

PERFORMANCE ENHANCEMENT OF CdS NANOROD ARRAYS/P3HT HYBRID SOLAR CELLS *VIA* N719 DYE INTERFACE MODIFICATION*

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Abstract Improved hybrid solar cells consisting of vertical aligned cadmium sulfide (CdS) nanorod arrays and interpenetrating polythiophene (P3HT) have been achieved *via* modification of CdS nanorod surface by using conjugated N719 dye. The complete infiltration of P3HT between CdS nanorods interspacing was verified by scanning electron microscopy. By employing absorption and photoluminescence spectra, and current-voltage characterization the interaction between N719 molecules and CdS nanorods/P3HT interface was explored, and the role of N719 dye on the improvement of device performance was discussed.

Keywords: CdS nanorods; Hybrid solar cells; N719; Interface modification.

INTRODUCTION

Hybrid solar cells (HSCs) based on conjugated polymers and inorganic nanostructures have been attracting enormous interest, as a derivative of polymer-based solar cells, due to the potential advantages of n-type inorganic semiconductors over the organic acceptors, including higher dielectric constant, higher electron mobility and affinity as well as better physical and chemical stability^[1–6]. Recent researches have demonstrated the unique stability of HSCs in kinds of architectures, such as oxide-based bilayer device, CdSe-based bulk-heterojunction (BHJ) device and ZnO or CdS-based ordered BHJ device^[6–10]. In these HSCs, the exciton separation efficiency, interface charge transport and recombination are strongly dependent on the morphology of the composite films and surface quality of the inorganic component. Inorganic nanorod arrays (NRA)-based polymer solar cells as the easiest realization form of ordered BHJ supply ideal three dimensional spatial morphology with bicontinuous charge transport channels, which can effectively improve the charge transport and reduce the carriers recombination, ultimately affecting the performance of devices^[5, 11–13]. To improve the compatibility between organic and inorganic components and to optimize the interface energetic, pyridine, benzoic acid derivatives and other small and low-conjugated molecule ligands were employed to modify inorganic surface, such as CdSe, TiO₂, ZnO and CdS^[14–20]. By modifying the physical or chemical properties of the inorganic surface with small molecule ligands, the performance of HSCs is improved significantly. Therefore, understanding and controlling of the surface properties and interfacial interactions between the organic molecules and inorganic semiconductors have been investigated intensively.

* This work was financially supported by the National Natural Science Foundation of China (Nos. 50990063, 51261130582 and 91233114).

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Invited paper dedicated to Professor Fosong Wang on the occasion of his 80th birthday

Received December 31, 2012; Revised January 25, 2013; Accepted January 31, 2013

doi: 10.1007/s10118-013-1274-z

In the present paper, we employ the relatively larger and high-conjugated surface ligand, N719 dye, as the modifier to change the surface quality of CdS NRA. The spectrum change of CdS NRA/P3HT composites after interface modification is investigated *via* UV-Visible absorption spectra and photoluminescence (PL) spectra. The modified CdS NRA/P3HT HSCs show us greatly improved device performance, and the interaction mechanisms between N719 dye and CdS NRA/P3HT composite are discussed based on the analysis of interfacial energy level arrangement and the fitting of photovoltaic characteristics.

EXPERIMENTAL

Fabrication of CdS NRA/P3HT HSCs

CdS NRAs were prepared via one-step hydrothermal method reported previously with slight modification^[21]. Prior to N719 dye modification, CdS NRA was annealed in air at 200 °C for 1 h. Then CdS NRA was immersed into 0.5 mmol/L N719 dye solution with mix-solvent composed of acetonitrile and *t*-butyl alcohol (1:1, *V/V*) at 60 °C for 12 h. After rinsed by acetonitrile three times and dried by nitrogen, CdS NRA was transferred into a glovebox immediately, and the P3HT film was spin-coated from a solution in dichlorobenzene (35 mg/mL) at 700 r/min for 60 s. P3HT was used as purchased from LumTec. The composite film was then placed in a covered Petri dish and allowed to dry over the course of 45 min. The dry sample was subsequently annealed at 225 °C for 1 min and allowed to cool naturally. Finally, the Au electrode was thermally evaporated at a pressure of 5.3×10^{-4} Pa with a thickness of 50 nm. The active area was 0.04 cm².

