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Electronic Supplementary Information

Tailoring the PbS/Metal Interface in Colloidal Quantum Dot Solar Cells for Improvements of Performance and Air Stability

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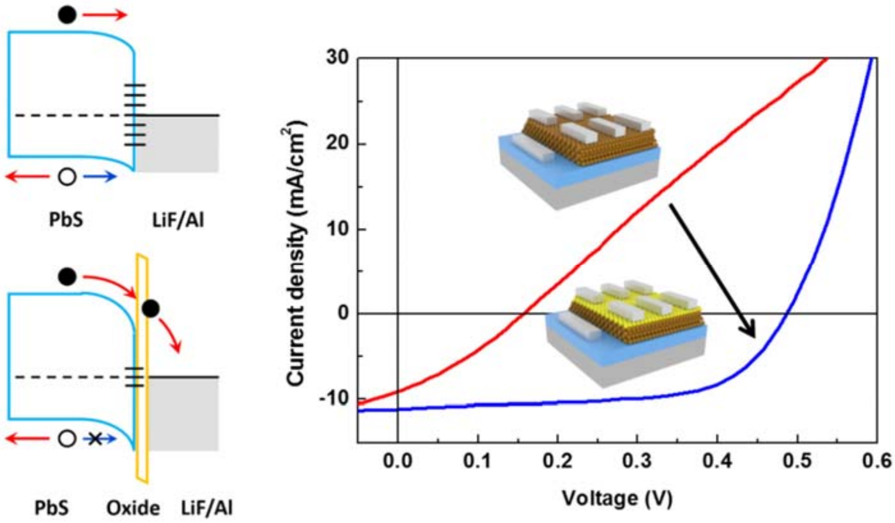

