PERSPECTIVE

Check for updates

The elusive photocatalytic water splitting reaction using sunlight on suspended nanoparticles: is there a way forward?

Hicham Idriss (iD) [ab]

For many decades hydrogen production by photocatalytic methods has been pursued over a variety of semiconductors with probably over a thousand formulations of powder catalysts in many structures and compositions. Yet, with the exception of a few reports, water splitting to molecular hydrogen and oxygen has remained elusive. The only reproducible results are those involving other additives to water: electron donors or acceptors yielding either hydrogen or oxygen, but not both. The consequence of this is a system unrelated to water splitting but simply driven by the organic or inorganic redox potential. One may argue that thermodynamic limitations indicate that an inorganic semiconductor with a band gap within the spectrum of sunlight, and that is stable in water, cannot split water. Otherwise, it would not have existed on earth.

Water splitting to molecular hydrogen and oxygen using sunlight to excite suspended semiconductor particles has been pursued for decades now.[1–3] Many materials were tested and many concepts have been tried, yet only a few have given evidence that a catalytic reaction indeed occurs. The water splitting reaction is as follows:

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2 \Delta G = +237 \text{ kJ mol}^{-1}$$
$$= +2.46 \text{ eV} = +1.23 \text{ eV per electron}$$
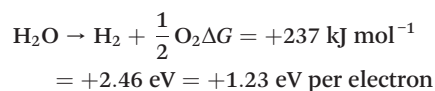
This reaction should give a H_2 to O_2 molar ratio equal to 2 with a turnover number (TON) more than one. In most papers dealing with water splitting over powder catalysts, these two simple requirements are not given and seldom met.

In the case of photocatalytic water splitting, a catalyst absorbs photon energy and consequently, electrons are transferred from its valence band to its conduction band. If its band gap is large enough, above that needed for water splitting (1.23 eV), and its band edges meet the thermodynamic requirement for the charge transfer to occur, then in principle, excited electrons can reduce hydrogen ions and holes can oxidize oxygen anions. For this reaction to occur many steps need to take place. Before addressing some of them, it is important to explain the statement about the absence of water splitting on wide band gap semiconductors. Wide band gap semiconductors in this case mean the ones that absorb light from the main part of the solar spectrum,

and these extend from $SrTiO_3$ and TiO_2 (up to 3.3 eV) to some halide perovskites (up to 1.5 eV or so). There are reports on pure water splitting for a short period at a negligible rate. Probably the most systematic study reported was by the team of Kondarides *et al.*[4] In this case the authors detected a decreasing production of molecular hydrogen (and importantly no molecular oxygen) over Pt/TiO_2 with time until the rates went to zero. The authors then measured the amount of H_2O_2 and found it to be increasing with time. From this observation, they postulated that some forms of dissociatively adsorbed H_2O_2 are present on the catalyst surface, which prevents further reactions from occurring ($2H_2O \rightarrow H_2 + H_2O_2$, although a more endothermic reaction than that to H_2 and O_2). This idea has initially been presented by Grätzel *et al.*[5] among others. It is however possible that some hydrocarbon contaminants on the surface of these semiconductor catalysts are responsible for this non-catalytic hydrogen evolution. It is also possible that the back reaction (hydrogen and oxygen recombination to water[6]) accelerated the decay of the reaction rate. The stability of a peroxo species ($_{(a)}$-O–O-$_{(a)}$, (a) stands for adsorbed) on the surface of TiO_2 is high enough to prevent further reactions (this is based on the DFT computation at the GGA level as well as using the hybrid functional HSE03 (ref. 7 and 8)). This has also been seen with RAIRS upon the adsorption of H_2O_2 over $TiO_2/Rh(111)$[9] and with IR spectroscopy over TiO_2 powder.[10] It is also the idea behind the use of some kind of catalyst to decompose these species. For example, it was proposed that "carbon quantum dots (CQDs)" when put on top of g-C_3N_4 have resulted in pure water splitting to H_2 and O_2 (with 2% solar to hydrogen efficiency (STH)). The reason

a Catalysis Department, SABIC-Corporate Research, and Development (CRD) Center at KAUST, Thuwal, Saudi Arabia. E-mail: idrissh@sabic.com
b Department of Chemistry, University College London, London, UK. E-mail: h.idriss@ucl.ac.uk

304 | *Catal. Sci. Technol.*, 2020, **10**, 304–310

This journal is © The Royal Society of Chemistry 2020

is that these QDs have the capacity to destabilize these species, although no specific studies were conducted to understand the possible fundamental reasons.[11] To date, this high STH (when compared to those of most other powder systems) has not been reproduced by others.

