Optimization of PbI$_2$/MAPbI$_3$ Perovskite Composites by Scanning Electrochemical Microscopy

Hsien-Yi Hsu, Li Ji, Minshu Du, Ji Zhao, Edward T. Yu, and Allen J. Bard

†Center for Electrochemistry, Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, United States
‡Microelectronics Research Center, Department of Electrical and Computer Engineering, University of Texas at Austin, Austin, Texas 78712, United States

ABSTRACT: A variety of PbI$_2$/MAPbI$_3$ perovskites were prepared and investigated by a rapid screening technique utilizing a modified scanning electrochemical microscope (SECM) in order to determine how excess PbI$_2$ affects its photoelectrochemical (PEC) properties. An optimum ratio of 2.5% PbI$_2$/MAPbI$_3$ was found to enhance photocurrent over pristine MAPbI$_3$ on a spot array electrode under irradiation. With bulk films of various PbI$_2$/MAPbI$_3$ composites prepared by a spin-coating technique of mixed precursors and a one-step annealing process, the 2.5% PbI$_2$/MAPbI$_3$ produced an increased photocurrent density compared to pristine MAPbI$_3$ for 2 mM benzoquinone (BQ) reduction at −0.4 V vs Fc/Fc+. As a result of the relatively high quantum yield of MAPbI$_3$, a time-resolved photoluminescence quenching experiment could be applied to determine electron-hole diffusion coefficients and diffusion lengths of PbI$_2$/MAPbI$_3$ composites, respectively. The diffusion coefficients combined with the exciton lifetime of the pristine 2.5% PbI$_2$/MAPbI$_3$ (τ$_{PL}$ = 103.3 ns) give the electron and hole exciton diffusion lengths, ~300 nm. Thus, the 2.5% PbI$_2$/MAPbI$_3$ led to an approximately 3.0-fold increase in the diffusion length compared to a previous report of ~100 nm for the pristine MAPbI$_3$ perovskite. We then demonstrated that the efficiency of liquid-junction solar cells for 2.5% excess PbI$_2$ of p-MAPbI$_3$ was improved from 6.0% to 7.3%.

INTRODUCTION

Organic–inorganic hybrid lead-based perovskites exhibit remarkable properties, including high absorption coefficients, long exciton lifetimes and diffusion lengths, high charge-carrier mobilities, and low exciton binding energies, and have yielded power conversion efficiencies (PCE) of ~20% in photovoltaic cells. These perovskitic cells usually are titanium dioxide (TiO$_2$) dye-sensitized solar cells (DSSC) and solid-state solar cells. In a previous paper, we described liquid junction PEC solar cells involving MAPbI$_3$ perovskites. The MAPbI$_3$ perovskites are extremely sensitive to moisture and unstable in polar solvents. However, dichloromethane (CH$_2$Cl$_2$) can be used for liquid junction PEC solar cells with reasonable stability because of its relatively higher dielectric constant and is also useful for fundamental studies. More importantly, the use of liquid electrolytes allows easy combinatorial synthesis and screening of new perovskite materials in arrays and testing the effects of various dopants on them. In this article, we describe such studies using robotic synthesis and rapid screening based on scanning electrochemical microscopy (SECM).

MAPbI$_3$ perovskites were synthesized with equimolar mixture of MAI and PbI$_2$. Dittrich et al. showed excess PbI$_2$ can be used to passivate perovskite grain boundaries and decrease carrier recombination lifetime for improving the performance of perovskite-based solar cells. Burda et al. then confirmed this passivation effect of excess PbI$_2$ by femtosecond time-resolved transient absorption spectroscopy (fs-TA) of MAPbI$_3$ perovskite films. The peak intensities of perovskite TA were used to estimate relative amounts of excess PbI$_2$ in the samples, while powder X-ray diffraction (XRD) can independently confirm the existence of excess PbI$_2$. Time-resolved transient absorption demonstrated that perovskite films with less excess PbI$_2$ displayed faster relaxation rates. These fast dynamics are assigned to charge carrier trapping at perovskite grain boundaries, and the slower dynamics in samples containing PbI$_2$ are attributed to a passivation effect. However, these studies did not show the amount of PbI$_2$ required for optimal passivation. Here, our contribution is to screen different quantitative combinations of PbI$_2$ and MAPbI$_3$ perovskites efficiently by utilizing SECM imaging.

