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Supplementary Information

High-efficient and low-temperature perovskite solar cells by employing a Bi-Hole Transport layer consisted of vanadium oxide and copper phthalocyanine

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Experimental details

Materials and Pre-formed perovskite film Preparation

PbI₂ (99.999 wt%) is purchased from Alfa Aesar and used as received. Vanadium triisopropoxy oxide (96%) is purchased from Alfa Aesar and diluted before using. CH₃NH₃I is prepared similar to a previously published method, in brief: 24 mL methylamine solution (33 wt% in ethanol, Sigma Aldrich) and 10 mL hydriodic acid (57 wt% in water, Sigma Aldrich) are diluted by 100 mL ethanol in a 250 mL round bottom flask by constant stirring at 60 °C for 2 h. The precipitate is washed with dry diethyl ether until the solid became white. The final product is dried at 60 °C in a vacuum oven for 24 hours.

Device completion

ITO/glass and ITO/PET substrates are cleaned sequentially by detergent, pure water, acetone for 20 min. The dried substrates are treated with ultraviolet ozone for 5 min for further clean. PEDOT: PSS solution (dissolved with deionized water in a mixture ratio of 1:3) are spun at 1000 rpm for 30 s and annealed at 120 °C for 20 min. For VO_x/CuPc B-HTL, vanadium-oxitriisopropoxide isopropanol solution is spin-coated on ITO substrates, then the substrates are staying at ambient atmosphere for 2 h. We transferred the substrates coated VO_x to a vacuum chamber. The CuPc buffer layer is sublimated under a pressure of 10⁻⁵ mbar at a rate of 0.2 Å/s.

PbI₂ film of 200 nm is sublimated at a rate of about 2 Å/s and resultant substrates are placed into the N₂-filled glovebox. Heated for 2 min at 55 °C, drops of 80 mg/mL MAI solution in isopropanol are loaded for 10 s, and then spin-coated at 2000 rpm on the ITO/HTL/PbI₂ substrate for 20 s. Afterward, the prepared films are drying at 60 °C for 2 h. To remove the unreacted excess of MAI, isopropanol solvent is spun at 2000 rpm upon the perovskite film for 30 s. The final film is annealed at 60 °C for 5 min. The hybrid perovskite film is further crystallized and inner-interface would be removed. Eventually, the devices are completed by consecutive vacuum deposited C₆₀ (30 nm), BCP (6 nm) and Ag cathode (140 nm) under 10⁻⁵ mbar.

Material and device characterization.

A field emission scanning electron microscope (SEM) (Quanta 250, FEI, USA) is used to investigate the morphology and crystallinity. The crystalline structure on ITO substrate is performed by a X-ray

diffractometer (Bruker D8 ADVANCE) with Cu K α radiation. The absorption and PL spectra are obtained by UV-Vis spectrophotometer (HITACHI U-3010, Japan) and Fluorescence Spectrometer (Fluoromax-4 spectrofluorometer) respectively. The W_F of VO $_x$ and VO $_x$ /CuPc thin films are measured using UPS (ESCALAB Xi+, Thermo Fisher Scientific) and Surface Kelvin Probe (Atomic-Force Microscopy, Bruker). The photovoltaic performance is estimated under an AAA solar simulator (XES-301S, SAN-EI), AM 1.5G irradiation with an intensity of 100 mW cm $^{-2}$. The photocurrent-voltage (J-V) curve is measured by a Keithley (2602 Series Sourcemeater), and the scan rates are performed with a 0.2 V s $^{-1}$ step. Incident photon-to-current conversion efficiency (IPCE) spectra are collected at AC mode by the solar cell quantum efficiency measurement system (SolarCellScan 100, Zolix instruments. Co. Ltd). The area of each device, calibrated by the shadow mask, is 7.06 mm 2 . Electrochemical impedance spectra (EIS) of the cells are evaluated using CHI-660E over the frequency range of 0.1 Hz to 100 KHz under the illumination (100mW cm $^{-2}$).

Mott-Schottky :

the built-in potential was derived according to the following equation:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 q A^2 N} (V_{bi} - V)$$

where C represents the measured capacitance, A is the active area, V is the applied bias, ϵ is the static permittivity, ϵ_0 is the vacuum permittivity, q is the elementary charge, and N is the doping density.

