ACS Photonics

Letter

pubs.acs.org/journal/apchd5

Strong Circularly Polarized Photoluminescence from Multilayer MoS_2 Through Plasma Driven Direct-Gap Transition

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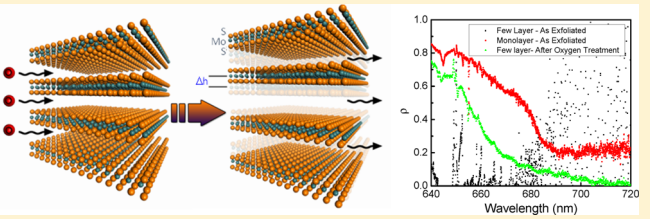
ABSTRACT: We report circularly polarized photoluminescence spectra taken from few layer MoS_2 after treatment with a remotely generated oxygen plasma. Here, the oxygen plasma decouples the individual layers in MoS_2 by perturbing the weak interlayer van der Waals forces without damaging the lattice structure. This decoupling causes a transition from an indirect to a direct band gap material, which causes a strong enhancement of the photoluminescence intensity. Furthermore, up to 80% circularly polarized photoluminescence is observed after plasma treatment of few layer MoS_2 flakes, consistent with high spin polarization of the optically excited carriers. A strong degree of polarization continues up to room temperature, further indicating that the quality of the crystal does not suffer degradation due to the oxygen plasma exposure. Our results show that the oxygen plasma treatment not only engineers the van der Waals separation in these TMDC multilayers for enhanced PL quantum yields, but also produces high quality multilayer samples for strong circularly polarized emission, which offers the benefit of layer index as an additional degree of freedom, absent in monolayer MoS_2.



KEYWORDS: *intercalation, symmetry breaking, transition metal dichalcogenides, circularly polarized photoluminescence*

While bulk transition metal dichalcogenides (TMDCs) are known to be indirect gap semiconductors, recent interest in this material system has been stimulated by the discovery of spin and pseudospin physics in atomically thin TMDCs.[1] In the monolayer limit, a direct band gap arises due to quantum confinement of electronic states,[2,3] making these materials attractive for potential optoelectronic device applications.[4−6] The crossover to a direct band gap in monolayer TMDCs is also accompanied by a breaking of inversion symmetry, which leads to several interesting physical phenomena, such as a coupling of spin and valley degrees of freedom and valley-dependent optical selection rules for interband transitions.[7] On the other hand, bilayer TMDCs show a unique interplay between spin, valley, and layer degrees of freedom. As previously described, the spin orientation in bilayer is locked to the layer index for a fixed valley.[8,9] Specifically, in the K valley, the up-spin resides primarily on one layer, and the down-spin resides primarily on the other layer. In the K′ valley, the spins are reversed. Optical probing of the spin layer locking has been achieved in bilayer WSe_2 in which the direct and indirect transitions are nearly degenerate. In MoS_2, optical measurement of these effects is harder to observe due to the indirect nature of the band gap, which dramatically reduces the photoluminescence (PL) quantum yields.

The photonic device performance of monolayer TMDCs is limited by their finite absorption (5−10% in the visible region of the electromagnetic spectrum).[10] Ideally, one would like to exploit the larger absorption cross section offered by multiple layer TMDCs while retaining the direct band gap structure and highly polarized light emission of monolayer TMDCs. The weak nature of the van der Waals coupling between individual TMDC layers opens up the possibility of perturbing these systems for band structure engineering, allowing one to create such a system ideally suited for spin-polarized optoelectronics.

Liquid phase intercalation of molybdenum disulfide with lithium ions has been shown to separate the individual layers of MoS_2.[11,12] The resulting lithium−MoS_2 complex is unstable and leads to "chemical exfoliation" of individual layers of the TMDC in solution.[13] In our previous work, we demonstrated that a low fluence of remotely generated oxygen plasma perturbs the crystal structure of few layer MoS_2, leading to a slight increase (about 1.5 Å) in interlayer separation.[14] This increased interlayer separation decouples the electronic states in the atomic layers of MoS_2, inducing an indirect-to-direct band gap transition accompanied by a huge enhancement (up to 20×) in the photoluminescence (PL) intensity. However,

Received: October 19, 2015

DOI: 10.1021/acsphotonics.5b00593
ACS Photonics XXXX, XXX, XXX−XXX

our previous study was performed using linearly polarized light, which prohibited us from exploring the layer-spin selective physics. In the work presented here, up to 80% circularly polarized photoluminescence is observed in plasma-treated, few layer MoS_2 flakes, consistent with our DFT calculations of weakly coupled TMDC multilayers.

