

Review

Single-Atom-Based Catalysts for Photocatalytic Water Splitting on TiO₂ Nanostructures

Seyedsina Hejazi ^{1,*}, Manuela S. Killian ^{1,*}, Anca Mazare ^{2,3,*} and Shiva Mohajernia ^{1,*}

¹ Department of Chemistry and Biology, Chemistry and Structure of Novel Materials, University of Siegen, Paul-Bonatz-Str. 9-11, 57076 Siegen, Germany

² Department of Materials Science and Engineering, Institute for Surface Science and Corrosion, Friedrich-Alexander-Universität ErlangenNürnberg, 91058 Erlangen, Germany

³ Advanced Institute for Materials Research (AIMR), National University Corporation Tohoku University (TU), 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

* Correspondence: manuela.killian@uni-siegen.de (M.S.K.); anca.mazare@fau.de (A.M.); shiva.mohajernia@uni-siegen.de (S.M.)

Abstract: H₂ generation from photocatalytic water splitting is one of the most promising approaches to producing cost-effective and sustainable fuel. Nanostructured TiO₂ is a highly stable and efficient semiconductor photocatalyst for this purpose. The main drawback of TiO₂ as a photocatalyst is the sluggish charge transfer on the surface of TiO₂ that can be tackled to a great extent by the use of platinum group materials (PGM) as co-catalysts. However, the scarcity and high cost of the PGMs is one of the issues that prevent the widespread use of TiO₂/PGM systems for photocatalytic H₂ generation. Single-atom catalysts which are currently the frontline in the catalysis field can be a favorable path to overcome the scarcity and further advance the use of noble metals. More importantly, single-atom (SA) catalysts simultaneously have the advantage of homogenous and heterogeneous catalysts. This mini-review specifically focuses on the single atom decoration of TiO₂ nanostructures for photocatalytic water splitting. The latest progress in fabrication, characterization, and application of single-atoms in photocatalytic H₂ generation on TiO₂ is reviewed.

Keywords: titanium dioxide; water-splitting; H₂ generation; single-atom



Citation: Hejazi, S.; Killian, M.S.; Mazare, A.; Mohajernia, S. Single-Atom-Based Catalysts for Photocatalytic Water Splitting on TiO₂ Nanostructures. *Catalysts* **2022**, *12*, 905. <https://doi.org/10.3390/catal12080905>

Academic Editor: Zupeng Chen

Received: 1 August 2022

Accepted: 12 August 2022

Published: 17 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Photocatalytic water splitting is the process of H₂ and O₂ production from water under light irradiation and in the presence of a catalyst, and follows the Equations (1)–(3) listed below.



Basically, in the photocatalytic pathway, photon energy (from solar energy) converts to chemical energy (hydrogen) in the presence of photocatalysts. The ground-breaking work of Fujishima and Honda [1] demonstrated the feasibility of photocatalytic hydrogen generation from water, using Pt/TiO₂ electrodes.

Currently, hydrogen is produced mainly from fossil fuels with a rate of ~50 billion kg per year [2]. Thus, solar water splitting can become a sustainable and renewable hydrogen production path, with the potential to mitigate the energy crisis.

Semiconductors are among the most suitable materials as photocatalysts for H₂ production from water splitting or photo-reforming of H₂O/alcohol mixtures, e.g., using methanol or ethanol (without or with the presence of co-catalysts). According to Takanabe [3], the process of water splitting on a semiconductor involves six major components

that occur sequentially (see Figure 1), which schematically summarizes the contribution of all the steps influencing the overall water splitting. In the first step, upon irradiation, electron-hole pairs are generated. This occurs when the photon energy is larger than the bandgap of the semiconductor. The second step is charge separation, followed by the third step of diffusion of the photogenerated charge carriers. Carrier diffusion (the third step) depends mainly on carrier lifetime, mobility, and diffusion length. Electrons and holes recombination is almost zero in an ideal photocatalyst with maximum efficiency. The fourth step is carrier transportation and is confined by the following characteristics of the system, conductivity, space charge layer, and flat band potential. The fifth major step is the catalyst's efficiency in terms of exchange current density, Tafel slope, electrocatalytic activity, activation energy, and charge transfer resistance. In the last step, mass transfer plays an important role and is under the control of mainly the iR drop in the solution, pH gradient, viscosity, and effective size of the ions in the electrolyte.

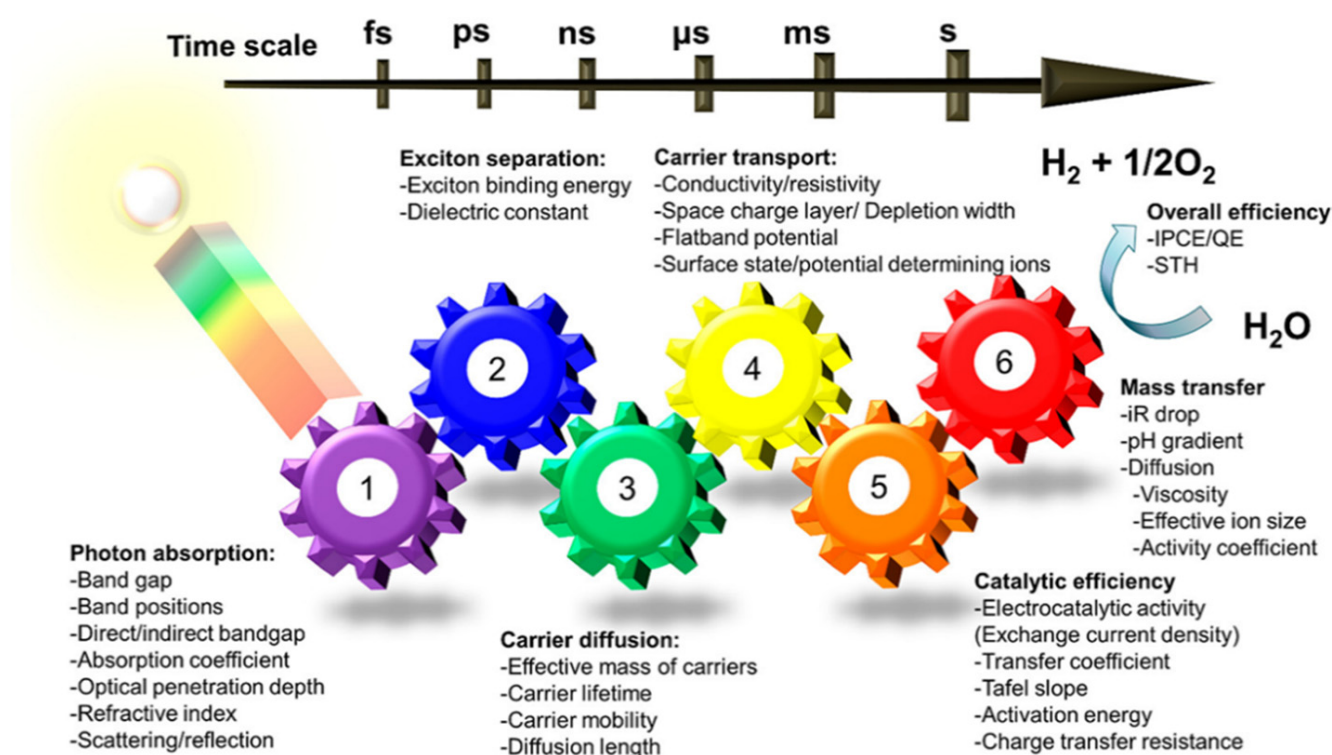


Figure 1. The parameters affecting the overall photocatalytic water splitting. The gear with the number indicates the order of the photocatalytic process to be successful for overall water splitting. The timescale for the reactions is also shown. Reprinted with permission from Ref [3], Copyright © 2017 American Chemical Society.

There are excellent review articles with respect to photocatalyst and photoelectrochemical water splitting, for example, refs. [4–10]. Of the multitude of investigated semiconductor materials, TiO_2 remains one of the most investigated photocatalysts as it provides excellent photo corrosion, non-toxicity, a low cost, and, most importantly, the conduction and valence band edges [11,12]. However, the solar to hydrogen (STH) conversion efficiency is still very low for TiO_2 , and the insufficient energy conversion efficiency in TiO_2 systems is mainly ascribed to the following factors: (i) the fast recombination of photogenerated charge carriers (electron-hole pairs), the recombination of electrons on the conduction band with the holes in the valence band causes unwanted heat or photon generation; (ii) the backward reaction, the reaction of H_2 and O_2 to form water, which occurs very fast; and (iii) the wide band gap of TiO_2 (3.2 eV) that allows only UV light absorption for H_2 production. Since only about 4% of the solar radiation energy is UV light the STH efficiency remains very low with pristine TiO_2 structures.

In general, rutile TiO_2 is the most stable phase among the TiO_2 polymorphs, compared to anatase and brookite, and has a smaller band gap. However, anatase is the preferred polymorph in photocatalytic applications due to a higher conduction band energy and a lower electron-hole recombination rate [12,13]. Different shapes of TiO_2 nanostructures have been synthesized to modify the electronic and optical properties, e.g., nanoparticles, nanobelts, nanosheets, nanoflakes, nanotubes [11]. From the different methods, the electrochemical anodization of Ti foil is a straightforward method to produce 1D nanostructures, and hydrothermal techniques as well provide scalable and convenient methods to produce 1D and 2D nanostructures. Additionally, designing anatase nanocrystals with 001 facet as the most active site using hydrothermal method is of great interest for enhancing the catalytic activities [14].

To tackle the above-mentioned issues and make photocatalytic water splitting feasible, tremendous efforts have been made to enhance the photocatalytic activity and visible light absorptions of TiO_2 . The following strategies prove to be the most efficient approaches to improving photocatalytic activity: (a) addition of hole scavengers (electron donors) [15–18], (b) addition of carbonate salts [19,20], (c) metal and non-metal doping [21], (d) self-doping (defect engineering) [22,23], and e) noble metal co-catalyst decoration [24]. Among the mentioned strategies, the use of noble metals as a co-catalyst for photocatalytic water splitting is one of the most efficient strategies. Platinum group metals (PGM) such as Pt, Pd, Rh, Ru, or Ir are among the least abundant elements on the earth and are thus expensive. However, they are the best-known catalysts for photocatalytic H_2 evolution [25]. Therefore, there is significant interest in utilizing noble metal catalysts in heterogeneous photocatalysis. For metal particles, the ultimate size limit is the single-atom catalyst, i.e., isolated atoms dispersed on supports. In addition to their small size that leads to a higher active surface area, a characteristic is also a low coordination environment that is ascribed to unsaturated bonding on the single-atoms [26,27]. Additionally, single-atoms have a distinctive HOMO–LUMO gap due to quantum size effects [28]. Furthermore, the chemical bonding between single-atom metals and supports facilitates the charge transfer between the single-atom co-catalysts and supports [29,30].

It should be noted that the development of the single-atom catalysis field largely relies on advances in both theoretical modeling and atomic-resolution characterization techniques. The present review is specifically focused on TiO_2 nanostructures for photocatalytic water splitting, using single-atom noble metals or transition metals as co-catalysts.

2. Fabrication of Single-Atom Co-Catalysts

Due to their small size, single atoms have high surface energy; thus, they often tend to agglomerate during the reaction process. One of the main goals in single-atom research is overcoming aggregation, which requires the formation of strong bonding between the single-atoms and the support material. This interaction directly influences the stability and efficiency of the reaction for which a single atom is adopted. The key to forming stable single-atom catalysts with high density is to enhance the anchoring sites. There are three types of anchoring sites for fabricating single-atom catalysts: (i) defects on the support material [31], (ii) unsaturated coordinated atoms [31], and (iii) excess O atoms on the support surface to form hollow sites [31]. Figure 2 illustrates the paths and key strategies for single-atom decoration [32], which will also be further discussed below.

In general, there are two main strategies for constructing single-atom catalysts with well-defined and separated atomistic structures, namely high vacuum physical deposition and wet chemical deposition

2.1. High Vacuum Physical Deposition

Vacuum deposition is a more suitable technique for fundamental studies mainly due to the superior control over the single-atom deposition and model catalyst formation. However, as a result of the low yield and high cost of this method, it is not yet feasible for

commercial catalyst production [33,34]. Mass-selected soft-landing [35] and atomic layer deposition (ALD) [36] techniques were further developed for the fabrication of single-atom catalysts. Mass-selected soft landing (Figure 2c) includes an ion source in gas form and a mass spectrometer to filter the nanoclusters according to their mass before their deposition onto a substrate [33].

