A Comparison of the Electronic Structure of Single Crystal Hybrid and Inkjet Printed Nanocrystalline Inorganic Perovskite Films

A. J. Yost,[1*] **T. Komesu,**[1] **C. C. Ilie,**[2] **F. Guzman,**[3] **B. L. Swanson,**[2] **I. R. Evans,**[2] **P. S. Costa,**[1] **J. D. Teeter,**[4] **M. Shekhirev,**[4] **N. Benker,**[1] **S. Sikich,**[5] **A. Enders,**[6] **P. A. Dowben,**[1] **A. Sinitskii**[4]

[1] *Department Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, Nebraska, USA 68588-0299*
[2] *Department of Physics, State University of New York-Oswego, Oswego, New York, USA 13126-3599*
[3] *Department of Physics, California State University-San Bernardino, San Bernardino, California, USA 92407-2318*
[4] *Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska, USA 68588-0304*
[5] *Department of Chemistry, Doane College, Crete, NE, USA 68333*
[6] *Physikalisches Institut, Universität Bayreuth, Bayreuth, Germany*

Halide based perovskite solar cells (HPSCs) have recently drawn plenty of attention due to their low cost, extraordinary power conversion efficiency, and long carrier lifetimes and diffusion lengths. Unfortunately organic based HPSCs have a few drawbacks including being sensitive to heat, moisture, and radiation induced degradation [1]. An alternative approach is the use of inorganic based HPSC materials as a way of circumventing some of the drawbacks.

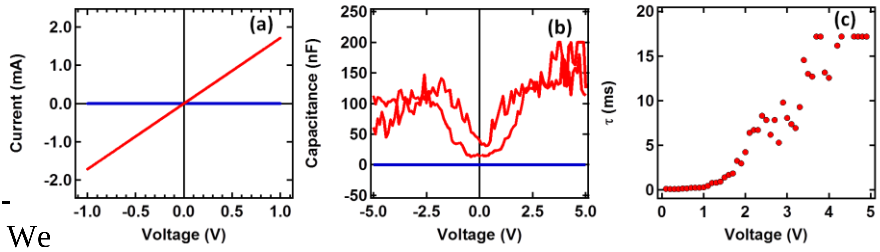

Figure 1. Transport measurements in dark (blue curve) and in light (red curve) (a) I-V (b) C-V (c) Photocarrier life time.

$CsPbBr_3$ quantum dot (QD) inks have been used in an inkjet printer to print photoactive-perovskite QD films. We discuss how these perovskite QDs differ from the single crystal hybrid perovskite $MAPbBr_3$ (MA= methyl- ammonium). The current-voltage I(V) and capacitance-voltage C(V) transport measurements indicate that the photocarrier drift lifetime, τ, can exceed 10 msec. for the $CsPbBr_3$ quantum dot printed perovskites films, as shown in Figure 1. The single crystal hybrid perovskite $MAPbBr_3$ exhibit significant mobilities, μ, leading to a significant diffusion carrier length equal to the product of $\mu\tau$ [2], but suffer from lead segregation to the surface [3]. The successful printing of photoactive-perovskite QD films of $CsPbBr_3$, indicates that the rapid prototyping of various perovskite inks and multilayers is realizable.

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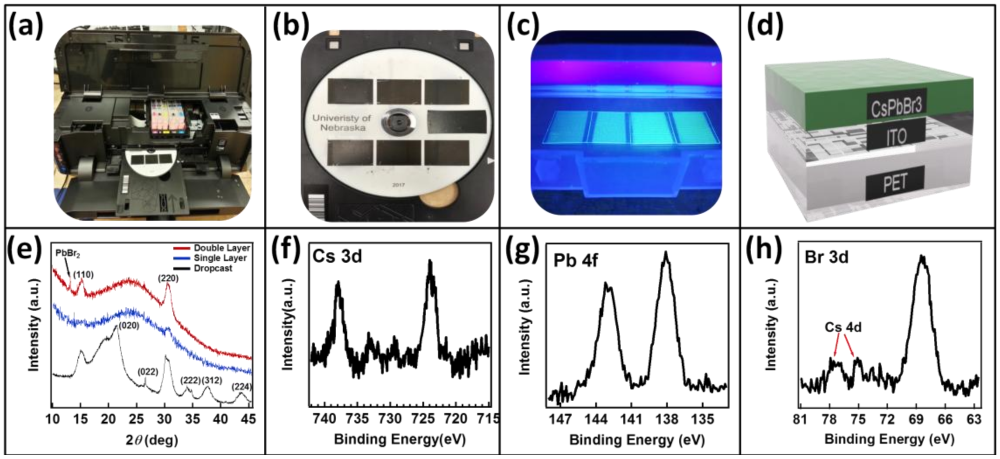
*author for correspondence: ayost3@unl.edu

