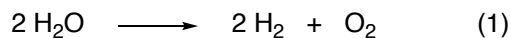


Photocatalytic Hydrogen Generation using Metal-Decorated TiO₂: Sacrificial Donors vs. True Water Splitting

The ubiquitous use of the term “water splitting” has made it virtually a synonym for hydrogen generation from water, even when sacrificial electron donors (SED) are used. Yet, the only true water splitting corresponds to the chemistry and stoichiometry of equation 1.¹



Given that hydrogen is truly a zero greenhouse gas (GHG) emissions fuel, a lot of effort has been devoted to solar water splitting mediated by a variety of photocatalysts, notably, modified TiO₂.² Unfortunately, true water splitting in the absence of sacrificial donors (that act as hole traps) and with catalysts that are not oxidized in the process is very inefficient.³ Photocatalytic hydrogen generation assisted by SED has been widely used as a surrogate for true water splitting, as hydrogen yields are much higher under these conditions. The use of SED for H₂ generation cannot be considered as water splitting, and its efficiency depends on both the catalyst and SED used. Thus, when comparing several TiO₂-based catalysts in true water splitting and in SED-assisted H₂ photogeneration, the overriding conclusion is that the knowledge acquired in one is not transferable to the other, thus putting to rest any expectation that sacrificial donors can be used to learn about true water splitting. While the SED approach has been severely criticized as it uses other valuable chemicals to generate hydrogen,⁴ we have recently proposed that water contaminants may be suitable sacrificial molecules, simultaneously making hydrogen and reducing water contaminant levels.⁵ For such strategies, the knowledge acquired through the SED-approach with a diversity of substrates is important, illustrated here with methanol and formic acid, both leading to excellent H₂ generation performance. While many forms of metal-decorated TiO₂ can be evaluated as catalysts, the discovery and eventual optimization of

catalysts that perform well with earth-abundant materials⁶ will open the path to practical applications in this field.

The use of methanol and formate as SED has been commonly explored;⁷⁻⁸ in both cases the radicals produced following hole trapping ($\cdot\text{CH}_2\text{OH}$ and $\cdot\text{CO}_2^-$) are themselves excellent electron donors. This leads to enhanced yields, sometimes described as a “doubling” effect.^{4,9} It has been frequently assumed that the H_2 generation, half of the water splitting reaction, is much the same whether just water or SED are used, as illustrated graphically in Figure 1a. Unfortunately, this is not quite true, as the cycle for H_2 generation involves the trapping of the photogenerated hole and subsequent reactions of the SED-derived radicals formed, and therefore the efficiency of hydrogen generation with SEDs such as methanol, simply reflects methanol splitting, Figure 1b. Indeed, experiments suggest hole lifetimes are strongly influenced by SED¹⁰ and that H_2 is generated by the reduction of two protons originating from both water and the SED.¹¹ This has led to severe criticism of the use of SED to study water splitting as the value of the information acquired and its significance in the understanding of water splitting becomes questionable.⁴

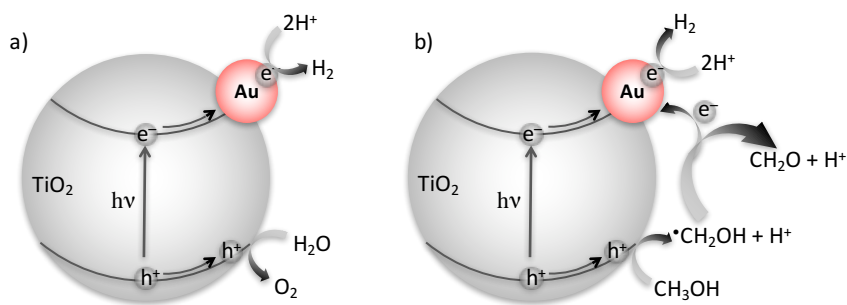


Figure 1. (a) Water splitting and (b) Methanol splitting upon UV excitation, illustrated for Au@TiO_2

While we agree with the questionable value of sacrificial donor strategies that result in the consumption of valuable chemicals, we have proposed that if common water contaminants, such as organic matter in river water can be the SED, then photocatalytic solar exposure could generate hydrogen while destroying pollutants, including bacterial water contaminants.⁵ While hoping that reported data on water splitting catalysts will be useful, several questions should be addressed: Is the knowledge acquired in true water splitting and in SED-mediated hydrogen production interchangeable? In other words, is catalyst performance in both processes correlated? Is the best catalyst for hydrogen generation from water splitting, also the best when SEDs are used? Finding an answer to these questions is the central subject of this viewpoint. Direct solar H₂ generation may pose major engineering challenges and while we acknowledge this issue, it is not an aspect discussed in this viewpoint.¹²⁻¹³