EXPERIMENTAL SECTION

Materials. Methylamine (CH$_3$NH$_2$, 2 M in methanol, Alfa Aesar), hydroiodic acid (HI, 57 wt % in water, Alfa Aesar), lead iodide (PbI$_2$, 99.9985% metals basis, Alfa Aesar), N,N-dimethylformamide (DMF, ≥99.9%, Sigma-Aldrich), methylene chloride (CH$_2$Cl$_2$, anhydrous, ≥99.9%, Sigma-Aldrich), tetrahydrofuran (THF, anhydrous, ≥99.9%, Sigma-Aldrich), ethyl acetate (EA, anhydrous, ≥99.8%, Sigma-Aldrich), p-benzoquinone (BQ, ≥99.5%, Sigma-Aldrich), tetrabutylammonium
hexafluorophosphate (TBAPF$_6$ ≥99.9%, Sigma-Aldrich). Fluorine doped tin oxide (FTO) coated glass was obtained from Pilkington (Toledo, OH) as a substrate of the electrodes. The 15 × 15 mm squares were cleaned by successive sonication in ethanol and 2-propanol and rinsed with deionized water. Phenyl-C61-butyric acid methyl ester (PCBM; Solenne BV) and 2,2′,7,7′-tetракис(Н,Н-ди-п-метиламинофенилен)9,9′-спироби–

**Preparation of Perovskite Film.** p-MAPbI$_3$ was spin-coated on FTO glass substrates from N,N-dimethylformamide (DMF) (Alfa Aesar) solution with the mixture of MAI and PbI$_2$. The weight percent of excess PbI$_2$ to MAPbI$_3$ was increased in the order of 0%, 1%, 2.5%, 5%, 7.5%, 10%, and 15%. If MAI was synthesized by stirring 27.86 mL of methylamine (2 M in methanol, Alfa Aesar) and 30 mL of hydroiodic acid (57 wt % in water, Alfa Aesar) in 250 mL round bottomed flask in an ice bath under an argon atmosphere for 3 h. After the reaction, the solvent was evaporated using a rotary evaporator. A white powder, methylammonium iodide (MAI), was washed with diethyl ether by stirring the solution for 30 min, which was repeated three times and then finally dried at 60°C in vacuum oven for 24 h. The synthesized MAI white powder was mixed with PbI$_2$ (Alfa Aesar) in DMF at 100°C for 1 h. The top quenchers were then deposited in air via spin-coating chlorobenzene solutions with the following conditions: PCBM at 30 mg/mL spin-coated at 1000 rpm and spiro-OMeTAD at 0.46 M spin-coated at 2000 rpm.

**Preparation of Photocatalyst Spot Array Electrodes.** Spot array electrodes (an electrode composed of spots with each spot having a different composition) were fabricated using a previously reported method$^{25}$ using a CH Instruments dispenser. The precursor solutions (0.518 M in DMF) were dispensed on the FTO substrate to create the spot array electrode. This was done by moving the piezo-dispensing tip to a programmed position over the FTO substrate and dispensing drops (~100 pL/drop) of the precursor solutions. The PbI$_2$ precursor solution was dispensed first in a preprogrammed pattern onto the FTO substrate, followed by a second MAI precursor solution dispensed onto the FTO in an overlay pattern. The distance between photocatalyst spots on the array was about 150 μm with a spot diameter of approximately 350 μm. Each spot had a total of 25 drops, and the spot composition is reported as the relative number of drops of each precursor solution. In all cases, the composition of the excess PbI$_2$ was controlled from 0 to 15 wt % PbI$_2$-to-MAPbI$_3$ ratio. The prepared arrays were annealed at 100°C for 1 h in air to form the MAPbI$_3$ perovskites.