Sample preparation begins with thin flakes of MoS_2 being mechanically exfoliated from bulk MoS_2 crystals onto a Si/SiO_2 wafer. Few layer flakes (2−6 layers) of MoS_2 are located using optical microscopy, and the layer thickness of the flakes is confirmed using PL spectroscopy, Raman spectroscopy, and atomic force microscopy (AFM). This study primarily focuses on indirect gap N-layer flakes (N between 2 and 6), which may be considered to be representative of bulk MoS_2, since the bandstructure of N-layer MoS_2 approaches that of the true bulk band structure in the limit of $N > 4$. The samples are then exposed to a stream of oxygen plasma (XEI Scientific, Inc.) for 2−3 min at a pressure of 200 mTorr. The plasma is generated from ambient air at low RF powers (20W), ensuring a low fluence of oxygen radicals. Furthermore, the sample is not placed directly between the RF electrodes for plasma generation (local plasma generation) but, instead, at a distance of about 10 cm from the plasma-generation electrodes (remote plasma generation). This remote plasma configuration ensures that the sample is not directly bombarded by ionic species being accelerated in a strong electric field. The time of exposure to plasma is somewhat important. While underexposed flakes of MoS_2 show no change in optical properties, overexposure to remote oxygen plasma does lead to damage of the MoS_2 crystal, and a drop in PL intensity, presumably due to defect creation. The optimal exposure time was found to be ∼2 min in this study. However, this time is dependent on parameters such as flake thickness, pressure in the plasma chamber, and the RF power used to generate plasma. A combination of the low RF power used and remote generation of plasma allows one to minimize any damage to the surface of MoS_2 from exposure to the oxygen plasma. Instead, as reported in our previous study, it is found that the interlayer separation in MoS_2 is increased by about 1.5 Å after exposure to oxygen plasma. Ab initio calculations showed that such an increase in interlayer separation is sufficient to cause a transition to a direct gap band structure in MoS_2.

f1 Figure 1a shows an optical microscope image of a typical exfoliated flake of MoS_2. The PL spectrum of the as-exfoliated flake, using linearly polarized 532 nm excitation, exhibits weak peaks at 1.85 and 2.05 eV, corresponding to the A and B excitonic states, split by spin orbit coupling in the valence band, as shown in Figure 1b. There is also a broad peak at 1.4 eV, which corresponds to emission from the indirect gap of this few layer MoS_2 flake. After oxygen plasma treatment, the PL emission from the A exciton (1.86 eV) is strongly enhanced (16×) with narrower line width, while the indirect band gap peak at 1.4 eV is no longer observed. All these observations imply a transition to a direct gap semiconductor. Raman spectra taken both before and after oxygen plasma treatment are shown in Figure 1c. The two observed Raman peaks correspond to the in-plane and out-of-plane vibrational modes. The separation between these two peaks is measured to be 22.5 cm^{-1}, indicating that the flake is about 3−4 layers in thickness, based on previous reports in literature.[15] This separation between the Raman peaks remains unchanged after exposure to oxygen plasma.