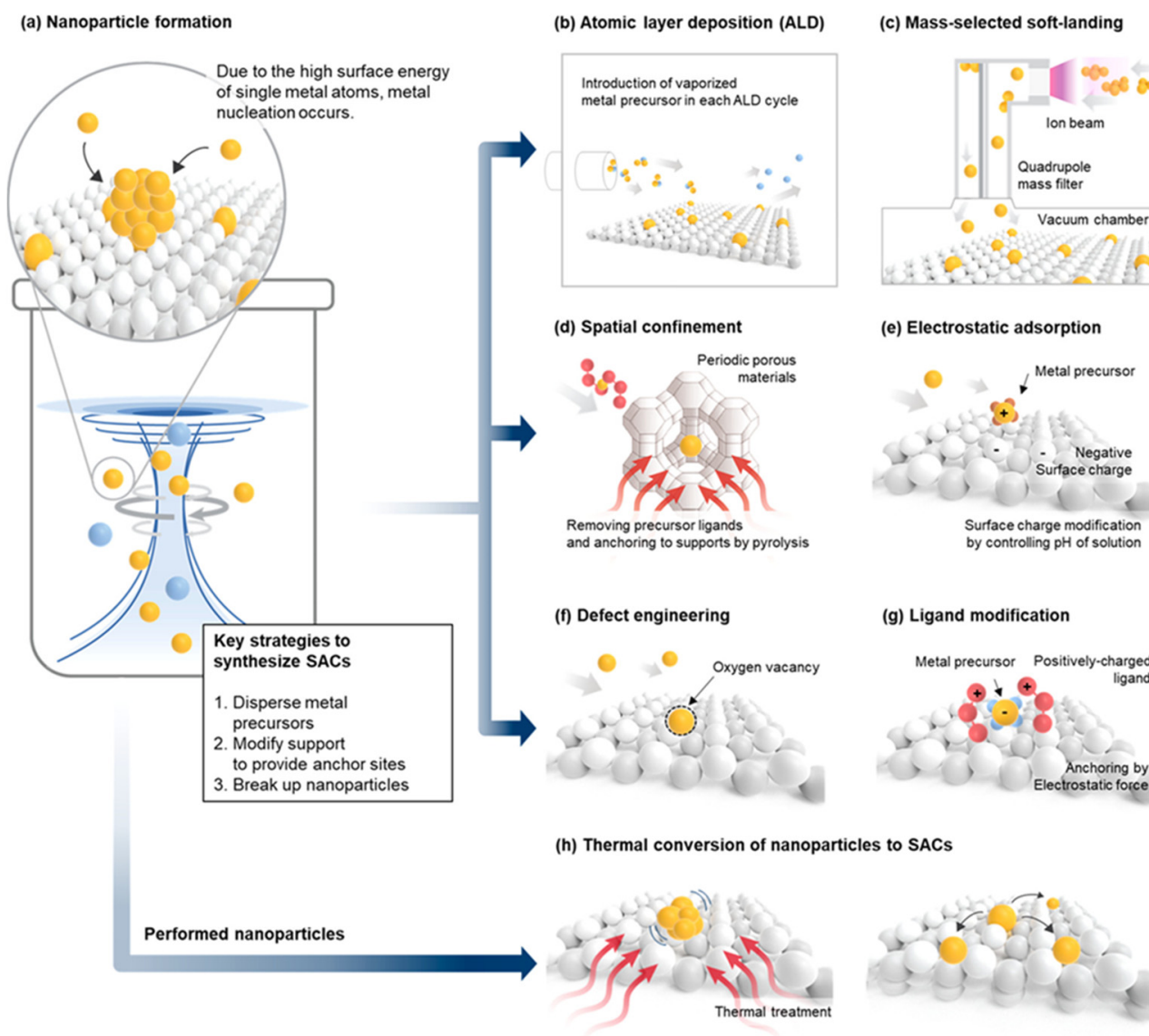


Figure 2. Schematic illustration of single-atom catalysts fabrication methods. Reprinted with permission from Ref [32], Copyright © 2020 American Chemical Society.

As a result, metal clusters with a well-defined number of atoms can be deposited (soft-landed) on a substrate. Kaden et al. [37] reported on the deposition of Pd clusters ($\text{Pd}(n)$, for $n = 1, 2, 4, 7, 10, 16, 20$, and 25) on clean rutile TiO_2 (110) to build a model catalyst for CO oxidation.

In ALD synthesis (shown schematically in Figure 2b), precursor molecules chemisorb on the support surface via gas-solid reactions and, in each reaction step, form less than a monolayer on the surface. Repeating this cycle, and depending on both the support and ALD-grown material, it is possible to form thin films, nanoparticles, and even single-atoms [38,39]. By optimizing the ALD conditions, namely temperature, counter-reactant, precursor, and pulse times, as well as selecting appropriate ALD approaches such as low-

temperature selective ALD [40] or modifying the pulsing sequences [41], one can design single-atom catalysts for a wide range of catalytic applications [42].

2.2. Wet Chemical Deposition

Wet-chemical approaches are more common and used routinely to synthesize single-atom catalysts as they do not require specialized equipment. According to the integration of the components, single-atom wet chemical synthesis is categorized into bottom-up methods, where single-atoms are anchored to the substrate by the reaction of the metal complexes with the anchoring sites on the substrate surfaces, or top-down methods, where metal nanoparticles are decorated on the surface of the support followed by dispersion into single-atoms [43].

In the bottom-up approach (Figure 2d–g), very dilute metal precursors are used as a source of the single-atom where the support material is dipped inside to be decorated by single-atoms and is usually followed by a calcination step, which results in single-atom catalysts on the support surface by a reduction or activation step [44]. Impregnation [45,46], galvanic replacement [47,48], electrostatic adsorption, and photochemical adsorption [49] are among the most common bottom-up methods for single-atom catalyst fabrication.

Nanostructures are turned into smaller pieces in a top-down strategy to obtain desirable characteristics and performance. For single-atom catalyst fabrication, the high-temperature atomic migration method represents a typical top-down approach (Figure 2h). The mechanism behind this method can be explained by Ostwald ripening. This process includes detaching metal atoms from nanoparticles, diffusion of the atoms on the substrate, and attachment to bigger particles [50] or immobilizing in defects [51]. For example, Ag single-atoms were prepared starting from Ag nanoparticles at 400 °C on MnO₂-based substrates [52], and Li et al. [51] showed that noble metal nanoparticles can be thermally converted to highly active and stable single-atoms (Pd, Au, Pt) at above 900 °C in an inert environment. Overall, this high-temperature atomic diffusion technique provides thermally stable and high-performance single-atom catalysts.

3. Characterization Methods for Single-Atom Co-Catalysts

Despite their extensive investigation, several key points related to the single-atom catalysts' physicochemical properties still remain unanswered or require further investigation, especially in view of understanding and correlation these properties to their photocatalytic efficiency. This includes the reliable evaluation and characterization of the single-atoms in their environment, considering their very low amounts (low weight loadings), strong metal-support interactions, and so on, characteristics which are necessary in order to identify their amount, charge state, electronic structure, atomic configuration, bonding interactions, etc.

The characterization techniques typically employed for nanoparticle characterization (with their corresponding optimization) cannot be used to confirm the presence of single-atom catalysts, though such techniques are useful for substrate characterization or as a negative control. Nowadays, with the progress achieved in characterization techniques, it is actually feasible to observe single metal atoms or sub-nanometric metal clusters of few atoms by means of aberration-corrected electron microscopy [53] or atomic-resolution scanning tunneling microscopy (STM) [54]. Moreover, their loading and coordination environment can be further evaluated by extended X-ray absorption fine-structure spectroscopy (EXAFS), X-ray absorption near-edge spectroscopy (XANES), X-ray absorption spectroscopy (XAS), and ambient pressure X-ray photoelectron spectroscopy (XPS). Recently, focus was also given to a more thorough understanding of these characterization techniques and their application to the single-atom catalysts field, see the comprehensive reviews in refs. [28,32,55–57]. It is also worth mentioning that supported single atoms are usually stabilized by chemical bonding to the inorganic support (e.g., on transition metal oxides, and zeolites), as previously discussed in the fabrication section. Such SA will show a limited geometric transformation under reaction

conditions, however, when supported on organic polymers with functional groups (like amine, carbonyl groups, thiol, etc.) SA may adapt their coordination environment under reaction conditions (as a result of the interaction between the single-atoms with the substrate molecules) [28]. Therefore, next we will discuss and exemplify characterization techniques for single atoms specifically decorated only on inorganic supports.

3.1. Transmission Electron Microscopy (TEM) for SA Evaluation

TEM is one of the most direct methods enabling the detailed evaluation of atomic-scale structural information of single-atom catalysts as well as their interaction with the support material. Moreover, aberration-corrected TEM either in both phase contrast TEM or sub-angstrom resolution high-angle annular dark-field STEM (HAADF-STEM) mode, was successful in imaging single-atom catalysts on various supports [58]. The advantage of HAADF-STEM lies in the fact that the imaging is based on Rutherford scattering (i.e., image intensity for the given atoms is proportional to the square of the element's atomic number), and this results in a brighter contrast of heavy metals atoms when on low mass background supports. Current literature includes the identification of single-atom on graphene-based supports (Au [59], Fe [60], Ru [61], etc.), graphitic carbon nitride (Pt [62]), carbon paper (Pt, Ru [63]) or inorganic semiconductors such as cerium oxide (Pt [64,65], Ru [66]), alumina (Pt [67]) or TiO₂ (Pt [45,68–75], Pd [71,76–81], Au [71,82,83], Ir [84,85], Rh [86]). This enabled a precise evaluation of the size and distribution of the single metal atoms, as well as their local structural information (metal species on the support) [55]. For example, HAADF-TEM images of typical Pt SAs on different inorganic semiconductors are shown in Figure 3a for Pt SAs obtained by the L-ascorbic acid (AA)-assisted reduction synthesis on CeO₂. Namely, Chen et al. [64] confirmed the presence of atomically dispersed Pt catalysts throughout the CeO₂ support (on the surface defects), showing also a uniform distribution of the co-catalyst on the support in the elemental mapping (Figure 3b). Similarly, Hejazi et al. [45] have shown that the Pt is present as SA on TiO₂ with a uniform distribution, see Figure 3c,d, and such a disperse SA loading was achieved by a dark deposition method based on wet impregnation.

Thus, TEM enables the direct imaging of supported co-catalyst particles and can identify structural and interfacial information of both the co-catalyst metals and substrate support, but only for specific positions on the sample, which means that it can lack a broader context of the investigated sample or in bulk. Therefore, it would prove helpful to combine TEM with other characterization methods to ensure that the observation is valid for the whole of the material. The recent comprehensive reviews of Kottwitz et al. [56] and Tieu et al. [87], detailing the use of advanced electron microscopy in single-atom catalysis, are also recommended for more details.

3.2. X-ray Absorption near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) for SA Evaluation

XANES and EXAFS are characterization techniques reflecting the oscillatory structure of the studied samples in correlation with the X-ray absorption coefficient [57,88]. The binding energy shifts and wiggles of the single metal atoms in XANES spectra represent the near-neighbor distances and their chemical coordination [57]. For example, XANES spectra would indicate complex structures, including the formation of additional bonds (M–N, M–C, etc.) which can disrupt the precise data associated to isolated metal atoms [57]. A significant advantage of these methods is their ability to provide insight into the chemical nature and stabilization structure of single atoms on supports, as well as the investigation of bulk materials. Combined with TEM, this would lead to the overall structure of metal SA compared to local, surface information [55,89]. The absence of metal-metal interactions can be a clear indication of the absence of particles in which, in general, single supported atoms are oxidized, and thus ruling out the presence of rafts/clusters/nanoparticles.

