

## Flame-made niobium doped zinc oxide nanoparticles in bulk heterojunction solar cells

Viruntachar Kruefu, Eric Peterson, Chantipa Khantha, Chawarat Siriwong, Sukon Phanichphant et al.

Citation: *Appl. Phys. Lett.* **97**, 053302 (2010); doi: 10.1063/1.3465866

View online: <http://dx.doi.org/10.1063/1.3465866>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v97/i5>

Published by the [American Institute of Physics](http://www.aip.org).

---

### Related Articles

Electrostatically driven collapsible Au thin films assembled using transfer printing for thermal switching  
*Appl. Phys. Lett.* **100**, 211904 (2012)

Structure and growth mechanism of quasi-aligned GaN layer-built nanotowers  
*Appl. Phys. Lett.* **100**, 213101 (2012)

Improved performance of non-volatile memory with Au-Al<sub>2</sub>O<sub>3</sub> core-shell nanocrystals embedded in HfO<sub>2</sub> matrix  
*Appl. Phys. Lett.* **100**, 203509 (2012)

Inhomogeneous nanostructured honeycomb optical media for enhanced cathodo- and under-x-ray luminescence  
*J. Appl. Phys.* **111**, 103101 (2012)

Nano-sized Ba<sub>2</sub>NaNb<sub>5</sub>O<sub>15</sub>-NaNbO<sub>3</sub> co-crystallized glass-ceramics in phosphoniobate system  
*Appl. Phys. Lett.* **100**, 201907 (2012)

---

### Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: [http://apl.aip.org/about/about\\_the\\_journal](http://apl.aip.org/about/about_the_journal)

Top downloads: [http://apl.aip.org/features/most\\_downloaded](http://apl.aip.org/features/most_downloaded)

Information for Authors: <http://apl.aip.org/authors>

## ADVERTISEMENT



**Goodfellow**  
metals • ceramics • polymers • composites  
70,000 products  
450 different materials  
**small quantities fast**

[www.goodfellowusa.com](http://www.goodfellowusa.com)

# Flame-made niobium doped zinc oxide nanoparticles in bulk heterojunction solar cells

Viruntachar Kruefu,<sup>1,2</sup> Eric Peterson,<sup>1</sup> Chanitpa Khantha,<sup>1,2</sup> Chawarat Siriwong,<sup>2</sup> Sukon Phanichphant,<sup>2,a)</sup> and David L. Carroll<sup>1,a)</sup>

<sup>1</sup>Center For Nanotechnology and Molecular Materials, Wake Forest University, Winston-Salem, North Carolina 27105, USA

<sup>2</sup>Nanosciences and Nanotechnology Program, Graduate School, Chiang Mai University, Chiang Mai 50200, Thailand

(Received 12 March 2010; accepted 9 June 2010; published online 2 August 2010)

We report fabrication and measurement of bulk heterojunction solar cells utilizing a poly(3-hexylthiophene) (P3HT), phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) composite loaded with different concentrations of niobium doped zinc oxide (Nb/ZnO) nanoparticles produced by flame spray pyrolysis. Nanoparticles with different niobium concentrations were compared, along with devices without Nb/ZnO nanoparticles and with undoped ZnO nanoparticles. It was found that niobium doping leads to a slight increase in open circuit voltage and an increase in short circuit current that scales with niobium concentration. Additional comparison was made between the nanoparticles with 3% niobium by weight to unloaded devices. These also showed a similar open circuit voltage increase and an increase in current that scales with Nb/ZnO nanoparticle concentration to 30% by volume and drops off at 33% Nb/ZnO by volume. Possible mechanisms for these improvements are discussed. © 2010 American Institute of Physics. [doi:10.1063/1.3465866]

Polymer solar cells are attractive sources of electrical energy because they combine flexibility with low-cost fabrication. The most efficient devices to date have been developed based on bulk-heterojunction (BHJ) systems, constructed by blending p-type conjugated polymers with n-type conjugated polymers,<sup>1–3</sup> fullerenes,<sup>4,5</sup> or inorganic semiconductor nanoparticles (NPs), such as TiO<sub>2</sub>, ZnO, CdSe, and C<sub>60</sub>.<sup>6–10</sup> Zinc oxide is a very promising metal oxide wide-band gap semiconductor for use in solar cells because of its abundance and low cost, nontoxicity, high electron mobility, low crystallization temperature, and ease of NP fabrication.

