



## Photocatalysis: HI-time for perovskites

Vesborg, Peter Christian Kjærsgaard

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PHOTOCATALYSIS: HI-time for perovskites

Organolead halide perovskite solar absorbers demonstrate high photovoltaic efficiencies but they are notorious for their intolerance to water. Now, methylammonium lead iodide perovskites are used to harvest solar energy - in water - via photocatalytic generation of hydrogen from solutions of hydriodic acid.

Peter C. K. Vesborg

The class of photoabsorbers based on organometal halide perovskites has seen the fastest efficiency rise of any photovoltaic technology, increasing from 3.8% in 2009<sup>1</sup> to more than 20% by 2015<sup>2</sup>. The success of this new class of solar absorber, which can be obtained using even simple liquid-phase synthesis, is owed to the material's remarkably good electronic properties<sup>3</sup>. Another distinct advantage, which the new perovskite absorbers share with silicon, is that they typically rely only on highly scalable chemicals, making implementation at the terawatt scale possible, in principle<sup>4</sup>. On the other hand, while the lead content and the slightly too high bandgap of the organo-lead-halide perovskites are probably manageable technological drawbacks, the more serious problem is the lack of stability in real-world photovoltaic application; the materials are sensitive to moisture, heat and perhaps even to illumination<sup>5</sup>. Now, writing in *Nature Energy*, Ki Tae Nam and colleagues at the Seoul National University show that hydrogen can be photocatalytically generated from aqueous solutions of hydriodic acid (HI) solution using methylammonium lead iodide perovskites (MAPbI<sub>3</sub>), providing an alternative approach to exploit perovskites' interactions with solar energy<sup>6</sup>.

The very first organolead halide perovskite solar cells operated in a liquid electrolyte (acetonitrile)<sup>1</sup> in a dye-sensitised-solar-cell (DSSC<sup>7</sup>) architecture, but given the near-instant ruinous effect of water on the perovskites, an analogous system based on an aqueous electrolyte would seem to be out of the question. While it is possible that the stability problems can be solved for photovoltaic applications<sup>8</sup>

the “wet” approach taken by Nam and colleagues represents a refreshing and counterintuitive way to put the new perovskite absorbers to work harvesting energy. Instead of eliminating moisture, the researchers put the perovskite into water, namely, into highly corrosive hydriodic acid solution. In this approach, the aqueous solution is saturated with the MAPbI<sub>3</sub> absorber, and the concentration of iodine ions and pH is tuned to enable a dynamic equilibrium between the dissolved species and the MAPbI<sub>3</sub> precipitate, which absorbs light and drives energetically-uphill redox reactions (Figure 1). In some respects, this approach is analogous to the “CoPI” family of dynamic oxygen evolution catalysts, where the active phase is not insoluble in the electrolyte, but dynamically exchanges species with the solution<sup>9</sup>.

**Comment [JG1]:** We tend to avoid Latin terms where possible to make the pieces easier to follow.

In the approach demonstrated by Nam and colleagues, the solar energy is harvested in the form of storable energetic chemicals (H<sub>2</sub> and I<sub>3</sub><sup>-</sup>) - as opposed to electricity in the photovoltaic approach. This is of course not a completely new idea, but rather a perovskite-based version of photocatalytic solar harvesting. For example, Texas Instruments did something very similar in 1981, splitting HBr to H<sub>2</sub> and Br<sub>2</sub> using solar excitation of silicon beads<sup>10</sup>. Such a strategy may be used to charge a flow battery (e.g. a H<sub>2</sub>/Br<sub>2</sub> flow battery) where the solar harvesting and the energy storage are truly integrated<sup>11</sup>. In this case, sunlight would “charge” the system during the day via the reaction  $2\text{HBr} \rightarrow \text{H}_2 + \text{Br}_2$  and a fuel cell running the reverse reaction would provide power after sundown, discharging the system. The approach by Nam and colleagues could perhaps also be used to drive some value-added chemistry such as solar-driven reduction of CO<sub>2</sub> to feedstocks, fuels or chemicals<sup>12</sup>.

