Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Ultra-broadband perovskite-PbS quantum dot sensitized carbon nanotube photodetector

Ibrahima Ka,*[a] Luis F. Gerlein,[a] Ivy M. Asuo,[a,b] Riad Nechache,*[a] Sylvain G. Cloutier*[a]

[a] Department of Electrical Engineering, École de Technologie Supérieure, 1100 Notre-Dame Ouest, Montréal, QC, H3C 1K3, Canada

[b] Institut National de la Recherche Scientifique INRS-Énergie, Matériaux et Télécommunications 1650, Blvd. Lionel-Boulet, Varennes, QC, J3X-1S2, Canada

*Correspondence and requests for materials should be addressed to Dr. Ibrahima Ka (email: ibrahima.ka.1@ens.etsmtl.ca) or Dr. Riad Nechache (email: riad.nechache@etsmtl.ca) or Prof. Sylvain G. Cloutier (email: sylvaing.cloutier@etsmtl.ca).

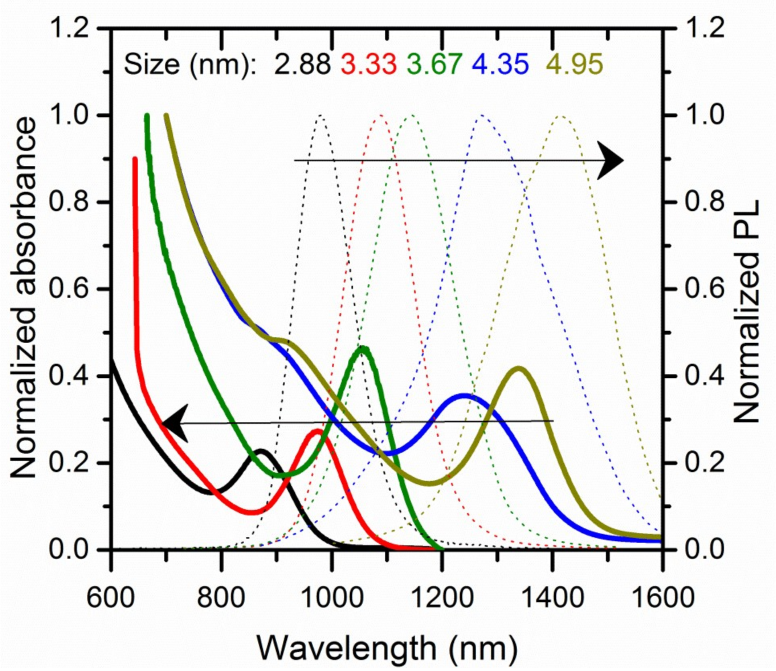

Fig. S1 Normalized absorption and photoluminescence of the PbS-QDs of different sizes used in this work. The estimation of the QDs sizes were determined using data reported by Sablon et al[1].

