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Air stability of TiO₂/PbS colloidal nanoparticle solar cells and its impact on power efficiency

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The short-term (less than 1 hour) exposure of TiO₂/PbS quantum dot photovoltaics to air increases the open circuit voltage (V_{oc}) and fill factor (FF) while slightly decreasing the short circuit current density (J_{sc}), leading to a power conversion efficiency above 4% and a peak external quantum efficiency over 80% for 1.1 eV PbS. The resulting J_{sc} , V_{oc} , and FF under 100 mW/cm² AM1.5 are 18.6 mA/cm², 0.517 V, and 42% for 1.1 eV PbS and 8.03 mA/cm², 0.655 V, and 35% for 1.7 eV PbS, respectively. Long-term air exposures result in much lower conductivities. Furthermore, short-term air exposure effects are fully reversible upon removal from air, and longer-term effects are mostly reversible through soaking in 1,2-ethanedithiol. © 2011 American Institute of Physics. [doi:10.1063/1.3617469]

Solar cells that contain quantum dots (QD) have the potential for combining lower cost with higher efficiency. While initial results have shown significant promise for obtaining high internal quantum efficiencies,^{1,2} overall power efficiencies are generally low compared to inorganic thin-film photovoltaics (PV) due to reduced absorption, open circuit voltages (V_{oc}), and fill factors (FF). Moreover, significant variation in the results between groups has been observed for similar device structures, making it challenging to compare results and understand how to improve overall device performance.^{3–5} A possible source for this variation is the condition in which the devices are fabricated and tested. While others have observed the impact of air-annealing on film and device performance,^{6,7} few systematic studies at short and long air exposure times have been reported, especially for devices with high initial short circuit current density (J_{sc}). Here, we systematically study the impact of air-exposure on TiO₂/PbS QD solar cells with initial $J_{sc} > 15$ mA/cm². We demonstrate that while air exposure can be used to increase both V_{oc} and FF and therefore overall power efficiency, it also preferentially decreases the IR-response of the external quantum efficiency (EQE).

The colloidal PbS QDs were provided by Solexant, the TiO₂ sol-gel was made using the standard procedure described earlier,⁸ and the TiO₂ nanoparticles (NP) were purchased from Solaronix. The devices (structure shown in the inset of Fig. 1(b)) were fabricated using a similar procedure described previously.⁵ We note that the sintering of the TiO₂ had very little impact on the indium tin oxide (ITO) and very similar results were observed for fluorine-doped tin oxide (FTO) and ITO.⁹ Current density-voltage (J-V) curves were taken using a calibrated solar simulator and a Keithley 2400 source meter, and EQE curves were taken using the solar simulator coupled into an Oriel monochromator. The J-V and EQE measurements were all taken in the nitrogen-filled

glove box, and the devices were not exposed to air between the PbS deposition and the initial J-V and EQE measurements. In air exposure experiments, the devices were moved out of the glove box and exposed to the air in normal indoor fluorescent light for the specified time, followed by immediate J-V and EQE measurements in glove box. The exposure to vacuum in the antechamber did not substantially impact the results.⁹ The optical properties of PbS QD films were obtained using a Varian Cary 50 UV-vis-NIR spectrometer and photothermal deflection spectroscopy (PDS).^{9,10}

In Fig. 1(a), the light J-V curves are shown for a TiO₂/PbS (1.1 eV) device as a function of 1 h of air exposure. Five minutes of air exposure leads to the greatest increase in performance, with a substantial increase in V_{oc} and FF; however, air exposure also results in a continuous decrease in J_{sc} . Dark curves show that dark saturation current reduces with air exposure time which results in the improved diode-like behavior and increased shunt resistance (inset of Fig. 1(a)), similar to observations in air-annealed PbS/fullerene derivative solar cells.⁷ The reduced conductivity also results in a decrease in J_{sc} which offsets the gains in V_{oc} and FF for long exposure times. As Fig. 1(b) shows, after 1 h of air exposure the EQE at longer wavelengths gradually decreases while the peak EQE remains mostly constant, indicating the reduction in current is due to reduced charge collection at the PbS/Au interface. Returning air-exposed devices to the glove box resulted in a transition back to the original values over several hours to days, demonstrating that the short-term air-exposure effect is reversible.

