Supporting Information

Tuning the Dimensionality of Organic-Inorganic Hybrid Perovskites towards Improved Photocatalytic Hydrogen Production

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TA experiment set-ups

A beam of ultra-short pulse laser with a wavelength of 800 nm is emitted from the regeneratively amplified Ti: sapphire laser system (Coherent; 800 nm, 70 fs, 6 mJ/pulse, and 1 kHz repetition rate) in the ultra-fast femtosecond laser system, which is split into two laser beams after passing through a 1:9 beam splitter. The larger 90% of the laser beam in the transmitted part passes through the optical delay line ODL and is frequency doubled to 400 nm by a BBO crystal as the pump beam. The pump beam passes through the center of the convex lens and is focused on the sample to be tested at a certain angle. The sample is excited from the ground state to the excited state. The less powerful 10% of the reflected portion is partially attenuated with a neutral density filter and focused into a 2 mm thick sapphire window to generate a white light continuum used for probe beam. The probe beam passes through the center of the convex lens and is focused together with the pump beam at the same location on the sample. And ensure that the pump beam and the probe beam are spatially coincident (spatial coincidence refers to the coincidence of the spots of the two beams) and temporally (at time zero, the laser pulses of the two beams arrive at the same position of the sample at the same time). In this way, the sample molecules excited from the ground state to the excited state will absorb the probe beam in the excited state. After passing through the sample, the pump beam incident on the sample at a certain angle will be blocked by the diaphragm and will not be received by the fiber probe, while the probe beam carrying the excited state information will be received by the fiber probe and then focused into fiber-coupled spectrometer with CMOS sensors with a detection frequency of 1 kHz. A variable neutral point control-density filter wheel was used to adjust the pump pulse intensity

during the experiment. A synchronous chopper cuts off the pump pulse at 500 Hz and the absorbance change is calculated with two adjacent probe pulses.

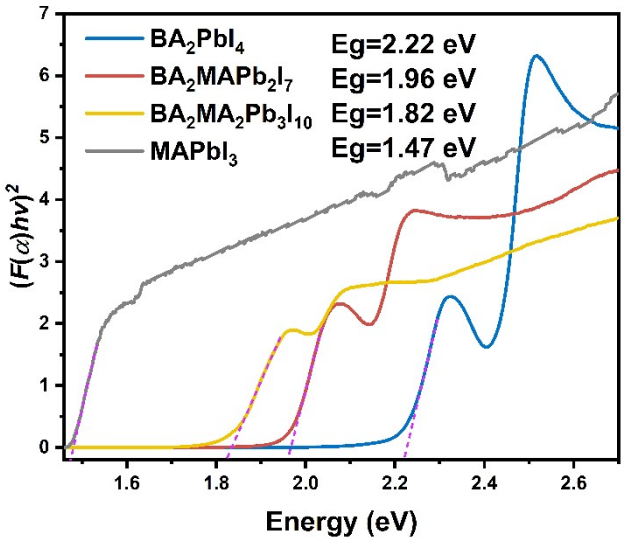

Figure S1. Band gap determination from Kubelka-Munk plots of 2D, quasi-2D, and 3D perovskite crystals.

