Electronic Supplementary Information

Perovskite Quantum Dots Embedded Paper Photodetector with High Flexibility and Self-Powered Operation

Xinwei Guan,†[a] Chien-Yu Huang,†*[b] Long Hu,[b] Dharmaraj Periyanagounder,[c] Zhihao Lei,[a] Jiyun Kim,[b] Md. Zahidur Rahaman,[b] Jing-Kai Huang,[d] Prashant Kumar,[a] Chun-Ho Lin*[b]

[a]*Global Innovative Centre for Advanced Nanomaterials, School of Engineering, Faculty of Engineering and Built Environment, The University of Newcastle, Callaghan, NSW, 2308 Australia*

[b]*School of Materials Science and Engineering, University of New South Wales (UNSW), Sydney, NSW, 2052 Australia*

E-mail: chienyu.huang@unsw.edu.au; chun-ho.lin@unsw.edu.au

[c]*Department of Engineering, University of Cambridge, Cambridge CB3 0FA, United Kingdom*

[d]*Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong*

†*These authors contributed equally to this work.*

Experimental Section

Preparation of the MQDs/CNFs paper devices: CNFs solution was prepared first, in which 210 mg of CNFs were dispersed in 20 mL of anhydrous dimethylformamide (DMF) with a purity of 99.8% (obtained from Sigma). This mixture was subjected to ultrasonic agitation for a duration of 4 h to ensure thorough dispersion. Then, the perovskite solution was also prepared by dissolving equimolar quantities of MABr (98% purity, supplied by Sigma) and $PbBr_2$ (99% purity, also from Sigma) in anhydrous DMF. The concentration of each component in the solution was maintained at 0.5 M. This solution was then stirred continuously at a temperature of 90 °C for 24 hours to achieve complete dissolution. Following the preparation of both solutions, CNFs and perovskite solutions were mixed at different weight ratios (10%, 20%, and 30%). The mixed solution did not contain oleic acid and oleylamine, which is different from conventional MQD synthesis approach. The combined solution was then exposed to ultrasonic agitation for an additional 2 h to ensure uniform mixing. The resultant mixture was subsequently passed through a filter membrane (Whatman, pore size of 20 nm) employing a vacuum filtration apparatus. The material amalgamating CNFs and MQDs was collected on the membrane and subjected to drying under a continuous vacuum for 24 h, leading to the formation of the MQDs/CNFs paper. The final step involves carefully detaching the MQDs/CNFs paper from the filter membrane for further testing. For the device fabrication, Au and Pt electrodes were deposited on the MQDs/CNFs, respectively, using E-beam evaporation through a shadow mask. Note that although 5% MQDs/CNFs samples were made, they were not investigated in this study due to their weak photoresponse, attributed to the insufficient quantity of MQDs.

Ion exchange of CNFs: To execute the ion exchange, CNFs were immersed in sulfuric acid (0.01 M) for 1 h and then filtered and dried in an oven for 48 h. After drying, the sulfated CNFs can be used for paper fabrication.

Preparation of conventional MQDs for comparison study: A solution of $MAPbBr_3$ with a concentration of 0.08 M was prepared by dissolving it in 5 mL of DMF. Subsequently, 200 μL of oleic acid and 50 μL of oleylamine were added to the solution, one after the other, under intense stirring until a clear solution was obtained. Following this, the precursor solution was transferred into 10 mL of toluene, again under intense stirring. For purification purposes, this mixture was then centrifuged at 7000 rpm for 10 minutes. The supernatant was removed, and the resulting pellet was redispersed in hexane. The MQDs films on glass substrates were prepared by spin coating method at 2500 rpm for 60 s.

