Single-Atom-Based Catalysts for Photocatalytic Water Splitting on TiO$_2$ Nanostructures

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Abstract: H$_2$ generation from photocatalytic water splitting is one of the most promising approaches to producing cost-effective and sustainable fuel. Nanostructured TiO$_2$ is a highly stable and efficient semiconductor photocatalyst for this purpose. The main drawback of TiO$_2$ as a photocatalyst is the sluggish charge transfer on the surface of TiO$_2$ 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 TiO$_2$/PGM systems for photocatalytic H$_2$ 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 TiO$_2$ nanostructures for photocatalytic water splitting. The latest progress in fabrication, characterization, and application of single-atoms in photocatalytic H$_2$ generation on TiO$_2$ is reviewed.

Keywords: titanium dioxide; water-splitting; H$_2$ generation; single-atom

1. Introduction

Photocatalytic water splitting is the process of H$_2$ and O$_2$ production from water under light irradiation and in the presence of a catalyst, and follows the Equations (1)–(3) listed below.

\[
2H^+ + 2e^- \rightarrow H_2 \quad (1)
\]

\[
2H_2O + 2h^+ \rightarrow \frac{1}{2} O_2 + 2H^+ \quad (2)
\]

\[
H_2O \rightarrow H_2 + \frac{1}{2} O_2 \quad (3)
\]

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/TiO$_2$ 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 H$_2$ production from water splitting or photo-reforming of H$_2$O/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.

![Diagram of the parameters affecting the overall photocatalytic water splitting.](image)

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, TiO2 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 TiO2, and the insufficient energy conversion efficiency in TiO2 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 H2 and O2 to form water, which occurs very fast; and (iii) the wide band gap of TiO2 (3.2 eV) that allows only UV light absorption for H2 production. Since only about 4% of the solar radiation energy is UV light the STH efficiency remains very low with pristine TiO2 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 electro-chemical 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].

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 (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-

Figure 2. Schematic illustration of single-atom catalysts fabrication methods. Reprinted with permission from Ref [32], Copyright © 2020 American Chemical Society.
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 TiO$_2$ (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 CeO$_2$. Namely, Chen et al. [64] confirmed the presence of atomically dispersed Pt catalysts throughout the CeO$_2$ 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 TiO$_2$ 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.
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 TiO$_2$ (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-STEM 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 CeO$_2$. Namely, Chen et al. [64] confirmed the presence of atomically dispersed Pt catalysts throughout the CeO$_2$ 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 TiO$_2$ 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.

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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 (Co$_3$O$_4$, CeO$_2$, ZrO$_2$, graphene) and comparing the data with that of Pt foil and PtO$_2$ (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 Co$_3$O$_4$ > ZrO$_2$ > CeO$_2$ > graphene [90]. The Pt SAs on the Co$_3$O$_4$ 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 TiO$_2$ nanoparticles [93] and for bi-metallic SAs of PtAu [94].
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 CoO3 > 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/CoO3 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-ordination (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 Pt6+ and Pt4+ (the peaks at 72.93 and 76.28 eV correspond to Pt6+4f7/2 and Pt6+4f5/2, whereas the peaks at 75.04 and 78.51 eV can
be attributed to Pt$^{4+}$4f$^7$/2 and Pt$^{4+}$4f$^5$/2, while for the Pt nanoparticle decoration peaks are mainly attributed to metallic Pt (4f$^7$/2 at 71.07eV) [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 Pt$_{6^+}$ 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]. Moreso, 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 facetted 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 Pt4f$^7$/2 at 73.0 (typically attributed to Pt$^{4+}$) are obtained, while for the Au4f peaks (Figure 5d) a shift of 0.2eV to more negative binding energies was observed for 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 facetted 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 284.8eV 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 TiO$_2$

Sluggish charge transfer, limited photoconversion, and fast electron-hole recombination rate are the bottlenecks of TiO$_2$ 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 TiO$_2$. 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 H$_2$ 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 TiO$_2$ 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 TiO$_2$ (MIL-125(Ti$_x$)) for photocatalytic H$_2$ 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 TiO$_2$ that trigger a reversible/self-healing and continuous photocatalytic process that effectively separates photoelectrons to reduce water to H$_2$. 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 Cud 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⁻¹ g⁻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).

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 mmol g$^{-1}$ 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.

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 \( \text{H}_2 \) evolution. They introduce two stable forms of Co single-atom on the (101)\( \text{TiO}_2 \) surface which are interstices and Co\(_1\)-substituted TiO\(_2\). They prove that the former exhibits better \( \text{H}_2 \) generation activity whereas the latter demonstrates increased hydrogen spillover effect in the \( \text{H}_2 \) atmosphere, producing surface O vacancies and Ti\(^{3+}\).

Calculating the free energy changes of hydrogen adsorption in a single-atom Ni/\( \text{TiO}_2 \) 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 \( \text{H}_2 \) evolution, and using DFT calculation, identified the active sites on the Ni single atom/\( \text{TiO}_2 \)(101) surface at different H coverages.

