the optimized CoPc/P-CN with abundant single-atom Co−N4 sites exhibits excellent photocatalytic activity for 2,4-dichlorophenol (DCP) degradation (shown in Figure 3f) and the possible mechanism of the oxidative degradation of 2,4-DCP over CoPc/P-CN is illustrated in Figure 3g. Moreover, the optimized 1.8CoPc/12P-CN photocatalyst was tested for selective oxidation of 2,4-DCP. The results are discussed in the context of the literature and are supported by experimental evidence. The mechanistic pathways for the photocatalytic reactions are elucidated in detail, providing insights into the design of efficient photocatalysts for various applications.
aromatic alcohols, exhibiting a 25.6% yield for producing benzaldehyde (Figure 3h).

Dehalogenation reaction of organic halides is considered as one of the most important transforming processes because of its potential use for detoxification and removal of harmful organic halides. Wu et al. used AgF as a photocatalyst for the selective dehalogenation of various organic halides under visible light illumination. Irradiated by visible light, AgF
The reduction reactions of widely available raw materials into fuels and value-added chemicals, such as H₂O₂ and aniline, have been successfully achieved on single-atom photocatalysts.

would be converted to Ag single atoms (Ag-SAs) and Ag nanoparticles, which could trigger hydro-deiodination or deiodination-phenylation of organic halides in a specific solvent. Recycling tests were performed to understand the key role of this photocatalytic reaction. The in situ electron spin resonance (ESR) spectroscopy studies and contrast experiment data confirm that Ag-SAs acts as the reactive center for photocatalytic deiodination reactions.

3. SINGLE-ATOM PHOTOCATALYSTS FOR EMERGING OXIDATION REACTIONS

As discussed in our previous work, selective photocatalytic oxidation is a promising strategy to produce various value-added chemicals. Although photocatalytic selective oxidation of organic compounds to form valuable chemicals has been extensively investigated, it is still challenging to achieve the high-selectivity yield of desired chemical products. Recent studies (shown in Table 2) indicate that single-atom photocatalysts can achieve the efficient activity, high selectivity, and strong stability toward selective oxidation reaction, thus generating target chemicals, such as phenol and imines.

Photocatalytic selective oxidation of organic compounds on single-atom photocatalysts is a promising strategy to produce various desirable value-added chemicals.

Phenol is utilized as a pivotal organic chemical intermediate and precursor to synthesize many important industrial products, e.g., phenolic resins, bisphenol A, cyclohexanol, polysulfone, carbonate, aniline, and o-cresol. However, the current industrial procedure to synthesize phenol from benzene requires multiple steps and indirect preparation, thus suffering from many drawbacks, e.g., complex preparation processes, severe depletion of raw materials, and serious environmental contamination. Hence, it is of great importance to discover cost-effective strategies for phenol production via benzene oxidation utilizing H₂O₂ from the industrial and social perspectives. This is also one of the most challenging tasks in the green chemistry field. Recently, Xiao et al. anchored single-atom Cu (SA-Cu) on tubular carbon nitride (TCN) for visible-light-induced photocatalytic benzene oxidation to generate phenol using H₂O₂. As demonstrated in Figure 4a, SA-Cu-TCN is synthesized via thermal treatment of melamine-based precursor containing chlorophyll sodium copper (CSC). The TEM results of SA-Cu-TCN and the enlarged marked area are displayed in Figure 4b and 4c. The corresponding elemental mapping images of N, C, and Cu are presented in Figure 4d–f, respectively. In particular, the uniform distribution of Cu element on the whole carbon nitride is confirmed in Figure 4f. The aberration-corrected HAADF-STEM image (Figure 4g) displays the detection of single-atom Cu, confirming the fabrication of single-atom Cu in SA-Cu-TCN. Moreover, X-ray absorption spectroscopy (XAS; see Figure 4h) study reveals the valence state of Cu in SA-Cu-TCN, as well as the coordination environment. Since its absorption edge is located in the middle of those edges of CuO and Cu₂O, both Cu(I) and Cu(II) are supposed to be present in SA-Cu-TCN. Figure 4i displays the Fourier transform of the k²-weighted EXAFS spectra for the Cu K edge on Cu foil, CSC, and SA-Cu-TCN. The predominant peak at ca. 1.6 Å is assigned to the Cu–N bond in SA-Cu-TCN, again confirming the loading of single-atom Cu on TCN. Since the local coordination environment intimately affects the form of X-ray absorption near edge structure (XANES) spectra, the authors employed FEFF9.6 code to calculate the spectra of two coordination structures (denoted as Cu–N₁ and Cu–N₂) as shown in Figure 4j and k, respectively. Also, the XANES results of SA-Cu-TCN are verified by the simulated spectra shown in Figure 4j and k. The construction of the Cu–N₁ structure is attributed to the interaction of Cu atom and three N atoms in the TCN layer. Meanwhile, the interaction between four N atoms from two CN monolayers and a single atom results in Cu–N₄ coordination. The calculated charge density differences between the Cu–N₁ and Cu–N₄ coordination of SA-Cu-TCN are shown in Figure 4l and m, respectively. The charge migration in Cu and its adjacent N atoms is disclosed. In Cu–N₄ coordination, the apparent charge migration along the z-direction is also manifested in Figure 4m. Hence, the aforementioned results indicate that these Cu–N configurations in SA-Cu-TCN generate novel charge migration channels for enhancing the charge movement within and between the carbon nitride planes. This will boost the photocatalytic performance. Moreover, the benzene-to-phenol conversion was used to test the photocatalytic oxidation performance on SA-Cu-TCN. No benzene-to-phenol conversion happened without the catalyst. In dark conditions, SA-Cu-TCN attained a benzene-to-phenol conversion efficiency of 41.2% with a selectivity of 88.3%. Using visible light, SA-Cu-TCN shows the conversion and selectivity of 92.3% and 99.9%, respectively (Figure 4n), much larger than those obtained on CN and TCN. Besides, SA-Cu-TCN also possesses good robustness for benzene oxidation to phenol. The outstanding photocatalytic performance arises from the formation of the Cu–Nₑ electron/hole migration path in SA-Cu-TCN, thus