Long term air exposure can result in substantial decrease in J_{sc} ; nonetheless, this reduction in J_{sc} was shown to be partly reversible for all devices studied by soaking the device in 1,2-ethanedithiol (EDT) solution, the same solution used in the ligand exchange as shown in Figs. 2(a) and 2(b).⁹ The presence of EDT in the solution was required for the improvement in conductivity, and the dark curves reveal that the EDT soak strongly increases conductivity,⁹ as may be

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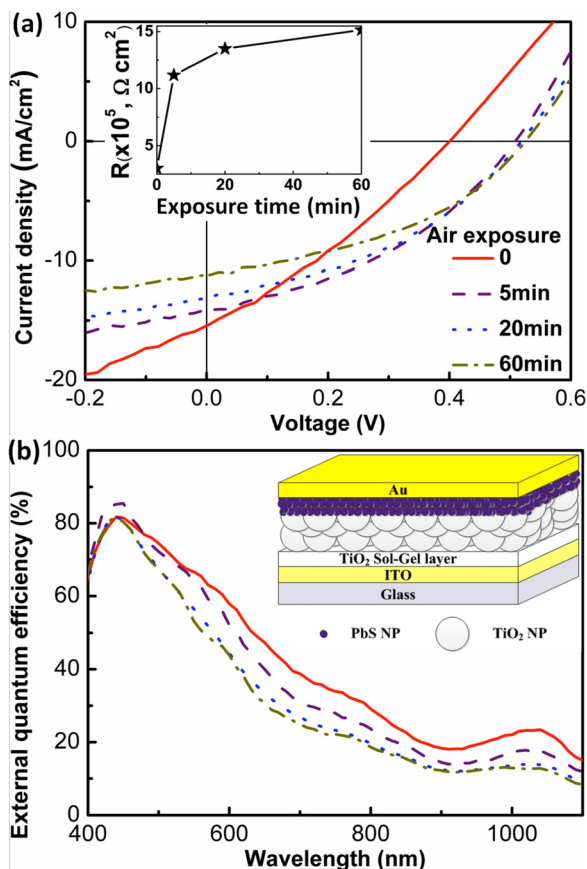


FIG. 1. (Color online) (a) J-V characteristics for a TiO_2/PbS (1.1 eV) device under 90 mW/cm^2 AM1.5 illumination in 1 h of air exposure under fluorescent lights. Inset: resistance (R) change of the device with air exposure time. Resistances are calculated from $\Delta V/\Delta I$ at $V = -0.3$ to 0 V for each J-V curve of the device in the dark. (b) EQE spectra for the corresponding device in 1 h of air exposure. Inset: Schematic of the TiO_2/PbS solar cell structure.

expected due to the impact of EDT on the overall mobility.⁶ However, we observe no bulk changes in the EDT ligands in the Fourier transform infrared spectrum measured before and after EDT and air exposure.

Several possibilities can explain the observed reduced dark current and resulting improved V_{oc} after air exposure as well as the reversibility of the effects. First, oxygen vacancies in the TiO_2 layer could have been filled after air exposure, resulting in lower conductivity and therefore reduced dark currents. The effect should be transient because the absorbed oxygen could be desorbed from the TiO_2 surface when the device is moved back to nitrogen-filled glove box.¹¹ However, this possibility can be eliminated because no abrupt improvement occurred in V_{oc} when the TiO_2 layer was exposed to a variety of treatments, including sintering in oxygen or treatment with oxygen plasma.⁹ Furthermore, similar effects have been observed for devices that do not contain TiO_2 .⁷ A second possibility is that the oxygen in air mainly affects the PbS layer when the devices are exposed to air. Oxygen is expected to create acceptor states on the PbS (Ref. 12) and PbSe (Refs. 12 and 13) QD films. The creation of these acceptor states results in the shifting of PbS's Fermi level towards the valence band, which causes bigger energy band bending and resulting improved rectification and V_{oc} . The falloff in the longer wavelength region of EQE spectra, observed in Fig. 1(b), supports that the decrease of the depletion