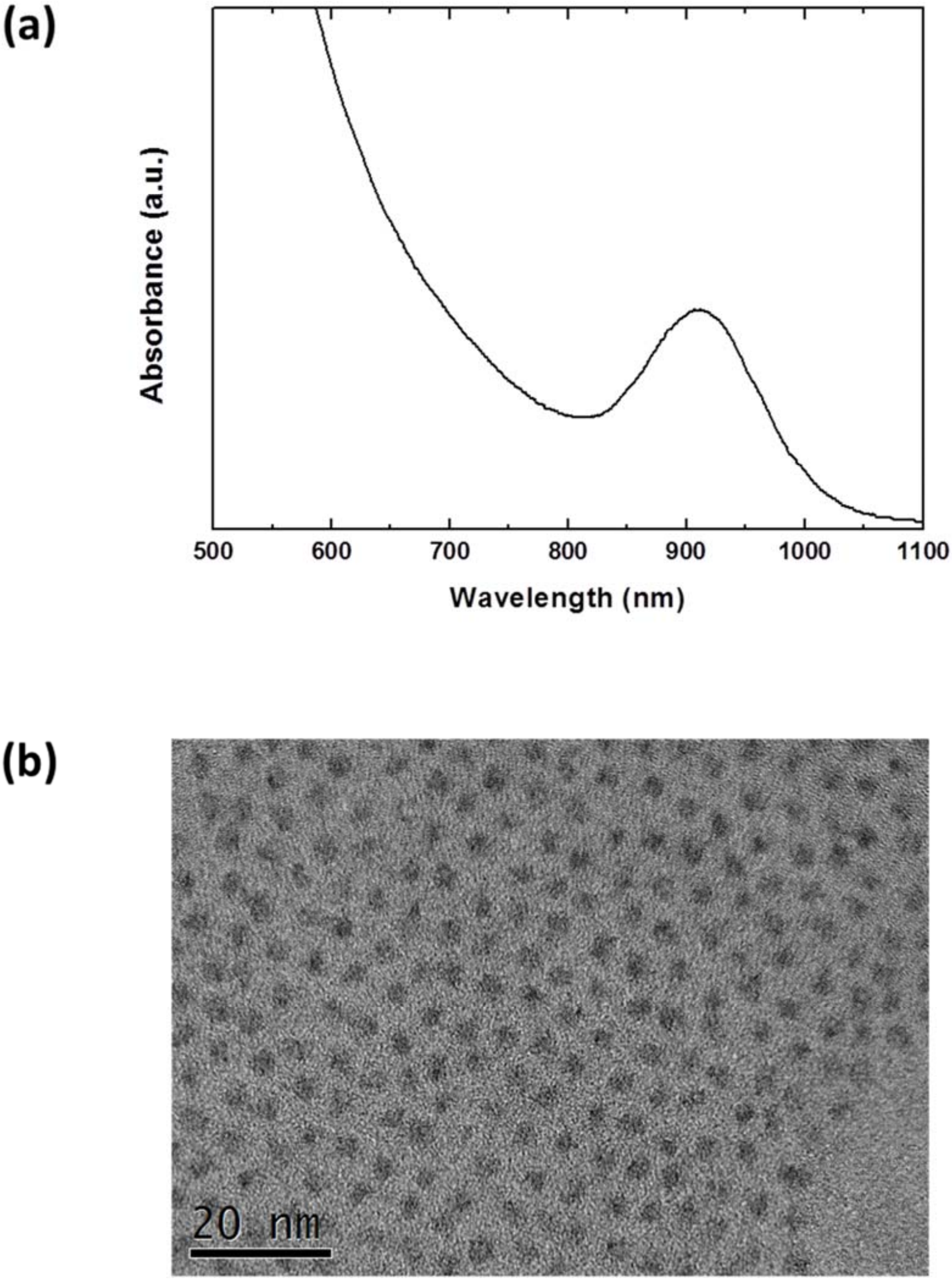

Figure S1. (a) UV-Vis absorption spectrum of as-synthesized PbS QDs dissolved in toluene. The first exciton peak is at 910 nm. (b) Transmission electron microscopy (TEM) images of PbS QDs with average diameter of 3 nm.

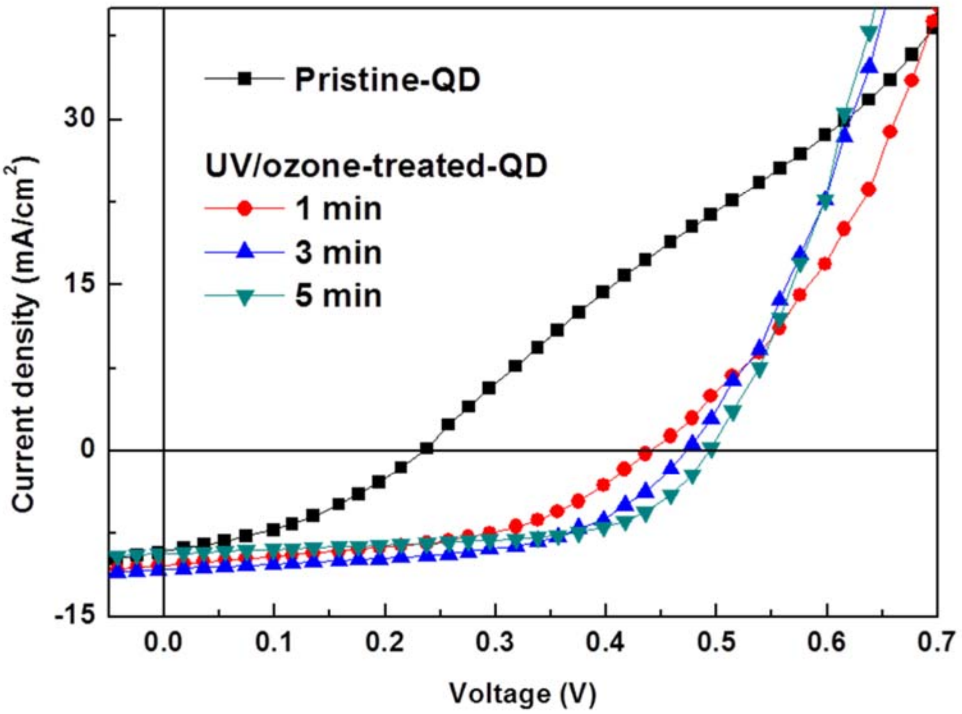

Figure S2. J-V characteristics of the UV lamp illuminated devices under AM1.5G illumination. UV lamp illumination was done in air with a 365 nm, 80 mW/cm^2 UV lamp.

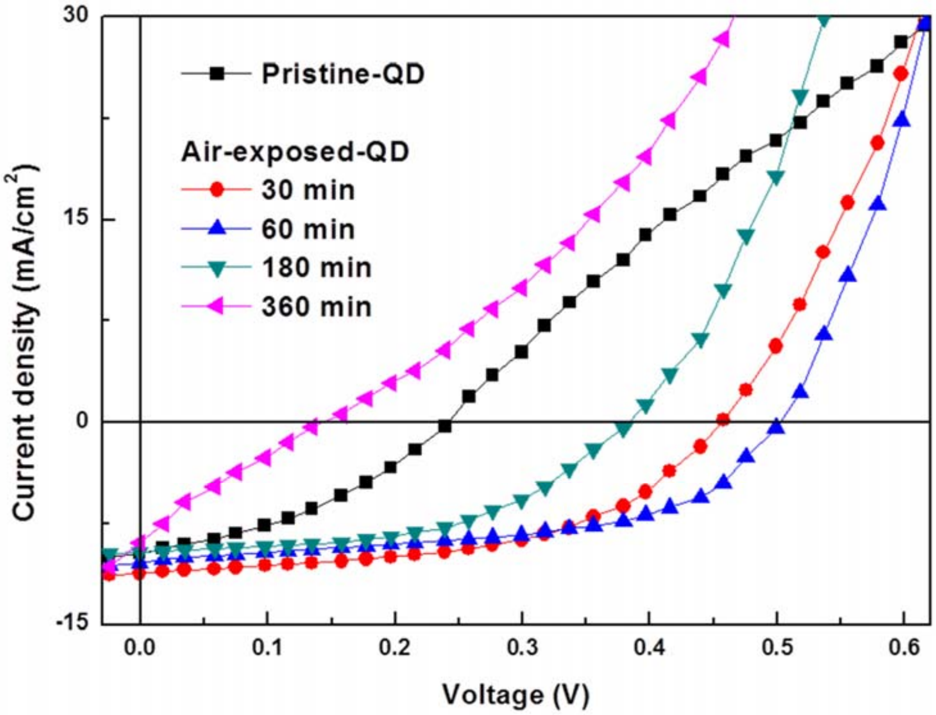

Figure S3. J-V characteristics of the air-exposed devices under AM1.5G illumination. The air exposure was performed in ambient conditions at room temperature.

