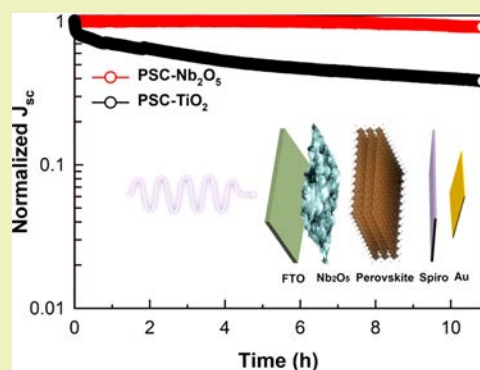


Solution Processed Nb<sub>2</sub>O<sub>5</sub> Electrodes for High Efficient Ultraviolet Light Stable Planar Perovskite Solar CellsZenghua Wang,<sup>†,‡</sup> Junjie Lou,<sup>†,‡</sup> Xiaojia Zheng,<sup>\*,‡,†</sup> Wen-Hua Zhang,<sup>\*,‡,†</sup> and Yong Qin<sup>\*,†,†</sup><sup>†</sup>Institute of Nanoscience and Nanotechnology, School of Physical Science and Technology, Lanzhou University, 222 South Tianshui Road, Lanzhou, Gansu 730000, China<sup>‡</sup>Sichuan Research Center of New Materials, Institute of Chemical Materials, China Academy of Engineering Physics, 596 Yinhe Road, Shuangliu, Chengdu 610200, China

## Supporting Information

**ABSTRACT:** TiO<sub>2</sub> is the most widely used electron transport layer (ETL) in high performance perovskite solar cells (PSCs). However, TiO<sub>2</sub> often induces a rapid decay in performance under ultraviolet (UV) light illuminations. So, high performance ETL is urgently needed for PSCs. Here, a new kind of Nb<sub>2</sub>O<sub>5</sub> nanoparticles ETL was developed for fabricating efficient planar PSCs with excellent UV stability. The matched band alignment between perovskites and Nb<sub>2</sub>O<sub>5</sub> promotes electron injection at the ETL/perovskite interface, and decreases the energy barrier for electron injection. Decreased energy loss during electron transfer from perovskite to Nb<sub>2</sub>O<sub>5</sub> and lower recombination rates in the devices contribute to the improved open-circuit voltage ( $V_{oc}$ ) of PSCs on Nb<sub>2</sub>O<sub>5</sub> compared to devices on TiO<sub>2</sub>. Power conversion efficiency (PCE) surpassing 20% with a high  $V_{oc}$  of 1.19 V was demonstrated for planar PSCs with Nb<sub>2</sub>O<sub>5</sub> ETL. The unencapsulated devices based on Nb<sub>2</sub>O<sub>5</sub> retained 93% of their initial short-circuit current density ( $J_{sc}$ ) after 10 h exposure to concentrated 365 nm UV light (46 mW/cm<sup>2</sup>), versus 40% for devices based on TiO<sub>2</sub>, which was attributed to the excellent chemical stability nature of Nb<sub>2</sub>O<sub>5</sub> under UV light.

**KEYWORDS:** Perovskite solar cell, Electron transport layer, Nb<sub>2</sub>O<sub>5</sub>, Solution process, Light stability



## INTRODUCTION

Organometal halide perovskites (OHPs) have emerged as a promising candidate for photovoltaic (PV) application owing to their high absorption coefficient, suitable band gap ( $E_g$ ), long and balanced charge diffusion length, robust fabrication process, etc.<sup>1–5</sup> A certified efficiency as high as 23.7% for a perovskite solar cell (PSC) has been achieved, which shows great promise for next-generation photovoltaic devices.<sup>6</sup> Despite the remarkable progress in PSCs, the instability of perovskite materials and corresponding devices is now one of the biggest challenges for their practical applications.<sup>7–9</sup> It is well-known that PSCs exceeding power conversion efficiency (PCE) of 20% have mainly been demonstrated by employing TiO<sub>2</sub> as the electron transport layer (ETL).<sup>10–12</sup> However, TiO<sub>2</sub> will result in a rapid decay in PCE under UV light illuminations.<sup>13–15</sup> Many efforts have been made to prevent the light-induced degradation, such as surface modification of TiO<sub>2</sub>,<sup>16–18</sup> doping of TiO<sub>2</sub> to reduce UV-induced photocatalysis,<sup>19–22</sup> and employing down-conversion phosphor in glass.<sup>23</sup> However, exploring a new type of ETL to replace TiO<sub>2</sub> for fabricating stable PSCs without damaging their performance is critically important and valuable.<sup>24,25</sup>

Many organic semiconductors and metal oxide thin films, such as PCBM,<sup>26</sup> C60,<sup>27</sup> BaSnO<sub>3</sub>,<sup>28</sup> ZnO,<sup>29</sup> Nb<sub>2</sub>O<sub>5</sub>,<sup>30</sup> WO<sub>3</sub>,<sup>31</sup> and SnO<sub>2</sub>,<sup>32</sup> have been prepared and employed as ETLs. PSCs

