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## Effects of bifunctional linker on the optical properties of ZnO nanocolumn-linker-CdSe quantum dots heterostructure

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### ABSTRACT

We study the effects of bifunctional linker on the optical properties of ZnO nanocolumn-linker-CdSe quantum dots heterostructure. The CdSe quantum dots are anchored on the surface of ZnO nanocolumns through either aliphatic linker of 3-aminopropyl trimethoxysilane (APS) or aromatic linker of p-aminophenyl trimethoxysilane (APhS). X-ray photoelectron spectroscopy is used to confirm the bifunctional linker bound onto CdSe quantum dots and onto the ZnO nanocolumns. The TEM study reveals a CdSe quantum dot shell of about 15 nm coated on the ZnO nanocolumns. The photoluminance (PL) spectroscopy and time-resolved PL spectroscopy of ZnO nanocolumn-linker-CdSe quantum dots reflects that the photo-induced electron transfer across the interface of ZnO and CdSe through the aromatic APhS is more efficient than the aliphatic APS. This study demonstrates that through the usage of appropriate surface linker, the charge transfer rate across the interfaces of donor/acceptor (D/A) heterostructure can be improved for potential photovoltaic cell applications.

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### 1. Introduction

Surface modification has been widely studied due to its various applications. The surface modification plays an important role for the fabrication of high performance electronic devices, such as biosensors [1], LEDs [2] and solar cells [3–6]. The interfaces between layers or materials show great influences on the performance of devices. In this study, we have fabricated the heterostructure of donor/acceptor (D/A) with interfacial molecular linker and studied the effects of interfacial linker on the properties of heterojunction of D/A. The heterojunction of D/A has been widely used in photovoltaic cell applications. In the heterojunction of D/A, electron donor harvests light and generate excitons. Excitons separate into electrons and holes at the interfaces between donor and acceptor instead of recombination. Finally, the electron is accepted by the acceptor. Efficient charge transfer across the D/A heterojunction is imperative for efficient photovoltaic energy conversion. The role of the interfacial modifier between donor and acceptor is essential in the charge separation procedures across the D/A interfaces [7–9].

In this study, a thin shell of CdSe quantum dots is coated on the surface of ZnO nanocolumns through utilizing bifunctional linkers.

The technique of self-assembly of linker exhibits the ability to achieve effective anchoring of CdSe quantum dots onto ZnO surface and allows a uniform coverage. This approach also allows a careful control of the quantum dot properties, like size and shape which is not possible with the direct growth of quantum dots on semiconductor surface [7]. The ZnO nanocolumn-linker-CdSe quantum dots we fabricated can be applied for a variety of photovoltaic device applications. The mercaptopropionic acid has been employed to link CdSe quantum dots to ZnO nanorod arrays to fabricate solar cell [8]. Other researchers have been employed mercaptopropionic acid, thiolacetic acid, mercaptohexadecanoic acid, thioglycolic and cysteine to link CdSe quantum dots to TiO<sub>2</sub> in photovoltaic cells. The performances of D/A heterostructure with linker molecules for photovoltaic devices have been widely studied [7,9,10].

The performances of CdSe/TiO<sub>2</sub> heterostructure with linker molecules for photovoltaic device have been studied [11–16] to gain deep insight into the influence of linker in the system. In this study, the CdSe quantum dot sensitized ZnO nanocolumn structure is considered as an alternative choice for the fabrication of quantum dot sensitized solar cells, due to it provides straight path for electron conduction [8,17]. Typically, the charge transfer at the interface of donor/acceptor structure is of critical to power conversion efficiency of photovoltaic cells. Since there are few studies on the CdSe quantum dot sensitized ZnO electrode, the interface properties between the CdSe and ZnO is not well known and believed not optimized. We would like to develop a CdSe sensitized ZnO

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nanocolumn structure with effective charge transfer at interface and is suitable for photovoltaic applications.

