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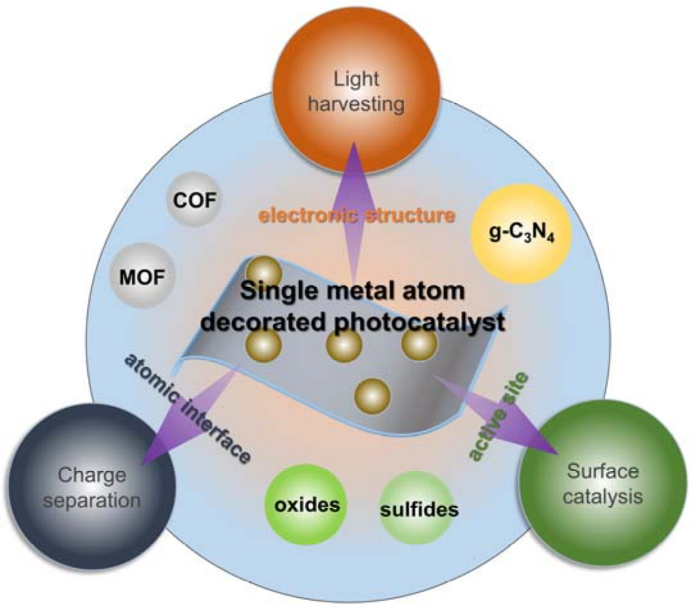
Single metal atom decorated photocatalysts: progress and challenges

Lei Zeng and Can Xue*

Nanyang Technological University, Singapore



This mini review summarizes recent progress on single metal atom decorated photocatalysts, and discusses the roles of the single metal atom catalysts in different types of host photocatalysts including organic, carbon-based and inorganic materials.

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Single metal atom decorated photocatalysts: progress and challenges

Lei Zeng[1], Can Xue[1] (✉)

[1] *School of materials science and engineering, Nanyang Technological University, 50 Nanyang avenue, 639798, Singapore*

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ABSTRACT

Photocatalysis has attracted intense attention due to its potential to solve the energy resource problem and environmental issues. The single metal atom decorated photocatalysts as a rising star become more and more popular because of the unique advantages of superior catalytic activities and ultrahigh atom utilization efficiency. The key function of single metal atom catalysts in photocatalytic reactions is boosting surface redox reactions by utilizing photogenerated charges, and has been verified by various spectroscopic and microscopic techniques. Nevertheless, the activities of the single metal atoms highly depend on the binding environment in the host photocatalyst that affect the adsorption and activation of reactants as well as the reaction energy barrier. Herein, this mini review summarizes recent progress on single metal atom decorated photocatalysts, and discusses the roles of the single metal atom catalysts in different types of host photocatalysts including organic, carbon-based and inorganic materials. The remaining challenges and future perspectives on the stability and activities of single atom catalysts in photocatalytic processes are elaborated in the end. We believe that this mini review will provide valuable overview on synthetic methods of different single atom photocatalysts for researchers towards future development of highly efficient photocatalysts.

KEYWORDS

Photocatalysis, single atom, carbon nitride, recent progress

1 Introduction

The photon energy from sunlight is one of the most attractive energy sources due to the abundance, cleanliness and sustainability. Inspired by nature, it is an ideal and economic solution to convert solar energy and store it in chemical bonds through generation of high value-added hydrocarbon compounds. To realize this conversion route, researchers have tried many kinds of semiconductors to harvest light and implement photocatalytic processes, in which the photogenerated electrons and holes are separated and consumed for different redox reactions.

To promote photocatalytic activities, catalysts are usually decorated on the surface of semiconductor photocatalysts to enhance the charge separation, boost the redox reaction rate, and improve the selectivity [1]. In particular, single atom catalysts (SACs) have attracted great research attention since 2011, when Zhang et al. reported that single Pt atoms on FeO_x support showed ultrahigh catalytic activity and stability on CO oxidation reaction [2]. Comparing with traditional catalysts of clusters or nanoparticles, SACs present some compelling advantages, such as well-defined active sites, superior catalytic efficiency and high metal atom utilization rate [3-9]. In fact, SACs have been successfully used in energy conversion [10] and environmental treatment [11].

including hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and other reactions [12-14].

In particular for photocatalysts, decoration of SACs can remarkably promote the surface redox reactions by regulating adsorption, desorption and activation of the reactants, intermediates and products [15]. In previous reports, people were incline to denote the photocatalyst decorated with uniformly distributed individual metal atoms or ions as “single atom photocatalyst” in order to emphasize the important functions of single metal atoms in the photocatalytic reactions. Actually, it has been proven that the introduction of SACs can tune the electronic structure, extend the light absorption range and improve the charge separation of host photocatalytic materials [16-18].

In this mini review, we aim to summarize the latest development of single atom photocatalyst and discuss the roles of single metal atoms in different host photocatalysts. As such, the discussion will be classified according to the types of host materials, including organic, carbon-based and inorganic materials. This will provide comprehensive understanding on the interactions between metal single atom and host photocatalytic material and offer valuable guidance on rational design of highly efficient photocatalysts for specific reactions. We believe that single atom photocatalyst is one of the most interesting and promising trends in the field of photocatalysis. Inevitably, the remaining challenges and future perspectives of single atom photocatalysts will be elaborated in the end.