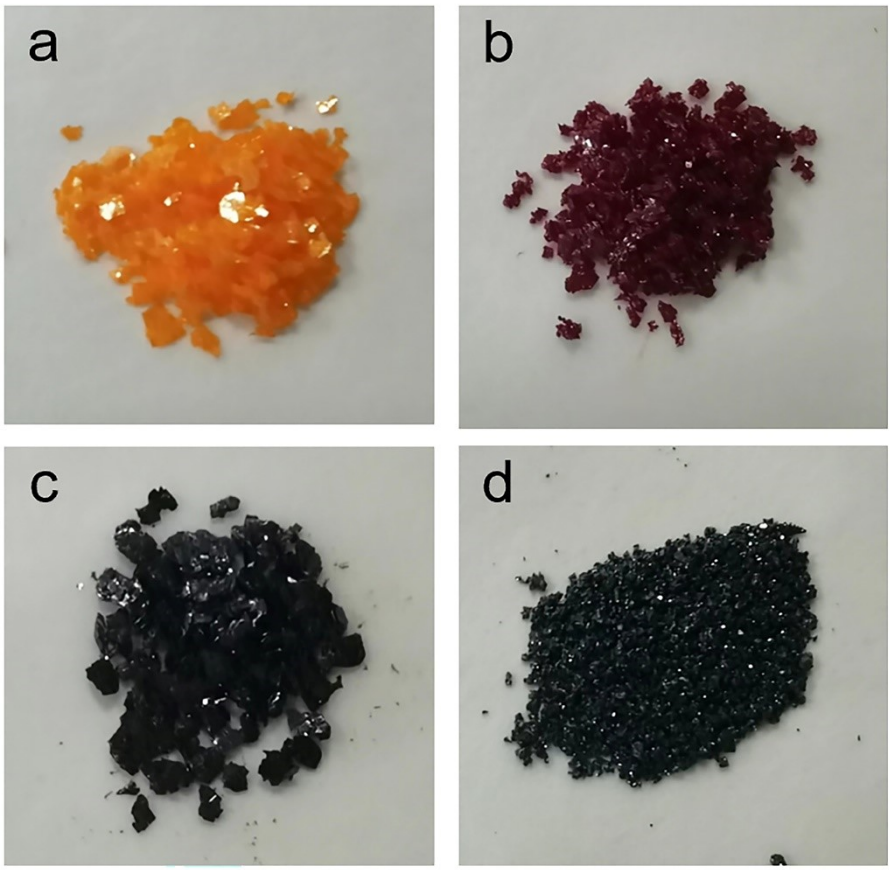

Figure S2. The photographic images of as-prepared perovskite crystals. (a) BA_2PbI_4, (b) $BA_2MAPb_2I_7$, (c) $BA_2MA_2Pb_3I_{10}$, and (d) $MAPbI_3$.

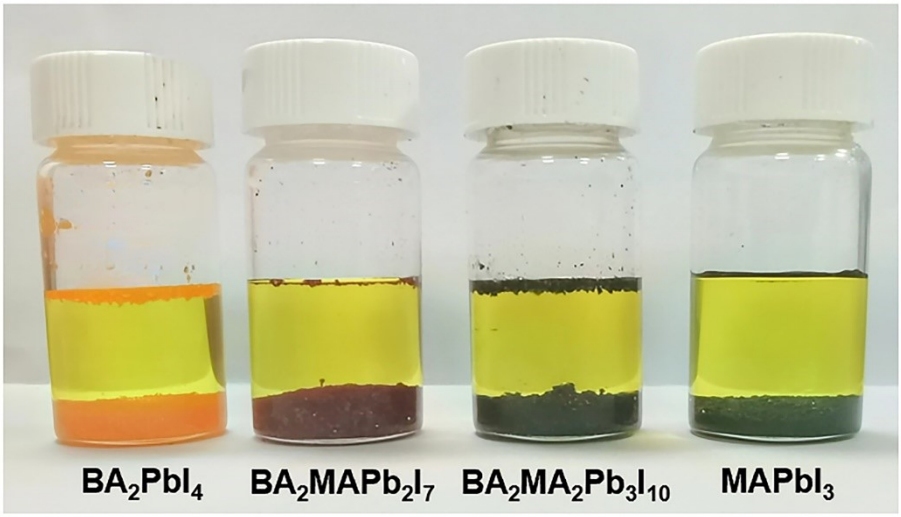

Figure S3. Photographs of 2D, quasi-2D, and 3D perovskites crystals stabilized in saturated HI solution.