| Type of SA | Type of Support | SA Loading | Light Source | \( \text{H}_2 \) Evolution Rate | Reaction System | Reference |
|-----------|----------------|------------|--------------|-------------------------------|----------------|-----------|
| Pt        | [001] \( \text{TiO}_2 \) 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] \( \text{TiO}_2 \) nanosheet | 0.35 at.% | 365 nm | 500 µL h\(^{-1}\) | 50 vol% methanol-water | [71] |
| Au        | [001] \( \text{TiO}_2 \) nanosheet | 0.35 at.% | 365 nm | 50 µL h\(^{-1}\) | 50 vol% methanol-water | [71] |
| Pt        | [001] \( \text{TiO}_2 \) nanosheet | 0.35 at.% | 365 nm | 200 µL h\(^{-1}\) | 50 vol% methanol-water | [71] |
| Pd        | [001] \( \text{TiO}_2 \) 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] \( \text{TiO}_2 \) nanosheet | 0.33 wt% | 300 W Xe lamp | 60 mmol h\(^{-1}\) g\(^{-1}\) | 10 vol% methanol-water | [94] |
| Pt/Au     | [101] \( \text{TiO}_2 \) nanosheet | 0.31 wt% | 300 W Xe lamp | 15 mmol h\(^{-1}\) g\(^{-1}\) | 10 vol% methanol-water | [94] |
| Cu        | MIL-125(Ti\(_v\)) (nanoparticles) | 1.5 wt% | simulated solar light irradiation | 101.7 mmol h\(^{-1}\) g\(^{-1}\) | H\(_2\)O/methanol with a ratio of = 1:2 | [116] |
| Cu        | \( \text{TiO}_2 \) 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] \( \text{TiO}_2 \) nanosheets | Pt 0.16/Co 0.18 wt% | 300 W Xe lamp | 45 mmol h\(^{-1}\) g\(^{-1}\) | 10 vol% methanol-water | [119] |
| Co        | \( \text{TiO}_2 \) nanosheets | 1.11 wt% | 300 W Xe lamp | 8 mmol h\(^{-1}\) g\(^{-1}\) | 1M NaOH solution with 20% methanol | [120] |
| Pt        | \( \text{TiO}_2 \) 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 \( \text{H}_2 \) evolution. They introduce two stable forms of Co single-atom on the (101)\( \text{TiO}_2 \) surface which are interstices and Co\(_1\)-substituted TiO\(_2\). They prove that the former exhibits better \( \text{H}_2 \) generation activity whereas the latter demonstrates increased hydrogen spillover effect in the \( \text{H}_2 \) atmosphere, producing surface O vacancies and Ti\(^{3+}\).

Calculating the free energy changes of hydrogen adsorption in a single-atom Ni/\( \text{TiO}_2 \) 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 \( \text{H}_2 \) evolution, and using DFT calculation, identified the active sites on the Ni single atom/\( \text{TiO}_2 \)(101) surface at different H coverages.

5. Conclusions and Future Outlook

Overcoming the kinetic barrier of photocatalytic water splitting half reactions, which are an \( \text{H}_2 \) 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.

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**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. 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]
10. Lee, K.; Mazare, A.; Schmuki, P. One-dimensional titanium dioxide nanomaterials: Nanotubes. *Chem. Rev.* 2014, 114, 9385–9454. [CrossRef] [PubMed]
11. Liu, J. Catalysis by Supported Single Metal Atoms. *Adv. Mater.* 2018, 30, 1801649. [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 KₓNb₂O₇ 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.; Mohajerinia, S. One-dimensional suboxide TiO2 nanotubes for electronics applications. *Electrochem. Commun.* 2012, 13, 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. Trassati, S. Work function, electronegativity, and photochemical 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 catalyst. *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. Wäng, 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. Fonsça, J.; Lu, J. Single-Atom Catalysts Designed and Prepared by the Atomic Layer Deposition Technique. ACS Catal. 2021, 11, 7018–7059. [CrossRef]
43. Li, H.; Wu, Z.; Li, 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 evolution. 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.; 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 catalytic. 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. Wiedendanger, 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.–Mater. Methods 2021, 1, 278–294. [CrossRef]
57. Zhang, L.; Li, 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 Diffraction of Materials. Graduate Texts in Physics; Springer: Berlin/Heidelberg, Germany, 2013; pp. 587–615. [CrossRef]
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.; Halem, 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]
83. Wang, X.; Pan, H.; Sun, M.; Zhang, Y. Au single atom-anchored WO

65. Bruix, A.; Lykhach, Y.; Matol

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/CoO Catalyst with High Activity and Stability for CO Oxidation. ACS Sustain. Chem. Eng. 2018, 6, 14054–14062. [CrossRef]

63. Wang, Z.; Yang, J.; Gan, J.; Chen, W.; Zhou, F.; Zhou, X.; Yu, Z.; Zhu, J.; Duan, X.; Yu, W. Electrochemical conversion of bulk platinum into platinum single-atom sites for the hydrogen evolution reaction. J. Mater. Chem. A 2020, 8, 10755–10760. [CrossRef]

62. Thang, H.V.; Pacchioni, G.; DeRita, L.; Christopher, P. Nature of stable single atom Pt catalysts dispersed on anatase TiO2. J. Catal. 2021, 437, 160–171. [CrossRef]

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 Atom Catalysts with Precise Numbers of Atoms. Nature. 2015, 500, 264–270. [CrossRef]

61. 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. J. Phys. Chem. C 2018, 122, 20065–20073. [CrossRef]

81. Lv, T.; Xiao, B.; Xia, F.; Chen, M.; Zhao, J.; Ma, Y.; Wu, J.; Zhang, J.; Liu, Q. Insights into synergistic effect of Pd single atom and Pt single atom on TiO2 nanosheets for enhanced photocatalytic H2 evolution. ACS Sustain. Chem. Eng. 2019, 7, 16100–16109. [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.E.; Jiang, Z.; Cui, Y.; Liu, J.; Li, J.; Zhang, T. Single-atom catalysis of CO oxidation using Pt/FeOx. 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, F.; 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. 2012, 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. 2017, 54, 194004. [CrossRef]

100. Daelman, N.; Capdevila-Cortada, M.; Lopez, N. Dynamic charge and oxidation state of Pt/CoO 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, 9533–9538. [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.; Spiesser, E.; et al. A facile “dark”-deposition approach for Pt single-atom trapping on facetted 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. Rh/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 analyses: 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.; Gai, 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]