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Supplementary Information

Depth-Resolved Band Alignments of Perovskite Solar Cells with Significant Interfacial Effects

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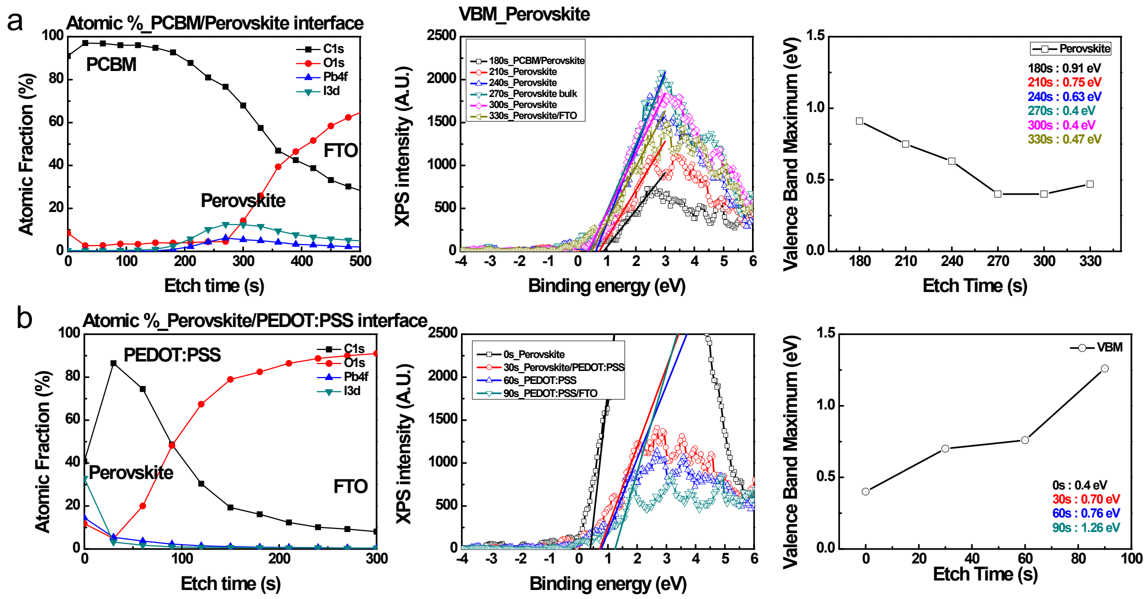
1. VB maximum energies extracted from VB edge XPS spectra

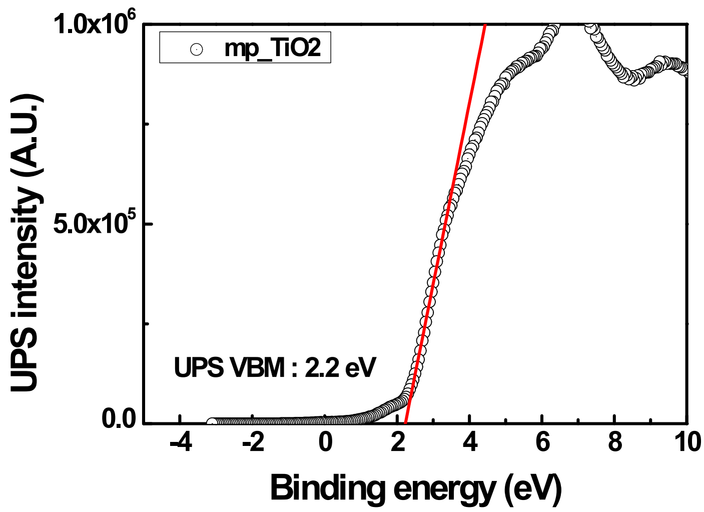
Figure S1. Atomic fraction (left), VB edge XPS spectra (middle), and VB maximum energies extracted from VB edge XPS spectra as a function of sputtering time (right) for (a) PCBM/perovskite and (b) perovskite/PEDOT:PSS interface.



2. UPS data of TiO_2 layer

The VB edge spectra of the UPS and XPS measurements of TiO_2 exhibit n-type characteristics with the Fermi energy level close to the CB minimum. In the UPS results (Figure S1.) for the mp-TiO_2 surface without Ar ion etching, the VBM was found to be 2.2 eV. Consequently, it was confirmed that the characteristics of typical n-type TiO_2 are deduced in combination with the bandgap of mp-TiO_2 (3.26 eV), as derived from a Tauc plot.