2 Different host materials decorated with single atom catalysts for photocatalysis

2.1 Organic host materials

2.1.1 Single atom catalysts in polymeric carbon nitride based photocatalysts

Polymeric carbon nitride (PCN) is a type of polymer

Address correspondence to First A. Firstauthor, email1; Third C. Thirdauthor, email2

semiconductor with tailorable bandgap of 2.2-2.8 eV. It has ideal energy levels of conduction band and valence band that enable many attractive reactions including proton reduction, water oxidation, CO_2 reduction and N_2 fixation. In the past decade, PCN has been extensively explored for various photocatalytic applications, such as pollutant degradation, hydrogen generation, and solar fuels production [19-21]. However, the fast recombination of photogenerated charge carriers and sluggish surface reactions restrict the photocatalytic efficiency of PCN. To address these issues, researchers have attempted to decorate PCN with different catalyst particles composed by metals or metal-based compounds [22-24]. Nevertheless, the utilization efficiency of metal atoms in the catalyst particles was usually quite low. In contrast, single metal atom catalysts do have this problem.

The typical PCN structure has enriched nitrogen atoms with lone-pair electrons that enable binding with metal atoms through coordination interactions. As such, individual metal atoms can be immobilized and uniformly distributed in the PCN matrix, and serve as active catalytic sites for chemical reactions. In addition, these trapped single metal atoms, usually having positive charge, may also attract photogenerated electrons and facilitate charge separation.

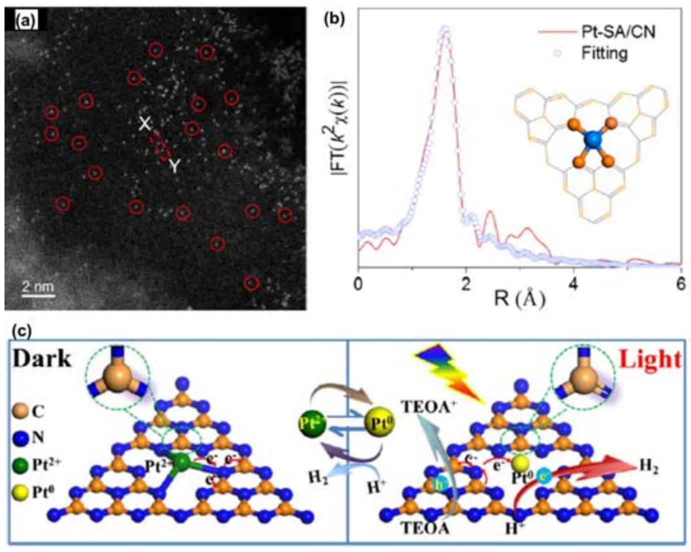

Figure 1. (a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Pt-SA/CN photocatalysts. (b) Fourier transform of the experimental extended X-ray absorption fine structure (EXAFS) spectrum and the best fitting result for Pt-SA/CN. Reproduced with permission from Ref. [27], © American Chemical Society 2018. (c) Illustration of charge transfer and bond variation on S-Pt-C_3N_4 catalysts for photocatalytic hydrogen evolution. Reproduced with permission from Ref. [29], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

In 2016, Li et al. firstly introduce single Pt atoms into PCN framework, attaining ~ 8.6 times higher photocatalytic H_2 evolution rate than Pt nanoparticle-decorated PCN [25]. They proposed that the isolated Pt single atoms induced intrinsic change of surface trap state of PCN, which significantly increased the lifetime of charge carriers. Similar studies reported by Ou et al. indicated that the Pt single atoms in PCN could facilitate charge separation of excited PCN and thus promote photocatalytic H_2 evolution [26]. Later, Cao et al. revealed that the single Pt atoms in PCN exist as Pt_1-N_4 configuration (Figs. 1(a) and 1(b)) [27]. The strong interaction between Pt and nearby N atoms led to redistribution of Pt valence electrons with highly vacant 5d orbital, and shift of d-band center toward the Femi level, which facilitated the adsorbed H to form H* and optimized the HER kinetics on the PCN surface. The studies by Su et al. also supported this conclusion [28]. They found that the high valence Pt^{II} single atoms anchored to N atoms could lead to downshift of PCN valence band and increase of mobile electrons around the Femi level, which provided a satisfactory thermodynamic condition for water oxidation. More recently, Zhang et al. presented direct observation of Pt−N bond evolution in single atom Pt/PCN during photocatalytic H_2 evolution by using synchronous illumination X-ray photoelectron spectroscopy [29]. They experimentally demonstrated that upon PCN excitation, the cleavage of Pt−N bond results in transformation of C−N bond into the C=N bond and creates active Pt^0 sites, which designates Pt0 and CN framework as separate sites for HER and oxidation reactions, respectively (Fig. 1(c)). This is considered as the intrinsic reason for dramatically enhanced photocatalytic H_2 activity of single-atom Pt loaded PCN.

Certainly, the overall photocatalytic activity is still dependent on the amount of decorated Pt single atoms. The electron-deficient PCN enriched with N−vacancies enables high-density decoration of Pt single atoms (0.35 mg/ m^2) through in-situ photoreduction at low temperature (< 0 °C) [30]. Recently, a different strategy was presented by Zeng et al. to achieve ultrahigh single Pt atom loading (8.7 wt.%) on PCN by using the interlayer space to accommodate the metal atoms [31]. The simulation studies showed that the PCN interlayer environment could delocalize the charge density of Pt atoms, which reduces HER energy barrier and promotes the photocatalytic activity for hydrogen generation.

Besides Pt, gold is also a typical noble metal that can be decorated as single atom catalyst on PCN for photocatalytic reactions. Su et al. introduced both Pt and Au atoms into PCN to gain atomically dispersed Pt_1N_x−Au_1N_x sites that act as electron donor-acceptor couple to improve electron-hole separation and greatly enhance the photocatalytic activity for water splitting [32]. When the PCN structure is enriched with amino groups, the Au single atom can be more readily trapped as Au^+ by three nearby N atoms, and can serve as the active site for CO_2 reduction upon excitation of the PCN host [33].

