Modulating Buried Interface with Natural Chemical VB$_2$ for TiO$_2$ Based Planar Perovskite Solar Cells

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1. Experimental

1.1 Materials

Titanium (IV) tetraisopropoxide, Acetylacetone in isopropanol, anhydrous solvents of chlorobenzene, Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO) and Di(acetylacetone)diisopropyl titanate were purchased from Sigma-Aldrich. Mesoporous titanium dioxide slurry, Lead iodide (PbI$_2$), Formamidinium iodide (FAI), Methylammonium chloride (MACl), Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI) and 4-tert-butylpyridine were purchased from Advanced Election Technology Co., Ltd. Co(III) TFSI (FK209) and 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (Spiro-OMeTAD) were purchased from Xi'an Yuri Solar Co., Ltd. Riboflavin (VB$_2$) was purchased from Energy Chemical. All of the used solvents and reagents were analytical grade, without further purification.

1.2 PSCs device fabrication

The n-i-p device configuration was adopted in this study (FTO/c-TiO$_2$/m-TiO$_2$/VB$_2$/Perovskite/Spiro-OMeTAD/Au). The FTO substrates were etched. The patterned substrate was cleaned by an ultrasonic bath with detergent soap water, deionized water, isopropanol, and acetone each cleaning step for 30 min and then

dried with a nitrogen stream. Preparation of dense titanium dioxide (c-TiO$_2$) solution: Dissolve 40 g of acetylacetone in 275 mL of isopropanol and shake thoroughly. Then slowly add 20 g of di(acetylacetone)diisopropyl titanate dropwise in a low-temperature environment and store it in the refrigerator for later use. The electron transporting c-TiO$_2$ layer was coated by spray-coating technique and annealed at 500 °C for 30 min. The substrates were treated with oxygen plasma for 15 min. The m-TiO$_2$ layer was deposited over the c-TiO$_2$ layer via spin coating at 5000 rpm for 30 sec followed by sintering at 100 °C for 15 min and 500 °C for 60 min. For modified TiO$_2$ film, VB$_2$ solution was spin-coated on the cooled TiO$_2$ films at 4000 rpm for 30 s and then annealed at 100 °C for 10 min. Before coating the perovskite layer, the substrate was treated with oxygen plasma for 15 min and transferred immediately to the glove box for further process. The FAPbI$_3$ perovskite precursor solution was prepared by mixing 682.3 mg PbI$_2$, 230.5 mg FAI and 33.8 mg MACl in DMF: DMSO (4:1) was spin-coated onto TiO$_2$ with two-step program: 1,000 and 3,000 rpm for 10 and 20 s, respectively. During the second step, 200 µL of chlorobenzene was drop-coated to treat the perovskite films. The substrate was dried on a hot plate at 150 °C for 10 min to produce FAPbI$_3$ halide perovskite thin film in a glovebox. Subsequently, the Spiro-OMeTAD was spin-coated on the perovskite layer at 3000 rpm for 30 s. The Spiro-OMeTAD solution was prepared by dissolving Spiro-OMeTAD (90 mg/mL) with chlorobenzene that contains 23 µL Li-TFSI (520 mg/mL in acetonitrile) ,10 µL FK-209 (320 mg/mL in acetonitrile) and 39 µL TBP. Finally, the 100 nm Au electrode was thermally evaporated on top of HTL layer to complete

device fabrication process. The active area of the device is 0.09 cm^2.

1.3 Characterization

The UV-Vis absorption spectra were measured using SHIMADZU. The SEM images were taken on a JEOL JSM-7800. The Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å) was used to detect XRD patterns of the sample. The photoelectron spectrometer (Thermo Scientific K-Alpha+) was used to measure the XPS spectra of the samples. PHI5000 VersaProbe III was performed to detect UPS patterns of the sample. Steady-state PL (excitation at 532 nm) measurements were carried out using an Edinburgh Instruments Ltd (FLS980). Electrochemical impedance spectroscopy (EIS) was performed using a two-electrode system under dark with electrochemical workstation (Zahner PP211). The light source for the photocurrent-voltage (*J-V*) measurement is an AM 1.5G solar simulator. The incident light intensity was 100 mW/cm^2 calibrated with a standard Si solar cell. The measurement of the incident-photon-to-current conversion efficiency (IPCE) was performed with CEL-QPCE3000 photoelectric chemical quantum efficiency testing and analysis system.