Table 2. Single-Atom Photocatalysts for Emerging Oxidation Reactions

| Photocatalyst       | Light source | Reactants                     | Oxidation reaction | Oxidation reaction | Activity | Stability | ref |
|---------------------|--------------|-------------------------------|--------------------|--------------------|----------|-----------|-----|
| Cu/C₃N₄            | λ > 420 nm   | benzene, H₂O₂, CH₃CN          | Benzene oxidation  | Phenol             | 92.3% conversion | 12 h      | 41  |
| Co/carbon quantum dots | 460 nm LED  | Benzylamine, CH₃CN           | Oxidative coupling | (E)-N-benzyl-1-phenylmethanimine | 83% conversion | 4 cycles | 93  |
Figure 4. (a) The synthesis process of SA-Cu-TCN. (b) TEM image of SA-Cu-TCN and (c) the enlarged TEM image of the marked area in Figure 4b and the elemental mapping images of (d) N, (e) C, and (f) Cu elements. (g) A typical HAADF-STEM image of SA-Cu-TCN. (h) XANES spectra of the Cu K edge for SA-Cu-TCN, CSC, Cu foil, Cu2O, and CuO samples. (i) Fourier transform (FT) of the K2-weighted EXAFS Cu K edge of SA-Cu-TCN, Cu foil, and CSC. (j, k) Experimental and computed XANES spectra of the Cu K edge for the samples with the corresponding structure models (inset). (l, m) Differential charge surfaces of the Cu−N3 and Cu−N4 coordination structures. (n) Catalytic activity of SA-Cu-TCN for oxidation of benzene performed at 50 °C using visible light illumination for 12 h. Reproduced with permission from ref 41. Copyright 2020 John Wiley & Sons, Inc.
tremendously advancing the in-plane and interplane charge migration.

