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A Multifunctional C+epoxy/Ag-paint Cathode Enables Efficient and Stable Operation of Perovskite Solar Cells in Watery Environments

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Supplementary Materials

Materials: Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich or J&K and used as received.

Preparation of CH_3NH_3I. CH_3NH_3I was prepared by reacting 24 mL of methylamine (40 wt. % in water, J&K) and 12 mL of hydroiodic acid (57 wt% in water, stored in refrigerator, J&K) in ice bath for 2 h with stirring. The precipitate was recovered by rotary evaporation at 50 °C and carefully removing the solvents with the help of low temperature circulator. It is noted that overheating resulted in dark yellow product due to the formation of I_2. The as-prepared CH_3NH_3I was re-dissolved in ethanol and precipitated with diethyl ether, which was repeated twice. Finally, the white solid was collected by filtration and dried at 60 °C in a vacuum oven overnight.

Preparation of PbI_2. PbI_2 was prepared by simply adding KI solution into $Pb(NO_3)_2$ solution (molar ratio: 2 : 1), collecting the yellow powder by filtration, washing by water and drying at 60 °C in vacuum oven overnight.

Modification of Ag paint: a commercial Ag paint (SPI, original solvent is a mixture of chloroform, ethyl acetate and butyl acetate) is firstly dried by rotary drying and re-dispersed in butyl acetate solvent for encapsulation application.

Device fabrication. The FTO glasses were sequentially cleaned in detergent solution, deionized water, acetone, ethanol and dried with compressed air.

Step 1: After UV-O_3 cleaning, the substrates were put on a heating plate and heated up to 500 °C, and a 50 - 100 nm TiO_2 compact layer was deposited by a home-made ultrasonic spray deposition equipment using titanium diisopropoxide bis(acetylacetonate) solution (0.05 M, ethanol). Then, a ~ 350 nm TiO_2 mesoporous layer by spin-coating (3,000 r.p.m, 20 s) using the diluted TiO2 paste solution (1 : 3.5 wt%, Dyesol 30 NRD). At last, the substrates were transferred into a home-made glove-box, which supplied a dry and closed working condition (note: lead is a highly poisonous metal, regardless if inhaled or swallowed).

Step 2: PbI_2 was dissolved in *N,N*-dimethylformamide (DMF) at a concentration of 460 mg mL^{-1} and kept at 100 ℃. The FTO/TiO_2 substrates were also pre-heated to 100 ℃ and the PbI_2 solution was then spin coated on the top of the TiO_2 layer at 2,000 r.p.m. for twice. After coating, the FTO/TiO_2/PbI_2 substrates were heated at 100 ℃ for 15 min and then cooled down to room temperature. When the substrates were cooled down to room temperature, the substrates were soaked in CH_3NH_3I isopropanol solution (10 mg mL^{-1}) for 30 min, dried by spin-coating and baked at 100 ℃ for 5 ~ 30 min.

Step 3: When the substrates were cooled down to room temperature, carbon paint (Guangzhou Seaside Technology Co., Ltd) is bladed on the perovskite layer directly and baked at 100 ℃ (30 min) for resin curing. Lastly, the modified silver paint was brushed on the cured carbon electrode and baked at 100 ℃ for another 30 min.

Material and device characterization. X-Ray diffraction (XRD) data was collected on an X'pert Pro (PANalytical) with Cu K□ radiation. Morphologies of the perovskite-related films were directly examined on JEOL6700F Scanning electron microscope (SEM) at an accelerating voltage of 5 kV. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) were carried out on a JEOL 2010 transmission electron microscope operating at 200 kV. Raman measurements were conducted on a Renishaw 2000 laser Raman microscope equipped with a

632.8 nm and 17 mW argon ion laser with a 1 μm spot size for excitation. Resistance and Hall Effect was conducted using a cured carbon paint thin in HL5500PC (Bio-Rad).