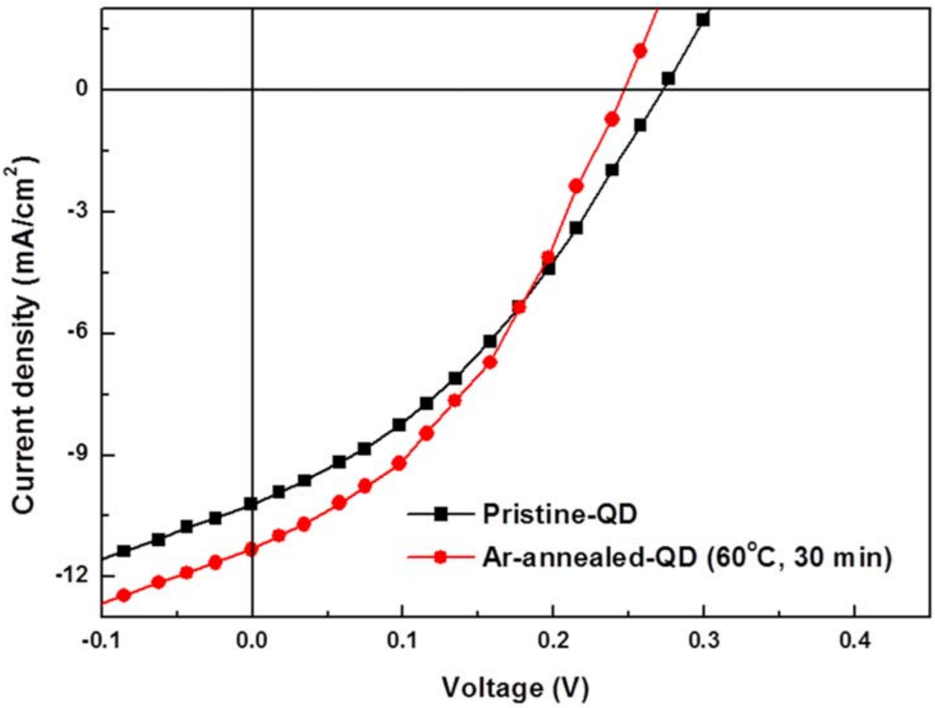

Figure S4. J-V characteristics of the pristine device and the device with thermal annealing in Ar-filled glove box under AM1.5G illumination.

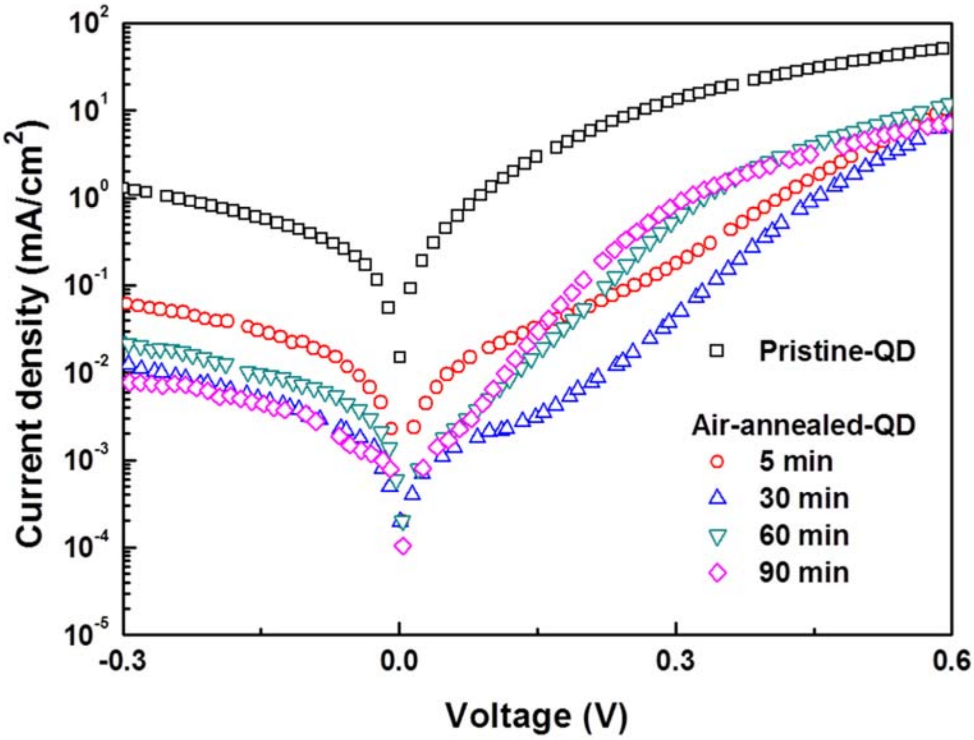

Figure S5. J-V characteristics of the devices with different air-annealing time in the dark. Air annealing was performed at 60 °C.

