Nanoimprinted Perovskite Micro- Nanostructures for Photovoltaics

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Perovskites (PS) have quickly emerged as a promising material for photovoltaics (PV) with 21% power conversion efficiency (PCE) in the shortest time in history of solar cells. To our best knowledge, there is no report yet on the use of nanoimprint lithography (NIL) on organic-inorganic perovskites $MAPbBr_{(3-x)}I_x$. It is not surprising that since $MAPbI_3$ is crystalline material without glass transition, it is expected to be not imprintable. On the other hand it is obvious that nanopatterning of perovskites, if it would be achieved, has a great potential to tune and improve the electronic properties via larger surface for charge collection, higher mobility, and longer life times, similar to nanoimprinted organic PV, and optical processes via better light absorption, comparable to the successes of NIL patterning for silicon PV.

Towards this end, here we report the use of nanoimprint to pattern perovskites into ordered micro and nanostructures with improved crystallinity and light absorption. Although PS are ionic solids and do not have a glass-transition behavior like polymer, it becomes "soft" enough to deform to fill in mold cavities upon applied heat and pressure (Fig. 1A), in particular with assistance from a underneath polymer hole transport layer in a "cushion" effect. SEM shows the successful NIL of $MAPbI_3$ films into nanogratings of well-defined crystalline groves and holes with no visible grain boundaries (Fig. 1C-1F). A simple hypothesis is that mechanism of deforming PS films during NIL is due to grain sliding/merging during the pressure driven squeezing flow of PS under elevated temperature into the mold cavities and fill film porosity, as shown at Fig. 1B. The initial porosity of the PS films plays a positive role, since they allow movement of PS grains under pressure (P~6 MPa) and temperature (T~100 °C). A microscopic mechanism of grains collision with formation of bigger grains, with better crystalline type can be understood in terms of sliding of small grains relative to each other and moving into openings of the mold, activated by high T and squeezing flow driven by high P. During the grain collision process, pinholes and boundaries that are associated with initial smaller grains are greatly reduced or even completely removed (Fig. 1D). Some of the broken gratings in the defect area show formation of single crystal PS sub-micron nanowires (Fig. 1E). Such freestanding or surface patterned perovskite nanowires may open up new opportunities to microlasing, nanoscale LED, photodetctors. The NIL patterns in PS (Fig 1G) also show the photonic crystal color effects, such as bright iridescence, suggesting that with proper structural design, favorable photon trapping for higher optical absorption is feasible.

We then use X-ray diffraction (XRD) to investigate crystallinity of the nanoimprinted $MAPbI_3$. The crystallite size before NIL and after NIL were determined using Rietveld refinement based on all *hkl* reflections to be 68.3 nm and 187.9 nm, respectively. The (220) reflection of before and after NIL are shown in Fig 2B. The narrower reflection in the red curve indicates the significantly increased crystallinity. For proof-of-concept, we are just able to make prototype devices using the successfully imprinted MAPbI3 films as shown in Fig. 1C on a PEDOT:PSS covered ITO glass. Fig. 3 shows the J-V curves of NIL- $MAPbI_3$ PSPV vs. flat PSPV. Clearly in first trials, the nanoimprinted PSPV shows dramatic effect of photocurrent enhancement likely due to significantly improved crystallinity. Low fill factor (FF) and low open circuit voltage V_{oc}~0.34 V are likely due to imprint defect areas of 1 cm^2 pixels, which will be mitigated in future work.