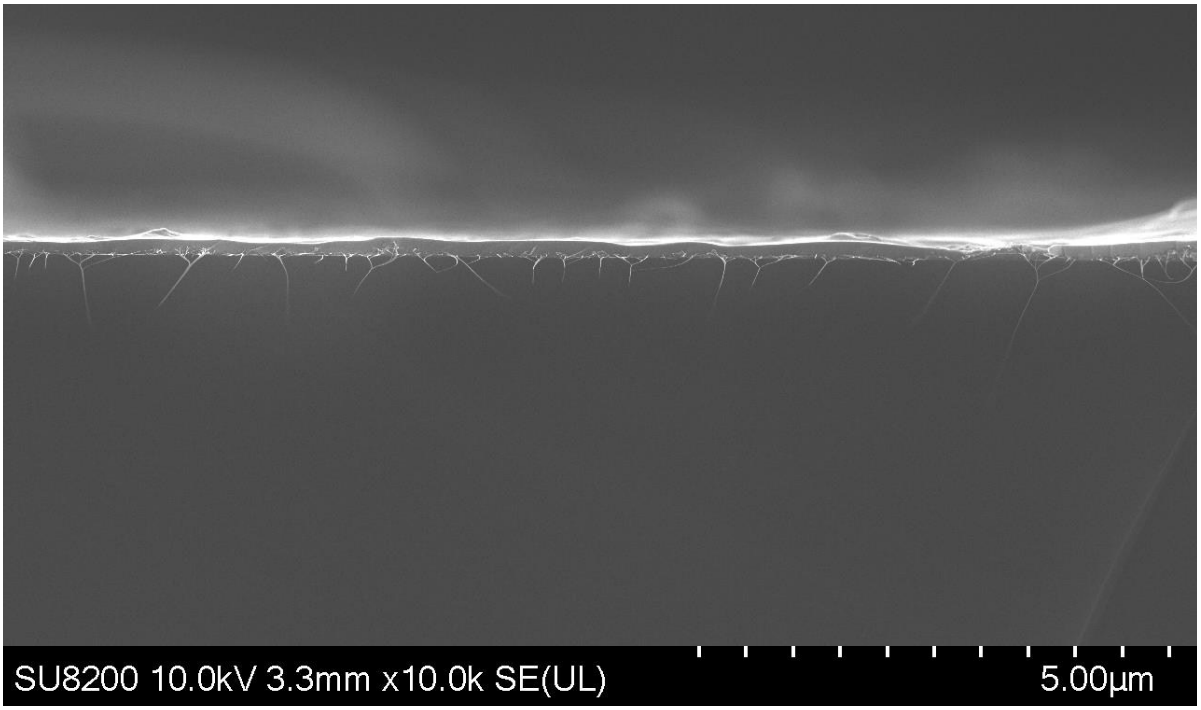

Fig. S2 Cross sectional SEM image of SWCNT/PbS-QDs/perovskite at low magnification, showing the uniformity of the hybrid film. The SWCNTs are deposited by spray-coating, the PbS-QDs are deposited by dip-coating and the perovskites are deposited by spin-coating.

