Photocatalytic hydrogen generation from hydriodic acid using methylammonium lead iodide in dynamic equilibrium with aqueous solution

Sunghak Park^{1†}, Woo Je Chang^{2†}, Chan Woo Lee¹, Sangbaek Park¹, Hyo-Yong Ahn¹ and Ki Tae Nam^{1,2*}

The solar-driven splitting of hydrohalic acids (HX) is an important and fast growing research direction for H_2 production. In addition to the hydrogen, the resulting chemicals (X_2/X_3^-) can be used to propagate a continuous process in a closed cycle and are themselves useful products. Here we present a strategy for photocatalytic hydrogen iodide (HI) splitting using methylammonium lead iodide (MAPbl₃) in an effort to develop a cost-effective and easily scalable process. Considering that MAPbl₃ is a water-soluble ionic compound, we exploit the dynamic equilibrium of the dissolution and precipitation of MAPbl₃ in saturated aqueous solutions. The I⁻ and H⁺ concentrations of the aqueous solution are determined to be the critical parameters for the stabilization of the tetragonal MAPbl₃ phase. Stable and efficient H₂ production under visible light irradiation was demonstrated. The solar HI splitting efficiency of MAPbl₃ was 0.81% when using Pt as a cocatalyst.

S plitting hydrogen iodide (HI) to generate H_2 has been extensively investigated, especially in thermochemical water splitting processes¹⁻³. When iodine and sulfur participate in this process, in the form of hydrogen iodide and sulfuric acid, hydrogen from the water splitting can be continuously generated with high efficiency in a large-scale closed system, known as the iodine–sulfur cycle. Because of the thermodynamic requirement for high temperatures, centralized production systems coupled with nuclear power have been explored the most⁴⁻⁷.

In addition to the merits that are applicable to the iodinesulfur water splitting cycle, solar-driven splitting of hydrohalic acids (HX) represents an important alternative process to water splitting. Relative to water splitting involving four electrons, a lower overpotential is required because only two electrons are involved^{8,9}. As a result, the overpotential is almost zero in the case of iodide ion oxidation^{10,11}. Furthermore, the concurrent oxidation reaction involved in HX splitting produces value-added chemicals such as I₂/I₃⁻, Br₂/Br₃⁻, or Cl₂, which have a variety of uses in the energy and hygiene industries¹²⁻¹⁴. Indeed, many pioneering works demonstrate successful HX splitting¹⁵⁻¹⁷. For example, a layered metal dichalcogenide selenide (WSe₂) has been used as the photoelectrochemical (PEC) electrode to split aqueous hydriodic acid, achieving a 4.2% solar HI splitting efficiency¹⁸. By applying a Nafion-separated silicon microwire PEC electrode, HI splitting has been achieved with a 0.6% efficiency and pure products¹⁹.

A major difficulty in materials selection and system design in solar-driven HI splitting lies in the fact that aqueous HI is a strong acid ($K_a = 10^{10}$). Thus, most semiconductors and metals, with a few exceptions, cannot be used reliably as PEC electrodes, photocatalysts, and cocatalysts in the presence of such an acid. For instance, transition metal oxides such as CoO cannot maintain their phases under acidic conditions as predicted by the Pourbaix diagram²⁰.

Methylammonium lead iodide (MAPbI₃), a representative hybrid organic–inorganic perovskite, is an ionic crystal consisting

of organic methylammonium cations and inorganic PbI_3^- anions. The crystal structure of MAPbI₃ is composed of a three-dimensional framework of PbI_3^- , which is formed by the corner sharing of lead iodide octahedra. The negative charges are compensated by methylammonium cations located in the cubo-octahedral sites. MAPbI₃ exhibits great optoelectronic properties, such as a high light absorption coefficient and high carrier mobility²¹⁻²⁵. Therefore, MAPbI₃ has recently been applied as a photoactive material in solar cells with a drastic enhancement of the photoconversion efficiency to above 20% (refs 26–29). Moreover, various optoelectronic devices using MAPbI₃ have been reported, such as lasers, light-emitting diodes, and photodetectors³⁰⁻³². At the same time, Pb-free perovskites, such as Sn- and Bi-based perovskites, have been studied because of the toxicity of Pb^{33,34}.

Despite the good optoelectronic properties of MAPbI₃, to the best of our knowledge MAPbI₃ has never been used as a photocatalyst or photoelectric catalyst due to its instability in humid conditions. Water molecules can interact with the MAPbI₃ crystal lattice via hydrogen bonding, resulting in the collapse of the MAPbI₃ crystal structure into hydrated forms such as (CH₃NH₃)PbI₃(H₂O) (monohydrate) or (CH₃NH₃)₄PbI₆(2H₂O) (dihydrate) when the MAPbI₃ is exposed to humid conditions. Additionally, MAPbI₃ decomposes into the PbI₂ precipitate, methylammonium cation, and iodide anion when it is exposed to liquid water. This is one factor causing the performance degradation of optoelectronic devices that use MAPbI₃ (refs 35,36). Because of the stability issues of MAPbI₃ under humid conditions or in liquid water, using MAPbI₃ as a photocatalyst in aqueous solutions for H₂ production is counterintuitive.