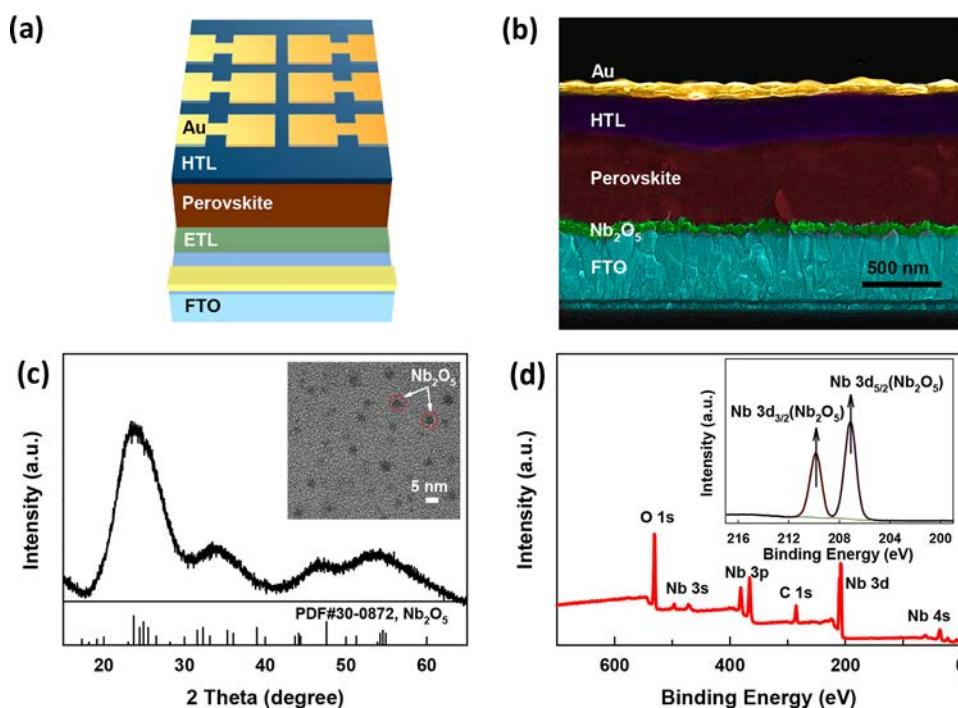
using BaSnO<sub>3</sub> and SnO<sub>2</sub> ETLs show excellent stability under light illumination.<sup>28,33</sup> Other than tin based oxides, Nb<sub>2</sub>O<sub>5</sub> has attracted considerable attention for its high optical transparency, chemical stability, outstanding conductivity, and well-matched energy levels to the conduction band minimum (CBM) of perovskites. Benefited from its excellent fundamental chemistry and physics, an improved open-circuit voltage ( $V_{oc}$ ) has been demonstrated in both dye sensitized solar cells (DSSCs) and PSCs.<sup>34–36</sup> PSCs with a PCE as high as 17.2%<sup>30</sup> and 18.59%<sup>37</sup> had been achieved by using sputtered Nb<sub>2</sub>O<sub>5</sub> thin film as an effective ETLs, displaying high promise for Nb<sub>2</sub>O<sub>5</sub> as ETL for efficient PSCs. Developing a new kind of Nb<sub>2</sub>O<sub>5</sub> ETL with much better anti-UV ability and higher PCE of PSCs is critically important and highly valuable.

Here, we report a low-temperature solution route to prepare Nb<sub>2</sub>O<sub>5</sub> nanoparticles, and further utilize them as ETL to fabricate PSCs. The PSC fabricated with the Nb<sub>2</sub>O<sub>5</sub> compact layer showed a PCE of 20.22% (stabilized PCE of 20.14%) with  $V_{oc}$  of 1.19 V. Moreover, these devices exhibited improved UV stability, retaining 93% of the initial short-circuit current density ( $J_{sc}$ ) under 365 nm UV light exposure (46 mW/cm<sup>2</sup>)

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**Figure 1.** (a) Schematic illustration of the perovskite solar cell. (b) Cross-sectional SEM image of PSCs employing  $\text{Nb}_2\text{O}_5$  as ETL. (c) X-ray diffraction spectrum and TEM image (inset) and (d) X-ray photoelectron spectra of the as-synthesized  $\text{Nb}_2\text{O}_5$  nanoparticles.

for 10 h, whereas the device based on  $\text{TiO}_2$  retained only 40% of its initial  $J_{sc}$ .

## EXPERIMENTAL SECTION

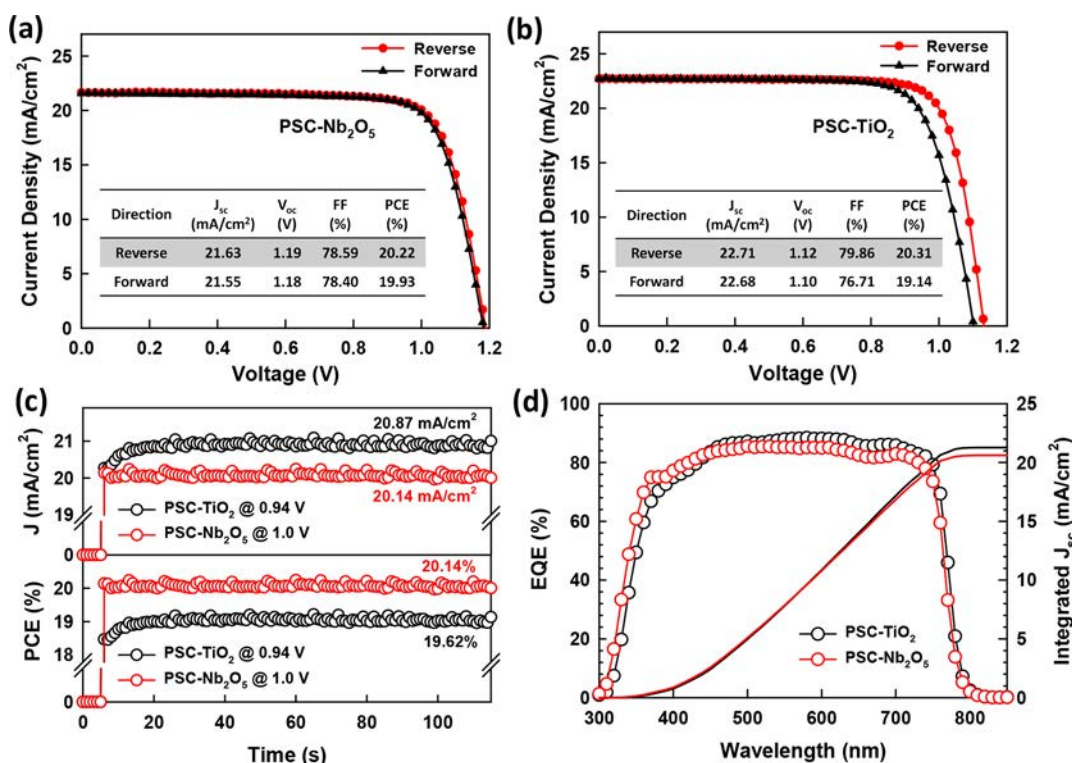
**Materials.** Lead iodide ( $\text{PbI}_2$ , 99.999%),  $\text{TiCl}_4$  (99.9%), cesium iodide (CsI, 99.999%), 4-*tert*-butylpyridine (TBP), Li-TFSI, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were purchased from Aldrich Sigma. Tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine) cobalt(III) bis(trifluoromethylsulfonyl)imide (FK209), formamidine iodide (FAI), methylammonium bromide (MABr), and lead bromide ( $\text{PbBr}_2$ ) were purchased from Xi'an p-OLED Corp. HCl (37%) was purchased from Xilong Scientific.  $\text{NbCl}_5$  (99.9%), benzyl alcohol (anhydrous), ethanol (anhydrous), and methylphenoxide (PhOMe) were purchased from Alfa Aesar. All chemicals used in this work were used as received.