Solar cell and water splitting performance evaluation. The solar light simulator (Newport solar simulator, model number 6255, 150 W Xe lamp, AM 1.5 global filter) was calibrated to 1 sun (100 mW cm^{-2}) using a silicon reference solar cell equipped with KG-5 filter. The cell active area is 0.07 cm^{-2}. Current density-voltage (*J–V*) characteristic curves of solar cells and current density-time curves of water splitting cells were recorded using an IM6x electrochemical workstation (ZAHNER-Elektrik GmbH & Co., KG, Germany). Incident-photo-to-current conversion efficiency (IPCE) spectra were recorded using IPCE kit developed by ZAHNER-Elektrik in AC mode with frequency of 1 Hz.

Supplementary results:

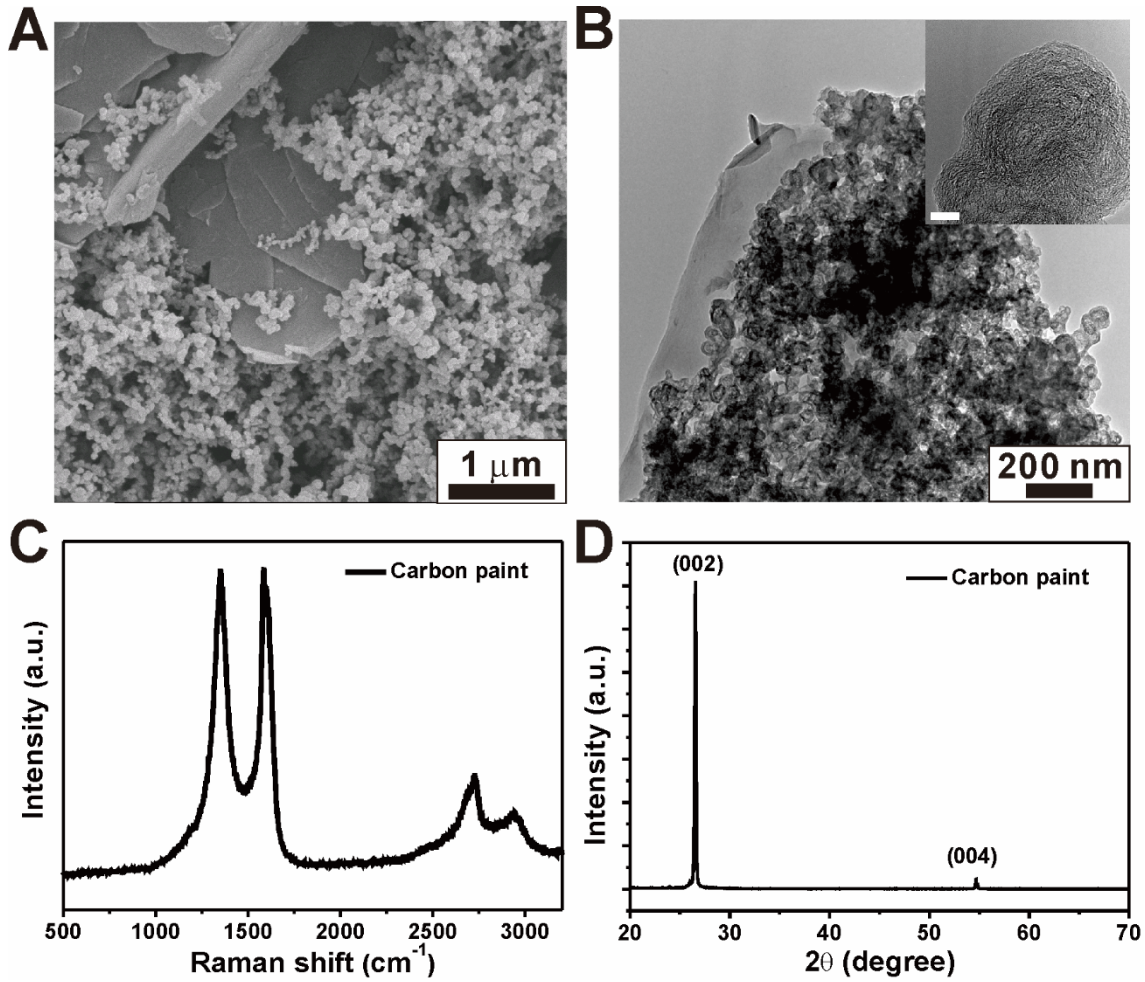
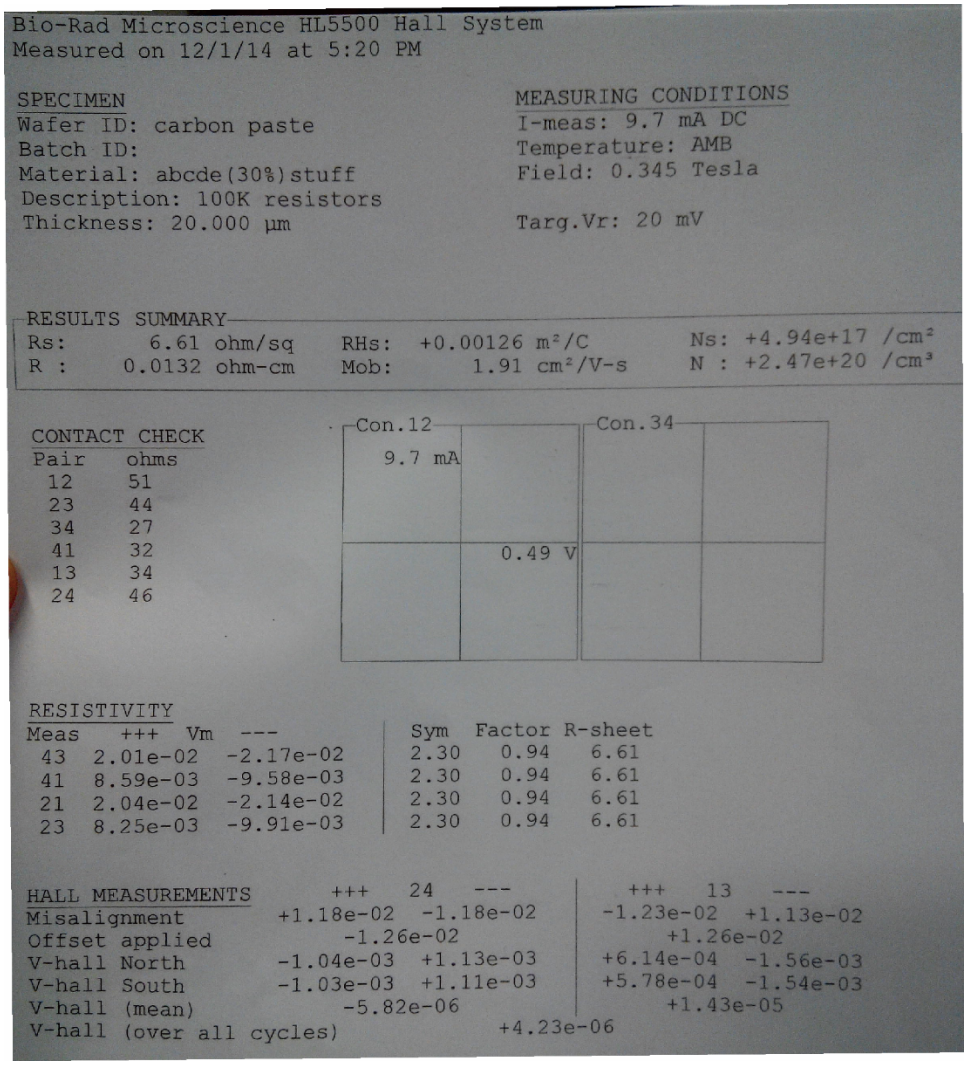


Figure S1. Characterization of C+epoxy thin film. (A) SEM image, (B) TEM image (the scale bar in the insert is 10 nm), (C) Raman spectrum and (D) X-ray diffraction spectrum.