Here we use MAPbI₃ as a photocatalytic material in dynamic equilibrium with aqueous HI solution. The dynamic equilibrium between the MAPbI₃ precipitates and the saturated aqueous solution is confirmed via substitution of iodine atoms with bromine. MAPbI₃ undergoes a phase transition to hydrated phases or PbI₂ at different

¹Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea. ²Interdisciplinary Program for Bioengineering, Seoul National University, Seoul 151-742, Korea. [†]These authors contributed equally to this work. *e-mail: nkitae@snu.ac.kr



Figure 1 | **Dynamic equilibrium between MAPbI₃ powder and aqueous HI solution. a**, Solutions of MAPbI₃ in aqueous HI solution at different concentrations. **b**, Solubility of MAPbI₃ in aqueous HI solution at different temperatures. Error bars in **b** are standard error values of three tests (*n* = 3). **c**, X-ray diffraction (XRD) patterns of powders after reaching dynamic equilibrium with a saturated HI solution and a saturated hydrobromic acid (HBr) solution. **d**, Schematic illustration of the MAPbI₃ powder in dynamic equilibrium with a saturated HI solution. Dotted lines represent dissolution and precipitation of MAPbI₃ crystal and ions.

ion activities in the aqueous solution, and is stable only in specific concentration ranges of I⁻ and H⁺. We found that the MAPbI₃ powder in the aqueous HI solution could effectively split HI into H₂ and I₃⁻ under visible light irradiation, the efficiency of which could be increased via thermal annealing in a polar solvent atmosphere and by using a Pt cocatalyst.

MAPbl₃ saturated aqueous HI solution system

Our idea for generating MAPbI₃ precipitates in an aqueous system was based on the fact that ionic crystals start to precipitate when the concentration of ions exceeds the solubility limit. Because MAPbI₃ is an ionic crystal that consists of methylammonium cations and PbI₃⁻ anions, MAPbI₃ crystals could form in saturated solutions similar to other general ionic crystals. To dissolve PbI₃⁻ anions in aqueous solutions, controlling the concentration of I⁻ is required because PbI₂ barely dissolves in pure water. PbI₂ exists in the solid state as a powder with very few Pb²⁺ and I⁻ ions ($K_{sp} = 4.4 \times 10^{-9}$ at 20 °C) (ref. 37). Instead, PbI₂ starts to dissolve in water as the I⁻ concentration increases, forming PbI₃⁻ or PbI₄²⁻ ions³⁸. Furthermore, controlling the hydrogen bond strength of the water molecules is very important to force MAPbI₃ to precipitate rather than to form hydrates. The hydrogen bond strength among water molecules becomes stronger as the acidity increases³⁹. Therefore, the hydrated phase would be suppressed under acidic conditions because water molecules will interact with themselves rather than with the MAPbI₃ crystal lattice. Therefore, controlling both the I⁻ and H⁺ concentrations would be required for MAPbI₃ formation in aqueous solution.

Aqueous HI, which has both I⁻ and H⁺ ions, was the ideal model system to verify our hypothesis. Synthesized MAPbI₃ powder was placed in 6.06 mol l⁻¹ aqueous HI with various amounts of MAPbI₃ powder (Fig. 1a). A small amount of MAPbI₃ fully dissolved into the aqueous HI, and the colour of the aqueous solution changed to yellow due to the formation of PbI_3^- ([MAPbI_3] $\leq 0.5 \text{ mol } l^{-1}$). As the amount of MAPbI₃ powder increased, the aqueous solution became saturated, and the MAPbI₃ powder remained stable in the aqueous solution ($[MAPbI_3] \ge 0.7 \text{ mol } l^{-1}$). This result is in agreement with the previous research studying MAPbI₃ single-crystal growth behaviour in HI solutions⁴⁰. To determine the solubility of MAPbI₃ in aqueous HI, the weight of the MAPbI₃ solute was measured by evaporating the solvent. Interestingly, the solubility was relatively high (0.645 mol l⁻¹) at 20 °C and increased as the temperature increased (Fig. 1b). This trend indicates that the interactions between the PbI₃⁻ anions and methylammonium cations are stronger than the solvent-solute interactions. On the basis of the measured solubility data, a saturated solution of MAPbI₃ powder was easily



Figure 2 | **Phase conversion of MAPbl₃ powder in aqueous HI solution with various [I⁻] and [H⁺]. a**, XRD patterns of excess precipitates in saturated solution at various HI concentrations. **b**, Constructed phase map as a function of [I⁻] and [H⁺]. Each symbol indicates the stable precipitate phases in saturated solutions at each [I⁻] and [H⁺] concentration. Main peaks of precipitated powder were unindexed at some conditions, expressed as empty boxes.

synthesized. To form this solution, 64.5 mmol of methylammonium iodide (MAI) and PbI_2 were placed in 100 ml of aqueous HI, and simple heating and cooling of the solution was sufficient. From the heating, a saturated solution could be obtained at higher temperatures as the solvent evaporated. Because the solubility is lower at lower temperatures, the hot saturated solution became supersaturated as the temperature decreased. Finally, MAPbI₃ precipitates formed in the saturated solution at room temperature.