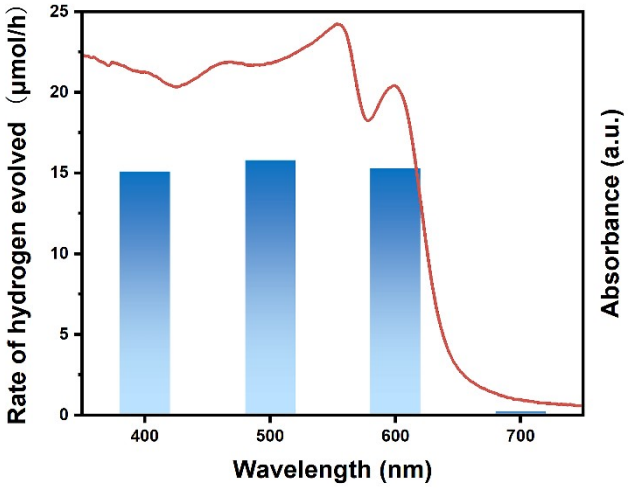

Figure S4. The rates of H_2 evolution on Pt (0.5 wt%)/ $BA_2MAPb_2I_7$ under photoirradiation of different wavelengths. Reaction conditions: 15 mL perovskite saturated solutions, 50 mg of perovskite photocatalyst, 300 W xenon lamp band pass filters of different wavelengths, reaction cell: top-irradiation cell with a Pyrex window.

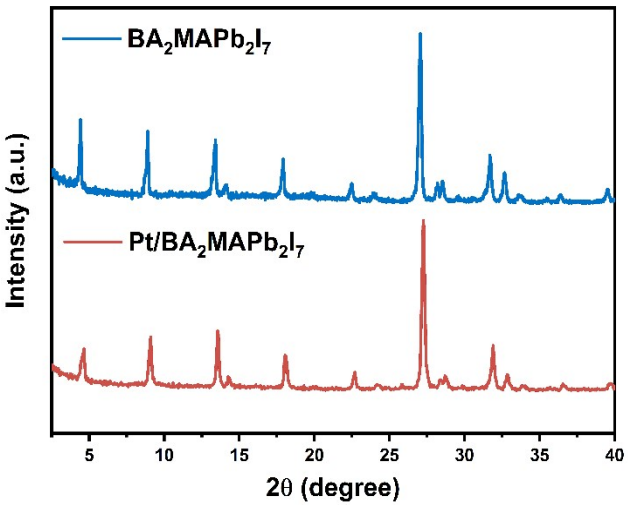

Figure S5. XRD patterns of $BA_2MAPb_2I_7$ perovskite samples before (blue) and after (red) photocatalytic reactions.