**Screening the Spot Array Electrodes.** A schematic SECM setup has been described previously.$^{25}$ Briefly, a 400 μm diameter optical fiber was connected to a 150 W xenon lamp (Oriel) and was attached to the tip holder of a CHI 900B SECM. A 420 nm long-pass filter (removing the UV portion of the spectrum) was used for visible light only illumination in rapid screening experiments. The perovskite array was used as the working electrode and was placed in the bottom of a custom designed Teflon SECM cell with an O-ring (exposed area: 1.0 cm$^2$). A Pt wire was used as the counter electrode, and a saturated Ag/AgNO$_3$ electrode was used as the reference electrode. The electrolyte consisted of 2 mM BQ and 0.1 M TBAPF$_6$ (supporting electrolyte). Light from the xenon lamp was passed through the optical fiber, positioned perpendicular to the working electrode ~200 μm above the surface, to illuminate one spot on the working electrode at a time. The optical fiber tip was scanned across the spot array electrode with a scan rate of 500 μm/s, while a potential of −0.4 V vs Ag/AgNO$_3$ was applied to the working electrode through the SECM potentiostat. Scanning over the spot arrays revealed two-dimensional images indicative of the generation of photocurrent on each spot.

**Photoelectrochemical Measurements.** The results on array electrodes were confirmed by PEC of perovskite films. The photoactivity of p-MAPbI$_3$ was measured in a photoelectrochemical cell. The films were used as working electrodes (0.27 cm$^2$) exposed to electrolyte solution and irradiation. All measurements were carried out in a borosilicate glass cell with a carbon counter electrode and Ag/AgNO$_3$ reference electrode (a silver wire immersed in 0.01 M silver nitrate in MeCN connected to the cell via a 0.10 M TBAPF$_6$ in deaerated CH$_3$Cl$_2$ salt bridge). All potentials are reported vs Fe/Fe$^+$ in deaerated CH$_3$Cl$_2$. The light source was irradiated through the electrolyte solution using full output of the Xen lamp with an incident light intensity of about 100 mW/cm$^2$. The supporting electrolyte was 0.1 M TBAPF$_6$ in deaerated CH$_3$Cl$_2$.

**Instruments.** A CH Instruments Model 760E electrochemical analyzer (Austin, TX) was used as a potentiostat for the experiments with the thin film electrodes. Illumination was with a xenon lamp (XBO 150 W, Osram) at full output for UV-visible irradiation. Glancing incidence angle X-ray diffraction (XRD) measurements were performed by using D8 ADVANCE (Bruker, Fitchburg, WI) equipped with a Cu Ka radiation source where the incident angle was 0.4°. The film thickness was measured by scanning electron microscopy (SEM, Quanta 650 FEG, FEI Company, Inc., Hillsboro, OR). In the solar cell measurements, current (I) and voltage (V) readings were taken between the working electrode and the carbon counter electrode without external power source using a Keithley Model 2400 electrometer and a xenon lamp solar simulator (Newport) equipped with an AM1.5G filter. Emission spectra were obtained by a front-face alignment on a Fluorolog-3 spectrophotometer (Jobin-Yvon) spectrophotometer. For precursor dispensing, a CH Instruments model 1550 dispenser (Austin, TX) with a piezoelectric dispensing tip (Micro Jet AB-01-60, MicroFab, Plano, TX) connected to an XYZ stage driven by a computer-controlled stepper-motor system (Newport) was used.

## RESULTS AND DISCUSSION

**SECM Scanning of Perovskite Arrays.** A method for rapid screening of semiconductor materials using a form of the modified SECM has been described previously.$^{26}$ In brief, arrays composed of ~350 μm diameter semiconductor spots with different compositions were deposited by a piezoelectric dispenser onto a conductive fluorine-doped tin oxide (FTO) substrate. The scanning tip of the modified SECM was replaced by a 300 μm fiber optic connected to a xenon lamp and was rapidly scanned over the array. This combinatorial screening technique can reduce the effort and material expended in the optimization process,$^{27,28}$ and evaluate the photocurrent response at the substrate of different elements in the semiconductor array.$^{29}$ In this study, we performed a rapid screening analysis on PbI$_2$/MAPbI$_3$ composites with a modified SECM. The arrays contained three rows and seven spots of columns. To test the reproducibility, the first and second seven-spot rows are pristine MAPbI$_3$ perovskites. The photocurrents of all 14 spots are almost the same (~5.6 ± 0.1 μA). The third seven-spot row we analyzed are spot arrays of MAPbI$_3$ perovskite blended with varying excess amounts of the PbI$_2$ precursor in compositions ranging...
from 0 to 15%. Time-resolved photoluminescence spectra on separate films at different concentrations were then monitored for the different ratios of PbI₂/MAPbI₃ composites. The SECM imaging and photoluminescence decay kinetics can yield further insight as to which factor primarily affects the resulting enhancement.

