# Wavelength-Tuned Light Emission via Modifying the Band Edge Symmetry: Doped SnO<sub>2</sub> as an Example

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### **Supporting Information**

**ABSTRACT:** We report the observation of ultraviolet photoluminescence and electroluminescence in indium-doped  $SnO_2$  thin films with modified "forbidden" bandgap. With increasing indium concentration in  $SnO_2$ , dominant visible light emission evolves into the ultraviolet regime in photoluminescence. Hybrid functional first-principles calculations demonstrate that the complex of indium dopant and oxygen vacancy breaks "forbidden" band gap to form allowed transition states. Furthermore, undoped and 10% indium-doped  $SnO_2$  layers are synthesized on p-type GaN substrates to obtain  $SnO_2$ -based heterojunction light-emitting diodes. A dominant visible emission band is observed in the undoped  $SnO_2$ based heterojunction, whereas strong near-ultraviolet emission peak at 398 nm is observed in the indium-doped  $SnO_2$ -based heterojunction. Our results demonstrate an unprecedented doping-based approach toward tailoring the symmetry of band edge states and recovering ultraviolet light emission in wide-bandgap oxides.



#### 1. INTRODUCTION

Recently, exploitation of wide-bandgap transparent oxide semiconductors has attracted much attention due to their potential applications in short-wavelength optoelectronic devices, such as ultraviolet (UV) light emitting diodes (LEDs), laser diodes, and photodiodes.<sup>1–15</sup> SnO<sub>2</sub>, as one of these wide-bandgap oxides, has been extensively applied in the fields of transparent conducting thin films, catalysis, gas sensors, and so on owing to its high chemical stability as well as excellent optical and electrical properties.<sup>16–19</sup> However, bulk SnO<sub>2</sub> cannot efficiently emit UV light due to the dipoleforbidden nature of its band edge quantum states, which has hindered its potential optoelectronic applications. Most studies reported a dominant broad visible emission band centered at around 540 nm instead of the near band edge (NBE) UV emission for bulk  $SnO_2$ .<sup>20-22</sup> To recover the optical activity of SnO<sub>2</sub> corresponding to the "forbidden" bandgap, and to use it as a UV light emitter, some researchers attempted to utilize SnO<sub>2</sub> nanostructures, including nanowires and quantum dots, to modify SnO<sub>2</sub> electronic structure so that the dipole forbidden rule can be broken.<sup>17</sup> Doping in semiconductors is the most adapted method to modify the electronic structures; in particular, defects and their complexes introduced by

dopants can serve as radiative recombination centers. For example, Gao et al. have reported that Sn dopants in  $In_2O_3$  can break the dipole-forbidden rule to realize UV light emission.<sup>23</sup> However, so far there has been no report on UV light emission in doped SnO<sub>2</sub> thin films. Furthermore, no electroluminescence (EL) in the UV regime has ever been demonstrated in doped SnO<sub>2</sub> thin films.

In general, defect complexes exist in compensated semiconductors—especially donor–acceptor complexes often form due to Coulomb attraction, which significantly affects the conductivity, magnetism, and optical properties of the semiconductors.<sup>24–30</sup> Since oxygen vacancies (V<sub>O</sub>) exist as main donor defects in SnO<sub>2</sub>, we expect the formation of acceptor– V<sub>O</sub> complex if acceptor dopants are induced into SnO<sub>2</sub>.<sup>19</sup> Indium (In) is an acceptor in SnO<sub>2</sub> through substituting Sn site (In<sub>Sn</sub>) due to its chemical valence of +3 and small atom size mismatch with the Sn atom. However, so far the formation of In<sub>Sn</sub>–V<sub>O</sub> complex and its effect on electronic and optical properties of SnO<sub>2</sub> have not been explored.

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Figure 1. Characterization and prediction of structural properties of the In-doped  $SnO_2$  using XRD patterns and first-principles calculations. (a) XRD patterns of the undoped and In-doped  $SnO_2$  thin films grown on quartz substrates. (b) Enlarged region of the (101) diffraction peaks in (a). (c) Corresponding (101) diffraction peak position as a function of In concentration. (d) Lattice constants of  $SnO_2$  without and with  $V_{O}$ ,  $In_{Sn}$ ,  $In_{Sn}$ ,  $V_{O}$ , and  $2In_{Sn}$ ,  $-V_O$  defects predicated by first-principles calculations.