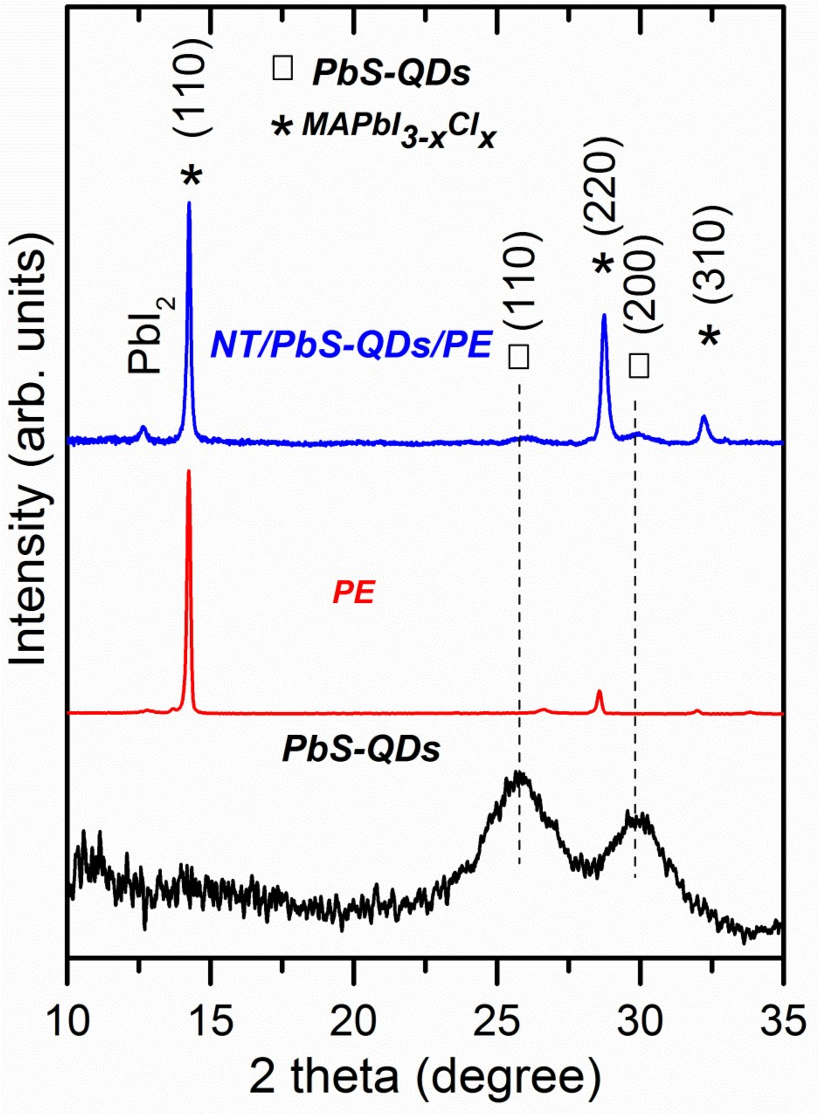

Fig. S3 X-ray diffraction measurements of the PbS-QDs, the $MAPbI_{3-x}Cl_x$ and the SWCNT/PbS-QDs/MAPbI3-xClx. The size of PbS-QDs used in these measurements is around 2.88 nm.

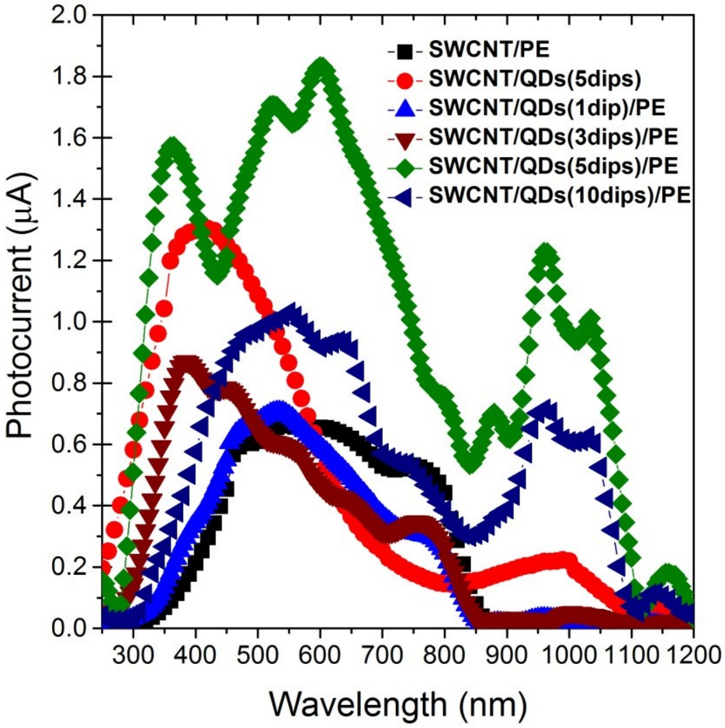

Fig. S4 Optimization of the number of dips of PbS-QDs through the photocurrent spectrum measurements. The addition of PbS-QDs as another sensitizer shows additional responses in the UV and the NIR regions. The samples made with 5 dips exhibits the highest response both in the NIR and the visible. The size of PbS-QDs used in these measurements is around 2.88 nm.

We call 5 dips our optimum based on the optimization data showed above (Fig. S4§). As can be seen, we obtained both higher photoresponse in the NIR (which means more contribution of the PbS-QDs) and in the visible region (which means that charge generated by the perovskites are efficiently collected by the carbon nanotubes). We believe that in the devices fabricated with 1 and 3 dips, the PbS-QDs film is not thick enough to absorb all the NIR photons, while in devices fabricated with 10 dips all the NIR are possibly absorbed. However, due to the thickness of the PbS-QDs film on the SWCNT the efficiency of the charge transfers (from the PbS-QDs and from the PE to the SWCNT) is reduced. Thus, 5 dip-coatings of PbS-QDs are considered to offer the best trade-off between the charge transfer and the photoresponse in the NIR.