It has taken the community a few decades to understand that the addition of an electron donor into a system (methanol, other primary alcohols, or polyols such as ethylene glycol) results in a reforming reaction (CO_2 and H_2). It is important to emphasize that all electrons in this case originate from the electron donors and none from water.[12,13] Many published reports that mention "water splitting" are actually about the redox of the additives or probably corrosion and therefore do not deal with water splitting.[14–17] From an energetic point of view, there is little advantage in producing hydrogen from alcohols, since the energy needed for producing them may offset the benefit from their decomposition unless they are of biological origin, although in this case their contribution to the overall energy budget would be marginal. It is also important to mention that the technology of converting alcohols back to hydrogen, steam reforming of methanol for example, is well established. Actually, the pure and complete decomposition of methanol to CO and H_2, which is based on the principle of "micro-reversibility" in catalysis, has been known since the pioneering work of Frolich *et al.*[18] 90 years ago over 30% Cu/70% ZnO catalysts (probably still the most active catalyst for the forward and backward reaction). While studying hydrogen production using these additives has provided considerable fundamental knowledge related to electron transfer reactions from the semiconductor/ metal interface to hydrogen ions,[19,20] which would eventually help in making a water splitting catalyst, this needs not be confused with the water splitting reaction.

The case of electron scavengers is more complex because of the four-electron requirement to make one molecule of oxygen. On powder catalysts, Ag cations were the most used in heterogeneous photocatalysis. The deposition of Ag cations on the surface of the semiconductor, an interesting subject on its own merit because of anisotropy (metal cation deposition on the surface of a semiconductor in the presence of light is sensitive to its structure with reasons linked to polarization due to electric fields[21,22]), dictates a relatively short time to measure the reaction rates. It does also open important questions related to the spatial and temporal properties of excited electrons propagating between the semiconductor bulk and its surface on which a metal cation is deposited.[23] In homogeneous Ir and Ru-based systems[24–26] (and in some cases heterogeneous[27] ones) the use of Ce^{4+} cations as electron scavengers is common (because the redox potential Ce^{4+}/Ce^{3+} is more favorable than that of hydrogen ion reduction). Again, as in the case of Ag^+/Ag^0, Ce oxides (Ce_2O_3/CeO_2) are deposited on the surface containing Ir or Ru (or making a compound in the case of a homogeneous system) with little information on the nature of interaction. As in the case of hole scavengers, the reaction is driven by the redox potential of the inorganic compound and is not related to water splitting.

There is an increasing fraction of work addressing pure water splitting with figures showing the production of molecular hydrogen and molecular oxygen with time.[28,29] These, however, need to be reproduced by others in particular because the catalysis community knows well how to make these catalysts. There have been also, more recently, some results on monolithic p-type InGaN wires,[30] on top of which a noble metal is deposited that is further protected by a metal oxide to prevent the back reaction (H_2/O_2 recombination reactions). It is however important to mention that GaN is a textbook example of photocorrosion[31] and in addition the conduction band of InGaN is always lower than that of GaN.[32]

Other studies have focused on plasmonic systems (mostly on gold nanoparticles) because they absorb light in the visible region for pure water splitting, and indeed a few reports have shown H_2/O_2 formation[33,34] from pure water. This field is progressing fast and because it focuses on pure water splitting, both H_2 and O_2 are actually measured, in particular within the *Z*-scheme configuration. It is too early to draw conclusions yet, or foresee a direction. The electric field strength of the oscillating charges within gold particles of nanometer size increases sharply with decreasing interparticle distance[35] in addition to being sensitive to the particle shape and medium. This well-studied field may provide improvement in the catalyst activity yet catalyst design is not at the level of theory yet.

There have been a few attempts focusing on the reasons why this reaction is elusive. In a recent review article on the same subject, the weak photon fluxes used in most laboratory studies may disfavor the reaction rate.[36] However, no known attempts are made with the use of high solar fluxes (probably at least three orders of magnitude higher than sunlight are needed to offset the kinetics of fast charge traps) for suspended semiconductor particles to drive pure photocatalytic water splitting. Another idea is related to orbital overlap, where for an electron transfer to occur between two species, a favorable orbital overlap is needed and this is not the case between the O2p of a surface hydroxyl and an empty state in the valence band (O2p of the oxide support),[37] while it works with alkoxides.[38] The use of an electric field to separate the excited charge carriers in quantum wells is known in the field of optoelectronics,[39] where in this case the electric field is high enough to decrease the wavefunction overlap between the holes and electrons at the two sides of the well[40] and therefore increase their lifetime. Most of these materials are however water sensitive preventing them from being used or tested as photocatalysts for water splitting.