In order to compare H₂ generation in the presence and absence of SED, seven TiO₂-based catalysts were examined under conditions of solar simulation (AM 1.5) or under 368 nm LED irradiation. Some of these catalysts were already described by our group as photocatalysts for different organic transformations.¹⁴⁻¹⁶ We established unequivocally that with all catalysts the rate of production of hydrogen using SEDs exceeded that under conditions of true water splitting. In order to establish to what extent we could distinguish the efficiency of SED and non-SED systems, we first tested one of the catalysts, Cu@TiO₂, in the presence of variable concentrations of the two selected SED, formic acid and methanol. We noted that for this particular catalyst formic acid is more efficient for H₂ generation than methanol, as expected.¹⁷ Indeed, pH effect and counter ion (Cl⁻) interference were ruled out as part of the higher efficiency denoted by formic acid (Table S2).

The use of a 368 nm LED as irradiation source can help to establish the relative performance under SED vs. non-SED conditions. The rationale behind this choice includes the fact that all catalysts have a single dominant absorber in the UV region, i.e., TiO₂, thus ensuring that the data for various systems are readily comparable. Notice that the presence of formic acid in the solution does not change the optical properties of the TiO₂ suspension (See SI). Thus, no charge-transfer complexes are formed between the SED selected and the semiconductor (many molecules do)¹⁸ and the mechanism under study can be considered to reflect the true photocatalytic activity of TiO₂.¹⁹ Notably, results using solar illumination show basically the same tendency described below (See SI). We note that in our nomenclature we always refer to metal@TiO₂, however in many of these systems the nanostructure can easily be oxidized (see XPS analysis in the SI for further details).

Additionally, at relatively high SED concentration the H₂ generation is linear with time, showing that at least in this time scale the photocatalyst performance does not deteriorate (Figure 2) in contrast at very low SED the plot shows curvature, as anticipated when reagents gradually deplete. Note that this curvature does not reflect catalyst deterioration, but rather a dramatic reduction in SED concentration, a desirable feature for applications in water decontamination.

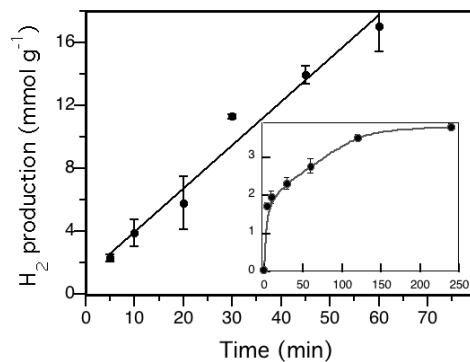


Figure 2: Kinetic plot for the generation of H₂ under 368 nm irradiation for 1% (main plot) and 0.01% (inset) formic acid SED using as catalysts Pd@TiO₂ (main plot) and Pt@TiO₂ (inset).

Figure 3 shows the rates of H₂ generation for the seven systems examined. Similar experiments in the absence (Figure 3A) or presence of SED (Figure 3B-C) show about two orders of magnitude larger efficiencies than true water splitting conditions as expected. The values in Figure 3A are significantly lower than the rates of H₂ generation in this spectral region (300-400 nm) found for gold nanoplate on multilayer graphene, to date one of the most efficient photocatalysts for “true water splitting” with rates up to 1.2 mol H₂/g h.²⁰

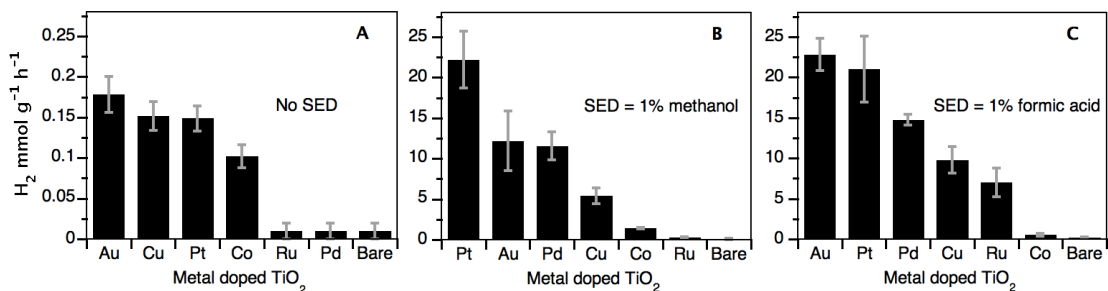


Figure 3: H₂ generation rates by different catalysts tested using 368 nm irradiation (0.33 Wcm⁻²) for (A) true water splitting conditions (rates for Ru@TiO₂, Pd@TiO₂ and pure TiO₂ are zero within experimental error), (B) in the presence of 1% of methanol and (C) in the presence of 1% of formic acid (pH ~ 2.2). Note scale for panel A is expanded x100 relative to panels B and C.

