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the formation of the solar system and was incorporated into planetesimal bodies. Consequently, if the formation of the solar nebula was typical, our work implies that interstellar ices from the parent molecular cloud core—including the most fundamental life-fostering ingredient, water—are widely available to all young planetary systems.

REFERENCES AND NOTES
17. Materials and methods are available as supplementary material on Science Online.

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WATER SPLITTING

Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts

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Although sunlit-driven water splitting is a promising route to sustainable hydrogen fuel production, widespread implementation is hampered by the expense of the necessary photovoltaic and photoelectrochemical apparatus. Here, we describe a highly efficient and low-cost water-splitting cell combining a state-of-the-art solution-processed perovskite tandem solar cell and a bifunctional Earth-abundant catalyst. The catalyst electrode, a NiFe layered double hydroxide, exhibits high activity toward both the oxygen and hydrogen evolution reactions in alkaline electrolyte. The combination of the two yields a water-splitting photocurrent density of around 10 milliamperes per square centimeter, corresponding to a solar-to-hydrogen efficiency of 12.3%. Currently, the perovskite instability limits the cell lifetime.

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Fig. 1. Performance of perovskite solar cell. (A) Current density–potential curve (J–V) of the perovskite solar cell under dark and simulated AM 1.5G 100 mW cm⁻² illumination. (B) IPCE spectrum of the perovskite solar cell and the integrated photocurrent with the AM 1.5G solar spectrum.

Comparing with other energy resources, solar energy is sustainable and far more abundant than our projected energy needs as a species; thus, it is considered as the most promising energy source for the future. Because of the diffuse nature of solar energy, large arrays of solar cells will have to be implemented. Currently, electricity produced by silicon (Si) solar cells is too costly to achieve grid parity. In contrast, the dye-sensitized solar cell (DSSC) (1, 2) uses cheap materials and facile solution processes. A related type of low-cost solution-processed solar cell based on a perovskite formulation has recently emerged (3–10). The rapid rise of the solar-to-electric power conversion efficiency (currently 17.9% certified) in less than 5 years makes it highly promising for large-scale commercialization (11). Long-term stability, however, is currently a challenge with these solar cells.

The conversion of solar energy directly into fuels is a promising solution to the challenge of intermittency in renewable energy sources, addressing the issues of effective storage and transport. In nature, plants harvest solar energy and convert it into chemical fuel via photosynthesis. Inspired by nature, artificial photosynthesis has been proposed as a viable way to store the solar energy as fuel (12, 13). Hydrogen, which is the simplest form of energy carrier, can be generated reversibly with solar energy through photoelectrochemical water splitting or by photovoltaic (PV)-driven electrolysis. Intensive research has been conducted in the past several decades to develop efficient photoelectrodes, catalysts, and device architectures for solar hydrogen generation (14–20). However, it still remains a great challenge to develop solar water-splitting systems that are both low-cost and efficient enough to generate fuel at a price that is competitive with fossil fuels (21). Splitting water requires an applied voltage of at least 1.23 V to provide the thermodynamic driving force.
force. Because of the practical overpotentials associated with the reaction kinetics, a substantially larger voltage is generally required, and commercial electrolysers typically operate at a voltage of 1.8 to 2.0 V (22). This complicates PV-driven electrolysis using conventional solar cells—such as Si, thin-film copper indium gallium selenide (CIGS), and cadmium telluride (CdTe)—because of their incompatibility with low-circuit voltages. To drive electrolysis with these conventional devices, three to four cells must be connected in series or a DC–DC power converter must be used in order to achieve reasonable efficiency. Multijunction solar cells—such as triple-junction silicon (28, 29), III–V–based solar cells (30), and most recently CIGS solar cells in tandem—have also been applied to water splitting at a voltage of 1.9 V (24). In contrast, perovskite solar cells have achieved open-circuit voltages of at least 0.9 V and up to 1.5 V according to recent reports (25–27), which is sufficient for efficient water splitting by connecting just two in series.

