



# Hydrogen production from water: past and present

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Hydrogen derived from sustainable materials may be an important energy vector in a post petroleum economy. The focus of this short review article is on the most studied methods for making hydrogen from water including: electrocatalytic, photocatalytic, and thermally driven reactions on reducible oxides. Hydrogen from renewables comes at a cost. Therefore, projected process cost issues are necessary in determining the best path forward. The most important challenge in the thermally driven reaction is finding a metal oxide that can be reduced at practical temperatures with acceptable reaction kinetics while the most important challenge for photocatalytic reactions is to find a stable semiconductor-based material capable of splitting water using a large fraction of sun light.

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Jules Verne in the Mysterious Island [1] indicated in 1874 that water would be the fuel of the future “*Someday the coal rooms of steamers and the tenders of locomotives will, instead of coal, be stored with these two condensed gases (hydrogen and oxygen), which will burn in the furnaces with enormous calorific power*”. Jules Verne knew of electrolysis of water which was discovered a century before, in 1789 on gold electrodes.

A few concepts that govern hydrogen production from water.

1 To split water one needs an input of energy of 1.23 eV ( $\Delta G^{\circ}_{298K}$ , 1 bar) or 1.48 eV ( $\Delta H^{\circ}$ ). The value of water is in charge carriers (electrons) and this in oxygen anions ( $O^{2-}$ ). Water dissociation occurs naturally on most surfaces ( $H_2O + M - X \rightarrow MOH + XH$ ; where M is a metal and X can be another M site, or a heteroatom in its ionic form such O, S or N anions). This is an acid-

base reaction (electrons are not transferred from an atom to the other) [2]. In other words, water dissociation results in hydrogen ions and oxygen anions, a process governed by the difference between the ionization potential and electron affinity. Therefore, water dissociation is only involved in the kinetics of the reaction. Water splitting is an ill-defined term. In the field it is understood as the production of  $H_2$  (a two-electron process) and  $O_2$  (a four-electron process). This means that for electron transfer to occur a third party (a catalyst or a material) is needed.

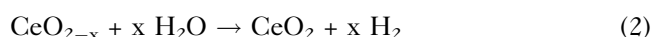
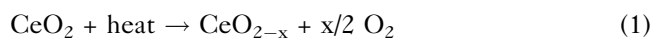
- 2 The reduction of a metal oxide, such as  $CeO_2$ , involves the removal of oxygen atoms from the surface (and from the bulk by diffusion). Oxygen ions in the lattice are stabilized due to the electrostatic attractive and repulsive forces (the Madelung Potential) [3]. An oxygen is removed from the lattice as an oxygen atom, leaving two electrons behind; these are located on the metal cations (partially reducing them). The location of these electrons is the subject of extensive work on  $CeO_2$  and  $TiO_2$  among other reducible oxides [4,5]. The reason is that electron affinity of oxygen atoms in the gas phase is zero. Oxygen atoms then react together to make a molecular oxygen.
- 3 A catalytic cycle needs to be maintained. Hydrogen and oxygen need to be produced in a molecular ratio of two otherwise the system may not be stable and the catalyst is consumed during the reaction (such as by corrosion).
- 4 While catalytic reactions are predominantly surface reactions, in the case of water splitting by thermal, electro and photo driven surfaces, bulk interaction dominates the process. While our understanding of thermal effect on surface-bulk dynamics and of electrocatalytic charge transfer is well advanced, this is not the case for photo-driven catalytic reactions because both light absorption and charge transfer kinetics occur at different time scales adding further complications.

Hydrogen production from water is poised to decrease the world reliance on fossil fuel for transportation, and the chemical industry. The world annual production of hydrogen is about 70 million metric tons of which about 50% is dedicated to ammonia synthesis. Most of hydrogen produced worldwide is made by methane reforming resulting in  $CO_2$  emission of about 830 million tons per year. The world annual  $CO_2$  emission is close to 35 billion tons of which about 25% is emitted while generating electricity and heat, 20% from industry, and about the same percentage from transportation. Because of the link between global warming and  $CO_2$  emission there is an increasing move towards taxation and finding alternative

ways for making molecular hydrogen. Hydrogen production from renewables is taking an increasingly important stage within this strategy. At present, the cost of hydrogen made by steam methane reforming (per kg) with CO<sub>2</sub> sequestration is between \$ 1.3 and 2.8 [6]. The cost of hydrogen from renewables (such as water using energy directly or indirectly from sun) needs to be competitive at least at a foreseen future. At present, this is not the case [7\*\*] although the present numbers are not too far and can be put in place relatively fast with government incentives.