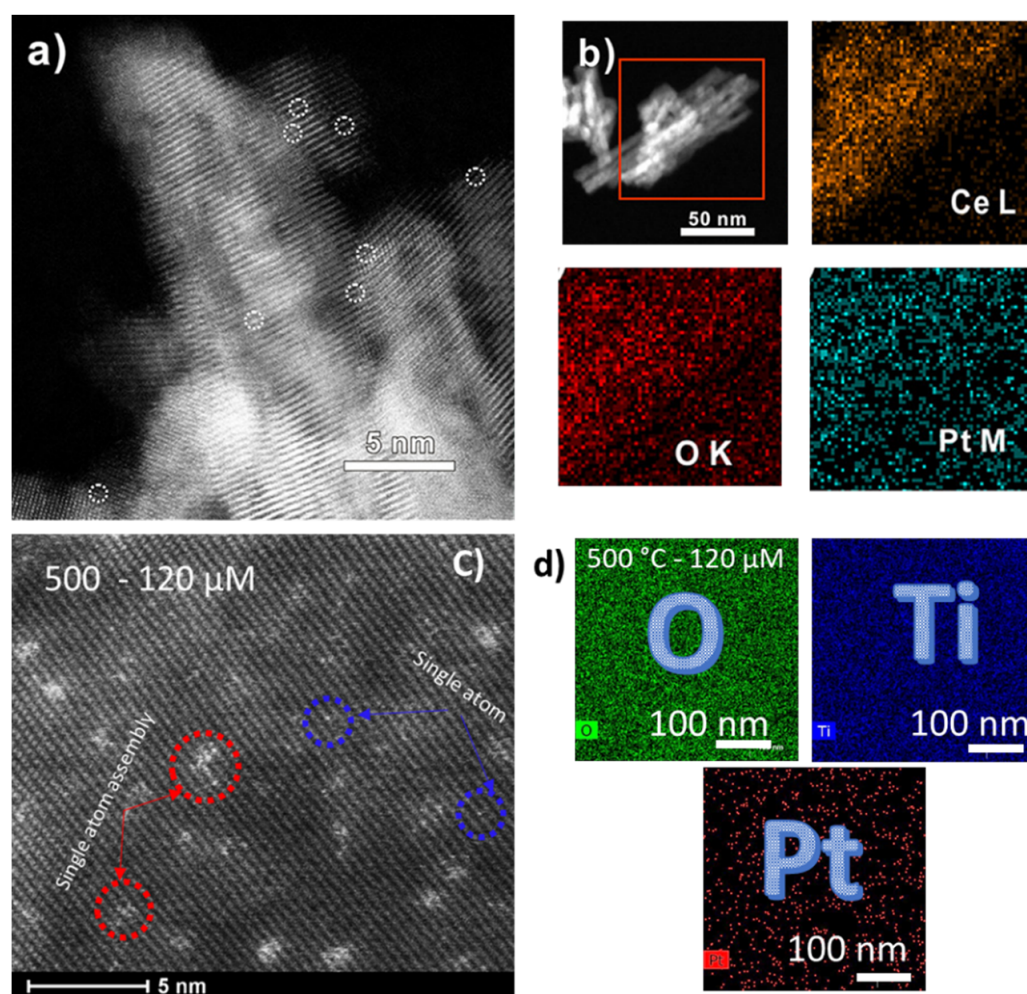


Figure 3. Pt on CeO₂: (a) Cs-corrected HAADF-STEM, (b) HAADF-STEM, and corresponding elemental mappings images of CeO₂-AA-Pt-cal. (c,d) Pt on TiO₂: (c) HAADF-TEM image and (d) EDS map of Pt-SA-decorated TiO₂ layer. Part (a,b) is adopted with permission from Ref [64] Copyright © 2018 American Chemical Society. Part (c,d) is adopted with permission from Ref [45], Copyright © 2020, John Wiley and Sons.

Especially for evaluating the electronic structure of metal SA, XANES measurements are useful for characterizing the electronic and structural properties of the absorbed SA, as shown by Li et al. [90] (Figure 4a). The authors [90] attribute the white line of the Pt L3 edge to the transition of 2p electrons to unoccupied 5d valence orbitals, thus providing information related to the population of unoccupied Pt 5d orbitals. Evaluating the Pt SA on various supports (Co₃O₄, CeO₂, ZrO₂, graphene) and comparing the data with that of Pt foil and PtO₂ (as references), resulted in establishing an explicit electronic correlation with the unoccupied Pt 5d states, having the following magnitude for the Pt SAs on the supports Co₃O₄ > ZrO₂ > CeO₂ > graphene [90]. The Pt SAs on the Co₃O₄ have shown a higher valence state of ~4⁺ and a larger population of unoccupied Pt 5d states [90]. Similar investigations were also performed to investigate the Pt 5d occupation state of Pt SA compared to small clusters or nanoparticles (on graphene) [91], for Pt SAs on FeOx [92] or on different polymorphs of TiO₂ nanoparticles [93] and for bi-metallic SAs of PtAu [94].

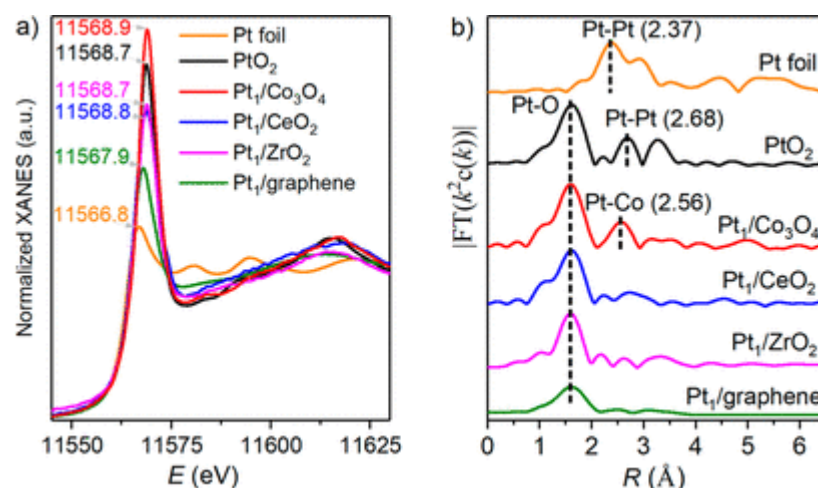


Figure 4. (a) XANES spectra of Pt₁/Co₃O₄, Pt₁/CeO₂, Pt₁/ZrO₂, and Pt₁/graphene single-atom catalysts as well as the Pt foil and PtO₂ reference at the Pt L3-edge. (b) The corresponding K₂-weighted Fourier transform spectra. With permission from Ref [90], Copyright © 2019 American Chemical Society.

Similarly, Li et al. [90] have further evaluated the EXAFS analysis of the Pt SAs on the various supports, see Figure 4b, and attributed to the coordination number of Pt–O (peak at 1.60 Å) the subsequent trend Co₃O₄ > CeO₂ > ZrO₂ > graphene, for the Pt SAs decorated different substrates, and the absence of the Pt–Pt coordination peak suggested the absence of Pt NPs or clusters. Additionally, the Pt/Co₃O₄ curve showed a second shell peak at 2.56 Å (attributed to Pt–Co coordination), distinct from those of Pt foil (2.37 Å) and PtO₂ (2.68 Å) [90]. Similarly, the coordination of Pt SAs on different supports (TiO₂ [93]) or of other SAs (Au on TiO₂ [82]) can also be evaluated. For example Wan et al. [82] reported on the isolated single atomic dispersion of Au on defective TiO₂, with an Au–O shell (R = 1.6 Å) and an Au–Ti shell (R = 2.4 Å), without Au–Au and Au–Cl coordination peaks (compared with Au foil and HAuCl₄ as reference).

XANES and EXAFS measurements are also advantageous for investigating single-atoms on MOF, zeolites, or graphitic layers, see as examples Ye et al. [95] for Co SAs on MOF (Co–N bonding detected in EXAFS), Yin et al. [96] for Co on N-doped carbon, or Choi et al. [97] for Pt on zeolites.

3.3. X-ray Photoelectron Spectroscopy (XPS) for SA Evaluation

XPS is a well-known characterization technique, universally used for evaluating the chemical and compositional properties of surfaces, and more specifically in catalysis of the catalysts and co-catalysts. XPS is a highly surface-sensitive technique ensuring analysis of the top 10 nm of the sample. Moreover, it has shown adaptability and precision to the field of supported metal SA catalysts [56,98], and can also be used in ambient pressure mode allowing for the evaluation of catalysts under the reaction atmosphere (e.g., Simonovis et al. [99], evaluating the behavior of singly dispersed Pt atoms on the surface of Cu(111) in an ambient pressure of CO).

Please note that the trapped metal single atom, denoted as M, shows a chemical shift of δ^+ due to the changed co-coordination (as a result of the oxygen coordination, see the case of Pt SAs on CeO₂, where the Pt is bound to oxygen instead of Pt [100]). Compared to classical metallic nanoparticles, noble metal SAs decorated on the same support material show a shift to higher binding energies, which is related to its surface coordination—please see the work of Wan et al. [82] showing a shift in the Au4f XPS spectra of Au SAs (85 eV) compared to Au NPs (84 eV) on TiO₂. Moreover, Figure 5a shows a similar shift to higher binding energies for Pt SAs/TiO₂, compared to their nanoparticle counterpart. The deconvolution of the Pt4f peak of the Pt SAs (see Figure 5b) results into Pt δ^+ and Pt $^{4+}$ (the peaks at 72.93 and 76.28 eV correspond to Pt δ^+ 4f_{7/2} and Pt δ^+ 4f_{5/2}, whereas the peaks at 75.04 and 78.51 eV can

be attributed to $\text{Pt}^{4+}4f_{7/2}$ and $\text{Pt}^{4+}4f_{5/2}$, while for the Pt nanoparticle decoration peaks are mainly attributed to metallic Pt ($4f_{7/2}$ at 71.07 eV) [45].

Literature confirms that when Pt is present in the SA state, it is coordinated to its trap environment, that is mainly oxygen atoms of the oxide surface, thus forming Pt-oxide-similar $\text{Pt}^{\delta+}$ and Pt^{4+} states (with Pt^{4+} as evidence of a strong Pt– TiO_2 interaction) [92,100–103]. Similar results were also obtained for other Pt single-atom decoration on different TiO_2 supports [69–71,104] or on other support materials, e.g., Pt on nanosized CeO_2 (no metallic Pt, only SA with +2 state) [105]. Moreover, XPS was used to evaluate the chemical state of a variety of other single-atoms co-catalysts, such as Pd [71,78], Au [71], Rh [86,106], and Ir [84], confirming the $\delta+$ state of the single-atom co-catalyst on the evaluated support material.

Recently Wei et al. [94] reported on the synthesis of bi-metallic single-atoms on different faceted TiO_2 ($\{001\}$, $\{101\}$), where the metal–support interactions that originated from the coordinatively unsaturated sites contributed to the anchoring of the atomic co-catalysts—namely, onto $\{001\}$ - TiO_2 through Pt–O and Au–O bonds, while on $\{101\}$ - TiO_2 preferentially for Pt–O and Au nanoparticles. This difference was also observed in the high-resolution XPS spectra, as for the Pt4f peaks (Figure 5c), binding energies for $\text{Pt}^{4+}4f_{7/2}$ at 73.0 (typically attributed to Pt^{4+}) are obtained, while for the Au4f peaks (Figure 5d) a shift of 0.2 eV to more negative binding energies was observed for $\text{PtAu}/\{101\}$ - TiO_2 (where Au is deposited as nanoparticles). The latter may be due to the changes in the binding environment of Au, as the weaker metal–support interactions lead to agglomeration and reduce the binding energies [71,94].