To better understand the dynamic equilibrium of the system, the exchange of halogen atoms between the MAPbI₃ precipitates and the saturated solution was observed. Here, dynamic equilibrium indicates that the MAPbI₃ precipitates dissolve in the saturated solution and are precipitated in the crystalline form at the same rate. MAPbI₃ powder was placed in saturated HBr solution, and the halogen atoms substitution was studied. We observed a rapid colour change from black to orange, indicating the substitution of Br atoms for I atoms in the MAPbI₃ powder (Supplementary Video 1). According to a previous study, the halogen component of MAPbI₃ (iodine) can be easily substituted by bromine atoms to form $(CH_3NH_3)Pb(I_{1-x}Br_x)_3$ $(MAPb(I_{1-x}Br_x)_3)$, and its phase is transformed from the tetragonal phase to the cubic phase (at $x \ge 0.2$; ref. 41). From the X-ray diffraction (XRD) patterns, we could confirm the phase transformation of the powder from the tetragonal phase (MAPbI₃) to the cubic phase $(MAPb(I_{1-x}Br_x)_3)$ after the MAPbI₃ powder was immersed in saturated HBr solution (Fig. 1c). The surface morphology of the MAPbI₃ powder also changed when the MAPbI₃ powder was in dynamic equilibrium with the saturated solution. The surface morphology of the MAPbI₃ powder synthesized from organic solvents was flat and smooth (Supplementary Fig. 1). After the synthesized powder was transferred to the saturated solution and reached dynamic equilibrium, the surface became rough, with protrusions (approximately 30 nm) and holes. This rough surface, which was an effect of dynamic equilibrium, was also observed on the MAPbI₃ powder prepared via a simple heating and cooling method of the saturated solution, as shown in Supplementary Fig. 2. Our results indicate that the MAPbI₃ precipitates and saturated solution are in dynamic equilibrium, as shown in the schematic illustration (Fig. 1d). MAPbI₃ dissolves in the saturated solution, forming methylammonium cations and PbI₃⁻ anions, and at the same time, methylammonium cations and PbI₃⁻ anions crystallize, forming MAPbI₃ crystals.

To investigate the effects of the I^- and H^+ ion concentrations, we studied the phase of the precipitated powder in aqueous HI solutions with varying I^- and H^+ concentrations. Three kinds of solutions were prepared. First, solutions with the same I⁻ and H⁺ concentrations ($[I^-] = [H^+]$) were made with 3.16, 2.51, 1, 0.1 mol l^{-1} HI $(-\log[HI] = -\log[H^+] = pH = -\log[I^-] = -0.5, -0.4, 0, 1.0)$ by diluting the 6.06 mol l^{-1} HI $(-\log[HI] = -\log[H^+] = pH =$ $-\log[I^{-}] = -0.78$) using deionized water. For higher I⁻ concentration ($[I^-] > [H^+]$), further KI powder was added, which was added as an I⁻ source to the diluted HI to form specific I⁻ and H⁺ concentrations. Similarly, HClO4 was added to the diluted HI for higher H⁺ concentrations ($[I^-] < [H^+]$). Next, MAPbI₃ powder was transferred into each solution, and the phase changes of the precipitates were confirmed using XRD analysis (Fig. 2a and Supplementary Fig. 3). On the basis of the XRD results, we could construct the phase map of the precipitates at each I^- and H^+ concentration (Fig. 2b). Interestingly, the precipitated powders are in the hydrated phase in the whole higher I^- concentration region ($[I^-] > [H^+]$). Note that the MAPbI₃ phase was stable only in the high ion concentration region at the same and lower I⁻ concentrations ([I⁻] \leq [H⁺]). The hydrated phase was stable in the middle concentration ranges of I^- and $H^+\!.$ The PbI_2 phase was observed in the low I^- and H^+ concentration regions. This result is consistent with our previous idea that the hydrated phase could form when the H⁺ concentration decreases due to the hydrogen bonding of water molecules with the MAPbI₃ crystal lattice, and that the PbI₂ phase would be formed when the I⁻ concentration decreases due to the lack of PbI₃⁻ anion formation at low I⁻ concentrations. From the phase map, we found the specific conditions needed to form the stable MAPbI₃ phase: $[I^-] \leq [H^+]$ is necessary to ensure that the MAPbI₃ phase is stable when the pH and $-\log[I^-]$ are less than -0.5 and -0.4, respectively.

