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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Size-Dependent Surface Photovoltage in CdSe-Based Nanocrystal Thin Films

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Three different sizes (2.0 nm, 2.8 nm, and 4.9 nm) of highly monodisperse zinc blende CdSe nanocrystals have been selected to construct heterojunctions with and without ZnO particles. To investigate photoinduced charge transfer at CdSe/ITO and CdSe/ZnO/ITO heterojunctions, surface photovoltage (SPV) and surface photovoltage spectroscopy (SPS) have been employed. All the SPV responses observed in CdSe/ITO junctions have involved a higher energy band corresponds than the band-gap excitation of CdSe. Based on the SPV measurements, the photovoltage response is a function of nanocrystal's sizes and it generally has a red shift as the diameter of CdSe nanocrystals increases. For CdSe/ZnO/ITO heterojunctions, photovoltage responses have been increased up to 10 times compared to bare CdSe. This suggests that good alignment of energy levels between CdSe and ZnO is formed and an efficient charge transfer may occur. From the studies of SPV transient spectra of these junctions, the excitations above the band gap of ZnO generally show fast decay rate.

1. Introduction

Conversion between photonic energy and electronic energy is technologically important and provides plenty of opportunities to study fundamental physical phenomena and apply in potential applications.¹⁻³ During the past decade, we have experienced rapid growth of inorganic semiconductor nanocrystal based solar cells, photodetectors, and light emitting diodes (LEDs).⁴⁻⁸ In particular, CdSe based nanocrystals as emissive layer has been sandwiched between a hole transport layer (HTL) and an electron transport layer (ETL) to fabricate stable and efficient LEDs, or as blending layer with conjugated polymers to form hybrid photovoltaic cells.⁷⁻¹⁰

Recent studies indicates that the device performance has been greatly improved with the incorporation of the ZnO nanoparticles as ETL⁷ in LEDs or as buffer layer⁸ in hybrid solar cells, which have the potential promise of future large-area displays, solid states lighting, and solar cells. The essence of photovoltaic effect harvests photonic energy and converts it to electronic form in solar cells. Conversely, the electroluminescence phenomena are converting electronic energy to photonic energy. As a result, there has been great interest in photoinduced charge transfer in LEDs and solar cells based on

inorganic nanocrystals. Understanding charge-transfer mechanisms at the junction of semiconductor nanocrystals and related metal oxides (such as ZnO) is a key issue to discover common physics governing both LED devices and solar cells. Therefore, we hope to gain intrinsic information about charge transfer behaviors across inorganic semiconductor junctions and provide further guidance in the design of LEDs and solar cells.

To monitor charge transfer across such inorganic semiconductor junction, surface photovoltage (SPV) and surface photovoltage spectroscopy (SPS) have been employed, which measure those optical absorption bands followed by charge transfer across the interfaces.¹¹⁻¹⁵ These are the optical absorption bands that contribute to the photovoltaic effect. In this paper, we have constructed CdSe/ITO and CdSe/ZnO/ITO heterojunctions using different sizes of CdSe nanocrystals with and without ZnO particles and investigated photoinduced charge transfer at their junctions. SPV and SPS are especially versatile for investigating charge-transfer phenomena, we have found that photoinduced charge transfer occurred at the CdSe/ITO and CdSe/ZnO/ITO junction. SPV of CdSe nanocrystals in CdSe/ITO junction is size-dependence, the smaller the size of CdSe nanocrystals, and the more blue shift of its SPV. For CdSe/ZnO/ITO junctions, its SPV responses have been increased up to 10 times compare to bare CdSe's SPV. This result may provide some fundamental information for the studies of charge transfer/separation behaviors in nanocrystals-based LED and solar cells.

2. Experimental

2.1 Materials

All reagents were used as received without further experimental purification. Cadmium oxide (CdO, 99.99%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), zinc acetate (99.99%), dimethyl sulphoxide (DMSO, 99.7%), tetramethylammonium hydroxide (TMAH, 97%), and selenium (Se, 99.99%, powder) were purchased from Aldrich. Hexanes (analytical grade), paraffin oil (analytical grade), ethanol (analytical grade), and methanol (analytical grade) were obtained from Beijing Chemical Reagent Ltd., China.