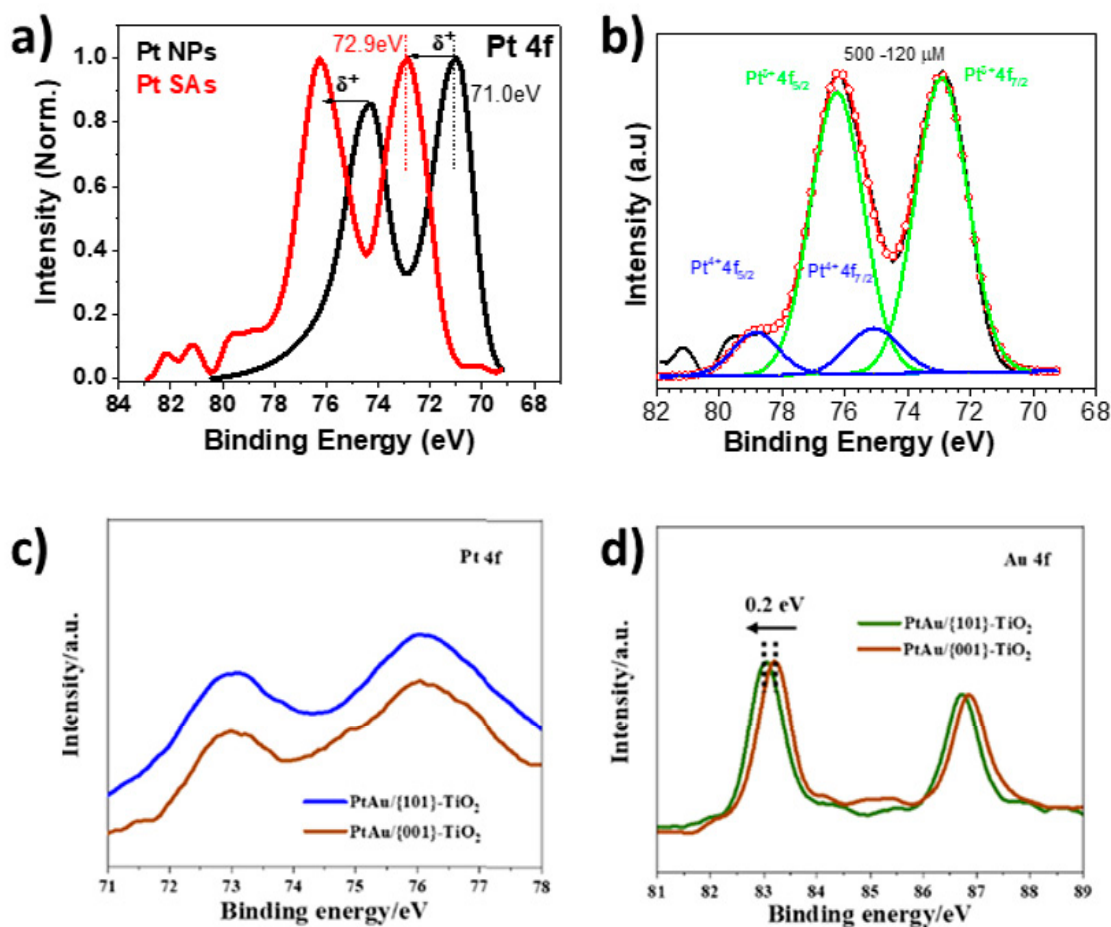


Figure 5. (a) XPS high-resolution spectra of SAs vs NPs for Pt on TiO_2 , (b) Peak fitting of the Pt SAs of (a). Bi-metallic SAs as exemplified for Pt–Au SAs on different faceted TiO_2 , showing the (c) Pt4f and (d) Au 4f. Part (a,b) reproduced with permission from Ref [45], Copyright © 2020, John Wiley and Sons. Part (c,d) reproduced With permission from Ref [94], Copyright © 2021 American Chemical Society.

With respect to the energy shift in XPS, two further aspects need to be mentioned, (i) first that both support and particle size could induce positive binding energy shifts (as shown for Pt nanostructures because of the reduction of effective atomic coordination numbers) [107], and (ii) second, in the case of comparing the different SA binding energies, careful consideration of the peaks used for calibration has to be made (especially if the C1s peak at 284.8 eV is employed [108–110]).

As a closing remark, a combination of characterization techniques has to be used to properly identify and quantify the atomic fractions of the SA. Additional characterization techniques adapted to single-atom characterization include (a) Fourier-transform infrared spectroscopy (FTIR)—molecular groups, chemical bonding (only specific molecules can be detected) [98] or diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)—which provides chemical and structural information related to surface species, commonly through measurement of adsorbed probe (e.g., CO) molecules in studies of catalytic reaction mechanisms, typically linearly adsorbed CO on an isolated metal atom site [56,105], (b) surface-enhanced Raman spectroscopy (SERS)—crystal structure, chemical bonding (though only working for specific elements) [98], (c) electron energy loss spectroscopy (EELS)—element and chemical state analysis [98], scanning tunneling microscopy (STM)—imaging of the supported individual single metal atoms (low temperature under ultrahigh vacuum) [28,98].

4. Photocatalytic Hydrogen Evolution on Single Atom Decorated TiO₂

Sluggish charge transfer, limited photoconversion, and fast electron-hole recombination rate are the bottlenecks of TiO₂ photocatalytic water splitting, and as mentioned earlier, this makes the introduction of a promising co-catalyst essential in order to improve the photocatalytic performance of TiO₂. Recently, single-atom catalysts have drawn significant attention due to enhanced active reaction sites, while decreasing the loading compared to conventional nanoparticle catalysts. The active and isolated metal atoms anchored onto the photocatalysts provide more water-molecule adsorption and thus enhance photocatalytic activity. However, the aggregation of SAs during the catalytic reaction is the major issue that leads to a significant drop in the performance of the photocatalysts. Therefore, obtaining a high concentration and highly dispersed single-atom catalysts is the bottleneck in photocatalytic water splitting using SAs. The single-atom catalysts are stabilized by covalent bonding with the carrier or neighboring surface atoms or interionic interaction. In this context, the catalytic activity of a single-atom can be tuned by metal-support interaction, coordination environment, quantum size effect, and so on [111].

Noble metals such as Pt, Au, and Pd are mainly used as co-catalysts in photocatalytic water splitting, and this is due to their efficient charge separation and low activation energy. To reach a more scalable water splitting system, earth-abundant transition metals such as Cu, Ni, Co, and Fe are promising alternatives for noble metals in photocatalysis [112–115]. Utilizing noble metals and transition metals as single atom co-catalysts for producing H₂ from water is known to result in higher efficiency and an overall lower cost. In this section, the most recent research on photocatalytic water splitting reactions using single-atom catalysts on TiO₂ will be discussed.

Zhang et al. [116] reported on a large loading amount (1.5 wt.% of Cu) and highly dispersed copper single-atom on nanoparticle TiO₂ (MIL-125(Ti_v)) for photocatalytic H₂ generation that exhibits a quantum efficiency of 56% under 365 nm irradiation (see Figure 6). A range of loading from 0.47 wt% to 2.57 wt% of Cu was evaluated in their experiments. The authors attributed this performance to the strongly anchored Cu single atoms on TiO₂ that trigger a reversible/self-healing and continuous photocatalytic process that effectively separates photoelectrons to reduce water to H₂. The results are supported with various spectroscopic and in-situ experiments as well as with DFT modelling results. Their study reveals the most efficient charge separation by Cu SA and proves the significance of the in-situ self-healing effect of Cu species during the photocatalytic reaction.

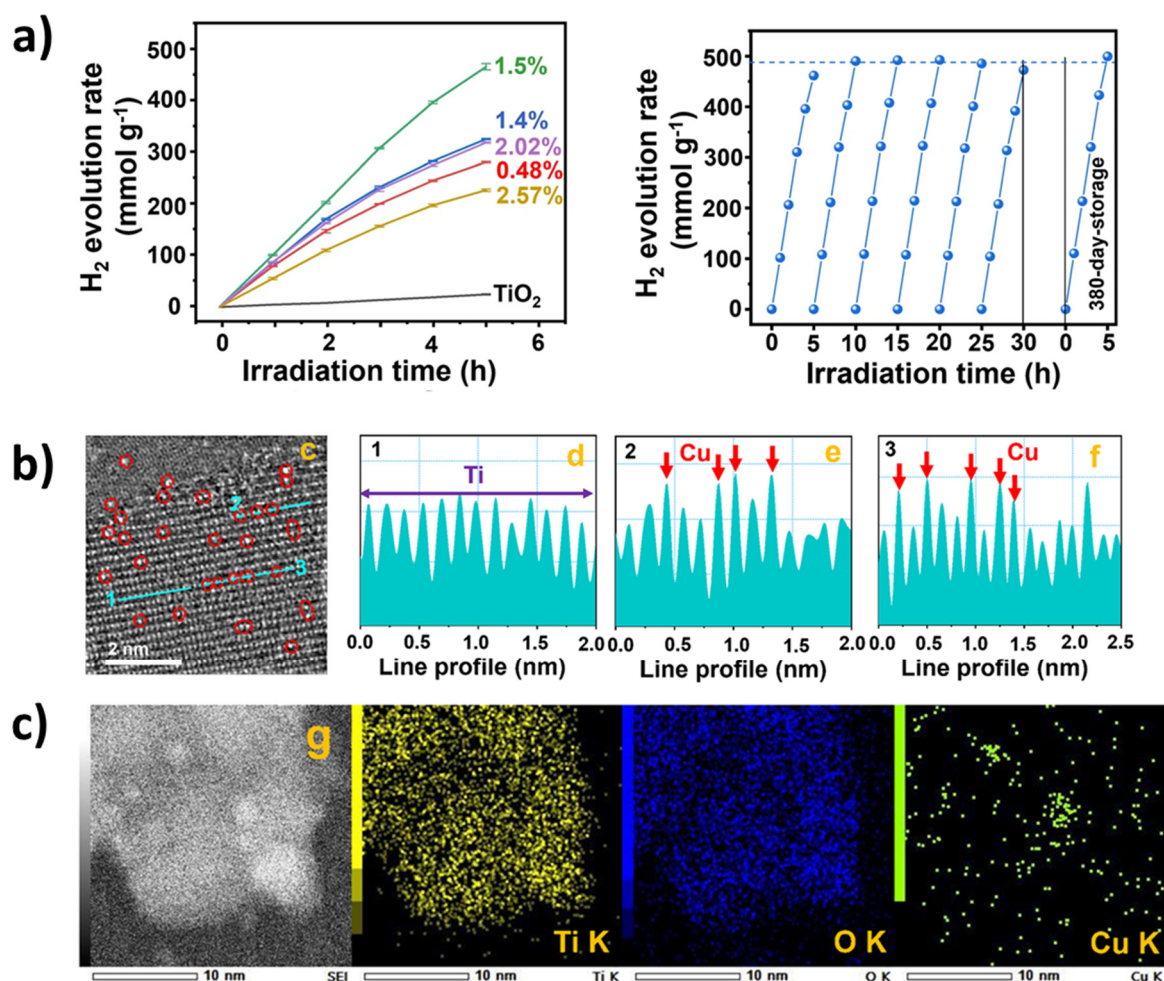


Figure 6. (a) The photocatalytic H₂ evolution rate of TiO₂ loaded with different ratios of Cu SA catalysts as a function of the irradiation time (left side) and right side—the photocatalytic activity of the ca. 1.5 wt% CuSA-TiO₂ for six cyclic water splitting experiments and the last run is the activity of the sample after storing in the lab for 380 days, (b) filtered HAADF STEM image and the corresponding line scan profiles, (c) STEM-EDS mapping of Ti, O, and Cu of the fresh CuSA-TiO₂. With permission from Ref [116], Copyright © 2021, Springer Nature.

In another approach on TiO₂ systems modified by Cu single-atoms, Lee et al. [117] reveal that the cooperative interplay of atomic catalysts and their environment has a significant influence on the properties and catalytic performance of the material. They suggest that the fundamental atomic-level cooperative interaction is very similar to homogeneous catalysts. Through ab initio nonadiabatic molecular dynamics, Long et al. [118] show simulations that Cu single-atoms on TiO₂ are inactive for water splitting, before light irradiation. However, after illumination, the deep trap state on the Cu d orbital is stabilized by the local distortion around the Cu single atom, decoupling it from the free charge thus providing a high photocatalytic hydrogen production activity.

It is also reported that bi- or multi-metallic catalytic sites show higher photocatalytic water splitting activity compared to regular single-atom catalysts. Wei et al. [94] show that bi-metallic Pt and an Au single atom on the {001}-TiO₂ presented a 1000-fold increase in the H₂ generation rate in comparison to pristine {001}-TiO₂. They show that by regulating the coordination environment of atoms, it is possible to disperse bimetal catalytic sites on faceted semiconductors. They show an H₂ evolution rate of 61.3 mmol h⁻¹g⁻¹, much higher than that of the TiO₂ modified by Pt or Au single-atoms. They explain the mechanism by the synergistic effect of PtAu dual-atom catalysts, which can decrease the Gibbs free energies of hydrogen adsorption by optimizing the electronic states of both Pt and Au sites.

Particularly, the Pt atom is activated by the Au atom and the activity of catalysts is further enhanced through the dimer interaction (see Figure 7).

