High-Performance Photodetectors Based on Solution-Processed Epitaxial Grown Hybrid Halide Perovskites

Li Ji,*‡,† Hsien-Yi Hsu,*‡,§,∥ Jack C. Lee,‡ Allen J. Bard,‡,* and Edward T. Yu*†

Abstract: Hybrid organic–inorganic halide perovskites (HOIPs) have recently attracted tremendous attention because of their excellent semiconducting and optoelectronic properties, which exist despite their morphology and crystallinity being far inferior to those of more mature semiconductors, such as silicon and III–V compound semiconductors. Heteroepitaxy can provide a route to achieving high-performance HOIP devices when high crystalline quality and smooth morphology are required, but work on heteroepitaxial HOIPs has not previously been reported. Here, we demonstrate epitaxial growth of methylammonium lead iodide (MAPbI₃) on single crystal KCl substrates with smooth morphology and the highest carrier recombination lifetime (~213 ns) yet reported for nonsingle crystalline MAPbI₃. Experimental Raman spectra agree well with theoretical calculations, presenting in particular a sharp peak at 290 cm⁻¹ for the torsional mode of the organic cations, a marker of orientational order and typically lacking in previous reports. Photodetectors were fabricated showing excellent performance, confirming the high quality of the epitaxial MAPbI₃ thin films. This work provides a new strategy to enhance the performance of all HOIPs-based devices.

Keywords: Perovskites, epitaxial, photodetectors, solution-processed

Hybrid organic–inorganic halide perovskites (HOIPs) have been intensively studied in recent years, because they are solution processable, require only earth-abundant elements and yield excellent semiconducting and optoelectronic properties.¹⁻¹⁷ Of particular interest have been applications in photovoltaics and optoelectronic devices with the certified efficiency of hybrid halide perovkite-based solar cells having increased from 3.8%¹⁸ to 22.1%¹⁹ in only 6 years. The theoretical limit of HOIP-based photovoltaic energy conversion efficiency has been estimated to be 31%,²⁰ which is very close to the Shockley-Queisser limit of GaAs solar cells (33%). In addition, HOIPs have shown great potential for photodetector applications.²¹⁻²³

For thin film optoelectronic devices, morphology and crystallinity are critical for obtaining high performance, as confirmed in previous studies of HOIP-based devices.¹⁵,²⁴⁻²⁸ Numerous approaches have been used to modify their film morphology and improve crystallinity, including but not limited to various postannealing methods, for example, vacuum-assist/pressure-assist/oxygen-assist/two-step annealing, optimizing precursor and Lewis acid–base adduct approaches.²⁶,²⁹⁻³² However, the morphology and crystallinity of thin film HOIPs remain far inferior to those of more mature photovoltaic materials, such as silicon and III–V compound semiconductors.

Heteroepitaxy-growth of a crystalline film atop a different substrate material surface with atomically aligned orientation is the basis for crystalline semiconductor multijunction solar cells, quantum cascade lasers, light-emitting diodes, and other optoelectronic devices in which high crystalline quality and smooth surface morphology are required. The prevailing approaches for heteroepitaxial growth generally rely on various vacuum deposition methods, such as molecular-beam epitaxy, atomic-layer epitaxy, and metal–organic vapor-phase epitaxy. However, the high cost of vacuum-based deposition techniques has driven interest in finding low cost alternatives, and growth of various heteroepitaxial films has also been demonstrated using low-cost solution-based processes.²⁵,²⁶ The compatibility of HOIPs with low cost solution-based processes suggests that this approach might enable heteroepitaxial growth of high quality HOIP thin films with substantially improved optoelectronic properties. However, no work has been reported to date on heteroepitaxial growth of HOIP thin films.

Though not sufficient, compatible crystal symmetry and lattice match are powerful factors influencing heteroepitaxial
growth. Methylammonium lead iodide (MAPbI₃), one of the most widely studied HOIPs, has a quasi-cubic (tetragonal, space group \( I\bar{4}/mcm \), \( Z = 4 \)) structure at room temperature with its quasi-cubic lattice constant being approximately 6.31 Å. Potassium chloride (KCl), a common rocksalt, has a face-centered cubic structure with lattice constant \( a = 6.29 \) Å. The lattice mismatch of MAPbI₃(110)/KCl(001) is calculated to be only 0.3% at room temperature, favorable for heteroepitaxy.

