Supporting Information

All-Inorganic Lead Halide Perovskite-Based Photocathode for Stable Water Reduction

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Materials

CsBr, $PbBr_2$ were purchased from Aladdin Chemistry Co. Ltd. Methanol, Isopropanol, N,N-dimethylformamidel (DMF), Dimethyl sulfoxide (DMSO), Trichloromethane, Nickel(II) acetate tetrahydrate, Zinc acetate dihydrate were from Sinopharm Chemical Reagent Co. Ltd. Ethanolamine, Ethylene glycol monomethyl ether were from Shanghai Lingfeng Chemical Reagent Co. Ltd. Silver paste was purchased from Guangzhou Kaixiang Electronics Co. Ltd. InBiSn alloy was from Northeastern Non-ferrous Market Co. Ltd. $H_2PtCl_6 \cdot 6H_2O$ was purchased from Shanghai Reagent Factory. All chemicals were used as received.

Precursor Preparation

Nickel oxide (NiO) precursor solution was prepared as follows. 0.3 M nickel (II) acetate tetrahydrate with 0.3 M ethanolamine was mixed in ethylene glycol monomethyl ether, and stirred at 70 °C for 1 h. Then the solution cooled down to room temperature and was kept for future use.

Zinc oxide (ZnO) nanoparticles were prepared in methanol via hydroxylation of zinc acetate by potassium hydroxide. 0.1 M zinc acetate dihydrate was dissolved in methanol (12.5 mL) with stirring at 65 °C. A solution of KOH (0.35 M) in methanol (6.5 mL) was then added dropwise. The reaction mixture was stirred for 2.25 h at 65 °C. After cooling to room temperature, the supernatant was decanted and the precipitate was washed twice with methanol. Chloroform was added to disperse the precipitate and produce a 2 wt.% ZnO nanoparticle solution.

Photocathode preparation

The pre-patterned FTO glass was spin-coated with the precursor solution of NiO at 3,000 r.p.m. for 30 s, and annealed at 400 °C for 1 h. Subsequently, a DMF/DMSO (v/v=9:1) solution of 1.4 M $PbBr_2$ was spin-coated onto the NiO layer at 2,000 rpm for 30 s and dried at 80 °C for 30 min. Then the substrate was dipped in a methanol solution of 0.07 M CsBr for different reaction time, rinsed with isopropanol, dried in air, and heated at 150 °C for 5 min on a hot plate to form a uniform layer of $CsPbBr_3$. ZnO nanoparticles were spin-coated on the perovskite surface at 2,000 r.p.m. for 30 s, and then annealed at 100 °C for 5 min. The silver paste was deposited on the $CsPbBr_3$ layer by doctor-blade coating and then heated at 90 °C for 10 min. A piece of InBiSn alloy was placed on the substrates and heated to 90 °C. Once the InBiSn alloy melted completely, the device was left to cool on the hot plate. Finally, a Pt co-catalyst was deposited onto the InBiSn alloy in an H_2PtCl_6 solution (2.2 mmol/L) by electrochemical deposition method. The deposition potential was -1 V vs. Ag/AgCl and the deposition time was 300s.

Sample Characterization

The morphology of samples was examined with a scanning electron microscope (Nova NanoSEM 230, FEI Co.). The crystal structure of the films was obtained by X-ray diffraction

(Ultima III, Rigaku Corp.). The absorption of samples was performed on an UV-visible-near-infrared (UV-Vis-NIR) spectrophotometer (Lambda 950, PerkinElmer). The steady-state fluorescence was characterized by fluorescence spectrophotometer (Cary eclipse, Varian).

Photoelectrochemical performance measurement

Photoelectrochemical properties of the photocathodes were measured in a conventional three-electrode cell using an electrochemical analyzer (CHI-630D, Shanghai Chenhua, China). An as-prepared photocathode, a Pt foil, and an Ag/AgCl/saturated KCl electrode were used as the working electrode, counter electrode, and a reference electrode, respectively. Since the encapsulating material, InBiSn alloy, may be easily corroded in the acidic environment, an aqueous solution containing 0.2 mol/L Na_2HPO_4/NaH_2PO_4 (pH = 8) was used as electrolyte. The light sources were a solar simulator (Oriel 92251A-1000, AM 1.5 G, 100 mW cm^{-2}) and a 500 W Xe lamp. The samples were illuminated from the glass side and a scanning rate of 50 mV s^{-1} was applied. Potentials of the working electrode can be calculated by the formula $V_{RHE}=V_{Ag/AgCl}+0.197V+ 0.059\times pH$, where V_{RHE} was the potential vs. a reversible hydrogen potential, $V_{Ag/AgCl}$ was the potential vs. Ag/AgCl electrode. The incident photon-to-current efficiency (IPCE) was determined under irradiation of different wavelengths of light generated by monochromatic filters. The IPCE was calculated as follow:

$$IPCE = \frac{1240 \times I_{ph}}{P \times \lambda}$$

Where I_{ph} is the photocurrent density (μA cm^{-2}), P and λ are the incident light intensity (μW cm^{-2}) and wavelength (nm), respectively. The incident light intensity was measured by a photometer (Newport, 840-C, USA). Faradaic efficiency was measured under Xe lamp illumination. The cell was sealed and purged by Ar for 30 min until no O_2 or N_2 was detected before the Faradaic efficiency measurement. Evolved H_2 gas was detected by a gas chromatograph (SHIMADZU, GC-8A).

