



Structural and optoelectronic properties of hybrid bulk-heterojunction materials based on conjugated small molecules and mesostructured TiO2

Hung Phan, Justin P. Jahnke, Bradley F. Chmelka, and Thuc-Quyen Nguyen

Citation: Applied Physics Letters **104**, 233305 (2014); doi: 10.1063/1.4883001 View online: http://dx.doi.org/10.1063/1.4883001 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/104/23?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

MgO-hybridized TiO2 interfacial layers assisting efficiency enhancement of solid-state dye-sensitized solar cells Appl. Phys. Lett. **104**, 063303 (2014); 10.1063/1.4864319

Self-powered solid-state photodetector based on TiO2 nanorod/spiro-MeOTAD heterojunction Appl. Phys. Lett. **103**, 261109 (2013); 10.1063/1.4858390

Structurally stabilized mesoporous TiO2 nanofibres for efficient dye-sensitized solar cells APL Mat. **1**, 032106 (2013); 10.1063/1.4820425

Synthesis and pore filling mechanism in anatase TiO2 nanostructured network mediated by PbS molecular adsorption J. Appl. Phys. **109**, 094904 (2011); 10.1063/1.3583648

Structural and electronic properties of pentacene-fullerene heterojunctions J. Appl. Phys. **104**, 114518 (2008); 10.1063/1.3040003



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 128.111.83.184 On: Sat, 21 Jun 2014 19:01:19



Structural and optoelectronic properties of hybrid bulk-heterojunction materials based on conjugated small molecules and mesostructured TiO₂

Hung Phan,¹ Justin P. Jahnke,² Bradley F. Chmelka,² and Thuc-Quyen Nguyen^{1,3,a)} ¹Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, USA ²Department of Chemical Engineering, University of California, Santa Barbara, California 93106, USA ³Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

(Received 31 March 2014; accepted 1 June 2014; published online 11 June 2014)

Improved hybrid bulk-heterojunction materials was fabricated by spin-casting a benchmark conjugated small molecule, namely, 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP(TBFu)₂), into mesostructured TiO₂. Due to both a reduced molecular size and less hydrophobic nature of the conjugated molecules (relative to conjugated polymers), homogeneous and improved infiltration into the mesoporous TiO₂ are achieved without the need for pre-treatment of the TiO₂. Remarkably, this small molecule can realize loadings of up to 25% of the total pore volume— $2.5 \times$ the typical loadings achieved for conjugated polymers. The small molecule loading was determined using dynamic secondary ion mass spectroscopy and absorption spectroscopy. Further characterization such as charge transfer and nanoscale conducting atomic force microscopy helps to demonstrate the promise and viability of small molecule donors for hybrid optoelectronic devices. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4883001]

Hybrid systems comprising of organic semiconductors (OSCs) and wide band-gap inorganic nanocrystals (i.e., ZnO, TiO_2) have great potentials for both scientific studies and the creation of practical optoelectronic materials. Among different inorganic materials, TiO2 has been intensively studied in hybrid devices since early 1990s.^{1–5} TiO₂ is an attractive material, due to its environmental stability, low-cost, and non-toxic properties. For most π -conjugated OSC, the electron affinity (\sim 3.0–4.0 eV) is less than that of TiO₂ (~4.2 eV). Therefore, photoexcited electrons through π - π^2 transition of OSC are thermodynamically allowed to transfer to the conduction band of TiO_2 , leaving holes in the OSC. The photoinduced charge transfer at the interface of TiO₂-organic hybrid materials enables it to be applicable in photo-sensing devices, such as photoconductors and photovoltaics. Upon charge transfer, electrons and holes transport in TiO₂ and organic material, respectively, then being collected at electrodes. There are three critical factors affecting the performance of such hybrid TiO₂-OSC devices: photon absorption, charge separation, and charge transport. Mesoporous TiO₂ has been utilized efficiently in different devices, especially in dye-sensitized solar cells (DSSCs),⁶ due to its high interfacial area for efficient charge separation. It should be noted that DSSC employs a third material as the hole transporter while dyes are used for light absorbing only. In another type of mesoporous TiO₂ hybrid devices, a single organic component is loaded into mesopores for both functions: absorbing light and conducting holes.^{5,7} In that case, high loading of OSC is desired to absorb more light and result in more photogenerated carriers. In addition, the organic domain, which is presumably the mesopore domain, should be continuous for hole transport and small enough

 $(\sim 5-20 \text{ nm})^{5,8}$ for excitons created in OSC to diffuse to the interface and undergo charge separation.