Here in this work, we demonstrate the heteroepitaxial growth of MAPbI₃ on KCl (100) with the resulting epitaxial films exhibiting excellent morphology, crystallinity, and carrier lifetime. A high-performance photodetector is fabricated to validate the high quality of these thin films.

Figure 1. Processing scheme for perovskite thin film via one-step spin coating and film morphology on various substrates (a) One-step spin-coating scheme for thin film deposition, using a 1:1 ratio (molar) of MAI and PbI₂ in DMF. (b) SEM characterization of MAPbI₃ thin films on KCl (001), KBr (001) and FTO coated-glass.

Figure 2. X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) characterization for determining crystal quality and epitaxial orientation. (a) Grazing incidence X-ray diffraction (GI-XRD) measured for MAPbI₃ on KCl (black line) and calculated spectra for tetragonal MAPbI₃ and PbI₂. (b) Rocking-curve spectra for MAPbI₃ on KCl at angle 2\( \theta \) = 28.3°. (c) Experimental measurements and simulations of pole figures from EBSD mapping for both MAPbI₃ and KCl. The simulations are obtained by gnomonic projection of MAPbI₃ (110) and/or KCl (001) on (001) and (111) planes. (d) Three-dimensional rendering of atomic arrangement for epitaxial MAPbI₃ on KCl. Colors represent the following: blue, K atom; green, Cl atom; heavy brown, I atom; light brown, Pb atom; pink, CH₃ and/or NH₃ cation groups. The inset is top view.
Figure 3. Optical properties of the perovskite films. (a) Steady-state photoluminescence (PL) spectra of MAPbI3 films on KCl at room temperature. The PL excitation wavelength was 530 nm. (b) Normalized time-resolved PL spectra taken at the peak emission wavelength of 770 nm for MAPbI3 films on KCl (green circles), on KBr (orange triangle), and on FTO glass (blue squares), respectively. Solid lines are single stretched exponential fits, with parameters listed in the inset table. Carrier lifetimes, \( \tau \), were extracted directly from the fitted curves. A pulsed laser diode (pulse duration <200 ps, fluence \(~30 \text{ nJ/cm}^2\)) at 530 nm was used as excitation source. All films were coated with PMMA to prevent degradation. (c) The measured Raman spectra of MAPbI3 on KCl (red line), on KBr and calculated spectra (black line). The laser excitation wavelength is 532 nm.

Thin Films Deposition and Characterizations. As illustrated in Figure 1a, a one-step spin-coating process is employed in which the inorganic and organic precursors are mixed in a single solution, a film is deposited by spin coating, and then annealing is used to form the appropriate crystalline phase. In general, it is challenging to form a smooth and continuous perovskite film by one-step solution coating. A noncontinuous perovskite film containing pin holes is usually obtained, and the incomplete coverage of the perovskite films typically results in poor device performance. In contrast, the approach employed here results in continuous thin films on KCl (001) substrates, as shown in Figure 1b. Furthermore, we observe highly oriented, aligned, mesh-like microstructure across the whole sample surface, suggesting that heteroepitaxial growth occurs over the entire substrate. The thickness of epitaxial films is 200–300 nm. However, for thin films on KBr for which the lattice constant is slightly larger (6.59 Å) and whose lattice mismatch with MAPbI3 is 4.4% the mesh-like microstructures seen in Figure 1b are not consistently oriented, which we attribute to nonepitaxial growth. The same occurs for thin films on amorphous FTO-coated glass, also shown in Figure 1b. For films deposited on both KBr and FTO, pin-holes and voids are present in the deposited film, as commonly seen in previous reports.35,36