**Synthesis of  $\text{Nb}_2\text{O}_5$  Nanoparticles.**  $\text{NbCl}_5$  (5 mmol) was dispersed by anhydrous ethanol (2 mL, stored in the fridge before use) under stirring to obtain a clear pale yellow solution. After the solution cooled down to room temperature, 10 mL of anhydrous benzyl alcohol was added. The original pale solution became bright yellow after the addition of benzyl alcohol. The mixed solution was loaded into a 20 mL flask, which was firmly sealed and stored without stirring in an oven at 70 °C for 10 h. A white and condensed colloid can be seen at the 6th hour. The product was then washed and precipitated twice as follows: 12 mL of ethanol was added to form a clear dispersion. 60 mL of diethyl ether was then used to precipitate the dispersion. The product  $\text{Nb}_2\text{O}_5$  nanoparticles were isolated by centrifugation at 5000 rpm for 4 min. The  $\text{Nb}_2\text{O}_5$  colloidal solution was obtained by dispersing the nanoparticles in anhydrous ethanol (concentration is  $\sim 6$  mg/mL).

**PSC Fabrication.** Fluorine-doped tin oxide (FTO) coated glass (NSG 10, Nippon sheet glass, Japan) was used as purchased. The  $\text{TiO}_2$  blocking layer was fabricated by a chemical bath deposition method.  $\text{TiCl}_4$  (0.2 mol) was added in 100 mL of iced deionized water dropwise. After the ice had completely melted, FTO electrodes were immersed in the solution and the hydrothermal growth was conducted in an oven at 80 °C for 70 min. After the reaction had finished, the FTO/ $\text{TiO}_2$  substrates were washed with deionized water and dried at 150 °C under ambient condition for 15 min.  $\text{Nb}_2\text{O}_5$

layers were deposited on bare FTO by spinning the colloidal solution at 2000 rpm for 25 s, and annealed on a hot plate at 150 °C for 15 min in ambient condition. The thickness of the  $\text{Nb}_2\text{O}_5$  layer was controlled by repeating the deposition process for 1–5 times. The thickness for the film is  $\sim 10$  nm for once spin-coating process, which almost linearly increases with spin-coating times. Before the deposition of the perovskite layer, the substrates were treated with UV-ozone for 15 min. The anti-solvent assisted crystallization (ASAC) method employing PhOMe as green anti-solvent was used for the deposition of perovskite layers. Perovskite precursor solution was prepared by dissolving FAI (1 M),  $\text{PbI}_2$  (1.1 M), MABr (0.2 M), and  $\text{PbBr}_2$  (0.22 M) in a 4:1 (V/V) mixture of anhydrous DMF:DMSO. Then, CsI (0.75 M) in DMSO was added to the above solution in 10:95 volume ratios. The mixed solution was aged for 12 h before use. The perovskite deposition process was conducted through a two-step spin-coating program (10 s at 1000 rpm and 40 s at 4000 rpm) with dripping PhOMe during the second step, 10 s before the end. The wet perovskite film was annealed at 110 °C for 20 min. Hole transport material solution containing Spiro-OMeTAD (68 mM), Li-TFSI (32 mM), FK209 (6 mM), and TBP (50 mM) in chlorobenzene and acetonitrile (19/1 in volume ratio) was spun at 4900 rpm for 25 s. Finally, a thin layer ( $\sim 80$  nm) of gold was deposited by thermal evaporation as electrode.

**Characterization.** X-ray diffraction (XRD) analyses were performed on an Empyrean X-ray diffractometer with  $\text{Cu K}\alpha$  radiation (Panalytical, 2°/min). Scanning electron microscope (SEM) images were obtained under an accelerating voltage of 5 kV (SIGMA HD ZEISS Company). X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo escalab 250Xi XPS system, with a 300  $\mu\text{m}$  spot size and energy steps of 0.1 eV. Transmission electron microscopy (TEM) image was obtained at 200 kV (Carl Zeiss SMT Pte, Ltd. Libra 200FE). UV–vis absorption spectra of all samples were recorded on an Evolution 201 spectrophotometer (Thermo Fisher Scientific Corporation). Atomic force microscopy (AFM) topography images were obtained using a Bruker Dimension Icon system in tapping mode under atmospheric condition. Kelvin probe force microscope (KPFM) measurements were performed using amplitude modulation mode with an MESP probe (Co/Cr coated). The work function of the probe was calibrated



**Figure 2.** Typical  $J$ - $V$  curves of the devices based on (a) Nb<sub>2</sub>O<sub>5</sub> and (b) TiO<sub>2</sub> ETLs measured under simulated AM1.5 illumination. (c) The corresponding stabilized current output and PCE around maximum power point as a function of time for the PSCs under 1 sun illumination and (d) EQE spectra of the PSCs.

by freshly cleaned highly ordered pyrolytic graphite (HOPG, with 4.60 eV of constant work function). Current density–voltage measurements were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a digital source meter (Keithley Model 2400) under simulated one sun AM 1.5G illumination at 100 mW/cm<sup>2</sup> (SSF5-3A, Class AAA Solar Simulator, Enlitech) in a glove box. A 50 ms scanning delay was adopted for each data point. Before the test, the exact light intensity was calibrated with a KG5-flited Si reference diode (SRC-2020-KG5-RTD, Enlitech). A metal mask of 0.09 cm<sup>2</sup> was applied for measurement. Electrochemical impedance spectroscopy (EIS) results were recorded by an electrochemical workstation (VMP3 Biologic instruments) at various applied bias under dark condition for frequency from 100 mHz to 100 kHz with an AC amplitude of 30 mV. The steady-state photoluminescence spectrum (PL) was measured with an Edinburgh Instruments Ltd. (FLS980). UV stability measurement was conducted at ambient condition (humidity ~ 40%, 25 °C) using a 365 nm LED light as UV source. The spectrum of the UV light was measured using an Ocean Optics spectrometer (QE-Pro). The intensity of UV light was calibrated with a photodetector (OPHIR NOVA II). Mott–Schottky (MS) plots for FTO and ETLs analysis were obtained using an electrochemical workstation (VMP3 Biologic instruments) in a standard three-electrode configuration with Ag/AgCl (in saturated KCl) as the reference electrode, and Pt mesh as the counter electrode in 0.1 M NaCl electrolyte. The frequency was 80 mHz, whereas the amplitude potential was 10 mV. External quantum efficiencies (EQE) were measured by a QE-R3011 Quantum Efficiency Measurement System (Enlitech) under direct current mode.