Probably the lack of progress in the field is ironically driven by the choice of the prototype semiconductor that most researchers have used, TiO_2. Because of its stability, conductivity, and ease of preparation it has been used as a benchmark in catalysis, photocatalysis for organic decomposition (oxidation),[41–43] surface science[44,45] and computation studies.[46–49] Yet, the realization that TiO_2

cannot split water is still not widely spread in the community. Again, this is because of the confusion between alcohol photoreforming (with the misleading terminology "sacrificial agent") and water splitting.

Among other semiconductors that have been extensively used is CdS; while its band gap is in the middle of the visible light region (2.5 eV or so) because of self-corrosion, it requires the use of hole scavengers. In other words, conceptually, it is not a different system from TiO_2, probably even inferior: the reaction rates are lower and the surface structure (and defects) is far less understood than in the case of TiO_2. Another system that has attracted attention is carbon nitride ($g-C_3N_4$) yet it also works only in the presence of an electron donor (tri-ethanol amine, TEA, oxalic acid, *etc.*). There is not much benefit in the use of $g-C_3N_4$ or CdS (in its various compositions, such as CdZnS, *etc.*) when compared to TiO_2: the rates are slower from an efficiency perspective and the difference in the band gap energy is marginal (up to 0.5 eV) within the solar conversion perspective. In addition, the ill-defined nature of their surfaces (in particular $g-C_3N_4$) prevents extraction of fundamental information.

High solar to hydrogen efficiency from pure water has been routinely reported however for at least two decades for integrated multi-junction solar cells connected to electrodes[50,51] or modified to make a complete catalyst.[52–54] The stability of these cells has been the issue,[55] although there are ways of resolving them.[56] Yet, the difference in the efficiency placed these systems in a different league when compared to powder systems. There is a misconception about them being expensive materials. While indeed they are expensive they can function at high sunlight concentrations (thousands of suns[57] in the laboratory and about 1000 suns in practical systems[58] at present) considerably decreasing their amount (although the need for sun tracker systems increases the process cost[59]). Yet, they have an important advantage: naturally, hydrogen and oxygen are produced separately. This is unlike powder systems where hydrogen and oxygen are produced together and the technology to separate hydrogen and oxygen is to date not available because of flammability issues. In other words, suspended particles at present do not offer a possible way forward for hydrogen production even with much improved rates.

Another point that may also need to be addressed more carefully is the use of current as a means of measurement of hydrogen or oxygen production instead of volumetric measurement for rates and ratio measurements. Because a material corroded under light illumination may give a stable high current, it is not advisable to use it as a measure of photocatalytic activity.[60]

A way forward

Focusing on the present best light harvesting materials, multi-junction solar cells with some approaching 45% efficiency and working with high light fluxes[61,62] and being converted into or mimicking heterogeneous catalysts would be a wise choice for

a few reasons. Charge separation, the essence of a photocatalyst, has been studied, designed, and made possible for many decades and may offer a wealth of information for those who are focusing on the daunting task of converting every particle of nanodimensions into a multi-junction catalyst (multi-junction semiconductors). The interfaces semiconductor–metal for the HER and/or semiconductor–metal ions for the OER require a multidisciplinary approach including electron and vibrational spectroscopy, microscopy, reaction kinetics, and the physics of light–matter interaction, in addition to material synthesis. Studies in surface science, traditional catalytic methods, and synchrotron-based operando studies of photocatalysis are needed. The wealth of information obtained for over a century in solid catalysis has not been well transferred into the field of photocatalysis and this may have contributed to its stagnation and probably in some cases, propagation of wrong knowledge, in particular, regarding the concept of catalyst surface orientations, atomic structures, surface defects and a few others. Putting an OER catalyst on one side and an HER catalyst on the other side of a multi-junction cell is not trivial when looked at from a fundamental point of view and is best studied on model surfaces (single crystals in particular) for metal/semiconductor and metal ion/ semiconductor interfaces of both sides (see ref. 17 and 63 for example). Moreover, on the front side of the cell (the illuminated side), light matter interaction at the metal/ semiconductor interface needs considerable work due to charge trapping (wave propagation would be affected by the presence of metal clusters), light scattering, a possible plasmonic role in the case of plasmonic materials, and anion defects. Another field of research that would help progress is time-dependent (TD) quantum-based computation (such as TD-density functional theory, TD-DFT). Since in photocatalytic reactions charge carriers' lifetime is an intrinsic part of the reaction rate, TD-DFT studies are very much needed, yet at present because of demanding computational resources, they are seldom conducted, mostly on clusters.[64–66] Another technique that is gaining momentum for measurement of charge carriers is pump–probe transient absorption spectroscopy (TAS).[67–69] While this technique is well developed for molecular studies as well as nanoparticles, it is not as well studied for single crystals and well defined thin films (epitaxy). Extracting fundamental information related to the nature of excited electron dynamics under reaction conditions may help progress the field in designing catalysts such as the metal and metal oxide particle size and dispersion effects and charge transfer from the bulk of the multi-junction semiconductor to the interface. The possible epitaxial layer on the front side of the cell protects it from corrosion yet allows the transfer of excited electrons to the metal particles at the interface with the electrolyte medium[70] to occur which would benefit the TAS studies. There is however a danger in overusing TAS because of the lack of a standard (unlike electron and vibrational spectroscopy). By definition, the signal ΔA (absorption difference between the ground and excited states) as a function of time is system dependent. With time and increasing use of