To determine the crystal quality and epitaxial orientation of MAPbI3 films deposited on KCl (001), X-ray diffraction (XRD) characterizations were performed. XRD patterns were obtained to characterize the crystallinity of MAPbI3 films on KCl, as shown in Figure 2a,b. The standard symmetrical scan mode for thin films is not suitable, as the peaks from the perovskite thin films are overwhelmed by the presence of strong peaks from the KCl substrate. We therefore employed grazing incidence X-ray diffraction (GI-XRD) to limit the substrate signal. In Figure 2a, XRD patterns calculated for PbI2 (blue line) and tetragonal MAPbI3 (red line) are shown, along with the GI-XRD experimental spectra for MAPbI3 on KCl (black line). No PbI2 peaks are observed in the experimental measurement, indicating complete formation of MAPbI3 after spin-coating and annealing. The peaks calculated for the tetragonal phase of MAPbI3 and those in the measured GI-XRD experimental pattern are in excellent agreement, confirming the good crystallinity and the dominant (110) phase. The peak associated with reflection from the (211) plane, which is the characteristic peak for distinguishing between the cubic and tetragonal phases, is labeled by an asterisk.

Rocking-curve (RC) measurements, performed by fixing the detector at the center of the expected Bragg reflection and tilting the sample, are a powerful way to characterize favored growth directions and heteroepitaxial quality. Defects such as mosaicity, dislocations, or curvature lead to broadening of RC peaks. For example, the broad RC peaks observed in previous studies (MAPbI3 on TiO2) were attributed to the poor favored orientation.37 Figure 2b shows the RC measured for MAPbI3/KCl at a Bragg angle of \( 2\theta = 28.3^\circ \), corresponding to the MAPbI3 (220) and KCl (002) diffraction peak visible in the \( \theta - 2\theta \) scan in Figure 2a. There is a clear MAPbI3 (220) peak in the RC plot with full width at half-maximum (fwhm) of 0.039°, indicating high quality heteroepitaxial growth.37,38

The RC spectrum in Figure 2b provides lattice constants in the out-of-plane direction, but for characterizing heteroepitaxial growth details for the in-plane direction are also required. Cross-sectional transmission electron microscopy (CS-TEM) is typically used to visualize the lattice match and heteroepitaxy directly. However, the low thermal tolerance and instability to humidity of hybrid trihalide perovskites make CS-TEM highly challenging. Here, EBSD is used as an alternative and serves to reveal the orientation of the epitaxial layer with respect to the crystalline substrate.38 To study the relative orientation, samples for EBSD were selected with a portion of the KCl substrate left uncovered by MAPbI3. First, a backscatter Kikuchi diffraction pattern (BKD) of the exposed KCl substrate is taken simultaneously to determine their relative orientation. Because every Kikuchi pattern contains complete information about the film or crystal orientation, texture pole figures can be obtained, as shown in Figure 2c. The expected KCl (001) orientation is confirmed by comparing the measured texture pole figures with EBSD simulations. For the MAPbI3 film, the texture pole figures agree well with simulations for MAPbI3 in the (110) orientation, proving the epitaxial relationship of MAPbI3 (110) relative to the KCl substrate. As illustrated in Figure 2d, the inorganic PbI4 octahedral cage in the MAPbI3 is well matched to the KCl lattice matrix. On the basis of the expectation that Pb/Cl and K/I should form strong ionic bonds, we suggest, as shown in Figure 2b, that Pb atoms are positioned atop Cl...
atoms and I atoms atop K atoms. MA⁺ cation groups in the intermediate interface sit on Cl sites, which is expected to stabilize the interfacial structures.

Direct optical characterization of the epitaxial films provides additional evidence confirming the high film quality. Figure 3a shows the steady-state room temperature photoluminescence (PL) spectrum of a representative MAPbI₃ film on KCl, exhibiting a strong peak at 770 nm. In order to prevent degradation during measurement, all samples for optical measurements were sealed by spin-coating a layer of poly methyl methacrylate (PMMA) atop thin films. Time-resolved PL measurements, obtained at the peak emission wavelength of 770 nm with a pulsed LED laser excitation at 530 nm, are shown in Figure 3b. Both time-resolved PL decay spectra were fitted using a single stretched exponential function

\[ I(t) = I_0 + I_1 e^{-(t/\tau)\beta} \]  