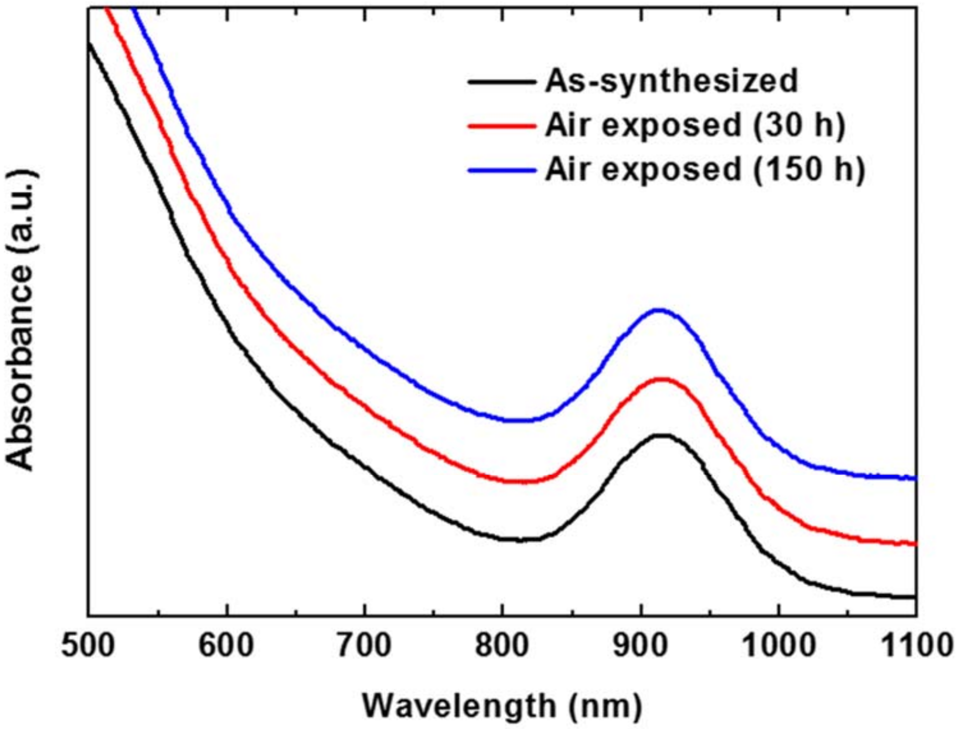

Figure S6. Almost invariant absorption spectra of PbS QDs capped with (long-chain) oleate in a toluene solution.