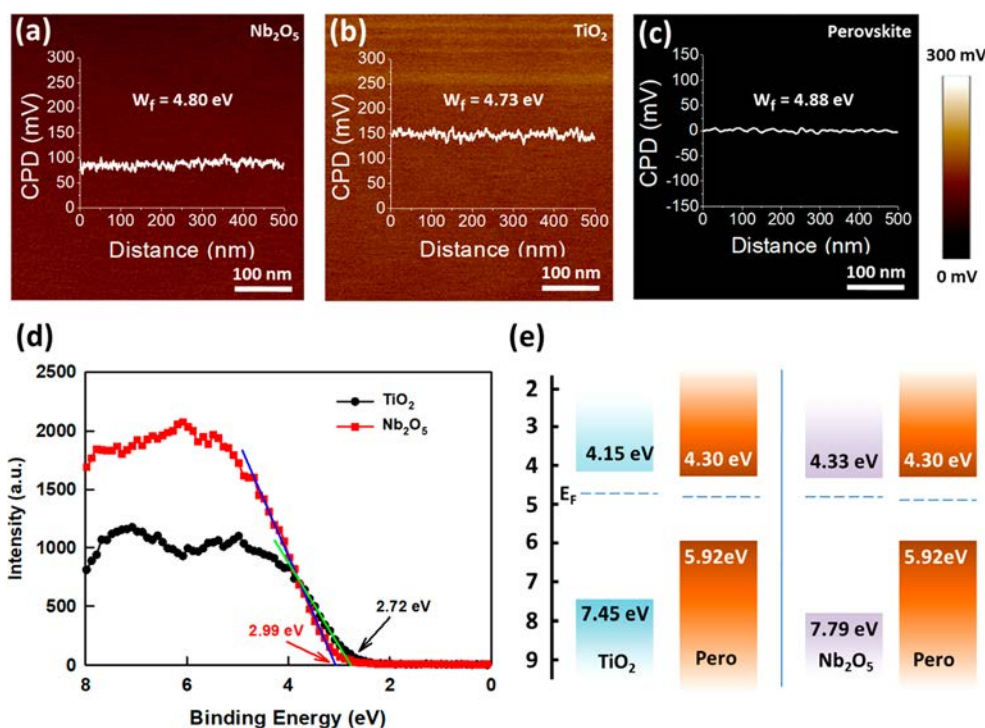
## RESULTS AND DISCUSSION

Devices were fabricated in a regular planar structure, as shown in Figure 1a. Figure 1b presents the typical cross-sectional SEM image of PSCs employing Nb<sub>2</sub>O<sub>5</sub> as ETL. A compact Nb<sub>2</sub>O<sub>5</sub> layer, prepared by spinning the colloidal solution on

top of FTO glass, was used as the hole blocking layer. A continuous, flat, and dense perovskite film with a thickness of ~550 nm was deposited by the anti-solvent assisted crystallization (ASAC) method with methoxybenzene (PhOMe) as the green anti-solvent. As shown in Figure 1b and Figure S1, the perovskite films show a smooth surface and 100% coverage, which is consistent with our previous work.<sup>38</sup> On the top of the perovskite layer, an ~300 nm thick spiro-OMeTAD was deposited as the hole transport material (HTM).

In this work, Nb<sub>2</sub>O<sub>5</sub> nanoparticles (NPs) were fabricated through a low-temperature (100 °C) solution process, and then were dispersed into ethanol to form a colloidal solution for film deposition. The Nb<sub>2</sub>O<sub>5</sub> NPs solution exhibits a typical Tyndall effect under red laser (Figure S2), confirming its colloidal characteristic.<sup>39</sup> Figure 1c displays the XRD and TEM characterizations of Nb<sub>2</sub>O<sub>5</sub> NPs used in this work. The broad peaks shown in the XRD pattern indicate the low crystallinity nature of Nb<sub>2</sub>O<sub>5</sub> NPs. The inserted TEM image in Figure 1c shows a 3–5 nm diameter of the used Nb<sub>2</sub>O<sub>5</sub> NPs. Figure 1d presents X-ray photoelectron spectroscopy (XPS) spectra of the Nb<sub>2</sub>O<sub>5</sub> NPs. A doublet of Nb 3d<sub>3/2</sub> and Nb 3d<sub>5/2</sub> appears, with binding energy (B.E.) values of 209.9 and 207.1 eV, confirming that the Nb element is in the 5<sup>+</sup> oxidation state.<sup>37</sup> There is no residual Cl observed in our low-temperature processed Nb<sub>2</sub>O<sub>5</sub>, indicating a pure Nb<sub>2</sub>O<sub>5</sub> product (Figure 1d). As a reference, PSCs based on TiO<sub>2</sub> ETL were also fabricated, and the device architecture is shown in Figure S3. More detailed information related to the Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> ETLs can be found in Figures S4 and S5.

It is well-known that the thickness of ETL can affect the device's performance obviously. The high series resistance introduced by too thick ETL will reduce both of the  $J_{sc}$  and fill



**Figure 3.** Surface potential images of (a) Nb<sub>2</sub>O<sub>5</sub>, (b) TiO<sub>2</sub>, and (c) perovskite obtained from KPMF measurement. (d) Valence band spectra of Nb<sub>2</sub>O<sub>5</sub> (red) and TiO<sub>2</sub> (black) from XPS measurement and (e) band alignment of ETLs and perovskite.