Experiments and characterization: The surface morphology of different MQDs/CNFs was analyzed using a Hitachi Regulus 8220 SEM. To assess the surface roughness of the MQDs/CNFs, an optical Zygo profilometer (NewView 7300) was utilized. The morphology of MQDs within the paper was examined through a Titan-CT TEM operating at 300 kV. XRD patterns for both the MQDs/CNFs and the pure CNFs were obtained using a Bruker D8 Advance diffractometer. PL spectra of the MQDs/CNFs were acquired with an Edinburgh Instruments Spectrofluorometer FS5, which is equipped with a 150 W xenon lamp and an excitation monochromator. The UV-vis absorption spectrum of the MQDs/CNFs was recorded using a Lambda 1050 spectrophotometer. XPS measurements were conducted with a Thermo Scientific ESCALAB 250Xi XPS system to analyze the binding energy. TRPL traces were examined using a Micro Time 200 (Picoquant) confocal microscope combined with TCSPC technique. The current-voltage (I–V) characteristics of the device, both in the absence of light and under AM 1.5G solar illumination, were determined using a Keithley 4200-SCS characterization system, coupled with an EverBeing CG-196-200 cryogenic probe station. The AM 1.5G can provide 1 sun solar light and a shadow mask with 1 cm x 1 cm open window was used, which allows light illumination to the entire channel of the photodetector device and was

focused on the channel center. The measurements were performed in the air under relative humidity of 60% at 20 °C.

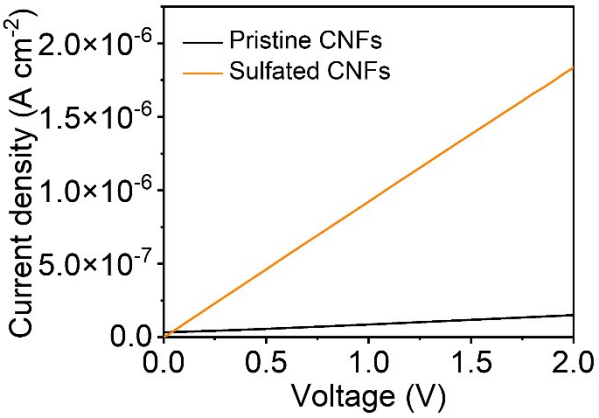

Fig. S1. Current density-voltage characteristics of pristine and sulfated CNFs papers.

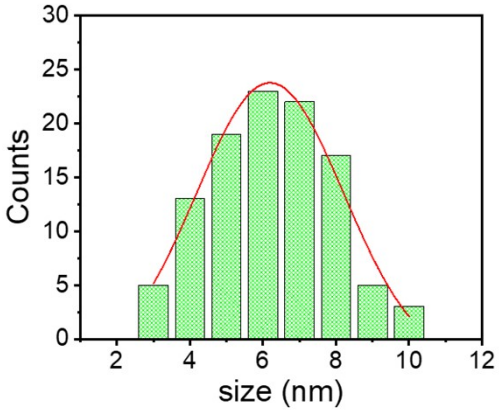

Fig. S2. MQDs size distribution (average size: 6.16 nm) synthesized by perovskite precursors and CNFs with weight ratios of 10%.