To construct the band diagram of the precipitated MAPbI₃ powder, absorbance spectroscopy and ultraviolet photoelectron spectroscopy (UPS) were performed. MAPbI3 powder shows a large light absorbance with a sharp onset in the visible light range (Fig. 3a). The light absorption coefficient $(F(\alpha))$ of the MAPbI₃ powder was calculated from the absorbance data using the Kubelka-Munk equation (Supplementary Fig. 4). From the relationship between the incident photon energy (hv) and $F(\alpha) hv$, the optical bandgap energy was determined to be 1.53 eV. To determine the valence band maximum position of the MAPbI₃ powder, UPS measurements were performed. Figure 3b shows the UPS spectrum of the MAPbI₃ powder sample with He I photon energy (21.2 eV) calibration. The valence band maximum position was determined to be -5.4 eV with respect to the vacuum level. From the determined optical bandgap and the valence band maximum position, the conduction band minimum position was determined to be -3.87 eV with respect to the



Figure 3 | **Characterization of MAPbl**₃ **powder for band diagram construction. a**, UV-Vis absorption spectrum of the MAPbl₃ powder. The inset shows the MAPbl₃ powder. **b**, Ultraviolet photoelectron spectroscopy of the MAPbl₃ powder. The inset shows the magnified spectrum and linear fitting of the Fermi level region. c, Schematic band diagram of the MAPbl₃ powder for the HI splitting photocatalytic reaction. CB, VB and NHE are the abbreviations for conduction band, valence band and normal hydrogen electrode, respectively.

vacuum level. These results were consistent with the previous results for an MAPbI₃ film fabricated via the spin coating method from an organic precursor solution⁴². The conduction band minimum and valence band maximum from the constructed band diagram of the precipitated MAPbI₃ powder corresponded to -0.6 V and 0.93 V versus the normal hydrogen electrode (NHE), respectively. These are suitable positions for hydrogen reduction (0.046 V versus NHE) and iodine oxidation (0.376 V versus NHE) in our designed system (6.06 mol l⁻¹ aqueous HI), as illustrated in Fig. 3c.

Photocatalytic HI splitting in MAPbl₃ saturated solution

The precipitated MAPbI₃ powder could efficiently split HI into H_2 and I_3^- when irradiated with visible light ($\lambda \ge 475 \text{ nm}$) at $pH = -log[I^-] = -0.78$ (Fig. 4). Electrochemically reduced HI was used in the saturated solution to eliminate the naturally existing I_3^- in the aqueous HI. H₂ gas evolution was verified using gas chromatography (GC) analysis. To determine the origin of the H₂ gas, the gas component was checked under dark conditions. Without light irradiation, no H₂ gas was detected (Supplementary Fig. 5a). Moreover, no H₂ gas was detected without the MAPbI₃ powder in the saturated solution under visible light irradiation (Supplementary Fig. 5b). From the above two results, it can be concluded that the H_2 was a product of the photocatalytic reaction of the MAPbI₃ powder. Furthermore, the H₂ evolution activity of the MAPbI₃ powder was certified by electrochemical experiments in the dark condition (Supplementary Fig. 6). By loading the MAPbI₃ powder on a carbon electrode, a higher current was obtained. The Faradaic efficiency of the H₂ evolution was almost 100% at -0.9 V versus the saturated calomel electrode, as shown in Supplementary Fig. 6b. Based on the fact that the band position of MAPbI₃ was appropriate for the hydrogen reduction reaction and the above experimental results, we confirmed that H₂ could be produced at the MAPbI₃ powder surface via photocatalytic reaction without any other additional cocatalysts.

To verify the existence of I_3^- ions, ultraviolet–visible (UV–Vis) spectra of the solution were collected after light illumination (Fig. 4b). Because the iodoplumbate ions are also dissolved in the saturated solution, and have a similar absorption wavelength range to I_3^- , a 1/200 dilution of the solution with deionized water was conducted to precipitate the iodoplumbate ions in the solution. The absorbance peaks at 287 nm and 353 nm increased as the photocatalytic reaction proceeded, which corresponded to the known absorption spectrum of I_3^- (ref. 43). This indicates that I_3^- was generated as the oxidation reaction product of the photocatalytic reaction. The concentration of I_3^- could be directly determined by matching the measured absorbance to the absorbance of standard I_3^- solutions (Supplementary Fig. 7). The I_3^- concentration of the solution was 2.2, 2.9, 4.1 mmoll⁻¹ at 1.5, 3, 9 h, respectively. Based on these quantification data, we checked the stoichiometry of the

evolved products and confirmed that full HI splitting occurs without side reactions (Fig. 4c). Because two electrons are needed to generate one H₂ molecule (2H⁺ + 2e⁻ \rightarrow H₂) and two holes are needed to generate one I₃⁻ ion (3I⁻ + 2h⁺ \rightarrow I₃⁻), the H₂ to I₃⁻ ratio should be one. The MAPbI₃ photocatalytic reaction produced almost the same amount of H₂ and I₃⁻. For example, after 1.5 h of photocatalytic reaction, 8.86 µmol of H₂ and 8 µmol of I₃⁻ accumulated in the photocatalytic system, and 25.72 µmol of H₂ and 27 µmol of I₃⁻ accumulated after 9 h of photocatalytic reaction.