While it has been established previously that the maximum photocurrent of photovoltaic devices may be increased by introduction of PbI₂ in MAPbI₃, SECM rapid screening of PbI₂/MAPbI₃ composite materials enables determination of the optimum amount of PbI₂ in the MAPbI₃ perovskite. Employing the SECM technique, we screened spot array electrodes to determine the dependence of photocurrent response on composition of PbI₂/MAPbI₃ composites with PbI₂ content ranging from 0 to 15 wt %. The rapid screening results showed that 2.5% of excess PbI₂ to MAPbI₃ gave rise to the highest photocurrent improvement under irradiation. When the excess amounts of PbI₂ to MAPbI₃ were more than 10%, the photocurrents were lower than that of the pristine MAPbI₃. Figure 1 presents a representative example of the SECM result of a PbI₂/MAPbI₃ spot array electrode under irradiation. The color represents the measured photocurrent shown in the scale bar above the SECM image. The first and second seven-spot rows are pure MAPbI₃ perovskites. The third seven-spot row represents the amount of excess PbI₂ in each spot in the array electrode. The photocurrent shown is for 2 mM BQ reduction with 0.1 M TBAPF₆ supporting electrolytes in CH₂Cl₂ measured at an applied potential of −0.4 V vs Fc/Fc⁺.

Figure 1. SECM images for a typical photocurrent response of PbI₂/MAPbI₃ composites under irradiation. The color represents the measured photocurrent shown in the scale bar above the SECM image. The first and second seven-spot rows are pure MAPbI₃ perovskites. The third seven-spot row represents the amount of excess PbI₂ in each spot in the array electrode. The photocurrent shown is for 2 mM BQ reduction with 0.1 M TBAPF₆ supporting electrolytes in CH₂Cl₂ measured at an applied potential of −0.4 V vs Fc/Fc⁺.

Characterization and Photoelectrochemistry with Thin Bulk Film Samples. A one-step deposition and annealing process made the MAPbI₃ perovskite films. Varying the amount of excess PbI₂ in MAI solution made MAPbI₃ containing PbI₂. The compositions of PbI₂/MAPbI₃ films were characterized by X-ray diffraction (XRD). Without adding excess PbI₂ only the β-phase of the MAPbI₃ is formed (Figure 2). PbI₂ can be easily detected by the (001) and (003) reflections at 2θ = 12.56° and 39.42°, respectively. The MAPbI₃ thin-film bulk electrodes were then introduced to characterize the PEC performance in order to verify the results of the rapid SECM screening tests. We compared the PEC responses of MAPbI₃ to 2.5% PbI₂/MAPbI₃, and 15% PbI₂/MAPbI₃, for BQ reduction by linear sweep voltammetry (LSV) with chopped light under irradiation (Figure 3). In Figure 3, the LSV was conducted from +0.45 to −0.40 V vs Fc/Fc⁺ at a scan rate of 50 mV/s. While the pristine MAPbI₃ resulted in a photocurrent of ~4.1 mA/cm², the 2.5% and 15% PbI₂/MAPbI₃ samples generated a photocurrent of 6.8 and 2.0 mA/cm² for BQ reduction, respectively. These results are consistent with those of the SECM screening process illustrated in Figure 1, confirming the validity of the SECM screening technique for determining the dependence of PEC performance on PbI₂/MAPbI₃ composite composition.

Steady-State Photoluminescence and Photoluminescence Decay Dynamics. Initially the MAPbI₃ film samples were prepared including solution preparation and spin coating. The steady-state photoluminescence spectrum for perovskite films was carried out at room temperature under optical excitation with monochromatic laser light at 485 nm, displayed in Figure 4. The photoluminescence of the MAPbI₃ films showed a strong band at 770 nm with a full width at half-maximum (fwhm) of 130 nm. Photoluminescence decay dynamics can be applied to determine carrier diffusion parameters in the perovskite
films in the absence and presence of the excess PbI₂. Time-resolved photoluminescence spectra of MAPbI₃ perovskite films were then recorded by using a time-correlated single photon counting (TCSPC) system to explore the photoluminescence decay dynamics. Excitation was provided by a 485 nm pulsed laser, which provided <200 ps pulses with the fluence of ~30 nJ/cm². The thickness of the MAPbI₃ films was approximately 200 nm, which is similar to the typical thickness in photovoltaic devices. The photoluminescence decay at the wavelength of 770 nm was monitored for perovskite films deposited on FTO glass substrates, shown in Figure 5.