### Thermal water splitting using metal oxides

This is a two-step reaction involving a reduction of an oxide material using heat, for simplicity in the case of a binary oxide, such as CeO<sub>2</sub>, the reaction is as follows



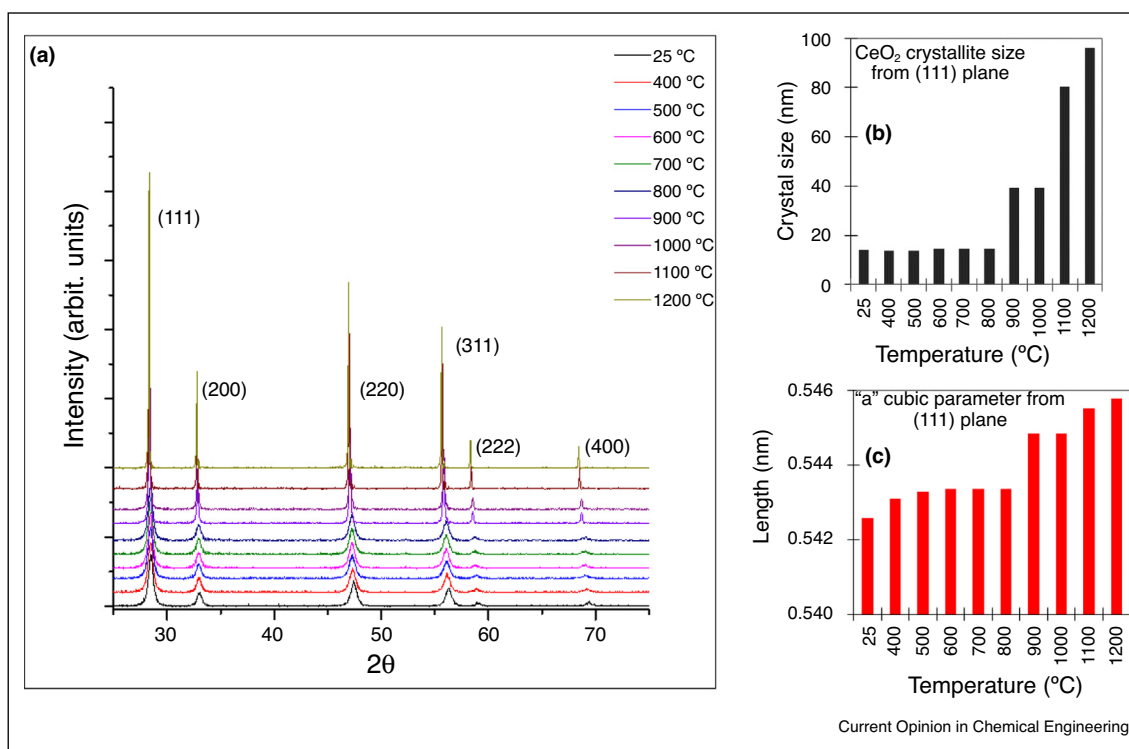
Reaction (1) requires an input of heat of around 1550°C [8] in order to generate enough oxygen vacancies with a reasonable reaction rate. The diffusion of oxygen ions in CeO<sub>2</sub> at this temperature is typically between 10<sup>-5</sup> and 10<sup>-4</sup> cm<sup>2</sup> s<sup>-1</sup> [9]. The second reaction (exothermic) occurs at temperatures around 1000°C for practical

reasons. There have been many prototype reactors such as those in reference [10\*].