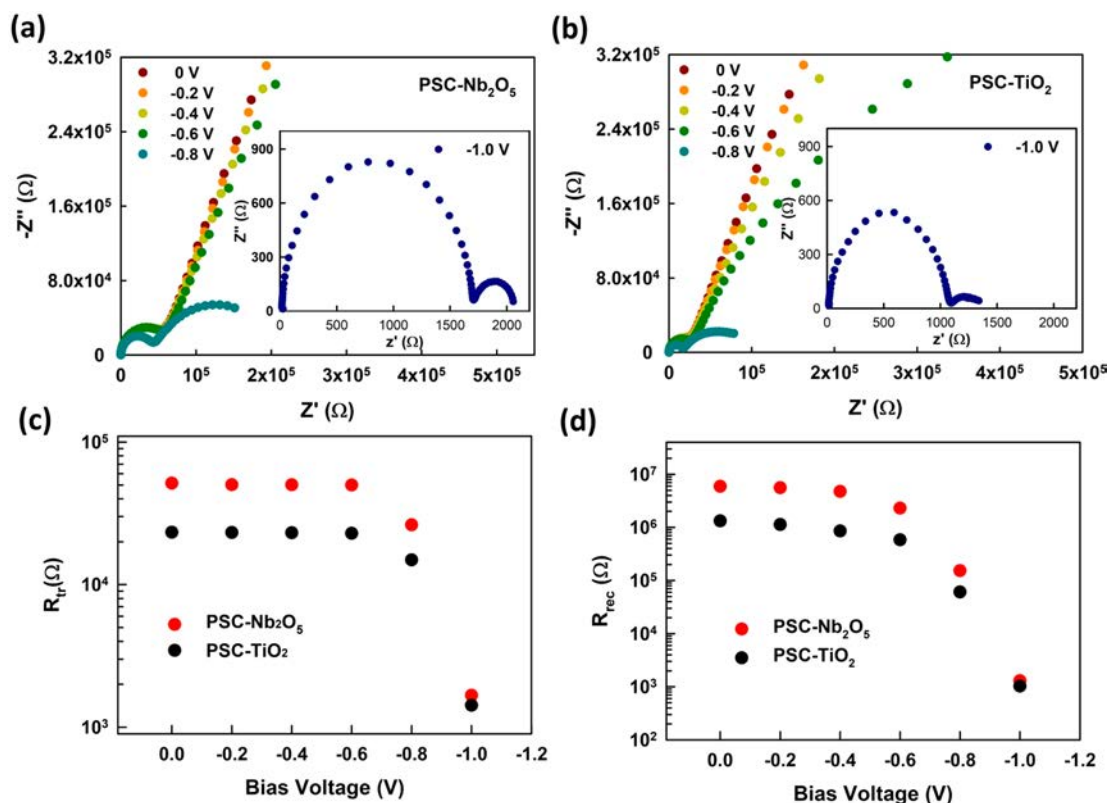
factor (FF) of the cell. However, prominent carrier recombination will happen when the ETL is too thin, due to that the direct contact between perovskite and FTO can result in inferior hole blocking properties. In this work, Nb<sub>2</sub>O<sub>5</sub> films with varying thicknesses were prepared by repeating the spin-coating process for 1–5 times (10 nm for one spin-coating process). It is found that the cell performance first increases and then decreases as the thickness of Nb<sub>2</sub>O<sub>5</sub> film increases (Figure S6). The photovoltaic parameters of the devices employing the Nb<sub>2</sub>O<sub>5</sub> film with different thicknesses are summarized in Table S1. The optimum thickness for the Nb<sub>2</sub>O<sub>5</sub> ETL is about 30 nm, which is achieved by repeating the spin-coating process for three times. Figure S7 shows the statistics of the performance for PSCs with optimized experimental condition using Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> ETLs. The narrow distribution indicates an excellent reproducibility for the devices. Figure 2a presents the typical current density–voltage (*J*–*V*) curves of the PSCs measured in reverse scan mode (*V*<sub>oc</sub> to *J*<sub>sc</sub>) and forward mode (from *J*<sub>sc</sub> to *V*<sub>oc</sub>) under AM 1.5G illumination (air mass 1.5 global) for PSCs on Nb<sub>2</sub>O<sub>5</sub>. The device exhibits a *V*<sub>oc</sub> of 1.19 V, a *J*<sub>sc</sub> of 21.63 mA/cm<sup>2</sup>, and an FF of 78.59% under reverse scan, producing a PCE of 20.22%. More importantly, devices based on Nb<sub>2</sub>O<sub>5</sub> ETL show negligible *J*–*V* hysteresis, showing a PCE of 19.93% under forward scan. In contrast, PSCs based on TiO<sub>2</sub> ETL show obvious *J*–*V* hysteresis, with a *V*<sub>oc</sub> of 1.12 V, a *J*<sub>sc</sub> of 22.71 mA/cm<sup>2</sup>, and an FF of 79.86%, yielding an overall PCE of 20.31% under reverse scan, and a *V*<sub>oc</sub> of 1.10 V, a *J*<sub>sc</sub> of 22.68 mA/cm<sup>2</sup>, and an FF of 76.71%, producing an overall PCE of 19.14% under forward scan (Figure 2b). These results clearly show that Nb<sub>2</sub>O<sub>5</sub> ETLs can obviously push the *V*<sub>oc</sub> of the devices to a much higher value, and 1.19 V is one of the best data for PSCs with similar light absorber in the literature. The steady output current density was monitored with time under an external bias, which is around the maximum power point

(Figure 2c). The voltage for maximum power point of PSCs based on Nb<sub>2</sub>O<sub>5</sub> ETL is obviously larger than that using TiO<sub>2</sub> ETL, owing to the improved *V*<sub>oc</sub>. The current density increased sharply for devices based on Nb<sub>2</sub>O<sub>5</sub> when we turned on the light and stabilized at ~20.14 mA/cm<sup>2</sup>, yielding a PCE of ~20.14%. The current density increased slowly for devices based on TiO<sub>2</sub> ETL when we turned on the light, and gradually stabilized at ~20.87 mA/cm<sup>2</sup>, yielding a PCE of ~19.62%. Faster dynamic current response always shows lower hysteresis, which agrees well with the *J*–*V* results.<sup>40,41</sup> It is worth pointing out that, despite that the PCE for PSCs on Nb<sub>2</sub>O<sub>5</sub> is lower than the device on TiO<sub>2</sub> under reverse scan, the stabilized PCE is higher, thanks to the negligible *J*–*V* hysteresis effect. The corresponding external quantum efficiency (EQE) spectrum for both cells shown in Figure 2d exhibits a broad plateau above 80% over the spectral range from 400 to 760 nm, indicating an efficient light absorbing, charge transfer, and charge collection in the device. The integrated *J*<sub>sc</sub> of 20.61 mA/cm<sup>2</sup> for PSCs on Nb<sub>2</sub>O<sub>5</sub> and 21.29 mA/cm<sup>2</sup> for PSCs on TiO<sub>2</sub> are well consistent with the *J*–*V* results.