It is of great importance to selectively oxidize benzylamine as well as its derivatives to form imines since they are pivotal electrophilic intermediates in pharmaceutical synthesis.91,92 In recent work, Wang et al. fabricated single-atom Co dispersed on carbon quantum dots (CoSAS@CD) for selective photocatalytic oxidation of benzylamine together with a range of its derivatives to yield imines in the presence of O2 using visible light illumination (Figure 5a).93 CoSAS@CD was fabricated through pyrolyzing vitamin B12 followed by hydrolysis in NaOH solution. CoSAS@CD was treated with an acid to yield the acid-treated CoSAS@CD (CoSAS@CD-acid). The TEM image of CoSAS@CD (Figure 5b) discloses that the as-prepared carbon dots are spherical with an averaged 9.0 nm diameter. Many bright dots (diameter <0.2 nm) observed in the aberration-corrected HAADF-STEM image (Figure 5c) could be ascribed to the single Co atoms. This result suggests that individual Co atoms are distributed on the carbon dots surface. Furthermore, the XANES Co K edge was recorded to study the chemical state of Co sites. As presented in Figure 5d, the absorption edges of CoSAS@CD and CoSAS@CD-acid are positioned between those for CoO and CoOOH, suggesting the existence of Co(II) and Co(III). Moreover, the Fourier transform (FT) k³-weighted EXAFS results show that only one major peak at ca. 1.9 Å is observed for both samples. This could be the first coordination shell of Co−N/C as that present in Co-porphyrin (CoPo). In particular, no apparent Co−Co peak located around ca. 2.5 Å and the HAADF-STEM result (Figure 5e) indicate the atomic dispersion of Co in CoSAS@CD. Then, benzylamine and its derivatives were selectively oxidized to yield imines in high conversion efficiency and excellent selectivity utilizing CoSAS@CD as the photocatalyst using visible light in the existence of O2. Moreover, CoSAS@CD exhibited excellent stability over four cycles (Figure 5f).

![Figure 5](image-url)

**Figure 5.** (a) Photocatalytic oxidative coupling of benzylamines with CoSAS@CD using visible light. (b) TEM image of CoSAS@CD; Figure 5b inset displays the size distribution of CoSAS@CD. (c) A typical HAADF-STEM image of CoSAS@CD. (d) XANES spectra of Co K edge for CoSAS@CD, CoSAS@CD-acid, Co foil, CoO, CoOOH, and Co-porphyrin (CoPo). (e) Fourier transform EXAFS spectra of Co K edge for CoSAS@CD, CoSAS@CD-acid, Co foil and CoPo. (f) The reaction conversion and selectivity of oxidative photocatalytic coupling of benzylamines on CoSAS@CD using visible light over 4 repeating cycles. Reproduced with permission from ref 93 (with CC-BY license). Copyright 2020 American Chemical Society.

| Photocatalyst | Light source | Reactants | Redox reaction | Main Product | Activity | Stability | ref |
|---------------|--------------|-----------|----------------|---------------|-----------|-----------|-----|
| Ru/Cu         | White light  | CH₄ and CO₂ | methane dry reforming | CO₂, H₂ | 34 mol H₂ mol⁻¹ s⁻¹ | 50 h | 78 |
| Co–P₃/CdS     | λ > 420 nm   | formic acid | dehydrogenation of formic acid | CO₂, H₂ | 102.9 mmol g⁻¹ h⁻¹ | 24 h | 94 |
| Pt/TiO₂       | Xe lamp      | acetone   | acetone dehydrogenation and C–C coupling | 2,5-hexanediol, H₂ | 3.87 mmol g⁻¹ h⁻¹ | 16 h | 42 |
| Fe/carbon nitride | 460 nm LED | Styrene, p-methylbenzenesulfonic acid | sulfonation of alkenes | β-ketosulphones | 94% conversion | 79 |
The reduction and oxidation products via redox reactions could be obtained as the target products simultaneously by utilization of photo-generated electrons and holes over single-atom photocatalysts.

