Photoinduced hydrogen fuel production and water decontamination technologies. Orthogonal strategies with a parallel future?

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The photochemical splitting of water into H_2 and O_2 has fascinated photochemists since the OPEC oil embargo in 1973, yet progress has been slow largely due to the challenge of oxidizing water, an energetically uphill reaction (1).[1] Much of this research has utilized solar light, semiconductor catalysis and "sacrificial electron donors" (SED); that is, molecules that facilitate H_2 evolution at the expense of the degradation of valuable chemicals. For instance, methanol splitting, where the reaction yields H_2 and CH_2O, is relatively facile, with a ΔG^0 = 64 kJ/mol compared with 238 kJ/mol for water splitting.[2-3] This approach has been criticized in a 2013 commentary that stated, "*…measuring H_2 gas formation in such a sacrificial system no longer generates any mechanistic information*.".[4] While the argument is indeed valid, it is clear that the sacrificial donor approach has helped with the understanding of the H_2 formation, half of the water splitting reaction.

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta G^0 = 238 \text{ kJ/mol or } 1.23 \text{ eV} \qquad (1)$$

Photochemical H_2 generation and water treatment fit well the useful concepts of *positive* and *negative* photocatalysis developed by Corma and Garcia;[5] these concepts separate catalysis aimed at the production of valuable chemicals (frequently organic) from catalysis aimed at water

remediation. The definition reflects the general perception that positive and negative catalysis are orthogonal, that is, photocatalytic processes are usually designed with either a positive or negative outcome in mind. We propose that in the context of H_2 generation positive and negative photocatalysis can be viewed as parallel or concurrent processes that in the future may provide simultaneous solutions to both hydrogen fuel generation and water decontamination (Figure 1).

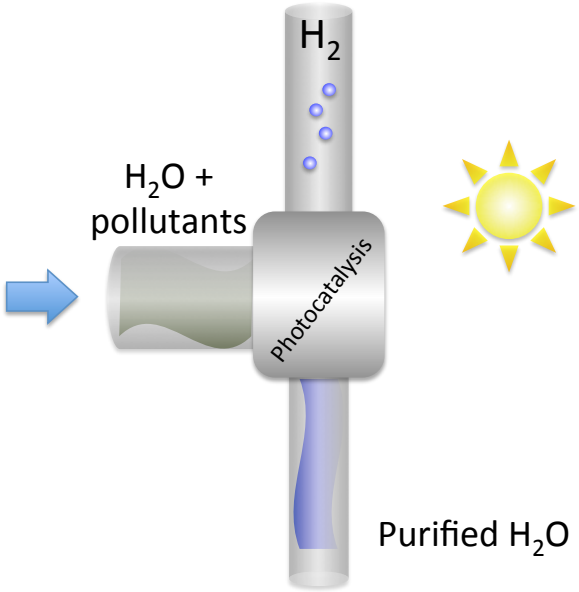

Figure 1. Hydrogen generation and pollutant remediation as coupled processes.

While the intimate understanding of the water splitting process may require pure water in the absence of any sacrificial donors, the same may not be true for the practical generation of H_2. Whereas alcohols have been the preferred choice for sacrificial donors,[6] the reality is that numerous molecules that can be easily oxidized can fulfill this role, including many of the contaminants that are present in polluted waters (Figure 2). Region-specific contaminants may add to traditional ones, such as fossil fuels, industrial discharges and the modern-age microplastic pollution, a subject of current concern.[7] Key to the performance of the mechanism of Figure 2 is the fate of the electron, which will depend on pH, oxygen availability, and the

nature and intrinsic affinity of the surface electron host,[8] all parameters that can be easily controlled.