306 | *Catal. Sci. Technol.*, 2020, **10**, 304–310

This journal is © The Royal Society of Chemistry 2020

model bulk semiconductor materials, the extracted transient wave and associated time constants will be better gauged. This technique, because of the relative simplicity of its set up, can be used for operando studies[71–73] and this is poised to help improve our understanding of photocatalytic processes at the metal/semiconductor interface.

At present, in order for water splitting to hydrogen systems to succeed, a 30–35% overall solar to hydrogen efficiency is needed in order to start competing with hydrogen provided from natural gas.[54] The 30% STH mark is far higher than what has been initially thought a decade[74] or even a few years ago.[75] This has been shown to be technically possible[76] using a "two system" approach and is achievable upon improving a one-system approach.[50] For this, probably a catalyst that works at around one thousand suns based on four-junction cells is needed.

One may transfer the above mentioned points to the case of CO_2 photo- (and/or electro-) catalytic conversion. With lessons learned from water splitting, it is important to focus on the fate of oxygen by measuring molecular oxygen rather than the relevant reaction product (CO or hydrocarbons) so as to ensure that the reaction is indeed catalytic. Some of the needed criteria for this reaction are given in the work of Teramura and Tanaka.[77] Other researchers have recently attempted to create a standard for one of the crucial catalytic reactions[78] (N_2 splitting followed by hydrogenation to ammonia at low temperatures) for precisely the same reasons, which were actually recognized early[79] on with the hope that this time, lessons will be learned and useful knowledge will be shared.

In summary, focusing on water splitting to molecular hydrogen and oxygen and re-iterating the conditions, all being known in the community and some already mentioned by others,[1] the following three points seem to be important. (i) A molar ratio of two, (ii) a catalytically acceptable turnover number (TON), and (iii) direct measurements (not current based) of molecular hydrogen and oxygen. These would be the minimum requirement needed for water splitting studies. This is to make sure that one is indeed dealing with a photocatalytic water splitting reaction.

Conflicts of interest

There are no conflicts to declare.

References

1 A. Miseki and Y. Kudo, Heterogeneous photocatalyst materials for water splitting, *Chem. Soc. Rev.*, 2009, **38**, 253–278.

2 F. E. Osterloh, Photocatalysis versus Photosynthesis: A Sensitivity Analysis of Devices for Solar Energy Conversion and Chemical Transformations, *ACS Energy Lett.*, 2017, **2**, 445–453.

3 J. W. Ager, M. R. Shaner, K. A. Walczak, I. D. Sharp and S. Ardo, Experimental Demonstrations of Spontaneous, Solar-Driven Photoelectrochemical Water Splitting, *Energy Environ. Sci.*, 2015, **8**, 2811–2824.

4 V. M. Daskalaki, P. Panagiotopoulou and D. I. Kondarides, Production of peroxide species in Pt/TiO2 suspensions under conditions of photocatalytic water splitting and glycerol photoreforming, *Chem. Eng. J.*, 2011, **170**, 433–439.

5 E. Yesodharan, S. Yesodharan and M. Grätzel, Photolysis of water with supported noble metal clusters, the fate of oxygen in titania based water cleavage systems, *Sol. Energy Mater.*, 1984, **10**, 287–302.

6 H. Yoshida, R. Yamada and T. Yoshida, Platinum Cocatalyst Loaded on Calcium Titanate Photocatalyst for Water Splitting in a Flow of Water Vapor, *ChemSusChem*, 2019, **12**, 1958–1965; and refrences therein.

7 H. Alghamdi and H. Idriss, Study of the modes of adsorption and electronic structure of hydrogen peroxide and ethanol over TiO_2 rutile (110) surface within the context of water splitting, *Surf. Sci.*, 2018, **669**, 103–113.

8 W. Huang, P. Raghunath and M. C. Lin, Computational Study on the Reactions of H_2O_2 on TiO_2 Anatase (101) and Rutile (110) Surfaces, *J. Comput. Chem.*, 2011, **32**, 1065–1081.

9 K. Mudiyanselage and H. Idriss, Characterization of peroxo species on TiO_x/Rh(111) single crystal, *Surf. Sci.*, 2019, **680**, 61–67.

