Sonochemical Hydrogen Production as a Potential Interference in Light-Driven Hydrogen Evolution Catalysis

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ABSTRACT: The use of sonication to dissolve or disperse solids in solvents is a common practice in catalytic studies. However, the frequency and power of commercial ultrasonic baths are within the right range to trigger unwanted sonochemical reactions that can be a source of interference. Based on our own experience, we have noted that sonication used to disperse heterogeneous photocatalysts in water—alcohol mixtures as the first step in light-driven hydrogen evolution can lead to hydrogen evolution, which is not related to any photochemical or photocatalytic process. Furthermore, “dark” hydrogen evolution continues even when sonication is stopped, which can cause significant problems for time-dependent studies. To the best of our knowledge, this phenomenon has not been described as a potential issue for light-driven hydrogen evolution studies, and it should, therefore, be brought to the attention of the energy conversion research community to avoid errors in ongoing and future hydrogen evolution studies.

INTRODUCTION

Photocatalytic water-splitting into H\textsubscript{2} and O\textsubscript{2} is a key technology for sustainable energy schemes. Current research is targeting both homogeneous and heterogeneous systems for the water-splitting reactions. In particular, photocatalytic water-splitting using heterogeneous catalysts holds great technological promise as it allows facile recovery and separation of the catalyst. A prime example is the TiO\textsubscript{2}-based water photolysis using UV light, which can simply be triggered by irradiation of an aqueous solution of TiO\textsubscript{2} particles.\textsuperscript{1} This discovery triggered an explosion in material development, and a wide range of heterogeneous semiconductors have been explored for the photochemical water-splitting reaction.\textsuperscript{2–5} For sunlight-driven full water-splitting, the semiconductor band gap needs to (a) be within the energy range of visible light and (b) feature more positive valence band edge redox potentials than the oxygen-evolution reaction (OER) \(E^0 = 1.23\ \text{V vs normal hydrogen electrode (NHE)}\) and more negative conduction band edge redox potentials than the hydrogen evolution reaction (HER) \(E^0 = 0\ \text{V vs NHE}\). As these requirements are not always met by new semiconductor materials, many studies first explore one half-reaction of the water-splitting process using a sacrificial electron donor or acceptor as a substitute for the second half-reaction. In the case of the HER, the sacrificial agent is often an alcohol such as methanol, ethanol, or glycerol. For homogeneous irradiation and reproducible results, the heterogeneous catalyst particles have to be well dispersed in the catalytic mixture, and sonication is a simple means of dispersing and de-aggregating nanoparticulate semiconductor catalyst particles. However, under sonication, cavitations within the solvent \(i.e.,\) the formation and collapse of gas bubbles) introduce significant amounts of energy into the system. This can even lead to the breaking of C–H or O–H bonds and give rise to the formation of hydrogen.\textsuperscript{5,7} This phenomenon has been explored for the sonolysis of pure water saturated with argon: spin-trapping experiments and product analysis\textsuperscript{8} have identified the formation of H\textsuperscript{*} and OH\textsuperscript{*} radicals by homolytic O–H bond cleavage. Recombination of these radicals leads to the formation of H\textsubscript{2}O, H\textsubscript{2}, and H\textsubscript{2}O\textsubscript{2}. While sonochemical reactions proceed to a very low extent in pure alcohol compared to aqueous solutions, water–alcohol mixtures have been observed to give sonochemical H\textsubscript{2} yields remarkably higher compared to pure water.\textsuperscript{9,10} To the best of our knowledge, this phenomenon has not been explored in the context of heterogeneous light-driven HER; however, based on earlier studies in sonochemistry, we note that changes of the solvent and sonication conditions can significantly affect the amounts of hydrogen evolved. The resulting challenges for catalytic studies and their reproducibility are further compounded by the fact that the operating power and sonication frequency of the ultrasonic baths vary greatly from lab to lab, as does the sonication time. Here, we set out to explore these phenomena in the context of light-driven heterogeneous hydrogen evolution after noticing the formation of hydrogen as a result of sonication in the course of our ongoing studies of materials for photocatalytic hydrogen evolution. We conducted experiments under conditions used typically in this research...
field and varied key parameters relating to the sonication process. This allows us to provide the first systematic overview of the consequences of sonication on the noncatalytic, sonication-induced hydrogen evolution under typical heterogeneous light-driven HER conditions. We believe that raising awareness of this potential experimental problem is important in a field that grows at a fast pace and attracts large numbers of new research groups. Our report, therefore, follows several other recent studies that emphasize the need for rigorous analysis when reporting new catalytic results.11–15