2.2 Synthesis of CdSe nanocrystals

CdSe nanocrystals were prepared according to the previous literature of our group.¹⁶ In a typical synthesis, CdO (0.0154 g, 0.12 mmol), oleic acid (0.36 mmol), and ODE were loaded in a

25 mL three-neck flask and heated to 240 °C under nitrogen flow to obtain a clear colorless solution, then it was heated to 280 °C, 2 mL Se precursor (0.237 g of Se and 30 mL of ODE were mixed in a 100 mL three-neck flask heated to 220 °C for 180 min, and then the reaction solution was cooled to room temperature.) was injected and maintained at 260 °C for certain time for the formation of different CdSe nanocrystals. Three sizes of CdSe nanocrystals with emission at 513 nm, 579 nm, and 634 nm were synthesized, respectively.

2.3 Synthesis of ZnO nanocrystals.

ZnO nanocrystals were synthesized by a solution-precipitation process using Zn acetate and TMAH.⁷ For a typical synthesis, a solution of zinc acetate in DMSO (0.5 M) and 30 mL of TMAH in ethanol (0.55 M) were mixed and stirred for 1 h in ambient air, then washed and dispersed in ethanol at a concentration of ~ 30 mg mL⁻¹.

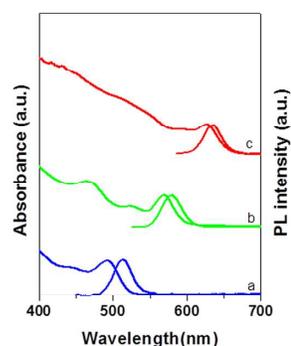


Fig 1. UV-vis absorption and photoluminescence spectra of CdSe nanocrystals with particle size of (a) 2.0 nm, (b) 2.8 nm, and (c) 4.9 nm, respectively. The fractions of CdSe nanocrystals were diluted to similar absorption intensity for the measurement. Note that the spectra are normalized and shifted for clarity.

2.4 Fabrication of CdSe and CdSe/ZnO thin films

CdSe and CdSe/ZnO thin films were fabricated on glass substrates coated with ITO with a sheet resistance of ~20 Ω sq⁻¹. The substrates were cleaned with deionized water, acetone, and isopropanol, consecutively, for 15 min each, and then treated for 15 min with ozone generated by ultraviolet light in air. To prepare CdSe thin films, these substrates were spin-coated using 60 μL of CdSe nanocrystal solutions (2,000 rpm for 30 s), followed by baking at 160 °C for 20 min in a vacuum oven. To fabricate CdSe/ZnO thin films, these substrates were first spin-coated using 40 μL of ZnO solutions (3,000 rpm for 30 s), immediately followed by another spin-coating with 60 μL of CdSe nanocrystal solutions (2,000 rpm for 30 s), then they were baked at 160 °C for 20 min in a vacuum oven. The spin speed is 2,000 rpm for the CdSe layer and 3,000 rpm for the ZnO layer to achieve layer thickness of ~ 20 nm and ~ 30 nm, respectively.

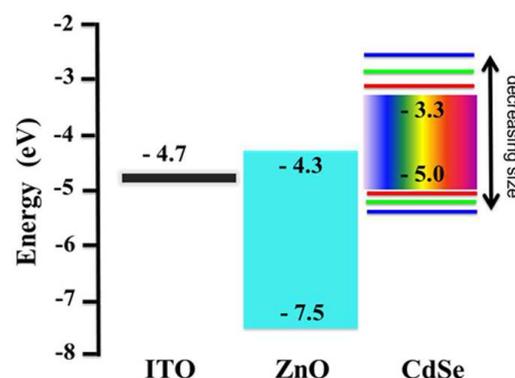
2.5 Kelvin Probe Measurements

A commercial Kelvin probe system (KP-6500 Digital Kelvin Probe System, McAllister Technical Services) was integrated with a light source to determine the work function changes. This apparatus measures the contact potential difference (CPD)

between a reference plate and the sample's surface. CPD is defined as the work function of the reference plate connected to the preamplifier minus the work function of the sample, that is, $\phi_m - \phi_{sam}$ (where ϕ_m is the work function of the reference plate (a constant), and ϕ_{sam} is the work function of the sample). By comparing the work function before and after deposition of CdSe or ZnO onto ITO substrate, the change in work function, $\Delta\phi_m$, after the deposition is obtained. The probe plate is made of stainless steel with a diameter of 2 mm. It was electrically connected via ground to the sample during the measurement. The typical distance between the reference plate of the probe and the sample was less than 1 mm and the oscillation frequency of the probe was 105 Hz.