Bio-Rad Microscience HL5500 Hall System
Measured on 12/1/14 at 5:20 PM

SPECIMEN
Wafer ID: carbon paste
Batch ID:
Material: abcde(30%)stuff
Description: 100K resistors
Thickness: 20.000 µm

MEASURING CONDITIONS
I-meas: 9.7 mA DC
Temperature: AMB
Field: 0.345 Tesla

Targ.Vr: 20 mV

RESULTS SUMMARY

Rs:	6.61 ohm/sq	RHs:	+0.00126 m²/C	Ns:	+4.94e+17 /cm²
R :	0.0132 ohm-cm	Mob:	1.91 cm²/V-s	N :	+2.47e+20 /cm³

CONTACT CHECK

Pair	ohms
12	51
23	44
34	27
41	32
13	34
24	46

Con.12 Con.34
9.7 mA
0.49 V

RESISTIVITY

Meas	+++	Vm ---	Sym	Factor	R-sheet
43	2.01e-02	-2.17e-02	2.30	0.94	6.61
41	8.59e-03	-9.58e-03	2.30	0.94	6.61
21	2.04e-02	-2.14e-02	2.30	0.94	6.61
23	8.25e-03	-9.91e-03	2.30	0.94	6.61

HALL MEASUREMENTS

	+++ 24	---	+++ 13	---
Misalignment	+1.18e-02	-1.18e-02	-1.23e-02	+1.13e-02
Offset applied	-1.26e-02		+1.26e-02	
V-hall North	-1.04e-03	+1.13e-03	+6.14e-04	-1.56e-03
V-hall South	-1.03e-03	+1.11e-03	+5.78e-04	-1.54e-03
V-hall (mean)	-5.82e-06		+1.43e-05	
V-hall (over all cycles)	+4.23e-06			

Figure S2. Resistance and Hall Effect test result of a C+epoxy paint thin film.

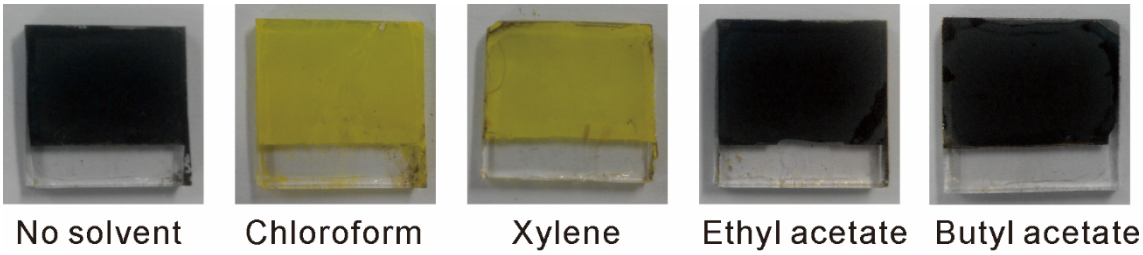


Figure S3. Perovskite stability test by soaking the perovskite thin film in different solvents. Based on this result, the original SPI Ag paint is firstly dried by rotary drying and re-dispersed in butyl acetate solvent for encapsulation application.