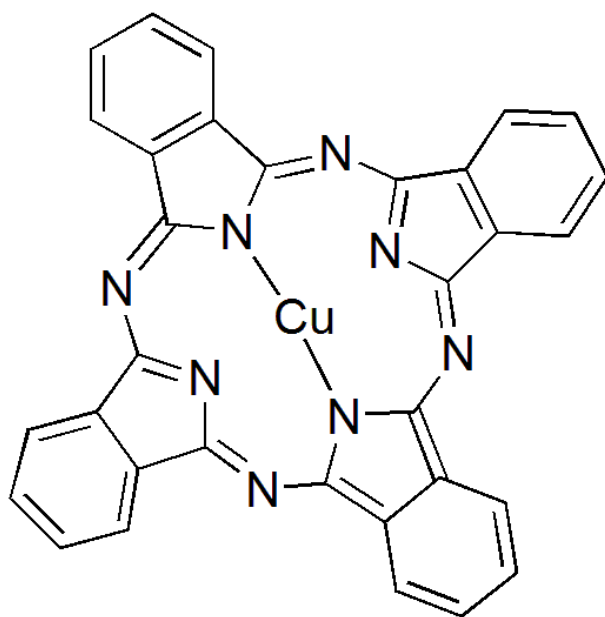


Figure S1. Molecular structure of copper phthalocyanine (CuPc).

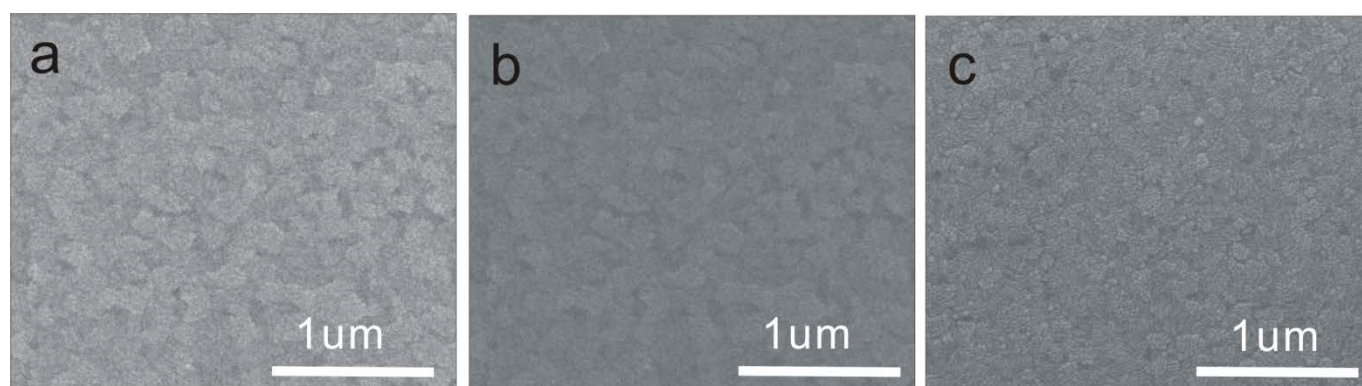


Figure S2. SEM images of (a)ITO substrate, (b)ITO/VO_x and (c)ITO/VO_x/CuPc.