The reduction of a fraction of Ce<sup>4+</sup> cations (typically between 1 and 10%) to Ce<sup>3+</sup> is associated with lattice expansion. The increase in size of Ce cations, Ce<sup>3+</sup> (1.02 Å) larger than Ce<sup>4+</sup> (0.87 Å) is often invoked as the cause of lattice expansion [11], although other interpretations have been reported [12\*]. Figure 1 shows XRD patterns of *in situ* heated CeO<sub>2</sub> in inert environment up to 1200°C. Two main points are worth mentioning. A decrease in width of the diffraction peaks with increasing temperature due to sintering. A shift in peaks position to lower angles (2θ) as a consequence of lattice expansion,  $n\lambda/2\sin(\theta) = d$ ; where  $d$  is the inter-planar distance,  $\lambda$  is the wavelength of X-rays, typically CuK<sub>α</sub> = 1.54 Å,  $\theta$  is the diffraction angle and  $n$  is the order of diffraction). Using Sheerer equation, one can determine the crystallite size and from Bragg's diffraction one can calculate the lattice dimension. Both are indicated in Figure 1.

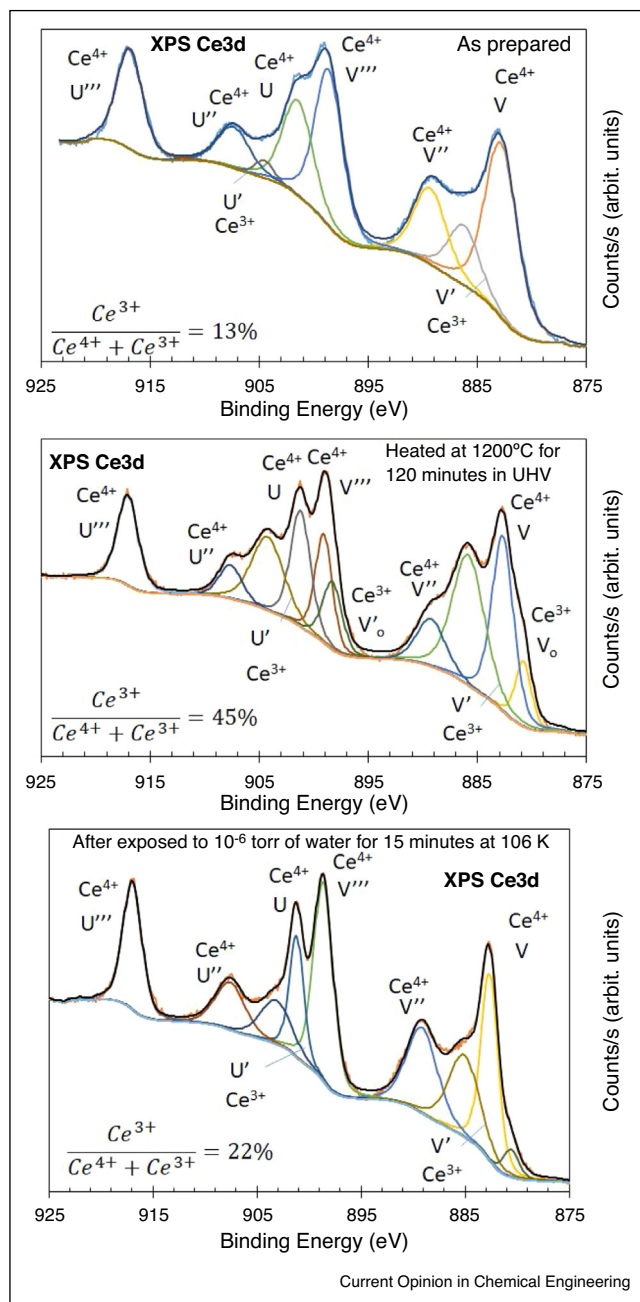
The redox properties of CeO<sub>2</sub> can be monitored by XPS when studied *in situ* or in operando conditions. Figure 2 presents XPS Ce3d of CeO<sub>2</sub> before and after heating inside an Ultra High Vacuum chamber at 1200°C. The

Figure 1



(a) *In situ* X-ray diffraction of CeO<sub>2</sub> particles annealed at the indicated temperatures. Note the shift in the diffraction line to lower 2θ as well as the decrease in the peak width with increasing annealing temperatures. (b) Crystallite size of CeO<sub>2</sub> at the indicated temperatures, extracted from Sheerer equation. (c) The CeO<sub>2</sub> cubic crystal lattice size,  $a$ , extracted from the  $d$  spacing ( $d = a/\sqrt{3}$ ).