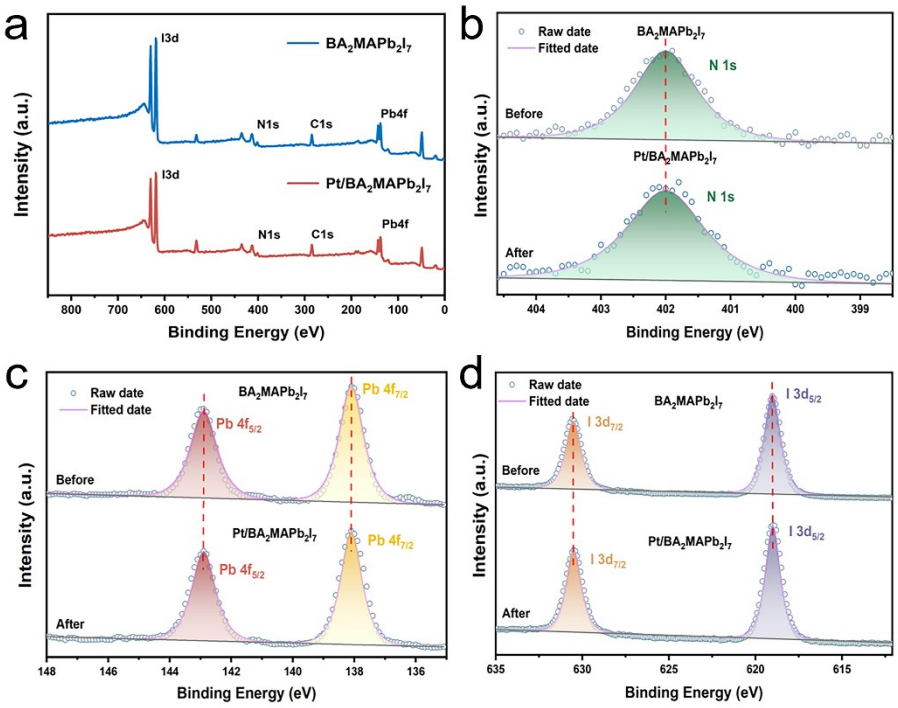

Figure S6. XPS spectra of $BA_2MAPb_2I_7$ perovskite samples before and after photocatalytic reactions. (a) Survey spectrum, (b) N 1s, (c) Pb 4f and (d) I 3d.

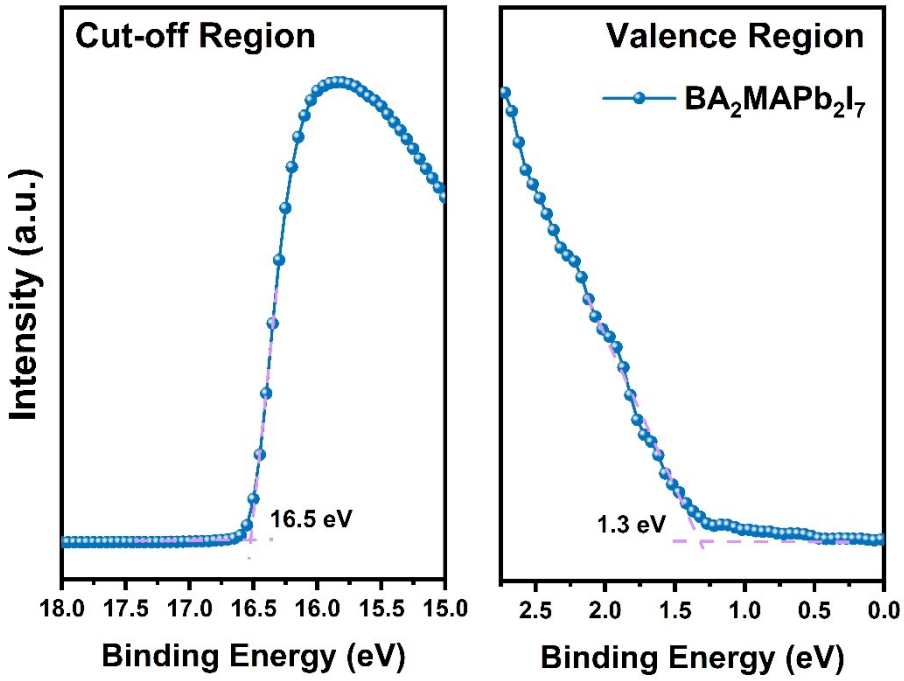

Figure S7. UPS spectra of $BA_2MAPb_2I_7$ perovskites.

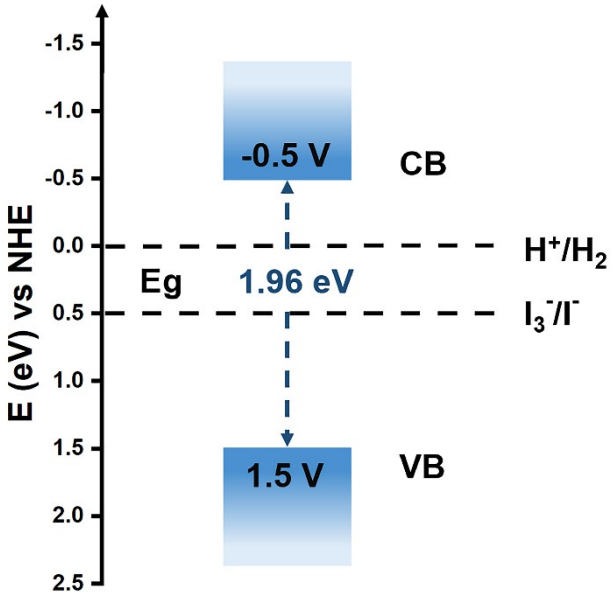

Figure S8. The schematic energy diagrams of $BA_2MAPb_2I_7$ perovskites relative to the redox potentials of HI splitting reaction.

