

In-situ Growth of CdS Nanorods in PTB7 by Solvothermal Process for Hybrid Organic Inorganic Solar Cell applications

Ramil K Bhardwaj^{1,2}, Vishal Bharti¹, Jitender Gaur^{1*}, Abhishek Sharma¹, Annu Sonania, Dibyajyoti Mohanty¹, Shilpa Jain¹, Gauri D Sharma¹, Neeraj Chaudhari¹, Suresh Chand¹ and Kamalika Banerjee²

¹CSIR-National Physical Laboratory, K S Krishnan Marg, New Delhi-110012, India

²School of Science, Indira Gandhi National Open University, Maidan Garhi, New Delhi-110068, India

E-mail: jitender.jnsri@gmail.com; gaurj@mail.nplindia.org

Abstract— We demonstrate a high yielding, green approach using solvothermal, *in-situ* growth of CdS nanorods (NRs) in a low band gap polymer, poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7). The use of chloroaniline dithiocarbamate and chloroaniline as ligands to functionalize the Cd (II) ions provides a new path for solubilization of Cd (II) complex in the chlorobenzene solvent. It removes use of volatile and hazardous chemicals such as pyridine as ligand which are conventionally used to enhance solubility of such complexes. It is the first example of solvothermal process used for *in-situ* growth of CdS NRs in a polymer matrix. This nanocomposite is used to fabricate hybrid-organic-inorganic-solar cells (HOISC) as donor-acceptor combination in the bulk heterojunction (BHJ) geometry. The incorporation of CdS NRs shows significant decrease in the band gap of PTB7 from 1.71 eV to 1.59 eV and the photoluminescence (PL) studies show significant quenching in the PL of PTB7 by the addition of CdS NRs. This suggests that the PTB7:CdS NRs is a potential nanocomposite for the bulk heterojunction active layer in the HOISCs. The HOISCs fabricated using the PTB7:CdS as donor-acceptor combination give power conversion efficiency of the order of 1.16%. This work has implication in the development of green economical and efficient HOISC by using highly controlled synthetic process.

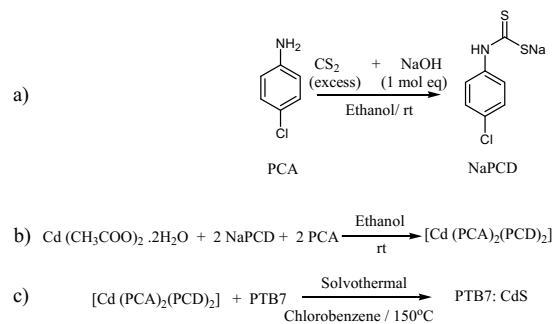
Index Terms— : Hybrid solar cell; Solvothermal; Nano rods; CdS; PTB7; Green chemistry.

I. INTRODUCTION

Semiconducting nanomaterials (SNMs) exhibit enhanced optical, electronic, photo-conducting and luminescent properties which are key features in their electronic applications. [1,2] SNMs show accelerated charge transfer rates when they are chemically bound with the organic polymer matrix, which lead to their application as electron acceptors in hybrid-organic-inorganic solar cells (HOISC).[3] SNMs such as CdS, CdSe have been synthesized in various morphologies using process such as sol-gel, solvothermal, solution phase and co-precipitation.[4-11] The morphology of the SNMs plays critical role in improving the efficiency of HOISC.[12] The conventional synthetic processes use hazardous chemicals such as pyridine and several surfactants leading to poor atom economy. [13,14] This aspect have been highlighted in our previous work where we have demonstrated green synthesis of CdS Quantum Dots (QDs) *in-situ* grown in the P3HT polymer network.[3] The solubility of the

P3HT:CdS QDs nano-composite in the non-polar organic solvents such as chlorobenzene remains as an obstacle in fabricating efficient HOISC.[9] In our present work we demonstrate for the first time, (i) solvothermal, *in-situ* growth of CdS nanorods (NRs) in the matrix of low band gap polymer poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl) carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) and (ii) the development of HOISC using the PTB7:CdS as donor-acceptor combination in the bulk-heterojunction (BHJ) geometry. The *in-situ* growth of CdS NRs results into (i) significant decrease in the band gap of PTB7 from 1.7 eV to 1.59 eV, (ii) adequate photoluminescence (PL) quenching of the PTB7 on incorporation of CdS NRs in PTB7 (PTB7:CdS) in 1:1 (w/w) ratio and (iii) the TEM and SEM images show homogenous distribution of CdS NRs in PTB7 matrix. Based on these findings we have prepared the HOISC using PTB7:CdS NRs as donor-acceptor combination in BHJ geometry and achieved power conversion efficiency (PCE) of the order of 1.16%.