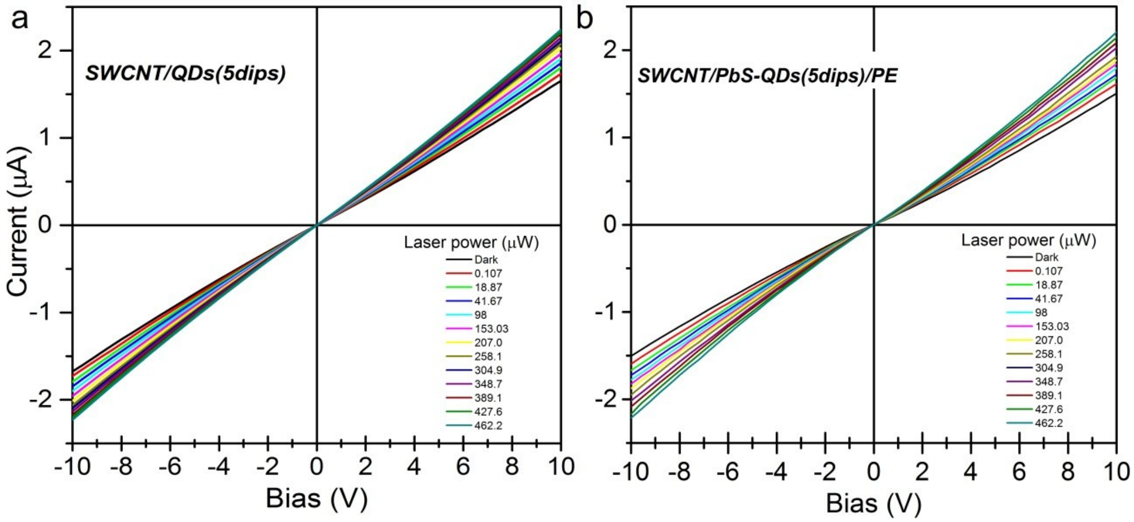

Fig. S5 Comparison of the I-V characteristics of devices made with (a) SWCNT/PbS-QDs and (b) SWCNT/PbS-QDs/PE hybrids illuminated with a 980 nm laser under different laser powers. The photocurrent generated in the two different samples is specifically from the PbS-QDs because perovskite are transparent at 980 nm. In Figure 4a in the manuscript, the photocurrent I_{ph} at each laser power is calculated as follows: $I_{ph} = I_{\text{under illumination}} – I_{\text{dark}}$. The size of PbS-QDs used in these measurements is around 3.33 nm.

After the deposition of the perovskite, we noticed a small decrease in the dark current. As we suspect that the DMF solvent is the cause of the increased resistance, we deposited a film of SWCNT in between to silver electrodes and measured its resistance before and after an addition of a DMF solvent. As expected, after the deposition of 40 µl of DMF (corresponding to the volume of perovskite solution deposited on SWCNT/PbS-QDs film) on the SWCNT film, the conductivity of the SWCNT has decreased by ~15% (see Fig. S6). This value is in agreement with the relative variation of the dark current of the SWCNT/PbS-QDs/PE device in comparison with the SWCNT/PbS-QDs device. This comparison clearly demonstrates that the lower dark current of the SWCNT/PbS-QDs/PE is due to the DMF reacting with the SWCNTs. DMF is composed of isolating molecules and these are known to be adsorbed on the surface of the nanotubes thereby impeding the electrical conductivity of the SWCNT network.