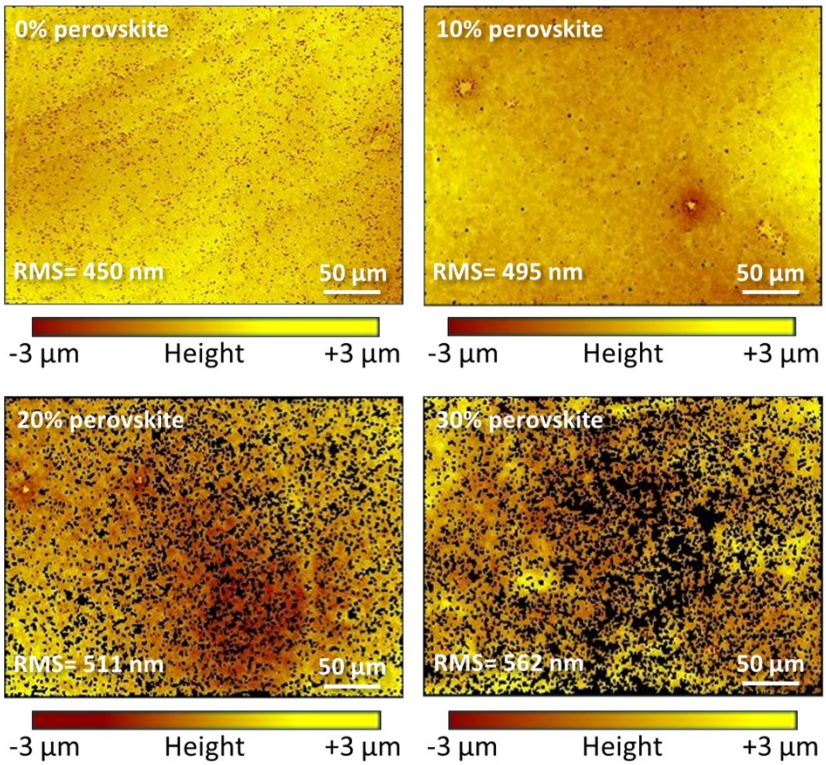

Fig. S3. Surface topography images of MQDs/CNF hybrid paper with perovskite concentration from 0% to 10%, 20%, and 30%.

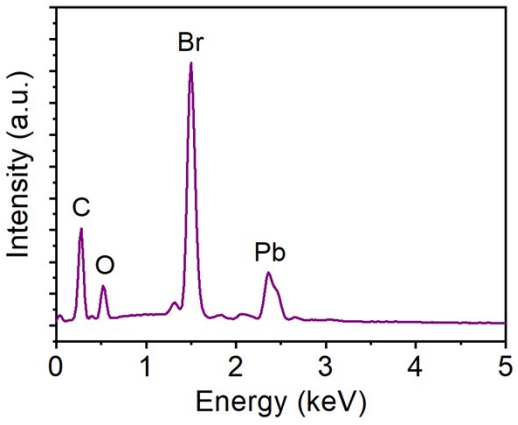

Fig. S4. SEM EDX spectrum of precipitated crystals on the surface of MQDs@30/CNF paper.

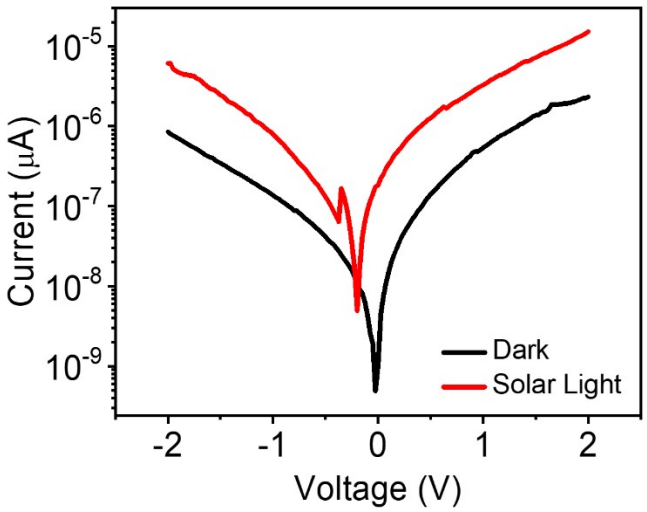

Fig. S5. Semilog plot of Au/MQDs@10/CNF/Pt under dark and solar light illumination.

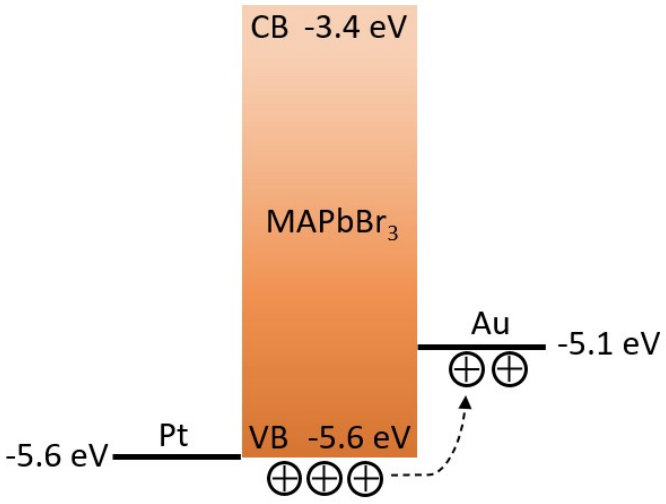

Fig. S6. Band diagram of $MAPbBr_3$-based paper photodetector contacted with Pt and Au electrodes. CB and VB represent the conduction band and valance band, respectively.

