

Atomically Dispersed Catalytic Sites for Photocatalytic Water Splitting

Subjects: Others

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SAPCs provide a new pathway for the construction of high performance cocatalyst/photocatalyst composites. For the past few years, the preparation method, characterization technology, theoretical modeling, and mechanism investigation of SAPCs have been developed rapidly, promoting the rational design and fabrication of more efficient SAPCs. As discussed above, benefitting from their low-coordination status, unique electric structures, and metal-support interactions, SAPCs can bring about unique advantages in comparison with the nanocluster-based, nanoparticle-based, and bulk catalysts.

Keywords: single atom ; cocatalyst ; photocatalytic water splitting ; hydrogen generation

1. Introduction

Since the pioneering discovery of water photolysis on TiO₂ electrodes in 1972, solar-driven water splitting has been recognized as one of the most promising ways to transform solar energy into renewable and clean hydrogen energy ^[1]. The photocatalysts are the key component of photocatalytic processes ^[2]. Over the past few decades, researchers have developed various photocatalysts toward the application of water splitting ^{[3][4][5]}. A typical photocatalytic water splitting reaction on semiconductor photocatalysts mainly involves three primary steps: (1) absorption of light to generate electron-hole pairs; (2) separation of the photogenerated electron-hole pairs and their migration to semiconductor surfaces; and (3) consumption of the photogenerated electrons and holes via surface redox reactions. Specifically, only the photogenerated electrons and holes that successfully reach the surface of the catalyst have the possibility to react with water. Therein, the water molecules can be reduced by photogenerated electrons to generate H₂ (hydrogen evolution reaction, HER), and at the same time oxidized by photogenerated holes to generate oxygen (Oxygen evolution reaction, OER), hydrogen peroxide, superoxide radicals, etc ^[6]. The problem is that the single-component photocatalyst always suffers from poor photocatalytic activities because of its narrow light harvesting range, serious electron-hole recombination, and weak adsorption and activation abilities for reactant molecules. To overcome these bottlenecks, strategies aiming to expand the light absorption range, construct interface heterojunctions, and engineer surface reaction sites by rational design of multicomponent photocatalysts have been developed ^{[7][8]}. Among these, the loading of a cocatalyst is an effective method to improve the functions of a photocatalyst ^[9]. For example, noble metals, such as Pt and Pd nanoparticles, are considered as efficient cocatalysts for promoting photocatalytic H₂ evolution ^[10]. However, the high cost of these noble metal particles strongly hinders their wide utilization.

Single-atom photocatalysts (SAPCs) with maximized atomic utilization can effectively improve the number of exposed reaction sites on surface while reducing the loading amount of the noble metal cocatalyst ^{[11][12]}. For SAPCs, the atomically dispersed metal atoms could be anchored on the support materials by forming coordination with the host atoms, which helps to prevent agglomeration of the monodispersed metal atoms with high surface energy ^[13]. Compared with metal nanoparticles, the coordination interaction with the support atoms makes the single metal atoms possess a unique local electronic and geometric structure ^[14]. In addition, the electron transfer and charge redistribution between the single metal atoms and supports may reduce the reaction barriers to enhancing catalytic performance ^[15]. Nevertheless, due to the high surface free energy of isolated atoms, their aggregation is always unavoidable, and this is significantly detrimental to photocatalytic activity and stability. Therefore, how to develop SAPCs with high activity, selectivity, and stability, and how to unravel the structure-activity relationship of SAPCs still remain as the research focus in this area. In this review, the recent advances in exploiting SAPCs as the new prototype of cocatalyst/photocatalyst composites toward water splitting are introduced, especially from the aspect of their atomic structure, synthetic strategy, and applications. Then, the challenges and future research directions of single-atom photocatalysts are discussed.

2. Structure of SAPCs

Metal oxides, metal sulfides, and other inorganic semiconductor materials with appropriate bandgaps such as TiO₂, ZnO, WO₃, ZrO₂, CdS, GaS, MoS₂, BiVO₄, BiOX (x= Cl, Br), SrTiO₃, etc. have been frequently used as photocatalysts [16][17][18][19][20]. The abundant coordination atoms of O, S in the lattice and surface of these materials can provide a strong anchoring effect for stabilizing the single metal atoms.

