

Conventional Solvent Oxidizes Sn(II) in Perovskite Inks

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The most efficient perovskite solar cell devices use Pb(II); however, the toxicity of lead and its decomposition products represent possible obstacles to their widespread commercial and carbon impact.^{1,2} Pb from hybrid perovskites may enter plants—and consequently the food cycle—10× more efficiently than do other Pb sources.³ Although consumer solar modules are encapsulated, there remain concerns about their distribution, maintenance, and recycling.⁴ Replacing lead with more environmentally benign metals, without compromising device efficiency, is of utmost importance.

Recent high-throughput computational studies evaluating the electronic properties of thousands of ABX₃ perovskites revealed that only lead and tin perovskites can deliver solar cell relevant bandgaps and absorption coefficients.^{5,6} Replacing Pb with Sn is a promising path; however, Sn(II) undergoes undesired oxidation forming Sn(IV) and charge carrier recombination centers, leading to a significant loss of photovoltage in solar cells.⁷ Innovative approaches, including dopant additives, a reducing atmosphere, and comproportionation, have increased the record power conversion efficiency for Sn-based devices, approaching currently only half of that for Pb-based solar cells.^{8–10}

In this Viewpoint, we report that the solvent conventionally used in the fabrication of perovskite films, dimethyl sulfoxide (DMSO), oxidizes Sn(II) to Sn(IV). Using the combination of nuclear magnetic resonance (¹H NMR) and X-ray absorption near-edge spectroscopy (XANES), we find that the DMSO/Sn(II) pair undergoes an irreversible redox reaction forming dimethylsulfide (DMS) and Sn(IV) in solution.

Recently, Hamill et al. showed that DMSO induces the conversion of methylammonium into dimethylammonium cation in CH₃NH₃I + PbI₂ solutions at 150 °C.¹² DMSO is also known as an oxidation agent for Sn(II) in acidic medium;¹¹ given that perovskite organic cations are Lewis acids, we hypothesized that DMSO can oxidize Sn(II) in perovskite solutions.

To check this hypothesis and provide insight into reaction/decomposition pathways in Sn(II)-containing perovskite solutions, we performed a series of experiments. We prepared a perovskite solution in DMSO by dissolving FAI (where FA is formamidinium cation) and SnI₂, sealed the vial, and heated it at 120 °C for 5 h, all in an inert atmosphere.

We noticed a significant change in color (Figure 1); the solution became much darker, indicating the oxidation of Sn(II).¹³ On the other hand, the dimethylformamide (DMF)-

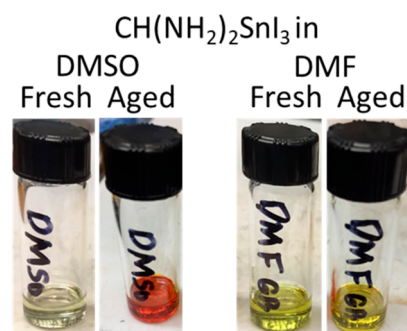


Figure 1. Fresh and aged (120 °C for 5 h) formamidinium tin iodide solutions.

based solution showed an only negligible change in color in the analogous experiment. Though perovskite solutions are generally not heated for such a long time, this accelerated test can provide insights about the processes that occur in solution when heating the solution to dissolve the precursors or annealing spin-coated film with the leftover DMSO. It does not take much Sn⁴⁺ doping (<0.1%) in ASnI₃ perovskites to turn the material's p-type conductors and render them inactive as solar photovoltaic absorbers.

¹H NMR measurements of the corresponding solutions revealed the presence of DMS (at 2.07 ppm)¹¹ even after 10 min of heat treatment at 120 °C (Figure 2a,b). Longer heat treatment led to more DMS formation (Figure S1). A blank sample without FAI and SnI₂ was treated in the same way, and it showed no DMSO decomposition (Figure S2). Notably, FAI or PbI₂ DMSO-based heat-treated solutions under the same conditions exhibited trace amounts of DMS (Figures S3–S5). Variable-temperature ¹H NMR measurements showed that DMS formation commences at 100 °C in the presence of Sn²⁺ ions (Figures S6 and S7).

We then conducted X-ray absorption near-edge spectroscopy (XANES) on the solutions before and after heat treatment. The XANES spectra of S K-edge confirmed that DMSO was

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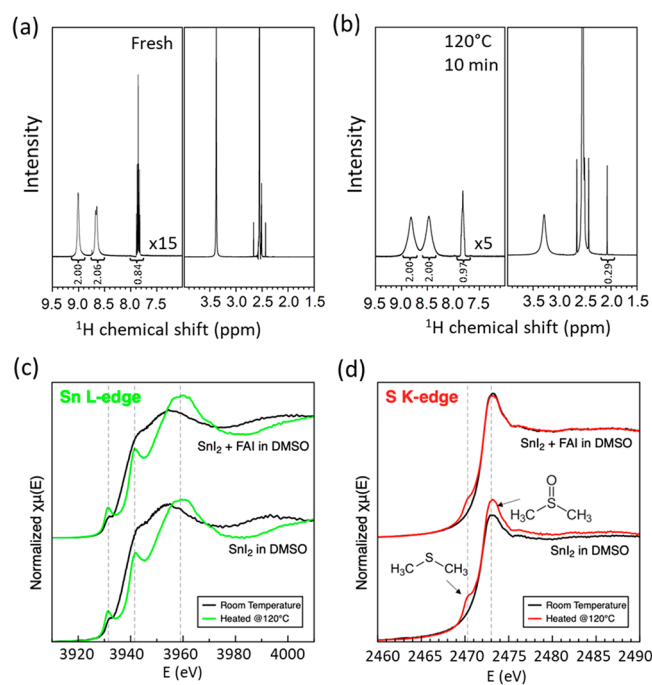
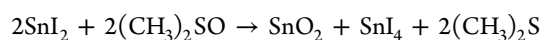


Figure 2. ¹H NMR spectra of DMSO sample solutions (a) before and (b) after heat treatment at 120 °C for 10 min. The peak at 2.07 ppm is assigned to the methyl protons of DMS. The peaks at 8.82 ppm and 8.47 ppm correspond to the (–NH₂) protons, while the peak at 7.86 ppm corresponds to the (–CH–) proton of formamidinium cation.¹⁸ XANES (c) Sn L-edge and (d) S K-edge spectra before and after heat treatment.

partially reduced to DMS (emergence of a peak at 2470.5)¹⁴ after annealing at 120 °C under an argon atmosphere (Figure 2c). Similarly, distinct peaks corresponding to Sn(IV) were observed in all the annealed solutions using the Sn L-edge,¹⁵ indicating Sn oxidation (Figure 2d). These findings indicate that the following reaction took place in solution:



Summary and Future Outlook. In sum, our work provides a piece of evidence that DMSO can oxidize Sn(II) at temperatures above 100 °C. DMSO has become a mandatory near-ubiquitous component in the fabrication of perovskite films, as it is known to be a good ligand in coordination chemistry, thus retarding crystallization and improving crystallite quality.^{16,17} Even the most minute Sn⁴⁺ amount in the structure can compromise solar cell photovoltage to <0.5 V, much less than the ~0.9 V expected from the bandgap. If Sn-based solar cells are going to match the performance of Pb-based ones, all potential oxidation pathways should be prevented, urging the development of new, DMSO-free solvent systems for the synthesis of Sn-based perovskites with suppressed defect densities.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnenergylett.0c00402>.

Sample preparation, characterization information, and additional NMR spectra (PDF)

■ AUTHOR INFORMATION

Complete contact information is available at:

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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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