The photoluminescence lifetime, \( \tau_{PL} \), was determined by fitting exponential functions to the measured decay curves, as shown in Table 1. The fitting parameters \( (\tau_1, \alpha_1, \tau_2, \alpha_2) \) and corresponding errors \( (\chi^2) \) of photoluminescence decay are summarized in Table S1. For the 2.5% PbI₂/MAPbI₃, the fast decay component, \( \tau_1 \), shows a time constant of \( \tau_1 = 9.0 \) ns, likely due to bimolecular recombination;\(^{33-36} \) the long decay component \( \tau_2 \) is assigned to recombination of free carriers in the radiative channel, which matches with the previously reported photoluminescence decay in MAPbI₃ films.\(^{22,37} \) The diffusion lifetime in 2.5% PbI₂/MAPbI₃ perovskite films was extended to 103.3 ns because the passivation effect results in the reduction of free carrier recombination. The pristine MAPbI₃ film exhibits a time constant of \( \tau_{PL} = 9.10 \) ns owing to electronic defects at grain boundaries that results in a serious recombination with the relatively lower photocurrent density. In comparison with 2.5% PbI₂/MAPbI₃ perovskite films, the long decay component, \( \tau_2 \), for 5.0% and 7.5% of excess PbI₂ in MAPbI₃ film decreased slightly to 101.6 and 86.7 ns, respectively, because the PbI₂ might become one of the main phases in the perovskite films.\(^{37} \) By adding 15% of excess PbI₂ in MAPbI₃ film, lifetime shortened to a time constant of \( \tau_{PL} = 4.43 \) ns since higher amount of PbI₂ becomes an insulating layer rather than a passivating layer.

The crucial parameters for enhancing the efficiency of photovoltaic devices are the diffusion coefficient and the diffusion length, \( D \) and \( L_D \), which can be determined by photoluminescence quenching measurements.\(^{38} \) By spin-coating either an electron-accepting fullerene [phenyl-C₆H₅-butyric acid methyl ester (PCBM)] or a hole-acceptor \([2′,7′,7′′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD)]\) on top of the perovskite films, quenching samples were fabricated. For the addition of electron and hole quenchers, PCBM and Spiro-OMeTAD, the lifetimes of MAPbI₃/PCBM and MAPbI₃/Spiro-OMeTAD were decreased with time constants \( \tau_{PL} \) of 2.9 ± 0.1 and 4.0 ± 0.1 ns, respectively (Figure S1). According to a 1-D diffusion model (equation S3, described in detail in Supporting Information),\(^{32} \) we calculated total decay rate, \( k = k_e + k_w = \beta \tau_{PL}^{-1} \), by using a stretched exponential function to fit photoluminescence decay curves of perovskite films in the absence of any quenchers. The boundary condition \( n(L_D) = 0 \), where \( n = 0 \) at the glass/perovskite interface and \( L \) is the perovskite film thickness, can be obtained by assuming that all charge carriers that reach the interface are quenched. And then we estimated the electron and hole diffusion coefficients, showing 0.010 ± 0.003 and 0.008 ± 0.002 cm²/s, respectively. The electron and hole diffusion lengths \( (L_D) \) were calculated to be \( L_D (c^-) = 135 \) nm and \( L_D (h^+) = 85 \) nm by utilizing \( L_D = (D \tau_{PL})^{1/2} \), where \( \tau_{PL} \) is the lifetime in the absence of quenching, tabulated in Table 1. The long transport lengths of MAPbI₃ perovskite films are due to its crystal structure containing corner-connected PbI₆ octahedral that form a three-dimensional framework.\(^{12} \) The diffusion length \( I \) measured for the pristine MAPbI₃ is close to the typical diffusion length for the MAPbI₃ perovskite film (~100 nm).\(^{32,37} \) In comparison to pure MAPbI₃, the \( L_D (c^-) \) and \( L_D (h^+) \) of 2.5% PbI₂/MAPbI₃ composites are 321 and 287 nm, which reached about 3.0-fold longer diffusion length than the 0% PbI₂/MAPbI₃ sample. We attribute that this result, a reduction in the number of trapping sites, was due to refilling the grain boundaries in the perovskite materials.\(^{22} \) We then demonstrated that short-circuit current density for 2.5% excess PbI₂ of p-MAPbI₃ was increased from 7.8 to 9.8 mA/cm², and the efficiency of a liquid-junction solar cell was improved.