Figure 2



XPS Ce3d line of CeO<sub>2</sub>. Top. As prepared. Middle: heated in UHV at 1200°C for 120 min. Bottom: exposed to water vapor (10<sup>-6</sup> torr) for 15 min at 106 K. Note the appearance of the considerable increase of the V' and U' of Ce<sup>3+</sup> cations upon heating at 1200°C due to the removal of oxygen anions. Upon exposure to water vapor the lines due to Ce<sup>3+</sup> have been largely attenuated due to oxidation. Binding energy positions of Ce 3d lines are given in Table 1.

surface was then exposed to water vapor at 100 K then Ce3d lines were collected again. Clear evidence of Ce<sup>3+</sup> consumption; more details regarding the Ce<sup>4+</sup> and Ce<sup>3+</sup> can be found in one of the original work by Mullins *et al.*

[13] Similar results were observed previously on UO<sub>2-x</sub> (which also has a fluorite structure) [14].

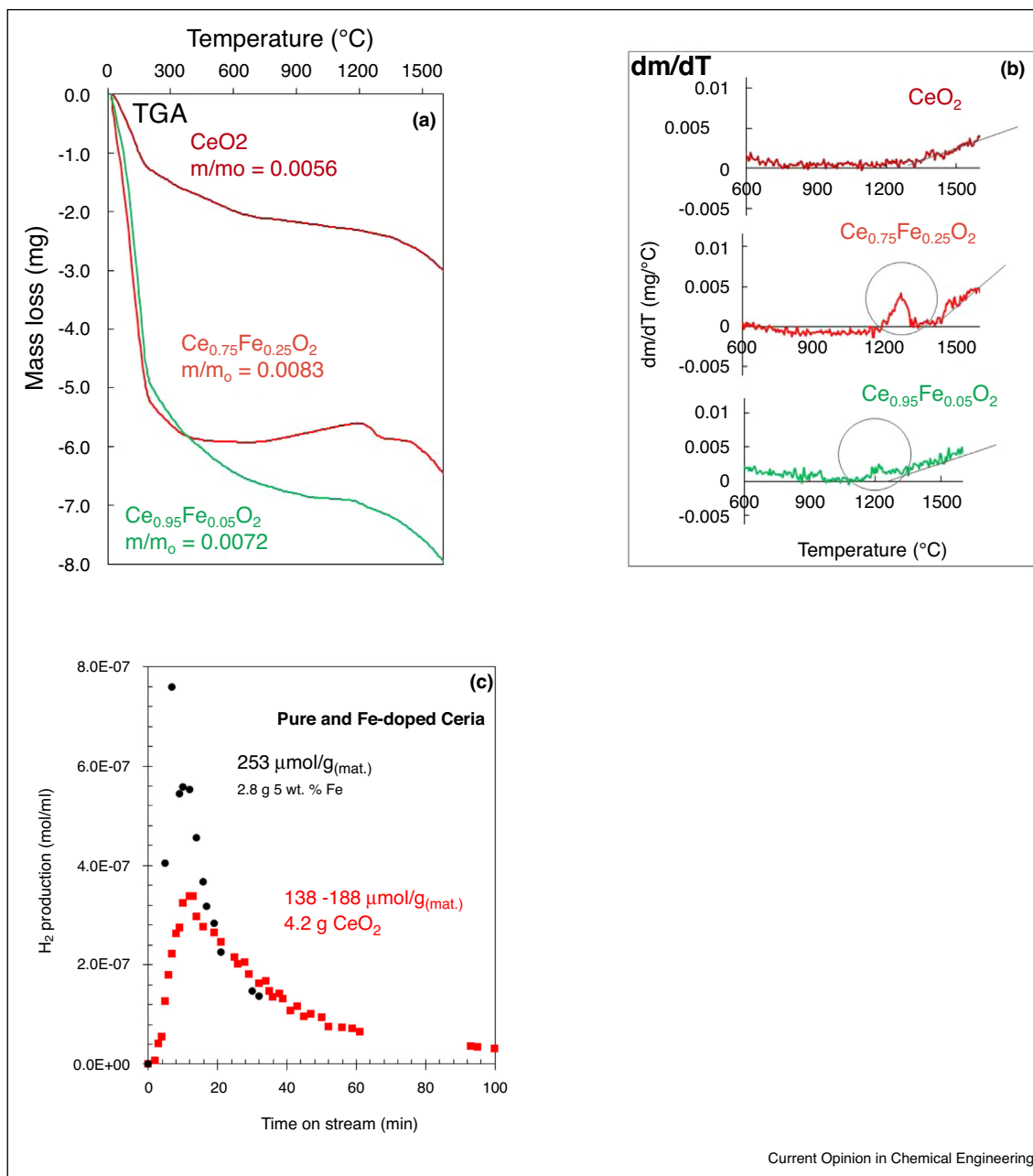
In order to increase the number and obtain faster kinetics with CeO<sub>2</sub>, doping with other metal cations has been conducted by many researchers. These can be grouped into three categories. 1. Compensation for lattice expansion, where Ce<sup>4+</sup> cations are substituted by Zr<sup>4+</sup> cations (much smaller: the size of Zr<sup>4+</sup> cations is 0.59 Å while that of Ce<sup>4+</sup> is 0.87 Å). Although, at the high temperature needed for reduction considerable segregation occurs [15]. 2. Additional charge transfer upon doping of CeO<sub>2</sub> by U<sup>4+</sup> cations occurs which results in increasing Ce<sup>3+</sup> concentration this is because UO<sub>2</sub> can accommodate non-stoichiometric amounts of oxygen anions up to UO<sub>2.25</sub> [16]. 3. Aliovalent doping where Fe<sup>3+</sup> cations substitute Ce<sup>4+</sup> resulting in non-charged vacancies, which in turn cause lattice distortion [17]. Figure 3 presents Thermo-gravimetric analysis of CeO<sub>2</sub>, Fe<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub> and Fe<sub>0.25</sub>Ce<sub>0.75</sub>O<sub>2</sub> powder materials together with results of hydrogen production over CeO<sub>2</sub> and Fe<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2</sub>. TGA shows that reduction occurs at lower temperature in the presence of Fe cations, which in turn was translated into higher hydrogen production from water.