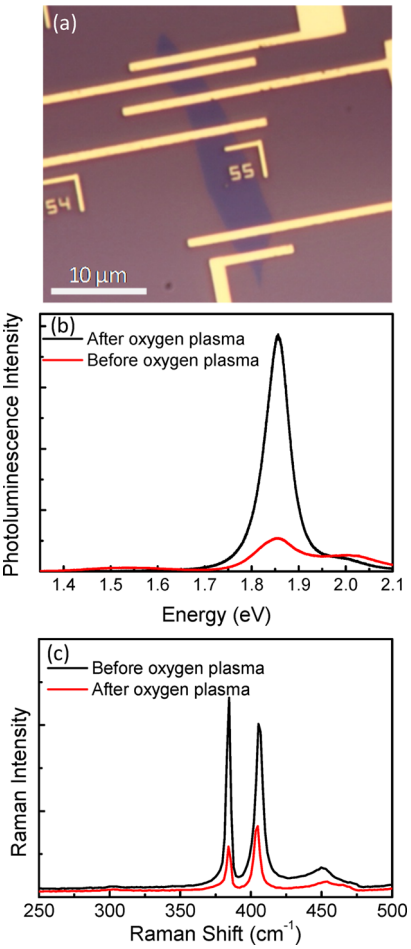


Figure 1. (a) Optical microscope image, (b) photoluminescence spectra, and (c) Raman spectra of a 3−4 layer flake of MoS_2 taken before and after the remote oxygen plasma treatment. The electrical lithographically patterned electrical contacts on the MoS_2 flake in (a) were not used in this study, which focuses on optical measurements.

We have also performed circularly polarized photoluminescence measurements on these oxygen-plasma-treated flakes of few-layer MoS_2, as shown in Figure 2. Excitation is provided by f2 a 633 nm HeNe laser at moderate laser powers (80 μW), to ensure heating effects are minimal. Figure 2 shows the normalized circularly polarized photoluminescence spectra measured at 30 K. The photoluminescence signal is strongly copolarized with either left (σ^+) or right (σ^-) circularly polarized excitation, as shown in Figure 2a,b. The sharp spectral features around 650 nm correspond to Raman peaks from the MoS_2 and the underlying silicon. These features were removed from the spectra before calculating the degree of polarization, which is given by $\rho = \frac{I^+ - I^-}{I^+ + I^-}$, where $I^{+(-)}$ is the intensity of PL emission of σ^+ (σ^-) polarization. As seen in Figure 2c, the PL emission is copolarized by up to 80% with the excitation polarization (at λ = 640 nm). In these spectra, the degree of polarization is most pronounced at shorter wavelengths (i.e., 640 nm) and tails off at lower energies due to intervalley scattering processes, consistent with previous studies on monolayer MoS_2. This is considerably higher in energy than the band gap (667 nm), but closest to the circularly polarized excitation (633 nm). The slight difference in the spectra in Figures 1 and 3 can be attributed to the differences in substrate f3 temperature, and excitation wavelength. The 633 nm excitation

DOI: 10.1021/acsphotonics.5b00593
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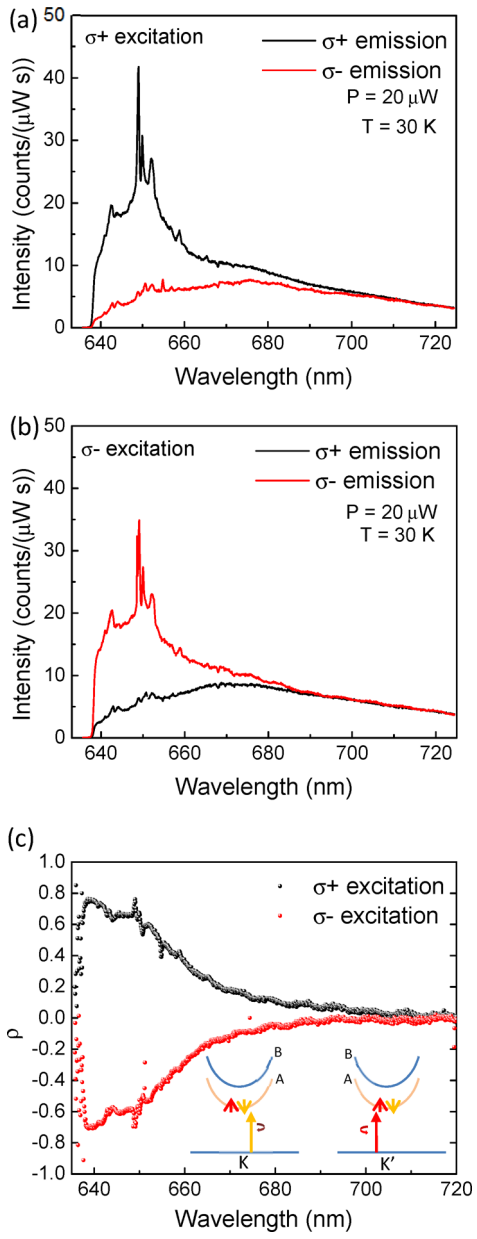

Figure 2. Circularly polarized photoluminescence spectra from an oxygen plasma treated few layer flake (3−4 layers) of MoS_2 collected at 30 K with (a) σ^+ excitation and (b) σ^- excitation. The degree of polarization, ρ, is plotted in (c). Inset shows the valley contrasted selection rules for optical transition, with strong oscillator strength, similar to the case observed for direct gap (monolayer) MoS_2.