Syngas comprised of CO and H2 is extensively utilized in industrial-scale processing. Syngas can be generated by MDR reaction, where two greenhouse gases could be transformed into a high-value chemical feedstock.95 However, the MDR reaction is not only kinetically and thermodynamically unfavorable but also suffering from coke deposition and the subsequent deactivation of catalysts. Moreover, high temperatures (700–1000 °C) are required to attain efficient reaction rates and reduce coke deposition. Thus, the photocatalytic MDR under light irradiation and tremendously milder reaction conditions is of great significance. Recently, Zhou et al. have prepared single-atom site Ru–Cu alloy as an antenna-reactor plasmonic photocatalyst via coprecipitation on the surface of a MgO/Al2O3 substrate (Figure 6a).78 In detail, a series of CuRu catalysts (i.e., Cu20, Cu19.9Ru0.1, Cu19.8Ru0.2, Cu19.6Ru0.4, and Cu19.5Ru0.5) was fabricated, where x and y are the percentages of Cu and Ru of metal contents in the photocatalysts. The as-synthesized photocatalysts were tested for light-driven MDR using white light illumination. Single-atom Ru–Cu alloy (Cu19.8Ru0.2) exhibited much higher photocatalytic MDR activity, stability, and selectivity than bare Cu NPs (Figure 6b and c). Besides, Cu19.8Ru0.2 shows a turnover frequency (TOF) of 34 molH₂ molRu⁻¹ s⁻¹ and excellent photocatalytic stability over 50 h. Moreover, due to the low coverage of Ru on the surface of Cu19.9Ru0.05, the exposed Cu on the surface (Figure 6d) catalyzed a large fraction of the reaction. However, the Cu atoms exposed are susceptible to coking. Since the Ru content is smaller than 0.2%, it is postulated that Ru is atomically loaded onto the surface of Cu, separating carbon intermediates on the surface and inhibiting the graphitic carbon generation (Figure 6e). For comparison, with larger Ru content (Cu19.5Ru0.5), the generated Ru assembles or some islands can be formed, which promote the carbon formation considering their proximity. Thus, dehydrogenated derivatives of CH₄ (CH₂) oligomerize and yield coke (Figure 6f). The robustness tests are also repeated to corroborate the above conclusions. Both CO probe molecule diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) and DFT-based computations are combined to support the single-atom Ru dispersion in Cu (Figure 6g). Moreover, the authors conducted periodic DFT +D3 calculations to further probe the reaction mechanism. They found that the most likely rate-limiting steps of FA dehydrogenation on Cu and CuRu are the first step of hydrogen dissociating from CH₄ (CH₄ → CH₃ + H) and the fourth step of hydrogen dissociating from CH intermediate (CH → C + H) (see Figure 6h and i). Hence, the embedded multiconfigurational n-electron valence second-order perturbation theory (e-NEVPT2) was applied to study the above two steps. It was predicted that the first dehydrogenation step on Cu and the fourth dehydrogenation step on CuRu possess the largest barriers. Their ground-state barriers are 2.51 and 1.10 eV, respectively (Figure 6i and k). Hence, the barrier of CH₄ dissociation can be reduced by incorporating Ru. In the above photocatalytic MDR process, the generation of hot carriers is deemed as the principal mechanism, thus leading to significantly different behavior from the thermocatalytic MDR process. Hot carriers play a key role in improving the activation rates of C–H on Ru sites and H₂ desorption off from the catalysts surface. The observed improvement results from the kinetic matching of production rates of H₂ and CO, thus minimizing the coking formation and reverse water gas shift (RWGS) rates. Thus, the reported photocatalytic MDR process is robust and selective.

The photocatalytic formic acid (FA) dehydrogenation to produce hydrogen (H₂) was achieved on the atomic-level well-dispersed Co–P₁ on CdS nanorods (NRs) photocatalyst.94 A facile impregnation–phosphorization strategy was adopted to prepare Co–P₁ with atomic dispersion onto CdS NRs. The distinct hexagonal-phase structured CdS NRs with ordered lattice spacings can be seen in the HAADF-STEM result (Figure 7a). This indicates that CdS crystal structure was not affected much in the aforementioned phosphatizing treatment at elevated temperature. The elemental mapping images in Figure 7a confirm the uniform dispersion of Co and P on the CdS NRs, and no apparent nanoparticles of Co and/or CoP are observed. Moreover, CoPSA-CdS exhibits a Co K edge higher than that of Co foil in the XANES spectra (Figure 7b).