II. EXPERIMENTAL DETAILS



Scheme 1: a) Synthesis of sodium salt of *p*-chloroaniline dithiocarbamate (NaPCD); b) synthesis of Cadmium complex, Cd(PCA)₂(NaPCD)₂; c) Synthesis of PTB7:CdS NRs

The synthesis of PTB7:CdS NRs is a three step reaction. The *p*-chloroaniline (PCA) is reacted with excess CS₂ followed by cadmium complex synthesis as illustrated in Scheme 1.[15] The cadmium complex is mixed with PTB7 in chlorobenzene poured in a Teflon lined solvothermal bomb. It

was kept at 150 °C for 4 hrs. After the treatment solution was concentrated under reduced pressure.

III. RESULTS & DISCUSSIONS

The metal complexes of dithiocarbamate are known to decompose into metal sulfide nano materials of controlled morphologies which depend on the synthetic conditions such as temperature, pressure, solvent, surfactants etc.[15] The solvothermal treatment of the cadmium complex, $\text{Cd}(\text{PCA})_2(\text{PCD})_2$ produces CdS NRs which were characterized by SEM images Fig. 1a. Same conditions were used for the *in-situ* growth of the CdS NRs in the PTB7 matrix. The SEM and TEM images of the PTB7:CdS NRs (Fig. 1 b&c) depicts that the CdS NRs are uniformly distributed in the PTB7 matrix. The EDS (inset Fig. 1c) indicates cadmium rich PTB7:CdS composite. The TEM image (Fig. 1 c) of the PTB7:CdS shows ~10 nm CdS NRs. The HRTEM image (Fig. 1 d) highlights the crystalline character of the CdS NRs in the PTB7 matrix. The HRTEM (Fig. 1d) shows fringe width of ~3.8 Å which corresponds to the $2\theta_{[001]} = 23.2^\circ$.

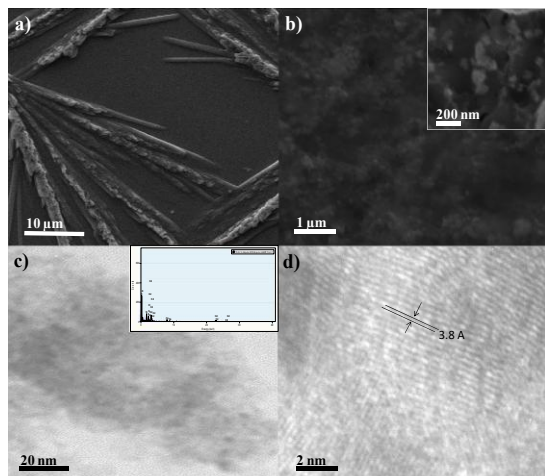


FIG 1:(a) SEM image of CdS NRs synthesized by thermal decomposition of the $\text{Cd}(\text{PCA})_2(\text{PCD})_2$; (b) SEM of drop cast film of PTB7:CdS composite; inset highlighting the cubical morphology of the material; (c) TEM of the PTB7:CdS composite, showing the growth of the CdS in the polymer matrix with particle size < 10 nm; inset: EDS of the composite at the encircled region. (d) HRTEM image of the PTB7:CdS showing the crystalline nature of the *in-situ* grown CdS NRs in the polymer matrix.

The PL spectra of the PTB7 for λ_{ex} 680 nm excitation is shown in Fig. 2a. It shows that there is a significant quenching of photoluminescence of the PTB7 on addition of the CdS NRs. The quenching implies the addition of CdS NRs leads to a significant charge transfer from PTB7 to CdS NRs. The quenching increases with the increase in the concentration of the CdS NRs from 1:0.5 to 1:1 (w/w) ratio in the PTB7:CdS. However, it can be seen from Fig. 2a that on increasing the amount of CdS in PTB7 (PTB7:CdS) to 1:2 (w/w) ratio there is a saturation in the quenching process. Therefore the

HOISCs were prepared for two cases viz., PTB7:CdS 1:0.5 and 1:1 (w/w) respectively.

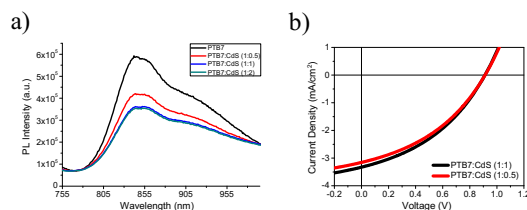


FIG.2. (a) PL spectra of PTB7 polymer and PTB7:CdS in 1:0.5 and 1:1 (w/w) ratios in chlorobenzene solvent. The PL spectrum of PTB7 shows a significant quenching after the addition of CdS NRs which implies a significant charge transfer from PTB7 to CdS NRs; (b) Solar cell device J vs V characteristics, there is an increase in the J_{sc} with the increase in the CdS NRs concentration however the V_{oc} remains constant.