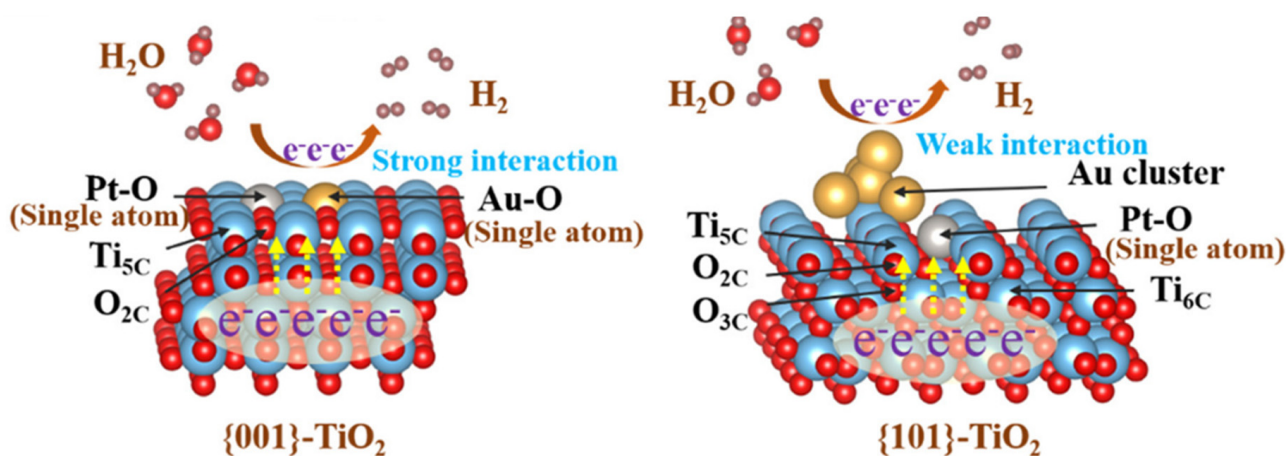


Figure 7. Schematic illustration of charge transfer in dual-site co-catalyzed {001} and {101}-faceted TiO_2 . Blue, red, gray, yellow, and brown spheres represent Ti, O, Pt, Au, and H atoms, respectively. With permission from Ref [94], Copyright © 2021 American Chemical Society.

In another study, Wang et al. [119] reported on the Co and Pt dual single-atom on TiO_2 with ultrahigh photocatalytic hydrogen generation efficiency. They attributed this enhancement to the oxygen-coordinated Co–O–Pt dimer coupling, which is able to optimize the electronic states of Pt and Co sites in order to weaken H^* binding. They further explain that the Pt single-atom activates the “mute” Co single-atom and the activity of the Pt atom itself is additionally improved by the dimer interaction. With this strategy, the authors show that the dual single-atom catalyst yields 13.4% dimer sites that lead to stable and highly active photocatalysts with an H_2 generation rate of $43.467 \text{ mmol g}^{-1} \text{ h}^{-1}$ and external quantum efficiency of $\approx 83.4\%$ at 365 nm.

Wu et al. [120] reported on the isolated Co atoms on TiO_2 nanosheets that significantly improve the charging kinetics via a Co–O electronic coupling. With experimental investigations and theoretical calculations, the authors show that the electron transfer and the hydrogen adsorption/desorption processes are facilitated by the effective atomic scale Co–O electronic coupling.

Several experimental and theoretical studies suggest that coupling Pt single atoms with the atomic scale defects in TiO_2 nanostructures is an efficient strategy for stabilizing SAs and to achieving an excellent photocatalytic H_2 generation activity compared to conventional nanoparticle decoration [45,68,121,122]. The role of oxygen vacancy in single-atom catalysts expands to Pd for instance, where Wang et al. [77] showed, by experimental and theoretical studies, that the presence of Pd SAs, clusters, and VOs on TiO_2 has a synergistic effect on improving the photocatalytic reaction. The authors explain the role of Pd SAs by facilitating the generation and stabilization of oxygen vacancies by the formation of the Pd–O– Ti^{3+} interface, at the same time Pd clusters are responsible for charge carrier separation and act as the optimum active sites for H_2 generation, while surface oxygen vacancies are the preferable sites for adsorption and activation/dissociation of reactant molecules. It has also been reported that oxygen vacancies on the surface of TiO_2 nanosheets act as traps for Pd single-atoms as cocatalysts for photocatalytic H_2 generation [71]. More interestingly, the photocatalytic performance of Pd single-atoms outperforms that of the Pt single-atoms, and according to the DFT calculations, this performance was ascribed to the charge localization on the noble metal single-atoms implanted in the TiO_2 surface [71].

Table 1 shows an overview of the photocatalytic H_2 evolution rate for various SA co-catalysts on TiO_2 support materials discussed above, taking also into consideration the morphology of the support material, the SA loading, light source, and reaction system used. From these data, it is evident that a clear-cut comparison between the different noble

metal single-atom decorations is not feasible, as either there is a significant difference in the noble metal loading amount, the light source used, the difference in the morphology of the support material and the amount of sacrificial agent used in the reaction system.

Table 1. Overview of the photocatalytic H₂ evolution rate for SA decorated TiO₂ nanostructures from literature, including the photocatalytic system (SA metal, SA loading, light source, and reactions system).

Type of SA	Type of Support	SA Loading	Light Source	H ₂ Evolution Rate	Reaction System	Reference
Pt	{001} TiO ₂ nanosheet	0.47 at%	325 nm	3.2 mL·h ⁻¹ ·cm ⁻²	50 vol% methanol-water	[45]
Pt	MIL-125(Ti _v)(nanoparticle)	-	300 W Xe lamp	14 mmol·h ⁻¹ ·g ⁻¹	20 vol% methanol-water	[61]
Pd	{001} TiO ₂ nanosheet	0.35 at. %	365 nm	500 µL·h ⁻¹	50 vol% methanol-water	[71]
Au	{001} TiO ₂ nanosheet	0.35 at. %	365 nm	50 µL·h ⁻¹	50 vol% methanol-water	[71]
Pt	{001} TiO ₂ nanosheet	0.35 at. %	365 nm	200 µL·h ⁻¹	50 vol% methanol-water	[71]
Pd	{001} TiO ₂ nanosheet	0.39 wt%	Xe lamp	600 µmol·h ⁻¹ ·g ⁻¹	N,N-dimethylformamide (DMF) 50, 0.5 mL deionized water and 0.5 mL benzylamine	[77]
Pt/Au	{001} TiO ₂ nanosheet	0.33 wt%	300 W Xe lamp	60 mmol·h ⁻¹ ·g ⁻¹	10 vol% methanol-water	[94]
Pt/Au	{101} TiO ₂ nanosheet	0.31 wt%	300 W Xe lamp	15 mmol·h ⁻¹ ·g ⁻¹	10 vol% methanol-water	[94]
Cu	MIL-125(Ti _v)(nanoparticle)	1.5 wt%	simulated solar light irradiation	101.7 mmol·g ⁻¹ ·h ⁻¹	H ₂ O/methanol with a ratio of = 1:2	[116]
Cu	TiO ₂ hollow nanoparticles	0.75 wt%	Xe lamp	17 mmol·h ⁻¹ ·g ⁻¹	water and methanol (volume ratio of 3:1)	[117]
Pt/Co	{001} TiO ₂ nanosheet	Pt 0.16/Co 0.18 wt%	300 W Xe lamp	45 mmol·h ⁻¹ ·g ⁻¹	10 vol% methanol-water	[119]
Co	TiO ₂ nanosheets	1.11 wt%	300 W Xe lamp	8 mmol·h ⁻¹ ·g ⁻¹	1M NaOH solution with 20% methanol	[120]
Pt	TiO ₂ nanobelts	1 wt%	simulated solar light (AM 1.5G)	90 mmol·mg ⁻¹	50 vol% methanol-water	[112]

Using first principle calculations, Yang et al. [123] shed light on the diversity and complexity of the confinement effect of transition metal SA in oxides for H₂ evolution. They introduce two stable forms of Co single-atom on the (101)TiO₂ surface which are interstices and Co₁-substituted TiO₂. They prove that the former exhibits better H₂ generation activity whereas the latter demonstrates increased hydrogen spillover effect in the H₂ atmosphere, producing surface O vacancies and Ti³⁺.

Calculating the free energy changes of hydrogen adsorption in a single-atom Ni/TiO₂ system using density functional theory, Bi et al. [124] reveal that the hydrogen generation reactions most probably take place on SA Ni and its surrounding O atoms. They also prove that hydrogen activity in this system is comparable to that of Pt as the best-known catalyst for H₂ evolution, and using DFT calculation, identified the active sites on the Ni single atom/TiO₂(101) surface at different H coverages.

5. Conclusions and Future Outlook

Overcoming the kinetic barrier of photocatalytic water splitting half reactions, which are an H₂ evolution reaction and oxygen evolution reaction, is the main challenge for converting solar light to hydrogen. The key to enhance the efficiency of the photocatalytic water splitting reaction is to increase the number and intrinsic activity of the active sites. Remarkably, reducing the size of the photocatalysts simultaneously improves the above-mentioned factors.

In this regard, research on single-atom catalysts has become a frontier in photocatalytic water splitting in the past few years and this is the direct result of the atomistic scale of the single-atoms which leads to a higher active surface area, lower loading amount compared to classical co-catalysts (thus more cost-effective), quantum size effects, facilitated charge transfer and new reaction pathways. The advances achieved in both theoretical modeling and atomic-resolution characterization techniques play key roles in the development of single-atom catalysts. For example, the atomic resolution characterization techniques used for the typical nanoparticulate co-catalysts were further developed and tailored to the detection and proper evaluation of the small size of the single atoms. Currently, there is no one characterization technique from which all physico-chemical data of the single-atom loading and their interaction with the surrounding environment can be obtained. There is, however, a mix of techniques which can bring a clear and detailed overview of these properties, and this includes: (i) transmission electron microscopy (HAADF-TEM)—size, distribution, and local structural information of the single metal atoms, combined with additional elemental mapping; (ii) X-ray absorption near edge structure (XANES) and extended X-Ray absorption fine structure (EXAFS)—electronic and structural properties of the absorbed single-atom and their coordination; (iii) X-ray photoelectron spectroscopy (XPS)—coordination state and loading amount of the single-atoms; (iv) or other additional methods such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), scanning tunneling microscopy (STM).

Modification of TiO_2 , as one of the most studied materials in photocatalysis, with single atoms as cocatalysts for photocatalytic water splitting has become an emerging field of study. The major challenges in single-atom catalysis are connected to the fact that the single-atom loading on the current photocatalysts is very low (<2 wt.%) and to the stability of the SAs, due to their high surface energy. Thus, the focus of research in this area is to enhance the stability and loading of single-atoms on the support material while avoiding the formation of/aggregation to nanoparticles, i.e., obtaining a high coverage of single-atoms on the substrate. In this respect, the interaction of single atoms with the support material has a substantial influence on the stability, loading, and overall photocatalytic activity of the developed SA/ TiO_2 photocatalytic system. For example, the in situ self-healing effect of Cu species on TiO_2 during the photocatalytic reaction resulted in a quantum efficiency of 56% under 365 nm irradiation [116]. Remarkably, the use of bi-metallic single-atoms on a suitable support proves to be an efficient approach in designing a highly efficient photocatalyst. In general, controlling the fabrication of single atoms and operando atomic scale characterizations are the keys to achieving a better understanding of the reactions occurring on single-atoms. Therefore, rapid development in single-atom catalysts for photocatalytic water splitting and, in general, other catalytic applications, is foreseeable.

Author Contributions: Writing original draft, review and editing, S.H.; Review and funding acquisition, M.S.K.; Supervision, writing original draft, review and editing, A.M.; Supervision, writing original draft, review and editing, S.M. This manuscript was written by the contributions of all authors. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by DFG researcher group FOR 1878 and KI 2169/2-1.