Characterization

The morphologies of CdS NRA and CdS NRA/P3HT composite films were observed on a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM). UV-Visible absorption spectra were obtained using a UV-2450 UV-Vis Shimadzu spectrophotometer. Photoluminescence (PL) spectra were recorded on an Edinburgh FLS920 spectrometer. The current-voltage characteristics of the HSCs were measured under simulated AM 1.5 G irradiation (100 mW/cm²) in air using Keithley 236 source measure unit and Thermo Oriel solar simulator. The light intensity was calibrated with a standard silicon photodiode.

RESULTS AND DISCUSSION

The typical SEM images of pristine CdS NRA, N719 capped CdS NRA and CdS NRA/N719/P3HT composite film are shown in Fig. 1. CdS NRA prepared from one-step hydrothermal method has similar morphology to our previous reports^[21]. The rod diameter is approximately 150 nm with an average length and the rod-to-rod distance of 400 and 150 nm, respectively (Fig. 1a). There are almost no morphology changes after N719 modification except the nanoscaled bulges on the top of nanorods (Figs. 1b–1c). These bulges could be thought as the recrystals of residual N719 dye after rinsing. Figure 1(d) shows the cross-sectional SEM image of CdS NRA/N719/P3HT composite film. It can be observed that the gaps between nanorods are fully infiltrated by P3HT. The thickness of CdS NRA/N719/P3HT composite film is about 450 nm with a pristine P3HT cover layer about 50 nm, as electron blocking layer.

Figure 2 shows the absorption spectra of CdS NRA and CdS NRA/P3HT composite film before and after N719 modification. We can find that there is an obvious absorption peak of the as-prepared CdS NRA at 500 nm with an extended band edge. No obvious change was observed after N719 modification except the slightly absorption enhancement in the range of 500–600 nm, benefited from the intrinsic absorption of N719 dye. The absorption of CdS NRA/N719/P3HT hybrid was dominated by the superposition of the individual absorptions of pristine CdS NRA and P3HT film with negligible contribution from N719 dye. However, the absorption intensity of CdS NRA/P3HT composite was obviously enhanced after N719 modification, which was different from the systems where small and low-conjugated molecules, such as pyridine, benzoic acid and its derivatives were employed to modify organic/inorganic interfaces^[16, 20, 22]. In the present CdS NRA/P3HT hybrid, the conjugated molecule of N719 dye can form strong π - π interaction with P3HT chain. On the other hand, the interaction between alkyl chain of N719 and P3HT chain can improve the spatial packing of P3HT. These two

kinds of interactions improved the absorption of CdS NRA/P3HT composite and made N719 a better modifier compared to other low-conjugated modifiers, in favor of the charge generation and transport in final devices.