In addition, the main peak of CoPSA-CdS located around ca. 1.63 Å in the EXAFS spectra (Figure 7c) is ascribed to the Co–P bond. The EXAFS fitting results further indicate that the centered Co atoms in CoPSA-CdS possess one Co–P₁ and two Co–Pᵢ, again supporting the atomic dispersion of Co atoms in CoPSA-CdS. Based on the aforementioned XAFS results, the theoretical computation was executed to construct the atomic geometry structure of CoPSA-CdS in Figure 7d. As displayed in Figure 7d, the Co atom is coordinated with one Co–P₁ and two Co–Pᵢ bonds. Then the catalytic performance of these samples was investigated via dehydrogenation of FA into H₂ and CO₂ under visible-light illumination at room temperature. In Figure 7e, CoPSA-CdS manifests the highest photocatalytic performance for FA dehydrogenation with a rate of 102.9 mmol·g⁻¹·h⁻¹, much higher than pristine CdS,
Figure 6. (a) Illustration of a single-atom Ru embedded Cu alloy photocatalyst. The reactants and products of MDR are displayed on the left panels. (b) Photocatalytic MDR activities and stabilities of pure Cu NPs (Cu20) and Ru/Cu alloys with different Ru contents (Cu19.95Ru0.05, Cu19.9Ru0.1, Cu19.8Ru0.2, and Cu19.5Ru0.5) using white light irradiation. The reactor for conducting the photocatalytic MDR reaction was maintained at room temperature. (c) Photocatalytic MDR selectivity of pure Cu NPs (Cu20) and Ru/Cu alloys with different Ru contents (Cu19.95Ru0.05, Cu19.9Ru0.1, Cu19.8Ru0.2, and Cu19.5Ru0.5) using white light irradiation. The reactor for conducting the photocatalytic MDR reaction was maintained at room temperature. The formation rate ratio of H2 to CO is defined as the selectivity. Schematic illustration for the influence of CuRu composition on the coke resistance for (d) Cu alone, (e) CuRu with low Ru loading content, and (f) CuRu with high Ru loading content. (g) Infrared spectra of CO adsorbed on single-atom Ru embedded Cu alloy surface at room temperature and saturation coverage following pretreatment at 200 °C in 10% CO in Ar (100 mL min⁻¹) for 60 min. Rate-determining (h) CH₄ and (i) CH activation on Cu (111) and CuRu (111), respectively. Left, middle, and right panels indicate reactant, transient state, and product structure, respectively. Ground- and excited-state energy curves for CH₄ activation on (j) Cu (111) and (k) Cu activation on CuRu (111) from e-NEVPT2. From the ground to the highest energy excited state, the color saturation of the curves turns from dark to light. Reproduced with permission from ref 78. Copyright 2020 Springer Nature.
Figure 7. (a) HAADF-STEM image and the relevant elemental mapping images of CoPSA-CdS. (b) X-ray absorption spectra of Co and (c) the corresponding $k^3$-weighted FT space at R space. (d) Atomic-level structure configuration of CoPSA-CdS based on first-principles simulation. (e) Comparison of the photocatalytic activities for FA dehydrogenation on all the as-prepared samples. The test of photocatalytic FA dehydrogenation reaction was conducted in the 100 mL 20 vol % FA aqueous solution using visible light illumination ($\lambda > 420$ nm) at room temperature. (f) Transient-state photoluminescence spectra of the as-prepared samples. (g) In situ IR spectrum analysis for photocatalytic dehydrogenation of FA on (g) CoPSA-CdS. (h) Free energy profiles calculated for the photocatalytic FA dehydrogenation process on P-CdS, CoSSA-CdS, and CoPSA-CdS. The differential charge density maps between CdS and adsorbed FA on (i) P-CdS, (j) CoSSA-CdS, and (k) CoPSA-CdS. (l) Photocatalytic FA dehydrogenation and H$_2$ evolution mechanism on CoPSA-CdS. Reproduced with permission from ref 94. Copyright 2020 John Wiley and Sons, Inc.
phosphatized CdS NRs (P-CdS), or S-coordinated Co single atom on CdS NRs (CoSSA-CdS). Besides, CoPSA-CdS presents an ca. 100% product selectivity for CO₂ and H₂ with a 1:1 ratio. Thus, the generation of byproducts was efficiently suppressed on CoPSA-CdS. Furthermore, CoPSA-CdS shows much higher activity than Ru-loaded CdS (Ru-CdS), Rh-loaded CdS (Rh-CdS), Pd-loaded CdS (Pd-CdS), or Pt loaded CdS (Pt-CdS) as displayed in Figure 7e. Additionally, CoPSA-CdS displays the highest mass activity of Co (34,309 mmol g⁻¹ h⁻¹), in contrast to the previous record. Such an outstanding activity of CoPSA-CdS was explored by both experimental characterizations and theoretical computations. Transient-state photoluminescence spectra (Figure 7f) indicate the most efficient charge migration in CoPSA-CdS compared to CdS, P-CdS, or CoSSA-CdS. Moreover, the in situ IR spectrum study of the photodriven FA dehydrogenation on CoPSA-CdS (Figure 7g) shows the apparent peak intensity reduction of the C—H bond in the IR spectra, suggesting the effective FA adsorption and C—H bond activation on CoPSA-CdS. Additionally, the apparent IR peak intensity improvement around 2324 cm⁻¹ was found for CoPSA-CdS (Figure 7g), indicating the marked generation of CO₂. Moreover, the DFT-based computations were executed to further probe into the reaction mechanism of the photocatalytic FA dehydrogenation. Figure 7h displays that the hydroxyl group of FA is inclined to dissociate between the adjacent P and Co atoms, ascribed to the *HCOO-H compound. Thus, the P-HCOO generation along with the H adsorption on Co atom are achieved on CoPSA-CdS. As presented in Figure 7h, this is a spontaneous reaction step based on the negative reaction energy (−0.29 eV). In comparison, both CoSSA-CdS and P-CdS show positive reaction energy. As regards CoPSA-CdS, its FA dehydrogenation activity is restricted by the hydrogen migration process between P atom and the adjacent Co atom during the reaction, with positive reaction energy (0.88 eV). Thus, CoPSA-CdS displays a smaller energy barrier toward FA dehydrogenation compared to that observed for P-CdS or CoSSA-CdS, agreeing with its highest photocatalytic performance. Moreover, Figure 7i–k exhibits the differential charge density between the CdS surface and FA owing to the pivotal role of the FA dissociation adsorption on the CdS surface. In comparison to CoSSA-CdS and P-CdS, CoPSA-CdS possesses the best capacity to transport electrons from FA to Co atom and the ability to bind with HCOO via a robust P—O bond as well (shown in Figure 7i–k). Based on these results, the proposed reaction route is illustrated in Figure 7l. When illuminated by visible-light, the photoinduced electrons and holes are transported to Co—P sites and adjacent Cd—S sites, respectively. Subsequently, photoinduced electrons on Co atoms reduce the adsorbed proton to generate H₂. Meanwhile, the photoinduced holes on Cd—S sites migrate to P sites and the adsorbed HCOO group is dehydrogenatively oxidized to generate CO₂.