Conjugated polymers (CPs) are the most widely studied materials to combine with mesoporous TiO₂ due to their high absorption coefficients and hole mobilities.⁴ In the TiO₂-conjugated polymer (TiO₂-CP) hybrid system, difficulty arises in gaining efficient infiltration into the pores using viscous polymer solutions that contain long polymer chains.^{9,10} Additionally, the hydrophilic nature of TiO_2 repels the hydrophobic CPs, leading to reduced polymer loadings and inefficient charge transfer from photo-excited conjugated polymers to TiO₂.¹¹ For example, it has been shown that the low loading of CPs in TiO₂-CP hybrid solar cells (HSCs) results in low short circuit current.^{12,13} Numerous efforts have been made to improve the loading and charge transfer of polymers to mesoporous TiO₂. One approach involves treating the surface of TiO₂ with interfacial modifiers, such as common dyes^{9,11,14,15} used in DSSCs or carboxylated oligothiophene derivatives,^{7,15} thus making it more energetically compatible with conjugated polymers. Using this method, charge transfer to the TiO₂ can be enhanced drastically.^{7,11,15} Even still, the infiltration of conjugated polymers into mesoporous TiO₂ is still challenging since the majority of loadings reported in literature without further surface treatment of TiO_2 is less than 10%.^{9,10}

We proposed an improved hybrid system comprises mesostructured TiO_2 and small conjugated molecules (SMs). First, mesostructured TiO_2 has high surface area and continuous mesopores for efficient charge separation and charge transport. In addition, its well-defined structure provides an appealing platform for both theoretical predictions and then experimental validation of the performance of HSCs.¹⁶ Second, SMs may be able to achieve higher loadings into mesoporous TiO_2 , compared to conjugated polymers, due to their smaller size, resulting in less viscous solutions and

^{a)}Author to whom correspondence should be addressed. Electronic mail: quyen@chem.ucsb.edu

facile diffusion into the mesopores. In addition, incorporation of heteroatoms like oxygen and nitrogen in the backbone of SMs makes them more hydrophilic than most conjugated polymers. This is expected to yield improved loadings and more efficient charge transfer to the hydrophilic TiO₂ network.¹⁷ To test our hypothesis, we used a benzofuran substituted diketopyrrolopyrrole, DPP(TBFu)₂,¹⁸ as a model small molecule; owing to its relatively low molecular weight and the presence of oxygen atoms in the benzofuran units, which makes it relatively more hydrophilic. DPP(TBFu)₂ has already achieved PCEs of around 5% using conventional bulk-heterojunction (BHJ) device architectures that use a fullerene derivative as the acceptor.¹⁸ In addition, it has been extensively characterized to understand the nanoscale morphology and optoelectronic properties of BHJ solar cells.^{18,19} In this study, we show that the hybrid TiO₂-small molecule system is a promising candidate for optoelectronic devices.

Mesostructured TiO₂ films were prepared following a method developed by Frey and coworkers and applied in polymer HSCs.^{20–22} The mesostructured TiO_2 films were prepared from a solution of THF in concentrated HCl (12.1 M) containing the TiO₂ precursor, tetraethylorthotitanate, and the triblock copolymer PluronicTM F127.²⁰ The films were spin-cast from solution onto glass or patterned indium-tin-oxide (ITO) substrates. Subsequently, the films were dried for several days and then calcined in air at 350 °C for 12h to introduce porosity. Small-angle X-ray scattering (SAXS) was used to confirm the presence of mesostructural order before and after calcination and the resulting patterns are shown in Figure 1. In both cases, a single reflection was observed at a 2θ angle of 0.7° , corresponding to a *d*-spacing of 12.5 nm, a value consistent with the cubic phase reported in the literature.²⁰ The lack of framework contraction upon calcination is likely due to the low temperature of the calcination. Porosimetry data of mesostructured TiO₂ film were also collected, and the films were found to have a surface area of 170 m²/g with a void fraction of 0.43 (Figure S1).²³ The calcined, spin-coated films were found to have thickness

of ca. 400 nm, as measured by profilometry and secondary ion mass spectrometry (SIMS). After calcination, a 10 mg/mlsolution of DPP(TBFu)₂ dissolved in chloroform was then spin-coated onto the TiO₂ film. The hybrid film was then annealed at $130 \,^{\circ}$ C before characterizations.