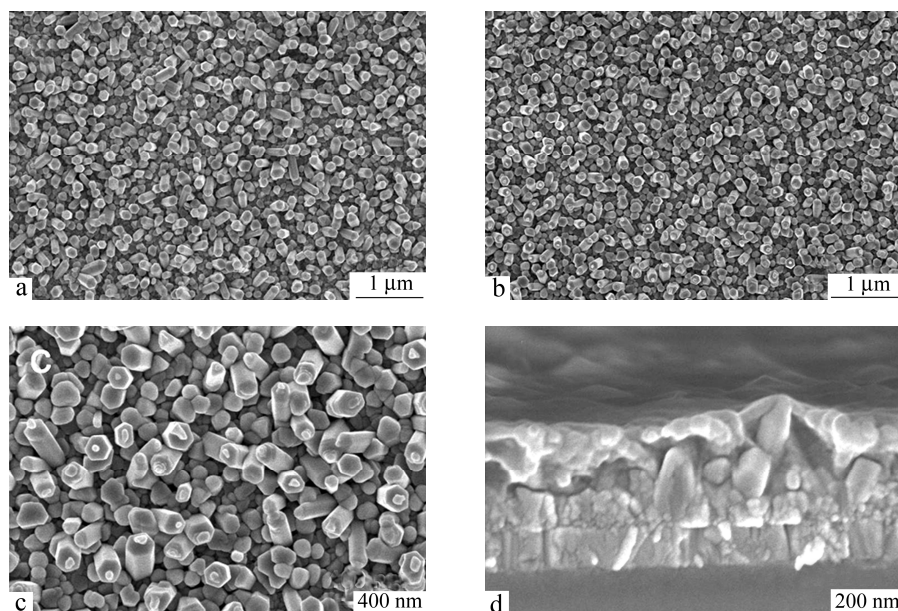


Fig. 1 Top view SEM images of (a) pristine CdS NRA, (b–c) N719 capped CdS NRA with different magnifications and (d) cross-sectional view of CdS NRA/N719/P3HT composite film

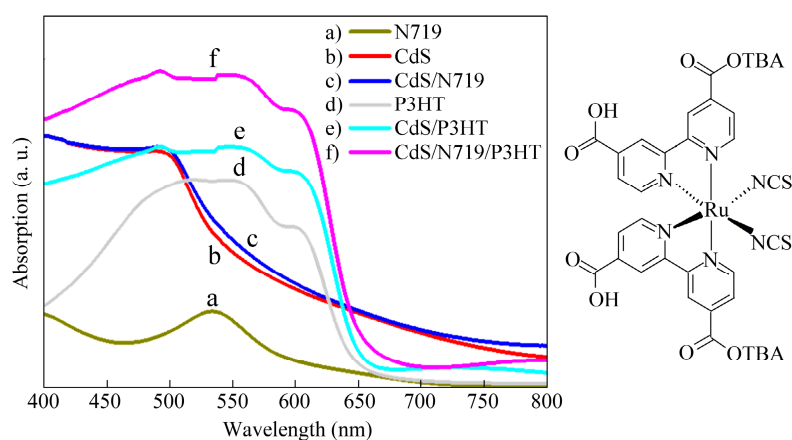


Fig. 2 UV-Vis absorption spectra of CdS NRA and CdS NRA/P3HT composite films before and after N719 modification
Inset shows the chemical structure of N719 dye.

The PL spectra of CdS NRA/P3HT composite after N719 modification (Fig. 3) showed significantly PL quenching by *ca.* 50%, illustrating apparently improvement of interface exciton separation. The strong interaction between the carboxyl group of N719 molecules and the surface Cd atoms of CdS NRA decreased the concentrations of surface dangling bonds and traps. Hereby, the surface trapping and recombination of separated electrons and holes at CdS NRA surface will be greatly decreased.

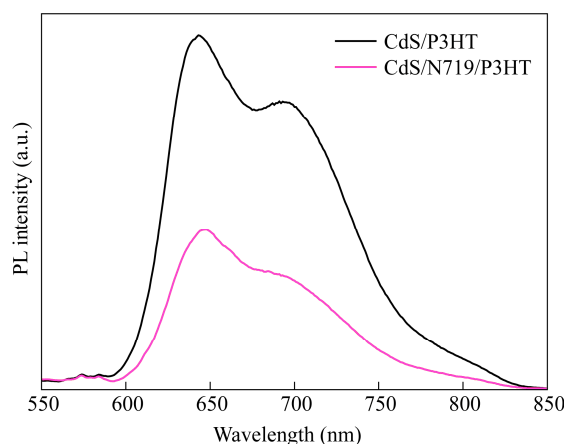


Fig. 3 PL spectra of CdS NRA/P3HT composites before and after N719 modification

The J - V characteristics of ITO/CdS NRA/P3HT/Au HSCs before and after N719 modification are shown in Figure 4(a). After immersing in N719 dye solution for 12 h, the short current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE) were improved by 53%, 219%, 59% and 684%, respectively, from 0.62 mA/cm², 0.16 V, 31.5% and 0.031% to 0.95 mA/cm², 0.51 V, 50.1%, and 0.243% (see Table 1).