Acknowledgments: The authors acknowledge the DFG researcher group FOR 1878 and KI 2169/2-1 for funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fujishima, A.; Honda, K. TiO_2 photoelectrochemistry and photocatalysis. *Nature* **1972**, *213*, 8656.
2. Armaroli, N.; Balzani, V. The Hydrogen Issue. *ChemSusChem* **2011**, *4*, 21–36. [[CrossRef](#)] [[PubMed](#)]
3. Takanabe, K. Photocatalytic Water Splitting: Quantitative Approaches toward Photocatalyst by Design. *ACS Catal.* **2017**, *7*, 8006–8022. [[CrossRef](#)]
4. Osterloh, F.E. Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. *Chem. Soc. Rev.* **2013**, *42*, 2294–2320. [[CrossRef](#)]

5. Maeda, K.; Domen, K. New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. *J. Phys. Chem. C* **2007**, *111*, 7851–7861. [\[CrossRef\]](#)
6. Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38*, 253–278. [\[CrossRef\]](#)
7. Maeda, K.; Domen, K. Photocatalytic Water Splitting: Recent Progress and Future Challenges. *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661. [\[CrossRef\]](#)
8. Sivula, K.; van de Krol, R. Semiconducting materials for photoelectrochemical energy conversion. *Nat. Rev. Mater.* **2016**, *1*, 15010. [\[CrossRef\]](#)
9. Ng, K.H.; Lai, S.Y.; Cheng, C.K.; Cheng, Y.W.; Chong, C.C. Photocatalytic water splitting for solving energy crisis: Myth, Fact or Busted? *Chem. Eng. J.* **2021**, *417*, 128847. [\[CrossRef\]](#)
10. Gopinath, C.S.; Nalajala, N. A scalable and thin film approach for solar hydrogen generation: A review on enhanced photocatalytic water splitting. *J. Mater. Chem. A* **2021**, *9*, 1353–1371. [\[CrossRef\]](#)
11. Lee, K.; Mazare, A.; Schmuki, P. One-dimensional titanium dioxide nanomaterials: Nanotubes. *Chem. Rev.* **2014**, *114*, 9385–9454. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Lan, Y.; Lu, Y.; Ren, Z. Mini review on photocatalysis of titanium dioxide nanoparticles and their solar applications. *Nano Energy* **2013**, *2*, 1031–1045. [\[CrossRef\]](#)
13. Chen, H.; Nanayakkara, C.E.; Grassian, V.H. Titanium dioxide photocatalysis in atmospheric chemistry. *Chem. Rev.* **2012**, *112*, 5919–5948. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Prashant, V. Kamat TiO₂ Nanostructures: Recent Physical Chemistry Advances. *J. Phys. Chem. C* **2012**, *116*, 11849–11851. [\[CrossRef\]](#)
15. Bamwenda, G.R.; Tsubota, S.; Nakamura, T.; Haruta, M. Photoassisted hydrogen production from a water-ethanol solution: A comparison of activities of Au/TiO₂ and Pt/TiO₂. *J. Photochem. Photobiol. A Chem.* **1995**, *89*, 177–189. [\[CrossRef\]](#)
16. Lee, S.G.; Lee, S.; Lee, H.-I. Photocatalytic production of hydrogen from aqueous solution containing CN[−] as a hole scavenger. *Appl. Catal. A Gen.* **2001**, *207*, 173–181. [\[CrossRef\]](#)
17. Gurunathan, K.; Maruthamuthu, P.; Sastri, M.V.C. Photocatalytic hydrogen production by dye-sensitized Pt/SnO₂ and Pt/SnO₂/RuO₂ in aqueous methyl viologen solution. *Int. J. Hydrogen Energy* **1997**, *22*, 57–62. [\[CrossRef\]](#)
18. Abe, R.; Sayama, K.; Domen, K.; Arakawa, H. A new type of water splitting system composed of two different TiO₂ photocatalysts (anatase, rutile) and a IO₃[−]/I[−] shuttle redox mediator. *Chem. Phys. Lett.* **2001**, *344*, 339–344. [\[CrossRef\]](#)
19. Arakawa, H.; Sayama, K. Solar hydrogen production. Significant effect of Na₂CO₃ addition on water splitting using simple oxide semiconductor photocatalysts. *Catal. Surv. Jpn.* **2000**, *4*, 75–80. [\[CrossRef\]](#)
20. Sayama, K.; Yase, K.; Arakawa, H.; Asakura, K.; Tanaka, A.; Domen, K.; Onishi, T. Photocatalytic activity and reaction mechanism of Pt-intercalated K₄Nb₆O₁₇ catalyst on the water splitting in carbonate salt aqueous solution. *J. Photochem. Photobiol. A Chem.* **1998**, *114*, 125–135. [\[CrossRef\]](#)
21. Basavarajappa, P.S.; Patil, S.B.; Ganganagappa, N.; Reddy, K.R.; Raghu, A.V.; Reddy, C.V. Recent progress in metal-doped TiO₂, non-metal doped/codoped TiO₂ and TiO₂ nanostructured hybrids for enhanced photocatalysis. *Int. J. Hydrogen Energy* **2020**, *45*, 7764–7778. [\[CrossRef\]](#)
22. Hejazi, S.; Pour-Ali, S.; Killian, M.S.; Mohajernia, S. One-dimensional suboxide TiO₂ nanotubes for electrochemical applications. *Electrochem. Commun.* **2022**, *136*, 107246. [\[CrossRef\]](#)
23. Naldoni, A.; Altomare, M.; Zoppellaro, G.; Liu, N.; Kment, Š.; Zbořil, R.; Schmuki, P. Photocatalysis with Reduced TiO₂: From Black TiO₂ to Cocatalyst-Free Hydrogen Production. *ACS Catal.* **2019**, *9*, 345–364. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Bumajdad, A.; Madkour, M. Understanding the superior photocatalytic activity of noble metals modified titania under UV and visible light irradiation. *Phys. Chem. Chem. Phys.* **2014**, *16*, 7146–7158. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Trasatti, S. Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *39*, 163–184. [\[CrossRef\]](#)
26. Van Hardeveld, R.; Hartog, F. The statistics of surface atoms and surface sites on metal crystals. *Surf. Sci.* **1969**, *15*, 189–230. [\[CrossRef\]](#)
27. Lopez, N.; Janssens, T.V.W.; Clausen, B.S.; Xu, Y.; Mavrikakis, M.; Bligaard, T.; Nørskov, J.K. On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation. *J. Catal.* **2004**, *223*, 232–235. [\[CrossRef\]](#)
28. Liu, L.; Corma, A. Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles. *Chem. Rev.* **2018**, *118*, 4981–5079. [\[CrossRef\]](#)
29. Valden, M.; Lai, X.; Goodman, D.W. Onset of Catalytic Activity of Gold Clusters on Titania with the Appearance of Nonmetallic Properties. *Science* **1998**, *281*, 1647–1650. [\[CrossRef\]](#)
30. Campbell, C.T. Electronic perturbations. *Nat. Chem.* **2012**, *4*, 597–598. [\[CrossRef\]](#)
31. Wang, A.; Li, J.; Zhang, T. Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* **2018**, *2*, 65–81. [\[CrossRef\]](#)
32. Weon, S.; Huang, D.; Rigby, K.; Chu, C.; Wu, X.; Kim, J.-H. Environmental Materials beyond and below the Nanoscale: Single-Atom Catalysts. *ACS EST Eng.* **2021**, *1*, 157–172. [\[CrossRef\]](#)
33. Liu, J. Catalysis by Supported Single Metal Atoms. *ACS Catal.* **2017**, *7*, 34–59. [\[CrossRef\]](#)
34. Wang, J.; Li, Z.; Wu, Y.; Li, Y. Fabrication of Single-Atom Catalysts with Precise Structure and High Metal Loading. *Adv. Mater.* **2018**, *30*, 1801649. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Vajda, S.; White, M.G. Catalysis Applications of Size-Selected Cluster Deposition. *ACS Catal.* **2015**, *5*, 7152–7176. [\[CrossRef\]](#)

36. Zhang, L.; Banis, M.N.; Sun, X. Single-atom catalysts by the atomic layer deposition technique. *Natl. Sci. Rev.* **2018**, *5*, 628–630. [\[CrossRef\]](#)
37. Kaden, W.E.; Wu, T.; Kunkel, W.A.; Anderson, S.L. Electronic Structure Controls Reactivity of Size-Selected Pd Clusters Adsorbed on TiO₂ Surfaces. *Science* **2009**, *326*, 826–830. [\[CrossRef\]](#)
38. Van Bui, H.; Grillo, F.; van Ommen, J.R. Atomic and molecular layer deposition: Off the beaten track. *Chem. Commun.* **2017**, *53*, 45–71. [\[CrossRef\]](#)
39. Miikkulainen, V.; Leskelä, M.; Ritala, M.; Puurunen, R.L. Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends. *J. Appl. Phys.* **2013**, *113*, 21301. [\[CrossRef\]](#)
40. Wang, H.; Wang, C.; Yan, H.; Yi, H.; Lu, J. Precisely-controlled synthesis of Au@Pd core-shell bimetallic catalyst via atomic layer deposition for selective oxidation of benzyl alcohol. *J. Catal.* **2015**, *324*, 59–68. [\[CrossRef\]](#)
41. Lu, J.; Stair, P.C. Low-Temperature ABC-Type Atomic Layer Deposition: Synthesis of Highly Uniform Ultrafine Supported Metal Nanoparticles. *Angew. Chem. Int. Ed.* **2010**, *49*, 2547–2551. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Fonseca, J.; Lu, J. Single-Atom Catalysts Designed and Prepared by the Atomic Layer Deposition Technique. *ACS Catal.* **2021**, *11*, 7018–7059. [\[CrossRef\]](#)
43. Li, Z.; Wang, D.; Wu, Y.; Li, Y. Recent advances in the precise control of isolated single-site catalysts by chemical methods. *Natl. Sci. Rev.* **2018**, *5*, 673–689. [\[CrossRef\]](#)
44. Chen, Y.; Ma, Z.; Tang, X. Single-Atom Heterogeneous Catalysts. In *Heterogeneous Catalysts: Advanced Design, Characterization and Applications, II*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2021; pp. 103–117. [\[CrossRef\]](#)
45. Hejazi, S.; Mohajernia, S.; Osuagwu, B.; Zoppellaro, G.; Andryskova, P.; Tomanec, O.; Kment, S.; Zbořil, R.; Schmuki, P. On the controlled loading of single platinum atoms as a Co-catalyst on TiO₂ anatase for optimized photocatalytic H₂ generation. *Adv. Mater.* **2020**, *32*, 1908505. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Moses-DeBusk, M.; Yoon, M.; Allard, L.F.; Mullins, D.R.; Wu, Z.; Yang, X.; Veith, G.; Stocks, G.M.; Narula, C.K. CO Oxidation on Supported Single Pt Atoms: Experimental and ab Initio Density Functional Studies of CO Interaction with Pt Atom on θ -Al₂O₃(010) Surface. *J. Am. Chem. Soc.* **2013**, *135*, 12634–12645. [\[CrossRef\]](#)
47. Speck, F.D.; Kim, J.H.; Bae, G.; Joo, S.H.; Mayrhofer, K.J.J.; Choi, C.H.; Cherevko, S. Single-Atom Catalysts: A Perspective toward Application in Electrochemical Energy Conversion. *JACS Au* **2021**, *1*, 1086–1100. [\[CrossRef\]](#)
48. Wang, L.; Li, H.; Zhang, W.; Zhao, X.; Qiu, J.; Li, A.; Zheng, X.; Hu, Z.; Si, R.; Zeng, J. Supported Rhodium Catalysts for Ammonia-Borane Hydrolysis: Dependence of the Catalytic Activity on the Highest Occupied State of the Single Rhodium Atoms. *Angew. Chem. Int. Ed.* **2017**, *56*, 4712–4718. [\[CrossRef\]](#)
49. Liu, P.; Zhao, Y.; Qin, R.; Mo, S.; Chen, G.; Gu, L.; Chevrier, D.M.; Zhang, P.; Guo, Q.; Zang, D.; et al. Photochemical route for synthesizing atomically dispersed palladium catalysts. *Science* **2016**, *352*, 797–800. [\[CrossRef\]](#)
50. Ouyang, R.; Liu, J.-X.; Li, W.-X. Atomistic Theory of Ostwald Ripening and Disintegration of Supported Metal Particles under Reaction Conditions. *J. Am. Chem. Soc.* **2013**, *135*, 1760–1771. [\[CrossRef\]](#)
51. Wei, S.; Li, A.; Liu, J.-C.; Li, Z.; Chen, W.; Gong, Y.; Zhang, Q.; Cheong, W.-C.; Wang, Y.; Zheng, L.; et al. Direct observation of noble metal nanoparticles transforming to thermally stable single atoms. *Nat. Nanotechnol.* **2018**, *13*, 856–861. [\[CrossRef\]](#)
52. Huang, Z.; Gu, X.; Cao, Q.; Hu, P.; Hao, J.; Li, J.; Tang, X. Catalytically Active Single-Atom Sites Fabricated from Silver Particles. *Angew. Chem. Int. Ed.* **2012**, *51*, 4198–4203. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Yang, J.C.; Small, M.W.; Grieshaber, R.V.; Nuzzo, R.G. Recent developments and applications of electron microscopy to heterogeneous catalysis. *Chem. Soc. Rev.* **2012**, *41*, 8179. [\[CrossRef\]](#)
54. Wiesendanger, R. Single-atom magnetometry. *Curr. Opin. Solid State Mater. Sci.* **2011**, *15*, 1–7. [\[CrossRef\]](#)
55. Cheng, N.; Zhang, L.; Doyle-Davis, K.; Sun, X. Single-Atom Catalysts: From Design to Application. *Electrochem. Energy Rev.* **2019**, *2*, 539–573. [\[CrossRef\]](#)
56. Kottwitz, M.; Li, Y.; Wang, H.; Frenkel, A.I.; Nuzzo, R.G. Single Atom Catalysts: A Review of Characterization Methods. *Chem.-Methods* **2021**, *1*, 278–294. [\[CrossRef\]](#)
57. Zhang, L.; Wang, Y.; Niu, Z.; Chen, J. Single Atoms on Graphene for Energy Storage and Conversion. *Small Methods* **2019**, *3*, 1800443. [\[CrossRef\]](#)
58. Fultz, B.; Howe, J. High-Resolution STEM and Related Imaging Techniques. In *Transmission Electron Microscopy and Diffractometry of Materials. Graduate Texts in Physics*; Springer: Berlin/Heidelberg, Germany, 2013; pp. 587–615.
59. Wang, H.; Li, K.; Cheng, Y.; Wang, Q.; Yao, Y.; Schwingenschlögl, U.; Zhang, X.; Yang, W. Interaction between single gold atom and the graphene edge: A study via aberration-corrected transmission electron microscopy. *Nanoscale* **2012**, *4*, 2920. [\[CrossRef\]](#)
60. Liu, D.; Wu, C.; Chen, S.; Ding, S.; Xie, Y.; Wang, C.; Wang, T.; Haleem, Y.A.; ur Rehman, Z.; Sang, Y.; et al. In situ trapped high-density single metal atoms within graphene: Iron-containing hybrids as representatives for efficient oxygen reduction. *Nano Res.* **2018**, *11*, 2217–2228. [\[CrossRef\]](#)
61. Zhang, C.; Sha, J.; Fei, H.; Liu, M.; Yazdi, S.; Zhang, J.; Zhong, Q.; Zou, X.; Zhao, N.; Yu, H.; et al. Single-Atomic Ruthenium Catalytic Sites on Nitrogen-Doped Graphene for Oxygen Reduction Reaction in Acidic Medium. *ACS Nano* **2017**, *11*, 6930–6941. [\[CrossRef\]](#)
62. Cao, Y.; Wang, D.; Lin, Y.; Liu, W.; Cao, L.; Liu, X.; Zhang, W.; Mou, X.; Fang, S.; Shen, X.; et al. Single Pt Atom with Highly Vacant d-Orbital for Accelerating Photocatalytic H₂ Evolution. *ACS Appl. Energy Mater.* **2018**, *1*, 6082–6088. [\[CrossRef\]](#)