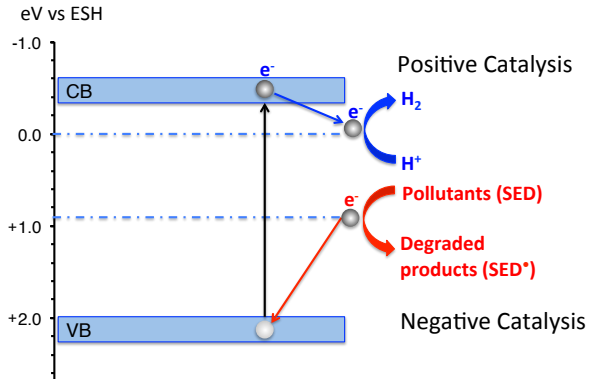

Figure 2: Hydrogen fuel production and water remediation can be coupled by using contaminants as sacrificial reducing agents. In many cases, hybrid materials incorporating surface metal or metal oxides may be the initial electron traps that also reduce electron-hole recombination rates.

In our own research with decorated TiO_2 we find that waters from regional river sources in Ontario and Quebec (Canada) generate much more hydrogen than pure water.[9] Further, addition of less valuable chemicals, such as glycerine (not shown), an abundant by-product of biofuel production, could also be employed. Preliminary results also show that the bacterial content in water is linked to the amount of H_2 generated; indeed, bacterial growth is inhibited under H_2 generation conditions.[10]

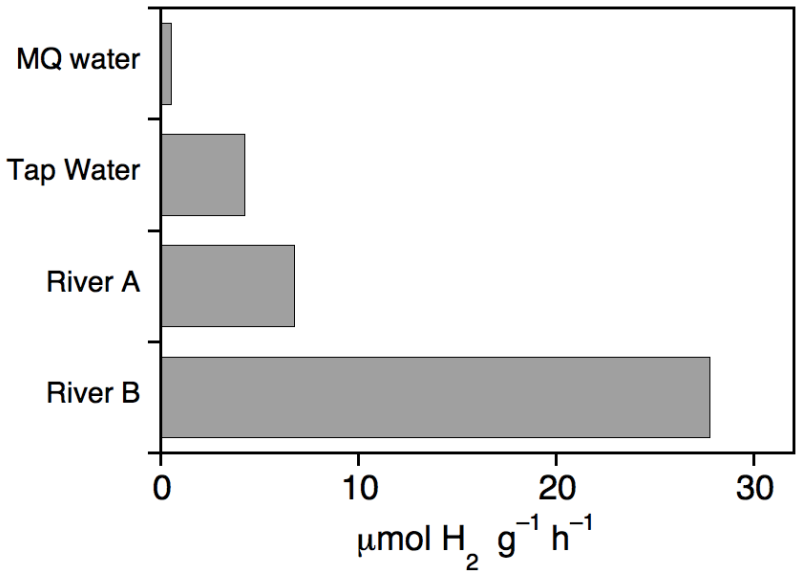

Figure 3: Hydrogen generation from different sources of water under solar simulated radiation. In this case MQ water is pure water from a Milli-Q system with 18.2 MΩ resistance. River A (Quebec) and river B (Ontario-Quebec border).

We propose a strategy in which H_2 gas generation and pollutant remediation are coupled processes (Figure 2) leading to water remediation on one side, and simultaneously to H_2 generation with higher efficiency than strict water splitting. The concomitant development of technologies that couple improved H_2 fuel production and water quality remediation using solar energy will eventually become important. Closely related, the use of wastewater in the energy field is a subject of current interest.[11] It is possible that geographical and economic realities will dictate whether H_2 generation, water remediation, or both will be initially exploited. Depending on the mode of utilization the choice of the preferred catalyst may change, reflecting the primary objective, but research on the development of photocatalysts will no doubt establish the performance and scope of individual catalysts.

We propose that parallel technologies that couple positive (H_2 generation) and negative (water quality) catalysis should be the preferred strategy and that strict water splitting, valuable for

fundamental research may not be the most practical, valuable of efficient route to hydrogen fuel generation.

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Notes

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