(1)

where \( t \) is time, \( \tau \) is the carrier lifetime, and \( \beta \) is the stretch index. As shown in the inset table of Figure 3b, the unquenched carrier lifetime for MAPbI₃ on KCl is 213 ns, the highest reported value for nonsingle crystalline MAPbI₃ thin films. The carrier diffusion length \( L_D \) can be estimated as \( L_D = \sqrt{D\tau} \), where \( D \) is the diffusion coefficient. Using the previously reported values for \( D \) of 0.036 cm²/s for electrons and 0.022 cm²/s for holes, the calculated diffusion lengths for electrons and holes in epitaxial MAPbI₃ thin films on KCl are 875 and 684 nm, respectively, much larger than the film thickness (200–300 nm). For MAPbI₃ on FTO glass, the carrier lifetime is 14 ns, most likely due to the poor crystalline quality and surface coverage of the thin films on FTO. The stretch index is only 0.47, suggesting a large degree of disorder in the material and/or large amount of nonradiative recombination at localized trap states or surface states.

Raman spectroscopy can also serve as a powerful probe of crystal quality, bonding configuration, and local molecular vibrational modes. However, only a limited number of Raman spectroscopic studies have been reported for MAPbI₃; these generally lack sharp peaks and often suffer from significant discrepancies between experimental results and simulations, due to the high sensitivity of Raman spectra to crystal quality, bonding configuration, and local molecular vibrational modes. However, only a limited number of Raman spectroscopic studies have been reported for MAPbI₃. Both performed theoretical simulations of MAPbI₃ Raman spectra using DFT calculations, assigning a peak at 95 cm⁻¹ to the stretching of Pb–I bonds, a 151 cm⁻¹ peak to a torsional mode of the MA⁺ cations and a 300 cm⁻¹ peak to a torsional mode of the MA⁺ cations. As shown in Figure 3c, the Raman spectra of the MAPbI₃/KCl thin films in this work contain a clear peak at 91 cm⁻¹, corresponding to the vibrational modes of the inorganic PbI₆ octahedra cage. The peak at 146 cm⁻¹ is attributed to librations of the organic cations, slightly red-shifted compared to the numerically simulated value. The torsional mode, corresponding to rotation of CH₃ units against the NH₃ units along the C–N axis in the tetragonal phase, is predicted to be around 300 cm⁻¹ by Brivio et al. and Quarti et al., however, this peak was not observed in their experiments. In this work, the restricted torsional mode of the MA⁺ cations is clearly observed at 290 cm⁻¹, in agreement with their theoretical calculations. It has been suggested that the organic cation rotation in tetragonal MAPbI₃ can lower the exciton binding energy and slow carrier recombination, critical for solar photovoltaic applications. Thus, the Raman results indicate the reduced capture of carriers by nonradiative trap...
Table 1. Device Performance Comparison between Epitaxial CH$_3$NH$_3$PbI$_3$ Thin Film Photodetectors in This Work and Other Reported CH$_3$NH$_3$PbI$_3$-Based Photodetectors from Literature