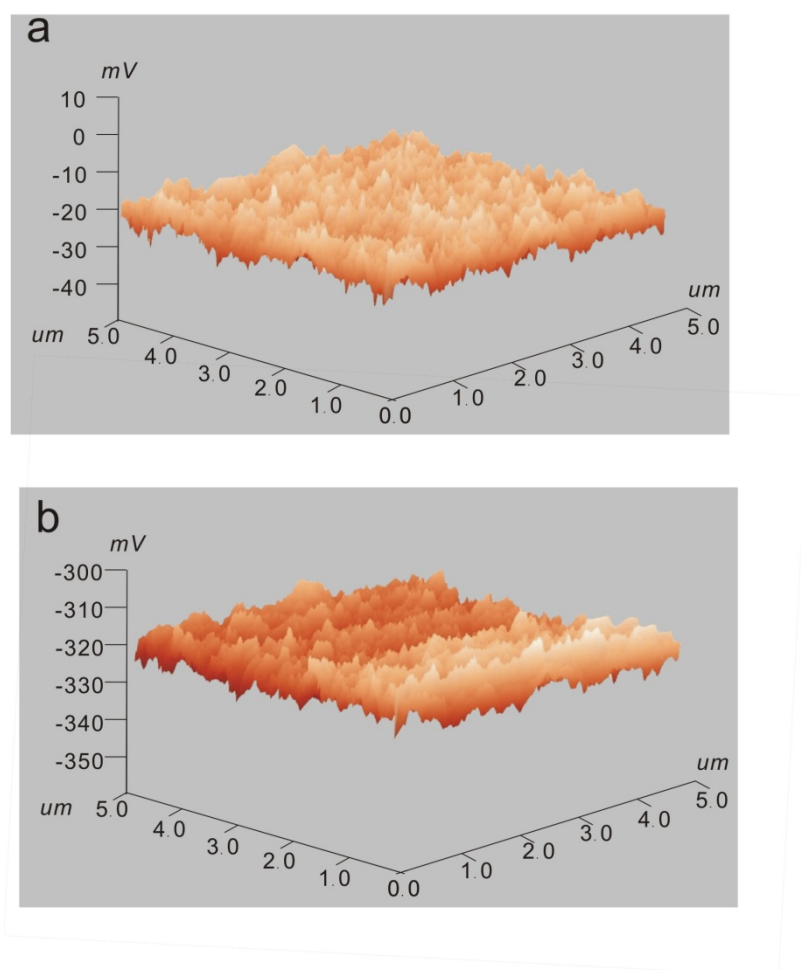


Figure S3. Surface Kelvin Probe measurements of the (a)ITO/VO_x and (b)ITO/VO_x/CuPc. (Here the Kelvin Probe is platinum with the $W_F=5.6\text{eV}$).

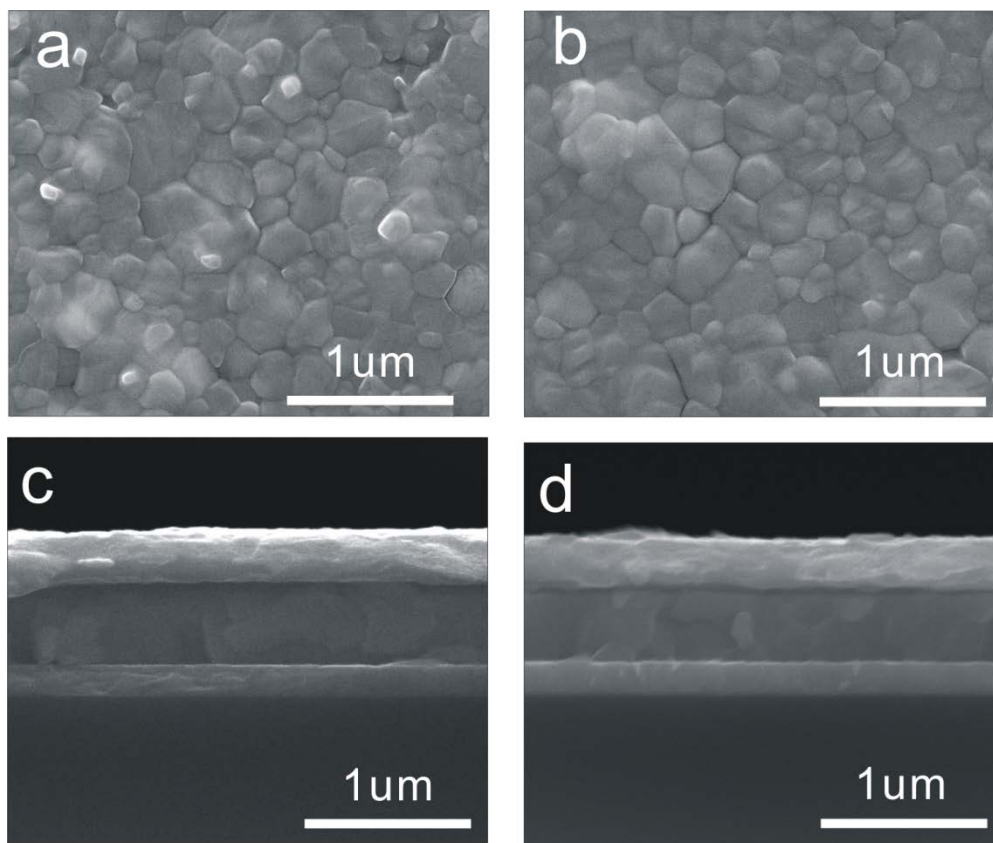


Figure S4. Top-view SEM images of perovskite on (a) PEDOT and (b) B-HTL, cross-section SEM images of perovskite on (c) PEDOT and (d) B-HTL.

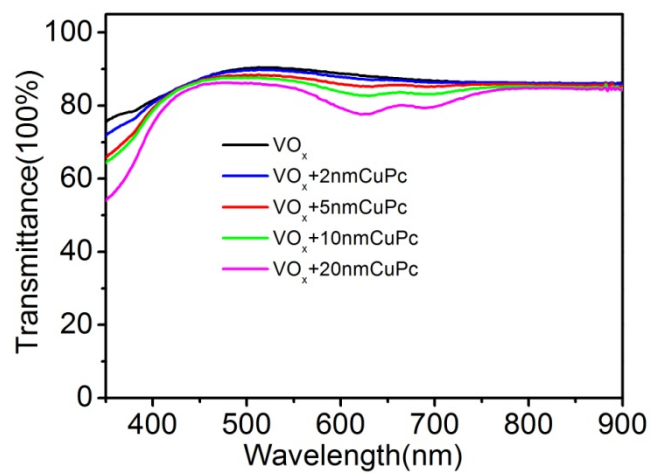


Figure S5. Transmittance of B-HTL with different thickness of CuPc.