In recent years, organic polymer semiconductors, especially g-C₃N₄, have attracted extensive attention in photocatalysis owing to their fascinating advantages such as appropriate energy band structure, good stability, nontoxicity, low cost, etc. [21][22][23]. It is worth noting that the bandgap of pristine g-C₃N₄ is about 2.7 eV, with the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) well fitted for driving water splitting from the aspect of thermodynamics [24]. At the same time, g-C₃N₄ possesses abundant N atoms with lone-pair electrons, which are ideal coordinating sites for anchoring single metal atoms [25]. It has been found that the isolated metal atoms anchored on g-C₃N₄ can serve as active centers for boosting photocatalytic HER and ameliorate the low separation efficiency of photogenerated charge carriers for pristine g-C₃N₄ [26][27]. Hence, g-C₃N₄ has been intensively explored as the support materials for hosting single atoms, giving birth to various SAPCs.

Carbon dots (CDs) are another attractive support material for hosting single atoms. Their bandgaps can be tuned by nitrogen doping to function as a good light-harvesting antenna [28]. Run Li et al. synthesized the CDs anchored with single Co atoms [29], in which the single Co atoms with a high loading content of 3.27% were stabilized through the Co-N₄ coordination structure. The authors unraveled that CDs played double functions in photocatalysis: the support for single-atom Co and the light-harvesting antenna. Meanwhile, the isolated Co atoms can boost the separation and directed migration of photogenerated charge carriers, and, more significantly, can gather the photogenerated holes for promoting oxidation reactions. As a result, the obtained photocatalyst exhibited excellent activity and stability in photocatalytic water oxidation (245 $\mu\text{mol/g}$, 4h), photocatalytic oxidative coupling of aromatic amines, and photodegradation of organic dye.

Due to their suitable Fermi level for trapping electrons and a low potential for H₂ evolution, noble metal Pt is an efficient cocatalyst for H₂ evolution and has been intensively studied in SAPCs [30][31][32][33]. Wu et al. reported a photocatalyst with significantly enhanced photocatalytic activity and maximized utilization of Pt [34], in which the isolated Pt atoms were incorporate into the sub-nanoporosity of 2D g-C₃N₄ (referred as Pt-C₃N₄, **Figure 1 b**) and acted as co-catalyst for photocatalytic HER. The intrinsic change of the surface trap states induced by single-atom Pt contributed to a longer lifetime of photogenerated electrons, which was the primary factor for the prominently improved photocatalytic performance. Bi et al. further investigated the in situ charge transfer and chemical bond evolution between the single-atom Pt and g-C₃N₄ during photocatalytic HER (**Figure 1 a**) [35]. The results showed that different from the metallic Pt decorated-g-C₃N₄ catalyst, within single-atom Pt/C₃N₄, the Pt-N bond broke to form Pt⁰ species and the C-N bond transformed into C=N bond of g-C₃N₄ under visible light irradiation. Such dynamic changes designated Pt⁰ and g-C₃N₄ as the reaction sites for reduction and oxidation reactions respectively, and this contributed to the remarkably enhanced H₂ evolution activity. Furthermore, it has been demonstrated that a higher loaded content of Pt single atoms can give much higher photocatalytic activity. For example, Zhou et al. developed a surfactant-stabilized coordination strategy to realize ultrahigh single-atom Pt loading of 12% within MOFs [36]. The resulting SAPCs exhibited an exceptionally high activity of 11320 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for photocatalytic HER under visible light.