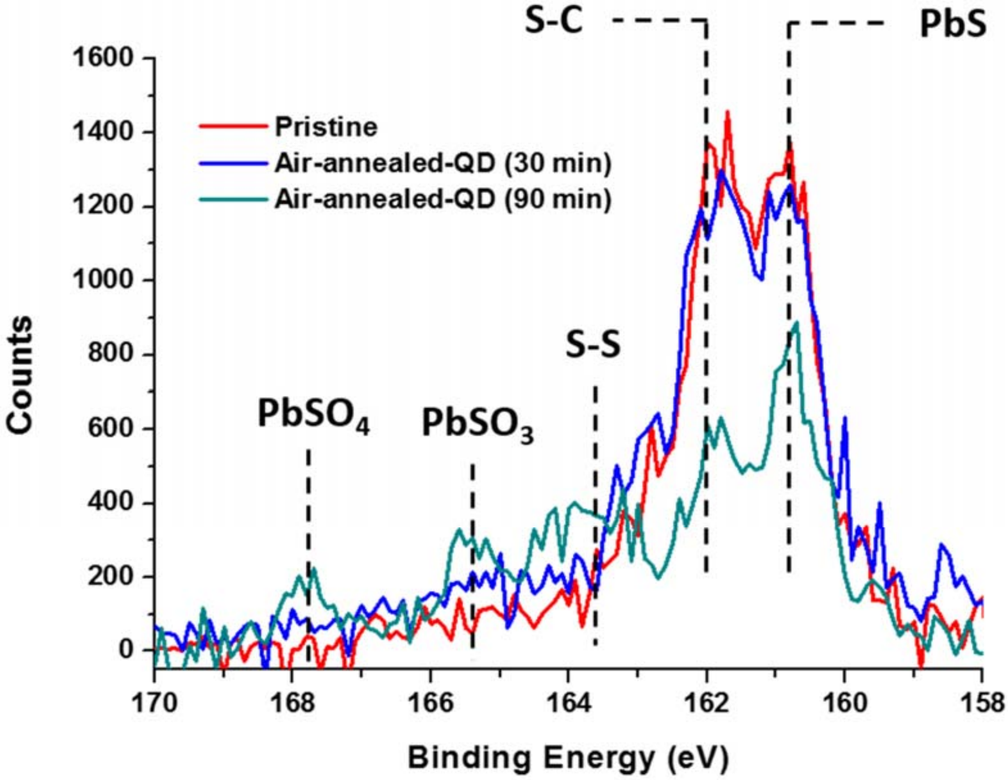

Figure S7. XPS S2p spectra of the air-annealed PbS QD film. Dashed lines indicate the different chemical bonding states of sulfur. (160.8 eV for PbS, 162.0 eV for S-C in ethandithiol, 163.7 eV for S-S in the oxidized form of ethanedithiol, 165.4 eV for $PbSO_3$, and 167.8 eV for $PbSO_4$).[1] Air-annealing for 30 min produced a small amount of lead sulfate and sulfite, while almost no change in sulfur in ethanedithiol. In contrast, 90-min-annealing significantly promoted the oxidation of ethanedithiol and the formation of lead sulfate and sulfite.

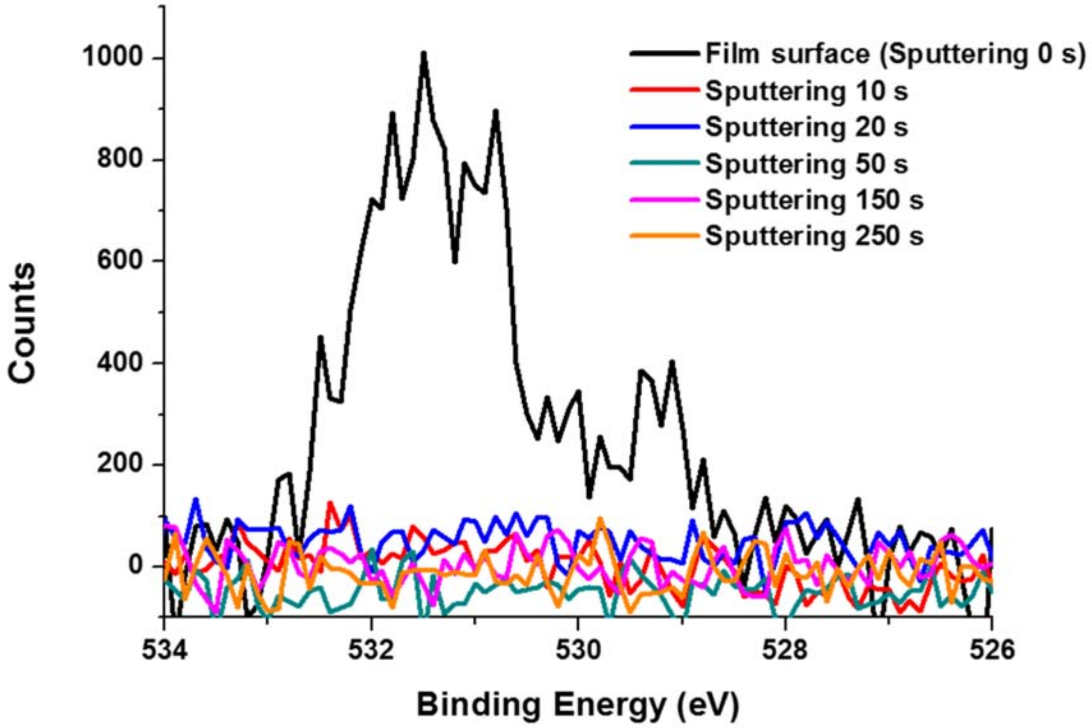

Figure S8. XPS O1s spectra of the 30-min-annealed PbS QD film with increasing Ar sputtering time. As shown in Figure 3c, the 160-nm-thick PbS QD film is mechanically etched with Ar^+ beam sputtering within 320 seconds, indicating an etching rate of 0.5 nm/s. The data show that the oxygen in the QD film is completely removed within sputtering time of 10 s, indicating that the upper limit of thickness of the oxidized layer is 5 nm.