Table 1. Photovoltaic parameters of ITO/CdS NRA/P3HT/Au HSCs before and after N719 modification

Modifier	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	R_s ($\Omega \cdot \text{cm}^2$)	$R_{sh} \times 10^{-4}$ ($\Omega \cdot \text{cm}^2$)	Rectification ratio (± 2 V)
No	0.62	0.16	31.5	0.031	2040	1	199
N719	0.95	0.51	50.1	0.243	200	256	10978

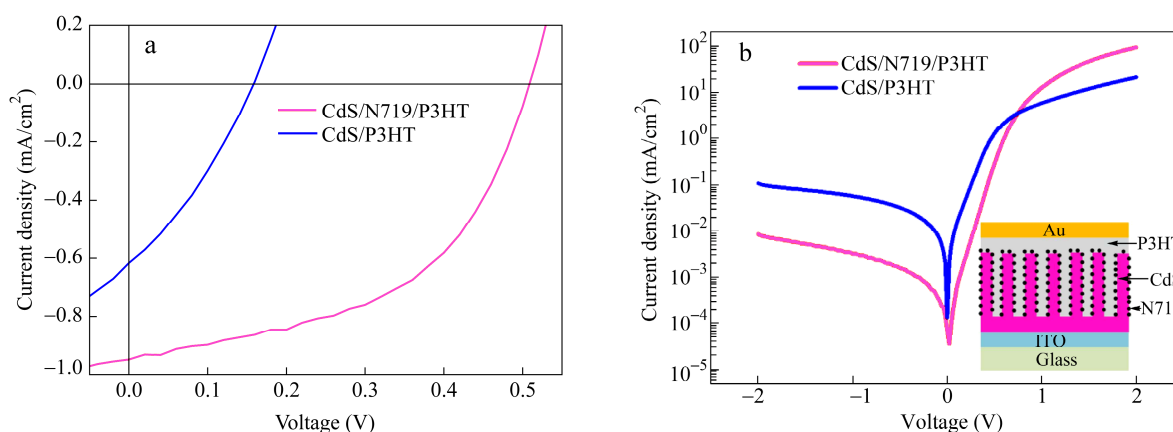


Fig. 4 Illuminated (a) and dark (b) J - V characteristics of ITO/CdS NRA/P3HT/Au HSCs before and after N719 modification

Inset shows the schematic diagram of ITO/CdS NRA/P3HT/Au device after N719 modification.

Figure 4(b) showed the dark J - V curve of CdS NRA/P3HT HSCs in semi-logarithmic scale with obvious diode characteristics. Rectification ratio at ± 2 V increased by two orders of magnitude from 199 to 10978. The reverse current density (-2 V) decreased while the forward current density ($+2$ V) increased, illustrating the improvement of charge transport after N719 modification. The series resistance (R_s) and the shunt resistance (R_{sh}) were obtained and summarized in Table 1 by fitting the dark J - V curve with the following equivalent circuit model equation^[23]:

$$J = \frac{R_{sh}}{R_s + R_{sh}} \left\{ J_s \left[\exp \left(\frac{q(V - jR_s)}{nkT} \right) - 1 \right] + \frac{V}{R_{sh}} \right\} \quad (1)$$

where J_s is the reverse saturation current density, k is Boltzmann constant, T is the temperature in Kelvin, q is the electron charge, and n is the ideal factor. As listed in Table 1, R_s decreased from $2040 \, \Omega \cdot \text{cm}^2$ to $200 \, \Omega \cdot \text{cm}^2$, while R_{sh} increased from $1 \times 10^4 \, \Omega \cdot \text{cm}^2$ to $2.56 \times 10^6 \, \Omega \cdot \text{cm}^2$, suggesting the effective improvement of device transportation and restriction of recombination. The improvement of R_s and R_{sh} not only contributes to J_{sc} but also to V_{oc} and FF.