In any case, the specifics of the system used by the researchers – HI splitting in a HI electrolyte – are not ideal. The main reason is that the triiodide product (I<sub>3</sub><sup>-</sup> ions) in the electrolyte absorbs much of the incoming light before it can reach the active MAPbI<sub>3</sub>, so the system deactivates itself due to product build-up. So, while the researchers show 160 hours solar harvesting – an uncommonly long experimental timescale when using MAPbI<sub>3</sub> as an absorber – they must continuously remove I<sub>3</sub><sup>-</sup> from the solution in order to maintain activity. The 6 M HI solution used is also a highly impractical electrolyte due to its corrosive effect on plumbing, and the solar-to-chemical efficiencies achieved are quite modest (< 1 %) and not relevant for large-scale energy harvesting. Clearly, new ideas are needed for a practical electrolyte, but the “saturated liquid” approach elevates the longevity from practically zero for a perovskite in contact with water to being on a par with some of the most stable perovskite-based solar cells reported so far<sup>13</sup>.

Thus, Nam and colleagues present the solar energy community with a new research challenge: to identify a practical electrolyte and energy harvesting process for a possible new photocatalytic role for perovskite absorbers. This work demonstrates that there might be more to the new perovskites than plain old “dry” solar cells.

Peter C. K. Vesborg in the Department of Physics, Technical University of Denmark (DTU)

B. 312, Fysikvej, DK-2800, Denmark

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Email: Peter.Vesborg@fysik.dtu.dk

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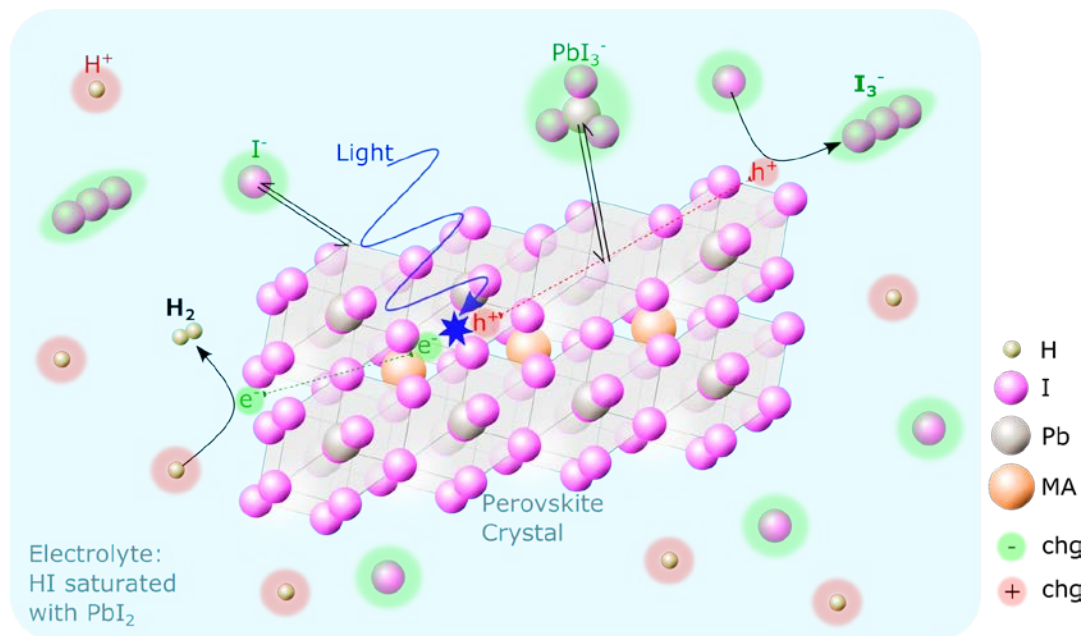
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**Figure 1. Photocatalytic generation of H<sub>2</sub> from hydriodic acid using methylammonium lead iodide.** The MAPbI<sub>3</sub> perovskite particles absorb light via band-gap excitation; the resulting electrons and holes drive proton reduction to dihydrogen and iodide oxidation to triiodide, respectively. Simultaneously, the perovskite particle dynamically-exchanges ions with the aqueous electrolyte, which is saturated with respect to those ions.