Dynamic SIMS was used to characterize the infiltration depth and uniformity of DPP(TBFu)₂ within the mesostructured TiO₂ films. Elemental fragments of the film are ejected from the sputtering of the sample by primary ion beam; and detected by a mass spectrometer as a function of time. The depth-profiling traces of different m/z fragments are shown in Figure 2. The m/z at 12, 26, 29, and 64 represent C, CN+C₂H₂, Si, and TiO, respectively (hereafter ¹²C, ²⁶CN, 29 Si, and 64 TiO). The 12 C and 26 CN signals are attributed to DPP(TBFu)₂ in the hybrid film while 64 TiO arises from the mesostructured TiO₂, and ²⁹Si is from glass substrate. It is clear that the relative counts from ¹²C, ²⁶CN, and ⁶⁴TiO remain constant until the interface with glass substrate is reached, at which point the ²⁹Si count significantly increases. This demonstrates that DPP(TBFu)₂ was infiltrated uniformly (within the sensitivity of the measurement) throughout the mesostructured TiO₂ film. This is a significant improvement compared to polymers, which usually efficiently infiltrate only after surface-modification of TiO2.9,10 As a result, all of the surface area of the mesostructured TiO_2 is expected to be available to form heterojunctions with DPP(TBFu)₂, which is vital for charge separation.

A high loading of DPP(TBFu)₂ is as important as achieving uniform and deep infiltration because DPP(TBFu)₂ is the only visible-light absorber in this hybrid structure. We quantify the loading of DPP(TBFu)₂ in mesoporous TiO₂ by means of film absorption and SIMS. In the absorption method, the loading of DPP(TBFu)₂ was estimated to be around 25% of total TiO₂ pore volume, by comparing the optical density at maximum absorption wavelength of hybrid TiO₂-DPP(TBFu)₂ film to that of a series of known-thickness neat DPP(TBFu)₂ films (Figure S2).²³ In the other method, we drop-casted the small molecule solution on mesostructured TiO2 film and characterized it by SIMS. Drop-casting results in a neat small molecule layer formed on top of hybrid layer. By comparing the ¹²C



FIG. 1. SAXS patterns of mesostructured TiO_2 film (a) before and (b) after calcinations.



FIG. 2. SIMS traces of a hybrid TiO_2 -DPP(TBFu)₂ spin-coat film. The arrow indicates the approximate film thickness up to the interface determined by profilometry after the SIMS measurements.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 128 111 83 184 On: Sat 21 Jun 2014 19:01:19



FIG. 3. Steady-state photoluminescence and transient photoluminescence (the inset) of neat DPP(TBFu)₂ and hybrid TiO_2 -DPP(TBFu)₂.

intensity from the top neat DPP(TBFu)₂ layer and the hybrid layer, we estimated the loading of DPP(TBFu)₂ to be around 29% of the total TiO₂ pore volume (Figure S3).²³ The higher loading of DPP(TBFu)₂ in the drop-cast film relative to the spin-cast film is likely, because drop-casting allows the molecules to infiltrate into the mesopores for a longer time compared to the spin-cast film. This is a notable result, given that the loading of polymer reported in literature without further surface treatment of TiO₂ is less than 10%.^{9,10} This validates our hypothesis that less hydrophobic small molecules in low viscosity solutions can be more easily introduced into hydrophilic mesoporous TiO₂ films and with significantly higher loadings than polymeric molecules.