It was shown recently that ZnO can be used as an electron acceptor to dissociate excitons formed in conjugated polymers, thus combining the advantages of organic semiconductors (flexibility, solutions processing) with those of inorganic semiconductors (stability, high mobility). Band gap engineering of ZnO has been demonstrated as an efficient way to increase open-circuit voltage and solar cell efficiency. Olson *et al.*<sup>11</sup> have demonstrated the beneficial effect of band gap tuning with Mg<sub>x</sub>Zn<sub>1-x</sub>O in the case of hybrid solar cells using poly(3-hexylthiophene) (P3HT) as the p-type light absorber. So far, the highest efficiencies have been obtained in the BHJ configuration, because that yields the highest interface area between the ZnO and conjugated polymer.

Unfortunately, the power conversion efficiencies of such hybrid polymer solar cells are too low, ~2.0% for inorganic/organic hybrid cells, for practical applications. Janssen and co-workers<sup>12</sup> have demonstrated 1.6% efficient BHJ structures by blending 5 nm diameter ZnO NPs with MEH-PPV and 0.9% efficient solar cells in blends of ZnO and P3HT. Many research groups have developed solar cells based on P3HT and conjugated fullerene composites.<sup>4,5,13</sup> Although much progress has been achieved, with several reported polymer solar cell devices providing power conversion effi-

ciencies of 3%–6%, there remains room for improvement.

Doping Nb into ZnO is quite attractive because there is a valence difference of three between Nb<sup>5+</sup> and Zn<sup>2+</sup>, thus each Nb atom can contribute more than one electron to the electrical conductivity.<sup>14</sup> To study the device efficiency as a function of the formulation and amount of niobium doped ZnO (Nb/ZnO) NP and find the optimal loading percentages for each, we synthesized highly crystalline NPs of pure ZnO and ZnO doped with 0.5, 1, and 3 mol % niobium by flame spray pyrolysis (FSP) technique, see Ref. 15 for specific methods of production of the NPs and photovoltaic devices. It is well known that the surface characteristics of ZnO, determined by the different fabrication processes, will influence the optical properties as well as the final degradation efficiency.<sup>16</sup> FSP is a very promising technique for synthesis of high purity nano-sized materials with controlled size and crystallinity. The method has been applied to prepare metal oxide-supported particles and heterogeneous catalysts. Niobium is a versatile

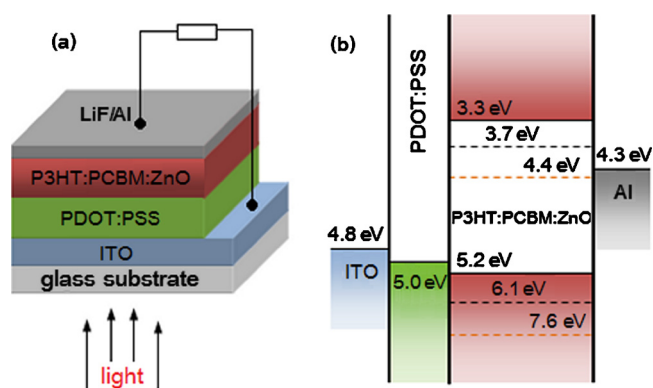


FIG. 1. (Color online) Device structure and energy level diagram of the components. (a) Schematic device structure for P3HT:PCBM BHJ solar cell with ZnO NPs. (b) Energy level diagram of the components of the device (relative to vacuum level).

<sup>a)</sup>Electronic mail: carrolldl@wfu.edu.

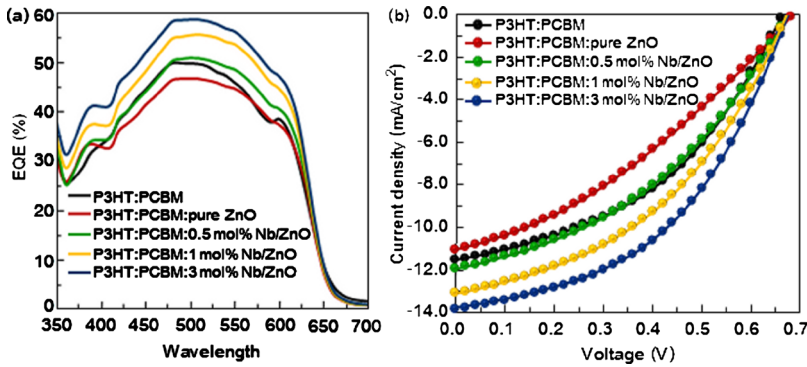


FIG. 2. (Color online) The effects of Nb/ZnO loading with different Nb concentrations on device performance. (a) EQE spectra and (b) J-V curves under 120 mW/cm<sup>2</sup> white light illumination.

dopant and is widely applied as catalytic metal oxide.<sup>17</sup>

The device structure and energy levels of the materials used in this work are shown in Fig. 1. Excitons are formed when P3HT absorbs photons. These excitons can be dissociated at the phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) and/or Nb/ZnO interfaces. ZnO and PCBM both can act as electron acceptor for P3HT. ZnO has a high electron mobility,<sup>18,19</sup> which can help charge-carrier collection and transport. The electrons at the lowest unoccupied molecular orbital level of PCBM (−3.7 eV) can be easily transferred to the conduction band of ZnO (−4.4 eV) (Fig. 1).