One of the advantages for employing Nb<sub>2</sub>O<sub>5</sub> as ETL in PSCs is the high *V*<sub>oc</sub>. For a solar cell, the *V*<sub>oc</sub> can be written as

$$V_{oc} = \frac{nkT}{q} \ln \left( 1 - \frac{G_{sh} V_{oc}}{J_0} + \frac{J_L}{J_0} \right) \quad (1)$$

where *J*<sub>0</sub>, *G*<sub>sh</sub>, *n*, *k*, and *J*<sub>L</sub> are the diode saturation current density, parallel conductance, diode ideality factor, Boltzmann constant, and photocurrent density, respectively. Considering *J*<sub>L</sub> ≫ *G*<sub>sh</sub>*V*<sub>oc</sub>, we know that *V*<sub>oc</sub> depends strongly on the *J*<sub>0</sub>, declining dramatically with the increase of *J*<sub>0</sub>. The diode equation provides an expression for the current through a diode as a function of voltage, which can be described by the following equation:



**Figure 4.** EIS of PSCs based on (a)  $\text{Nb}_2\text{O}_5$  and (b)  $\text{TiO}_2$  ETLs recorded under different applied bias. The inserted figures show the corresponding Nyquist plots measured under the bias of  $-1.0$  V. (c)  $R_{\text{tr}}$  and (d)  $R_{\text{rec}}$  derived from the Nyquist plots.

$$J = J_0(e^{qV/nkT} - 1) \quad (2)$$

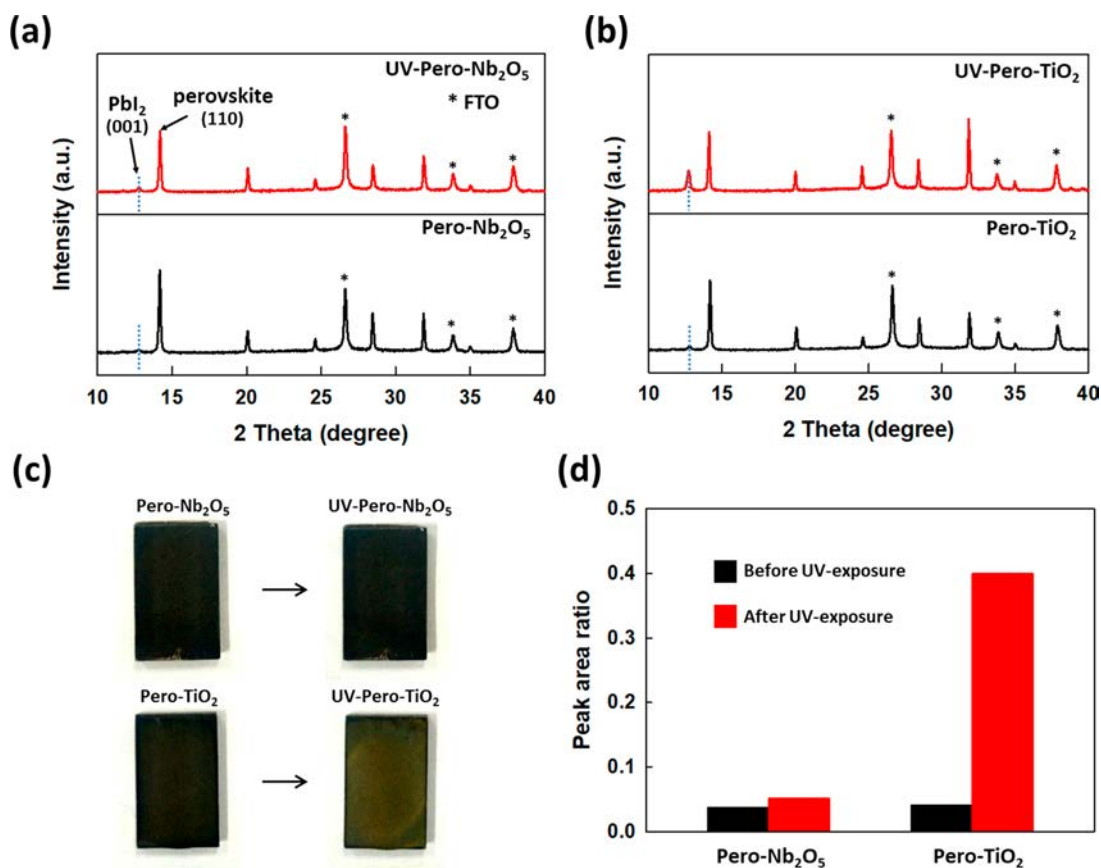
We measured both the dark  $J$ - $V$  curves for the PSCs based on  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$  ETLs. From the semi-logarithmic plots shown in Figure S8, the PSC employing  $\text{Nb}_2\text{O}_5$  ETL shows lower  $J_0$  value, which accounts for improved  $V_{\text{oc}}$  in the device.