Figure 5 shows the energy band diagram of ITO/CdS NRA/N719/P3HT/Au devices. The cascaded position of N719 dye serves as the transition energy level between CdS and P3HT. The positions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels for both N719 dye and P3HT are favorable for electron injection towards CdS and hole transport towards the Au electrode. The interfacial dye molecules also prohibit the recombination of electrons and holes at interface due to the special separation of the two types of carries^[22, 24]. Additionally, the better electronic coupling between the absorbed N719 dye and CdS due to chemical bonding could also improve the electron collection efficiency.

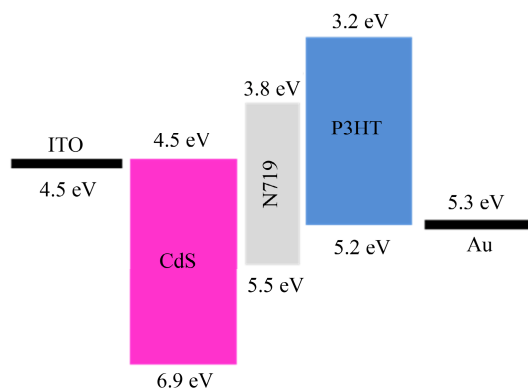


Fig. 5 Energy band diagram of ITO/CdS NRA/N719/P3HT/Au devices. Energy level values of CdS, P3HT and N719 come from Refs. [24–26].

On the other hand, molecules like N719 dye with high carboxyl density always show negative dipole. A dipolar layer towards polymer formed once these negative molecular dipoles were introduced at organic/inorganic interface. This dipolar layer, when attached to CdS surface, induced a step in the local vacuum level due to the electric field across this layer, leading to the shift of CdS conduction level towards the local vacuum level of P3HT^[18]. Eventually, the gap between the bottom of CdS conduction level and HOMO level of P3HT increased, suggesting an enlarged V_{oc} . In addition, this less-protonated N719 dye resulted in a CdS conduction level closer to the vacuum level and also caused a higher V_{oc} .

CONCLUSIONS

Performance enhancement in HSCs composed of CdS NRA and P3HT was successfully realized by introducing conjugated N719 dye as interface modifier. N719 dye can form strong π - π interaction with P3HT chain, improve the spatial packing of P3HT, quench the surface dangling bonds and traps, and serve as the transition energy level between CdS NRA and P3HT, leading to the improved interfacial exciton separation and charge transport as well as the reduced recombination, and thus, enhance the device performance with improved series and parallel resistance. N719 dye can also form interface dipolar layer and change the relative position of local energy level, which will improve the interface energy level difference, giving a higher V_{oc} .