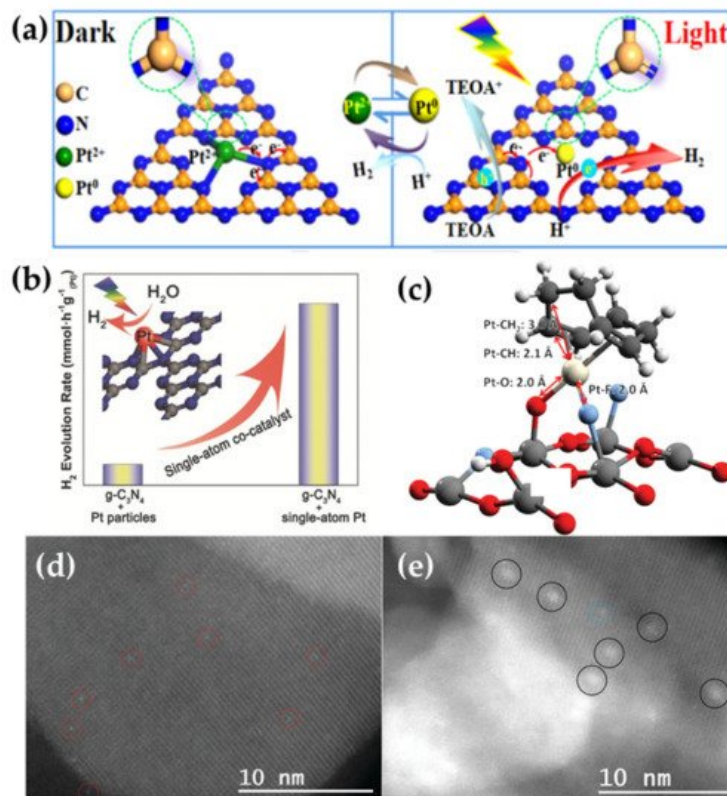


Figure 1. (a) Illustration of the charge transfer and bond variation on S-Pt-C₃N₄ catalysts for photocatalytic hydrogen evolution [35]; (b) Photocatalytic activity comparison of g-C₃N₄ with Pt nanoparticles and single atoms, respectively. Inside is the structure model of Pt-C₃N₄ [34]; (c) O-Pt-F DFT-optimized structure, used as the initial model for EXAFS fitting; (d,e) HAADF-HRSTEM images of the 0.5%Pt_{GR}:TiO₂ [37]; (d) and 0.5%Pt_{NP}:TiO₂ (e). Single atoms are denoted by red circles, clusters by blue circles, and nanoparticles by black circles [37].

3. Synthesis of SAPCs

A simple and effective synthesis method is one critical factor for the practical application of SAPCs [38]. It is essential to construct strong coordination interactions between single metal atoms and support materials to avoid the aggregation of these isolated atoms with high surface free energy during synthesis and reaction processes [39]. This can be achieved through various strategies including defect engineering, coordinated design, and spatial confinement [40]. In the following section, the commonly used synthesis methods for SAPCs are summarized.

The impregnation method is a typical and flexible method for the synthesis of single-atom catalysts. The support materials are immersed in a solution containing appropriate metal precursors. In this condition, the metal ions could be anchored or absorbed on the support surface through coordination, electrostatic adsorption, or spatial confinement. This is followed by drying and activation treatment, which can make the single metal atoms stably anchored on the supports. Here, the bonding with coordination atoms in supports such as, O, N, P, S, etc. is the key to keep the metal atoms spatially isolated with restricted migration.

As for the co-precipitation method, single atoms are immobilized on the supports during their formation process. This method is suitable for support materials such as g-C₃N₄, MOF, metal sulfides, and metal [41][42][43]. For example, Lu et al. prepared a series of single-atom Mo catalysts by calcining low-cost primary material of urea with various amounts of Mo(VI) salts [44]. The isolated Mo atoms were incorporated into g-C₃N₄ through MoN₂ species in the polymerization process. The coordinatively unsaturated Mo sites acted as reaction centers for N₂ chemisorption and activation during photocatalysis. With regard to the metal supports, the atomic ratio of metal precursor to support is a key factor that should be precisely controlled for preparation of single atoms in metal supports. For example, Yang et al. synthesized a single-atom Pt 1Ag 24 alloy cocatalyst on g-C₃N₄, and the resulting composite (referred as Pt 1Ag 24/ g-C₃N₄) was applied in photocatalytic HER [45]. The H₂ evolution rate of Pt 1Ag 24/g-C₃N₄ reached 39.7 μmol/h, which was four times higher than that of Ag 25/g-C₃N₄. The precise composition of single-atom Pt 1Ag 24 alloy cocatalyst was tuned by carefully tuning the molar ratio of Ag and Pt precursors during the nucleation and growth process.

(a) Formation of the hollow nanotube MOF and the single atom-immobilized hollow nanotube MOF, which are denoted as HNTM and HNTM-M, respectively [46]; (b) Schematic illustration of the icing-assisted in-situ photocatalytic reduction method for preparing the supra-high-density PtSAs-loaded g-C₃N₄. Scale bar: 2 nm [47]; (c) Schematic illustration of the

4. Applications of SAPCs for Photocatalytic Water Splitting

H₂ produced from photocatalytic water splitting is an ideal clean energy to replace fossil fuels. However, great challenges remain for developing high-activity, durable, and economical photocatalysts that can realize practical applications toward photocatalytic H₂ generation. The creation of SAPCs provides a new clue for the development of water splitting photocatalysts with excellent activity, selectivity, and stability, as well as high atomic utilization of noble metals to lower the cost of the catalyst. **Table 1** summarizes the recent progress in this research area. As discussed above, the single metal sites in SAPCs have been intensively used as efficient cocatalysts for promoting photocatalytic H₂ evolution.