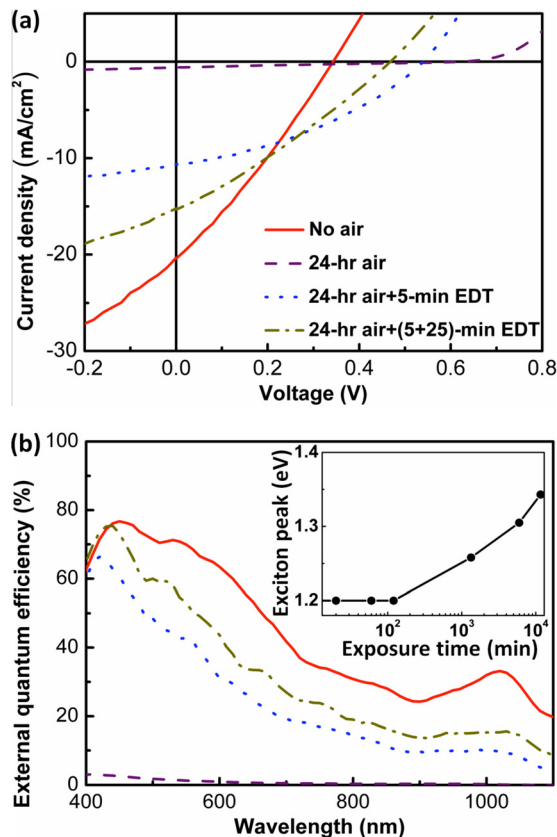


FIG. 2. (Color online) (a) J-V characteristics for a TiO_2/PbS (1.1 eV) device under 100 mW/cm^2 AM1.5 illumination before and after 24-h air exposure and subsequent 5 and 30-min of EDT soak. (b) EQE spectra for the corresponding device. Inset: the change in the exciton peak extracted from absorption data with air exposure time.

width in the PbS film is due to acceptor doping as photons with lower energy are absorbed farther from the depletion region in the PbS film with air exposure time and contribute less to the photocurrent. However, acceptor doping is inconsistent with the rapid decrease in the dark current observed. An alternative explanation is that the air exposure reduces electron mobility as oxygen is a known electron trap. Since the red photons are absorbed much further from the transparent electrode than the blue photons, the lower mobility electrons generated near the Au interface will not be as efficiently collected at the TiO_2 interface.

The reversibility is likely caused by reversible physical adsorption of oxygen on the PbS surfaces. At low oxygen exposures, Norris *et al.*¹³ reported the reversibility in charge mobilities and conductivities of their PbSe QD films and ascribed the effect to the formation of reversible superoxide-like complexes. As shown in the inset of Fig. 2(b), no obvious blue shifts of the excitonic energy⁹ occurred for our PbS films in the first 2 h of air exposure under room lighting conditions, indicating that similar reversibly adsorbed structures on our PbS layer are also possible for short-term air exposure.

As the time of air exposure increases, the probability of the physically adsorbed oxygen molecules to dissociate and form chemical bonds with the PbS surface increases. These irreversible reactions likely produce some oxides (e.g., PbO , PbSO_3 , and PbSO_4) on the PbS QD surface, similar to the case of PbSe QD film.¹³ Indeed, as shown in the inset of Fig. 2(b), the blue shift of exciton peak (from 1.20 to 1.26 eV)