The evolved I₃⁻ could interfere with the light absorption of MAPbI₃ because the solution colour became dark brown as the I₃⁻ concentration increased. Even though the maximum absorption peak positions of I_3^- are at wavelengths of 287 nm and 353 nm, high concentrations of I_3^- absorbed a wider range of visible light up to 700 nm (Supplementary Fig. 8). As a result, the light absorption by MAPbI₃ was blocked by the absorption of I₃⁻, resulting in diminished light absorption by the MAPbI₃ powder and a decreased H₂ evolution rate. For this reason, further system design is needed, such as a flow system to simultaneously remove I₃⁻ to overcome the rate reduction of the photocatalytic HI splitting and achieve stable long-term H₂ production. In this study, we added H₃PO₂ to our saturated solution system as a selective reducing agent for $I_3^{\,-}.\ H_3PO_2$ is known to be a good reducing agent for the $I_3^{\,-}$ to I⁻ reaction⁴⁴. H₃PO₂ was electrochemically inactive without further oxidation reactions in the potential range from 0.2 to 1 V versus the reversible hydrogen electrode (RHE) without I₃⁻ (Supplementary Fig. 9). Therefore, photogenerated holes are only consumed for I⁻ oxidation without direct H₃PO₂ oxidation. Furthermore, there was no significant difference in the H₂ evolution rate between the case with added H₃PO₂ and the electrochemically reduced HI case for up to 1 h of irradiation. Surprisingly, by adding H₃PO₂ in the saturated solution, the colour of saturated solution did not change during photocatalytic reaction, and the H₂ evolution rate was consistently maintained, as shown in Fig. 4a.

Indeed, we found that the photocatalytic performance of MAPbI₃ can be kept constant even after 160 h of continuous illumination, as shown in Fig. 4d. No phase change of powder was observed after photocatalytic reaction (Supplementary Fig. 10). This superior stability was due to the quasi-stable property of the dynamic equilibrium between MAPbI₃ powder and the saturated solution. Continuous regeneration of the new surface could be achieved due to the simultaneous, fast exchange of ions such as I⁻, PbI₃⁻, and methylamine cations at the interface of the MAPbI₃ powder and the saturated solution. Cycling tests were performed by evacuating the reactor with Ar twice after five hours of visible light illumination (Supplementary Fig. 11). The slight increase in the H₂ production rate after the purging procedure is due to the increase in the amount of MAPbI₃ as a result of solvent evaporation.



Figure 4 | **Photocatalytic reaction results of the MAPbl**₃ **powder in a saturated solution system for HI splitting. a**, Photocatalytic H₂ evolution from the MAPbl₃ powder in a saturated solutions were prepared by electrochemical reduction (black squares) and H₃PO₂ addition (red circles), respectively. **b**, Photocatalytic reaction time-dependent UV-Vis spectra of diluted saturated solutions for I_3^- titration. The saturated solution was made by adding MAPbl₃ powder to the electrochemically reduced HI solution. **c**, Quantitative comparison between the evolved H₂ and I_3^- . **d**, Stable photocatalytic H₂ evolution produced by the MAPbl₃ powder in the saturated solution for 160 h. H₃PO₂ was added to the HI solution.

To optimize our photocatalytic system to achieve higher efficiency, the amount of powder in 50 ml of solution was changed (Supplementary Fig. 12). In the experiments, 200 mg of MAPbI₃ powder shows consistent and efficient H₂ evolution. The light irradiation area was controlled by masking the reactor surface to ensure uniform irradiation (Supplementary Fig. 13). Further enhancement of the H₂ production could be achieved by thermal annealing of the MAPbI₃ powder in a polar solvent atmosphere and by Pt cocatalyst deposition (Fig. 5a). It is known that efficient charge carrier transfer to the surface of the photocatalyst material is crucial for high photocatalytic activity⁴⁵. To improve the charge carrier diffusion length, we used thermal annealing of the MAPbI₃ powder in a polar solvent atmosphere. In solar cell research, thermal annealing of MAPbI₃ films in polar solvent atmospheres, such as dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), could improve their charge carrier diffusion lengths by increasing the crystallinity and decreasing the number of recombination sites⁴⁶. The same annealing method was applied to the MAPbI₃ powder, and increased crystallinity was confirmed by XRD (Supplementary Fig. 14). Notably, approximately 2 times and 2.8 times more H₂ were generated using the MAPbI₃ samples that were thermally annealed in DMF and DMSO atmospheres. To maximize the efficiency, Pt deposition was used on the MAPbI₃ that was thermally annealed in a DMSO atmosphere, resulting in an additional 1.8 times H₂ evolution. Finally, approximately $57 \,\mu mol g^{-1} h^{-1} H_2$ was evolved from the sample with deposited Pt. The final solar HI splitting efficiency was 0.81%. For comparison, the performances of other groups are summarized in Supplementary Table 1. The mol to mol

 $\rm H_2$ evolution activities of the $\rm MAPbI_3$ powders with the different treatments are shown in Supplementary Table 2.

In addition, we tested the photocatalytic activity of MAPbI₃ at various light intensities. Because MAPbI₃ is a good light absorber with a large light absorption coefficient throughout the visible light range (10⁵ cm⁻¹) (ref. 47), MAPbI₃ powder would also efficiently split HI at low light powers. The H₂ evolution rate was checked at light intensities of 100, 20, 3, 0.5 mW cm⁻² using a solar simulator $(\lambda \ge 475 \text{ nm})$. H₂ was consistently generated over the whole range of light intensities (Fig. 5b). Even under commercial light-emitting diode (LED) irradiation, H₂ could be generated. The reaction order of the light intensity was analysed by fitting the H₂ evolution rate and the light intensity on a logarithmic scale. The conventional photocatalytic reaction model suggests that the reaction order of the light intensity has a value from 1 to 0.5 as the light intensity increases⁴⁸. The reaction order of the light intensity for our system was 0.4, which is close to 0.5, suggesting that second-order recombination of photoexcited carriers occurs in our system (Fig. 5c).