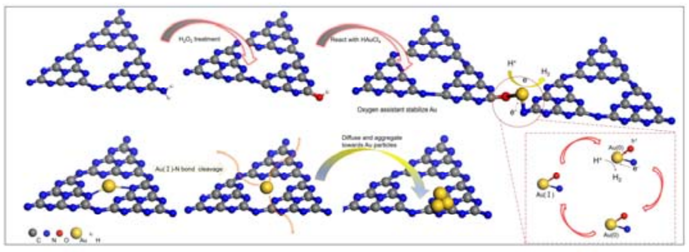

Figure 2. Schematic of structural evolution of CNUHAu and CNUAu during photocatalytic H_2 evolution reaction. Reproduced with permission from Ref. [34], © Royal Society of Chemistry 2019.

The stability of single Au atom in photocatalytic reaction has been a major concern. Zeng et al. demonstrated that pre-treatment of PCN with H_2O_2 enables formation of robust Au−O bond to stabilize gold single atom on PCN during photocatalytic H_2 generation [34]. The Au−O bond can effectively restrict the diffusion of intermediate Au(0) and prevent formation of Au nanoparticle, which allows for maintaining the status of single Au atoms as active sites for proton reduction towards H_2 evolution (Fig. 2).

Pd is also a well-known HER catalyst. Cao et al. have constructed atomically dispersed Pd atoms bridged adjacent layers in PCN nanosheets [35]. The Pd single atoms can provide directional charge transfer channels and collect photogenerated electrons from excited PCN for HER. Similarly, Liu et al. showed that very low loading amount of Pd single atoms on PCN significantly enhanced the photocatalytic H_2 generation rate, which could be 10 times higher than that on the PCN loaded with Pd nanoparticles [36].

In addition to noble metals, transition metals (e.g. Co, Fe, Ni) have been widely used as single atom catalysts on PCN for various photocatalytic reactions. Due to the stability issues, these transition metals usually exist as metal ions in the PCN matrix with different coordination environment.

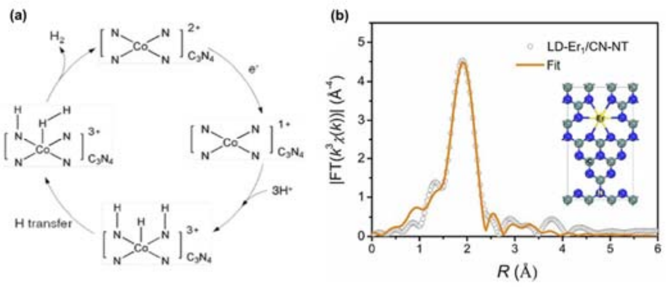

Figure 3. (a) Proposed reaction path of photocatalytic H_2 evolution on single-site Co_1-N_4. Adapted permission from Ref. [37], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2017. (b) The EXAFS R-space fitting curves; Inset: Schematic model of LD-Er_1/CN-NT, Er (yellow), N (blue), and C (green). Reproduced with permission from Ref. [43], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

Yao group reported atomically dispersed Co atoms covalently grafted on PCN nanosheets by forming Co_1−N_4 structure via atomic layer deposition [37]. Theoretical investigations revealed that the coordinated donor nitrogen increased the electron density and lowered the formation barrier of key Co hydride intermediate, thereby accelerating H−H coupling to facilitate H_2 generation (Fig. 3(a)). Further, they modified the Co-decorated PCN through phosphidation to create single Co_1−P_4 site confined on PCN, which showed steady photocatalytic activities for overall water splitting [38]. Moreover, the PCN decorated with single Co^{2+} sites could also exhibit excellent activity for CO_2 photoreduction with high selectivity towards CO formation [39]. When anthraquinone was simultaneously introduced together with atomically dispersed cobalt ions on PCN, the product could be quite efficient for photocatalytic H_2O_2 production [40]. The spatial separation of these two catalysts was achieved by trapping cobalt ions in the void center of PCN for enhanced water oxidation activity, and anchoring anthraquinone at the PCN edges for improved H_2O_2 production selectivity.

Comparing with cobalt, iron and nickel are more environmentally friendly. Zhang et al. showed that single-site dispersed Fe^{2+} ions anchoring on PCN could shift the Fermi level, which enables more effective interfacial electron transfer to the active iron sites towards higher photocatalytic H_2 generation rate [41]. Jin et al. prepared PCN decorated with partially oxidized Ni single atoms having abundant unpaired d-electrons, which increased visible light responses, improved charge carrier mobility in PCN, and enabled 30-fold enhancement for photocatalyic H_2 production rate [42].

More recently, Ji et al. [43] found that rare-earth single erbium (Er) atoms loaded on carbon nitride nanotubes (Er_1/CN−NT) could greatly enhance CO_2 photoreduction performance in CO_2-saturated water. The X-ray spectroscopy results indicated that, unlike other typical M−N_4 or M−N_3 configuration, the Er atoms are coordinating with six nearby N atoms (Fig. 3(b)). The majority product of CO_2 photoreduction was CO under the Er−N_6 configuration because Er was not favored in binding proton to produce active hydrogen species to transform CO to CH_4. Indeed, other rare-earth metal (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb, Lu) single atoms could also be decorated on the carbon nitride nanotubes through similar methods.

Some metal atoms, such as Cu and Mo, show specific binding capability with the nitrogen molecule (N_2), and thus are suitable for use as single atom catalyst for photocatalytic N_2 fixation, which has been considered as an alternative way to replace the high energy consumption Haber-Bosch process for ammonia synthesis [44]. Huang et al. demonstrated that the NH_3 production rate of copper single atom decorated PCN reached 186 μmol/ (h · g) under visible light irradiation with quantum efficiency achieved 1.01% at 420 nm [45]. The characterization and simulation results suggest that the Cu atoms could readily generate isolated valence electrons from the conjugated π electron cloud of PCN. These valence electrons could be excited and turn to free electrons under light irradiation, which promoted the photo-induced ammonia production process. Single-atom molybdenum immobilized on carbon nitride (Mo-CN) was also employed to fix nitrogen in pure water for photocatalytic ammonia synthesis [46]. Further investigations revealed that the unsaturated Mo atoms could strongly adsorb nitrogen molecules with elongation of the N≡N bond. By this way, the weakened N≡N bond can more be easily activated by accepting the photogenerated electrons towards ammonia production.