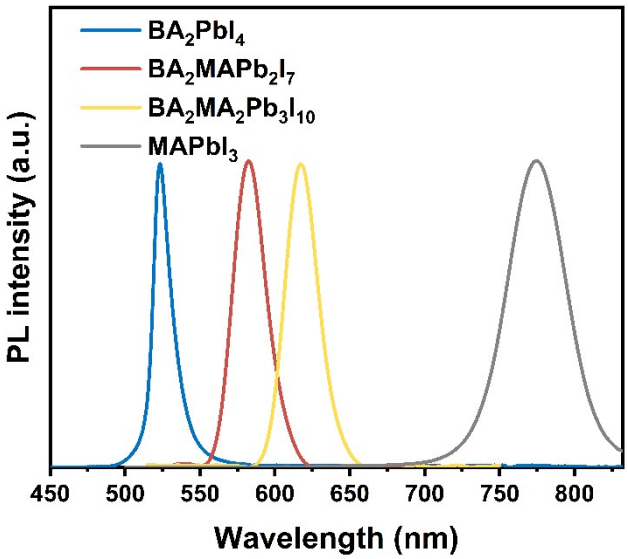

Figure S9. The PL spectra of 2D, quasi-2D, and 3D perovskite crystals.

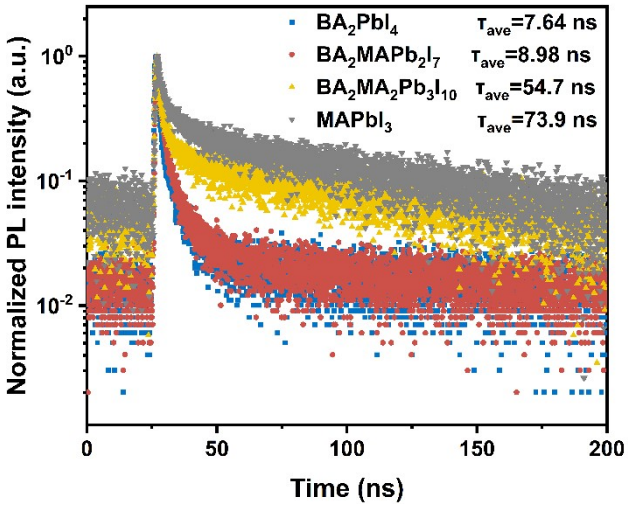

Figure S10. The TRPL decay curves of 2D, quasi-2D, and 3D perovskite crystals.