10 R. Nakamura, A. Imanishi, K. Murakoshi and Y. Nakato, In Situ FTIR Studies of Primary Intermediates of Photocatalytic Reactions on Nanocrystalline TiO_2 Films in Contact with Aqueous Solutions, *J. Am. Chem. Soc.*, 2003, **125**, 7443–7450.

11 J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.-T. Lee, J. Zhong and Z. Kang, Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway, *Science*, 2015, **347**, 970–974.

12 Z. H. N. Al-Azri, A. Chan, W.-T. Chen, T. Ina, H. Idriss and G. I. N. Waterhouse, On the role of metals and reaction media in photocatalysis for hydrogen production. Performance evaluation of M/TiO$_2$ photocatalysts (M = Pd, Pt, Au) for H$_2$ Production in different alcohol-water mixtures, *J. Catal.*, 2015, **329**, 355–367.

13 Z. H. N. Al-Azri, M. Al-Oufi, A. Chan, G. I. N. Waterhouse and H. Idriss, Metal particle size effects on the photocatalytic hydrogen ion reduction, *ACS Catal.*, 2019, **9**, 3946–3958.

14 X. Chen, L. Liu, P. Y. Yu and S. S. Mao, Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals, *Science*, 2011, **331**, 746–749.

15 P. Kalisman, Y. Nakibli and L. Amirav, Perfect Photon-to-Hydrogen Conversion Efficiency, *Nano Lett.*, 2016, **16**, 1776–1781.

16 Y. Miseki and K. Sayama, Photocatalytic Water Splitting for Solar Hydrogen Production Using the Carbonate Effect and the Z-Scheme Reaction, *Adv. Energy Mater.*, 2019, **9**, 1801294; and references therein.

17 J. Yang, X. Zeng, L. Chen and W. Yuan, Photocatalytic water splitting to hydrogen production of reduced graphene oxide/SiC under visible light, *Appl. Phys. Lett.*, 2013, **102**, 083101.

18 P. K. Frolich, M. R. Fenske, P. S. Taylor and C. A. Southwich, Jr., Catalysts for the Formation of Alcohols from Carbon Monoxide and Hydrogen Synthesis of Methanol with

This journal is © The Royal Society of Chemistry 2020

Catal. Sci. Technol., 2020, **10**, 304–310 | **307**

Catalysts Composed of Copper and Zinc, *Ind. Eng. Chem.*, 1928, **20**, 1327–1330.

19 S. Tan, H. Feng, Y. Ji, Q. Zheng, Y. Shi, J. Zhao, A. Zhao, J. Yang, Y. Luo, B. Wang and J. G. Hou, Visualizing Elementary Reactions of Methanol by Electrons and Holes on TiO2(110) Surface, *J. Phys. Chem. C*, 2018, **122**, 28805–28814.

20 K. Katsiev, G. Harrison, G. Thornton and H. Idriss, Metal-semiconductor interaction in photo-catalysis. Cluster size and coverage effects on hydrogen production over $TiO_2(110)$ rutile single crystal, *ACS Catal.*, 2019, **9**, 8294–8305.

21 J. L. Giocondi, P. A. Salvador and G. S. Rohrer, The origin of photochemical anisotropy in $SrTiO_3$, *Top. Catal.*, 2007, **44**, 529–533.

22 W. Song, P. A. Salvador and G. S. Rohrer, Influence of the Magnitude of Ferroelectric Domain Polarization on the Photochemical Reactivity of $BaTiO_3$, *ACS Appl. Mater. Interfaces*, 2018, **10**, 41450–41457.

23 R. Qiana, H. Zonga, J. Schneiderc, G. Zhoua, T. Zhaoa, Y. Lid, J. Yange, D. W. Bahnemannf and J. H. Pana, Charge carrier trapping, recombination and transfer during TiO_2 photocatalysis: An overview, *Catal. Today*, 2019, **335**, 78–90.

24 R. G. Menendez, A. Bucci, R. Hutchinson, G. Bellachioma, C. Zuccaccia, H. Idriss and A. Macchioni, Extremely Active, Tunable, and pH-Responsive Iridium Water Oxidation Catalysts, *ACS Energy Lett.*, 2016, **2**, 105–110.

25 R. Tagore, H. Chen, H. Zhang, R. H. Crabtree and G. W. Brudvig, Homogeneous water oxidation by a di-μ-oxo dimanganese complex in the presence of Ce^{4+}, *Inorg. Chim. Acta*, 2007, **360**, 2983–2989.

26 Q. Yin, J. Miles Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle and C. L. Hill, A Fast Soluble Carbon-Free Molecular Water Oxidation Catalyst Based on Abundant Metals, *Science*, 2010, **328**, 342–345.