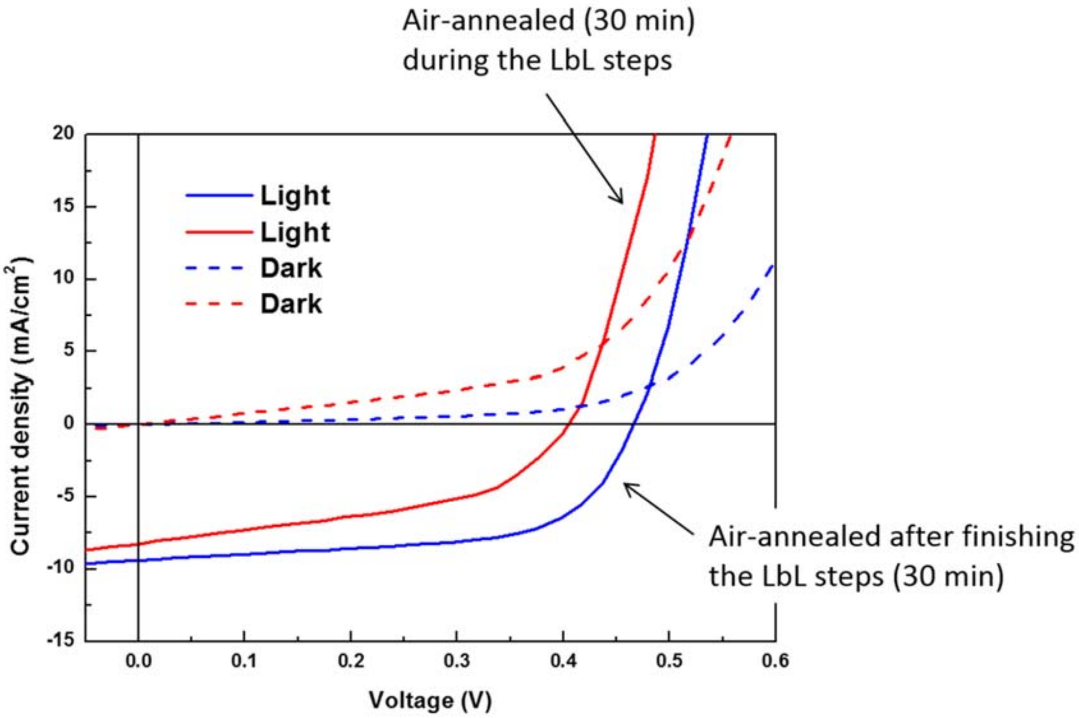

Figure S9. J-V characteristics of the devices with air annealing during the LbL deposition steps (red) and after finishing the LbL deposition (blue) under AM1.5G illumination. Blue line indicates the device with the oxidized layer at the surface and red line shows the device composed of overall oxidized-QDs. Improved device performance and onset of the dark forward current indicates that oxidation provides positive effect at the surface, while oxidation inside the film decreases the device performance.