<table>
<thead>
<tr>
<th>device type</th>
<th>materials/structure</th>
<th>responsivity $R$ (A W$^{-1}$)</th>
<th>detectivity $D^*$ (Jones)</th>
<th>rise time $\tau_r$ ($\mu$s)</th>
<th>voltage (V)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>photoconductors (lateral structure)</td>
<td>CH$_3$NH$_3$PbI$_3$ NW</td>
<td>13.57</td>
<td>$5.2 \times 10^{12}$</td>
<td>200</td>
<td>5</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$PbI$_3$ epitaxial thin film</td>
<td>20.7</td>
<td>$6.5 \times 10^{13}$</td>
<td>$&lt;17$</td>
<td>5</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$PbI$_3$ thin film</td>
<td>3.49</td>
<td></td>
<td>100</td>
<td>3</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$PbI$_3$ thin film</td>
<td>0.055</td>
<td></td>
<td>50</td>
<td>10</td>
<td>53</td>
</tr>
<tr>
<td>photoconductors (vertical structure)</td>
<td>CH$_3$NH$_3$PbI$_3$ NW</td>
<td>1.30</td>
<td></td>
<td>200</td>
<td>30</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$PbI$_3$ NW</td>
<td>0.005</td>
<td></td>
<td>300</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>photodiodes (three terminals)</td>
<td>TiO$_2$/CH$_3$NH$_3$PbI$_3$/SpiroOMETAD</td>
<td>0.35</td>
<td>$1.02 \times 10^{12}$</td>
<td>300</td>
<td>10</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>ITO/CH$_3$NH$_3$PbI$_3$/TPD-Si$_2$</td>
<td>4.95</td>
<td>$2 \times 10^{13}$</td>
<td>100</td>
<td>2</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$PbI$<em>3$/I$</em>{PD}$/Si</td>
<td>1.2</td>
<td>$1 \times 10^{8}$</td>
<td>3000</td>
<td>1</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$PbI$_3$/Graphene</td>
<td>1.9 $\times 10^6$</td>
<td>$2.7 \times 10^8$</td>
<td>10000</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$PbI$_3$/MoSe$_2$</td>
<td>1.9 $\times 10^6$</td>
<td>$1.3 \times 10^4$</td>
<td>600000</td>
<td>5</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>silicon diode</td>
<td>0.6</td>
<td>$1 \times 10^{13}$</td>
<td>10 ns</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

states. This result also helps to explain the long carrier lifetimes obtained in this work.

**Performance of Photodetectors.** For HOIP device studies, it is typical to fabricate a photovoltaic device for characterizing optoelectronic performance, usually employing a vertical device architecture. In this work, however, KCl is a nonconducting substrate so that a horizontal architecture must be used. Using shadow mask patterning, we fabricated photodetectors with two metal contacts deposited atop MAPbI$_3$ thin films, as illustrated in Figure 4a. To characterize the photodetector, we used a light-emitting diode operating at 520 nm as a monochromatic light source. Typical $I$–$V$ characteristics of the detectors at different illumination intensities are shown in Figure 4b. The dark current is extremely low, $\sim 0.2$ pA at 1 V bias, and the photocurrent to dark current ratio is very high: $I_{\text{light}}/I_{\text{dark}} > 1 \times 10^4$ at 20 mW/cm$^2$ and $I_{\text{light}}/I_{\text{dark}} > 1 \times 10^5$ at 2 uW/cm$^2$.

The performance of photodetectors is conventionally assessed using several figures of merit. Responsivity ($R$), which relates the generated photocurrent to a given incident power, indicates how efficiently the detector responds to an optical signal. The spectral responsivity is expressed as $R = \frac{I_{\text{light}}}{P}$, where $I_{\text{light}}$ is the photocurrent density and $P$ is incident light intensity. As shown in Figure 4c, $R$ is as high as 20.7 A/W at 5 V bias with 2 uW/cm$^2$ illumination under 520 nm. Photocductive gain, given by $G = R \times E_{\text{int}}$, which quantifies the ability to provide multiple electrical carriers per single incident photon where $E_{\text{int}}$ is the energy of the incident photon, is shown in the inset to Figure 4c. The responsivity and gain, which are very high in comparison to values in the literature for HOIPs or conventional semiconductors as shown in Table 1, are attributed to the high carrier mobility and long carrier lifetime of epitaxial film. Detectivity ($D = \frac{I_{\text{light}}}{P \times (2qI_{\text{dark}})^{1/2}}$), another important figure of merit for photodetectors, reflects the ability to detect weak optical signals. As shown in Figure 4c, the maximum detectivity is $6.5 \times 10^{13}$ Jones, the highest value yet reported for nonsingle crystalline MAPbI$_3$ thin films, leading to outstanding performance of lateral photodetectors fabricated from these films. This work demonstrates a new strategy for engineering hybrid halide perovskite-based devices, including photovoltaic, photodetectors, and light-emitting devices.

In summary, in this work we demonstrate the heteroepitaxial growth of hybrid organic–inorganic halide perovskites, which we achieve using closely lattice matched rock salt substrates. The epitaxial relationship with the substrate and high crystalline quality of MAPbI$_3$ films on KCl substrates are confirmed using X-ray diffraction, EBSD, and Raman spectroscopy. Time-resolved PL reveals carrier lifetimes that are the longest yet reported for nonsingle crystalline MAPbI$_3$ thin films, leading to outstanding performance of lateral photodetectors fabricated from these films. This work demonstrates a new strategy for engineering hybrid halide perovskite-based devices, including photovoltaic, photodetectors, and light-emitting devices.