Many other binary, tertiary and higher mixed metal oxides are investigated with considerable knowledge gained at the materials, reaction and reactor design levels [18,19]. The main hurdles are three. 1. Finding a reducible material that can work at practical levels up to a maximum of 1000°C. 2. Producing hydrogen with a rate fast enough to warrant applications. 3. The cost of light concentrators and reactor materials due the high temperature and corrosive nature of the process. At present, these three main hurdles are compromising this route. One of the main advantages however is the utilization of a very large fraction of sun light unlike most other methods.

### Electrocatalytic water splitting

Electrocatalytic water splitting is the most mature technology for making hydrogen from water with many commercial systems available for small and large-scale applications. With respect to making hydrogen from renewable, electro-catalysis is attractive because electricity can be generated from photovoltaic cells. At present, this system offers probably the least expensive method for making hydrogen with an estimated cost of hydrogen between \$1.5 and \$2/kg<sub>H2</sub> if electricity is provided at a cost of \$0.02/kWh, which is three to four times lower than the present cost [20]. Commercial electrolyzers work either at neutral pH in this case using noble metals for both electrodes and Proton-Exchange Membrane, this is mostly for small-scale applications, or in alkaline environment. In alkaline media, electrodes are made of mixed metal oxides based on Fe, Ni, and Co cations. Considerable progress has been made on membrane technology