■ RESULTS AND DISCUSSION

The current report is based on our observation of irreproducible hydrogen evolution data during screening studies of heterogeneous metal oxide semiconductor HER studies. We noted that during sample preparation, our samples were sonicated for a few minutes in deaerated H2O/alcohol (8:2, v/v) (alcohol = ethanol or methanol) to ensure homogeneous dispersion. While analyzing the possible sources of error, we performed a blank reference experiment where the pure, catalyst-free solvent was sonicated (but not irradiated), and we observed the formation of hydrogen by headspace gas chromatography. We followed the hydrogen evolution of this sample over time, leading to the H2 evolution curve shown in Figure 1.

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c03110)

**Figure 1.** Hydrogen evolution over time for a H2O/EtOH (8:2, v/v) mixture sonicated for 5 min after taking the first reading at \( t = 0 \) h. The mixture was vigorously stirred throughout the experiment.

After ruling out any other source of hydrogen (e.g., glassware contamination, GC malfunction, etc.), the only remaining explanation was that H2 is formed by sonication. This was supported by literature analysis, which showed that there are a few reports discussing the phenomenon; however, there are no systematic studies of the amounts of hydrogen produced depending on the sonication conditions. However, this type of information is critical to inform future experiment planning in the HER community.

Next, we explored the principal factors that affect H2 formation under sonication to give other research groups a better understanding of how these factors might affect their HER activity (and unexpected changes thereof). This is based on literature analysis of the factors that affect cavitation formation; these include ultrasonic frequency, dissolved gas, acoustic power, and temperature as well as solution volume, vessel shape and vessel material, and position of the vessel in the sonication bath.16,17 As shown in Figure 2, a simple change of the Schlenk flask position from the center to the corner of the sonication bath results in significant H2 evolution changes. We have used Margulis and Mal’tsev’s calorimetric method18,19 as described in the literature to estimate the acoustic power that gets dissipated during sonication in both positions, observing a sharper increase in temperature during the first minutes of sonication in the flask positioned in the center compared to that in the corner. This is reflected in the estimated acoustic power values of ca. 2800 and ca. 1250 mW, respectively (280 and 125 mW/cm²), which explain the difference in the amount of hydrogen produced. Next, we tried to reproduce hydrogen evolution by sonication by replicating the identical experiment four times using our standard experimental setup (10 mL of H2O/MeOH (8:2, v/v), identical Schlenk flask in the center of the bath, sonication time 5 min, not stirred after sonication).

As shown in **Figure S1**, the four experimental runs show significant deviations in terms of quantitative hydrogen evolution and can essentially be considered irreproducible. This is in line with previous studies by Christman et al. who highlighted that cavitation is a difficult phenomenon to quantify, as the observed results are combinations of “random” events, so that reproducibility is simply unattainable.6 Note that **Figure S1** represents the range of typical values obtained for this experiment type; however, identical experiments sometimes led to significantly lower or higher amounts of H2; see **Figure S2**. We also note that even sonication times as low as 1 min lead to observable hydrogen formation. Thus, this phenomenon seems virtually ubiquitous for sonicated samples containing water–alcohol mixtures, highlighting that much care is needed when studying the performance of catalytic hydrogen evolution. This is of particular importance when
small amounts of catalyst are used or when the catalyst is not showing high performance, while it becomes less problematic if larger catalyst amounts are used or if the catalyst produces high amounts of H₂.