Having established the excellent infiltration and loading of DPP(TBFu)₂ into mesostructured TiO₂, we now consider optical and electrical characterization of the hybrid TiO_2 -DPP(TBFu)₂ film. First, the absorption spectra of neat $DPP(TBFu)_2$ and hybrid films are comparable (Figure S4),²³ suggesting that there is no chemical change of DPP(TBFu)₂ in the hybrid film. Steady-state and transient photoluminescence (PL) quenching were then used to probe the efficiency of charge transfer from DPP(TBFu)₂ to TiO₂ in the hybrid system, as these techniques have been widely used to establish the electron transfer from photo-excited conjugated polymer moieties to TiO₂.^{24,25} The steady-state PL of neat DPP(TBFu)₂ film and hybrid DPP(TBFu)₂ film of comparable optical density are shown in Figure 3. The PL quenching efficiency of DPP(TBFu)₂ by TiO₂ was estimated, from both the steady-state and transient PL, to be around 70%, reflecting efficient electron transfer from excited state DPP(TBFu)₂ to TiO₂. Transient PL of neat DPP(TBFu)₂ (inset of Figure 3) exhibited monoexponentially decaying intensity with a lifetime of 1.0 ns. By comparison, analogous measurements of transient PL intensity for a hybrid TiO₂-DPP(TBFu)₂ film decayed biexponentially with two lifetimes of 230 ps and 1.0 ns. The former lifetime may reflect the excitons formed within their diffusion lengths near TiO₂ interface that are quenched immediately by electron transfer to TiO₂. The latter lifetime corresponds to the excitons formed further away from TiO₂, which decayed in local environments that are similar to those in neat DPP(TBFu)2. The PL quenching can likely be improved by adsorption of interfacial modifiers onto the TiO₂ surface, as has been demonstrated for other hybrid TiO₂-conjugated polymer materials.^{7,9,11,14,15,26}

Conducting and photoconducting atomic force microscopy (c-AFM and pc-AFM, respectively) were employed to simultaneously probe morphology, charge extraction, and photosensitivity of the hybrid TiO₂-DPP(TBFu)₂ system. These are powerful techniques to characterize and correlate the nanoscale morphologies and electrical properties the film materials.^{19,27-29} Hybrid TiO₂-DPP(TBFu)₂ and TiO₂-P3HT (Poly(3-hexylthiophene-2,5-diyl)) films were prepared by spin-coating the donor materials into mesostructured TiO₂ for c-AFM and pc-AFM characterization. Though the hybrid TiO₂-P3HT system has been intensively studied, nanoscale electrical properties have not been investigated using c-AFM and pc-AFM. In our c-AFM experiments, the gold-coated silicon AFM tip is scanning the sample in contact mode, to map out topography and current images. The structure of the devices ITO/TiO₂: DPP(TBFu)₂ or P3HT/Au-tip resembles the structure of hole-only diode devices, since the work function of Au (~5.1 eV) and ITO (~4.8 eV) is much closer to the HOMO of P3HT (\sim 5.0 eV) and DPP(TBFu)₂ (\sim 5.2 eV). As negative bias is applied to the ITO substrate, holes are injected from the Au tip and collected at the substrate. The pc-AFM experiment set-up is similar to c-AFM, except the fact that the sample is illuminated by a Xe-lamp light source with a light spot approximately 160 μ m in diameter.^{19,30}

Figure 4 shows the morphology, dark conductivity, and photoconductivity collected at the ITO bias of -3V for TiO₂-DPP(TBFu)₂ ((a), (b), and (c)) and TiO₂-P3HT ((d), (e), and (f)). The surface morphology of TiO₂-P3HT shows coarser features compared to that of TiO₂-DPP(TBFu)₂. While the TiO₂-P3HT surface more closely resembles that of neat P3HT morphology (g), the TiO₂-DPP(TBFu)₂ surface is more similar to that of TiO_2 (i). This suggests that more P3HT remains on top of TiO₂ surface as a neat P3HT layer. Compared to TiO₂-P3HT, the dark and photo-currents of the TiO₂-DPP(TBFu)₂ hybrid are quite homogeneous throughout the surface, which can lead to more continuous conduction pathways for carrier transport in solar cells. Most interestingly, the increase from dark to photocurrent of TiO_2 -DPP(TBFu)₂ ((e) to (f)) is around 200 times while that of TiO_2 -P3HT ((b) to (c)) is only around six times. It implies that the carrier density of TiO₂-DPP(TBFu)₂ is much higher than that of TiO₂-P3HT under illumination. This can be attributed to the higher loading of DPP(TBFu)2 in the mesostructured TiO₂ film and more efficient charge transfer between the two, resulting in more photo-generated carriers and hence higher photoconductivity. The intense photoresponse of TiO₂-DPP(TBFu)₂ system suggests that this structure may be utilized in a hybrid photoconductor device. The further modification of TiO₂ surface and/or using higher compatible small molecules can be utilized to improve the photocurrent at zero bias which is more relevant for solar cells operation.