As a key chemical extensively applied in biofuel and medicinal chemistry, 2,5-hexanedione (HDN) is usually prepared using costly chemicals through complicated and harsh reaction processes. Hence, it is of great significance to prepare HDN from renewable and inexpensive biomass, e.g., acetone, via cost-effective and environmentally benign solar photocatalysis under mild conditions. Recently, C—H activation of the methyl group in acetone and the subsequent cross-coupling of two CH₃COCH₂• radicals to produce HDN was achieved on single-atom Pt dispersed P25 TiO₂(PtSA-TiO₂)₃⁻¹ H₂, as a green fuel and important chemical, was also generated via dehydrogenation of acetone in the above photocatalytic process. In detail, the DFT computation was first performed to acquire the energy profiles of the acetone dehydrogenation reaction on various single metal atoms dispersed on P25 TiO₂. The computation results indicate that the methyl dehydrogenation and generation of a CH₃COCH₂• radical are the major rate-limiting processes. Thus, among the TiO₂-supported single metal atoms, PtSA-TiO₂ possesses the smallest energy barrier toward dehydrogenation of acetone. Indeed, PtSA-TiO₂ is confirmed to be the most effective photocatalyst with 3.87 mmol g⁻¹ h⁻¹ of 2,5-hexanedione production rate and 93% selectivity. In the reaction procedure, the photoinduced holes from TiO₂ activated methyl groups, thus leading to their dehydrogenation into H species on Pt single atoms and CH₃COCH₂• radicals on TiO₂. Subsequently, two CH₃COCH₂• radicals can achieve C=C coupling and produce 2,5-hexanedione; while two photoinduced electrons reduce two H to H₂ gas. Both in situ IR and ESR techniques confirm the above process.

