

Supporting Information for

A photovoltaic-hydrovoltaic coupled carbon-based, all-inorganic CsPbBr₃ perovskite solar cell

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Experimental section

1. Fabrication of the PSC devices

The inorganic Cs_{0.91}Rb_{0.09}PbBr₃ photoactive layer for carbon-based, all-inorganic PSCs was made by a solution-processable multi-step method. In particular, all processes were carried out in the air by controlling the humidity at around 20% RH. Firstly, a satisfactory patterned FTO substrate was obtained by the etching process with zinc powders and 2 M HCl, and then it was thoroughly cleaned in detergent, deionized water, ethanol, and isopropanol. The TiO₂ film includes a compact and a mesoporous layer. The compact layer was spin-coated onto an FTO using an ethanol solution (0.5 M titanium isopropoxide and 0.5 M diethanolamine) at 7000 rpm for 30 s, and annealed at 500 °C for 120 min. Secondly, the mesoporous layer was then spin-coated on the compact layer surface with the as-prepared TiO₂ paste for 30 s before being calcined in air at 450 °C for 30 min. Last, the above substrate was immersed in the 0.04 M TiCl₄ aqueous solution at 70 °C for 30 min, and then annealed at 450 °C 30 min. The above operations are in an atmospheric environment.

The perovskite film was fabricated by a multi-step solution-processing technology. In detail, 1 M PbBr₂ in *N,N*-dimethylformamide solution was spin-coated on the TiO₂ film surface at 2000 rpm for 30 s, and dried at 90 °C for 1 h. Then, the mixed solution (0.07 M CsBr and 0.007 RbBr) methanol was spin-coated on PbBr₂ film at 2000 rpm for 30 s, and heated at 250 °C for 5 min. This step was repeated five times to obtain the suitable perovskite films. After that, the perovskite films were rinsed with isopropanol and dried at 250 °C for 5 min. Finally, a carbon electrode was coated on the perovskite film with carbon paste (Shanghai MaterWin New Materials Co., Ltd.). The active area was controlled at 0.09 cm².

Following that, a paste composed of 30 mg of CB and 30 mL of isopropanol was coated on the as-prepared carbon electrode surface to form the nanochanneled carbon electrode with a thickness of 30 μm. Upon drying at 60 °C in vacuum, the carbon electrode was treated with air plasma (pressure 100 Pa, RF power 60 W) for 120 s in a plasma cleaner

(Dongxin, TS-PL05). Finally, two current-collecting electrodes made from copper wires were set at the top and bottom of the nanochanneled carbon electrode and subsequently encapsulated by ethylene-vinyl acetate copolymer to avoid vapor attacks.

2. Characterizations

The photovoltaic tests were performed in ambient air conditions (20% RH, 25 °C) under illumination by a solar simulator (Newport, 91195A) at AM 1.5G simulated solar illumination (100 mW cm^{-2}). A black mask was applied to the solar cell surface to avoid stray light. The incident photo-to-current conversion efficiency (IPCE) spectra of various devices were recorded by a power source (Newport 300 W xenon lamp, 66920) with an amonochromator (Newport Cornerstone 260). The electrical performances of all-inorganic PSCs in flowing vapor were measured with self-made equipment, including control systems for temperature, flow velocity, and relative humidity. The voltage and current signals were measured on a CHI660E electrochemical workstation. A fan with controllable speed was used to tune the vapor velocity, and the flow velocity was monitored by a digital anemometer (Smart Sensor AS816). A humidity generator was used to control the relative ambient humidity, and the relative humidity and temperature were monitored by a Center 311 Humidity Temperature Meter. The top view of a carbon electrode was observed by a scanning electron microscope (Hitachi, SU8220). The functional groups were determined by a Raman spectrometer (Thermo DXR Raman Microscope, 532nm laser). The contact angles of water droplets at the carbon electrode were measured by a Zhongchen JC2000DM contact angle meter.

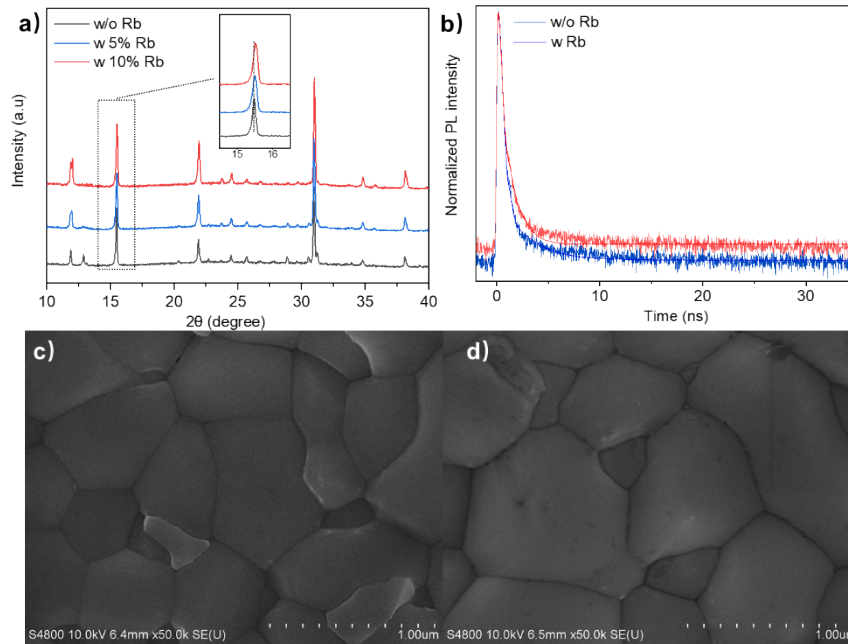


Figure S1 (a) The XRD patterns and (b) normalized time-resolved decay spectra of perovskite film w/ and w/o Rb⁺ doping. Top-view SEM images of (c) w/o and (d) w/ Rb⁺ doping.