### Table 1. Fitted Decay Times (\( \tau_{PL} \)) and Diffusion Lengths (\( L_D \)) of PbI₂/MAPbI₃ Composite Perovskite Films Containing 0.0, 1.0, 2.5, 5.0, 7.5, 10, and 15 wt % of Excess PbI₂

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>( \tau_{PL} ) (ns)</th>
<th>( L_D (c^-) ) (nm)</th>
<th>( L_D (h^+) ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% PbI₂/MAPbI₃</td>
<td>9.1 ± 0.1</td>
<td>135</td>
<td>85</td>
</tr>
<tr>
<td>1% PbI₂/MAPbI₃</td>
<td>90.7 ± 0.2</td>
<td>301</td>
<td>269</td>
</tr>
<tr>
<td>2.5% PbI₂/MAPbI₃</td>
<td>103.3 ± 0.2</td>
<td>321</td>
<td>287</td>
</tr>
<tr>
<td>5.0% PbI₂/MAPbI₃</td>
<td>84.6 ± 0.1</td>
<td>291</td>
<td>260</td>
</tr>
<tr>
<td>7.5% PbI₂/MAPbI₃</td>
<td>71.3 ± 0.2</td>
<td>267</td>
<td>239</td>
</tr>
<tr>
<td>10% PbI₂/MAPbI₃</td>
<td>8.2 ± 0.1</td>
<td>91</td>
<td>81</td>
</tr>
<tr>
<td>15% PbI₂/MAPbI₃</td>
<td>4.4 ± 0.1</td>
<td>67</td>
<td>60</td>
</tr>
</tbody>
</table>

---

**Figure 4.** Steady-state photoluminescence spectrum of MAPbI₃ film under excitation at 485 nm.

**Figure 5.** Photoluminescence decay monitored at 770 nm for PbI₂/MAPbI₃ composite perovskite films containing 0.0, 1.0, 2.5, 5.0, 7.5, 10, and 15 wt % of excess PbI₂, along with stretched exponential fits. To easily compare lifetimes of all perovskite samples, \( \tau_{PL} \) are acquired with a biexponential decay function.
We demonstrated that 2.5% excess PbI$_2$ conductors on the FTO substrate. The PCE of liquid-junction solar cells was increased from 6.0% to 7.3% under irradiation with 100 mW/cm$^2$, as plotted in Figure 6.

**SUMMARY AND CONCLUSIONS**

We have used a modified SECM imaging apparatus equipped with an optical fiber as a screening tip for determining the optimum amount of excess PbI$_2$ in MAPbI$_3$-based liquid-junction PEC cells. We demonstrate that 2.5% excess PbI$_2$ of p-MAPbI$_3$ showed stronger photoresponse, higher diffusion length, and longer carrier lifetime in a photoelectrode array system containing excess PbI$_2$ in p-MAPbI$_3$ perovskite semiconductors on the FTO substrate. The PCE of liquid-junction solar cells was increased to 7.3% as a result of the passivation effect of PbI$_2$. Hence, the longer diffusion lifetime with less recombination processes leads to higher photocurrent density.

**ASSOCIATED CONTENT**

<table>
<thead>
<tr>
<th>Supporting Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07850.</td>
</tr>
<tr>
<td>Time-resolved photoluminescence, diffusion modeling, and parameters of photoluminescence decay (PDF)</td>
</tr>
</tbody>
</table>

**AUTHOR INFORMATION**

**Corresponding Author**
*E-mail: ajbard@mail.utexas.edu. Phone: +1-5124713761.

**Author Contributions**
*These authors contributed equally to this work

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge the U.S. Department of Energy SISGR (DE-FG02-09ER16119) and the Robert A. Welch Foundation (F-0021).

**REFERENCES**


21. Wang, L.; McCleese, C.; Kovalsky, A.; Zhao, Y.; Burda, C. Femtosecond Time-Resolved Transient Absorption Spectroscopy of...