Conclusions

In summary, we have identified the conditions for the formation of stable MAPbI₃ precipitates in aqueous solution by controlling the I⁻ and H⁺ concentrations. The tetragonal MAPbI₃ phase is stable only at specific I⁻ and H⁺ concentrations ([I⁻] \leq [H⁺], pH \leq -0.5, and $-\log[I^-] \leq$ -0.4). In such a saturated solution, continuous dissolution and precipitation occur in dynamic equilibrium, and stable photocatalytic splitting of HI to evolve H₂ can be achieved. We expect that our study will improve understanding of



Figure 5 | H₂ evolution activity of various MAPbl₃ catalyst systems and at various light intensities. a, Photocatalytic H₂ evolution from MAPbl₃ powder that was thermally annealed in a polar solvent atmosphere with and without a Pt cocatalyst. **b**, H₂ evolution activity as a function of the light intensity. Even commercial LED light irradiation could generate H₂. **c**, The HI splitting reaction order of MAPbl₃ powder in a saturated solution system based on the light intensity. Red line was fitted using least-squares linear regression.

the characteristics of dynamic equilibrium of MAPbI₃ powder in saturated solution and its applications for photocatalytic HI splitting, as well as contribute to the development of organic–inorganic perovskites catalysts in aqueous solutions with high efficiency and durability for solar-driven hydrogen fuel production.

Methods

Chemicals and materials. PbI₂ (99.999%), KI (99%), gamma-butyrolactone (99%), *N*,*N*-dimethylformamide (anhydrous, 99.8%) and dimethyl sulfoxide (anhydrous, 99.9%) were purchased from Sigma Aldrich. HI (7.6 mol l⁻¹, 57 wt%, in water, unstabilized), and HBr (48 wt%, in water) were purchased from ACROS ORGANICS. Methylamine (40% in methanol) and H₂PtCl₆ · 6H₂O were purchased from TCI Chemical. Ethyl alcohol, diethyl ether, and standard I₃⁻ solution (0.05 mol l⁻¹) were purchased from Daejung Chemicals. H₃PO₂ (50 wt%, in water) and HClO₄ (70%) were purchased from Junsei.

Synthesis of methylammonium halide. Methylammonium halide (MAX) (X = Br, I) was prepared by reacting a 1:1 molar ratio of methylamine and HX solution. The reacting solution was stirred at 0 °C for 2 h. The solvent was removed by rotary evaporation at 50 °C for 1 h. The precipitates were dissolved in ethanol, and diethyl ether was added. The solution then mixed for recrystallization. This recrystallization process was repeated twice. After recrystallization, the product (MAX) was dried in a vacuum oven at 60 °C for 2 h.

Fabrication of MAPbI₃ **powder.** MAPbI₃ was prepared from organic solvent by dissolving 1.23 moll⁻¹ of MAI and PbI₂ in 20 ml of gamma-butyrolactone at 50 °C. The temperature was raised to 100 °C and held overnight to grow the crystal. The MAPbI₃ crystal was washed with diethyl ether and dried in a vacuum oven at 50 °C. MAPbI₃ was synthesized from aqueous solution by dissolving 0.645 moll⁻¹ of MAI and PbI₂ in 100 ml of aqueous HI. The aqueous HI was prepared by adding 50 wt% H₃PO₂ to 57 wt% HI in a 4:1 volume ratio or electrochemically reduced HI to adjust the pH value to -0.78. The solution was heated at 100 °C for 1 h, then cooled to room temperature to obtain the saturated solution with MAPbI₃ precipitates.

MAPbI₃ powder that was thermally annealed in polar solvent atmosphere was prepared by placing 1 g of MAPbI₃ powder on a hot plate at 130 °C, and 200 μ l of *N*,*N*-dimethylformamide (DMF) was sprayed near the MAPbI₃ powder and sealed under a glass Petri dish to contain the DMF vapour. The MAPbI₃ powder was annealed for 3 h. MAPbI₃ powder treated with dimethyl sulfoxide (DMSO) was prepared using the same method.

Solubility measurement. First, 500 mg of MAPbI₃ powder was added to 1 ml of aqueous HI solution. The solution with added powder was sonicated and shaken for 30 min at different temperatures to reach dynamic equilibrium. After that, 100 µl of the supernatant liquid from each solution was dropped on plasma-treated silicate glass and annealed for 20 min at 110 °C to evaporate all of the solvent. The solute weight was calculated from the mass difference between the weight before and after solution dropping. Using the solute MAPbI₃ weight, the solubility was calculated at each temperature.

Halogen atom substitution and phase mapping experiment. To verity the halogen atom exchange between the powder and the saturated solution, a methylammonium lead bromide (MAPbBr₃) saturated solution was prepared

using a method similar to the MAPbI₃ saturated solution synthesis, except that HBr was used instead of HI. No $\rm H_3PO_2$ addition or electrochemically reducing process was needed for the MAPbBr₃ saturated solution. Next, 300 mg of synthesized MAPbI₃ powder was transferred into 5 ml of MAPbBr₃ saturated HBr solution, stirred for 5 min, and filtered. The XRD pattern of the filtered powder was obtained.