Here, we present our results on water splitting using state-of-the-art perovskite solar cells. Our cell was based on CH3NH3PbI3, which is proficient for efficient water splitting by connecting conventional solar cells (28). The current density–voltage (J–V) characteristic of a representative perovskite solar cell is shown in Fig. 1A under simulated AM 1.5G solar irradiation (100 mW cm−2) and in the dark. The cell has a short-circuit photocurrent density, open-circuit voltage, and fill factor of 21.3 mA cm−2, 1.06 V, and 0.76, respectively, yielding a solar-to-electric power conversion efficiency (PCE) of 17.3%. The incident photon-to-current conversion efficiency (IPCE) (Fig. 1B) shows that the perovskite solar cell is active from the ultraviolet to 800 nm, which is in good agreement with the band gap (1.5 eV). An integration of the IPCE spectrum with the AM 1.5G solar photon flux yields a current density of 21.1 mA cm−2, corroborating the value that we obtained from the J–V measurements.

With the highly efficient perovskite solar cell in hand, the next step was to overcome the large water-splitting overpotentials that are typically required to generate H2 and O2 at a practical rate. For this purpose, efficient electrocatalysts must be implemented. Our intention was to avoid using the conventional expensive noble metals of low abundance, such as Pt, RuO2, and IrO2. In the past decades, tremendous efforts have been devoted to developing low-cost and high-efficiency electrocatalysts for water splitting—for example, MoS2 and NiMo for the H2 evolution reaction (HER) (29–31), and cobalt-phosphate, metal oxides, and hydroxides for the O2 evolution reaction (OER) (17, 32–34). For sustained overall water splitting, the catalysts for the HER and OER must be operated in the same electrolyte. Furthermore, in order to minimize overpotentials in the electrolyte, water splitting should be carried out in either highly active or alkaline electrolyte (35). This requirement is a challenge for most of the Earth-abundant catalysts because a highly active catalyst in acidic electrolyte may not be active or even stable in basic electrolyte. For example, MoS2 is highly active for the HER in acidic electrolyte (36), but it is unstable in basic. Similarly, most of the metal oxides and hydroxides for the OER are not stable in acidic electrolyte. Thus, it is crucial to develop a bifunctional catalyst that has high activity toward both the HER and OER in the same electrolyte (either strongly acidic or strongly basic). Moreover, the use of a bifunctional catalyst simplifies the system, lowering the manufacturing cost and thus the cost of the resulting hydrogen.

Nickel (Ni) foam is used as the electrode for commercial alkaline electrolysers because of its Earth-abundance and porous three-dimensional structure (22). Recently, Ni(OH)2 has received great attention for the OER (33–38), and it has been shown that the activity could be improved by the incorporation of iron (39–41). Furthermore, the Ni(OH)2 modified nickel surface has shown an HER rate around four times higher than bare nickel in alkaline electrolyte (42, 43). The high performance of Ni(OH)2 toward both the HER and OER in strongly basic solutions makes it an exceptional bifunctional catalyst. Here, we incorporated iron (Fe) into Ni(OH)2 to form NiFe layered double hydroxides (LDHs), which were directly grown on the surface of the Ni foam by a simple one-step hydrothermal growth method (28, 40). For comparison, pristine Ni foam, Ni(OH)2 on Ni foam, and Ni foam with ~3.5-nm Pt nanoparticles (deposited by sputtering on both sides of the foam) electrodes were also studied. The OER characteristics of these different electrodes in 1 M NaOH are shown in Fig. 2A at a scan rate of 1 mV s−1, with the scan direction from positive to negative on the reversible hydrogen electrode (RHE) scale (currents...
are uncorrected and thus include resistive losses in the electrolyte). In the three-electrode configuration, the NiFe LDH/Ni foam electrode requires an overpotential (\(\eta_{RER}\)) of only 240 mV to reach a (projected geometric area) current density of 10 mA cm\(^{-2}\). This potential is 100 mV less than the Pt/Ni foam electrode, whereas Ni(OH)\(_2\)/Ni foam electrode has nearly the same performance as the Pt/Ni foam for the OER. All of the modified electrodes show improved performance compared with pristine Ni foam. The small cathodic peak at 1.3 V versus RHE is due to the reduction of the oxidized NiFe LDH.