To further elucidate the mechanism behind the phenomenon of  $V_{\text{oc}}$  increase, the band alignment scheme for PSCs was studied. The linear part of Tauc plots extracted from UV-vis absorbance measurements was used to calculate the band gap of ETLs and perovskite (Figure S9). We then used Kelvin probe force microscopy (KPFM) to measure contact potential difference (CPD) of the functional layers, from which the work function ( $W_f$ ) or the position of the Fermi level ( $E_f$ ) can be inferred. The resulting  $W_f$  values are shown in Figure 3a–c. These results are consistent with the flat band potential ( $U_{\text{fb}}$ ), which is derived from the Mott–Schottky (MS) plots (Figure S10). X-ray photoelectron spectroscopy (XPS) has been proved as a suitable method for valence band maximum (VBM) measurements (energy relative to the Fermi level), especially for perovskites.<sup>42</sup> Here, the VBMs for all  $\text{Nb}_2\text{O}_5$ ,  $\text{TiO}_2$ , and perovskite layer were obtained by XPS study, which are shown in Figure 3d and Figure S11. Thus, the energy band diagram for the PSCs can be obtained, which is shown in Figure 3e. The better energy level matching between the perovskites and  $\text{Nb}_2\text{O}_5$  can decrease the energy barrier for electron extraction, thus decreasing the energy loss during charge transfer at the ETL/perovskite interface, and thereby resulting in a higher  $V_{\text{oc}}$ .<sup>43</sup>

To gain further insight into how  $\text{Nb}_2\text{O}_5$  would affect the performance of PSCs, we conducted electrochemical impedance spectroscopy (EIS) to investigate the charge transport

and recombination kinetics in PSCs. Nyquist plots shown in Figure 4a,b were measured with AC amplitude of 30 mV at various applied bias under dark condition. There are two typical arcs, where the first arcs at high frequency can be mainly attributed to the charge transport features in bulk materials and the semicircles in the low frequency range mainly represent the charge recombination process at interface.<sup>44,45</sup> The EIS data were fitted with the equivalent circuit diagram given in Figure S12. The equivalent circuit model contains both high frequency elements and low frequency elements. The charge transport resistance ( $R_{\text{tr}}$ ) is ascribed to the small semicircle at high frequency, and the recombination resistance ( $R_{\text{rec}}$ ) assigned to the large arc at low frequency. Due to the same fabrication process except for ETL, so the difference between the  $R_{\text{tr}}$  and  $R_{\text{rec}}$  should originate from the ETLs and ETL/perovskite interface. As shown in Figure 4c,d, both  $R_{\text{tr}}$  and  $R_{\text{rec}}$  are increased for PSCs based on  $\text{Nb}_2\text{O}_5$ . The higher  $R_{\text{tr}}$  means a larger transport resistance for electrons in the device, which may be caused by a thicker film for  $\text{Nb}_2\text{O}_5$  (30 nm) when compared to  $\text{TiO}_2$  (10 nm), as well as its inferior crystallinity nature. This higher  $R_{\text{tr}}$  will deteriorate the  $J_{\text{sc}}$  value of the devices, which is consistent with the  $J$ - $V$  results shown in Figure 2. The increased  $R_{\text{rec}}$  for PSC based on  $\text{Nb}_2\text{O}_5$  can be associated primarily with better electron extraction at the ETL/perovskite interface, which results in lower recombination rates, thereby giving higher  $V_{\text{oc}}$  in PSCs.<sup>46</sup> The steady-state photoluminescence (PL) results shown in Figure S13 also confirm a better electron extraction for  $\text{Nb}_2\text{O}_5$  film.

Stability under light illumination is one of the challenges for the practical application of PSCs.<sup>47</sup> Therefore, it is better to avoid using  $\text{TiO}_2$  ETL for completely overcoming the intrinsic UV light-induced degradation in PCEs.  $\text{Nb}_2\text{O}_5$  exhibits better



**Figure 5.** X-ray diffraction spectra of triple cation perovskite films deposited on (a) Nb<sub>2</sub>O<sub>5</sub> and (b) TiO<sub>2</sub> before and after UV aging for 10 h. (c) Corresponding optical photograph of the perovskite thin films on different substrates before and after UV irradiation. (d) Peak area ratio of the PbI<sub>2</sub> (001) plane to perovskite (110) plane.

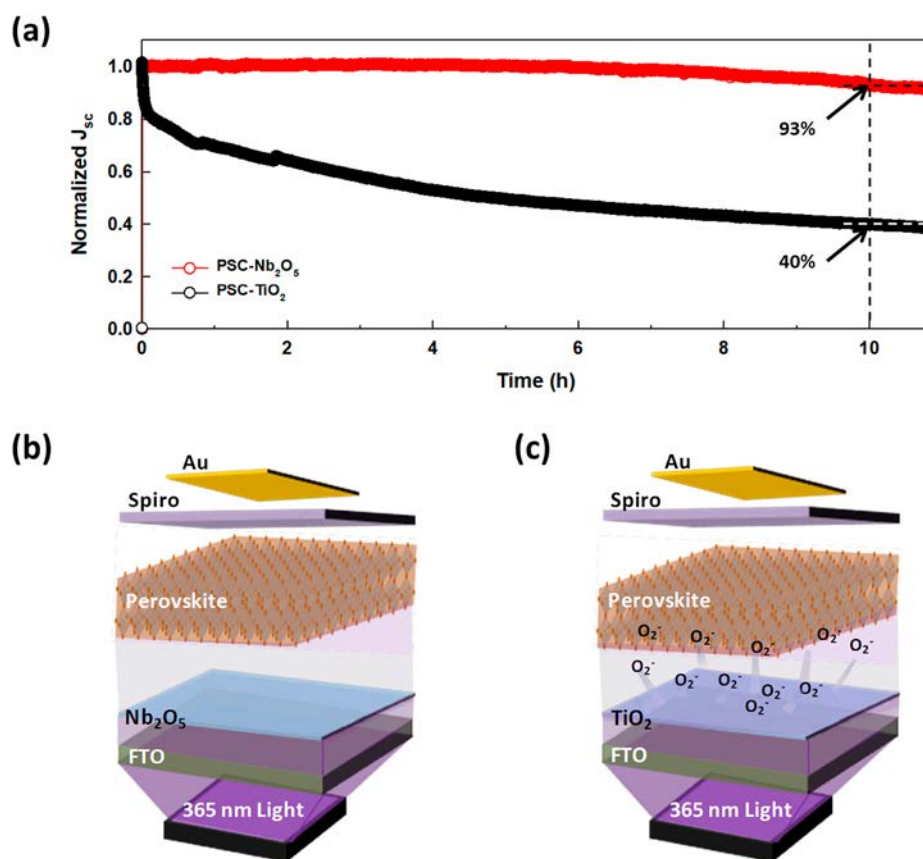
chemical stability relative to that of TiO<sub>2</sub>,<sup>48</sup> which may be a benefit for light stability of PSCs. Here, we investigated the stability of perovskite materials deposited on TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> ETLs under UV light illumination (we denoted the samples as Pero-TiO<sub>2</sub> and Pero-Nb<sub>2</sub>O<sub>5</sub>, respectively). The UV light was generated by a 365 nm LED light, which showed a half-peak width of 11 nm (Figure S14). The intensity was set to be 46 mW/cm<sup>2</sup>, which is about 10 times stronger than the UV section in AM 1.5G.<sup>49</sup> The comparison of diffraction peak areas of PbI<sub>2</sub> (001) at 12.7° and perovskite (110) at 14.16° was used to evaluate the decomposition behavior of perovskite.<sup>50,51</sup> As shown in Figure 5a, after 10 h UV exposure at ambient condition (humidity ~ 40%), there is no obvious change in their XRD pattern and color (Figure 5c) for Pero-Nb<sub>2</sub>O<sub>5</sub>. In contrast, we can see an obvious increase of the diffraction peak for PbI<sub>2</sub> when using TiO<sub>2</sub> as the substrate, indicating a low stability of the Pero-TiO<sub>2</sub> (Figure 5b). The color change from dark brown to yellowish after the 10 h UV exposure also indicates an instability nature of Pero-TiO<sub>2</sub> (Figure 5c). Figure 5d further presents the peak area ratio change for (001) of PbI<sub>2</sub> and (110) of perovskite after UV light illumination. The peak area ratio value of Pero-TiO<sub>2</sub> increases by about 10 times, indicating that some perovskite has been decomposed into PbI<sub>2</sub>. Meanwhile, the change for Pero-Nb<sub>2</sub>O<sub>5</sub> is much smaller. Thus, our results indicate Nb<sub>2</sub>O<sub>5</sub> can improve the UV stability of perovskite significantly when compared to TiO<sub>2</sub>.