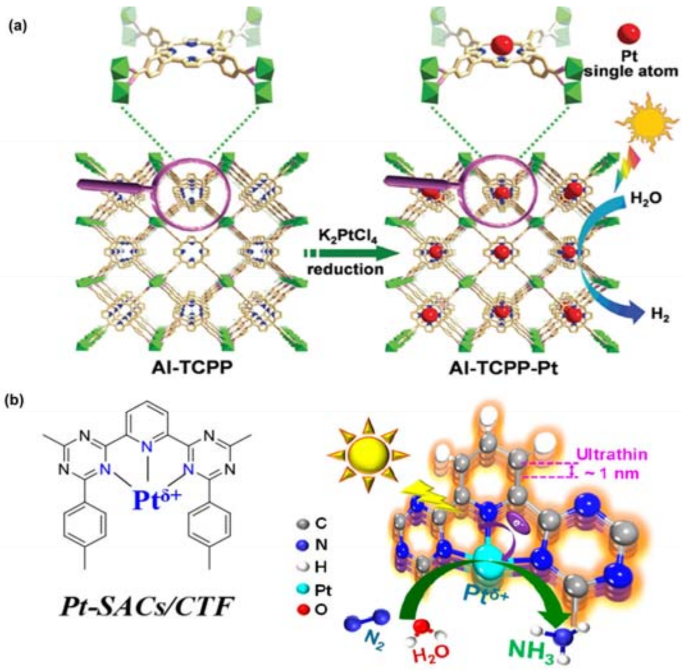

Figure 4. (a) Schematic illustration showing the synthesis of Al-TCPP-Pt for photocatalytic hydrogen production. Reproduced with permission from Ref. [54], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2018. (b) The photocatalytic N_2 fixation mechanism of the Pt-SACs/CTF catalyst. Reproduced with permission from Ref. [66], © American Chemical Society 2020.

2.1.2 Single atom catalyst in metal organic framework (MOF) based photocatalysts

As a type of porous crystals formed through coordination bonds between metal ions and organic ligands, MOFs possess tailorable structures, high specific surface area and flexible functionalities. Hence, MOFs have attracted great research interest for extensive applications including heterogeneous catalysis, non-linear optics, compound separation, gas storage, drug delivery, and biomedical sensing [47-49]. In particular, MOFs can serve as excellent scaffolds to coordinate with single metal atoms for efficient photocatalysis [50-53].

Fang et al. have firstly demonstrated that single Pt atoms could be confined in a MOF (Fig. 4(a)), in which the photogenerated electrons from visible-light-excited MOF could transfer to the Pt atoms for HER [54]. Similar studies were also reported by Zhou's group by introducing single Pt atom coordinated porphyrin precursors into ultrathin MOF nanosheets to achieve efficient photocatalytic H_2 evolution [55]. Li et al. employed MOF-88 and ethylenediaminetetraacetic acid (EDTA) to trap single Pt ions at well-defined positions in the MOF architecture [56], which exhibit excellent activities for photocatalytic hydrogen evolution rate with apparent quantum efficiency of 67.6% at 420 nm.

Besides Pt, the active single Co^{I} sites were also incorporated in the MOF structure, Ru-UIO67(bpy), for efficient visible-light-driven H_2 generation [57]. Further, Zhang et al. synthesized MOF-525 with implanted single Co atoms [58], which could selectively capture and photoreduce CO_2 under visible light irradiation. The photogenerated excitons could directionally migrate from porphyrin to single Co atoms, supplying long-lived electrons for the CO_2 reduction at the coordinatively unsaturated Co centers.

2.1.3 Single atom catalyst in covalent organic framework (COF) based photocatalysts

In the COF-based photocatalysts, the periodic organic building blocks create special 2D structure that enables delocalization of charges in the conjugated framework, and provides continuous pores for mass transfer [59]. More importantly, the catalytic active sites, such as single metal atoms, can be confined within the COF framework via coordination interactions between the metal atoms and binding groups in the COFs [60]. In addition, the heteroatom-rich pore walls of COFs could also facilitate molecular adsorption and charge transfer for more efficient catalytic reactions [61]. Hence, using COFs as the host for anchoring single metal atoms can be expected to bring new opportunities for developing highly efficient photocatalysts. For example, Zhong et al. reported a 2,2′-bipyridine-based COF supporting single Ni atoms (Ni-TpBpy) for selective photoreduction of CO_2 to CO in aqueous media [62]. The special Ni-TpBpy sites provide much higher affinity of CO_2 over H^+, which enables more effective activation of CO_2 towards CO formation and suppression of the competitive H_2 evolution process.

As a type of special COF, the two-dimensional covalent triazine-based framework (CTF) with high visible light harvesting capacity could serve as an ideal photocatalyst host for anchoring SACs due to its abundant, adjustable and well-defined bonding sites [63-65]. For instance, single-atom Pt anchored ultrathin CTF nanosheets (Pt-SACs/CTF) have been successfully synthesized by Li et al. for photocatalytic N_2 fixation [66]. The well-defined Pt−N_3 sites in the CTF (Fig. 4(b)) could not only enable adsorption of N_2 molecules, but also attract photogenerated electrons to implement reduction reactions towards NH_3 formation.