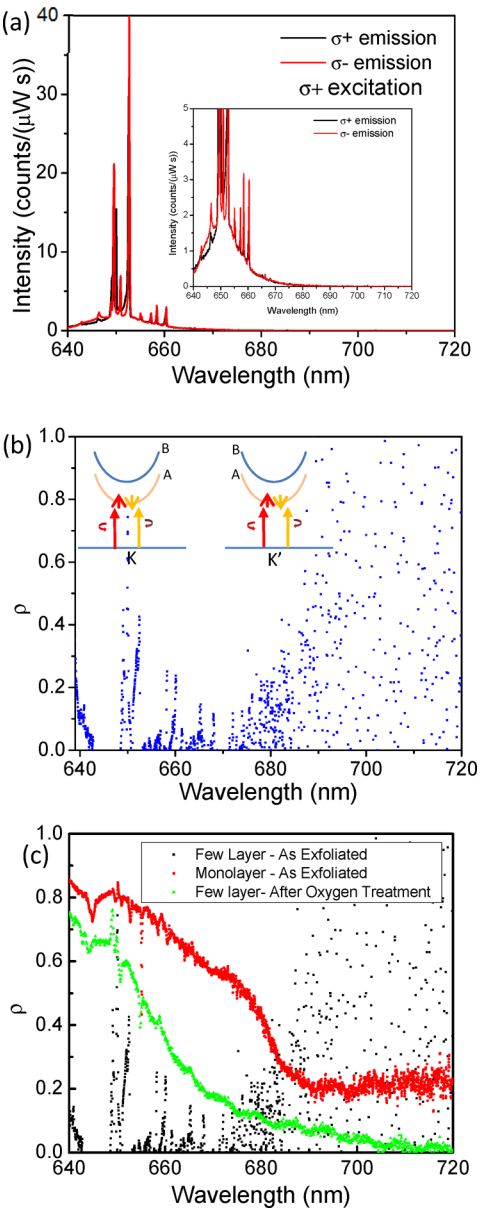

Figure 3. Circularly polarized photoluminescence spectra from a "as-exfoliated" few layer flake of MoS_2. The emission spectra, collected using σ+ excitation at 633 nm are shown in (a). The spectra for σ^+ and σ^- polarization are nearly identical, exhibiting only a weak (~10%) degree of polarization below 640 nm, shown in (b). The inset represents the absence of valley contrasted selection rules for optical transitions. The degree of polarization from few layer MoS_2 before and after plasma treatment is compared to that of pristine "as-exfoliated" monolayer MoS_2 in (c).

also uses a long pass filter with a cutoff around 640 nm, which slightly distorts the emission line shape. The large background observed in the PL spectra in Figure 2 emerges as a red-shifted shoulder peak at low temperatures and has been previously attributed to defect related sub-band gap states. In this work, we find that this background is largely unpolarized (Figure 2c), as expected for emission from subgap states. Circularly polarized photoluminescence spectra were also collected on as-exfoliated few layer MoS_2 flakes (before exposure to remote oxygen plasma), as shown in Figure 3. As expected, the PL emission from few layer flakes shows a negligible degree of polarization, even at 30 K. The lower quantum yield of PL emission in the indirect gap few layer MoS_2 leads to weaker PL signals. Thus, the degree of polarization is dominated by sharp spectra features such as the Raman peaks of MoS_2 and the underlying silicon substrate. At wavelengths longer than 680 nm, the raw spectra are dominated by the detector shot noise, leading to large fluctuations in the calculated degree of polarization, ρ.