Here, we demonstrate the wavelength tuning of PL and EL properties of  $SnO_2$  films from the visible to the near-ultraviolet (NUV) regime via doping and electronic structure engineering. In acceptors in  $SnO_2$  can compensate for the dominant donor defects of  $V_0$  to form donor–acceptor complex, which in turn serves as radiative recombination centers. Our results indicate that such defect complexes with modified wave function symmetry play important roles in enabling the optical dipole transition and realizing the NUV light emission. Furthermore, we fabricate and demonstrate an electrically pumped LED based on In-doped  $SnO_2$  thin films.

## 2. EXPERIMENTAL AND FIRST-PRINCIPLES CALCULATIONS SECTION

The undoped and In-doped SnO<sub>2</sub> (SnO<sub>2</sub>:In) thin films were synthesized on quartz substrates using the sol-gel method. The tin chloride pentahydrate  $(SnCl_4)$  and indium chloride  $(InCl_3)$ were used as precursors for preparing the SnO<sub>2</sub>:In films. First, to prepare the sols solution, SnCl<sub>4</sub> were mixed into10 mL of ethanol and stirred using a magnetic stirrer for 1 h at 80 °C. The different amount of InCl<sub>3</sub> was also hydrolyzed in ethanol (10 mL) and stirred for 3 h. Then the two presolutions were spin-coated on clean quartz substrates. After spin-coating, the films were baked at 180 °C for 5 min. Finally, the films were annealed under an oxygen pressure of  $1 \times 10^{-3}$  mbar in a horizontal quartz-tube furnace at 900 °C for 1 h. The In concentrations in the SnO<sub>2</sub>:In films were determined to be 0, 6%, and 10% by energy dispersive X-ray spectroscopy (EDS); the samples are denoted as T0, T6, and T10, respectively. For the preparation of SnO2-based heterojunction LEDs, the undoped and 10% In-doped SnO<sub>2</sub> layers were synthesized on p-type GaN substrates, respectively, to obtain SnO<sub>2</sub>/p-GaN and SnO2:In/p-GaN heterojunction. The Ni/Au electrodes were deposited through a shadow mask on the p-type GaN layers and served as the p-type electrode. In metal was sintered on the SnO<sub>2</sub> or SnO<sub>2</sub>:In layers and served as the n-type electrode. For structural characterizations, X-ray diffraction was carried out

using a powder diffractometer with a Cu K $\alpha$  radiation. The optical absorption measurements were performed using a UV–vis–near-IR spectrophotometer. The PL measurements were performed using a He–Cd laser with a 325 nm line as the excitation source.

First-principles calculations were carried out using the VASP code with the projector augmented wave (PAW) potentials.<sup>31-34</sup> The calculations were performed using the hybrid functional as proposed by Heyd, Scuseria, and Ernzerhof (HSE).<sup>35,36</sup> For the Sn and In atoms, d states were treated as valence states. We constructed a 72-atom 2  $\times$  2  $\times$  3 SnO<sub>2</sub> supercell with the rutile structure. To simulate the SnO<sub>2</sub> with a single V<sub>O</sub> defect, an oxygen atom is removed from the supercell. For a substitution defect of In<sub>Sn</sub>, a Sn atom is replaced by an In atom. To simulate the  $In_{Sn}-V_O$  defect complex in  $SnO_{2}$ , a Sn atom is replaced by an In atom and the nearest-neighbor (NN) oxygen atom is removed. We also calculated the 2In<sub>Sn</sub>-V<sub>O</sub> configurations for completely passivating the double donor nature of V<sub>O</sub>. The cutoff energy for the plane-wave basis set is 400 eV. In the calculations, all the atoms are allowed to relax until the Hellmann-Feynman forces acting on them become less than 0.01 eV/Å. The optimized a- and c-axis lattice constants of perfect SnO<sub>2</sub> are 3.224 and 4.768 Å with a small error of 0.6% and 1.1% with respect to experimental values, respectively, indicating our calculation is reasonable and reliable. The optimized lattice constants of SnO<sub>2</sub> with various defect complex are shown in Figure 1d. Although the calculated bandgap of pure SnO<sub>2</sub> is underestimated within HSE framework (2.77 eV), i.e. smaller than the experimental value,<sup>17</sup> it does not affect our discussion on the results.