We further examined the UV stability of the planar PSCs on Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>. The UV light soaking experiment was conducted employing PSCs with PCE ~ 20%. And the *J*-*V*

curves and parameters presented in Figure S15 and Table S2 were obtained by measuring the devices under one sun illumination in a N<sub>2</sub> atmosphere before and after UV light soaking. The devices made on Nb<sub>2</sub>O<sub>5</sub> show substantially improved stability relative to TiO<sub>2</sub> under UV light. A negligible reduction in PCE was witnessed for PSCs using Nb<sub>2</sub>O<sub>5</sub> ETL (from 19.97% to 19.51%). On the contrary, the TiO<sub>2</sub> based device suffered an obvious reduction of 20.14% to 12.68% in PCE. The normalized *J*<sub>sc</sub> shown in Figure 6a was recorded without encapsulation at ambient condition. Devices based on Nb<sub>2</sub>O<sub>5</sub> can retain 93% of their initial *J*<sub>sc</sub>, whereas those devices based on TiO<sub>2</sub> can only retain 40% of their initial *J*<sub>sc</sub>. Figure 6b,c illustrates the degradation diagram upon UV light exposure for these devices. TiO<sub>2</sub> is known to contain many oxygen vacancies (or Ti<sup>3+</sup> sites) which interact with molecular oxygen at the surface to form a charge transfer complex (O<sub>2</sub><sup>-</sup>-Ti<sup>4+</sup>).<sup>52-54</sup> The absorbed O<sub>2</sub> on the TiO<sub>2</sub> substrate could generate superoxide anion (O<sub>2</sub><sup>-</sup>) under UV light, which might be the primary reason for the decomposition of perovskite in solar cells under light soaking.<sup>55</sup> By replacing TiO<sub>2</sub> with Nb<sub>2</sub>O<sub>5</sub>, the light-induced O<sub>2</sub><sup>-</sup> is suppressed owing to the better chemical stability of Nb<sub>2</sub>O<sub>5</sub>. Therefore, PSCs with improved UV stability were obtained.

## CONCLUSION

In summary, we report a low-temperature solution-processed Nb<sub>2</sub>O<sub>5</sub> nanoparticle-formed film as electron transport layer to fabricate PSCs, yielding the highest PCE of 20.22% (stabilized PCE of 20.14%) with a very high *V*<sub>oc</sub> of 1.19 V. And PCE of



**Figure 6.** (a) Normalized  $J_{sc}$  of unencapsulated PSCs. Degradation diagrams of (b) Nb<sub>2</sub>O<sub>5</sub> and (c) TiO<sub>2</sub> based PSCs upon UV exposure.

20.22% and  $V_{oc}$  of 1.19 V are the best data for PSCs using Nb<sub>2</sub>O<sub>5</sub> as ETL. Moreover, these devices exhibited improved UV stability; a negligible reduction in PCE (from 19.97% to 19.51%) was witnessed for Nb<sub>2</sub>O<sub>5</sub> based PSCs before and after UV light soaking, whereas the devices based on TiO<sub>2</sub> showed an obvious reduction from 20.14% to 12.68%. The normalized  $J_{sc}$  of Nb<sub>2</sub>O<sub>5</sub> PSC retained 93% of the initial  $J_{sc}$  under continuous 365 nm UV light exposure (46 mW/cm<sup>2</sup>) for 10 h, whereas the TiO<sub>2</sub> based PSCs retained only 40% of their initial  $J_{sc}$ .

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b00991.

Figures S1–S16, showing the morphology of perovskite thin film, ETLs, and PSCs, performance for PSCs using Nb<sub>2</sub>O<sub>5</sub> ETL with different thicknesses,  $J$ – $V$  curves for PSCs measured under dark condition, Mott–Schottky plots of different ETLs, valence band spectra of perovskite on different ETLs from XPS measurement, equivalent circuit diagram for Nyquist plots fitting, photoluminescence spectrum of perovskite on various substrates, spectrum of the 365 nm UV light,  $J$ – $V$  curves for PSCs measured before and after UV light soaking,  $J$ – $V$  curves for flexible PSCs, and Tables S1 and S2, showing photovoltaic parameters (PDF)

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### Notes

The authors declare no competing financial interest.

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