In summary, we have demonstrated an important step toward using hybrid TiO₂-SM in optoelectronic devices. For the model system described, DPP(TBFu)₂ can be uniformly loaded into mesostructured TiO₂ to approximately 25% of the pore volume without additional surface modification of the TiO₂. This is a vast improvement when compared to the



FIG. 4. (a)–(f) Surface morphology, dark-current, and photo-current images from conducting and photoconducting atomic force microscopy of ((a), (b), and (c)) TiO₂-P3HT film and ((d), (e), and (f)) TiO₂-DPP(TBFu)₂ film, respectively. (g)–(i) The morphology of neat P3HT (g), DPP(TBFu)₂ (h), and mesostructured TiO₂ (i).

much poorer loadings achieved using conjugated polymers. Charge transfer from photo-excited DPP(TBFu)₂ to TiO_2 is efficient and promising for solar cell and photoconductor applications. Both the loading and charge transfer efficiency could be further improved by modifying TiO₂ surface and functionalizing small molecules so that they would interact with TiO₂ more favorably. Interestingly, the intense photoresponse of TiO₂-DPP(TBFu)₂ hints to a high performance hybrid TiO₂-SM photoconductors. We are currently exploring HSC and photoconductor devices that take advantage of the higher loadings and promising charge transfer properties of small molecule donor materials. In a broader context, with high loading, efficient charge transfer, intense photo-response, hybrid TiO2-SM systems are useful for assessing the effects of interfacial interactions between TiO₂ and non-metal organic dyes on their optoelectronic properties. For instance, these properties and the relatively simple small molecular structure of SMs facilitate the use high resolution characterization technique, such as solid-state 2D NMR, to gain molecular-level understanding of the chemical composition and structure of inorganic-organic interface.²⁰

This work was funded by the NSF-SOLAR grant and by the Institute for Collaborative Biotechnologies through Grant No. W911NF-09-0001 from the U.S. Army Research Office. H.P. thanks Dr. Thomas E. Mates for helping with SIMS; Dr. Alexander Mikhailovsky for helping with steady state and transient photoluminescence experiments; and Peter Zalar for constructive discussions and revisions of the manuscript. SIMS equipment belongs to MRL Shared Experimental Facilities which are supported by the MRSEC Program of the NSF under Award No. DMR 1121053; a member of the NSF-funded Materials Research Facilities Network (www.mrfn.org). J.P.J. acknowledges the U.S. NSF for an IGERT Fellowship under Grant No. NSF-DGE 0801627. The content of the information does not necessarily reflect the position or the policy of the U.S. Government, and no official endorsement should be inferred.

