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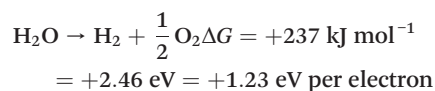
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The elusive photocatalytic water splitting reaction using sunlight on suspended nanoparticles: is there a way forward?

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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:



This reaction should give a H₂ to O₂ 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 SrTiO₃ and TiO₂ (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/TiO₂ with time until the rates went to zero. The authors then measured the amount of H₂O₂ and found it to be increasing with time. From this observation, they postulated that some forms of dissociatively adsorbed H₂O₂ are present on the catalyst surface, which prevents further reactions from occurring (2H₂O → H₂ + H₂O₂, although a more endothermic reaction than that to H₂ and O₂). 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 water⁶) 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 TiO₂ 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 H₂O₂ over TiO₂/Rh(111)⁹ and with IR spectroscopy over TiO₂ 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-C₃N₄ have resulted in pure water splitting to H₂ and O₂ (with 2% solar to hydrogen efficiency (STH)). The reason

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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 heterogeneous²⁷ ones) the use of Ce^{4+} cations as electron scavengers is common (because the redox potential $\text{Ce}^{4+}/\text{Ce}^{3+}$ is more favorable than that of hydrogen ion reduction). Again, as in the case of Ag^+/Ag^0 , Ce oxides ($\text{Ce}_2\text{O}_3/\text{CeO}_2$) 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 photocorrosion³¹ 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 distance³⁵ 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 well⁴⁰ 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 TiO₂, probably even inferior: the reaction rates are lower and the surface structure (and defects) is far less understood than in the case of TiO₂. Another system that has attracted attention is carbon nitride (g-C₃N₄) 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-C₃N₄ or CdS (in its various compositions, such as CdZnS, *etc.*) when compared to TiO₂: 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-C₃N₄) 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 suns⁵⁷ in the laboratory and about 1000 suns in practical systems⁵⁸ at present) considerably decreasing their amount (although the need for sun tracker systems increases the process cost⁵⁹). 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 medium⁷⁰ 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



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 decade⁷⁴ or even a few years ago.⁷⁵ This has been shown to be technically possible⁷⁶ 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 CO₂ 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 reactions⁷⁸ (N₂ splitting followed by hydrogenation to ammonia at low temperatures) for precisely the same reasons, which were actually recognized early⁷⁹ 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.

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