2.2 Carbon-based host materials

Due to the excellent conductivity, graphene-based host materials have been widely used for anchoring single metal atoms for various catalytic applications [67-69]. Similar to organic host, the structurally-modified graphene can bind with the metal atoms through coordination effect with oxygen (or nitrogen)-containing functional groups. For instance, the partially oxidized graphene nanosheets can be used to immobilize isolated single Co atoms through electrostatic force and coordination interactions between Co^{2+} and negatively charged oxygen-containing functional groups on the graphene surface. In this case, the graphene bridges the $Ru(bpy)_3$ photosensitizer and single Co atom catalytic sites to effectively transfer photogenerated electrons for CO_2 reduction [70]. The isolated Co atoms are coordinated with carbon and residue oxygen on the graphene surface and serve as catalytic sites for CO_2 reduction. The graphene works as conductive channel to transfer the electrons generated from $Ru(bpy)_3$ photosensitizer to Co catalytic sites. Moreover, the band structure of graphene is not altered by the incorporation of Co single atoms. The high turnover number is attributed to the fast transfer of received electrons to Co catalytic sites toward CO_2 reduction.

Nitrogen-doped graphene (N-graphene) is also a suitable host for single metal atoms through coordinative binding with surface nitrogen atoms. Xu's group showed that the N-graphene decorated with Co (or Ni) single atoms can be as efficient catalysts to couple with CdS for enhanced photocatalytic H_2 generation [71, 72]. For the Ni single atom, it can be anchored on the vacancies in nitrogen-doped graphene (Ni-NG). In the Ni-NG/CdS composite photocatalyst, the Ni-NG not only serves as an electron storage medium to suppress electron-hole recombination but also as an active site for proton reduction. The activation energy barrier of hydrogen evolution reaction is reduced by the introduction of Ni-NG as well. Zhou et al. have decorated N-graphene with atomically dispersed Pd single-atoms (Pd_1/N-graphene) by a freeze-drying-assisted method [73]. The Pd_1/N-graphene sample presented outstanding activity for acetylene hydrogenation under light irradiation at 125 °C with 93.5% selectivity to ethylene. The strong local coordination interactions between Pd atoms and nitrogen atoms suppressed the aggregation of Pd atoms and enabled durable catalytic activity for Pd_1/N-graphene during the photothermal reaction.

Unlike graphene, the carbon dots doped with nitrogen have easily tunable bandgap and thus can behavior as photocatalysts. This advantage allows N-doped carbon dots to function as an ideal light-responsive host for single metal atom catalysts. For example, through pyrolysis of vitamin B12, Wang et al. have prepared N-doped carbon dots that have anchoring sites for single cobalt atoms with well-defined Co−N_4 configuration [74]. In this system, carbon dots worked as both light-harvesting antenna and support for high-loading cobalt atoms, which acted as active sites with strong oxidative ability. Thus, the photocatalytic activity of the carbon dots for water oxidation, imine selective formation and complete photodegradation of organic dyes were all improved.

2.3 Inorganic host materials

2.3.1 Single atom catalyst in metal oxide-based photocatalysts

Metal oxide-based semiconductors (e.g. ZnO, TiO_2, WO_3 et al.)

have been extensively explored for various photocatalytic applications. On the metal oxide surface, the catalyst metal atoms can bind with the surface oxygen, creating individual active sites for 1) more effective molecular adsorption and activation; 2) trapping photogenerated electrons/holes to promote charge separation and redox reaction rate. Hence, the single metal atom catalysts enable fairly minimal loading amount on the metal oxide photocatalyst surface to achieve high efficiencies for the reactions.

For example, single Cu(Ⅱ) and Fe(Ⅲ) catalytic sites could be anchored on rutile TiO_2 surface to enhance photocatalytic degradation of 4-chlorophenol in water [75]. Trofimovaite et al. introduced single Cu(I) atoms in mesoporous TiO_2 with very low Cu concentration (< 0.1 wt.%) and achieved striking promotion on photocatalytic H_2 generation and Methyl Orange degradation [76]. More recently, Lee et al. demonstrated that the anatase TiO_2 incorporated with site-specific single copper atoms (Cu/TiO_2) exhibited reversible and cooperative photo-activation processes [77]. When all isolated Cu atoms were reduced by the photogenerated electrons from Cu^{2+} to Cu^+, it subsequently induced activation of nearby TiO_2 by converting adjacent Ti^{4+} to Ti^{3+} and significantly enhanced photocatalytic performance.

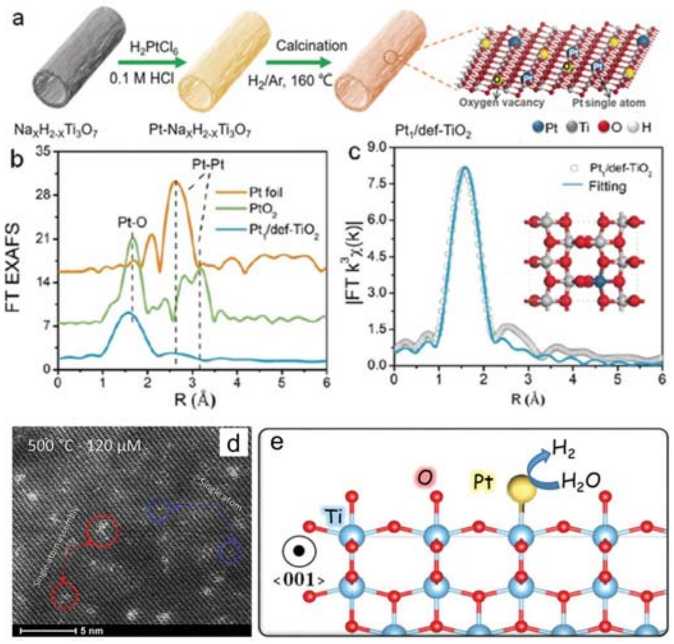

Figure 5. (a) The preparation process of the Pt1/def-TiO_2 catalyst. (b) FT-EXAFS spectra of Pt_1/def-TiO_2 catalyst, Pt foil and PtO_2. (c) EXAFS R space fitting curve (blue line) and the experimental one (circle) of Pt_1/def-TiO_2 catalyst. Reproduced with permission from Ref. [81], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020. (d) HAADF-STEM image of Pt-SA-decorated TiO_2 layer. (e) Schematic of Pt-SA-decorated TiO_2 for H_2 evolution application. Reproduced with permission from Ref. [82], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