Table S1. Statistical performance of MQDs@10/CNF paper photodetector under solar illumination.

Average responsivity of a device for 20 tests	Average responsivity of 5 devices
0.0278±0.0016 (mA/W)	0.0249±0.0065 (mA/W)

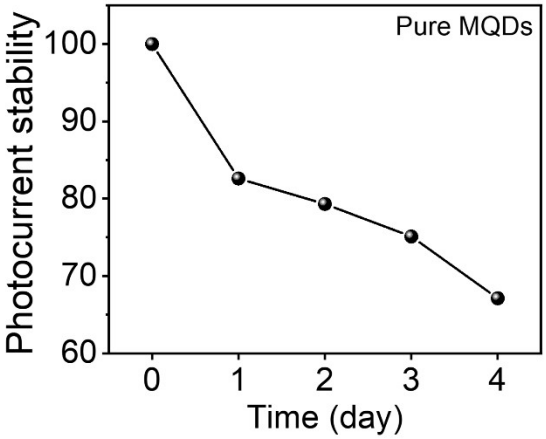

Fig. S7. Time-dependent photocurrent of pure MQDs thin film under RH of 60% at 20 °C.

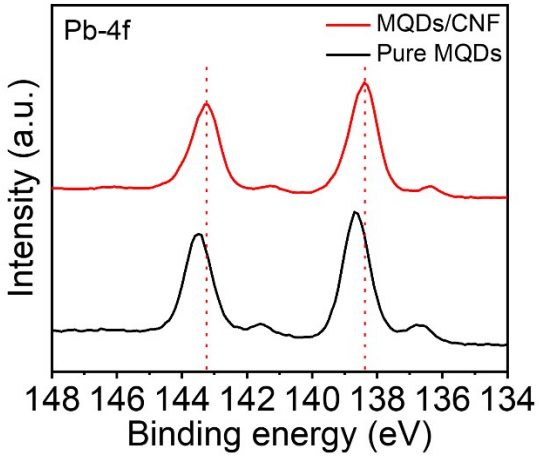

Fig. S8. XPS Pb-4f spectra of MQDs/CNF and pure MQDs for comparison.

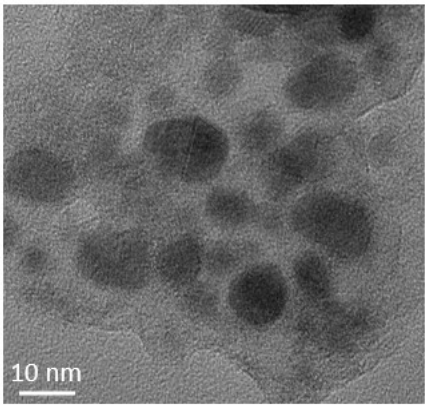

Fig. S9. TEM image of MQDs@20/CNF paper (perovskite to CNFs weight ratios: 20%). The average MQD size is calculated to be 9.31 nm.

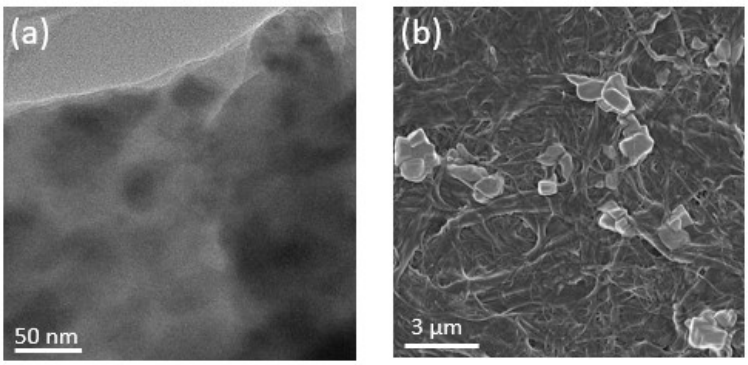

Fig. S10. (a) TEM and (b) SEM images of MQDs@30/CNF paper (perovskite to CNFs weight ratios: 30%). The perovskite grain is significantly enlarged without clear boundaries and a certain amount of large perovskite crystals appear on the paper surface.