Apart from the potential excellent electron transport of ZnO nanocolumn and the ease of control over the size, size distribution of quantum dot for linker assisted attachment [7], an additional advantage in the CdSe quantum dot-bifunctional linker-ZnO nanocolumn is the uniform coverage of the CdSe layer. A former study reported that a dense and continuous CdSe/CdS core-shell nanoparticle film on ZnO nanocolumn can be obtained by using the bifunctional linker [18]. The coverage and loading of the CdSe layer is important to the performance of photovoltaic cells [19]. The low loading and coverage of quantum dots on TiO<sub>2</sub> surface in some of the quantum dot sensitized nano-porous films has been attributed to two main reasons [12], one of which is much of the porous surface is inaccessible due to small pores. The second is competitive adsorption due to free capping groups or other molecular impurities that may interfere with desired surface attachment reaction. The metal oxide substrate consisting of nanowires and nanotubes can enable and improve the access of quantum dots to its surface with higher loadings [12].

The structure of linker molecule between the quantum dots and the ZnO can affect both the electronic structure at the interface [8] and leads to different charge transfer rate at interface upon illumination. The optical and electronic properties of the ZnO nanocolumn-bifunctional linker-CdSe quantum dots heterojunction can be varied by utilizing different type of linker. Two linkers, 3-aminopropyl trimethoxysilane (APS) and p-aminophenyl trimethoxysilane (APhS) are used in this study. Differences in optical properties, photoluminance (PL) and time-resolved PL decay spectra, for ZnO nanocolumn-bifunctional linker-CdSe quantum dots are obtained due to the influence of linker structure on the kinetics of charge separation. The photogenerated electron transfer from CdSe quantum dots to ZnO nanocolumns is more efficient by aromatic linker: p-aminophenyl trimethoxysilane.

## 2. Materials and methods

ZnO nanocolumns were grown in a 2 inch quartz tube which was inserted to a two-temperature-zone furnace [20]. Zinc acetylacetonate (98%, Alfa Aesar) placed on a cleaned Pyrex glass container and Si(100) substrates were loaded into the low-temperature and the high-temperature zones of the furnace, respectively. A N<sub>2</sub>/O<sub>2</sub> flow was employed to carry the vaporized Zn precursor to the high-temperature zone for ZnO nanocolumn growth. The temperatures for vaporizing Zn precursor and ZnO nanocolumn growth are 125 and 600 °C, respectively. A total pressure of 200 torr was maintained during growth. The materials were purchased and used as received.

The CdSe nanoparticles were grown according to procedures described in the literature [21]. The reaction mixture was heated up to 320 °C, and then was cooled down to 240 °C. As the colour of the solution changed from brick red to transparent, the solution of Se powder (0.025 g, 99%, Aldrich) dissolved in tri-n-butylphosphine (TBP, 1 ml 95%, Acros) was added into the flask. The obtained CdSe quantum dots were allowed to age at 240 °C for 1 min before cooling to room temperature. By adding 1.5 ml of methanol (99.99%, Acros) into the reaction flask, quantum dots of CdSe were precipitated and collected by centrifugation. To remove excess TOPO, repeated methanol washings were performed and followed by centrifugation. Finally, TOPO passivated CdSe quantum dot powder is obtained.

The preparation method of the hetero-structures of ZnO-linker-CdSe has been described in other reports [18,22]. To obtain the 3-aminopropyl trimethoxysilane (APS, Acros) modified ZnO nanocolumn, a ZnO nanocolumn film on substrate (0.5 × 0.5 cm<sup>2</sup>) was

firstly immersed in 6 g of anhydrous dimethyl sulfoxide (DMSO, Acros). Then 0.54 g of APS was injected into this system at room temperature. After the mixture was being heated to 130 °C for 2 h, it was cooled to room temperature. To remove excess APS, the obtained ZnO nanocolumn film was washed three times with ethanol. To prepare ZnO-APS-CdSe film on substrate, the CdSe nanoparticles (0.03 g) were dispersed in 3 ml of toluene and the APS modified ZnO film on substrate was immersed into the mixture and then stirred for 24 h. The produced ZnO-APS-CdSe film on substrate was then washed three times with toluene to remove excess CdSe nanoparticles.