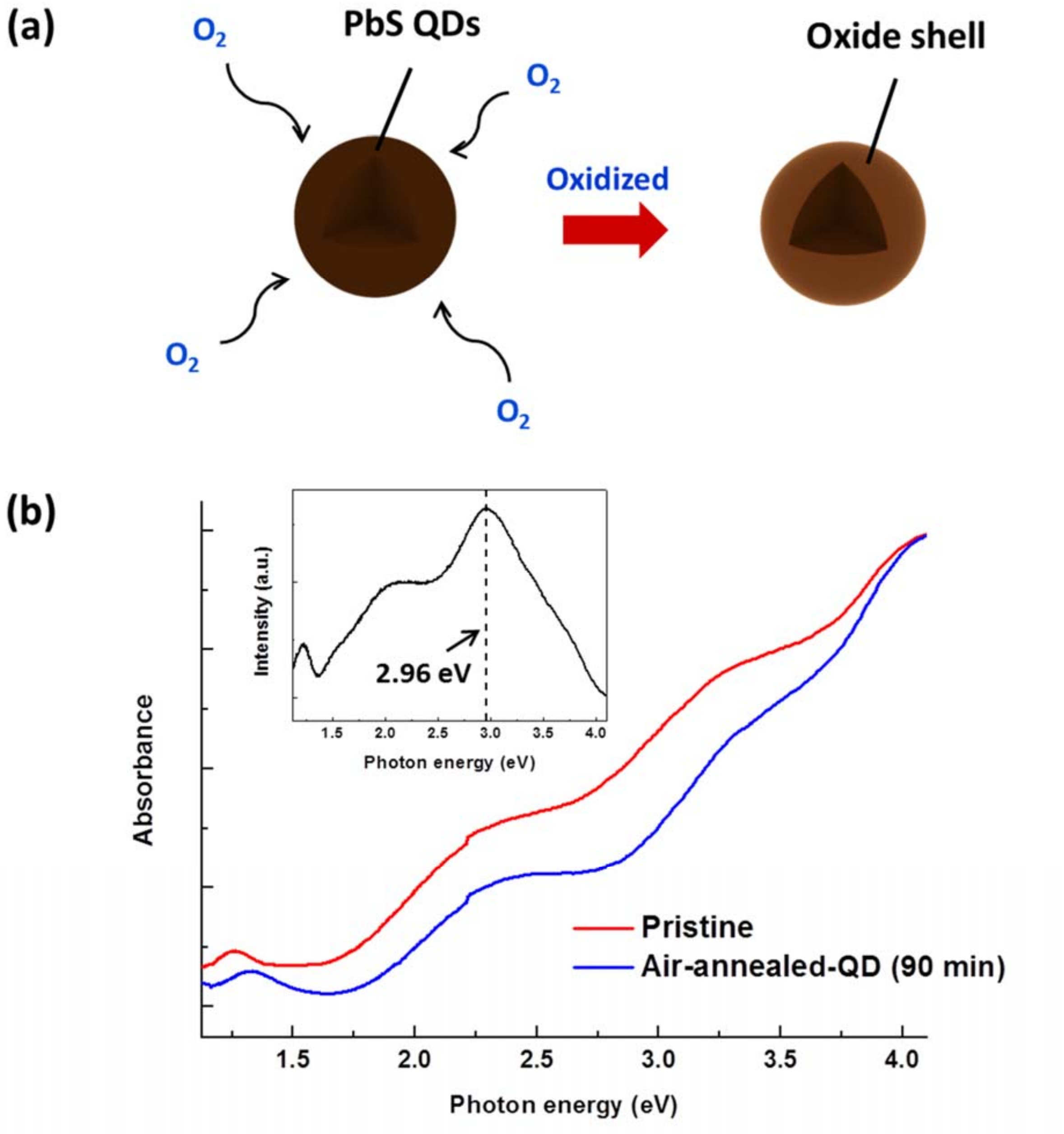

Figure S10. The oxidation progress in PbS QDs is indicated in (a). The outer surface of the PbS QDs is converted to oxide compounds, which results in light absorption loss and decreasing size of QDs.[1, 2] This suggests that the oxide shell in the PbS QDs is a wide-band-gap material that cannot absorb visible light. On the basis of this fact, we estimated the optical band gap of the oxide compounds from the UV-Vis absorption spectrum. We prepared a thin 30-nm-thick PbS QD film on ITO glass and annealed it in air at 60 °C for 90 min, in order to increase the portion of oxide compounds in the PbS QD film. (b) The UV-Vis absorption spectrum of the oxidized-film was compared with that of the pristine film. The inset data in (b) indicates the difference in light absorption between the pristine film and the oxidized-film. This difference decreases rapidly after the illuminated photon energy exceeds 2.96 eV, which means that the oxide compounds in the film absorb light above 2.96 eV.

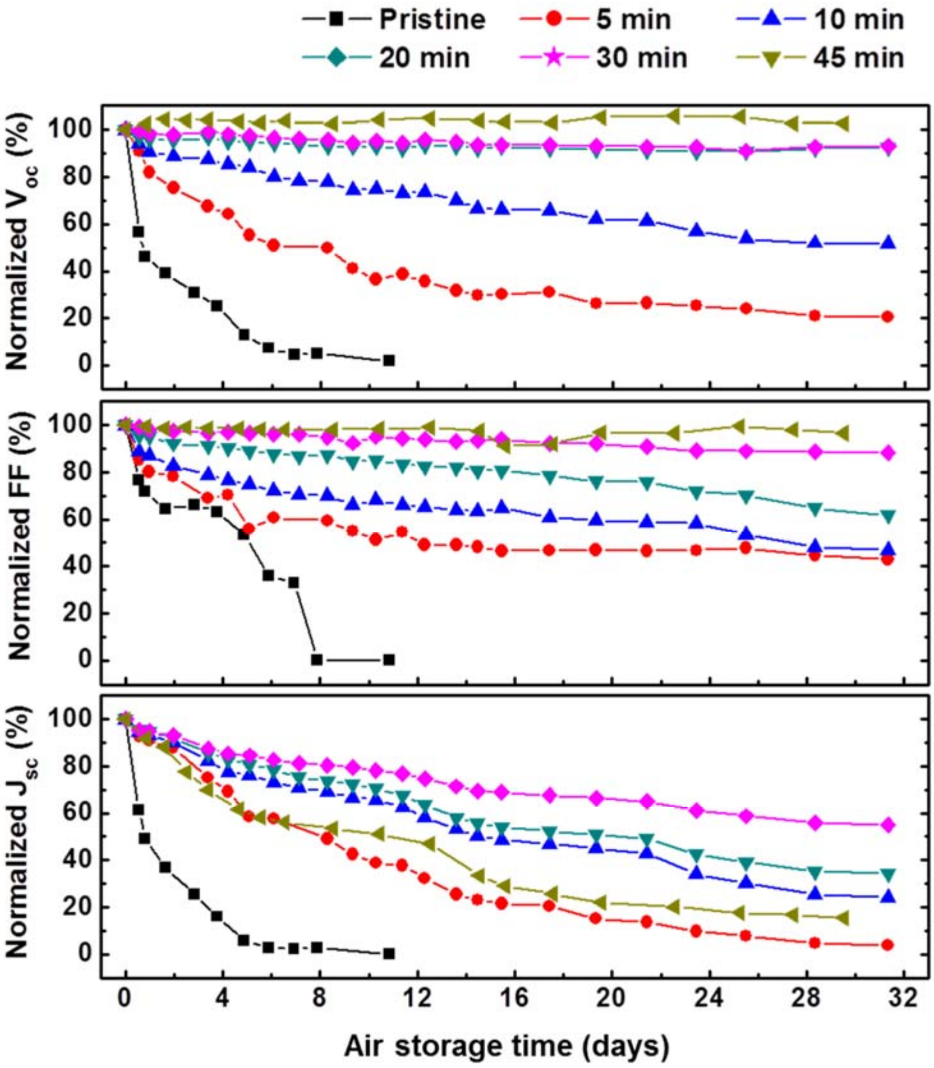

Figure S11. Normalized V_{OC}, FF, and J_{SC} values of the air-annealed-QD devices.