**Methods. Material Synthesis and Characterization.** Methylamine iodide (MAI) was prepared by reacting methylamine, 33 wt % in ethanol (Sigma-Aldrich) with hydriodic acid (HI) 57 wt % in water (Sigma-Aldrich) at room temperature. After drying at 100 °C, white powder was formed, followed by overnight drying in a vacuum oven. To form the...
precursor solution, MAI and PbI$_2$ (Sigama-Aldrich) were dissolved in anhydrous N,N-dimethylformamide (DMF) at a 1:1 molar ratio. The prepared precursor was spin-coated on KCl(001) substrate at 2000 rpm in a Ar-filled glovebox. After the spin-coating, the films were annealed at 100 °C for 20 min. For photodetector fabrication, Au metal contacts were deposited directly onto perovskite thin film by e-beam evaporation through a stainless steel shadow mask. The temperature was monitored and kept under 40 °C during deposition.

A field emission scanning electron microscopy (SEM) system (Zeiss) was used to acquire SEM fl pules with the photoexcited using a laser head pulsed, providing <200 ps kV to minimize electron-induced damage. Steady-state and time-resolved PL measurements were acquired using a time-correlated single photon counting setup. Film samples were photoexcited using a laser head pulsed, providing <200 ps pulses with the fluence of ∼30 nJ/cm$^2$. The Raman measurements were performed with excitation lines of 532 nm. Laser power density was 1 mW. XRD were obtained using a double-axis high resolution X-ray diffractometer, using CuKα ($\lambda = 1.5405$ Å) radiation source. The X-ray generator was set to 40 kV and 45 mA. The EBSD patterns were obtained in a SEM (Mahwah, NJ) APEX 2 integrated EDS and EBSD system by focusing the electron beam onto the sample surface at a tilt angle of 70° with respect to the horizontal. The scanned data were post analyzed using the EDAX TSL OIM 5.0 software.

**Photodetector Characterization.** Photodetectors were characterized using a B1500A Semiconductor Device Analyzer (Agilent Technologies) and Summit 11000 AP probe station (Cascade Microtech). The monochromatic light at different wavelengths was provided by light-emitting diode (LED) illumination and the intensity was calibrated by an optical power meter (1830-C, Newport). For transient response measurement, the LED was powered by a pulse pattern generator (Agilent 8110A). Photocurrent from the photo-detectors was amplified via a low noise current preamplifier (SR570, Stanford) and the output signal was monitored by measuring voltage across a 100 ohm resistor by a digital oscilloscope (3034T, Agilent) with 50 ohm input impedance. Dark current noise was measured using a SR830 lock-in- ter (Stanford) and the output signal was monitored by

**ACKNOWLEDGMENTS**

This work was performed in part at the University of Texas Microelectronics Research Center, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (Grant ECCS-1542159). This work was partially supported by the Global Climate and Energy Project (GCEP, Agreement No. 60853646-118146). The authors acknowledge the Judson S. Swearingen Regents Chair in Engineering at the University of Texas at Austin. The authors also acknowledge financial support from the Strategic Research Grant (Grants 7004928, 6000595, 7200525, and 9680208) and SZSTI Grant (Grant R-IND12301) at City University of Hong Kong.

**REFERENCES**


The authors declare no competing financial interest.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b04445.

Details of device fabrication and characterization (PDF)

**AUTHOR INFORMATION**

*Corresponding Authors*

**E-mail:** nmgjili@utexas.edu.

**E-mail:** sam.hyhsu@cityu.edu.hk.

**E-mail:** ety@ece.utexas.edu.

**ORCID**

Li Ji: 0000-0002-2004-230X
Allen J. Bard: 0000-0002-8517-0230

**Author Contributions**

1L.J. and H.-Y.H. contributes equally.

**Notes**

The authors declare no competing financial interest.