Figure 3



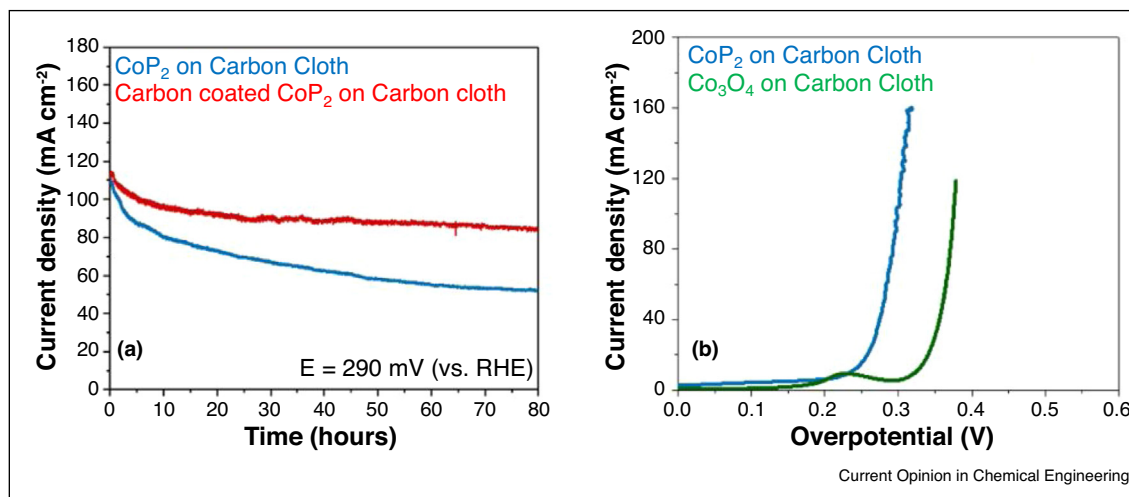
(a) Thermo-gravimetric analysis (TGA) of  $\text{CeO}_2$ ,  $\text{Fe}_{0.25}\text{Ce}_{0.75}\text{O}_2$  and  $\text{Fe}_{0.05}\text{Ce}_{0.95}\text{O}_2$ . (b) Differential of the data in (a). Hydrogen production at  $1200^\circ\text{C}$  following reduction at  $1500^\circ\text{C}$  for two hours of  $\text{CeO}_2$  and  $\text{Fe}_{0.05}\text{Ce}_{0.95}\text{O}_2$ . The indicated amounts in  $\mu\text{mol/g}$  are those of the sum of hydrogen produced.

Table 1

 Binding energy positions of XPS Ce3d lines for  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  cations in  $\text{CeO}_2$ 

Line	$V_o$	V	$V'$	$V''$	$V'''$	U	$U'$	$U''$	$U'''$
BE (eV)	881.5	883.5	886.6	888.8	899.4	902.0	904.3	908.9	917.6

Figure 4



(a) Time-dependent performance of pristine CoP<sub>2</sub>/Carbon Cloth and Carbon coated@CoP<sub>2</sub>/Carbon Cloth formed at 650°C in 1 M KOH(aq) solution for 80 hour at 0.85 V versus Ag/AgCl. (b) Polarization curves for CoP<sub>2</sub>/Carbon Cloth (650°C) and as-prepared Co<sub>3</sub>O<sub>4</sub>/Carbon Cloth at a scan rate of 0.05 mV s<sup>-1</sup> in 1 M KOH(aq) electrolyte solution. CoP<sub>2</sub> is used as the anode (oxygen evolving electrode). Figure adapted from Ref. [26].

with at present alkaline membranes working with current density of 0.5 A/cm<sup>2</sup> are commercially available [21]. Electrolysis is still a very active field of research mostly focusing on two aspects. 1. To replace Pt cathodes by less expensive and less prone to poisoning metals such as NiMo [22] (CO on Pt has an adsorption energy of about 1.5 V) [23]. The fact that Pt has a very low overpotential, the amount of energy needed to drive the reaction in addition to that required to split water, which is less than 0.1 eV, makes its replacement by less noble metals a difficult task. Yet, for large scale and wide spread application Pt availability may become the bottleneck of the process if no replacement is found. 2. The anode side where losses of 0.3 eV or more occur; this is because of the four-electron requirement for molecular oxygen to form. Among some promising materials are those based on Co cations such as CoP<sub>2</sub>. Figure 4 presents an example of CoP<sub>2</sub> electrode that has been shown active with good stability for the reaction; although the extent of oxidation is not known and it seems to have a small improvement when compared to Co oxide [24].