#### 3. RESULTS AND DISCUSSION

**3.1. Structural, Photoluminescent, Optical, and Electrical Properties of In-Doped SnO<sub>2</sub> Thin Films.** Figure 1a shows the XRD patterns of the undoped and In-doped SnO<sub>2</sub> thin films grown on quartz substrates. All thin films are polycrystalline with tetragonal rutile structure. No detectable

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secondary phase exists in these samples. Figure 1b shows the enlarged region of the (101) diffraction peaks. It is found that the diffraction angle decreases with increasing In concentration, indicating that the lattice constant progressively increases as In is doped into  $SnO_2$ . The (101) diffraction peak as a function of In concentration is shown in Figure 1c. The lattice expansion is attributed to the larger  $In^{3+}$  ionic size than the  $Sn^{4+}$  (0.81 Å vs 0.71 Å). It should be noted that V<sub>0</sub>, which is a main kind of defect in SnO<sub>2</sub>, leads to a decrease of lattice constant. Hence, it is necessary to check the variation of lattice constant since both In impurities and V<sub>O</sub> defects may coexist in SnO<sub>2</sub>. For this purpose, we optimized the crystal structure of In-doped SnO<sub>2</sub> with several different configurations using the first-principles calculations. These configurations include single Vo, perfect SnO<sub>2</sub>, In<sub>Sn</sub>-V<sub>O</sub>, In<sub>Sn</sub>, and 2In<sub>Sn</sub>-V<sub>O</sub> complex. The optimized aand c-axis lattice constants of SnO2 with these configurations are shown in Figure 1d. Although Vo defects coexist in SnO2, In-related impurities consistently lead to lattice expansion. This calculated result is in agreement with the XRD patterns and well supports the experimental observation of lattice expansion of SnO<sub>2</sub> after doping.

Figure 2a shows room temperature normalized PL spectra of the undoped and In-doped SnO<sub>2</sub> thin films grown on quartz



Figure 2. Room temperature PL spectra of the (a) undoped and Indoped  $SnO_2$  thin films as well as (b) p-type GaN wafer.

substrates. For the undoped SnO<sub>2</sub> thin films (T0), we observed a strong broad emission band at ~540 nm and a weak shoulder at ~440 nm in the visible region. No near band edge (NBE) emission in the UV region was observed due to the dipoleforbidden rule. In comparison, for the 6% In-doped SnO<sub>2</sub> film (T6), a dominant emission peak centered at 409 nm is observed, and the deep level emission band becomes weak. Further, for the higher In-doped SnO<sub>2</sub> film (T10), the dominant emission peak is significantly narrowed, and its center blue-shifts to 392 nm; meanwhile, the visible emission band nearly disappears. The visible emission band is attributed to the radiative recombination relevant to the deep level defects, such as  $V_0$ .<sup>19,37</sup>

In our previous work, the strong and dominant UV emission was observed in the nanocrystals/amorphous hybrid-structured SnO<sub>2</sub> films.<sup>17</sup> To determine whether the UV emission in the Indoped SnO<sub>2</sub> film is also derived from such a hybrid structure with nanocrystals imbedded in amorphous matrix, we directly examined the structural properties of the undoped and the Indoped SnO<sub>2</sub> films using transmission electron microscopy (TEM). Figure 3a-d shows the cross-sectional TEM image of the undoped and the 10% In-doped SnO<sub>2</sub> films and their corresponding magnified regions. It was clearly observed that both films are completely crystallized with nanoscale grains, differing from the previously reported case of nanocrystals in amorphous matrix.<sup>17</sup> The completely crystallization, which originates from the annealing at high temperature of 900 °C, leads to the absence of UV band edge emission in undoped  $SnO_2$  as a result of the dipole-forbidden rule. It should be noted that the TEM images show largely the same polycrystalline structure for both films. However, the UV emission was observed only in the In-doped  ${\rm SnO}_2$  film, which unambiguously suggests that the breakdown of the dipole-forbidden rule in the doped films should be attributed to the In doping, not the nanoscale grains. Furthermore, the In atoms substituting the Sn sites in SnO<sub>2</sub> are acceptor dopants. Taking a large amount of donor defects of  $V_{\rm O}$  in  ${\rm SnO}_2$  into consideration, the In acceptors will compensate for the Vo donors to form acceptordonor complexes, i.e.,  $In_{Sn}{-}V_O$  or  $2In_{Sn}{-}V_O$  complex. Such high-concentration complexes likely lead to the formation of impurity band in the energy gap and serve as radiative recombination centers. Therefore, it can be speculated that the acceptor-donor complex related impurity band is responsible for recovering the UV emission in doped SnO2. In addition, this scenario can explain the fact that the intensity of the visible emission band decreases with increasing In concentration due to the compensation effect of the acceptor impurities regarding to the donor defects.