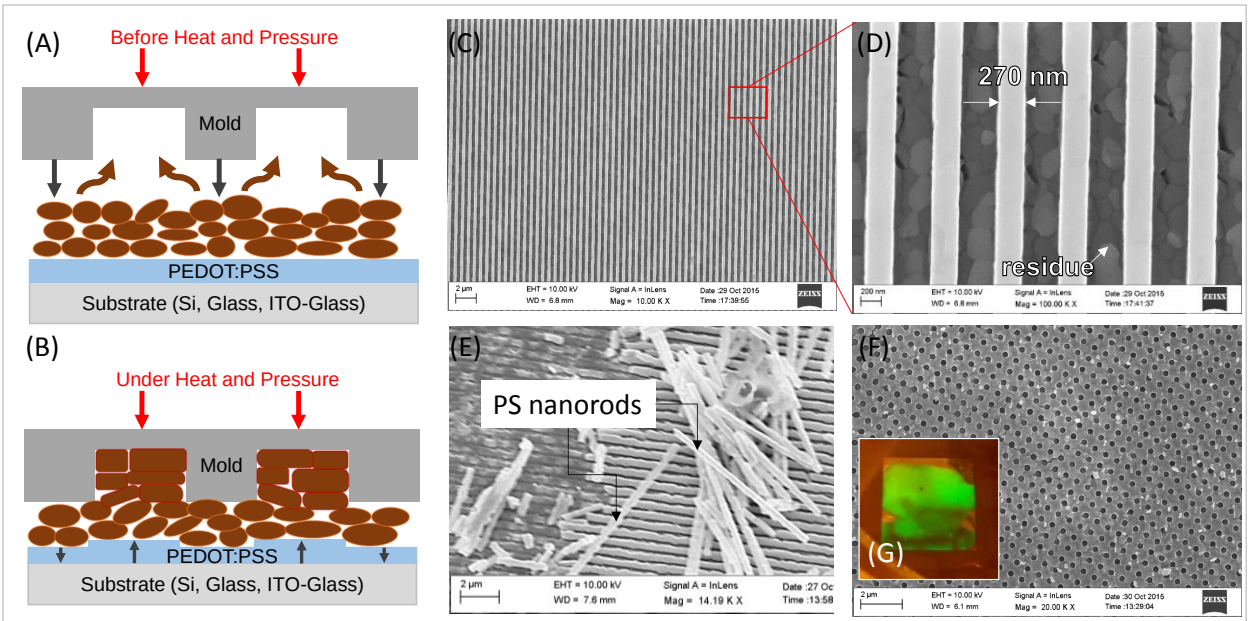

FIG 1: (A) Proposed mechanism of imprinting perovskite films (before stamping) and (B) after stamping by densification and grains agglomeration into larger crystallites. (C) Imprinted PS gratings is uniform across 90% of 1 cm^2. (D) SEM of 270 nm PS gratings show random crystallites in residue layer, while highly aligned crystallites with no visible grain boundaries. (E) Lifted freestanding PS nanorods of 8-10 µm in length, appearing to be single crystalline material induced by NIL. (F) Imprinted 300 nm periodic pores in PS film. (G) Imprinted PS nanopore sample shows clear greenish iridescence, typical for structural colors of photonic crystals.

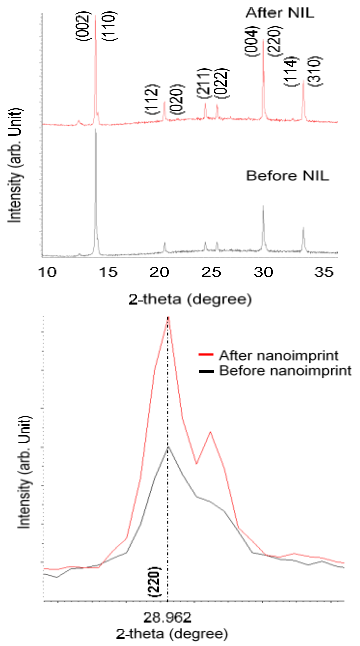

FIG 2: (A) Out of plane XRD data for $CH_3NH_3PbI_3$ on PEDOT before and after NIL using a 270 nm line and space gratings over an area of 1 cm^2. The crystallinity of PS can clearly indexed in the XRD spectrum. (B) The narrower reflection at (220) reflection of PS films indicates the increased crystallinity. (Corresponding to 28.9° in XRD spectrum).

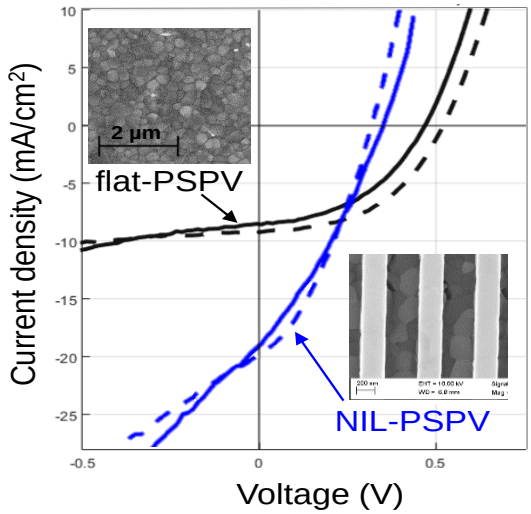

FIG 3: J-V curves of NIL- MAPbI3 PSPV vs. flat PSPV. Flat-PSPV with no groves shows reasonably high J_{sc} = 8-9 mA/cm^2, good FF, V_{oc}~0.5V. While NIL-PSPV demonstrates high J_{sc} of 18-20 mA, but low FF and low V_{oc}~0.34 V likely due to imprint defect areas of 1cm square pixels. Inset SEM shows the grain morphology of NIL and flat PS films. The >100 % increased photocurrent is a clear evidence of expected benefits of NIL patterning. What is the actual origin of such huge enhancement of Jsc is not certain yet, but likely due to greatly enhanced crystallinity as evidenced from XRD data and Figure 1E.