For the measurement of the catalytic activity toward the HER, the electrodes were swept at 1 mV s\(^{-1}\) from negative to positive potential on the RHE scale. The performance of the NiFe LDH/Ni foam electrode is much better than the bare Ni foam and slightly better than Ni(OH)\(_2\)/Ni foam, but worse than the Pt/Ni foam electrode (Fig. 2B). The NiFe LDH/Ni foam electrode requires an overpotential (\(\eta_{HER}\)) of 210 mV to achieve a current density of 10 mA cm\(^{-2}\), which is 100 mV greater than the Pt/Ni foam electrode. The gains that we achieve on the practical level through the use of Earth-abundant catalysts offset the small loss in voltage that we observe. Considering that the HER activity in strong base is usually two to three orders lower than in acidic solution (43), the performance of this electrode is remarkable.

To go a step closer to the real application, overall water splitting in a two-electrode configuration was investigated (Fig. 2C). Overall, the NiFe LDH/Ni foam electrode shows nearly the same performance as the Pt/Ni foam electrode, with 10 mA cm\(^{-2}\) water-splitting current reached by applying just 1.7 V across the electrodes. To confirm the bifunctional activity of the NiFe LDH/Ni foam electrodes, the evolved gaseous products were quantified by means of gas chromatography. We confirmed quantitative Faradaic gas evolution at the predicted 2:1 ratio for hydrogen and oxygen, within experimental error (Fig. 2D). The exceptional bifunctionality, high activity, and low cost of the NiFe LDH/Ni foam electrode make it highly competitive for potential large-scale industrial applications.

The stability of the catalyst is very important because a practical water-splitting device should ideally last for several years (the longer the lifetime of the device, the lower the cost of the resulting hydrogen). To assess the stability of the NiFe LDH/Ni foam catalyst electrode, 1.8 V was applied to the electrodes, and there is a small degradation over a 10-hour test (fig. S1). However, the performance of the catalyst electrodes fully recovered in the second and third repeat experiments on the same electrode. Thus, although the mechanism of this decrease is yet unclear, the system benefits from the diurnal cycle, in which any slight reduction in photocurrent during daytime illumination is recovered at night. Further characterization of the catalyst electrodes can be found in figs. S2 to S4 and movie S1.

Using the above-demonstrated high-efficiency, low-cost perovskite solar cell and bifunctional water-splitting catalyst, an overall water-splitting cell was assembled (28). The schematic diagram of the device is shown in Fig. 3A. The perovskite solar cells were placed side by side and connected with wires to the immersed catalyst electrodes, and simulated solar irradiation provided the energy to split water. A generalized energy diagram is shown in Fig. 3B of the two perovskite solar cells connected in series as a tandem cell for water splitting. The tandem cell used in the integrated device exhibited the \(J\)-\(V\) response depicted in Fig. 3C, yielding a \(V_{OC}\) of 2.00 V while retaining a high PCE of 15.7%. The predicted operating current density of the combined system (normalized to the total illuminated area of the solar cells) is defined by the intersection of the \(J\)-\(V\) curves of both the perovskite tandem solar cell and the catalyst electrodes in the two-electrode configuration (Fig. 3C), giving a value of 10.0 mA cm\(^{-2}\). This operating current, which corresponds to a solar-to-hydrogen efficiency of 12.3%, was confirmed with measurement in the standalone, unbiased light-driven configuration (Fig. 3D). To show the current more clearly, we present only the results of the initial 8 min in Fig. 3D. The performance of the device is further characterized under AM 1.5G chopped light illumination without applying any external bias for 2 hours (fig. S5). The fluctuation of the current under illumination is caused by bubble formation on the surface, which affects the effective surface area. The overall decrease in current on longer time scales is mainly due to the instability of the perovskite solar cell, a challenge that could be addressed by proper passivation and encapsulation techniques. A second representative device, featuring cells with greater stability but lower overall efficiency, is shown in fig. S6.