Supplementary Page



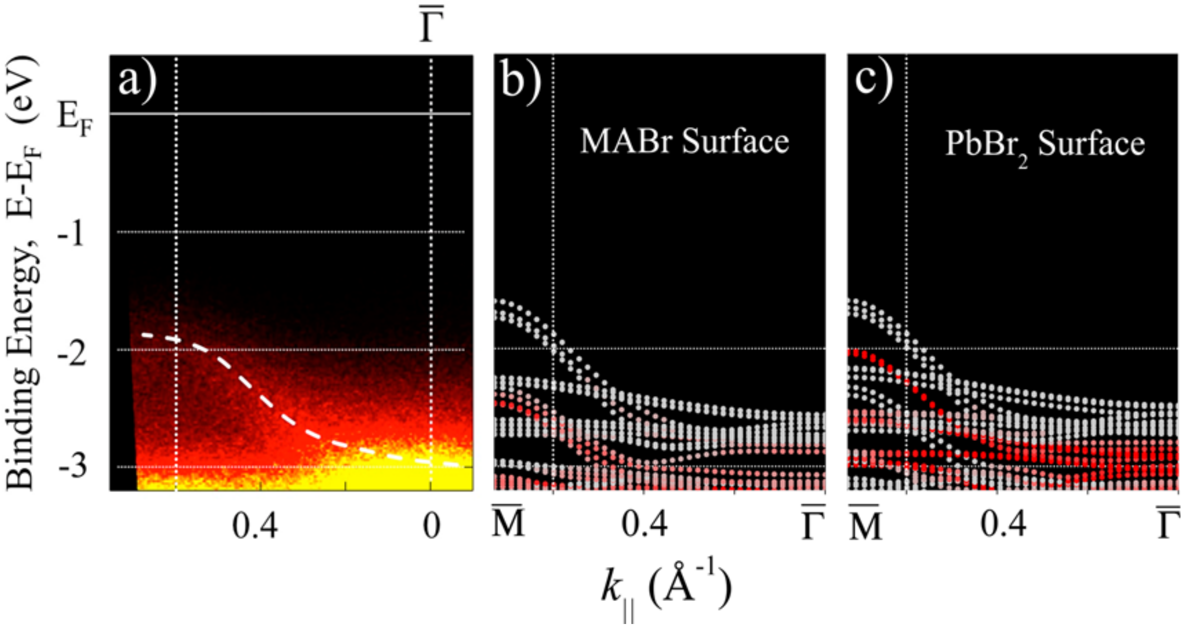
S1 (a) the inkjet printer set up with $CsPbBr_3$ inks loaded; (b) the printing template with flexible substrates in place; (c) luminescent films after printing; (d) schematic of printed device; (e) X-ray diffraction of as synthesized inks before printing (black curve), single printed layer (blue curve), and double printed layer (red curve); X-ray photoelectron spectroscopy of (f) Cs 3d core level (g) Pb 4f core level (h) Br 3d core

An inkjet printer was used to print all the inorganic halide perovskite QD thin films, as shown in S1 (a). Indium tin oxide (ITO) coated polyethylene terephthalate (PET) flexible substrates were attached to a compact disc and inserted into the inkjet printer's CD tray, as shown in S1(b) and (d). The thin films of $CsPbBr_3$ quantum dots were printed onto the substrates and checked for luminescence, as seen in S1(c). A detailed description of the $CsPbBr_3$ quantum dots inks and further characterization was reported in an earlier publication: for interested readers please see the work published by Shekhirev et al. [4]. The XRD investigation indicates that the crystalline $CsPbBr_3$ QD inks are robust, and the perovskite structure is established after the inkjet printing process. The XRD data, as seen in S1(e), indicates the as-synthesized (dropcast) $CsPbBr_3$ QD inks are in the orthorhombic room temperature phase for $CsPbBr_3$ perovskite in good agreement with reports in literature [6-8]. The bonding environments of the Cs, Pb, and Br constituents were investigated with XPS as shown in S1 (f-h). All peaks for Cs, Pb, and Br agree well with reported literature values for a $CsPbBr_3$ perovskite structure further confirming, in conjunction with XRD, the films are of high quality and experience no degradation after exposure to ambient conditions [5,7,9,10], without exhibiting the surface lead segregation of $MAPbBr_3$.

The I(V) and C(V) measurements were taken for each printed layer in dark and light conditions, as shown in Figure 1. The astonishingly high on/off ratios, greater than 1 x 10^9, are several orders of magnitude larger than the highest reported literature values to date, for solution processed $CsPbBr_3$ QDs [10,11]. As can be seen in Figure 1b, the films experience extremely low capacitance under dark conditions once again indicating a very low density of carriers, in agreement with the dark I(V) measurements. Under light illumination the zero-bias measured capacitance increases and the appearance of a significant current and capacitance, indicates that both films are photoactive. Furthermore, the roughly linear I-V characteristics under light illumination in both devices indicate that a good ohmic contact has been made. The lack of kinks and absence of hysteresis in the I(V) curves under illumination, also suggests that there is negligible ion migration present

[1,11]. This is quite different from the surface lead segregation observed with $MAPbBr_3$ which suggests the presence of ion migration [3].

The I(V) and C(V) data were used to extract an effective carrier lifetime plotted against the voltage in Figure 1(c). At low bias voltage the lifetimes die off and it is likely that deep trap states exist which act as recombination centers for non-radiative recombination of the charge carriers. At high bias voltage, the lifetimes extends to well above 10 msec., increasing until saturation occurs. The single crystals of $MAPbBr_3$, on the other hand, have fairly high mobilities of 115 cm^2/V.sec., but photocarrier lifetimes less than 1 μsec. [2]. The mobilities of the single crystal $MAPbBr_3$ is, however, consistent with the very low effective mass, evident in the band structure [3], as seen in S2.



S2 Electronic band structure of $MAPbBr_3$. (a) The experimental band structure obtained from angle resolved photoemission spectroscopy (ARPES), acquired at a photon energy of 34 eV. (b,c) The calculated band structure of a $MAPbBr_3$(001) surface with MABr surface termination (b) and $PbBr_2$ surface termination (c) along the high symmetry $\bar{M}$ to $\bar{\Gamma}$direction of the surface Brillouin Zone (SBZ). The color in (b,c) indicates contributions from the surface (red) or the bulk (light gray) to various bands [3].

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