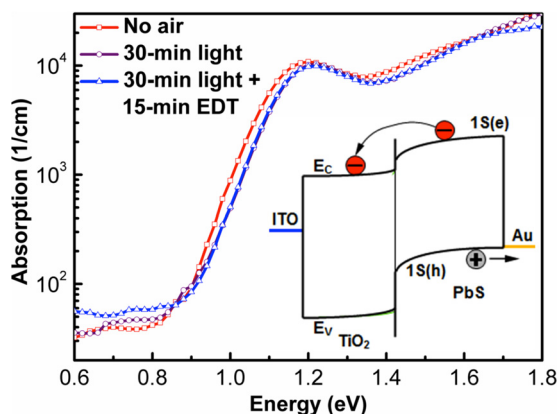


FIG. 3. (Color online) The photothermal deflection spectra of PbS QD film before air exposure and after 30-min aggressive oxidation in air by soaking in 100 mW/cm² of AM1.5 light, followed by a subsequent 15 min of EDT soak. Inset: the flat energy level diagram of device; E_c and E_v are the conduction and valence band edges.

was observed after about 24 h of air exposure, indicating that an insulating layer is forming on the PbS surface that reduces the overall QD size. The marked reduction of EQE over the full range spectrum, as well as the more notable blue-shift in the exciton peak, is due to the formation of oxides, which blocks the transportation of the carriers among PbS QDs. Previous results^{6,7} suggest that EDT can remove and/or transform the formed insulating layer on the PbS surface which can explain the EDT soaking effect that we observed; however, the removal of this oxide does not result in the recovery of the QD size, i.e., the QDs become increasingly smaller and less conductive. These results are shown in the PDS data presented in Fig. 3. For the PDS measurements, the sample was soaked in air for 30 min under a more aggressive AM1.5 illumination, instead of the indoor fluorescent light, to accelerate the degradation process. The aggressive exposure of the device to light soaking in air causes the expected increase in the band gap energy; however, subsequent exposure to EDT does not affect the bandgap energy, indicating that the EDT only dissolves away the insulating shell and does not rebuild the QD size to its pre-oxidation state. Subsequent exposures to oxygen and EDT will lead to increasingly smaller QDs and eventually device failure, as is observed. The PDS data taken within the bandgap also reveal that the mid-gap states, and therefore the doping, are not substantially impacted by air exposure or EDT treatment.¹⁰

The NREL group demonstrated remarkable stability for PbS QD solar cells on ZnO (Ref. 4); however, the J_{sc} obtained are lower (<10 mA/cm²) than those observed for other QD solar cells based on PbS (Refs. 3 and 5) or PbSe (Refs. 14 and 15). A question that remains is whether ZnO plays an important role in the device stability. To answer this question, we also made ZnO/PbS devices and observed a slightly slower, but similar, decrease in J_{sc} in comparison to our TiO₂ devices made from the same QD solutions.⁹ The discrepancy in our results with the NREL results could be explained by the different surface chemistry among PbS QDs caused by the timing of the air exposure.⁹

Using 5 min of air exposure, we were able to improve the device efficiency to above 4% for 1.1 eV PbS and increase the V_{oc} up to 0.65 V for 1.7 eV PbS, as shown in Fig. 4 and

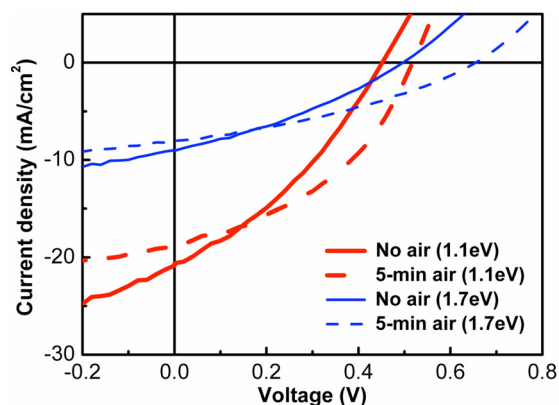


FIG. 4. (Color online) J-V characteristics of representative solar cells composed of two different sizes of PbS QDs before and after 5 min of air exposure under 100 mW/cm² AM1.5 illumination.

Supplementary Table.⁹ More importantly, our results show that small changes in environmental conditions can cause significant impact in conclusions drawn, calling into question the helpfulness of reporting results without careful consideration of the environmental conditions. We further note that being able to report internal quantum efficiencies above 100% requires accurately measuring the EQE and the absorption simultaneously since any changes in time and atmospheric exposure result in the measurement of a different material and device, potentially leading to incorrect conclusions.

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