As described above, bilayer TMDCs introduce a layer degree of freedom that couples to the spin and valley degrees of freedom. That is, in the K valley, the up-spin resides primarily in the lower layer, and the down-spin resides primarily in the upper layer. The spins are reversed in the K′ valley. The layer index is treated as a pseudospin with layer amplitudes c_L for the lower layer and c_U for the upper layer. For a given spin and

DOI: 10.1021/acsphotonics.5b00593
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valley, analysis of the low-energy, $\boldsymbol{k}\cdot\boldsymbol{p}$ Hamiltonian described in ref 7 shows that the magnitude of the layer polarization is

$$||c_U|^2 - |c_L|^2| = \lambda/\sqrt{\lambda^2 + t_p^2} \quad (1)$$

where λ is the valence band spin−orbit splitting and t_p is the interlayer coupling. This value is the same for each spin and each valley. This degree of layer polarization is also the degree of spin polarized absorption from circularly polarized light given by $\frac{|P^+_{K\uparrow}|^2 + |P^+_{K'\uparrow}|^2 - |P^+_{K\downarrow}|^2 - |P^+_{K'\downarrow}|^2}{|P^+_{K\uparrow}|^2 + |P^+_{K'\uparrow}|^2 + |P^+_{K\downarrow}|^2 + |P^+_{K'\downarrow}|^2}$, where P^+ is the interband matrix element of the canonical momentum $P_x + iP_y$ for the indicated valley and spin. Even for an unperturbed bilayer of MoS_2, the spin polarization is large. Using values of λ = 73.5 meV and t_p = 43 meV, the magnitude of the layer polarization and the spin polarization of the absorption is 0.86.

The O_2 plasma treatment increases the thickness of the sample, presumably by intercalating O_2 between the layers pushing them apart. As the layers are pushed apart, the interlayer coupling t_p is reduced, and the polarization given by eq 1 is enhanced. To understand the effect of layer separation (d) on the value of t_p in the low-energy $\boldsymbol{k}\cdot\boldsymbol{p}$ Hamiltonian, we perform density functional theory calculations as described previously, however, now we turn off the spin−orbit coupling so that the valence band splitting $\Delta K_v = 2t_p$ resulting from the interlayer coupling is not obscured by the spin−orbit coupling. Values for t_p resulting from an increase in the interlayer distance (Δd) are shown in Figure 4. At the equilibrium

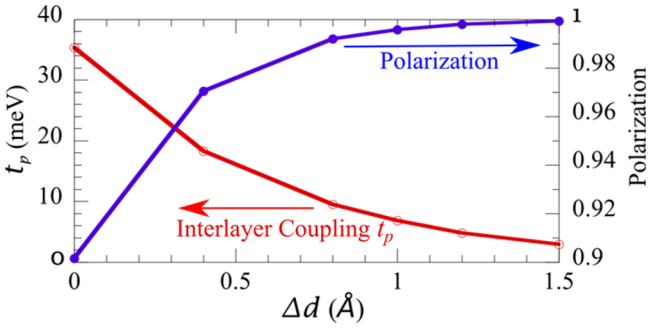

Figure 4. Calculated interlayer coupling parameter t_p and the polarization corresponding to the localization within the top or bottom layer of each spin in each valley and also the spin polarization of the excited carriers due to circularly polarized optical absorption.

position (d = 3.12 Å, Δd = 0), our value of t_p = 35.3 meV is close to the value of 43 meV from ref 3. At Δd = 1.0 Å, t_p = 4.8 meV, and the polarization is 0.998. These calculated values are in close agreement with the recent work of Liu et al.[16] Values of Δd between 1.0 to 1.5 Å are required to cause the indirect to direct transition in few layer MoS_2. Therefore, for the O_2 treated samples, we expect nearly complete spin polarization of the excited carriers. Experimentally, the degree of circularly polarized PL will rely on the spin lifetime and the radiative relaxation time of the excitons, which depends on the quality of the samples. The interpretation of these circularly polarized PL spectra using eq 1 is strictly valid in the long carrier lifetime limit, and a more rigorous model would also include any change in the carrier lifetimes brought about by exposure to remote oxygen plasma. However, intervalley scattering processes are strongly suppressed in TMDCs as they must be accompanied by a spin flip, which leads to long carrier lifetimes. Hence, only in highly defective samples is this assumption likely to be invalid, and to a first order, we expect that the change in interlayer coupling, and not a change in carrier lifetimes, plays a dominant role in the degree of polarization.