To prepare p-aminophenyl trimethoxysilane (APhS, Gelest) modified ZnO nanocolumns, the preparation method is similar to that of APS modified ZnO nanocolumns. A ZnO nanocolumn film on substrate (0.5 × 0.5 cm<sup>2</sup>) was immersed in 6.0 g of anhydrous DMSO (Acros) and then 0.64 g of p-aminophenyl trimethoxysilane was added into the system at room temperature. After the mixture was being heated to 130 °C for 2 h, it was cooled to room temperature. The obtained ZnO nanocolumn film was washed three times with ethanol to remove excess APhS. To prepare ZnO-APhS-CdSe film on substrate, the CdSe nanoparticles (0.03 g) were dispersed in 3 ml of toluene and the APhS modified ZnO film on substrate was immersed into the mixture and then stirred for 24 h. The produced ZnO-APhS-CdSe film on substrate was then washed three times with toluene to remove excess CdSe nanoparticles. Through the preparation procedures of hetero-structures of ZnO-linker-CdSe, a fraction of the TOPO on CdSe may be removed and this has led to slightly aggregation of CdSe nanocrystals.

The study of X-ray photoelectron spectroscopy (XPS) was performed by using an electron spectroscope for chemical analysis system (VG Scientific ESCALAB 250) under ultra high vacuum. For this study, both Mg and Al anodes driven at 400 W were used. All scans were obtained using the 0.5 cm<sup>2</sup> aperture and the typical surveys were collected for 5 min.

The steady-state photoluminescence (PL) spectroscopy was gathered by exciting the samples with a continuous wave He-Cd laser (325 nm). The obtained emission spectra were analyzed using a Jobin-Yvon TRIAX 0.55 m monochromator and were detected by a photomultiplier tube and standard photocounting electronics. Time-resolved PL spectra were obtained with a time-correlated single photon counting (TCSPC) spectrometer (Picoquant, Inc.). A pulse laser (375 nm) with an average power of 1 mW utilized for excitation was operating at 40 MHz with duration of 70 ps.

## 3. Results and discussion

Fig. 1 depicts the surface modification procedures of ZnO nanocolumns to obtain CdSe bound onto ZnO surface. The fabrication of the ZnO-linker-CdSe heterostructures follows the concept in the literature [18]. Bifunctional linkers with short chain length were selected to ensure the short distance between the two semiconductors enabling efficient electron transfer. The distance has dramatic effect on the interaction between two semiconductors. The extent of emission quenching is increased greatly with decreasing linker length [12,14,15]. While two semiconductors are coupled through a linker, this coupling is linker and temperature dependent. When a bridge between a donor and acceptor is made from conjugated molecules, it can better couple the donor and acceptor electronic states as compared to that made of saturated hydrocarbons [16]. The coupling through linker depends on the conformation of the linker, which is temperature dependent [16].

We have used the high temperature chemical vapor deposition method to grow good quality ZnO nanocolumns on Si substrate to minimize the detection of defect emission aside from CdSe quantum dots [21]. The morphology of the ZnO nanocolumns is

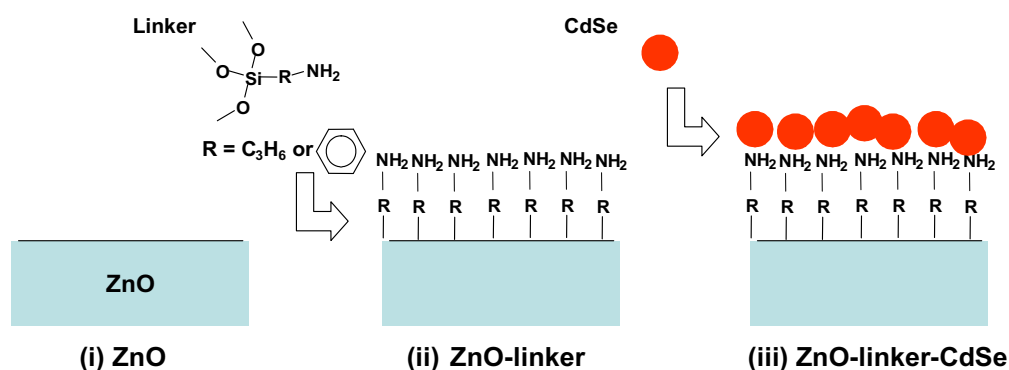


Fig. 1. Schematic illustration of the binding of CdSe quantum dots to ZnO nanocolumns by linker.

shown in Fig. 2. The size of the ZnO nanocolumns is about  $100\text{ nm} \times 400\text{ nm}$ .