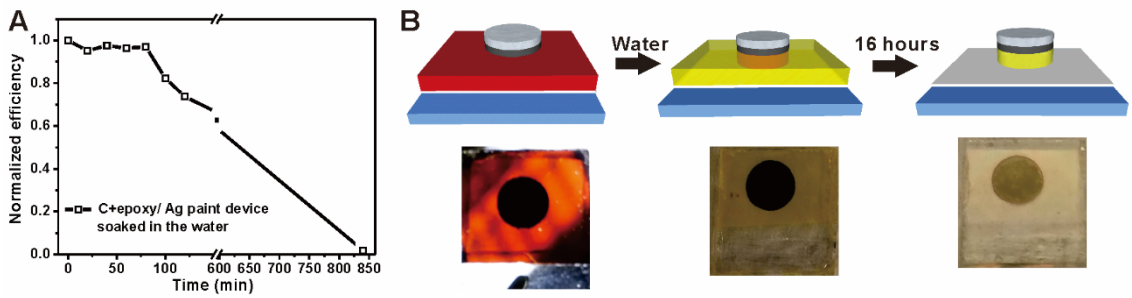


Figure S4. Waterproof capability of C+epoxy/Ag paint-based device. (A) Normalized efficiency as a function of soaking time in water (measured by recording *J-V* curves of the PSCs immersed in water). (B) Left: a device with only a circle of perovskite active material is covered by C+epoxy/Ag paint cathode. Middle: when the device is immersed in water for 1 s, it is found that only the circle of perovskite (black brown) is protected and others perovskite decompose into PbI_2 immediately (yellow). Right: after 16 hours, the perovskite circle decomposes completely into PbI_2 too and rest PbI_2 outside the circle has been dissolved in the water.

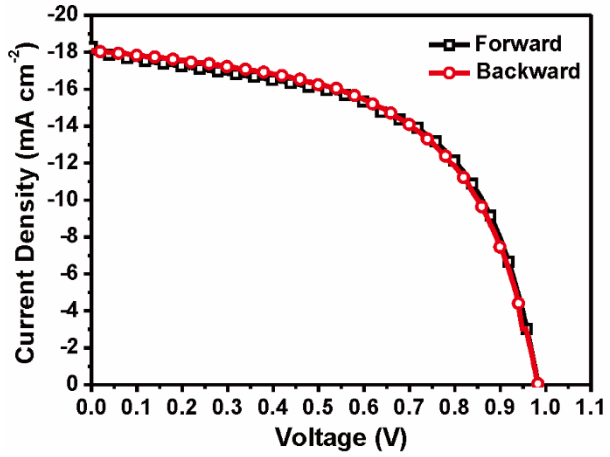


Figure S5. Forward and backward *J-V* curves (scan rate: 10 mV s^{-1} and delay time: 100 ms) of the as-fabricated C+epoxy/Ag paint-based perovskite solar cell.

