Hydrogen evolution from a spurious source

The prospect of green hydrogen (H_2) as a sustainable fuel has sparked intense research in electrocatalytic and photocatalytic methods for H_2 production. To qualify as a sustainable fuel, evolved H_2 should ideally emanate from catalytic splitting of water (or another abundant non-fossil fuel source) rather than from the breakdown of a sacrificial agent. Therefore, in complex reaction media, the source of H_2 evolution must be unambiguously identified for the research to be meaningful and impactful for energy generation. Here, we report how H_2 can emanate from a spurious source, which could give researchers the mistaken impression of successful green H_2 production.

In our recent studies of photochemical H_2 production using molybdenum oxide nanostructures, a control experiment performed in the absence of the photocatalyst produced H_2 in yields similar to experiments performed with the photocatalyst. In our quest to track down the source of the H_2, we found that merely nanopure water heated to 70 °C in a clean vial produced H_2. We ultimately traced this H_2 evolution to stir bars (VWR Spinbar, flea micro, 0.315" × 0.118", Product No: 76001-878) used for mixing in these experiments. We ruled out contamination of the stir bar because we thoroughly wash stir bars prior to use to remove any metal contaminants. Because contaminants stuck to the surface and inside cracks in the Teflon coating of the stir bar cannot be thoroughly removed by washing,[1–4] we wash stir bars in aqua regia—a mixture of nitric and hydrochloric acid—to dissolve away any metal contaminants, which is a common practice in the field.[4] Taking this step into account raised our suspicion that aqua-regia-washed stir bars may be the source of the spurious H_2 evolution. To test this hypothesis, we used a new stir bar with no aqua regia washing. No H_2 production was observed. This implicated aqua regia washing.

Examination of stir bars by optical microscopy (Fig. 1) showed the presence of cracks in the Teflon-coating, which was the case even for a new stir bar (Fig. 1b). These small cracks can allow acidic solution to seep into the core of the stir bar during aqua regia washing (Fig. 1a). The acid can react with iron (Fe) in the magnetic Alnico alloy core of the stir bar to produce H_2:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

$$2Fe + 6H^+ \rightarrow 2Fe^{3+} + 3H_2$$

$$Fe + H_2O \rightarrow FeO + H_2$$

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 3H_2$$

We separately confirmed that Fe powder can indeed react with an acidic solution, e.g., 0.1 M H_2SO_4, to result in H_2 evolution (Fig. 2). While these reactions involve water oxidation, they are not catalytic and involve stoichiometric consumption of Fe and acid. Although we rinse the stir bars thoroughly with water prior to use in a photocatalytic experiment, the acid may remain trapped inside the small cracks and continue to react with Fe in the core over time, releasing H_2 and causing the cracks to enlarge.

The aforementioned processes were visualized through optical microscopy: after washing of a new, i.e., previously unused, stir bar with aqua regia and rinsing with water, small yellow

droplets were observed near the cracks in the stir bar (Fig. 1c). Even upon further rinsing in water, the droplets persisted and even grew over time. While we do not know the identity of the droplets, they demonstrate a reaction occurs below the subsurface of the coating leading to material leaching out of the cracks. After a day (Fig. 1d), rust-colored patches were observed along the surface of the stir bar, which we suspect is a mixture of iron oxides and salts left over from the reaction of the acid with the Fe-containing core.

To further examine the conditions that lead to spurious H_2 evolution, we evaluated H_2 generated from new and aqua-regia-washed stir bars in aqueous solutions of acidic, neutral, and basic pH (Fig. 2). With new stir bars, no H_2 evolution was observed even in 0.1 M H_2SO4. However, exposure of stir bars to the extremely acidic conditions extant in aqua regia washing was sufficient to induce appreciable H_2 evolution even when the stir bar was removed from acidic conditions. The stir bars used in these experiments had not been used before; but since use is known to cause damage,[1,2] we expect that a well-used stir bar washed in aqua regia prior to experiments could evolve even higher levels of H_2.

Researchers studying photocatalytic and electrocatalytic methods of H_2 production must perform proper control experiments and/or accounting of mass balance to ensure that H_2 observed is not from a spurious source or contamination. As reported here, even something as innocuous as a stir bar, despite having been cleaned to remove trace metal contaminants, can lead to H_2 evolution, which could be easily mistaken for catalytic water splitting. Deuterium labeling, i.e., replacing H_2O with D_2O, would be insufficient to rule out that the evolved H_2 is from the reaction of Fe and residual acid. This is because of the exchange of deuterons of D_2O with protons of the acid. Secondly, Fe could react under acidic conditions with deuterons of D_2O to generate D_2, which could be misattributed to D_2O splitting. To avoid spurious H_2 evolution of the kind reported in our study, we recommend that researchers use new stir bars cleaned with mild solvents or use borosilicate stir bars, if aqua regia washing is indispensable.