27 G. Pastori, K. W. Wahab, A. Bucci, G. Bellachioma, C. Zuccaccia, J. Llorca, H. Idriss and A. Macchioni, Heterogenized water oxidation catalysts prepared by immobilizing Kläui-type organometallic precursors, *Chem. – Eur. J.*, 2016, **22**, 1–6.

28 H. Lyu, T. Hisatomi, Y. Goto, M. Yoshida, T. Higashi, M. Katayama, T. Takata, T. Minegishi, H. Nishiyama, T. Yamada, Y. Sakata, K. Asakura and K. Domen, An Al-doped $SrTiO_3$ photocatalyst maintaining sunlight-driven overall water splitting activity for over 1000 h of constant illumination, *Chem. Sci.*, 2019, **10**, 3196–3201.

29 Y. He and D. Wang, Toward Practical Solar Hydrogen Production, *Chem*, 2018, **4**, 399–408; and references therein.

30 M. G. Kibria, H. P. T. Nguyen, K. Cui, S. Zhao, D. Liu, H. Guo, M. L. Trudeau, S. Paradis, A.-R. Hakima and Z. Mi, One-Step Overall Water Splitting under Visible Light Using Multiband InGaN/GaN Nanowire Heterostructures, *ACS Nano*, 2013, **7**, 7886–7893.

31 D. Zhuang and J. H. Edgar, Wet etching of GaN, AlN, and SiC: a review, *Mater. Sci. Eng., R*, 2005, **48**, 1–46.

32 P. G. Moses, M. Miao, Q. Yan and C. G. Van de Walle, Hybrid functional investigations of band gaps and band alignments for AlN, GaN, InN, and InGaN, *J. Chem. Phys.*, 2011, **134**, 084703.

33 W. Zhang, Y. Hu, C. Yan, D. Hong, R. Chen, X. Xue, S. Yang, Y. Tian, Z. Tie and Z. Jin, Surface plasmon resonance enhanced direct Z-scheme TiO_2/ZnTe/Au nanocorncob heterojunctions for efficient photocatalytic overall water splitting, *Nanoscale*, 2019, **11**, 9053–9060.

34 S. Wang, Y. Gao, Y. Qi, A. Li, F. Fan and C. Li, Achieving overall water splitting on plasmon-based solid Z-scheme photocatalysts free of redox mediators, *J. Catal.*, 2017, **354**, 250–257.

35 S. K. Cushing, J. Li, F. Meng, T. R. Senty, S. Suri, M. Zhi, M. Li, A. D. Bristow and N. Wu, Photocatalytic activity enhanced by plasmonic resonant energy transfer from metal to semiconductor, *J. Am. Chem. Soc.*, 2012, **134**, 15033–15041.

36 N. Serpone, A. V. Emeline, V. K. Ryabchuk, V. N. Kuznetsov, Y. M. Artemev and S. Horikoshi, Why do Hydrogen and Oxygen Yields from Semiconductor-Based Photocatalyzed Water Splitting Remain Disappointingly Low? Intrinsic and Extrinsic Factors Impacting Surface Redox Reactions, *ACS Energy Lett.*, 2016, **1**, 931–948.

37 C. Di Valentin and D. Fittipaldi, Hole Scavenging by Organic Adsorbates on the TiO_2 Surface: A DFT Model Study, *J. Phys. Chem. Lett.*, 2013, **4**, 1901–1906.

38 J. N. Muir, Y. M. Choi and H. Idriss, DFT study of Ethanol on TiO2 (110) rutile surface, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11910–11919.

39 G. Bastard, E. E. Mendez, L. L. Chang and L. Esaki, Variational calculations on a quantum well in an electric field, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1983, **28**, 3241–3245.

40 L. Calcagnile, G. Coli, M. De Vittorio, R. Rinaldi, P. V. Giugno, R. Cingolani, L. Vanzetti, L. Sorba and A. Franciosi, Excitonic nonlinearities in wide gap II-VI multiple quantum wells, *J. Cryst. Growth*, 1996, **159**, 793–799.

41 D. S. Bhatkhande, V. G. Pangarkar and A. A. C. M. Beenackers, Photocatalytic degradation for environmental applications – a review D. S Bhatkhande, V. G Pangarkar, and A. ACM Beenackers, *J. Chem. Technol. Biotechnol.*, 2001, **77**, 102–116.

42 O. Carp, C. L. Huisman and A. Reller, Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.*, 2004, **32**, 33–177.

43 I. Dhada, P. K. Nagar and M. Sharma, Challenges of TiO_2-Based Photooxidation of Volatile Organic Compounds: Designing, Coating, and Regenerating Catalyst, *Ind. Eng. Chem. Res.*, 2015, **54**, 5381–5387.