1.4 Trap density calculation

The V_{TFL} can be used to determine the trap density (N_{trap}) in view of Equation (1).

$$N_{trap} = \frac{2\varepsilon\varepsilon_0 V_{TFL}}{qL^2} \tag{1}$$

where q is the electric charge, ε stands for the relative dielectric constant, ε_0 is the vacuum permittivity and L is the perovskite film thickness. (L≈750 nm, ε≈71.45)
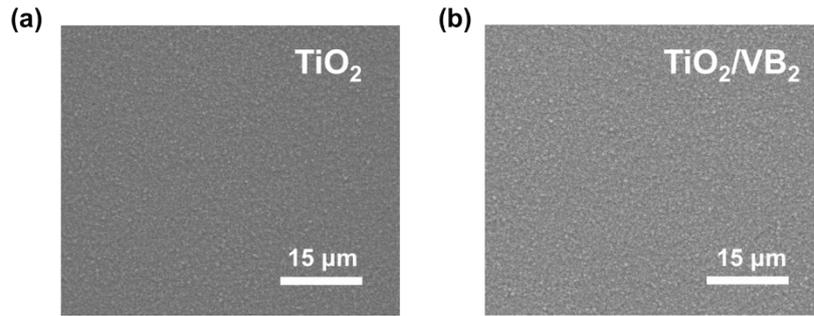
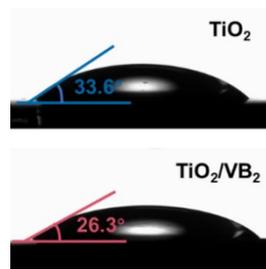**Figure S1.** (a) and (b) SEM images of pristine TiO_2 film and VB_2 modified TiO_2 films.

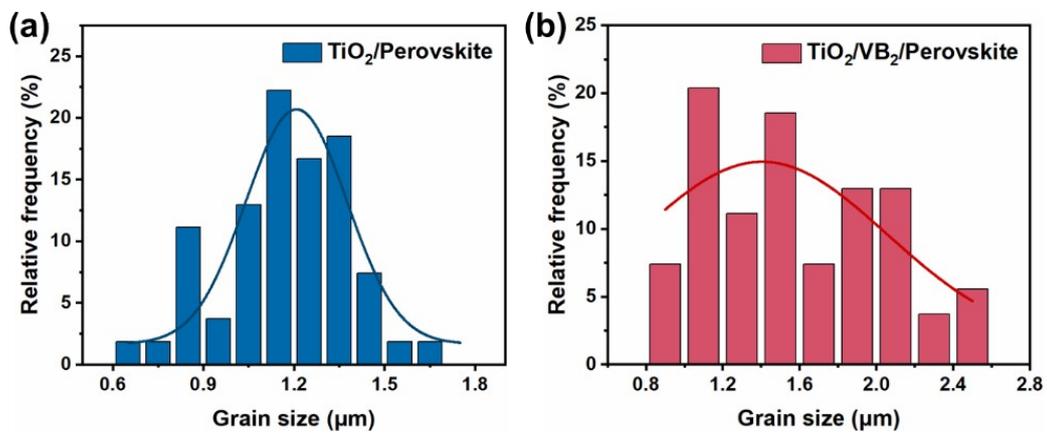**Figure S2.** Water contact angle measurements of TiO_2 and TiO_2/VB_2 films.

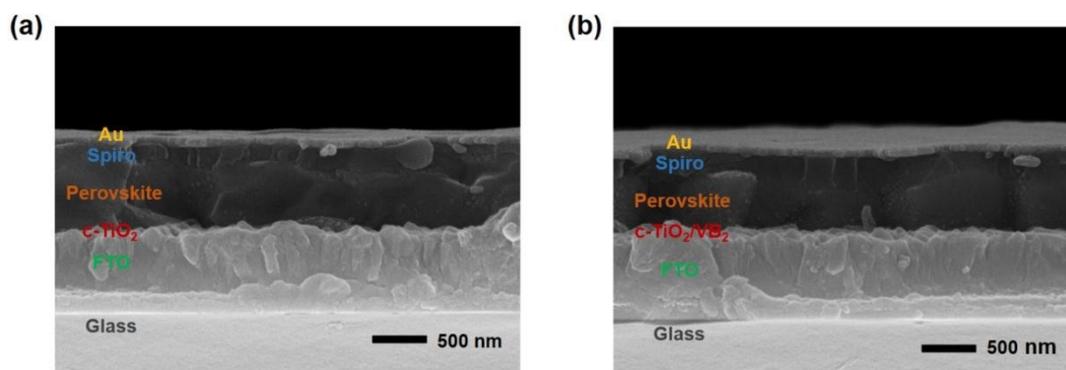**Figure S3.** Grain size of the perovskite without and with VB_2.

Figure S4. The cross-sectional SEM image of (a) pristine and (b) VB$_2$ modified perovskite films.
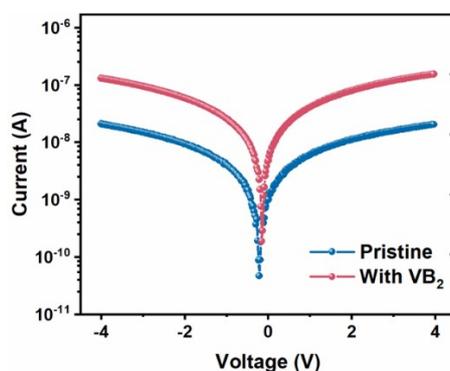