The peak locates at 2theta of 14°~17° slightly shifts to high angles due to the doping of Rb⁺ cation. The TRPL spectra are fitted by the equation $I=Ae^{-(t-t_0)/\tau_1}+Be^{-(t-t_0)/\tau_2}$, where A and B are constants for the baseline offset, τ_1 is related to the nonradiative-recombination of defects, τ_2 refers to the radiative recombination of electron-hole separation. The device with Rb shows the smallest τ_1 and largest τ_2 ($\tau_1=0.1869$ ns, $\tau_2=2.476$ ns) in comparison to the τ_1 of 0.1589 ns and τ_2 of 1.106 ns for a pristine solar cell. This result demonstrates the nonradiative-recombination in the carbon-based all-inorganic CsPbBr₃ PSC is dramatically inhibited by using the Rb doping. The SEM images reveal large crystals in the Cs_{0.91}Rb_{0.09}PbBr₃ film, which has been shown to be beneficial for the photovoltaic metrics.

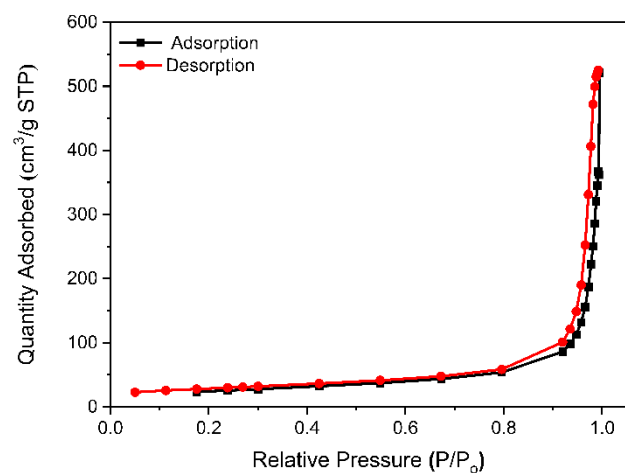


Figure S2. The nitrogen adsorption-desorption analysis of the carbon black. The isotherm indicates that the carbon black have a porosity characterization with a distinct hysteresis loop at relative pressure (P/P_0) between 0.8-1.0. Calculated by the multipoint Brunauer-Emmett-Teller (BET) method, the porous carbon nanoparticle has a high surface area of $\sim 86 \text{ m}^2/\text{g}$.

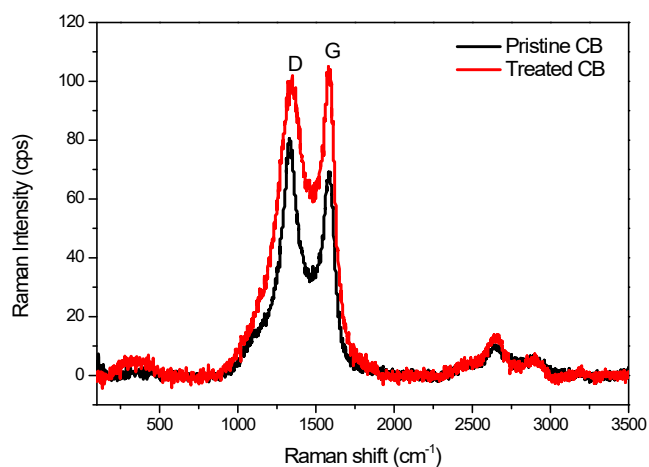


Figure S3. Raman spectra of the carbon black film. The black and red curves are the Raman spectra of pristine and treated CB, respectively. The two peaks centred at 1360 cm^{-1} (G peak) and 1580 cm^{-1} (D peak). There is only one peak at 1580 cm^{-1} for complete single crystal graphite, but there will be another peak at 1360 cm^{-1} for incomplete single crystal graphite. $R(I_d/I_g)$ characterizes the degree of graphitization of the carbon material. The results indicate that the carbon black possess the structure analogous to that of graphite with abundant disorder.

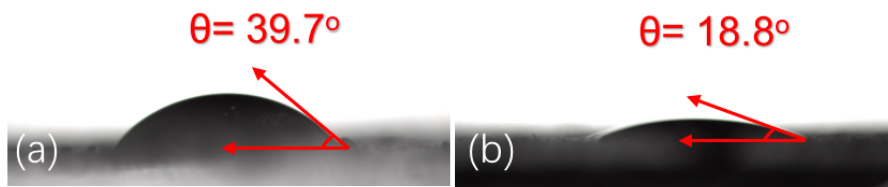


Figure S4. Water contact angles of the carbon black films. Pristine CB is hydrophilic. And it can be seen by contrast that the hydrophilicity of treated CB increases dramatically.