2.6 Surface Photovoltage Spectroscopy (SPS)

For SPV response, the samples were illuminated from the backside of transparent substrate by monochromatic light, which was obtained by passing light from a 450-W xenon lamp through a monochromator (IHR 320). SPV spectra were obtained by scanning the wavelength of the incident light from the visible to UV range (300 - 600 nm) with grating #1 (range: 300 - 750 nm), or (400 - 800 nm) with grating #2 (range: 300 - 1500 nm) and 400 nm long pass color filter at a typical scanning rate of 30 nm/min. The raw SPV data were not corrected for the spectrum of the xenon lamp.



Scheme 1. Energy levels for CdSe, ZnO, and ITO, respectively.

3. Results and discussion

Figure 1 shows the UV-vis and photoluminescence (PL) spectra of highly monodisperse zinc blende CdSe nanocrystals in 3 different sizes. They have very sharp features in the absorption spectra, the estimated sizes of CdSe nanocrystals are 2.0 nm, 2.8 nm, and 4.9 nm by TEM images (Figure S1). Only band gap emissions have been observed, and are located at 513 nm, 579 nm, and 634 nm, respectively. The PL FWHMs are successfully controlled below 30 nm, and quantum yields are around 30 to 60% without any size sorting. As-synthesized CdSe nanocrystals were purified by repeated precipitation with methanol and redispersion in hexanes several times to remove free surface ligands. Then, they were stored in hexanes for further studies.

SPS has been proven to be a useful technique to study charge transfer/separation behaviors between heterojunction multilayers.¹¹⁻¹³ Therefore, it has been used here to study CdSe nanocrystals based thin films' photo-induced behaviors. First, a

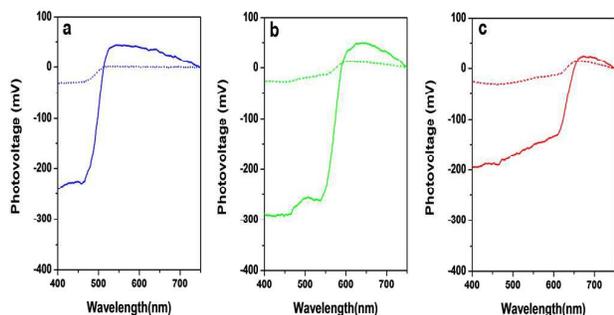


Fig 2. Surface photovoltage spectra of CdSe/ITO (dot lines) and CdSe/ZnO/ITO (solid lines). Particle sizes of CdSe nanocrystals are 2.0 nm (blue), 2.8 nm (green), and 4.9 nm (red), respectively.

solution-based spin-coating method has been used to construct CdSe nanocrystal based CdSe/ITO junction. Because of widely used as the electron injection/transfer layer on ZnO particles, we adopted it as an adjacent layer between CdSe nanocrystals and ITO to form CdSe/ZnO/ITO junction. The corresponding flat band energy level diagram is shown in Scheme 1 and these values are taken from the literature.¹⁷ The position of ITO is located at -4.7 eV, the conduction and valence bands of ZnO are located at -4.3 eV and -7.5 eV, respectively. For CdSe, the band gap energy of 1.7 eV, which is the bulk value. The CdSe nanocrystal's conduction band minimum and band gap energy values will change according to the size of the CdSe nanocrystals. Because of the small electron effective mass ($m_e=0.13m_0$) versus the significantly larger hole mass ($m_h=1.14m_0$), most of the band gap increase has been seen as a shift in the conduction band to more negative potentials (vs NHE).¹⁸ As the size of the CdSe nanocrystals decreases to the smallest size of 2.0 nm with a band gap energy of ~ 2.4 eV, this causes the conduction band minimum to rise to ~ 2.6 eV on the vacuum energy level diagram.