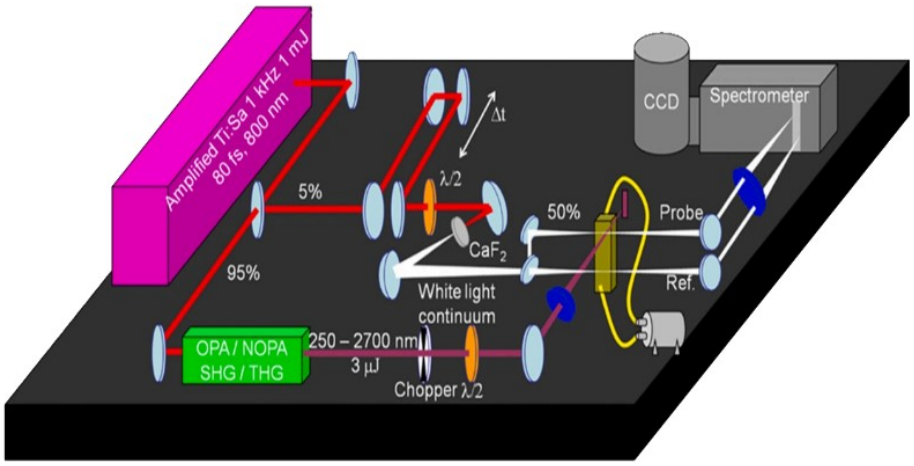

Figure S11. Schematic of the transient absorption setup with laser system and transient spectrometer.

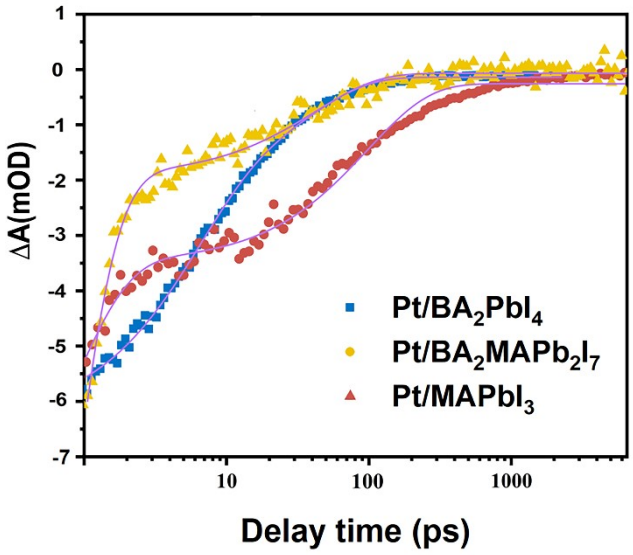

Figure S12. The exciton bleach kinetics of the Pt/BA_2PbI_4, Pt/$BA_2MAPb_2I_7$, and Pt/$MAPbI_3$ samples. The pink solid lines are bi-exponential decay model fit to the kinetics.

Table S1. TA decay lifetime of BA_2PbI_4, $BA_2MAPb_2I_7$, and $MAPbI_3$ samples.

Sample	BA_2PbI_4	$BA_2MAPb_2I_7$	$MAPbI_3$
τ_{ave} (ps)	44.5	296.5	7171.7

Kinetics fitting models. The TA kinetics of the perovskites are fitting to a bi-exponential decay:

$$S \propto A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (1)$$

where A_1, A_2 and τ_1, τ_2 are the relative amplitude and time constant. According to the relative amplitude and time constant obtained by the bi-exponential fitting, the average electron transfer, hole transfer and charge recombination time constants (τ_{ave}) of the carrier is calculated by the following formula:

$$\tau_{ave} = \tau_1 * A_1/(A_1+A_2) + \tau_2 * A_2/(A_1+A_2) \quad (2)$$

Table S2. TA decay lifetime of Pt/BA_2PbI_4, $Pt/BA_2MAPb_2I_7$, and $Pt/MAPbI_3$ samples.

Sample	Pt/BA_2PbI_4	$Pt/BA_2MAPb_2I_7$	$Pt/MAPbI_3$
τ_{ave} (ps)	35.6	89.3	134.2

Table S3. Interfacial charge transfer efficiency between perovskites and Pt co-catalysts.

Sample	Pt/BA_2PbI_4	$Pt/BA_2MAPb_2I_7$	$Pt/MAPbI_3$
Charge transfer efficiency	55.6%	76.9%	98.2%

The charge separation efficiency (η) of Pt/perovskite samples can be calculated using the following expression:

$$\eta = \tau_{ave}*\tau_{int} /(\tau_{ave}*\tau_{ave}+\tau_{ave}*\tau_{int}) \quad (3)$$

where τ_{ave} corresponds to the averaged lifetime constant for the Pt/perovskite samples; τ_{int} is the averaged lifetime constant for the pure perovskite samples.