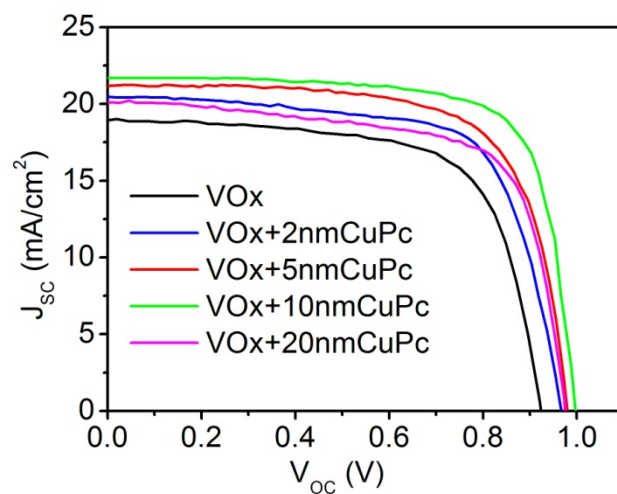


Figure S6. Typical J-V curves of PSCs with different B-HTLs.

Table S1 Performance parameters of PSCs with different B-HTLs (30 devices for each type)

Structure	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE(%)
ITO/PEDOT/MAPbI ₃ /C ₆₀ /BCP/Ag	0.902±0.017	20.27±0.84	0.717±0.022	13.69±0.64
ITO/VO _x /MAPbI ₃ /C ₆₀ /BCP/Ag	0.922±0.018	18.87±0.74	0.681±0.017	11.86±0.72
ITO/VO _x /CuPc(2nm)/MAPbI ₃ /C ₆₀ /BCP/Ag	0.968±0.016	20.31±0.77	0.693±0.021	13.63±0.88
ITO/VO _x /CuPc(5nm)/MAPbI ₃ /C ₆₀ /BCP/Ag	0.975±0.012	21.25±0.81	0.696±0.012	14.47±0.54
ITO/VO _x /CuPc(10nm)/MAPbI ₃ /C ₆₀ /BCP/Ag	0.996±0.015	21.68±0.61	0.738±0.011	15.98±0.47
ITO/VO _x /CuPc(20nm)/MAPbI ₃ /C ₆₀ /BCP/Ag	0.979±0.017	20.26±0.72	0.678±0.021	13.45±0.64

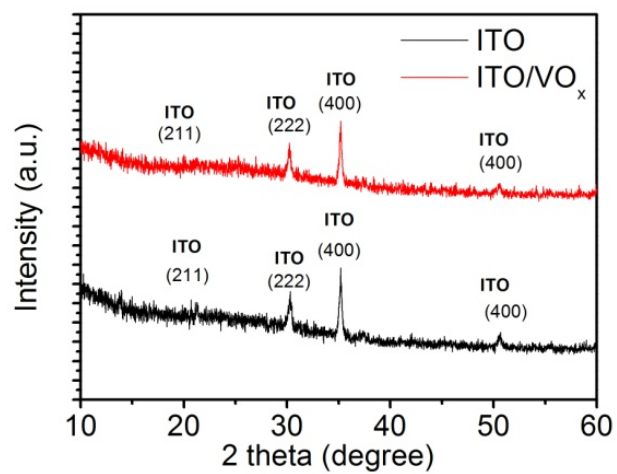


Figure S7. XRD measurement of pure ITO and ITO/VO_x.

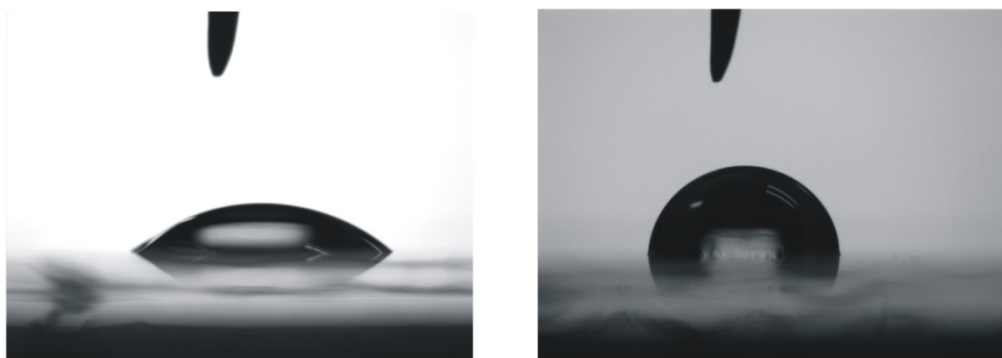


Figure S8. Contact angle of the PEDOT (left) and B-HTL(right).