Table 1. Summary of SAPCs for photocatalytic water splitting. The order is arranged by the time of publication.

	Supports	Single Atoms	Coordination	Loaded Content	Synthesis Methods	Products	Production Rate	AQE
1 [50]	TiO ₂ nanosheet	Rh	Rh-O	2.6 at.%	co-precipitation	H ₂	51 umol h ⁻¹	/
2 [34]	g-C ₃ N ₄	Pt	Pt-N	0.16 wt.%	impregnation	H ₂	318 umol h ⁻¹	/
3 [51]	g-C ₃ N ₄	Pt ²⁺	Pt-N	0.18 wt.%	co-precipitation	H ₂	605 umol g ⁻¹ h ⁻¹	/
4 [52]	g-C ₃ N ₄	Co	Co ₁ -N ₄	1 wt.%	ALD	H ₂	10.8 umol h ⁻¹	10.3%, 420 nm
5 [45]	Ag cluster	Pt	Pt-Ag	4 at.%	co-precipitation	H ₂	39.7 umol h ⁻¹	/
6 [53]	P doped g-C ₃ N ₄	Co	Co ₁ -P ₄	0.40. %	impregnation	H ₂ , O ₂	126.8 umol g ⁻¹ h ⁻¹	0.16%, AM 1.5 illumination
7 [32]	g-C ₃ N ₄	Pt	Pt-N (maybe)	/	impregnation	H ₂	12.7 umol g ⁻¹ , 4h	/
8 [16]	TiO ₂	Pt	Pt-O	0.6 wt. %	photo-deposition	H ₂	85.4 umol h ⁻¹	/
9 [54]	NG	Co	/	0.25 wt. % (Co-NG)	impregnation	H ₂	1382 umol h ⁻¹	50.5%, 420 nm
10 [55]	g-C ₃ N ₄	Pd	surface:Pt-N; interlayer: Pt-N, Pt-C	0.33 wt. %	photo-deposition	H ₂	6688 umol g ⁻¹ h ⁻¹	4%, 420 nm
11 [56]	g-C ₃ N ₄	Pt	Pt ₁ -N ₄	0.11 wt. %	photo-deposition	H ₂	42.1 umol h ⁻¹	/
12 [31]	Al- porphyrinic MOF	Pt	Pt-N	0.29 wt. %	impregnation	H ₂	129 umol g ⁻¹ h ⁻¹	/
13 [46]	Zr-porphyrinic MOF	Ir, Pt, Ru, Au, Pd	Pt-N ₄ Cl ₂	1.41 (Ir), 2.74 (Pt), 1.92 (Ru), 1.18 (Au), 3.68 (Pd), wt. %	impregnation	H ₂	201.9 umol g ⁻¹ h ⁻¹	/
14 [57]	g-C ₃ N ₄	Pt ^{II}	Pt-N	/	impregnation	H ₂	140 umol g ⁻¹ h ⁻¹	1.5%, 420 nm
15 [58]	mesoporous TiO ₂	Cu	Cu-O _{2.5}	<0.3 wt. %	impregnation	H ₂	/	/
16 [59]	CdS nanowires	Pt	Pt-S ₄	0.27–0.98 wt. %	impregnation	H ₂	47.41 mmol g ⁻¹ h ⁻¹	/