We investigated the effect of niobium doping on both the ZnO NPs and on composite solar cells made using the Nb/ZnO NPs. As shown in the supplementary methods, increasing the amount of niobium used when synthesizing the ZnO NPs resulted in smaller particles with more surface area. The P3HT:PCBM solution was doped with 31% by volume of Nb/ZnO in 1-butanol as well as ZnO NPs without niobium doping. As the niobium doping percentage is increased, there was an increase in the filling factor (FF) over a standard P3HT:PCBM device. There was also increase in short-circuit current density ( $J_{sc}$ ). The J-V (current-voltage) measurements and the EQE measurements are shown in Fig. 2.

Nb/ZnO particles synthesized with 3 mol % concentration of niobium were then used to investigate the effect of different loadings of NPs on the photovoltaic characteristics of devices (illuminated at 120 mW cm<sup>−2</sup>). Again, there is a small increase in open circuit voltage ( $V_{oc}$ ) for Nb/ZnO doped devices. The Nb/ZnO solution-blended P3HT:PCBM films exhibited higher values of  $J_{sc}$  with the maximum value 13.9 mA cm<sup>−2</sup> obtained for the 30 vol % Nb/ZnO system (11.5 mA cm<sup>−2</sup> for the unmodified device), although this started to decrease at the 33 vol % loading. The increased  $J_{sc}$  and  $V_{oc}$  lead to enhanced power conversion efficiency. This power conversion efficiency was a 21% improvement from the standard cell to the most efficient loading (from 2.85% to 3.62%). The FF of all devices are within what would be

expected for standard devices made with this P3HT and annealed for 3 min. The EQE measurements show an increase in photon collection, and thus photocurrent, across all wavelengths absorbed as seen in Fig. 3. There is a prominent increase at 375 nm, corresponding to the probable band gap of the Nb/ZnO particles.

One possible explanation is that the Nb/ZnO particles act as scatterers within the active layer of the device. This scattering effect could lead to better absorption via optical confinement within the device. Competing scattering effects (scattering within the active layer and scattering out of the active layer) could explain the current drop off from 30 to 33 vol % devices, with reflection out of the device beginning to dominate. Charge transport could also be changed significantly with high NP content, leading to suboptimal device characteristics (improved or degraded charge carrier mobility can affect the overall charge balance of the device). This could also be the reason that niobium doped particles have a positive effect on the device as opposed to the negative effect evidenced by the ZnO particles as the niobium could have an effect on how the NPs integrate into the BHJ film (via band structure changes). The slight increase in  $V_{oc}$  can be attributed to the change in band alignment caused by the introduction of the Nb/ZnO NPs, a similar effect is seen with undoped ZnO NPs. Scattering effects could be enhanced by the smaller particle sizes that are created by increased niobium doping (effectively increasing the scattering cross section).

In conclusion, we have demonstrated that doping P3HT:PCBM BHJ solar cells with certain amounts of niobium doped ZnO NPs resulted in efficiency increases via increases in primary photon conversion. Possible sources for this increase have been suggested. Further research will focus on optical measurements to determine changes in the index of refraction due to Nb/ZnO doping. Devices constructed without PCBM will also be researched.