Phase mapping of MAPbI₃ under different I⁻ and H⁺ concentrations was performed. The ion concentrations of the solutions were controlled by adding deionized water, HClO₄, and KI into the solution. First, 300 mg of MAPbI₃ powder was added to 400 µl of prepared solution and sonicated for 5 min. Then, the solution with the powder was shaken for 30 min for phase stabilization. The powder in the solution was filtered for phase verification by X-ray diffraction (XRD) pattern measurement. The XRD data were collected using an X-ray diffractometer (D-8 Advance, Brucker) in the Bragg–Brentano $\theta/2\theta$ geometry with Cu K α radiation ($\lambda = 1.54056$ Å) at 40 kV–40 mA. The scan range was from 10° to 60°, with a step size of 0.02° and scan speed of 5° per minute.

Surface morphology of powder at dynamic equilibrium. An MAPbI₃ saturated HI solution without precipitates was prepared by obtaining the supernatant of a solution of the two compounds. Then, 300 mg of MAPbI₃ powder prepared in organic solution was ground, added to the saturated HI solution, stirred, and then filtered. The surface of the MAPbI₃ powder was measured using a field-emission scanning electron microscope (FE-SEM, MERLIN Compact, Zeiss) at an operating voltage of 2kV.

Absorbance spectroscopy and UPS measurements. The absorption spectrum of the MAPbI₃ powder was analysed by means of a UV/Vis/NIR spectrophotometer (Cary 5000, Agilent Technology) using the diffuse reflectance mode. The UPS measurement was conducted using MAPbI₃ powder prepared from an aqueous HI solution with He I photon energy (21.2 eV) calibration, and the pass energy was 2.95 eV. The step size was 0.025 eV, the time was 20 ms, and five scans were conducted.

Electrochemical measurements. Electrochemical measurements were performed using a potentiostat (CHI 760E, CHInstrument) with a conventional three-electrode system. A Pt foil was used as the counter electrode. A Pt foil pseudo-reference electrode and a calomel reference electrode (CHI150, CHInstrument) were used for voltammetry and bulk electrolysis experiments, respectively. First, 30 ml of saturated HI solution was added to the H cell. In the case of MAPbI3 catalysis for the hydrogen evolution reaction, 100 µl of MAPbI3 saturated HI solution was dropped on 2 cm² of carbon fibre paper and dried on a 110 °C hot plate for 20 min. In the case of pure HI solution hydrogen evolution, carbon fibre paper with an active area of 2 cm^2 was used without any treatment. The current-voltage curve was measured via linear sweep voltammetry analysis in a sealed H cell with an Ar atmosphere at a scan rate 50 mV s⁻¹. The resistance between the electrode and the solution was also compensated for, thus observing only the catalytic effect. Bulk electrolysis was performed for 15 min in an Ar-purged H cell with tight sealing to ensure gas capture. After the bulk electrolysis, the gas in the working electrode compartment was measured using gas chromatography (GC, DS Science, iGC7200) and a thermal conductivity detector (TCD). Current-voltage curves were produced for comparisons of the solutions with both H_3PO_2 and HI (7.6 mol l^{-1} HI 8 ml + 50 wt% H_3PO_2 2 ml), deionized water, $HClO_4$, and H_3PO_2 (deionized water 2.76 ml + 70 wt% $HClO_4$ $5.24 \text{ ml} + 50 \text{ wt}\% \text{ H}_3 \text{PO}_2 2 \text{ ml}$), and the solution with only $\text{H}_3 \text{PO}_2$ (deionized water 8 ml + 50 wt% H₃PO₂ 2 ml); 0.3 cm² of Pt foil was used as the working electrode. The scan rate was 50 mV $\rm s^{-1}.$

Product analysis of MAPbI3 photocatalytic reaction. Two kinds of reduced HI solution were used for the gas product analysis. First, the electrochemically reduced HI solution was synthesized as below. A H cell was used to separate the anode and cathode compartment, and a Nafion 115 membrane was placed between each compartment. Then, 15 ml of 6.06 mol l-1 HI solution was placed in the anode compartment, and 15 ml of 6.06 mol l-1 HI solution was placed in the cathode compartment. Carbon fibre paper with an active area of 3 cm² was used for both the cathode and the anode. Before electrolysis, Ar purging was conducted for 10 min in the cathode compartment. Next, 800 mA of current was applied using a power supply for 1.5 h, and Ar purging was sustained during electrolysis. Deionized water was added to adjust the pH value to -0.78. In contrast, H₃PO₂ was added to the pure HI solution to prepare the reduced HI solution. First, 7.6 mol l^{-1} HI and H_3PO_2 were mixed in a 4:1 volume ratio (pH = -0.78). Then, 10 ml of the reduced HI solution was mixed with 4.2 g of MAPbI₃ powder prepared in a HI solution under Ar atmosphere to prevent oxidation of the reduced HI solution. To saturate the reduced HI solution with MAPbI₃, stirring was continuously performed for 3 h under an Ar atmosphere to synthesize the saturated solution in the dark. A solar simulator (HAL-302, Ashai Spectra) was used as the light source, and the irradiation spectrum was controlled using a 475 nm cutoff filter that passed wavelengths longer than 475 nm. The light intensity was fixed as 100 mW cm⁻² in this case. Fan cooling was used on the reactor to prevent the temperature of the reactor increasing due to the light source. The temperature difference before and after the light irradiation was only about 0.5 °C. The evolved hydrogen was measured using GC. To measure the evolved I3⁻, the same sample was prepared and measured under the same light conditions. At certain times, 0.01 ml of solution was obtained and diluted to 1/200 with deionized water. Finally, the diluted solution was analysed using a UV/Vis/NIR spectrometer (Cary 5000, Agilent Technology). The absorbance value at 353 nm was compared to a standard curve of I3- solutions to calculate the amount of I₃⁻ in the solution. The standard I₃⁻ solution was prepared by diluting the standard iodine solution with 0.01 mol l⁻¹ of KI solution to the desired concentration.