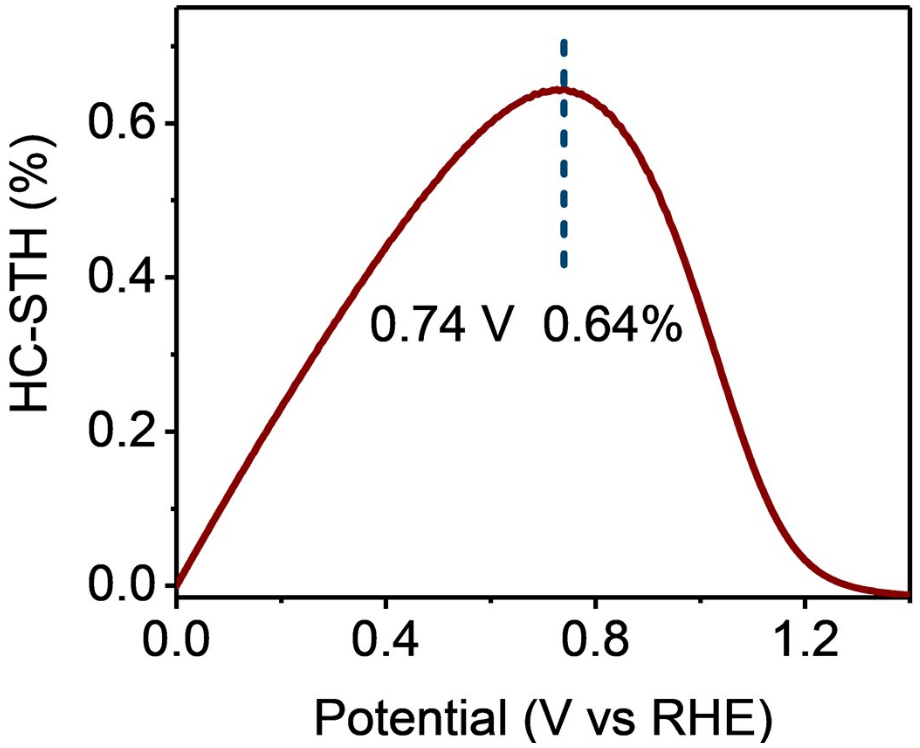

Figure S1. Half-cell solar to hydrogen efficiency of $CsPbBr_3$-based photocathode.

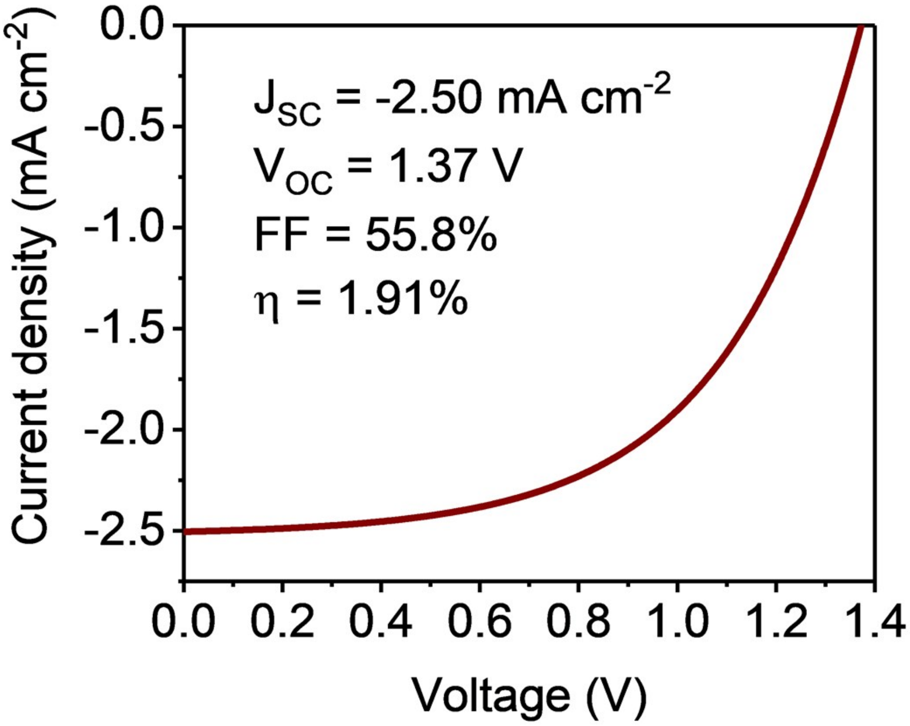

Figure S2. The current density–voltage curve for the inverted $CsPbBr_3$-based solar cell under simulated AM 1.5 G solar light.