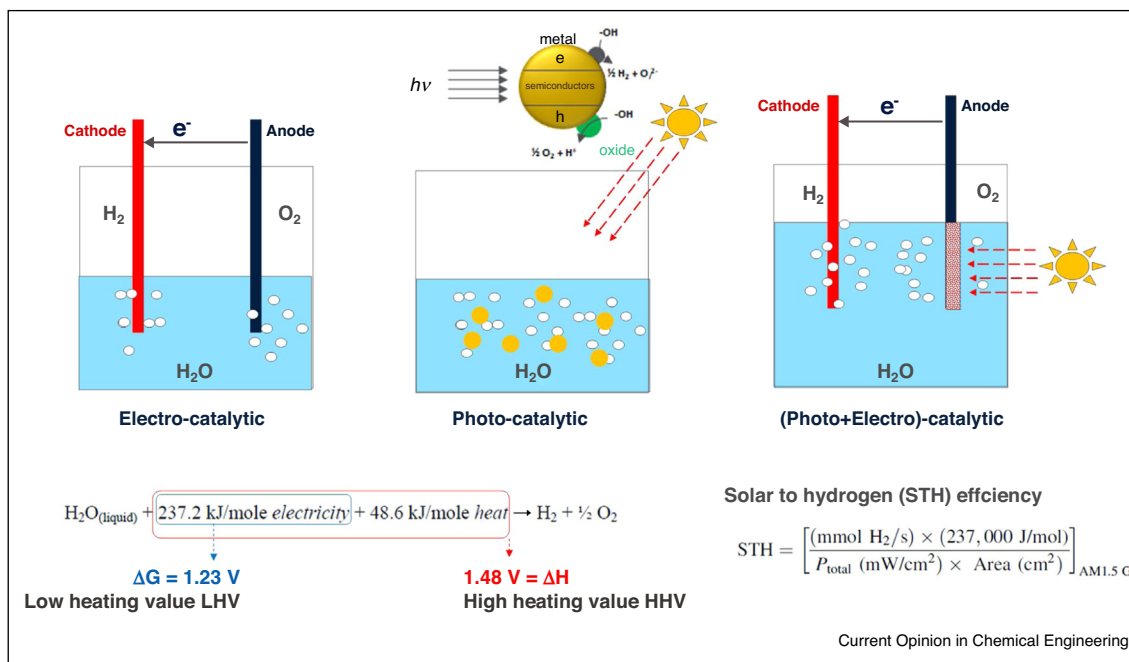
### Photocatalytic and photo-electrocatalytic water splitting

The largest fraction of work on water splitting in the last two decades up to now is on both photo-catalytic and photo-electrocatalytic systems. In that regard, one needs to make a few distinctions. First photo-electrocatalytic reactions requires a bias, such as the one used in the initial work by Fujishima and Honda in their seminal paper [25] or a connection between the anode and cathode. Second, the most important part of the reaction is at the anode side

in the case of photo-electrocatalytic reaction or in the water oxidation side on unbiased particle-based systems either dispersed or in the form of thin films. Third, light harvesting is at the essence of the photocatalytic systems. 1.23 eV (or about 1000 nm) falls in the middle of the solar spectrum. In order to harvest sun light efficiently one needs to make a photocatalyst that absorbs up to that energy (or about 50% of sun light). Since one needs two photons for each molecule of hydrogen, solar to hydrogen efficiency (defined in Figure 5) is at most 25%.

Figure 5 presents a schematic of these systems. There have been a large number of concepts involved to improve the reaction efficiency. These include, synergism of multiple phases of a semiconductor [26,27] p-n junction [28,29], Z-scheme [30,31], plasmonics [32], photonic band gap materials, [33,34] upconversion luminescence [35,36] to name a few. Because of the complexity of the reaction, researchers have focused on half of the reaction by using sacrificial agents. These include alcohols as electron donors (hole trapping) [37,38] for H<sub>2</sub>-production and metal cations as electron acceptors (electron trapping) [39,40] for O<sub>2</sub>-production. Electron donors results ultimately in the formation of CO<sub>2</sub> (a process called photo-catalytic reforming) [41] while electron acceptors are deposited on the surface of the catalyst [42], a known structure-sensitive reaction for decades [43]. Both systems while resulted in a wealth of information are different from a pure water splitting and there is now the realization that most work initially considered as water-splitting is actually a redox reaction of these organic and inorganic compounds. Economically these systems

Figure 5



Schematic description of electro-catalysis, photo-catalysis, and photo-electro-catalysis. Also shown are the low and high heating values for water splitting as well as solar to hydrogen efficiency.