A second key factor for hydrogen evolution by sonication is the solvent composition and the type of alcohol used. To this end, we explored how five commonly used alcohols20,21 (methanol, ethanol, 2-propanol, ethylene glycol, and glycerol) will affect hydrogen evolution under otherwise identical reaction conditions (H₂O/alcohol (8:2, v/v), identical Schlenk flask in the center of the bath, sonication time 5 min, not stirred after sonication). Our results are summarized in Figure 3 and show the H₂ formation order MeOH > EtOH > 2-
propanol > ethylene glycol ≈ glycerol. This is in line with previous studies, which report that the major contributing factors are surface tension22 and viscosity,23 as they affect the ability to form bubbles during the cavitation process. In addition, heat capacity and volatility of the solvent affect the maximum temperature reached inside of the cavitation bubbles10,24. Note that this sonolytic hydrogen evolution capacity is different to photochemical HER formation depending on different types of alcohol, where completely different orders of reactivity were reported.20,21 This could of course lead to dramatic changes in data interpretation depending on the expected versus real mechanism of HER.

We have mentioned several times that we note an increase of hydrogen concentration in the headspace of the reaction vessel even after sonication has finished; see also Figures 1–3. In more detail, we have noted that if the mixture is stirred after sonication, the amount of hydrogen in the headspace increases quickly and stabilizes after ~2 h (Figures 1 and 2). When the mixtures are not stirred, the hydrogen concentration in the gas phase increases at much smaller rates and follows a linear trend, which does not reach a plateau even after 7 h (Figures S1–S3). To the best of our knowledge, this “delayed sonication effect” has not been reported yet. Based on our initial experiments, we suggest that this is due to slow (without stirring) or fast (with stirring) diffusion of hydrogen from the liquid to the gas phase.

Finally, we explored how to overcome this undesired hydrogen evolution by sonication, as we believe that the
amounts produced are so irreproducible that a baseline correction using reference values is virtually impossible. One viable route is to bubble argon through the catalytic mixtures after the sonication step, as some researchers are already doing.25,26 We note that this is possible under our conditions, and 15 min vigorous Ar bubbling (for 10 mL of solvent after 5 min sonication) removes the hydrogen present.

## CONCLUSIONS

In summary, we report the unexpected formation of hydrogen by sonication of catalytic test reactions containing water–alcohol mixtures. This leads to “false positive” data or contributes to experimental errors in determining the actual catalytic performance. We demonstrate the main factors, which affect the amounts and rates of hydrogen production, and we show that hydrogen is still released from the liquid—presumably by diffusion—for hours after the sonication has stopped. Finally, we propose a degassing protocol that allows sample sonication while removing the hydrogen formed from the reaction mixtures. This report therefore raises awareness for undesired, noncatalytic hydrogen formation by sonication under conditions that are often employed for heterogeneous light-driven hydrogen evolution catalysis.

## EXPERIMENTAL SECTION

### Experimental Remarks.

Reagents: Methanol 99.9% was obtained from Across Organics, ethanol 99.5% and isopropanol 98% were obtained from VWR, glycerol 86.5% was obtained from Omikron, and ethylene glycol 98% was obtained from Roth.

Water and alcohols were thoroughly deaerated by Ar bubbling before mixing them. Alcohol–water mixtures (10 ml) were prepared in Schlenk flasks under an Ar atmosphere using a Schlenk line.

Hydrogen in the headspace was quantified using gas chromatography, the headspace volume of the Schlenk flasks being 10.5 mL.

Gas chromatography was performed on a Bruker Scion GC/MS, with a thermal conductivity detector 15 (column: molecular sieve SA, 75 m × 0.53 mm; oven temperature 70 °C; flow rate 25 mL/min; detector temperature 200 °C) with argon as a carrier gas. Calibration was performed by direct injection of known amounts of H₂ gas.

The ultrasonic bath used was a USC 600 TH from VWR (frequency 45 kHz).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03110.

Hydrogen evolution for four experimental runs of our standard experimental setup (10 mL of H₂O/MeOH (8:2, v/v), identical Schlenk flask in the center of the bath, sonication time 5 min, not stirred after sonication) (Figure S1); sample of unusually high hydrogen evolution data for the same experimental setup as S1 (Figure S2); hydrogen evolution depending on the position of the flask in the ultrasonic bath when the mixture is not stirred (Figure S3) (PDF)
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**Author Contributions**
All authors conceived the experiments. I.R. carried out the experimental studies. The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript.

**Notes**
The authors declare no competing financial interest.

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