The two ratio combinations synthesized here were used to fabricate the solar cells in configuration of, device 1: ITO/PEDOT:PSS/PTB7:CdS (1:0.5)/Al and device 2: ITO/PEDOT:PSS/PTB7:CdS(1:1)/Al. Fig. 2b shows current density and voltage (J - V) characteristics of the two devices. The open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) values for each set of devices are given in Table 1. It is seen that the solar cell parameters are almost similar in both the cases except for slight increase in J_{sc} , in the case of device 2. This slight enhancement in J_{sc} is revealed in the corresponding increase in PCE from 1.10 % to 1.16 %. This has been attributed to better charge transport process between donor and acceptor molecules vi z. PTB7 and CdS NRs which is also supported by the enhancement in the PL quenching for the case of PTB7:CdS 1:1 (w/w) ratio as compared to the PTB7:CdS 1:0.5 (w/w) ratio.

TABLE 1: Device parameters from PTB7:CdS PSCs measured under illumination intensity of 1000 W/m^2 .

Devices	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
PTB7:CdS (1:0.5)	3.25	0.91	37.5	1.10
PTB7:CdS (1:1)	3.44	0.91	37.0	1.16

IV. CONCLUSIONS

In conclusion we demonstrate a green and economically viable approach of *in-situ* growth of CdS NRs in PTB7 matrix by solvothermal process and first time report of achieving PCE of the order of 1.16 % in HOISC fabricated using PTB7:CdS donor-acceptor nanocomposite in BHJ configuration. UV-Vis study shows that our approach gives a band gap modulation of electron donor polymer PTB7.

V. ACKNOWLEDGEMENTS

The authors thank the director, NPL, for his kind support in this R & D work. One of the authors (RKB) thanks Vice

Chancellor and Director, IGNOU, Delhi. Authors are also thankful to DST, Govt. of India, for providing financial support under the India-UK joint initiative project entitled “Advancing the efficiency and production potential of excitonic solar cells (APEX)”.

VI. REFERENCES

- [1] B. Lebeau and P. Innocenzi, *Chem. Soc. Rev.*, 2011, **40**, 886-906.
- [2] H. Dong, H. Zhu, Q. Meng, X. Gong and W. Hu, *Chem. Soc. Rev.*, 2012, **41**, 1754-808.
- [3] R. K. Bhardwaj, H. S. Kushwaha, J. Gaur, T. Upreti, V. Bharti, V. Gupta, N. Chaudhary, G. D. Sharma, K. Banerjee and S. Chand, *Mater. Lett.*, 2012, **89**, 195-197.
- [4] W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science*, 2002, **295**, 2425-2457.
- [5] S. Dayal, N. Kopidakis, D. C. Olson, D. S. Ginley and G. Rumbles, *Nano Lett.*, 2010, **10**, 239-242.
- [6] W. U. Huynh, X. G. Peng and A. P. Alivisatos, *Adv. Mater.*, 1999, **11**, 923-927.
- [7] B. Q. Sun, H. J. Snaith, A. S. Dhoot, S. Westenhoff and N. C. Greenham, *J. Appl. Phys.*, 2005, **97**, 14914 (1-6).
- [8] Y. Zhou, Y. C. Li, H. Z. Zhong, J. H. Hou, Y. Q. Ding, C. H. Yang and Y. F. Li, *Nanotechnology*, 2006, **17**, 4041-4047.
- [9] L. Wang, Y. S. Liu, X. Jiang, D. H. Qin and Y. Cao, *J. Phys. Chem. C*, 2007, **111**, 9538-9542.
- [10] C. Kaito, Y. Saito and K. Fujita, *Jpn. J. Appl. Phys.*, 1987, **26**, L1973-1975.
- [11] D. R. Baker and P. V. Kama, *Adv. Funct. Mater.*, 2009, **19**, 805-811.
- [12] M. Wright and A. Uddin, *Sol. Cells*, 2012, **107**, 87-111.
- [13] H. C. Leventis, S. P. King, A. Sudlow, M. S. Hill, K. C. Molloy and S. A. Haque, *Nano Lett.*, 2010, **10**, 1253-1258.
- [14] S. Dowland, T. Lutz, A. Ward, S. P. King, A. Sudlow, M. S. Hill, K. C. Molloy and S. A. Haque, *Adv. Mater.*, 2011, **23**, 2739-2744.
- [15] K. D. Karlin, John Wiley & Sons, Inc., Hoboken, New Jersey, 2005, Volume 53.