- ¹J. Takada, H. Awaji, M. Koshioka, A. Nakajima, and W. A. Nevin, Appl. Phys. Lett. **61**, 2184 (1992).
- ²K. Kajihara, K. Tanaka, K. Hirao, and N. Soga, Jpn. J. Appl. Phys., Part 1 35, 6110 (1996).
- ³K. Kajihara, K. Tanaka, K. Hirao, and N. Soga, Jpn. J. Appl. Phys., Part 1 **36**, 5537 (1997).
- ⁴T. J. Savenije, J. M. Warman, and A. Goossens, Chem. Phys. Lett. 287, 148 (1998).
- ⁵P. A. van Hal, M. P. T. Christiaans, M. M. Wienk, J. M. Kroon, and R. A. J. Janssen, J. Phys. Chem. B **103**, 4352 (1999).
- ⁶B. O'Regan and M. Grätzel, Nature 353, 737 (1991).
- ⁷J. Yu, T. Shen, W. Weng, Y. Huang, C. Huang, W. Su, S. Rwei, K. Ho, and L. Wang, Adv. Energy Mater. **2**, 245 (2012).
- ⁸J. D. A. Lin, O. V. Mikhnenko, J. Chen, Z. Masri, A. Ruseckas, A. Mikhailovsky, R. P. Raab, J. Liu, P. W. M. Blom, M. A. Loi, C. J. García-Cervera, I. D. W. Samuel, and T.-Q. Nguyen, Mater. Horiz. 1, 280 (2014).
- ⁹A. Abrusci, I.-K. Ding, M. Al-Hashimi, T. Segal-Peretz, M. D. McGehee, M. Heeney, G. L. Frey, and H. J. Snaith, Energy Environ. Sci. 4, 3051 (2011).
- ¹⁰G. P. Bartholomew and A. J. Heeger, Adv. Funct. Mater. 15, 677 (2005).
- ¹¹S.-J. Moon, E. Baranoff, S. M. Zakeeruddin, C.-Y. Yeh, E. W.-G. Diau, M. Grätzel, and K. Sivula, Chem. Commun. 47, 8244 (2011).
- 12 F. Gao, S. Ren, and J. Wang, Energy Environ. Sci. 6, 2020 (2013).
- ¹³T. Xu and Q. Qiao, Energy Environ. Sci **4**, 2700 (2011).
- ¹⁴R. Zhu, C. Jiang, B. Liu, and S. Ramakrishna, Adv. Mater. **21**, 994 (2009).
- ¹⁵Y.-C. Huang, J.-H. Hsu, Y.-C. Liao, W.-C. Yen, S.-S. Li, S.-T. Lin, C.-W. Chen, and W.-F. Su, J. Mater. Chem. **21**, 4450 (2011).
- ¹⁶L. J. A. Koster, O. Stenzel, S. D. Oosterhout, M. M. Wienk, V. Schmidt, and R. A. J. Janssen, Adv. Energy Mater. 3, 615 (2013).
- ¹⁷P. Ravirajan, S. A. Haque, J. R. Durrant, D. D. C. Bradley, and J. Nelson, Adv. Funct. Mater. **15**, 609 (2005).
- ¹⁸B. Walker, A. B. Tamayo, X. Dang, P. Zalar, J. H. Seo, A. Garcia, M. Tantiwiwat, and T. Nguyen, Adv. Funct. Mater. **19**, 3063 (2009).
- ¹⁹X.-D. Dang, A. B. Tamayo, J. Seo, C. V. Hoven, B. Walker, and T.-Q. Nguyen, Adv. Funct. Mater. 20, 3314 (2010).
- ²⁰S. Neyshtadt, J. P. Jahnke, R. J. Messinger, A. Rawal, T. Segal Peretz, D. Huppert, B. F. Chmelka, and G. L. Frey, J. Am. Chem. Soc. **133**, 10119 (2011).
- ²¹T. Segal-Peretz, O. Leman, A. M. Nardes, and G. L. Frey, J. Phys. Chem. C 116, 2024 (2012).

- ²²S. Neyshtadt, M. Kalina, and G. L. Frey, Adv. Mater. **20**, 2541 (2008).
- 23 See supplementary material at http://dx.doi.org/10.1063/1.4883001 for porosimetry data of mesostructured TiO₂ and loading calculation of DPP(TBFu)2 in hybrid film., (n.d.).
- ²⁴P. A. van Hal, M. M. Wienk, J. M. Kroon, and R. A. J. Janssen, J. Mater. Chem. **13**, 1054 (2003).
- ²⁵J. Bouclé, S. Chyla, M. S. P. Shaffer, J. R. Durrant, D. D. C. Bradley, and J. Nelson, Adv. Funct. Mater. 18, 622 (2008).
- ²⁶J. Liu, E. N. Kadnikova, Y. Liu, M. D. McGehee, and J. M. J. Fréchet, J. Am. Chem. Soc. **126**, 9486 (2004).
- ²⁷O. Douhéret, L. Lutsen, A. Swinnen, M. Breselge, K. Vandewal, L. Goris, and J. Manca, Appl. Phys. Lett. 89, 032107 (2006).
- ²⁸D. C. Coffey, O. G. Reid, D. B. Rodovsky, G. P. Bartholomew, and D. S. Ginger, Nano Lett. 7, 738 (2007).
- ²⁹Z. He, H. Phan, J. Liu, T.-Q. Nguyen, and T. T. Y. Tan, Adv. Mater. 25, 6900 (2013).
- ³⁰M. Guide, X.-D. Dang, and T.-Q. Nguyen, Adv. Mater. **23**, 2313 (2011).