More generally, we underscore a need for greater transparency in reports and publications about the source of H_2 production: H_2 production by the catalytic splitting of water is a fuel-forming process, whereas H_2 production by dehydrogenation of a substrate, such as formic acid or ethanol, is a sacrificial process. Increased care and transparency about the true source of H_2 evolution can improve the reliability and impact of research in this field.

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Figures

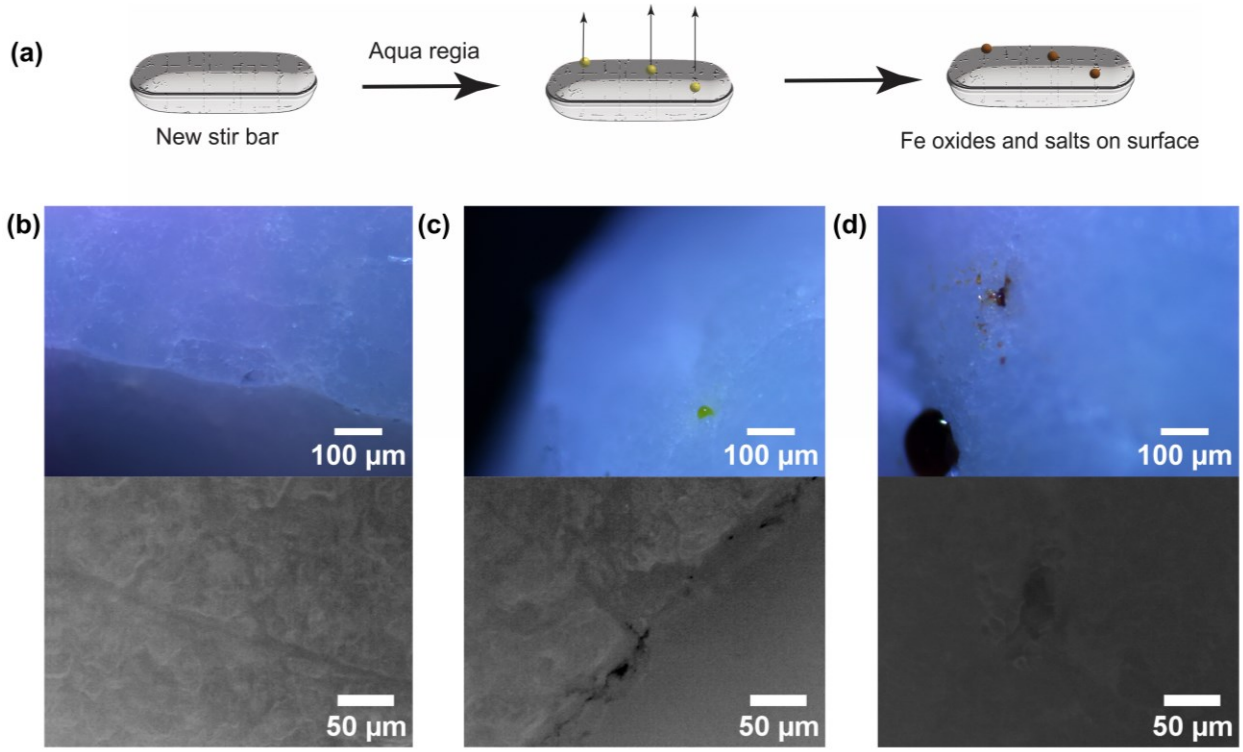

Figure 1. (a) Graphical scheme of the processes leading to spurious H_2 evolution from stir bars washed with aqua regia. (b–d) Selected optical microscopy images collected at 4× magnification on (top row) and at 10× magnification (bottom row) of a previously unused stir bar (b) before, (c) immediately after, and (d) at least 24 h after washing in 4 mL of aqua regia. For the top row images, the stir bar (VWR Spinbar, flea micro, 0.315" × 0.118", Product No: 76001-878) was placed on a glass slide (VWR Micro Slides, 25 × 75 mm, 1 mm thick, Product No: 48300-026) and imaged on an Ecoline D-EL2 digital microscope. For the bottom row images, the stir bar (VWR Spinbar, flea micro, 0.315" × 0.118", Product No: 76001-878) was placed on a glass coverslip (VWR Micro Cover Glass, 24 × 60 mm, 0.13 to 0.17 mm thick, Product No: 48404-455) and imaged on an Olympus IX51 microscope.