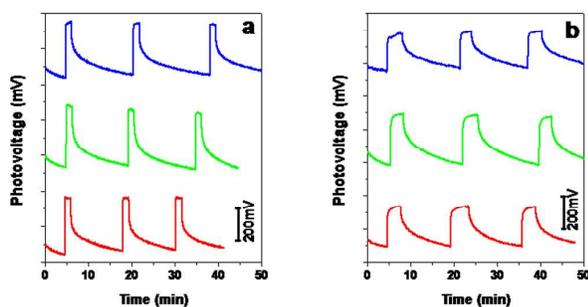


Fig 3. Surface photovoltage transient spectra of CdSe/ZnO/ITO junction at different wavelengths. (a) Excitation at 350 nm, which correspond to the ZnO band gap; (b) Excitation at 462 nm, 536 nm, and 610 nm, which correspond to 2.0 nm (blue), 2.8 nm (green), and 4.9 nm (red) CdSe nanocrystals, respectively.

In fact, photo-induced charge transfers between inorganic semiconductor (CdSe, CdS *etc.*) nanocrystals and metal oxides (SiO_2 , SnO_2 , TiO_2 , and ZnO *etc.*) heterojunctions have being widely studied recently, the majority method of these studies was using ultrafast transient absorption spectroscopy.¹⁹⁻²¹ Photo-induced electron transfers have been observed from inorganic nanocrystals to metal oxide nanoparticles and generally showed the agreement of the many-state Marcus model.²⁰ Here we use

SPS technique to study photo-induced charge transfers between ZnO and CdSe nanocrystals interfaces. Figure 2 shows the SPV spectra from CdSe/ITO and CdSe/ZnO/ITO junctions. First, we started with measuring SPV spectra for CdSe nanocrystals only. Three sizes of CdSe nanocrystals have been used to build CdSe/ITO junctions. For 2.0 nm CdSe nanocrystals, there was one broad peak, centered at 462 nm with a photovoltage of ~ 25 mV. We observed a photovoltage of ~ 25 mV at 536 nm for 2.8 nm CdSe nanocrystals/ITO junction. Similar photovoltage response has also been observed when 4.9 nm CdSe nanocrystals was used, there was only one peak located at 610 nm with a value of ~ 30 mV. It is clearly shown that the SPV is size-dependence. The smaller the size of CdSe, the more blue shift of its SPV. Thereafter, all the SPV responses show higher energy bands correspond than the band-gap excitation of CdSe.

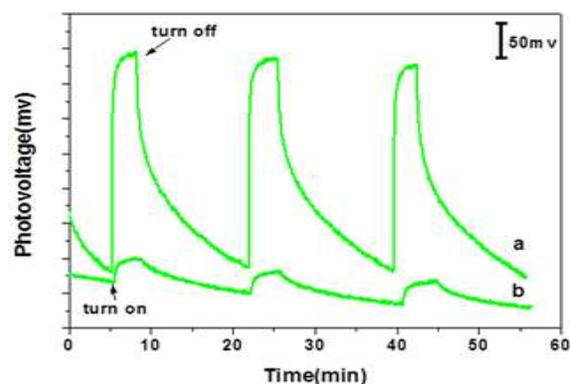


Fig 4. The comparison of surface photovoltage transient spectra of 2.8 nm CdSe nanocrystals in (a) CdSe/ZnO/ITO junction and (b) CdSe/ITO junction. Excitation at 536 nm, which correspond to the CdSe band gap.

For CdSe/ZnO/ITO junctions, photovoltage responses have been increased greatly, especially in the range above the band gap of related CdSe nanocrystals. For example, the photovoltage of ~ 270 mV at 462 nm has been obtained when 2.0 nm CdSe nanocrystals was used to form CdSe/ZnO junction. It is about 10 times increase compare to bare CdSe's SPV. This suggests that an efficient charge transfer may occur and good alignment of energy levels between CdSe and ZnO is formed. SPS of CdSe/ZnO ranges from 300 nm to 600 nm have been shown in Figure S3. A new peak positioned at 350 nm is contributed from the band gap of ZnO. Recent report also indicates that there is strong charge transfer between nanocrystal layers and ZnO layers. And such interfacial charge transfer processes may enhance the emission stability of nanocrystal emitters.¹