The optical bandgap generally will narrow if a large amount of donor-acceptor pair complexes constitute a passivated impurity band in the bandgap. To check the dependence of In concentration on optical bandgap, optical absorption spectra of undoped and In-doped SnO<sub>2</sub> films were carried out. Figure 4 shows the optical absorption spectra of In-doped SnO<sub>2</sub> with various In concentrations. The narrowing of bandgap with increasing In concentration was observed. Furthermore, using the relation  $\alpha(h\nu) \propto (h\nu - E_{\rm g})^{1/2}$ , the optical bandgaps  $E_{\rm g}$  of the films were evaluated to be 3.75, 3.66, and 3.40 eV, respectively. The bandgap as a function of In concentration is shown in the inset of Figure 4. The narrowing of bandgap as In doped into SnO<sub>2</sub> indicates that the transition of electrons is relevant to the defect states of In doping. Therefore, the defect states relevant to In impurities play a key role in breaking the dipole-forbidden rule.

Electrical transport properties of undoped and In-doped  $\text{SnO}_2$  thin films were measured, and the data are listed in Table 1. The undoped  $\text{SnO}_2$  film shows an n-type conduction with resistivity and concentration of 32.4  $\Omega$ -cm and  $1.7 \times 10^{17}$  cm<sup>-3</sup>, respectively. As the In concentration increases, the resistivity/ electron concentration significantly increases/decreases, suggesting a result of compensation of the intrinsic V<sub>O</sub> donors by the In acceptors. The variations of the electrical properties further support our speculation on the formation of donor–acceptor complex in In-doped SnO<sub>2</sub>.

3.2. Physical Mechanism of Breaking Dipole-Forbidden Rule in In-Doped SnO<sub>2</sub>. To better understand the role



Figure 3. Cross-section TEM images of the (a, b) undoped and (c, d) 10% In-doped SnO<sub>2</sub> films. (b) and (d) are the corresponding magnified images marked in (a) and (c), respectively.



Figure 4. Optical absorption spectra of the undoped and In-doped  $SnO_2$  thin films grown on quartz substrates. The inset shows the optical bandgap as a function of In concentration.

Table 1. Electrical Properties of Undoped and In-Doped  $SnO_2$  Thin Films

sample no.	resistivity ( $\Omega$ ·cm)	carrier concentration (cm <sup>-3</sup> )	$\begin{array}{c} \text{mobility} \\ (\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \end{array}$	carrier type
Т0	32.4	$1.7 \times 10^{17}$	1.7	n
T6	$2.0 \times 10^{2}$	$4.5 \times 10^{16}$	0.7	n
T10	$5.2 \times 10^{2}$	$2.4 \times 10^{16}$	0.5	n