are not sustainable. While some small applications might be suitable such as production of hydrogen from waste streams, they have marginal contribution into the overall energy budget. At present, there are no reproducible work for pure water splitting on suspended stable powder materials. Although reports have given 1 and 2% STH [44,45]; these even confirmed and found to be stable are 10–20 times lower than any acceptable reaction rate that can be of a practical application. Most importantly, if such a high STH is reached, it is unlikely that it will be of much value because process related issues. In order to separate  $\text{H}_2$  from  $\text{O}_2$  one needs to pressurize them but because of flammability these need to be diluted, the cost of such a process makes it unrealistic at present [46]. This has motivated researchers to separate hydrogen and oxygen from the beginning. Some work has addressed these using for example a membrane in between two types of catalysts [47,48] one for hydrogen and one for oxygen production but the use of a redox system to close each loop is found to add further complications including irreversible deposition of ions on the catalysts [49].

Activities on a different system has started almost in parallel for decades [50,51]. Largely without being noticed by the powder photocatalyst community. Researchers working on multijunction GaAs-based solar cells that have much higher efficiency; this is because they are tuned to absorb the maximum amount of light from the sun [52]. These are based on epitaxial growth of

semiconductors of different band gaps extending all the way to Ge (band gap = 0.67 eV) [53]. Like any electronic device, they cannot function in aqueous environment so most of the work has focused on stabilizing them [54\*\*]. One of their important properties is that the charge carriers' density scales linearly with the photon flux with simulation results up to 10 000 sun available [55]. Commercially systems are available with concentrations approaching 1000 sun [56].

Many of the earlier reported performance of catalysts based on these cells are conducted using photocurrent density measurements. There is an increasing realization that this can be misleading because photo-corrosion can lead to stable photocurrent and production of hydrogen [57], an increasing number of work at present shows stoichiometric hydrogen and oxygen production, for some periods. These type of systems with such a high performance dwarfs that of the suspended powder-based catalysts. Put more simply a photocatalyst is PV and electrolysis in one step, and since these multijunction solar cells are already available (as a fruit of many decades of work) understanding, using, and mimicking them would be a sensible approach. In particular, once the realization that when it comes to charge carriers transfer to make a catalytic reaction one needs a perfect medium for their propagation and this is provided by single crystals and not by particles with nano-dimension (where the high surface to bulk ratio means high number of defects). Actually,

even in thermal catalytic reactions, increasing the surface is not necessarily a good property. There are ample examples of catalytic systems, where a small surface areas are required [58]; because active sites can be structure-sensitive and increasing surface areas may lead to a decrease in selectivity. This is precisely the same thing in the case of photo-catalysis where an increase in selectivity in this case means less loss of charge carriers' density at the surface and interface. The present drawback of these cells is the generation of a large unwanted voltage for the water splitting reaction to occur (typically >3 eV at one sun for triple junctions cells); this far more than needed for one catalyst and less than the energy needed for two catalysts. Yet with the manufacturing of four-junctions, cells [59] the voltage can be increased enough to 3.5 eV or above making the use of two systems connected to one cell possible [60] This has then the potential of getting a solar to hydrogen efficiency above 35%; probably the threshold for commercialization of the complete system to hydrogen from water.

*In summary*, at present solar thermal hydrogen production suffers from a very costly and complex reactor system (light harvesting and energy transfer) and from a slow kinetics because of a reducible and stable oxide material at practical temperatures, roughly of 1000°C is yet to be found. While electro-catalysis is a mature technology, it may become competitive when electricity from renewables drops to below \$0.02/kWh. Photocatalysis on powder nanoparticles has no future for water splitting because of lack of performance and the impractical operating conditions. Multijunction solar cells either as a source of electricity to electrolyzers or as a complete standalone one step, unbiased photo-electro catalytic system, may compete with hydrogen from methane reforming once the process cost is dropped (in particular because of the cost of sun concentrators). Other alternatives to curb CO<sub>2</sub> emission, for a transitional period, would include carbon sequestration and capture methods, or by modified traditional methane reforming processes to reduce CO<sub>2</sub> formation in the entire life-cycle production [61]. Generating the needed electricity from nuclear powered plants (in off peaks for example) is also a possible alternative although building a nuclear power plant takes many years and comes with its associated chronic environmental problems.

### Conflict of interest statement

Nothing declared.

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