Generally, the dynamic nature of interfaces and junctions can be determined by photovoltage transient.^{11,13} Photoinduced transitions and recombination transitions among certain states may be monitored by switch the light on and off at related wavelength. In the early stage of light-on process, photovoltage increases because the build-in barrier diminishes. Steady photovoltage is reached when photoinduced and recombination rates are balanced. The SPV transient spectra of the CdSe/ZnO/ITO junction excited at different wavelengths have been shown in Figure 3. For the excitation energy at the band gap of ZnO (350 nm), SPVs reach its highest response rapidly for all

three sizes of CdSe nanocrystals. The decay rate is fast too and they can easily drop back to the ground value when the light is turned off. Similar SPV transient response has also been observed in TiO₂ nanoparticles.¹³ This indicates that the photo-induced charge transfer/separation behaviors have very high efficiency when the excitations above the band gap of metal oxides. If the excitations below the band gap of ZnO, but around CdSe's band gap, it needs a longer time to reach a steady SPV response. For CdSe/ITO junction, the SPV response is weak and will take long time for photovoltage to reach a steady response. The comparison of photovoltage transient spectra of 2.8 nm CdSe nanocrystals in CdSe/ZnO/ITO or CdSe/ITO junction is shown in Figure 4. When the light at 536 nm is turned on, the SPV reached ~300 mV for CdSe/ZnO/ITO junction, only ~34 mV is observed for CdSe/ITO junction.

4. Conclusions

In summary, three different sizes of highly monodisperse zinc blende CdSe nanocrystals have been chosen to construct heterojunctions with and without ZnO particles. Surface photovoltage (SPV) and surface photovoltage spectroscopy (SPS) have been employed to study the photo-induced charge transfer/separation behaviors at these heterojunctions. For CdSe/ITO junctions, all the SPV responses observed have involved a higher energy band corresponds than the band-gap excitation of CdSe. The smaller the size of CdSe, the more blue shift of its SPV. Therefore, it is clearly shown that the SPV is size-dependence. For CdSe/ZnO/ITO junctions, photovoltage responses have been increased greatly, especially in the range above the band gap of related CdSe nanocrystals. It is up to 10 times increase compare to bare CdSe's SPV. This suggests that an efficient charge transfer may occur and good alignment of energy levels between CdSe and ZnO is formed. The studies of SPV transient spectra of the CdSe/ITO and CdSe/ZnO/ITO junction excited at different wavelengths indicate that different SPV response rates have been observed. Generally, fast decay rate has been caught when the excitations above the band gap of ZnO. The importance of these findings may provide useful guidance on how to choose suitable nanocrystal thin films and adjust related heterojunctions in QLED and solar cell applications, such as to monitor charge transfer efficiency and optimize energy level's alignment by using SPS technique.

Acknowledgements

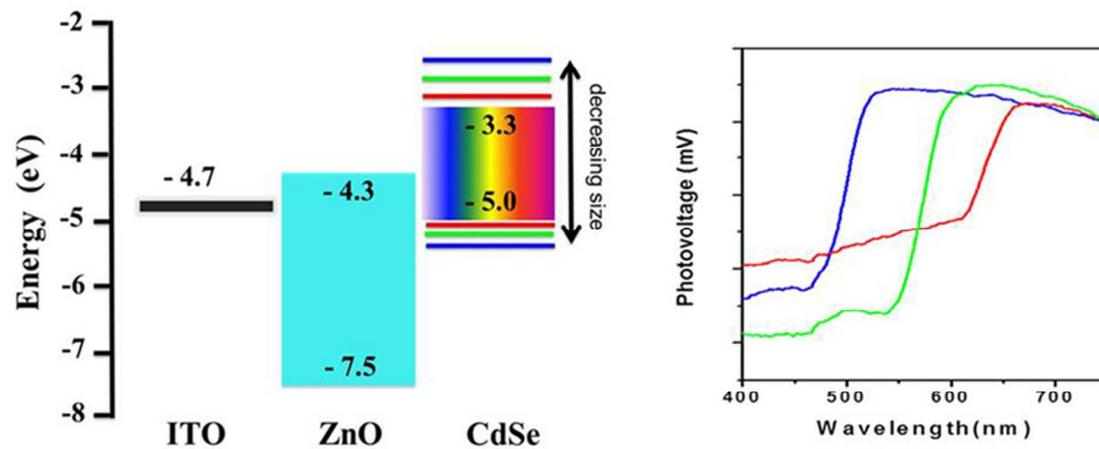
This work was financially supported by the research project of the National High Technology Research and Development Program of China (863 Program) (NO. 2013AA032204), National Natural Science Foundation of China (61474037), and Program for Changjiang Scholars and Innovative Research Team in University, (No. PCS IRT1126).