As the temperature is increased, the degree of polarization reduces due to phonon assisted intervalley scattering. However, as shown in Figure 5, a strong degree of copolarization with the

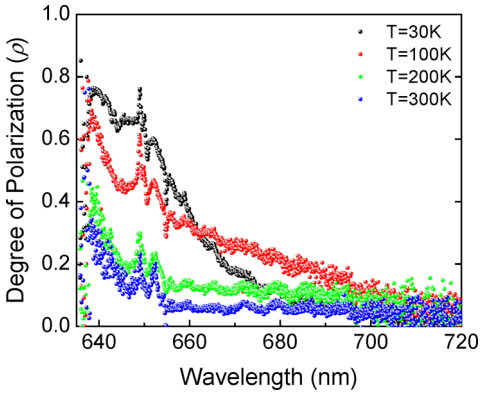

Figure 5. Temperature dependence of the degree of polarization of circularly polarized photoluminescence spectra, showing strong copolarization with the excitation up to T = 300 K.

excitation is observed up to a temperature of about 300 K, in agreement with previous reports on pristine monolayer MoS_2 samples. In highly defective samples with a high density of localized scattering sites, one would expect to see strong intervalley scattering. The measured temperature dependence of the degree of circular polarization confirms that the crystal quality of the MoS_2 is not degraded by exposure to this remote oxygen plasma. In contrast, before oxygen plasma treatment, few layer MoS_2 shows a weak degree of polarization, even at 30 K.

Optical access to the valley and spin degrees of freedom would be essential for future spintronic devices. However, the indirect gap nature and rapid relaxation of excited carriers to the Γ point in multilayers dramatically suppresses the quantum yields in the light emission from K valleys, which makes the observation of these effects challenging. Our results show that, by engineering the van der Waals separation in these TMDCs, it is possible to observe strong circularly polarized emission and absorption from multilayer MoS_2 with enhanced photoluminescence, which offers the additional benefit of layer index as an additional degree of freedom, absent in monolayer MoS_2. The transition to a direct gap semiconductor is corroborated by the large enhancement in photoluminescence quantum yield observed. Although bilayer indirect gap TMDCs such as WSe_2 and WS_2 have shown some degree of circular polarization[17] due to spin-layer-locking, previous measurements of bilayer MoS_2 show a much weaker degree of circularly polarized PL emission (~15%), due to the larger energy difference between the direct and indirect transitions. Furthermore, the quantum yield for PL emission is considerably lower in bilayer MoS_2, due to the indirect band gap. In this work, up to 80% circular polarization in the PL emission spectrum is observed for samples 3−4 layers in thickness. Also, the PL quantum yield is far stronger when compared with previous studies on multilayer MoS_2, due to the transition to a direct band gap. Other approaches to modifying the van der Waals gap, such as the application of cross-plane tensile strain could potentially also give rise to similar effects.

DOI: 10.1021/acsphotonics.5b00593
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In conclusion, we observe circularly polarized photoluminescence from few layer MoS_2 flakes after treatment with a remote oxygen plasma. These results confirm the transition from an indirect to a direct band gap material induced by plasma assisted decoupling of the electronic states in the individual layers of few layer MoS_2. An up to 20-fold enhancement of PL emission is observed due to the direct gap transition. While as-exfoliated MoS_2 exhibits only a weak degree of polarization, the PL resulting from circularly polarized excitation is 80% polarized at T = 30 K, consistent with the predictions of Liu et al. This simple and robust technique offers the possibility of creating efficient multilayer TMDC spin polarized optoelectronic devices. Multilayer molybdenum disulfide not only offers a higher absorption cross section, but is also significantly less sensitive to surface scattering phenomena. Engineering the bandstructure by plasma assisted layer decoupling gives multilayer MoS_2 the advantages of single layer MoS_2 (i.e., direct band gap) without sacrificing layer thickness.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The experimental portion of this work carried out at USC was supported by DOE Award No. DE-FG02-07ER46376. The work at UW is supported by DE-SC0012509. The theoretical and computational work was supported by the National Science Foundation (NSF) Grant No. 1307671 and FAME, one of six centers of STARnet, a Semiconductor Research Corporation program sponsored by MARCO and DARPA. The computational work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by NSF, Grant No. ACI-1053575.

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DOI: 10.1021/acsphotonics.5b00593
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