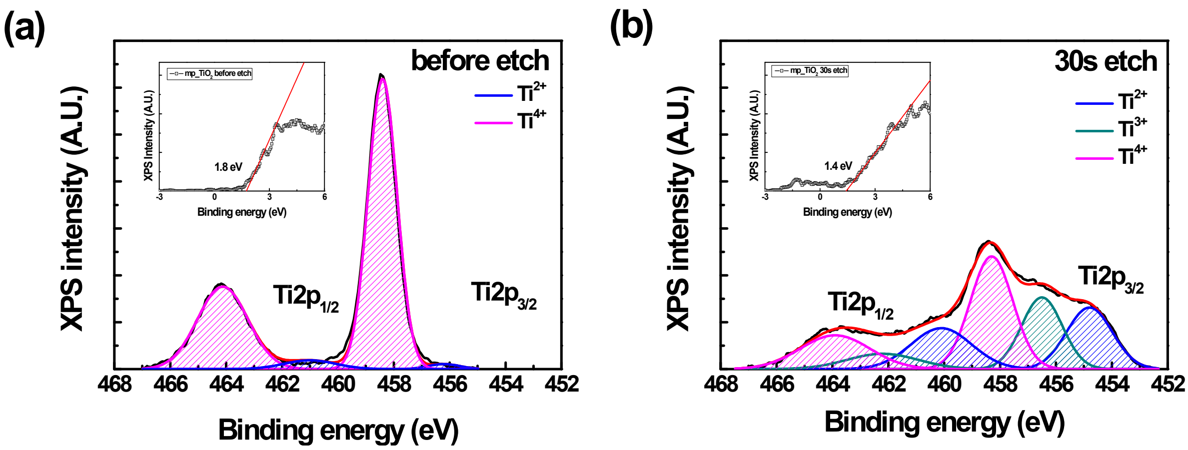
Figure S2. UPS data for mp-TiO_2 layer



3. XPS data of mp-TiO_2 before and after Ar ion sputtering

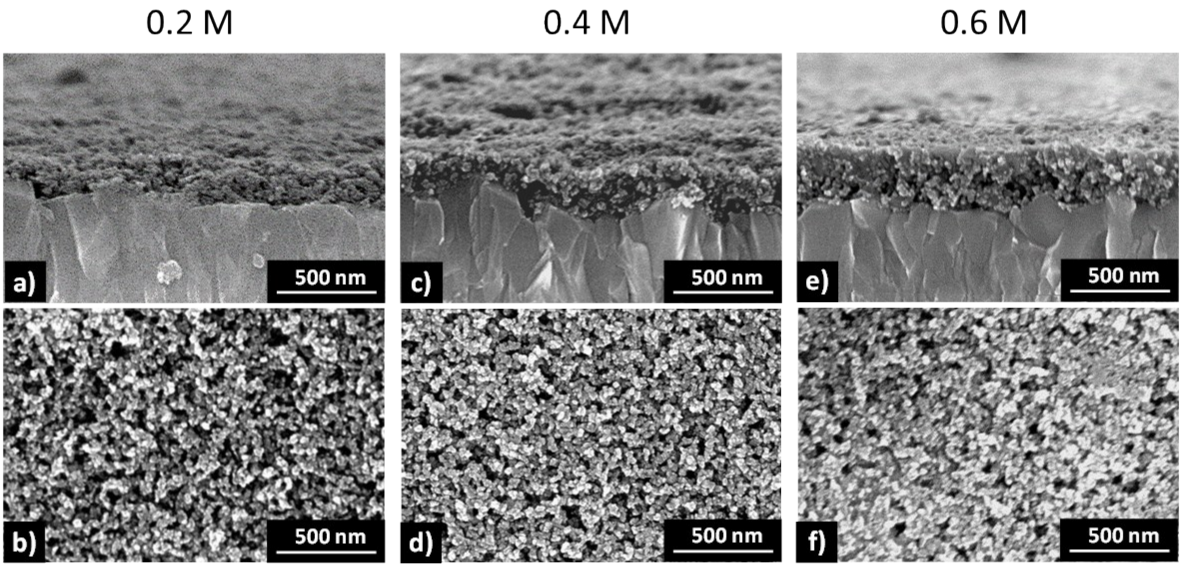
In Figure S2, the Ti2p XPS spectrum shows the Ti^{4+} peak ($Ti2p_{3/2}$: 458.4 eV, $Ti2p_{1/2}$: 464.1 eV) dominant binding states before Ar ion sputtering, which is the typical chemical property of regular TiO_2. The VBM value was also measured at 1.8 eV with n-type characteristics. However, after Ar ion sputtering for 30 s for 5- to 10-nm depth analysis from the top surface, the Ti2p spectrum revealed reduced TiO_x bond characteristics with peak components of Ti^{2+} ($Ti2p_{3/2}$: 454.8 eV, $Ti2p_{1/2}$: 460.1 eV), Ti^{3+} ($Ti2p_{3/2}$: 456.5 eV, $Ti2p_{1/2}$: 462.1 eV). In addition, VBM was also slightly negative-shifted to 1.4 eV, while the high sub-VB edge states overlapped at 0 eV of the E_F level. This is clear evidence of partially reduced TiO_x as a result of the Ar-sputter-induced bond-breaking, since mp-TiO_2 has a porous structure, which preferentially loses O ions from the lattice as a result of Ar ion bombardment. Therefore, non-destructive XPS analysis should be performed for an mp-TiO_2/perovskite interface.

Figure S3. XPS Ti2p narrow scan peak and VBM (a) before etch, (b) 30s Ar ion etched



4. SEM images of samples with different perovskite concentration

Figure S4. Cross sectional and plane-view SEM images for perovskite (upper layer) cross sectional (lower layer) plane-view



5. Average performances of PSCs

Table S1. Average solar cell parameters of planar and mesoporous (mp) structure PSCs

	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill Factor	PCE (%)
mp structure	0.98 ± 0.03	22.43 ± 0.81	0.61 ± 0.03	13.2 ± 0.90
planar structure	0.89 ± 0.04	18.48 ± 0.48	0.68 ± 0.03	11.2 ± 0.67

± represents standard deviation.