MAPbI₃ photocatalytic reaction rate with various treatments. The desired amount of MAPbI₃ powder was placed in 50 ml of saturated HI solution (H₃PO₂ mixed) and stirred for 30 min to reach dynamic equilibrium. The solution was placed in a quartz vessel and stirred vigorously during the photoreaction. The solar simulator was used as the light source. The irradiation spectrum was controlled by the 475 nm cutoff filter. Before the photocatalytic reaction, the vessel was purged with Ar for 15 min. The generated H₂ gas was measured using GC. The light irradiation area was controlled by masking the surface of the reactor. To reduce the light irradiation area, we masked a 0.5 cm by 0.5 cm area of the reactor and the light source. The light intensity was measured using a thermopile sensor (Newport, Model 818P-001-12).

Pt deposited MAPbI₃ preparation. 200 mg of thermally annealed MAPbI₃ powder in a polar solvent atmosphere was mixed with 2 ml of saturated HI solution. Then, 9 mg of $H_2PtCI_6 \cdot 6H_2O$ was mixed with the solution. Next, by using the solar simulator with a 475 nm cutoff filter, photodeposition was conducted under Ar atmosphere for 2 h. The sample consisting of 200 mg of MAPbI₃ powder with photodeposited Pt and 2 ml of saturated HI solution was transferred into 48 ml of saturated HI solution in a quartz reactor and purged with Ar for 15 min. The photocatalytic performance was analysed using GC under a solar simulator with a light filter that passes only wavelengths longer than 475 nm.

Calculation of the efficiency. The solar HI splitting efficiency, so-called solar-to-chemical conversion efficiency, is the ratio of solar light converted to break the chemical bonding of HI. It could be calculated by means of the standard redox potential of I⁻ oxidation and the H⁺ reduction potential. Our calculation for HI splitting efficiency is based on the amount of evolved hydrogen. The standard hydrogen reduction potential is 0 V (versus RHE), and the I⁻ oxidation potential to I₃⁻⁻ is 0.53 V (versus RHE). Because the concentration of HI we used was 6.06 mol I⁻¹ and the I₃⁻⁻ ion concentration in the reduced HI solution was 1.40 × 10⁻³ mol I⁻¹, the redox potential could be determined from the Nernst equation.

 $E(2H^+ + 2e^- \rightarrow H_2) = 0 - 0.0592 \times \log(1/6.06) = 0.046 \text{ V(versus NHE)}$

 $E(3I^- \rightarrow I_3^- + 2e^-) = 0.53 + 0.0592/2 \times \log(1.40 \times 10^{-3}/6.06^3)$

= 0.376 V(versus NHE)

For this reason, the total potential for the 6.06 mol l^{-1} of HI solution splitting could be calculated as 0.376~V-0.046~V=0.330~V.

By using this potential, the solar HI splitting efficiency could be estimated from the following equation:

Solar HI splitting efficiency = $[Evolved H_2(mol) \times 6.02 \times 10^{23} \times 2 \times 0.330 (eV)]$

 $\times 1.6 \times 10^{-19}] / [P_{sol}(W cm^{-2}) \times Area(cm^{2}) \times time(s)] \times 100$

For instance, in the case of the MAPbI₃ powder with Pt deposited, 57 μ mol of H₂ could be generated after 5 h of light irradiance at 100 mW cm⁻². Because our light irradiation area was 0.25 cm², the solar HI splitting efficiency could be calculated as 0.81%.

Data availability. The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files. Extra data are available from the corresponding author upon request.

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Author contributions

K.T.N. conceived and supervised the project. S.P. conceived, synthesized and characterized the MAPbI₃ inside the aqueous solution system, designed experiments and co-wrote the manuscript. W.J.C. characterized the photocatalytic reaction and co-wrote the manuscript. C.W.L. and S.P. supported analysis of the GC data of HI splitting reaction. H.-Y.A. measured the SEM image of MAPbI₃ powder. The manuscript was mainly written and revised by K.T.N., S.P. and W.J.C. All authors discussed the results and commented on the manuscript.

Additional information

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Competing interests

The authors declare no competing financial interests.