According to Fig. 1, the reaction of the ZnO nanocolumns with 3-aminopropyl trimethoxysilane (or p-aminophenyl trimethoxysilane) produces APS-bound ZnO columns (or APhS-bound ZnO columns). In a subsequent reaction with TOPO-stabilized CdSe quantum dots in toluene, the coupling to yield CdSe quantum dots coated ZnO nanocolumns is undergone. In this reaction, the primary amine group from APS (or APhS) can attach the CdSe surface. CdSe, ZnO, ZnO-none-CdSe, ZnO-APS-CdSe, and ZnO-APhS-CdSe used here in this report represent TOPO capped CdSe quantum dot film, ZnO nanocolumn film, CdSe quantum dot film on ZnO nanocolumn film without linkers, APS as a linker between ZnO nanocolumns and the anchored CdSe quantum dot shell, and APhS as a linker between ZnO nanocolumns and the anchored CdSe quantum dot shell, respectively. TEM images of Fig. 3a and b shows that the CdSe quantum dots are coated on the ZnO surface by linkers, APS and APhS, respectively. From the EDS spectra in Fig. 3a and b, the Cd, Se, Zn, O peaks are observed indicating that the CdSe quantum dots are coated on ZnO nanocolumns. The Cd and Se peaks come from the CdSe quantum dots coated on ZnO nanocolumns, the Zn and O peaks come from the ZnO nanocolumns, and the P and C peaks come from the surfactant, TOPO, on the surface of the CdSe quantum dots. The film thickness of CdSe quantum dot on ZnO-APS-CdSe and ZnO-APhS-CdSe is about 15 nm. The size of CdSe quantum dots used here is about 3 nm. Thus, a thin shell of CdSe quantum dots is coated on the surface of ZnO.

High-resolution XPS spectra are used to study the surface chemistry of CdSe quantum dot coated ZnO nanocolumns (Fig. 4). The

spectrum shows that the TOPO capped CdSe quantum dots with Cd 3d5/2 peak ranged from 405 to 406 eV, which has a normal distribution centered at 405.6 eV in agreement with previously reported data[23] of  $405.5 \pm 0.2\text{ eV}$  (Fig. 4a). The Cd 3d5/2 and Cd 3d3/2 of XPS spectra of both ZnO-APS-CdSe and ZnO-APhS-CdSe deviate from those of the CdSe. This implies their surface states are different from those of the TOPO capped CdSe quantum dots. The deviations come from the linker binding on the surfaces of the CdSe quantum dots. Oxide peaks (CdO) as a doublet near 405 eV for Cd 3d [23] are not observed for CdSe, ZnO-APS-CdSe, and ZnO-APhS-CdSe. From above discussion, these indicate that the CdSe quantum dots are successful bound on the surface of the ZnO nanocolumns and the bound quantum dots are in good quality. In order to confirm that the CdSe quantum dots are bound

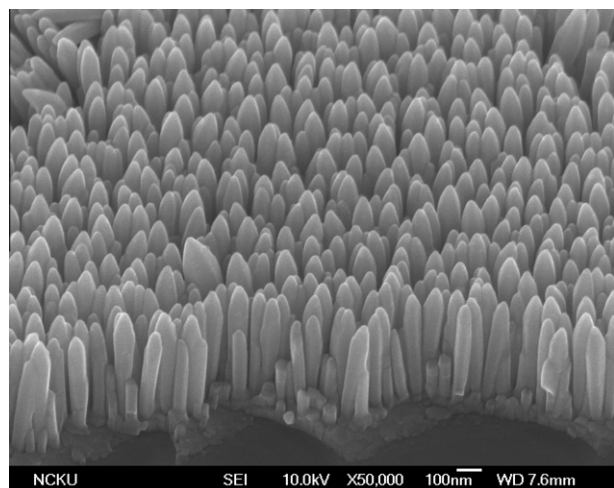


Fig. 2. SEM image of ZnO nanocolumns.