63. Wang, Z.; Yang, J.; Gan, J.; Chen, W.; Zhou, F.; Zhou, X.; Yu, Z.; Zhu, J.; Duan, X.; Wu, Y. Electrochemical conversion of bulk platinum into platinum single-atom sites for the hydrogen evolution reaction. *J. Mater. Chem. A* **2020**, *8*, 10755–10760. [\[CrossRef\]](#)
64. Chen, J.; Wanyan, Y.; Zeng, J.; Fang, H.; Li, Z.; Dong, Y.; Qin, R.; Wu, C.; Liu, D.; Wang, M.; et al. Surface Engineering Protocol To Obtain an Atomically Dispersed Pt/CeO₂ Catalyst with High Activity and Stability for CO Oxidation. *ACS Sustain. Chem. Eng.* **2018**, *6*, 14054–14062. [\[CrossRef\]](#)
65. Bruix, A.; Lykhach, Y.; Matolínová, I.; Neitzel, A.; Skála, T.; Tsud, N.; Vorokhta, M.; Stetsovych, V.; Ševčíková, K.; Mysliveček, J.; et al. Maximum Noble-Metal Efficiency in Catalytic Materials: Atomically Dispersed Surface Platinum. *Angew. Chem. Int. Ed.* **2014**, *53*, 10525–10530. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Chen, L.; Qi, Z.; Peng, X.; Chen, J.-L.; Pao, C.-W.; Zhang, X.; Dun, C.; Young, M.; Prendergast, D.; Urban, J.J.; et al. Insights into the Mechanism of Methanol Steam Reforming Tandem Reaction over CeO₂ Supported Single-Site Catalysts. *J. Am. Chem. Soc.* **2021**, *143*, 12074–12081. [\[CrossRef\]](#)
67. Zhang, Z.; Zhu, Y.; Asakura, H.; Zhang, B.; Zhang, J.; Zhou, M.; Han, Y.; Tanaka, T.; Wang, A.; Zhang, T.; et al. Thermally stable single atom Pt/m-Al₂O₃ for selective hydrogenation and CO oxidation. *Nat. Commun.* **2017**, *8*, 16100. [\[CrossRef\]](#)
68. Hu, X.; Song, J.; Luo, J.; Zhang, H.; Sun, Z.; Li, C.; Zheng, S.; Liu, Q. Single-atomic Pt sites anchored on defective TiO₂ nanosheets as a superior photocatalyst for hydrogen evolution. *J. Energy Chem.* **2021**, *62*, 1–10. [\[CrossRef\]](#)
69. Wu, Z.; Hwang, I.; Cha, G.; Qin, S.; Tomanec, O.; Badura, Z.; Kment, S.; Zboril, R.; Schmuki, P. Optimized Pt Single Atom Harvesting on TiO₂ Nanotubes—Towards a Most Efficient Photocatalyst. *Small* **2022**, *18*, 2104892. [\[CrossRef\]](#)
70. Qin, S.; Denisov, N.; Will, J.; Kolařík, J.; Spiecker, E.; Schmuki, P. A Few Pt Single Atoms Are Responsible for the Overall Co-Catalytic Activity in Pt/TiO₂ Photocatalytic H₂ Generation. *Sol. RRL* **2022**, *6*, 2101026. [\[CrossRef\]](#)
71. Cha, G.; Hwang, I.; Hejazi, S.; Dobrota, A.S.; Pašti, I.A.; Osuagwu, B.; Kim, H.; Will, J.; Yokosawa, T.; Badura, Z.; et al. As a single atom Pd outperforms Pt as the most active co-catalyst for photocatalytic H₂ evolution. *iScience* **2021**, *24*, 102938. [\[CrossRef\]](#)
72. Han, B.; Guo, Y.; Huang, Y.; Xi, W.; Xu, J.; Luo, J.; Qi, H.; Ren, Y.; Liu, X.; Qiao, B.; et al. Strong Metal–Support Interactions between Pt Single Atoms and TiO₂. *Angew. Chem. Int. Ed.* **2020**, *59*, 11824–11829. [\[CrossRef\]](#)
73. Thang, H.V.; Pacchioni, G.; DeRita, L.; Christopher, P. Nature of stable single atom Pt catalysts dispersed on anatase TiO₂. *J. Catal.* **2018**, *367*, 104–114. [\[CrossRef\]](#)
74. Therrien, A.J.; Hensley, A.J.R.; Marcinkowski, M.D.; Zhang, R.; Lucci, F.R.; Coughlin, B.; Schilling, A.C.; McEwen, J.S.; Sykes, E.C.H. An atomic-scale view of single-site Pt catalysis for low-temperature CO oxidation. *Nat. Catal.* **2018**, *1*, 192–198. [\[CrossRef\]](#)
75. Weon, S.; Suh, M.-J.; Chu, C.; Huang, D.; Stavitski, E.; Kim, J.-H. Site-Selective Loading of Single-Atom Pt on TiO₂ for Photocatalytic Oxidation and Reductive Hydrodefluorination. *ACS EST Eng.* **2021**, *1*, 512–522. [\[CrossRef\]](#)
76. Fujiwara, K.; Pratsinis, S.E. Single Pd atoms on TiO₂ dominate photocatalytic NO_x removal. *Appl. Catal. B Environ.* **2018**, *226*, 127–134. [\[CrossRef\]](#)
77. Wang, T.; Tao, X.; Li, X.; Zhang, K.; Liu, S.; Li, B. Synergistic Pd Single Atoms, Clusters, and Oxygen Vacancies on TiO₂ for Photocatalytic Hydrogen Evolution Coupled with Selective Organic Oxidation. *Small* **2021**, *17*, 2006255. [\[CrossRef\]](#)
78. Ge, X.; Zhou, P.; Zhang, Q.; Xia, Z.; Chen, S.; Gao, P.; Zhang, Z.; Gu, L.; Guo, S. Palladium Single Atoms on TiO₂ as a Photocatalytic Sensing Platform for Analyzing the Organophosphorus Pesticide Chlorpyrifos. *Angew. Chem. Int. Ed.* **2020**, *59*, 232–236. [\[CrossRef\]](#)
79. Kuai, L.; Chen, Z.; Liu, S.; Kan, E.; Yu, N.; Ren, Y.; Fang, C.; Li, X.; Li, Y.; Geng, B. Titania supported synergistic palladium single atoms and nanoparticles for room temperature ketone and aldehydes hydrogenation. *Nat. Commun.* **2020**, *11*, 48. [\[CrossRef\]](#)
80. Guo, Y.; Huang, Y.; Zeng, B.; Han, B.; Akri, M.; Shi, M.; Zhao, Y.; Li, Q.; Su, Y.; Li, L.; et al. Photo-thermo semi-hydrogenation of acetylene on Pd₁/TiO₂ single-atom catalyst. *Nat. Commun.* **2022**, *13*, 2648. [\[CrossRef\]](#)
81. Lv, T.; Xiao, B.; Xia, F.; Chen, M.; Zhao, J.; Ma, Y.; Wu, J.; Zhang, J.; Zhang, Y.; Liu, Q. Insights into synergistic effect of Pd single atoms and sub-nanoclusters on TiO₂ for enhanced photocatalytic H₂ evolution. *Chem. Eng. J.* **2022**, *450*, 137873. [\[CrossRef\]](#)
82. Wan, J.; Chen, W.; Jia, C.; Zheng, L.; Dong, J.; Zheng, X.; Wang, Y.; Yan, W.; Chen, C.; Peng, Q.; et al. Defect Effects on TiO₂ Nanosheets: Stabilizing Single Atomic Site Au and Promoting Catalytic Properties. *Adv. Mater.* **2018**, *30*, 1705369. [\[CrossRef\]](#)
83. Wang, X.; Pan, H.; Sun, M.; Zhang, Y. Au single atom-anchored WO₃/TiO₂ nanotubes for the photocatalytic degradation of volatile organic compounds. *J. Mater. Chem. A* **2022**, *10*, 6078–6085. [\[CrossRef\]](#)
84. Zhou, X.; Hwang, I.; Tomanec, O.; Fehn, D.; Mazare, A.; Zboril, R.; Meyer, K.; Schmuki, P. Advanced Photocatalysts: Pinning Single Atom Co-Catalysts on Titania Nanotubes. *Adv. Funct. Mater.* **2021**, *31*, 2102843. [\[CrossRef\]](#)
85. Wang, Y.; Xu, W.; Chen, X.; Li, C.; Xie, J.; Yang, Y.; Zhu, T.; Zhang, C. Single-atom Ir₁ supported on rutile TiO₂ for excellent selective catalytic oxidation of ammonia. *J. Hazard. Mater.* **2022**, *432*, 128670. [\[CrossRef\]](#)
86. Tang, Y.; Asokan, C.; Xu, M.; Graham, G.W.; Pan, X.; Christopher, P.; Li, J.; Sautet, P. Rh single atoms on TiO₂ dynamically respond to reaction conditions by adapting their site. *Nat. Commun.* **2019**, *10*, 4488. [\[CrossRef\]](#) [\[PubMed\]](#)
87. Tieu, P.; Yan, X.; Xu, M.; Christopher, P.; Pan, X. Directly Probing the Local Coordination, Charge State, and Stability of Single Atom Catalysts by Advanced Electron Microscopy: A Review. *Small* **2021**, *17*, 2006482. [\[CrossRef\]](#) [\[PubMed\]](#)
88. Van der Linden, M.; van Bunningen, A.J.; Amidani, L.; Bransen, M.; Elnaggar, H.; Glatzel, P.; Meijerink, A.; de Groot, F.M.F. Single Au Atom Doping of Silver Nanoclusters. *ACS Nano* **2018**, *12*, 12751–12760. [\[CrossRef\]](#) [\[PubMed\]](#)
89. Tyo, E.C.; Vajda, S. Catalysis by clusters with precise numbers of atoms. *Nat. Nanotechnol.* **2015**, *10*, 577–588. [\[CrossRef\]](#)