As a pivotal category of organic molecules containing sulfone, β-ketosulfones have been extensively applied for synthesizing pharmaceuticals and organic functional materials. Especially, significant attention has been drawn recently by β-ketosulfones owing to their interesting biological activities and key preparation applications. Unfortunately, the previously reported homogeneous photocatalytic preparation and functionalization processes of β-ketosulfones suffer from a narrow light absorption range, restricted substrate scope, and unrecoverable catalysts. Hence, it is important to explore highly efficient, recoverable, and environmentally friendly heterogeneous photocatalysts to prepare β-ketosulfones. Wen et al. adopted a facile molecule coupling approach to fabricate carbon nitride-hemin (CNH) composite photocatalyst. The atomic-resolution HAADF-STEM image of CNH exhibits the bright spots with sizes of ca. 0.20 nm, ascribed to the loading of single atom Fe on CNH. The as-prepared CNH with single-atom Fe dispersion exhibits the excellent catalytic performance for olefins sulfonation, yielding β-ketosulfones under the condition of room temperature and normal pressure using visible light and/or near-infrared light. It is proposed that O₅⁻ and singlet oxygen O₂, which are generated by reduction of molecular oxygen using photoinduced electrons, together with photoinduced holes participate in the sulfonation of olefins to produce β-ketosulfones.

5. Conclusion and Outlook

Nowadays an increasing number of single-atom photocatalysts are designed and fabricated toward the emerging reactions yielding the highly desirable chemicals and/or energy carriers. These chemicals and energy carriers are conventionally synthesized under harsh conditions at a high cost. In contrast, single-atom photocatalysts could achieve outstanding activities, selectivity, and/or stabilities toward these reactions in mild conditions by using clean and renewable solar energy. A series of advanced characterization methods, e.g., aberration-corrected scanning transmission electron microscopy (AC-STEM), synchrotron radiation-based X-ray absorption spectroscopy (XAS), in situ Fourier transform infrared spectroscopy (FT-IR), and in situ ESR spectroscopy, are integrated with DFT-based calculations to uncover the insightful and overall structure–performance relationship for single-atom photocatalysts. Besides, detailed and in-depth photocatalytic mechanisms for these reactions are also explored.
Though many breakthroughs have been made in the above field, there are still many challenging obstacles to overcome. For instance, the rational design and synthesis of appropriate single-atoms (e.g., Fe, Ni, Ru, Rh, Pd, Ag, Pt, and Au) with desirable coordination environments (e.g., M-N\textsubscript{4}, M-P\textsubscript{3}, M-N/O, and M-N/P) showing high activity and selectivity toward specific reactions is of great importance. Besides, it is highly desirable to seek suitable strategies for achieving strong metal–support interactions in single-atom photocatalysts, assuring long-term stable activity and selectivity. For instance, supports with abundant coordination sites (e.g., N\textsubscript{4}, P\textsubscript{3}, N/O, and N/P) should be designed and synthesized for anchoring large amounts of single atoms as active sites. Moreover, supports with sufficient cation/anion vacancies can also be utilized to stabilize suitable single atoms to achieve strong metal–support interactions. Furthermore, more approaches should be discovered for the controllable, scaled-up, and cost-effective production of single-atom photocatalysts via eco-friendly routes. On the other hand, a variety of powerful in situ or operando characterization techniques, in situ transmission electron microscopy (TEM), in situ X-ray photoelectron spectroscopy (XPS), and in situ Raman spectroscopy, can be adopted to disclose the real-time morphologies, structures, compositions, and surface chemical states of photocatalysts as well as intermediate/product compositions and contents for important reaction processes. The above measurements and calculations can be further utilized to understand the true structure–activity relationship for these photocatalysts as well as the actual and precise reaction mechanisms. Moreover, an increasing advancement of computation methods permits better integration of experimental and computational approaches to elaborate the structure–activity correlation and/or reaction mechanisms for single-atom photocatalysts. Furthermore, it is of great significance to achieve a high-throughput screening of novel photocatalysts via theoretical computations, followed by experimental design and fabrication of these photocatalysts toward specific reactions. The acquired knowledge and achievements are anticipated to tremendously advance the widespread utilization of high-performance and brand-new single-atom photocatalysts in the near future.

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**Notes**

The authors declare no competing financial interest.

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