Figure S5. Conductivity of pristine and VB$_2$ modified device.
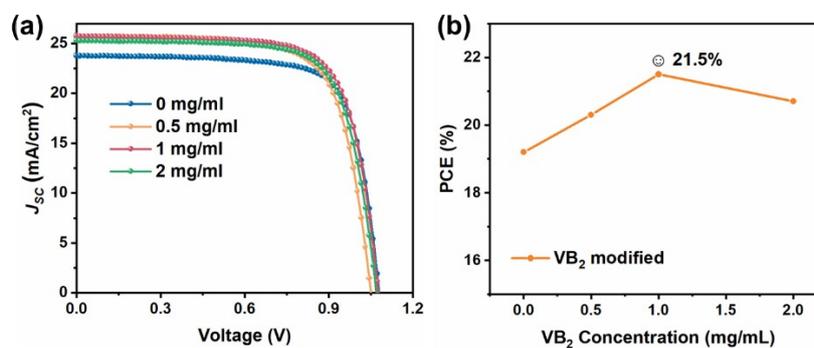

Figure S6. (a) *J-V* curves of VB$_2$ modified PSCs with different concentrations (the corresponding photovoltaic performance parameters are shown in Table S3). (b) The dependence of device performance on the concentration of VB$_2$ solution.
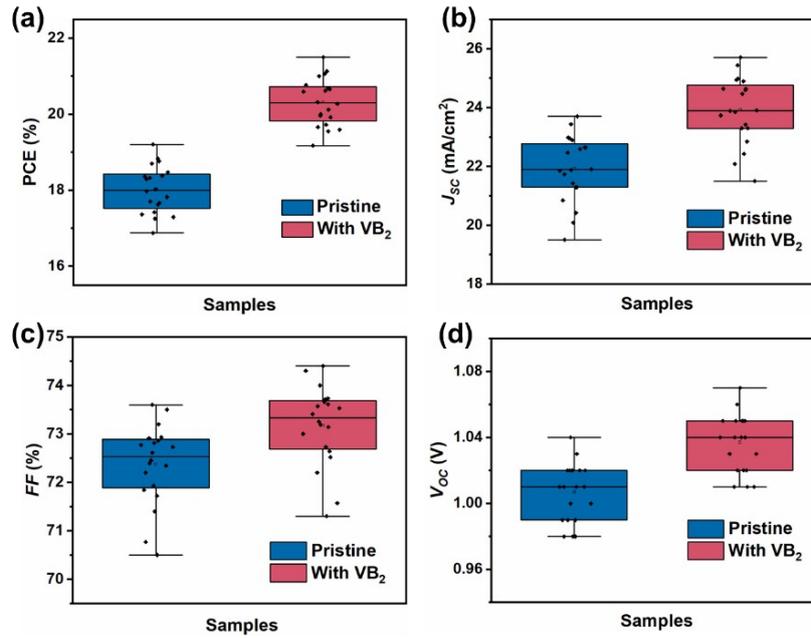
Figure S7. The statistical photovoltaic parameters (a) PCE, (b) J_{SC}, (c) *FF* and (d) V_{OC}. Distributions of 20 devices obtained from pristine device and VB$_2$ modified device in one batch.
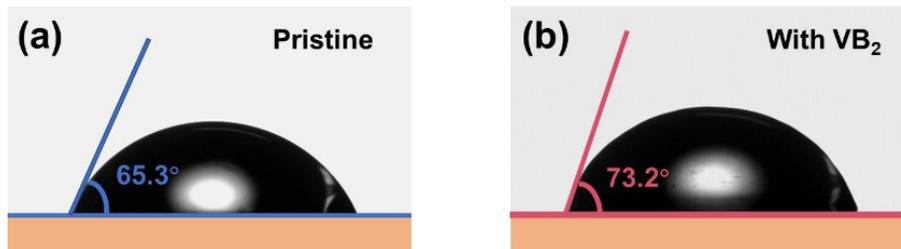

Figure S8. Water contact angle measurements of (a) pristine and (b) VB$_2$ modified perovskite films.

Table S1. The fitted parameters of perovskite films with and without VB$_2$ modified deposited on glass/Al$_2$O$_3$ substrates from TRPL spectra.

Parameters	A$_1$	τ_1	A$_2$	τ_2	τ
Pristine	32.38	6.73	67.62	352.18	240.32
With VB$_2$	67.33	2.08	32.67	145.09	48.80

Note: $\tau = \dfrac{A_1 \tau_1^{\,2} + A_2 \tau_2^{\,2}}{A_1 \tau_1 + A_2 \tau_2}$

Table S2. Photovoltaic performance parameters of champion devices.

	PCE (%)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)
Pristine	19.2	23.7	1.05	73.6
With VB$_2$	21.5	25.3	1.07	76.4

Table S3. Photovoltaic performance parameters of VB$_2$ modified PSCs with different

concentrations.

Concentration(mg/mL)	PCE (%)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)
0	19.2	23.7	1.05	73.6
0.5	19.5	25.6	1.05	71.9
1	21.5	25.3	1.07	76.4
2	20.4	25.2	1.07	73.3