Yuan et al. decorated mesoporous anatase TiO_2 with atomically dispersed Cu(II) species that underwent reduction to Cu(I) and eventually to Cu(0) during photocatalytic CO_2 reduction. They further proposed that the Cu(I)/Cu(0) mixtures could efficiently accumulate the photogenerated electrons to accelerate the multielectron reduction of CO_2 to CH_4 [78]. In contrast, Jiang et al. reported selective reduction of CO_2 to CO over the ultrathin TiO_2 nanosheets loaded with atomically dispersed Cu under solar irradiation [79]. The authors attributed the improved photocatalytic activity to the reduction of Cu^{2+} directly to Cu^0 that facilitated the separation of charge carriers.

Comparing with Cu, the Pt single atoms would be more suitable catalysts to anchor on TiO_2 particularly for photocatalytic hydrogen generation. Jeantelot et al. have grafted isolated Pt atoms on anatase TiO_2 through reacting the organometallic precursor, (1,5-cyclooctadiene)dimethylplatinum(II), with the surface hydroxyl groups of TiO_2 powder [80]. By assembling single Pt atoms on the defective TiO_2 surface, Chen et al. constructed Pt−O−Ti^{3+} atomic interface that facilitates electron-hole separation towards remarkable performance in photocatalytic H_2 production [81]. The single Pt atoms can not only be proton reduction sites here, but also promote the neighboring TiO_2 units to generate surface oxygen vacancies and form a unique Pt−O−Ti^{3+} atomic interface, which leads to fast separation and migration of charge carriers from Ti^{3+} defective sites to single Pt atoms, and consequently, outstanding performance in photocatalytic hydrogen evolution (Figs. 5(a)-(c)). Indeed, the strategy of oxygen vacancy engineering, by annealing TiO_2 in Ar/H_2 at different temperature to create well-defined Ti^{3+}-O_v defect sites[82], enables effective trapping of single Pt atoms for photocatalytic HER (Fig. 5(e)). A similar strategy of creating oxygen vacancies has also been applied to decorate Ru single atoms on TiO_2 nanosheets for photocatalytic N_2 fixation [83]. In fact, the isolated Ru atoms played important roles in the enhancement of N_2 photofixation, including weakened the hydrogen evolution, promoted N_2 absorption, and improved charge separation.

The ultrahigh activity of photocatalytic HER induced by single metal atoms may also be employed as a sensing platform. As an example, Guo's group have demonstrated a photocatalytic sensing strategy for detecting chlorpyrifos by using Pd single atoms decorated TiO_2 (PdSA/TiO_2) [84]. The strong binding capability of chlorpyrifos on the single Pd atom effectively inhibit its high activity for HER. The photocatalytic H_2 evolution rate over PdSA/TiO_2 decreased linearly with increasing chlorpyrifos content, giving a detection limit of 0.01 ng /mL. More recently, the PdSA/TiO_2 photocatalyst has also been utilized for NO removal due to the high resistance of isolated Pd sites to nitrate poisoning and their high selectivity for NO conversion to nitrate [85].

The non-noble metal Ni can also be atomically dispersed on TiO_2 to improve photocatalytic H_2 evolution. A new molten salt method has been reported for decoration of Ni single atoms on TiO_2 nanoparticle (NiSA/TiO_2) [86]. The molten salt provided a liquid environment to produce atomic dispersion of Ni ions on TiO_2 by space confinement effect. Similar to Pt−O−Ti^{3+} structure on defective TiO_2, the Ni atoms also facilitated the formation of oxygen vacancies on the neighboring surface of TiO_2, which greatly improve charge separation. As such, the NiSA/TiO_2 photocatalyst exhibited four times enhancement in H_2 evolution rate as compared to the Ni nanoparticle-loaded TiO_2.

In addition to TiO_2, some other metal oxide semiconductors have also been used as hosts for loading of single atom catalysts. For example, Liu's group have incorporated isolated Co single atoms into Bi_3O_4Br atomic layers [87]. The Co atoms binding with surrounding lattice oxygen showed a valence state of nearly 2+, and could lower CO_2 activation energy barrier, which boosted the activity of Bi_3O_4Br for CO_2 photoreduction.

2.3.2 Single atom catalyst in metal sulfide-based photocatalysts

Comparing with the common metal oxide photocatalysts, many metal sulfide semiconductors have relatively smaller bandgaps and higher conduction band levels, which allows for wider range of light harvesting and stronger reduction capability of photogenerated electrons. In order to incorporate single atom catalysts on metal sulfides, we need to either create surface defect sites during crystal formation or construct specific binding sites by post-treatment.

For instance, Wu et al. have successfully decorated isolated Pt atoms onto the surface step edges of CdS nanowires to promote photocatalytic HER [88]. The unsaturated sulfur atoms were enriched at the step terrace and served as anchoring sites via Pt−S bonding formation. In addition, the long-lived electrons can be supplied consecutively for photocatalytic hydrogen evolution due to the directional migrations of photogenerated excitons from conduction band of CdS to single Pt atoms. Similarly, Qiu et al. also anchored Pt single atoms on CdS nanosheets decorated with carbon dots through Pt−S bond [89]. More specifically, the Pt single atoms exhibit strong capacity to trap photo-generated electrons because of the Pt−S bonding with a coordination number of 4. The introduction of Pt single atoms creates more new empty bands produced near Fermi level, which facilitate the accommodation of photogenerated electrons. Thus, the highly efficient hydrogen evolution performance is expected.