	Supports	Single Atoms	Coordination	Loaded Content	Synthesis Methods	Products	Production Rate	AQE
17 [60]	g-C ₃ N ₄	Pt	Pt-C/Pt-N	0.17–1.7%	impregnation	H ₂	34.2 mmol h ⁻¹	/
18 [61]	MOF	Co	Co-N ₂ Cl ₂ O	3.3 wt. %	co-precipitation	H ₂	27.853 mmol g ⁻¹ , 40h	/
19 [62]	NG	Co	Co-N ₂ C	3.5 wt. % (Co-NG)	impregnation	H ₂	677.44 umol g ⁻¹ h ⁻¹	/
20 [63]	NG	Ni	Ni-N	0.26 wt. %	impregnation	H ₂	1351.1 umol h ⁻¹	48.2%, 420 nm
21 [37]	TiO ₂	(CH ₃) ₂ Pt(COD)	O-Pt-O	/	impregnation	H ₂	/	12%, 225–387 nm
22 [64]	TiO ₂	Cu, Co, Fe, Ni, Rh	Cu-O	0.75 wt. %	impregnation	H ₂	16.6 mmol g ⁻¹ h ⁻¹	45.5%, 340 nm
23 [65]	GaS nanosheet	Ru(IV)	Ru ₁ -S ₆	2.4 wt. %	impregnation	H ₂ , O ₂	340 umol g ⁻¹ h ⁻¹	/
24 [33]	MOF-808-EDTA	Pt	Pt-N ₂ O ₂	0.98 wt. %	impregnation	H ₂	68.33 mmol g ⁻¹ h ⁻¹	67.6%, 420 nm
25 [66]	g-C ₃ N ₄	Pd	Pd-N	0.1 wt. %	impregnation	H ₂	728 umol g ⁻¹ h ⁻¹	/
26 [67]	CdS@CDs	Pt	Pt-S	1.15%	impregnation	H ₂	45.5 mmol g ⁻¹ h ⁻¹	29.8%, 400 nm
27 [68]	zeolitic imidazole framework	Co	/	0.57%	co-precipitation	H ₂	6420 umol g ⁻¹ h ⁻¹	/
28 [69]	g-C ₃ N ₄	Pt, Au	Pt-N, Au-N	0.6 Pt, 0.8 (Au), wt. %	impregnation	H ₂ , O ₂	H ₂ : 285 umol g ⁻¹ h ⁻¹ , H ₂ :O ₂ = 2:1	/
29 [28]	N doped CDs	Co	Co-N ₄	3.27 wt. %	co-precipitation	O ₂	245 umol g ⁻¹ , 4h	/
30 [70]	g-C ₃ N ₄	Au	Au-O	0.18 wt. %	impregnation	H ₂	789.1 nmol h ⁻¹	/
31 [71]	g-C ₃ N ₄	Fe	Pt-N (DFT)	0.5 at. %	impregnation	H ₂	3390 umol g ⁻¹ h ⁻¹	6.89%, 420 nm
32 [47]	g-C ₃ N ₄	Pt	Pt-N/O/Cl	0.35 mg m ⁻²	photo-deposition	H ₂	174.5 mmol g ⁻¹ h ⁻¹	0.544%, 420 nm
33 [36]	MOF	Pt	Pt-N	12 wt. %	co-precipitation	H ₂	11320 umol g ⁻¹ h ⁻¹	/
34 [72]	TiO ₂	Pt	Pt-O	0.36 wt. %	photo-deposition	H ₂	1077 umol h ⁻¹	21.7%, 365 nm
35 [30]	defective TiO ₂	Pt	Pt-O	0.02wt%	impregnation	H ₂	4458 umol g ⁻¹ h ⁻¹	/
36 [73]	g-C ₃ N ₄	Rh	Rh-P	/	impregnation	H ₂	166.28 umol, 4h	/
37 [74]	g-C ₃ N ₄	Co	Co-P	0.13 wt. %	impregnation	O ₂ , H ₂ O ₂	O ₂ : 15.5 umol, 4h;	/
38 [75]	TiO ₂	Pt	/	0.03–0.47 at. %.	impregnation	H ₂	/	/
39 [76]	g-C ₃ N ₄	Ag	Ag-C ₂ N ₂	3.7 wt. %	co-precipitation	H ₂	1.8 mmol g ⁻¹ h ⁻¹	/