REFERENCES

- 1 Huynh, W.U., Dittmer, J.J. and Alivisatos, A.P., *Science*, 2002, 295: 2425
- 2 Helgesen, M., Sondergaard, R. and Krebs, F.C., *J. Mater. Chem.*, 2010, 20: 36
- 3 Huynh, W.U., Dittmer, J.J., Libby, W.C., Whiting, G.L. and Alivisatos, A.P., *Adv. Funct. Mater.*, 2003, 13: 73
- 4 Beek, W.J., Wienk, M.M. and Janssen, R.A., *Adv. Funct. Mater.*, 2006, 16: 1112
- 5 Gonzalez-Valls, I. and Lira-Cantu, M., *Energy Environ. Sci.*, 2009, 2: 19
- 6 Kuo, C.Y., Tang, W.C., Gau, C., Guo, T.F. and Jeng, D.Z., *Appl. Phys. Lett.*, 2008, 93: 033307
- 7 Lira-Cantu, M. and Krebs, F.C., *Sol. Energy Mater. Sol. Cells*, 2006, 90: 2076
- 8 Qian, L., Yang, J., Zhou, R., Tang, A., Zheng, Y., Tseng, T.K., Bera, D., Xue, J. and Holloway, P.H., *J. Mater. Chem.*, 2011, 21: 3814
- 9 Olson, D.C., Shaheen, S.E., Collins, R.T. and Ginley, D.S., *J. Phys. Chem. C*, 2007, 111: 16670
- 10 Nan, Y.X., Chen, F., Yang, L.G., Jiang, X.X., Zuo, L.J., Zhang, J.L., Yan, Q.X., Shi, M.M. and Chen, H.Z., *Sol. Energy Mater. Sol. Cells*, 2011, 95: 3233
- 11 Gnes, S., Neugebauer, H. and Sariciftci, N.S., *Chem. Rev.*, 2007, 107: 1324
- 12 Hochbaum, A.I. and Yang, P., *Chem. Rev.*, 2010, 110: 527
- 13 Chen, F., Qiu, W., Chen, X., Yang, L., Jiang, X., Wang, M. and Chen, H.Z., *Solar Energy*, 2011, 85: 2122
- 14 Fu, W., Shi, Y., Qiu, W., Wang, L., Nan, Y., Shi, M., Li, H. and Chen, H.Z., *Phys. Chem. Chem. Phys.*, 2012, 14: 12094
- 15 Wang, L., Liu, Y., Jiang, X., Qin, D. and Cao, Y., *J. Phys. Chem. C*, 2007, 111: 9538
- 16 Lin, Y.Y., Chu, T.H., Chen, C.W. and Su, W.F., *Appl. Phys. Lett.*, 2008, 92: 053312
- 17 Ravirajan, P., Peir, A.M., Nazeeruddin, M.K., Graetzel, M., Bradley, D.D., Durrant, J.R. and Nelson, J., *J. Phys. Chem. B*, 2006, 110: 7635
- 18 Goh, C., Scully, S.R. and McGehee, M.D., *J. Appl. Phys.*, 2007, 101: 114503
- 19 Lin, Y.Y., Chu, T.H., Li, S.S., Chuang, C.H., Chang, C.H., Su, W.F., Chang, C.P., Chu, M.W. and Chen, C.W., *J. Am. Chem. Soc.*, 2009, 131: 3644
- 20 Jiang, X., Chen, F., Qiu, W., Yan, Q., Nan, Y., Xu, H., Yang, L. and Chen, H.Z., *Sol. Energy Mater. Sol. Cells*, 2010, 94: 2223
- 21 Chen, F., Zhou, R., Yang, L., Shi, M., Wu, G., Wang, M. and Chen, H.Z., *J. Phys. Chem. C*, 2008, 112: 13457
- 22 Lin, Y.Y., Lee, Y.Y., Chang, L., Wu, J.J. and Chen, C.W., *Appl. Phys. Lett.*, 2009, 94: 063308
- 23 Band, B.P., Burk, D.P. and Forrest, S.R., *Phys. Rev. B*, 2007, 75: 115327
- 24 Tai, Q., Zhao, X. and Yan, F., *J. Mater. Chem.*, 2010, 20: 7366
- 25 Jiang, X., Chen, F., Xu, H., Yang, L., Qiu, W., Shi, M., Wang, M. and Chen, H.Z., *Sol. Energy Mater. Sol. Cells*, 2010, 94: 338
- 26 Thompson, B.C. and Fréchet, J.M. J., *Angew. Chem. Int. Ed.*, 2008, 47: 58