90. Li, J.; Guan, Q.; Wu, H.; Liu, W.; Lin, Y.; Sun, Z.; Ye, X.; Zheng, X.; Pan, H.; Zhu, J.; et al. Highly Active and Stable Metal Single-Atom Catalysts Achieved by Strong Electronic Metal-Support Interactions. *J. Am. Chem. Soc.* **2019**, *141*, 14515–14519. [\[CrossRef\]](#)
91. Sun, S.; Zhang, G.; Gauquelin, N.; Chen, N.; Zhou, J.; Yang, S.; Chen, W.; Meng, X.; Geng, D.; Banis, M.N.; et al. Single-atom catalysis using Pt/graphene achieved through atomic layer deposition. *Sci. Rep.* **2013**, *3*, 1775. [\[CrossRef\]](#)
92. Qiao, B.; Wang, A.; Yang, X.; Allard, L.F.; Jiang, Z.; Cui, Y.; Liu, J.; Li, J.; Zhang, T. Single-atom catalysis of CO oxidation using Pt₁/FeO_x. *Nat. Chem.* **2011**, *3*, 634–641. [\[CrossRef\]](#)
93. Qin, S.; Denisov, N.; Sarma, B.B.; Hwang, I.; Doronkin, D.E.; Tomanec, O.; Kment, S.; Schmuki, P. Pt Single Atoms on TiO₂ Polymorphs—Minimum Loading with a Maximized Photocatalytic Efficiency. *Adv. Mater. Interfaces* **2022**, *9*, 2200808. [\[CrossRef\]](#)
94. Wei, T.; Ding, P.; Wang, T.; Liu, L.-M.; An, X.; Yu, X. Facet-Regulating Local Coordination of Dual-Atom Cocatalyzed TiO₂ for Photocatalytic Water Splitting. *ACS Catal.* **2021**, *11*, 14669–14676. [\[CrossRef\]](#)
95. Zhang, H.; Wei, J.; Dong, J.; Liu, G.; Shi, L.; An, P.; Zhao, G.; Kong, J.; Wang, X.; Meng, X.; et al. Efficient Visible-Light-Driven Carbon Dioxide Reduction by a Single-Atom Implanted Metal-Organic Framework. *Angew. Chem. Int. Ed.* **2016**, *128*, 14522–14526. [\[CrossRef\]](#)
96. Yin, P.; Yao, T.; Wu, Y.; Zheng, L.; Lin, Y.; Liu, W.; Ju, H.; Zhu, J.; Hong, X.; Deng, Z.; et al. Single Cobalt Atoms with Precise N-Coordination as Superior Oxygen Reduction Reaction Catalysts. *Angew. Chem. Int. Ed.* **2016**, *55*, 10800–10805. [\[CrossRef\]](#)
97. Choi, C.H.; Kim, M.; Kwon, H.C.; Cho, S.J.; Yun, S.; Kim, H.-T.; Mayrhofer, K.J.J.; Kim, H.; Choi, M. Tuning selectivity of electrochemical reactions by atomically dispersed platinum catalyst. *Nat. Commun.* **2016**, *7*, 10922. [\[CrossRef\]](#) [\[PubMed\]](#)
98. Qi, P.; Wang, J.; Djitcheu, X.; He, D.; Liu, H.; Zhang, Q. Techniques for the characterization of single atom catalysts. *RSC Adv.* **2022**, *12*, 1216–1227. [\[CrossRef\]](#) [\[PubMed\]](#)
99. Simonovis, J.P.; Hunt, A.; Waluyo, I. In situ ambient pressure XPS study of Pt/Cu(111) single-atom alloy in catalytically relevant reaction conditions. *J. Phys. D Appl. Phys.* **2021**, *54*, 194004. [\[CrossRef\]](#)
100. Daelman, N.; Capdevila-Cortada, M.; López, N. Dynamic charge and oxidation state of Pt/CeO₂ single-atom catalysts. *Nat. Mater.* **2019**, *18*, 1215–1221. [\[CrossRef\]](#)
101. Lang, R.; Xi, W.; Liu, J.-C.; Cui, Y.-T.; Li, T.; Lee, A.F.; Chen, F.; Chen, Y.; Li, L.; Li, L.; et al. Non defect-stabilized thermally stable single-atom catalyst. *Nat. Commun.* **2019**, *10*, 234. [\[CrossRef\]](#)
102. Huang, D.; de Vera, G.A.; Chu, C.; Zhu, Q.; Stavitski, E.; Mao, J.; Xin, H.; Spies, J.A.; Schmuttenmaer, C.A.; Niu, J.; et al. Single-Atom Pt Catalyst for Effective C–F Bond Activation via Hydrodefluorination. *ACS Catal.* **2018**, *8*, 9353–9358. [\[CrossRef\]](#)
103. Tran, N.-D.; Farnesi Camellone, M.; Fabris, S. Probing the Reactivity of Pt/Ceria Nanocatalysts toward Methanol Oxidation: From Ionic Single-Atom Sites to Metallic Nanoparticles. *J. Phys. Chem. C* **2018**, *122*, 17917–17927. [\[CrossRef\]](#)
104. Cha, G.; Mazare, A.; Hwang, I.; Denisov, N.; Will, J.; Yokosawa, T.; Badura, Z.; Zoppellaro, G.; Tesler, A.B.; Spiecker, E.; et al. A facile “dark”-deposition approach for Pt single-atom trapping on faceted anatase TiO₂ nanoflakes and use in photocatalytic H₂ generation. *Electrochim. Acta* **2022**, *412*, 140129. [\[CrossRef\]](#)
105. Kottwitz, M.; Li, Y.; Palomino, R.M.; Liu, Z.; Wang, G.; Wu, Q.; Huang, J.; Timoshenko, J.; Senanayake, S.D.; Balasubramanian, M.; et al. Local Structure and Electronic State of Atomically Dispersed Pt Supported on Nanosized CeO₂. *ACS Catal.* **2019**, *9*, 8738–8748. [\[CrossRef\]](#)
106. Ghosh, T.K.; Nair, N.N. Rh₁/γ-Al₂O₃ single-atom catalysis of O₂ activation and CO oxidation: Mechanism, effects of hydration, oxidation state, and cluster size. *ChemCatChem* **2013**, *5*, 1811–1821. [\[CrossRef\]](#)
107. Sun, Y.; Wang, Y.; Pan, J.S.; Wang, L.; Sun, C.Q. Elucidating the 4f Binding Energy of an Isolated Pt Atom and Its Bulk Shift from the Measured Surface- and Size-Induced Pt 4f Core Level Shift. *J. Phys. Chem. C* **2009**, *113*, 14696–14701. [\[CrossRef\]](#)
108. Greczynski, G.; Hultman, L. Reliable determination of chemical state in X-ray photoelectron spectroscopy based on sample-work-function referencing to adventitious carbon: Resolving the myth of apparent constant binding energy of the C 1s peak. *Appl. Surf. Sci.* **2018**, *451*, 99–103. [\[CrossRef\]](#)
109. Greczynski, G.; Hultman, L. The same chemical state of carbon gives rise to two peaks in X-ray photoelectron spectroscopy. *Sci. Rep.* **2021**, *11*, 11195. [\[CrossRef\]](#) [\[PubMed\]](#)
110. Biesinger, M.C. Accessing the robustness of adventitious carbon for charge referencing (correction) purposes in XPS analysis: Insights from a multi-user facility data review. *Appl. Surf. Sci.* **2022**, *597*, 153681. [\[CrossRef\]](#)
111. Zhang, D.; Li, Y.Y.; Li, Y.Y.; Zhan, S. Towards single-atom photocatalysts for future carbon-neutral application. *SmartMat* **2022**, 1–30. [\[CrossRef\]](#)
112. Barroso, M.; Cowan, A.J.; Pendlebury, S.R.; Grätzel, M.; Klug, D.R.; Durrant, J.R. The Role of Cobalt Phosphate in Enhancing the Photocatalytic Activity of α-Fe₂O₃ toward Water Oxidation. *J. Am. Chem. Soc.* **2011**, *133*, 14868–14871. [\[CrossRef\]](#)
113. Wang, G.; He, C.-T.; Huang, R.; Mao, J.; Wang, D.; Li, Y. Photoinduction of Cu Single Atoms Decorated on UiO-66-NH₂ for Enhanced Photocatalytic Reduction of CO₂ to Liquid Fuels. *J. Am. Chem. Soc.* **2020**, *142*, 19339–19345. [\[CrossRef\]](#) [\[PubMed\]](#)
114. Xiao, M.; Zhang, L.; Luo, B.; Lyu, M.; Wang, Z.; Huang, H.; Wang, S.; Du, A.; Wang, L. Molten-Salt-Mediated Synthesis of an Atomic Nickel Co-catalyst on TiO₂ for Improved Photocatalytic H₂ Evolution. *Angew. Chem. Int. Ed.* **2020**, *59*, 7230–7234. [\[CrossRef\]](#) [\[PubMed\]](#)
115. Xie, J.; Jin, R.; Li, A.; Bi, Y.; Ruan, Q.; Deng, Y.; Zhang, Y.; Yao, S.; Sankar, G.; Ma, D.; et al. Highly selective oxidation of methane to methanol at ambient conditions by titanium dioxide-supported iron species. *Nat. Catal.* **2018**, *1*, 889–896. [\[CrossRef\]](#)

-
116. Zhang, Y.; Zhao, J.; Wang, H.; Xiao, B.; Zhang, W.; Zhao, X.; Lv, T.; Thangamuthu, M.; Zhang, J.; Guo, Y.; et al. Single-atom Cu anchored catalysts for photocatalytic renewable H₂ production with a quantum efficiency of 56%. *Nat. Commun.* **2022**, *13*, 58. [[CrossRef](#)]
 117. Lee, B.-H.; Park, S.; Kim, M.; Sinha, A.K.; Lee, S.C.; Jung, E.; Chang, W.J.; Lee, K.-S.; Kim, J.H.; Cho, S.-P.; et al. Reversible and cooperative photoactivation of single-atom Cu/TiO₂ photocatalysts. *Nat. Mater.* **2019**, *18*, 620–626. [[CrossRef](#)]
 118. Cheng, C.; Fang, W.-H.; Long, R.; Prezhdo, O.V. Water Splitting with a Single-Atom Cu/TiO₂ Photocatalyst: Atomistic Origin of High Efficiency and Proposed Enhancement by Spin Selection. *JACS Au* **2021**, *1*, 550–559. [[CrossRef](#)]
 119. Wang, C.; Wang, K.; Feng, Y.; Li, C.; Zhou, X.; Gan, L.; Feng, Y.; Zhou, H.; Zhang, B.; Qu, X.; et al. Co and Pt Dual-Single-Atoms with Oxygen-Coordinated Co–O–Pt Dimer Sites for Ultrahigh Photocatalytic Hydrogen Evolution Efficiency. *Adv. Mater.* **2021**, *33*, 2003327. [[CrossRef](#)]
 120. Wu, X.; Zuo, S.; Qiu, M.; Li, Y.; Zhang, Y.; An, P.; Zhang, J.J.; Zhang, H.; Zhang, J.J. Atomically defined Co on two-dimensional TiO₂ nanosheet for photocatalytic hydrogen evolution. *Chem. Eng. J.* **2021**, *420*, 127681. [[CrossRef](#)]
 121. Cai, J.; Cao, A.; Wang, Z.; Lu, S.; Jiang, Z.; Dong, X.-Y.; Li, X.; Zang, S.-Q. Surface oxygen vacancies promoted Pt redispersion to single-atoms for enhanced photocatalytic hydrogen evolution. *J. Mater. Chem. A* **2021**, *9*, 13890–13897. [[CrossRef](#)]
 122. Wang, X.; Zhang, L.; Bu, Y.; Sun, W. Interplay between invasive single atom Pt and native oxygen vacancy in rutile TiO₂(110) surface: A theoretical study. *Nano Res.* **2022**, *15*, 669–676. [[CrossRef](#)]
 123. Yang, K.; Zhou, G. Hydrogen evolution/spillover effect of single cobalt atom on anatase TiO₂ from first-principles calculations. *Appl. Surf. Sci.* **2021**, *536*, 147831. [[CrossRef](#)]
 124. Bi, H.; Zhang, L.; Wang, Z.; Zhou, G. Identification of active sites available for hydrogen evolution of Single-Atom Ni₁/TiO₂ catalysts. *Appl. Surf. Sci.* **2022**, *579*, 152139. [[CrossRef](#)]