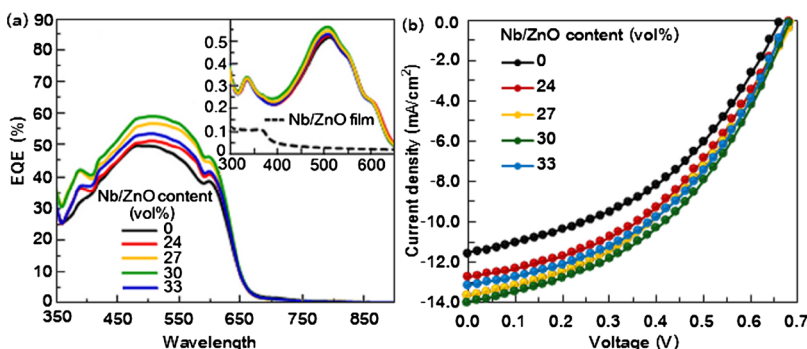


FIG. 3. (Color online) The effects of the 3 mol % Nb/ZnO concentration on device performance. (a) EQE spectra of the device fabricated using BHJ films with 3 mol % Nb/ZnO concentration of 24, 27, 30, and 33 vol %. The inset shows absorption spectra of P3HT:PCBM:Nb/ZnO films at various concentrations of Nb/ZnO solution blended into the P3HT:PCBM active layer. (b) The J-V curves of P3HT:PCBM:Nb/ZnO solar cells measured in the ambient atmosphere with 120 mW cm<sup>−2</sup> white-light irradiation.

The authors gratefully acknowledge the financial support from the Royal Thai Government, Ministry of Science and Technology, Thailand and the Thailand Research Funds. Particles synthesis was carried out in the Nanoscience Research Laboratory, Chiang Mai University, Thailand. This research was supported in part by a grant from the U.S. Dept. of Energy under Grant No. 07ER46428. E.D.P. is an NSF graduate research fellow. The solar-cell experimental characterization was done at Center for Nanotechnology and Molecular Materials, Wake Forest University, USA.

<sup>1</sup>J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Nature (London)* **376**, 498 (1995).

<sup>2</sup>S. C. Veenstra, W. J. H. Verhees, J. M. Kroon, M. M. Koetse, J. Sweelssen, J. J. A. M. Bastiaansen, H. F. M. Schoo, X. Yang, A. Alexeev, J. Loos, U. S. Schubert, and M. M. Wienk, *Chem. Mater.* **16**, 2503 (2004).

<sup>3</sup>G. Yu and A. J. Heeger, *J. Appl. Phys.* **78**, 4510 (1995).

<sup>4</sup>G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789 (1995).

<sup>5</sup>M. Svensson, F. Zhang, S. C. Veenstra, W. J. H. Verhees, J. C. Hummelen, J. M. Kroon, O. Iganas, and M. R. Andersson, *Adv. Mater.* **15**, 988 (2003).

<sup>6</sup>C. Y. Kwong, A. B. Djurisic, P. C. Chui, K. W. Cheng, and W. K. Chan, *Chem. Phys. Lett.* **384**, 372 (2004).

<sup>7</sup>W. J. E. Beek, M. M. Wienk, and R. A. J. Janssen, *Adv. Mater.* **16**, 1009 (2004).

<sup>8</sup>W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, *Science* **295**, 2425 (2002).

<sup>9</sup>W. J. E. Beek, M. M. Wienk, and R. A. J. Janssen, *Mater. Chem.* **15**, 2985 (2005).

<sup>10</sup>B. Sun, E. Marx, and N. C. Greenham, *Nano Lett.* **3**, 961 (2003).

<sup>11</sup>D. C. Olson, S. E. Shaheen, and M. S. A. White, *Adv. Funct. Mater.* **17**, 264 (2007).

<sup>12</sup>W. J. E. Beek, M. M. Wienk, and R. A. J. Janssen, *Adv. Funct. Mater.* **16**, 1112 (2006).

<sup>13</sup>K. Kim, J. Liu, M. A. G. Namboothiry, and D. L. Carroll, *Appl. Phys. Lett.* **90**, 163511 (2007).

<sup>14</sup>J. M. Lin, Y. Z. Zhang, Z. Z. Ye, X. Q. Gu, X. H. Pan, Y. F. Yang, J. G. Lu, H. P. He, and B. H. Zhao, *Appl. Surf. Sci.* **255**, 6460 (2009).

<sup>15</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3465866> for specific methods of production of the NPs and photovoltaic devices.

<sup>16</sup>H. Wang, C. Xie, W. Zhang, S. Cai, and Z. Gui, *J. Hazard. Mater.* **141**, 645 (2007).

<sup>17</sup>A. Teleki, N. Bjelobrck, and S. E. Pratsinis, *Sens. Actuators B* **130**, 449 (2008).

<sup>18</sup>M. Law, L. E. Greene, J. C. Johnson, R. Saykally, and P. D. Yang, *Nature Mater.* **4**, 455 (2005).

<sup>19</sup>E. M. Kaidashev, M. Lorenz, H. von Wenckstern, A. Rahm, H. C. Semmelhack, K. H. Han, G. Benndorf, C. Bundesmann, H. Hochmuth, and M. Grundmann, *Appl. Phys. Lett.* **82**, 3901 (2003).