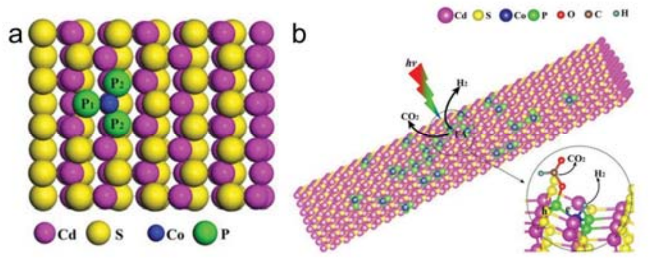

Figure 6. (a) Geometry structure of CoPSA-CdS at the atomic level from the first-principles simulation. (b) Mechanism of FA dehydrogenation and hydrogen production on CoPSA-CdS. Adapted permission from Ref. [90]. © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

Unlike Pt, some transition metals can anchor on CdS surface by replacing surface Cd^{2+} to bind with neighboring S atoms. For example, by simply impregnating CdS nanorods in $CoCl_2$ solution, Zhou et al. have prepared Co single atom loaded CdS nanorods,[90] and found that subsequent phosphorization could create very active Co-P_3 species on CdS nanorods (Fig. 6) to achieve significantly increased H_2 generation rate in photocatalytic formic decomposition. A different surface modification strategy was demonstrated by Zhang et al. [91], who decorated CdS nanorods with atomically dispersed Ni ions that bound with surface hydroxyl groups generated by photochemical methods. In this report, single Ni atom can enrich more electrons, which is similar with the aforementioned single Pt atom decorated CdS. The electronic properties of CdS and hydrogen binding energy can be optimized by the introduction of Ni single atom. Hence, the visible-light-driven H_2 evolution rate of Ni_1/CdS shows 30-fold enhancement as compared to that of pure CdS.

Some metal sulfides have layered structure and the weak van der Waals interlayer interactions enable intercalation of individual metal atoms that can not only serve as catalysts but also facilitate transport of photogenerated charges between adjacent layers. Li et al. have demonstrated that Ru single atoms can be confined in the interlayer of GaS nanosheets by forming a hexagonal structural configuration of Ru_1−S_6 (Fig. 7) [92]. The intercalated Ru atoms can effectively promote transportation of photogenerated electrons through the interlayers of GaS nanosheets, and serve as HER catalyst for more efficient H_2 production under visible light irradiation.

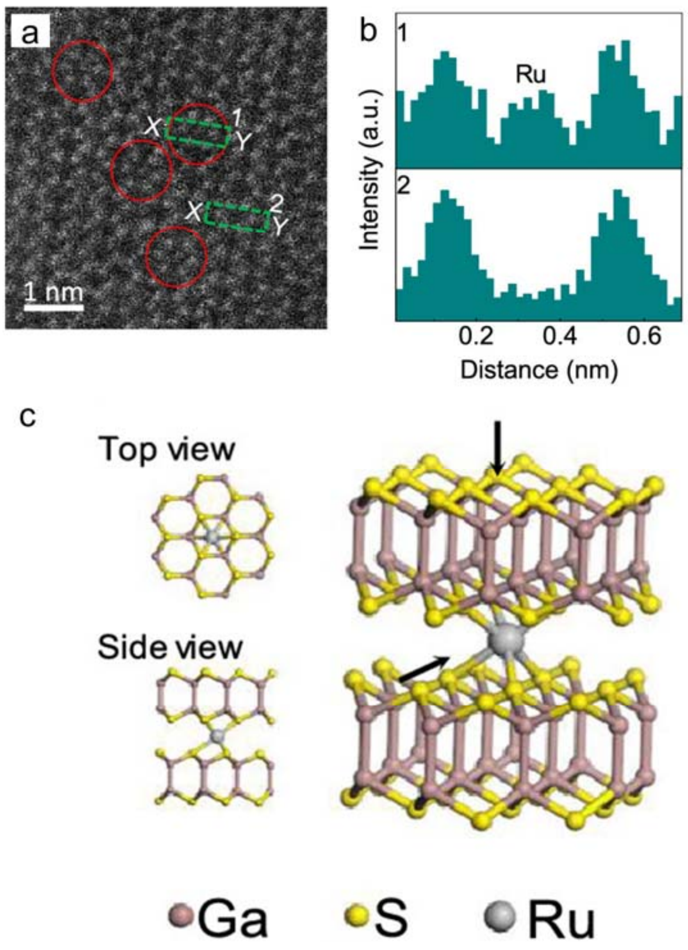

Figure 7. (a) Representative HAADF-STEM image of Ru−GaS NSs. (b) Intensity profiles along the X−Y lines at positions 1 and 2 in the HAADF-STEM image. (c) Structural model of the Ru−GaS NSs. Reproduced with permission from Ref. [92], © American Chemical Society 2019.

3. Summary and outlook

Nowadays, researchers -phave widely recognized that single metal atom catalysts can significantly boost the efficiency of semiconductor photocatalysts. However, the development of single atom photocatalysts still encounters many serious challenges in terms of stability, synthetic approaches and catalytic activities. Herein, we would like to discuss some challenges and future perspectives of the single atom photocatalyst.

(1) Stability

The high activity of the metal atoms usually relies on the available orbitals that enable strong coordination interactions for adsorption and activation of the reactants. However, the catalyst poisoning effect is a nonnegligible issue. Unlike the particle catalysts, which might be just partially poisoned due to the different binding capability on different crystal facet, single metal atom catalyst would be completely deactivated if the intermediate or by-product could also strongly bind with it. One way to solve this issue might be reactivating the SACs through “blank” photocatalytic reaction because the excited photocatalysts can supply active electrons or holes that can migrate to the metal atom sites to facilitate removal of those unwanted adsorbates.