Notice in Figure 3 the catalysts are arranged in their order of performance, and while the order in panels B and C is not identical, their bear a strong resemblance. In contrast, the order for true water splitting (Figure 3A) is quite different. In other words, using Figure 3B-C it would be impossible to predict the catalytic performance in true water splitting shown in Figure 3A. Additionally, the relative increases in H₂ production rates are illustrated in Figure 4 and range

from 5-to-130, thus, while SED bring a major increase in H₂ generation, it is clear that these increases are extremely different depending on the catalyst used. Note that Ru@TiO₂ is such a poor performer that the ratio has large uncertainty and the errors are hard to estimate (See also Figures 3). For the top performers, Au, Pd and Pt the effect of 1% SED is almost the same for methanol or formic acid, suggesting that at least for the examples examined, SED-assisted performance may be rather insensitive to the specific donor used, a desirable characteristic for applications in water treatment. Naturally this may not apply to electron-poor contaminants or to molecules (such as indoles) that associate with the TiO₂ surface.¹⁸ Thus, knowledge about catalytic performance in true water splitting and SED-assisted systems is simply not transferable.

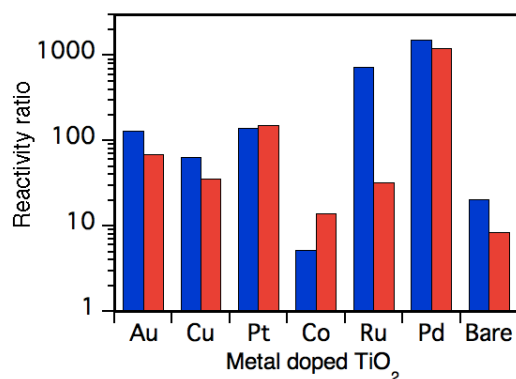


Figure 4: Relative rate for H₂ production (H₂ generation when a SED is used, relative to the data for true water splitting (i.e., Figure 3A)) in the presence and absence of 1% SED, for formic acid (blue) and methanol (red). The semi logarithmic scale used facilitates the comparison of extremely different systems such as Co and Pd.

The fact that SED-assisted hydrogen generation does not track true-water splitting is perhaps a simple reflection that electron and hole behavior are not independent and thus trying to influence one half of the water splitting reaction provides limited information. On the other hand, hydrogen generation using SEDs can be two orders of magnitude more efficient than true water splitting.

Rather than dismiss SED use as irrelevant, perhaps the key resides in finding SEDs with zero value; in the case of water contaminants one could argue that in fact they have a negative value, as their destruction enhances the uses and value of the waters that contain them. If contaminant-assisted H₂ generation has a future, then catalysts must be optimized, be robust (i.e., durable), must make use of the visible spectral region and ideally be able to perform in flow systems. Clearly challenging, but not insurmountable problems.

In conclusion, this viewpoint demonstrates the validity of SED utilization for the parallel objectives of water purification and hydrogen fuel formation with results that concentrate on the latter. Although catalysts are not optimized, it is nice to see that an earth-abundant element such as Cu@TiO₂ shows a competitive performance with other catalysts that utilize some of the scarce elements in the earth's crust.^{6, 21} Implementation of these technologies would require catalyst optimization including good performance in the visible region, where solar light is about ten times more abundant than in the UV region. Our results establish unequivocally that knowledge about performance in true water splitting and in SED-assisted systems is simply not transferable. At the same time, the fact that the performances with formic acid or methanol are similar (Figure 4) gives us hope that one will be able to build a generalized paradigm for a diversity of SED molecules, hopefully including those that are common water contaminants.

Developing SED-assisted processes requires a good understanding of the free radical chemistry that evolves from hole trapping that can lead to “doubling” processes as they relate to hydrogen formation or electrochemical performance.^{4, 9, 11}

Further, while a batch approach may be useful for hydrogen generation, it would be desirable to develop fixed-bed catalysts, more suited to solar flow photochemistry as will be required in

water purification applications. Performance, durability, cost and toxicity all will need to be considered in the development of catalysts that can truly make a difference in both the energy and potable water fields.

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ASSOCIATED CONTENT

Supporting Information. Details of materials and instruments, synthesis and composition of metal-decorated TiO₂, details of photoinduced hydrogen generation and H₂ detection, performance details, TEM images and diffuse reflectance and XPS data. The Supporting Information is available free of charge on the ACS Publications website.

NOTES

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

The authors declare no competing financial interest.

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