of donor-acceptor complex in recovering UV emission, we performed first-principles calculations. We constructed two 72atom 2 × 2 × 3 rutile SnO<sub>2</sub> supercells with In<sub>Sn</sub>-V<sub>O</sub> and 2In<sub>Sn</sub>-V<sub>O</sub> complexes, respectively. The calculation details are described in section 2. We first checked the stability of the complexes in SnO<sub>2</sub>. The binding energies of In<sub>Sn</sub>-V<sub>O</sub> and 2In<sub>Sn</sub>-V<sub>O</sub> and 2In<sub>Sn</sub>-V<sub>O</sub> complexes in SnO<sub>2</sub> can be expressed as  $E_b(In_{Sn}-V_O) = E_{tot}(In_{Sn}-V_O) + E_{tot}(SnO_2) - E_{tot}(In_{Sn}) - E_{tot}(V_O)$  and  $E_b(2In_{Sn}-V_O) = E_{tot}(2In_{Sn}-V_O) + 2E_{tot}(SnO_2) - 2E_{tot}(In_{Sn}) - E_{tot}(In_{Sn}) -$   $E_{\rm tot}(V_{\rm O})$ , respectively, where  $E_{\rm tot}$  is the total energies of the system calculated with the same supercell.<sup>38,39</sup> A negative  $E_{\rm b}$  indicates that the complex tends to bind to each other. The calculated binding energy  $E_{\rm b}$  for the  $\ln_{\rm Sn}-V_{\rm O}$  and  $2\ln_{\rm Sn}-V_{\rm O}$  complexes are -1.7 and -3.8 eV, respectively, indicating that both complexes are stable with respect to the isolated In dopant and  $V_{\rm O}$  defect. More importantly, the  $2\ln_{\rm Sn}-V_{\rm O}$  complex has a much lower energy than the  $\ln_{\rm Sn}-V_{\rm O}$  complex. Thus, the  $2\ln_{\rm Sn}-V_{\rm O}$  complex is more stable and may have a high concentration in the In-doped SnO<sub>2</sub>. In addition, the calculated absorption spectrum of SnO<sub>2</sub> with the  $\ln_{\rm Sn}-V_{\rm O}$  complex is inconsistent with the experimental absorption spectrum (Figure S1, Supporting Information),<sup>40</sup> indicating its insignificant population in the doped thin films.

Figures 5a and 5b show the energy band structures of the  $SnO_2$  systems without and with the  $2In_{Sn}-V_O$  complex, respectively. The calculated fundamental bandgaps of the  $SnO_2$  systems are 2.77 and 2.34 eV for without and with  $2In_{Sn}$ - $\mathrm{V}_{\mathrm{O}}$  complex, respectively, indicating narrowing of fundamental bandgap as In<sub>Sn</sub> compensating V<sub>O</sub>. To better understand the transition between conduction band and valence band, polarized optical absorption spectra of the SnO<sub>2</sub> without and with the  $2In_{Sn}-V_{O}$  complex were calculated, as shown in Figure 5c. For the perfect  $SnO_2$ , the onset of the polarized (denoted as  $\alpha_{zz}$  and  $\alpha_{xx}$  in Figure 5c) optical absorption edge is much higher than the fundamental bandgap, indicating that the band edge transition is forbidden in perfect SnO<sub>2</sub>. For the SnO<sub>2</sub> with the 2In<sub>Sn</sub>-V<sub>O</sub> complex, the polarized optical absorption edge moves down and the transition between CBM and VBM is allowed, in agreement with the results of the optical absorption spectra and PL spectra. The corresponding (110) plane contour plots of partial charge density mapping of CBM and VBM, as shown in Figure 5d,e, further confirm that the  $2In_{Sn}$ -V<sub>O</sub> complex is likely responsible for the band edge transition and bandgap narrowing.

**3.3. Ultraviolet Light Emission from In-Doped SnO<sub>2</sub> Heterojunction LED.** To exploit the UV luminescence

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**Figure 5.** First-principles calculated energy band structures of a 72-atom SnO<sub>2</sub> supercell (a) without and (b) with the  $2In_{Sn}-V_O$  complex within the hybrid functional method. (c) The corresponding polarized optical absorption spectra, denoted as  $\alpha_{zz}$  and  $\alpha_{xx}$ . The (110) plane contour plots of the partial charge density on the (d) CBM and (e) VBM of the SnO<sub>2</sub> with the  $2In_{Sn}-V_O$  complex.

property of the In-doped SnO<sub>2</sub> thin films in the field of UV light emission, we fabricated In-doped SnO<sub>2</sub> heterojunction LEDs and carried out EL experiments. For this purpose, we synthesized undoped and 10% In-doped SnO<sub>2</sub> thin films on p-type GaN substrates to fabricate two SnO<sub>2</sub>-based heterojunction LEDs: SnO<sub>2</sub>/p-GaN and SnO<sub>2</sub>:In/p-GaN heterojunctions. To unambiguously determine the origin of UV emission in the heterojunctions, we chose the p-type GaN wafer whose PL emission peaks are not overlapped with the UV emission peaks of the SnO<sub>2</sub>:In films. The PL spectrum of the p-type GaN wafer, as shown in Figure 2b, shows an emission band centered at 440 nm, different from the PL spectra of the SnO<sub>2</sub> films.