Notes and references

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1. B. S. Mashford, M. Stevenson, Z. Popovic, C. Hamilton, Z. Zhou, C. Breen, J. Steckel, V. Bulovic, M. Bawendi, S. Coe-Sullivan and P. T. Kazlas, *Nature Photonics*, 2013, **7**, 407-412.
2. M. G. Panthani, J. M. Kurley, R. W. Crisp, T. C. Dietz, T. Ezzyat, J. M. Luther and D. V. Talapin, *Nano Lett.*, 2014, **14**, 670-675.
3. M R Kim and D L Ma, *J. Phys. Chem. Lett.*, 2015, **6**, 85-99.
4. V. L. Colvin, M. C. Schlamp and A. P. Alivisatos, *Nature*, 1994, **370**, 354-357.
5. I. L. Medintz, H. T. Uyeda, E. R. Goldman and H. Mattoussi, *Nature Materials*, 2005, **4**, 435-446.
6. Q. J. Sun, Y. A. Wang, L. S. Li, D. Y. Wang, T. Zhu, J. Xu, C. H. Yang and Y. F. Li, *Nature Photonics*, 2007, **1**, 717-722.
7. L. Qian, Y. Zheng, J. Xue and P. H. Holloway, *Nature Photonics*, 2011, **5**, 543-548.
8. L. Qian, J. H. Yang, R. J. Zhou, A. W. Tang, Y. Zheng, T. K. Tseng, D. Bera, J. G. Xue and P. H. Holloway, *J. Mater. Chem.*, 2011, **21**, 3814-3817.
9. H. B. Shen, Q. L. Lin, H. Z. Wang, L. Qian, Y. X. Yang, A. Titov, J. Hyvonen, Y. Zheng and L. S. Li, *ACS Appl. Mater. Interfaces.*, 2013, **5**, 12011-12016.
10. H. B. Shen, X. W. Bai, A. Q. Wang, H. Z. Wang, L. Qian, Y. X. Yang, A. Titov, J. Hyvonen, Y. Zheng and L. S. Li, *Adv. Funct. Mater.*, 2014, **24**, 2367-2373.
11. L. Kronik and Y. Shapira, *Surf. Sci. Rep.*, 1999, **37**, 1-206.
12. L. S. Li, Q. X. Jia and A. D. Q. Li, *Chem. Mater.*, 2002, **14**, 1159-1165.
13. A. D. Q. Li and L. S. Li, *J. Phys. Chem. B.*, 2004, **108**, 12842-12850.
14. D. Gross, I. Mora-Seró, T. Dittrich, A. Belaidi, C. Mauser, A. Houtepen and E. D. Coco, *J. Am. Chem. Soc.*, 2010, **132**, 5981-5983.
15. L. Barnea-Nehoshtan, S. Kirmayer, E. Edri, G. Hodes and D. Cahen, *J. Phys. Chem. Lett.*, 2014, **5**, 2408-2413.
16. H. B. Shen, H. Z. Wang, Z. J. Tang, J. Z. Niu, S. Y. Lou, Z. L. Du and L. S. Li, *CrystEngComm*, 2009, **11**, 1733-1738.
17. G. Chris, W. Van de and J. Neugebauer, *Nature*, 2003, **423**, 626-628.
18. O. B. Dabbousi, J. Rodriguez-Viejo and V. F. Mikulec, *J. Phys. Chem. B.*, 1997, **101**, 9463-9475.
19. I. Robel, M. Kuno and V. P. Kamat, *J. Am. Chem. Soc.*, 2007, **129**, 4136-4137.
20. K. Tvrđy, P. A. Frantsuzov and P. V. Kamat, *PNAS*, 2011, **108**, 29-34.
21. T. B. Spann, V. S. Bhat and Q. Nian, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10669-10678.



Surface photovoltage spectroscopy (SPS) has been employed to study photovoltage responses of CdSe nanocrystal based heterojunctions with and without ZnO particles.