Besides poisoning, aggregation is another noteworthy issue of SAC during photocatalytic reactions. In many cases, the photocatalysts need to have high conduction band level to supply sufficient reduction capability for the photogenerated electrons that can also convert the trapped metal ions Mn$^+$ (e.g. Au$^+$, Pt^{2+} et al.) to M^0. These zero-valence metal atoms may have weaker interactions with the surrounding binding atoms such as N and O, and thus tend to aggregate to form small clusters or nanoparticles (Figure 8a). Some transition metals (e.g. Fe, Ni, Co et al.) do not have the aggregation issue due to the very high reduction potential required for producing zero-valence metal atoms. Nevertheless, the individual ions of these metals are readily hydrolyzed in a basic solution because the hydroxyl ions could heavily attack the metal ions and compete with the existing binding ligands, which eventually results in particle formation of metal hydroxide or metal oxide (Figure 8b). Therefore, it is critical to carry out the photocatalytic reactions involving SACs under appropriate conditions to avoid their degradation towards nanoparticles.

(2) Loading amount of single metal atoms

Currently the widely used impregnation-adsorption method usually leads to very low loading amount of single metal atoms (<1 wt%), which means that only trace amount of metal precursors can be incorporated into the host photocatalysts and converted to single atom catalysts. Indeed, the maximal loading amount of SAC is determined by the available binding sites on the photocatalyst surface. Generally, surface modifications of the photocatalysts would be necessary to increase the specific binding sites for intense loading of SACs. Common surface modification strategies include 1) creation of vacancies by high-temperature annealing or treating with strong reduction/oxidation reagents; 2) doping with strong binding element (e.g. N, P, S, et al.); 3) grafting functional groups (e.g. –NH_2, –OH, -COO-, pyridine, et al.) that has specific binding capability with the metal atoms. Besides, the pyrolyzing coordinated polymer (PCP) method is an alternative strategy to load single atoms and it’s also promising for high-loading of single atoms. This method requires mixing of appropriate solvents, metal precursor and monomers to coordinate thoroughly. Then it is necessary to remove the solvents through a non-destructive approach, such as vacuum freezing dry technique and rotary evaporation prior to the polymer pyrolysis step. Wang’s group[93] have presented a successful example for the synthesis of gram-scale high loading single atom catalysts by using this method.

(3) Activity for multi-reagent redox reactions

Some redox reactions are relatively complicated involving two or more reactants with different mechanism of adsorption, activation, and charge transfer. In the case of single metal atom catalyst, these reactants would have to compete for the binding with the metal atoms, while each individual metal atom can only accommodate one reactant molecule. For example, in the photoreduction of CO_2 with H_2O over SAC-decorated photocatalyst, both CO_2 and H^+ are able to adsorb on the metal atom catalyst such as Pt and Au, and may be reduced by photogenerated electrons into different intermediate species. As such, it is challenging to manage the reaction over a single atom catalyst in terms of reaction path control and product selectivity. To address this issue, one can decorate the photocatalyst surface by individual atomic catalytic sites of two different metals (denoted as dual-metal-atom catalysts) with or without linkage between them. This would need sophisticated surface modifications to achieve controllable confinement of the two different metal atoms. If each metal atom site is mainly responsible to one selective reactant (Figure 8c), tuning the loading ratio of the two metal elements would allow for fine control over the reaction path and product selectivity. We believe that the dual-metal-atom catalyst decorated photocatalyst is one of the most promising future directions for optimizing the photocatalytic processes at atomic level.

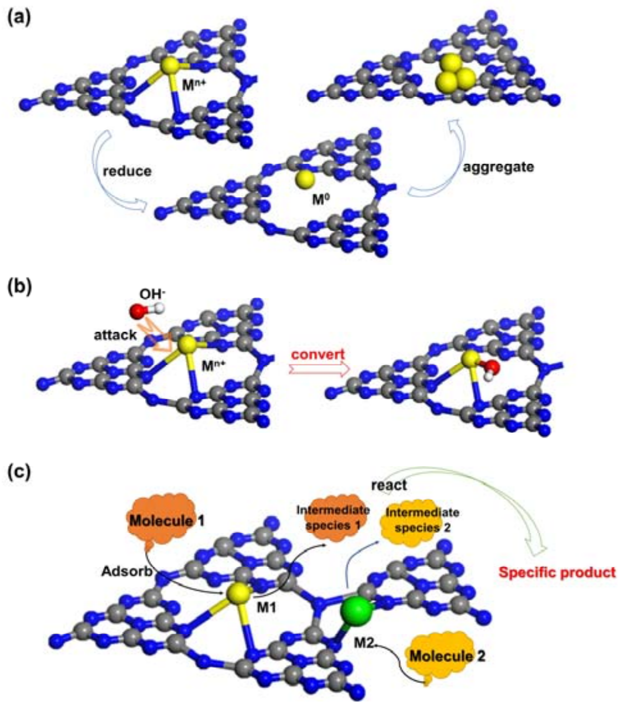

Figure 8. (a) Schematic illustration showing the evolution from single atom to cluster upon reduction; (b) Schematic illustration showing the degradation of single metal atom site to metal hydroxide in basic solution; (c) Schematic illustration of bi-atom catalyst that can be responsible to two different reactants, respectively, giving different intermediates for final reaction towards specific product.

In summary, the single metal atom decorated photocatalysts have presented superior advantages as comparing with the nanoparticle-loaded photocatalysts. Nevertheless, well-designed synthetic methods are required to achieve large loading amount of single atoms with high stability towards the ultimate goal of highly efficient and scalable photocatalytic reactions.

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