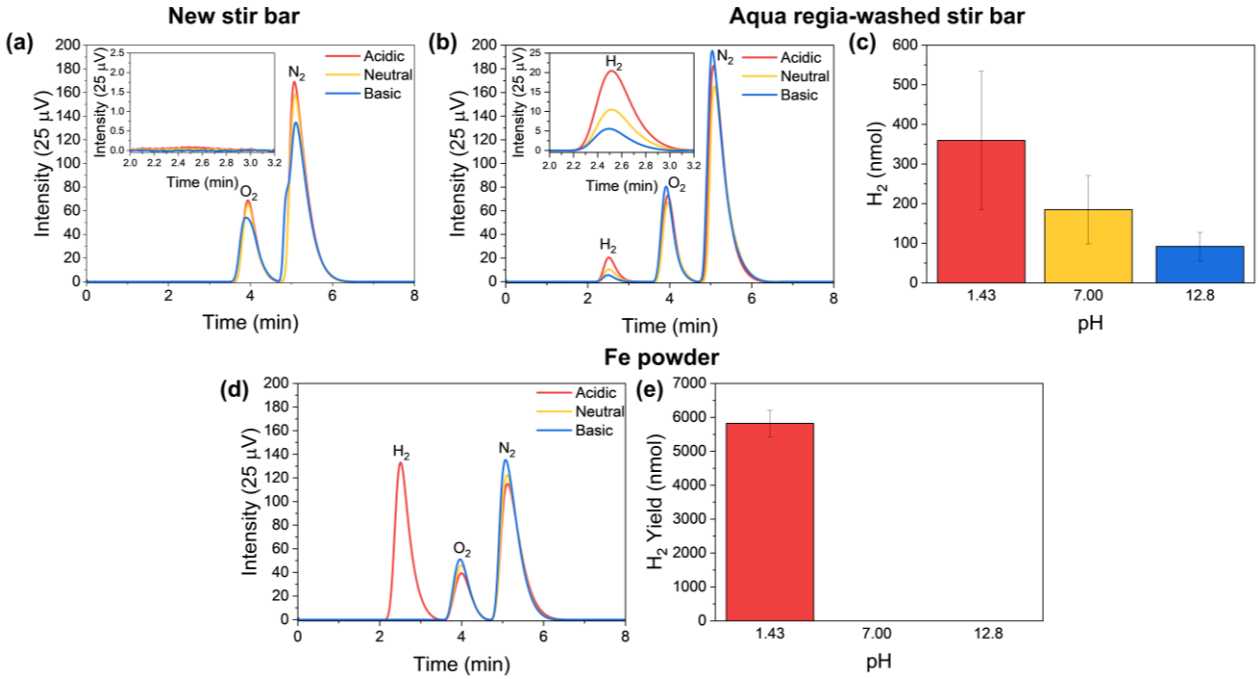

Figure 2. (a) GC–TCD chromatograms showing no H_2 production from new stir bars submerged in 3 mL of an aqueous solution at acidic (pH = 1.43), neutral (pH = 7.0), or basic conditions (pH = 12.8) in a sealed, 5 mL vial, which was heated to a temperature of 70.1 °C and maintained there for 2 h. (b) GC chromatograms and (c) corresponding bar plots of the molar amount of H_2 produced with stir bars washed in aqua regia overnight and then submerged in 3 mL of an aqueous solution at acidic (pH = 1.43), neutral (pH = 7.0), or basic conditions (pH = 12.8) in a sealed, 5 mL vial, which was heated to a temperature of 70.1 °C and maintained there for 2 h. (d) GC chromatograms and (e) corresponding bar plots of the molar amount of H_2 produced when 50 mg of Fe powder is exposed to a drop of water for a few seconds followed by the addition of 1 mL of an aqueous solution at acidic (pH = 1.43), neutral (pH = 7.0), or basic conditions (pH = 12.8) and left at room temperature for 20 min in a sealed, 5 mL vial. Acidic conditions were achieved using 0.1 M H_2SO_4 and basic conditions were achieved using 0.1 M NaOH. In each case, 300 µL of the vial headspace was extracted and subjected to GC–TCD analysis. Each chromatogram presented here is an average of chromatograms from three equivalent trials with three stir bars (a–b) or Fe powder (d). All chromatograms were subjected to a baseline correction prior to averaging. Peaks corresponding to H_2, O_2, and N_2 are labeled. Insets of (a) and (b) highlight the H_2 peak region of the chromatograms. Each data point in the bar graph is a mean of measured values from three trials; the error bar represents the standard error.