The operating point of the water-splitting cell occurs very close to the maximum power point of the perovskite tandem cell (9.61 mA cm\(^{-2}\) at 1.63 V) (Fig. 3C), indicating that minimal energy is lost in converting electrical to chemical energy in this system. In fact, we have achieved close to the maximum solar-to-hydrogen efficiency possible with the current state-of-the-art perovskite solar cell (in a side-by-side configuration). However, a solar-to-hydrogen efficiency up to 15% is reasonably possible with the fast development of perovskite solar cells (the theoretical upper limit for hydrogen generation in this configuration, as defined by a 1.5 eV band gap and the solar flux, is 17.8%). Improved stability of the device performance can be achieved through passivation of the perovskite solar cells. Furthermore, in the current study, the solar cells are wired with the Ni foam electrodes; however, alternative architectures are possible, for example, by directly attaching the water-splitting catalysts onto the back sides of the solar cells to form an integrated system.

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**Fig. 3. Combination of the perovskite tandem cell with NiFe DLH/Ni foam electrodes for water splitting.** (A) Schematic diagram of the water-splitting device. (B) A generalized energy schematic of the perovskite tandem cell for water splitting. (C) \(J\)-\(V\) curves of the perovskite tandem cell under dark and simulated AM 1.5G 100 mW cm\(^{-2}\) illumination, and the NiFe/Ni foam electrodes in a two-electrode configuration. The illuminated surface area of the perovskite cell was 0.318 cm\(^2\), and the catalyst electrode areas (geometric) were ~5 cm\(^2\) each. (D) Current density–time curve of the integrated water-splitting device without external bias under chopped simulated AM 1.5G 100 mW cm\(^{-2}\) illumination.

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**Note:** The diagram includes voltage graphs, current density-time curves, and energy schematics that illustrate the water-splitting process and the integrated system. The text explains the experimental setup and results, emphasizing the efficiency and stability of the perovskite tandem cell coupled with the NiFe LDH/Ni foam electrodes for water splitting. The discussion includes the practical implications of achieving high efficiencies and the potential for integrating the devices for real-world applications.

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**References:**

1. (43) The citation is not provided in the text, but it is implied that the reader should consult the journal for further details.

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**Additional Information:**

- The experiments involved the use of perovskite solar cells and NiFe LDH/Ni foam electrodes for water splitting.
- The performance metrics include current density, overpotential, and efficiency under various illumination conditions.
- The device stability and potential for large-scale applications are discussed.
- The study highlights the potential for integrating such devices into practical energy systems.
Infrared-driven unimolecular reaction of CH₃CHOO Criegee intermediates to OH radical products

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Ozonolysis of alkenes, an important nonphotolytic source of hydroxyl (OH) radicals in the lower atmosphere, proceeds through energized Criegee intermediates to drive hydrogen transfer from the methyl group to the terminal oxygen to generate vinyl hydroperoxide (VHP, H₂C=CHOOH). This leads directly to O-O bond breaking, yielding OH radical and vinyl hydroxide products. A different mechanism is predicted for substituted Criegee intermediate CH₃CHOO, the focus of the present study. (See table S1 for chemical structures of relevant species.) Concurrent detection of Criegee intermediates and OH products by photoionization mass spectrometry also shows a large increase in OH yield for alkyl-substituted Criegee intermediates compared to CH₃OO (11, 12).

The efficient production of OH radicals upon ozonolysis of alkenes has been proposed to follow a 1,4-hydrogen atom shift mechanism for alkyl-substituted Criegee intermediates. The computed reaction coordinate, depicted in Fig. 1 for the more stable syn-conformer of CH₃CHOO, involves passage over a transition state with a five-membered, ringlike structure and migration of a hydrogen on the methyl group (an α-hydrogen) to the terminal oxygen to generate vinyl hydroperoxide (VHP, H₂C=CHOOH). This leads directly to O-O bond rupture, yielding OH radical and vinyl hydroxide products. A different mechanism is predicted for CH₃OO (and anticonformers of Criegee intermediates), with a substantially higher barrier to reaction that leads to dioxirane (33, 34) and, based on kinetic studies, a much smaller yield of OH products under laboratory and atmospheric conditions (9).

This study focuses on infrared (IR) activation of cold Criegee intermediates to drive unimolecular decay to OH products. Specifically, we used IR excitation of syn-CH₃CHOO in the CH stretch overtone (2ν(CH)) region near 6000 cm⁻¹ to surmount the barrier associated with 1,4-hydrogen transfer.