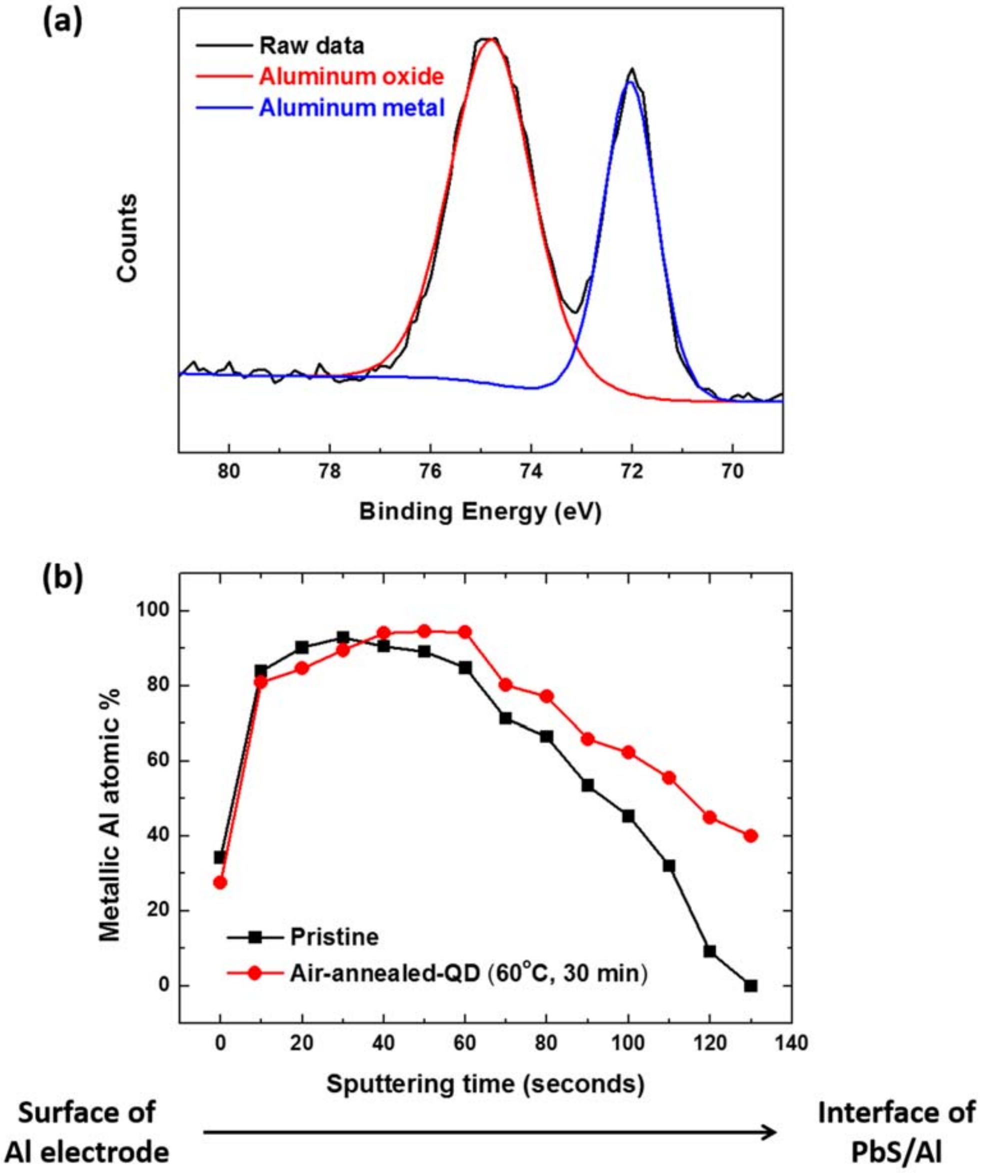

Figure S12. An XPS depth profiling experiment was performed to investigate the mechanism of improved air stability by the oxidized interfacial layer. (a) Al2p XPS spectra. Aluminum is easily oxidized in air, and thus the XPS spectra from the sample surface clearly shows the existence of two binding energies for aluminum metal and aluminum oxide. (b) XPS depth profiling analysis results for the Al electrode. We fabricated the pristine-QD device and 0-min-annealed-QD device using aluminum as a metal electrode. After storing the devices in air for 3 days, an XPS depth profiling test was performed with a 3 keV Ar^+ beam at a current of 1 μA.

References

1. J. Tang, L. Brzozowski, D. A. R. Barkhouse, X. H. Wang, R. Debnath, R. Wolowiec, E. Palmiano, L. Levina, A. G. Pattantyus-Abraham, D. Jamakosmanovic and E.H. Sargent, ACS Nano, 2010, 4, 869-878.

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3. Zhao, N.; Osedach, T. P.; Chang, L. Y.; Geyer, S. M.; Wanger, D.; Binda, M. T.; Arango, A. C.; Bawendi, M. G.; Bulovic, V. *Acs Nano* **2010,** 4, (7), 3743-3752.