44 K. A. Connelly and H. Idriss, The Photoreaction of TiO_2 and Au/TiO_2 single crystal and powder surfaces with organic adsorbates. Emphasis on hydrogen production from renewable, *Green Chem.*, 2012, **14**, 260–280.

45 A. Fujishima, X. Zhang and D. A. Tryk, TiO_2 photocatalysis and related surface phenomena, *Surf. Sci. Rep.*, 2008, **63**, 515–582.

46 V. L. Deringer and G. Csányi, Many-Body Dispersion Correction Effects on Bulk and Surface Properties of Rutile and Anatase TiO_2, *J. Phys. Chem. C*, 2016, **120**, 21552–21560.

308 | *Catal. Sci. Technol.*, 2020, **10**, 304–310

This journal is © The Royal Society of Chemistry 2020

47 J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo and D. W. Bahnemann, Understanding TiO2 Photocatalysis: Mechanisms and Materials, *Chem. Rev.*, 2014, **114**, 9919–9986.

48 D. Selli, G. Fazio and C. Di Valentin, Using Density Functional Theory to Model Realistic TiO_2 Nanoparticles, Their Photoactivation and Interaction with Water, *Catalysts*, 2017, **7**, 357.

49 A. Vittadini, M. Casarin and A. Selloni, Chemistry of and on TiO_2-anatase surfaces by DFT calculations: a partial review, *Theor. Chem. Acc.*, 2007, **117**, 663–671.

50 O. Khaselev, A. Bansal and J. A. Turner, High-efficiency integrated multijunction photovoltaic/electrolysis systems for hydrogen production, *Int. J. Hydrogen Energy*, 2001, **26**, 127–132.

51 E. Verlage, S. Hu, R. Liu, R. J. R. Jones, K. Sun, C. Xiang, N. S. Lewis and H. A. Atwater, A monolithically integrated, intrinsically safe, 10% efficient, solar-driven water-splitting system based on active, stable earth-abundant electrocatalysts in conjunction with tandem III–V light absorbers protected by amorphous TiO_2 films, *Energy Environ. Sci.*, 2015, **8**, 3166–3172.

52 J. L. Young, M. A. Steiner, H. Döscher, R. M. France, J. A. Turner and T. G. Deutsch, Direct solar-to-hydrogen conversion via inverted metamorphic multi-junction semiconductor architectures, *Nat. Energy*, 2017, **2**, 17028.

53 Y. Yang, J. Gu, J. L. Young, E. M. Miller, J. A. Turner, N. R. Neale and M. C. Beard, Semiconductor interfacial carrier dynamics via Photoinduced electric fields, *Science*, 2105, **350**, 1061–1065.

54 B. Turan, J.-P. Becker, F. Urbain, F. Finger, U. Rau and S. Haas, Upscaling of integrated photoelectrochemical water-splitting devices to large areas, *Nat. Commun.*, 2016, **7**, 12681.

55 W.-H. Cheng, M. H. Richter, M. M. May, J. Ohlmann, D. Lackner, F. Dimroth, T. Hannappel, H. A. Atwater and H.-J. Lewerenz, Monolithic Photoelectrochemical Device for Direct Water Splitting with 19% Efficiency, *ACS Energy Lett.*, 2018, **3**, 1795–1800.

56 A. Khan, P. Varadhan, H. He Jr. and H. Idriss, Metal Foil Protective Layer for Photovoltaic cells, *US Pat.*, 201862/891,659, 2019.

57 J. Zeitouny, E. A. Katz, A. Dollet and A. Vossier, Band Gap Engineering of Multi-Junction Solar Cells: Effects of Series Resistances and Solar Concentration, *Sci. Rep.*, 2017, **7**, 1766.

58 http://www.sharp-world.com/corporate/news/130614.html.

59 T. T. Isimjan, S. Al-Sayegh, R. Varjian and H. Idriss, Methanol Production by H_2 Generated from Water Using Integrated Ultra High Concentrated Solar Cells-Electrolysis and Captured CO_2: A Process Development and Techno-Economy Analysis, *SABIC-TechnoEconomy Analysis Report*, December 2018 – Classified.

60 M. A. Khan, P. Varadhan, R. Vinoth, H. Idriss and J.-H. He, Importance of O_2 measurements during photoelectrochemical water-splitting reactions, *ACS Energy Lett.*, 2019, **4**, 2712–2718 (Perspective).

61 M. S. Leitel and H. A. Atwater Device Modeling of an Optimized Monolithic All Lattice-Matched 3-Junction Solar Cell with Efficiency> 50%, *38th IEEE Photovoltaic Specialists Conference*, 2012, DOI: 10.1109/PVSC.2012.6318006.

62 M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, Solar cell efficiency tables (version 48), *Progr. Photovolt.: Res. Appl.*, 2016, **24**, 905–913.