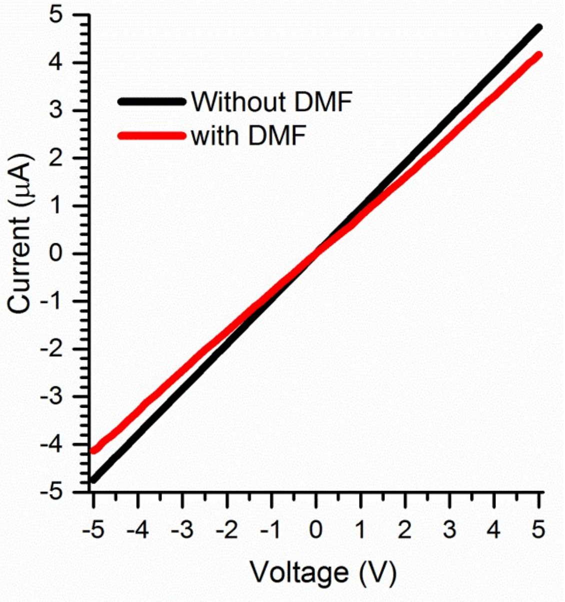

Fig. S6. I-V curves of a given SWCNT film before and after an addition of DMF, demonstrating that the lower dark current from the SWCNT/PbS-QDs/PE device is due to the DMF solvent that is used in the synthesis of the perovskite solution.

For the calculation of the detectivity, as previously shown in the revised version, we used the following formula widely used in the literature:[2, 3] $D^* = \frac{\sqrt{A}R}{\sqrt{2qI_d}}$, where A is the active area, R is the responsivity, q is the elementary charge and I_d is the dark current. Below are presented the values used in the calculation. The detectivities of our best SWCNT/PbS-QDs/PE based device are 1.4 x 10^{11} Jones and 0.9 x10^{11} at 500 nm and 1300 nm, respectively.

- At 1V and 500 nm: R = 0.48 A.W^{-1}, I_d = 0.125 x 10^{-6} A, A= 300 x 10^{-5} cm x 1.15 cm and q = 1.6 x 10^{-19} C.

- At 1 V and 1300 nm: R = 0.34 A.W^{-1}, I_d = 0.125 x 10^{-6} A, A= 300 x 10^{-5} cm x 1.15 cm and q = 1.6 x 10^{-19} C.

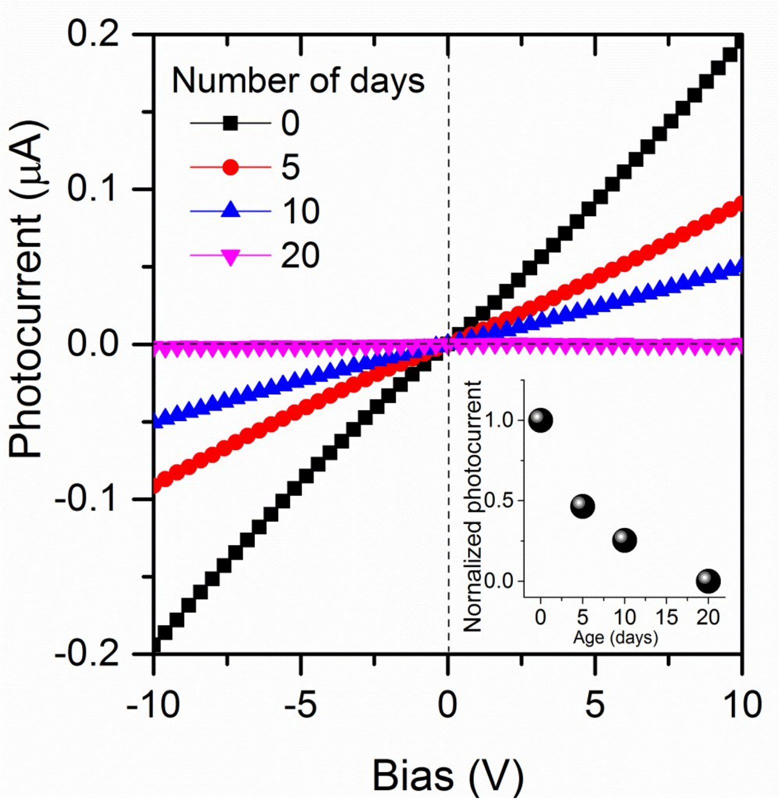

Fig. S7. Typical variation of the photocurrent over 20 days in ambient air. The bottom inset shows the normalized variation of the photocurrent**.**