We first performed the measurement of I-V characteristics for both SnO<sub>2</sub>-based LEDs. Figure 6 shows the I-V curves of the SnO<sub>2</sub>/p-GaN and the SnO<sub>2</sub>:In/p-GaN heterojunctions. Although both devices show large values of series resistance under the forward bias, a rectification behavior was clearly observed. The large series resistance can be derived from (i) high resistivity of the SnO<sub>2</sub> layers, (ii) SnO<sub>2</sub>/GaN junction resistance, and (iii) contact resistance from electrodes. Most likely, this large series resistance has more than one origin. The SnO<sub>2</sub>:In/p-GaN heterojunctions shows a larger series resistance than the SnO<sub>2</sub>/p-GaN heterojunction, which is due to the higher resistivity of the In-doped SnO<sub>2</sub> layer. In a previous report, Yang et al. also observed the I-V characteristics with a large series resistance in SnO<sub>2</sub> nanowires/p-GaN heterojunction LEDs.<sup>41</sup>



**Figure 6.** Room temperature I-V characteristics of the SnO<sub>2</sub>/p-GaN and SnO<sub>2</sub>:In/p-GaN heterojunction LEDs.

Figure 7a,b shows the room temperature EL spectra of the  $SnO_2/p$ -GaN and  $SnO_2$ :In/p-GaN heterojunction LEDs under various forward excitation currents. For both junctions, the EL intensity gradually enhances with increasing excitation current. The EL spectra of the  $SnO_2/p$ -GaN heterojunction exhibit a broad luminescence band centered at 547 nm in the visible regions, which is in good agreement with the result in the PL spectrum of the undoped  $SnO_2$  film. It indicates that the visible



**Figure 7.** Room temperature EL spectra of the (a)  $\text{SnO}_2/\text{p-GaN}$  and (b)  $\text{SnO}_2:\text{In/p-GaN}$  heterojunction LEDs under various forward excitation currents. The insets in (a) and (b) show the photographs of both LEDs biased under forward currents.

emission is derived from the SnO<sub>2</sub> layer. Additionally, a weak 449 nm emission peak was also observed. Its possible origin is ascribed to the SnO<sub>2</sub> layer or the p-type GaN wafer because the PL spectra of both show the emission peaks at 440 nm. The photograph of the SnO<sub>2</sub>/p-GaN LED under a forward bias captures the bright yellow-green light, as shown in the inset of Figure 7a. For the SnO<sub>2</sub>:In/p-GaN heterojunction, there is a dominant NUV emission peak at 398 nm and a weak one at 449 nm, as shown in Figure 7b. The result is significantly different from the SnO<sub>2</sub>/p-GaN heterojunction. Through comparing with the PL spectra of the SnO<sub>2</sub>:In and the p-type GaN samples, we can conclude that the NUV emission peak and the weak one are derived from the SnO<sub>2</sub>:In layer and the ptype GaN layer, respectively. The inset of Figure 7b shows the photograph of the SnO2:In/p-GaN LED under a forward current, where blue-violet light was clearly observed in the junction region. Therefore, In doping plays a key role in realizing UV EL based on SnO<sub>2</sub>.

#### 4. CONCLUSION

Unlike the nanostructure-engineered  $SnO_2$  where the surface states play an important role in breaking the dipole forbidden rule, the emergence of NUV emission observed in our In-doped  $SnO_2$  thin films is not a result of structural modification, but accomplished through the doping route. Our results demonstrate that by doping In to form defect complexes with the donor Vo defects, the nature of the "forbidden" gap is modified, which effectively tuned the light emission from the visible to the NUV regime. Furthermore, as we demonstrated here, a NUV LED based on In-doped  $SnO_2$  thin film was fabricated, which may find potential applications in the future display and solid-state lighting devices.

### ASSOCIATED CONTENT

#### Supporting Information

Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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