63 S.-H. Yoo, N. Siemer, M. Todorova, D. Marx and J. Neugebauer, Deciphering Charge Transfer and Electronic Polarization Effects at Gold Nanocatalysts on Reduced Titania Support, *J. Phys. Chem. C*, 2019, **123**, 5495–5506.

64 M. Pastore and F. De Angelis, First-Principles Modeling of a Dye-Sensitized TiO_2/IrO_2 Photoanode for Water Oxidation, *J. Am. Chem. Soc.*, 2015, **137**, 5798–5809.

65 J. J. Lutz, X. F. Duan and L. W. Burggraf, Semiconductor color-center structure and excitation spectra: Equation-of-motion coupled-cluster description of vacancy and transition-metal defect photoluminescence, *Phys. Rev. B*, 2018, **97**, 115108.

66 D. Cho, K. Chul Ko, O. Lamiel-García, S. T. Bromley, J. Yong Lee and F. Illas, Effect of Size and Structure on the Ground and Excited State Electronic Structure of TiO2 Nanoparticles, *J. Chem. Theory Comput.*, 2016, **12**, 3751–3763.

67 P. Maity, K. Katsiev, O. F. Mohammed and H. Idriss, Bulk Defect Mediated Photoexcited Charge Recombination in Anatase and Rutile TiO_2 Single Crystals, *J. Phys. Chem. C*, 2018, **122**, 8925–8932.

68 X. Wang, A. Kafizas, X. Li, S. J. A. Moniz, P. J. T. Reardon, J. Tang, I. P. Parkin and J. R. Durrant, Transient Absorption Spectroscopy of Anatase and Rutile: The Impact of Morphology and Phase on Photocatalytic Activity, *J. Phys. Chem. C*, 2015, **119**, 10439–10447.

69 A. Yamakata, J. J. M. Vequizo and H. Matsunaga, Distinctive Behavior of Photogenerated Electrons and Holes in Anatase and Rutile TiO_2 Powders, *J. Phys. Chem. C*, 2015, **119**, 24538–24545.

70 S. A. Chambers, Y. Du, R. B. Comes, S. R. Spurgeon and P. V. Sushko, The effects of core-level broadening in determining band alignment at the epitaxial $SrTiO_3(001)$/p-Ge(001) heterojunction, *Appl. Phys. Lett.*, 2017, **110**, 082104.

71 M. Fracchia, P. Ghigna, A. Vertova, S. Rondinini and A. Minguzzi, Time-Resolved X-ray Absorption Spectroscopy in (Photo)Electrochemistry, *Surfaces*, 2018, **1**, 138–150.

72 K. E. Knowles, M. D. Koch and J. L. Shelton, Three applications of ultrafast transient absorption spectroscopy of semiconductor thin films: spectroelectrochemistry, microscopy, and identification of thermal contributions, *J. Mater. Chem. C*, 2018, **6**, 11853–11867.

73 M. Barroso, S. R. Pendlebury, A. J. Cowan and J. R. Durrant, Charge carrier trapping, recombination and transfer in hematite (α-Fe_2O_3) water splitting photoanodes, *Chem. Sci.*, 2013, **4**, 2724–2734.

74 K. Maeda and K. Domen, Photocatalytic Water Splitting: Recent Progress and Future Challenges, *J. Phys. Chem. Lett.*, 2010, **1**, 2655–2661.

This journal is © The Royal Society of Chemistry 2020

Catal. Sci. Technol., 2020, **10**, 304–310 | 309

75 M. R. Shaner, H. A. Atwater, N. S. Lewis and E. W. McFarland, A comparative technoeconomic analysis of renewable hydrogen production using solar Energy, *Energy Environ. Sci.*, 2016, **9**, 2354–2371.

76 J. Jia, L. C. Seitz, J. D. Benck, Y. Huo, Y. Chen, J. Wei Desmond Ng, T. Bilir, J. S. Harris and T. F. Jaramillo, Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%, *Nat. Commun.*, 2016, **7**, 13237.

77 K. Teramura and T. Tanaka, Necessary and sufficient conditions for the successful three-phase photocatalytic reduction of CO_2 by H_2O over heterogeneous photocatalysts, *Phys. Chem. Chem. Phys.*, 2018, **20**, 8423–8431.

78 S. Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Nørskov and I. Chorkendorff, A rigorous electrochemical ammonia synthesis protocol with quantitative isotope measurements, *Nature*, 2019, **570**, 504–508.

79 D. L. Boucher, J. A. Davies, J. G. Edwards and A. Mennad, An investigation of the putative photosynthesis of ammonia on iron-doped titania and other metal oxides, *J. Photochem. Photobiol., A*, 1995, **88**, 53–64.