	Supports	Single Atoms	Coordination	Loaded Content	Synthesis Methods	Products	Production Rate	AQE
40 [77]	g-C ₃ N ₄	Ni	Ni-C/N	0.5 at%	impregnation	H ₂	354.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$	/
41 [78]	N-doped CDs	Pt	Pt-C	0.2 wt. %	photo-deposition	H ₂	175.3 $\mu\text{mol h}^{-1} \text{cm}^{-1}$	/
42 [42]	Zn _{0.25} Cd _{0.75} S QDs	Ni	Ni-S	0.15-0.125 at%	co-precipitation	H ₂	18.87 $\text{mmol g}^{-1} \text{h}^{-1}$	/
43 [44]	coordination polymers	Cu	Cu-N	/	co-precipitation	H ₂	57.64 $\text{mmol g}^{-1} \text{h}^{-1}$	/
44 [49]	g-C ₃ N ₄	Pt	Pt-N	8.7 wt. %	ion exchange	H ₂	22650 $\mu\text{mol g}^{-1} \text{h}^{-1}$	22.5%, 420 nm
45 [79]	CdS	Ni	Ni-O	2.85 wt. %	photo-deposition	H ₂	630.1 $\text{mmol g}^{-1} \text{h}^{-1}$	/
46 [80]	TiO ₂ spheres	Ru	Ru-O	0.93 wt. %	impregnation	H ₂	7.2 $\text{mmol g}^{-1} \text{h}^{-1}$	/
47 [35]	g-C ₃ N ₄	Pt	Pt-N	/	impregnation	H ₂	14.7 $\text{mmol g}^{-1} \text{h}^{-1}$	38.8%, 435 nm
48 [81]	CdS	Pt	Pt-S	0.50 wt. %	impregnation	H ₂	24.17 $\text{mmol g}^{-1} \text{h}^{-1}$	46%, 420 nm
49 [82]	TiO ₂ nanosheet	Co	Co-O	1.11 wt. %	impregnation	H ₂	1.682 $\text{mmol g}^{-1} \text{h}^{-1}$	/
50 [83]	g-C ₃ N ₄	Pt	Pt-C4	1 wt. %	Photo-deposition	H ₂	25.4 $\mu\text{mol h}^{-1}$	0.5%, AM 1.5 illumination
51 [84]	Cs ₂ SnI ₆	Pt	Pt-I ₃	0.12 wt. %	impregnation	H ₂	430 $\mu\text{mol g}^{-1} \text{h}^{-1}$	/
52 [85]	unimolecular micelles	Pt	Pt-N, Pt-C-N	4.1 wt. %	co-precipitation	H ₂	49465 $\mu\text{mol g}_{\text{Pt}}^{-1} \text{h}^{-1}$	/

In particular, benefitting from the high redox potential and work function, Pt in the form of atomically dispersed single atoms on TiO₂, g-C₃N₄, and MOF have manifested excellent performance in photocatalytic H₂ evolution [56][57]. Li et al. reported an efficient photocatalyst (referred as Pt 1/def-TiO₂) by dispersing single Pt atoms on defective TiO₂ [30]. Due to the hydrogen spillover effect, the atomically dispersed Pt atoms caused the formation of surface oxygen vacancies in neighboring TiO₂ units, giving birth to the Pt-O-Ti³⁺ atomic interface. According to the experimental results and DFT calculations, the Pt-O-Ti³⁺ atomic interface effectively facilitated the transfer of photogenerated electrons from Ti³⁺ defective sites to single Pt atoms, thereby enhancing the separation of electron-hole pairs. This unique structure allowed Pt 1/def-TiO₂ to exhibit an exceptionally high turnover frequency of 51,423 h⁻¹, which was 591 times higher than that of the Pt nanoparticles-supported TiO₂ photocatalyst.

SAPCs with non-noble metals such as Co, Ni, etc. have also been developed as cocatalysts to give excellent performance in photocatalytic water splitting. Importantly, apart from the benefits for H₂ evolution reaction, it has been reported that the cocatalyst of single-atom Co could facilitate the oxidation of water for O₂ evolution half reaction or even overall water splitting [86]. For example, Wei et al. developed a single-atom, Co-based photocatalyst (referred as Co/g-C₃N₄) with single Co atoms confined within phosphide doped-g-C₃N₄ nanosheets. [53] The Co 1-phosphide sites with coordination unsaturated Co sites exhibited oxygen evolution activity by effectively promoting water molecular adsorption and activation, and also helped to suppress electron-hole recombination. Meanwhile the phosphide dopants accelerated the electric conductivity of Co/g-C₃N₄. As a result, in photocatalytic overall water splitting reaction, Co/g-C₃N₄ afforded a H₂ evolution rate as high as 410.3 $\mu\text{mol h}^{-1}$, with the carrier lifetime over 20 times prolonged compared to the pristine g-C₃N₄.

Summary of SAPCs for photocatalytic water splitting. The order is arranged by the time of publication.

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