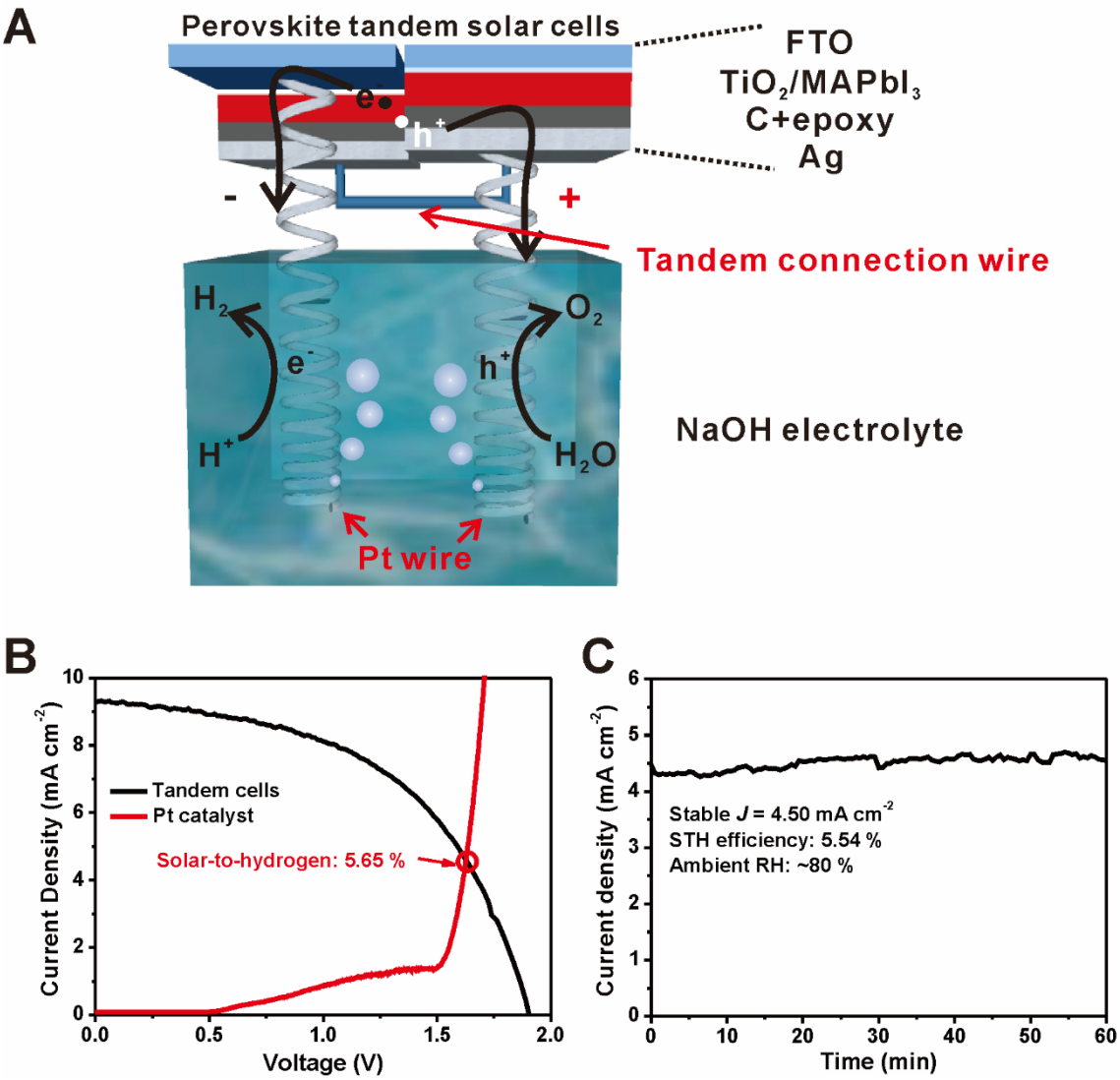


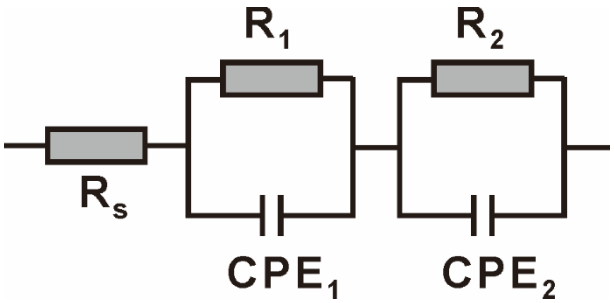
Figure S6. (A) Schematic diagram of an electrolysis cell fabricated by connecting a tandem C+epoxy/Ag paint-based perovskite solar cells and Pt catalyst: the two single cells are tandem connected by a metal wire firstly, then two Pt wires are connected to the as-fabricated tandem cells. (B) *J-V* curves of the tandem perovskite solar cells and Pt catalyst (oxygen evolution curve), where the intersection point indicating a solar-to-hydrogen (STH) efficiency of 5.65 %. (C) Timing profile of stabilized current density output of the electrolysis cell, which shows a stable solar-to-hydrogen efficiency of 5.54 % for 60 min.

The solar-to-hydrogen efficiency can be calculated according to equation:

$$\eta(\%) = \frac{J \times 1.23 \times \eta_F}{P_{In}} \times 100 \qquad (1)$$

Where η is the solar-to-hydrogen efficiency, *J* is the measured photocurrent density, η_F is the faradaic efficiency of catalyst and P_{In} is the illumination power density (100 mW cm^{-2} at standard AM 1.5G conditions).

Table S1. Fitting parameters obtained from EIS data (Figure 2E) and the corresponding equivalent circuit.



Samples	R_s (ohm)	R_1(ohm)	R_2 (ohm)
C based PSC	28.3	89	420
C+epoxy based PSC	28.8	--	214
C+epoxy/Ag paint based PSC	20.3	--	215