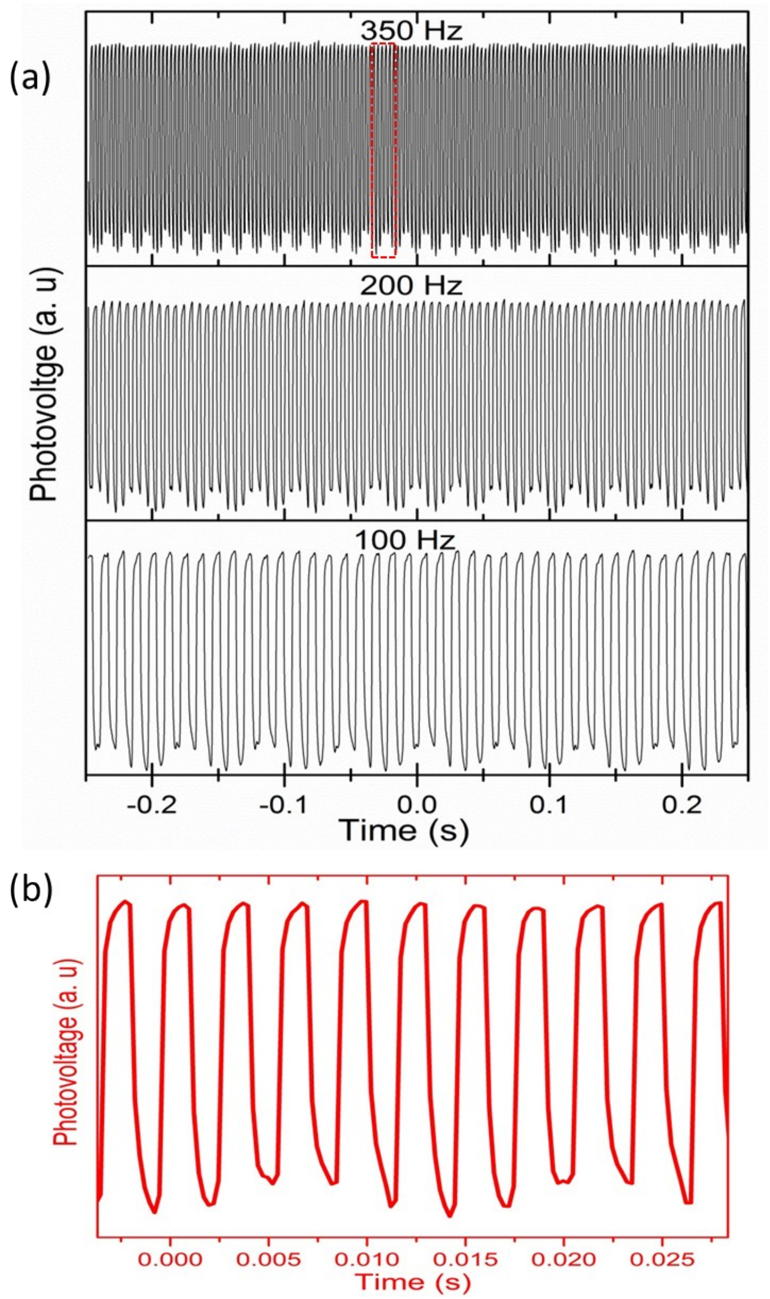

Fig. S8 a) Typical time response measurements of the NT/PbS-4.35nm/PE device measured at 2 V and under repetitive on/off cycles, using a chopper at different frequencies 100 Hz, 200 Hz and 350 Hz. The illumination was a continuous laser at 532 nm. b) Zoom-in of the red rectangle in upper of (a).

References

1. K. A. Sablon, A. Sergeev, S. Najmaei and M. Dubey, *Nanophotonics*, 2017, **6** 1263–1280.
2. J. Ding, S. Du, Z. Zuo, Y. Zhao, H. Cui and X. Zhan, *J. Phys.Chem. C*, 2017, **121**, 4917-4923.
3. L. Dou, Y. M. Yang, J. You, Z. Hong, W. H. Chang, G. Li and Y. Yang, *Nat. Comm.*, 2014, **5**, 5404.