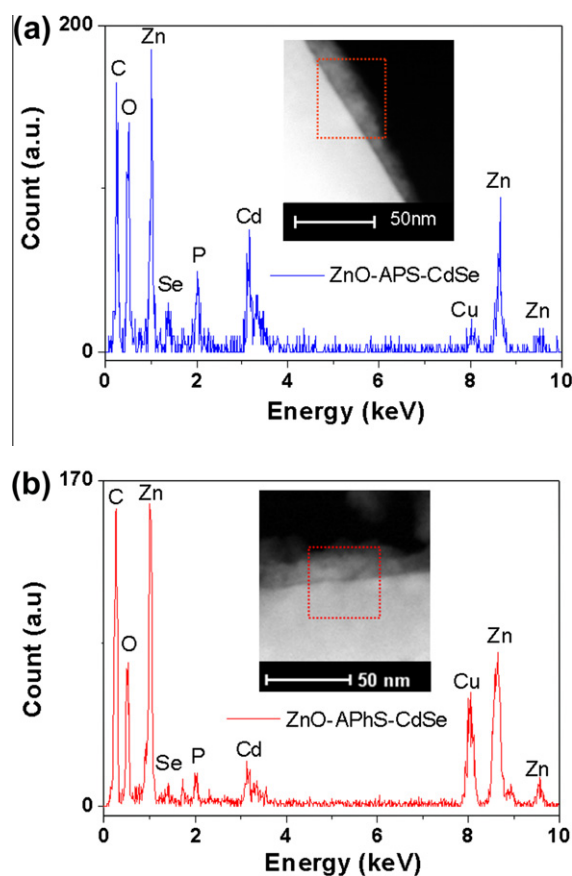


Fig. 3. EDS spectra and TEM images (inset) of (a) ZnO-APS-CdSe, and (b) ZnO-APhS-CdSe. Red lines of squares in (a) and (b) represent EDS range. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

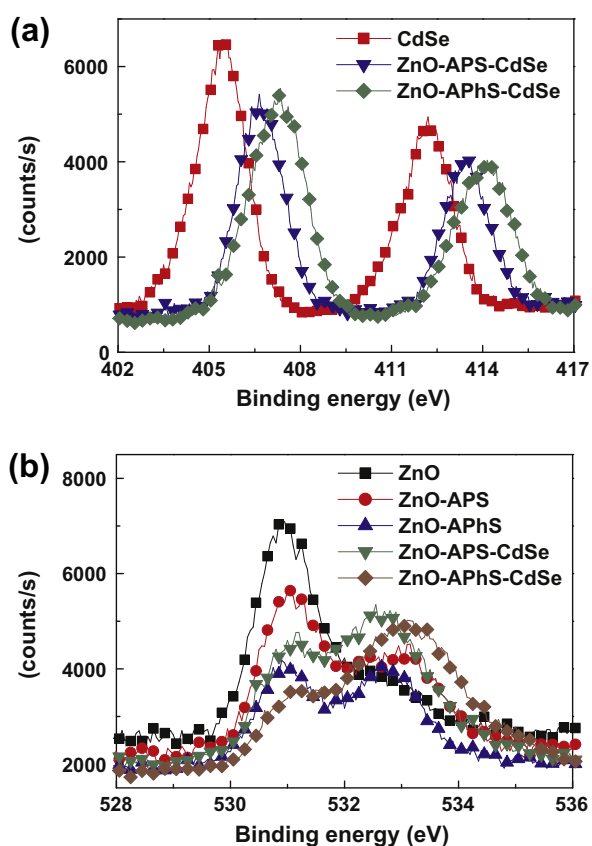


Fig. 4. XPS peaks of CdSe quantum dots coated on ZnO nanocolumns in two regions: (a) Cd 3d, (b) O 1s.

on the surfaces of ZnO nanocolumns through silane linker reacting with the Zn-OH on the surface of ZnO and forming Zn-O-Si, the O region of XPS spectra are taken. The O atoms of Zn-O are monitored for the O 1s peak position and found to be ranged from 530 to 532 eV, with a normal distribution centered about 530.7 eV [24]. The O atoms of Si-O are monitored for the O 1s peak positions of ZnO-APS, ZnO-APhS, ZnO-APS-CdSe, and ZnO-APhS-CdSe, and found to center about 533 eV [25]. The 533 eV peak position of ZnO nanocolumns represents the Si-O bond from using a silicon substrate in the XPS experiments. These results reflect that the CdSe quantum dots are successfully bound on the surface of ZnO nanocolumns by linker.

The PL spectrum of ZnO nanocolumns is shown in Fig. 5. The emission wavelength of ZnO nanocolumns is at 376 nm, which comes from the direct recombination of photon-generated charge carriers (excitonic emission) [26]. From Fig. 5, there is a very weak defect band (about at 530 nm) in our ZnO nanocolumns film. The defect band is caused by the intrinsic defects or oxygen vacancies in the ZnO [27,28]. The very weak defect emission implies that the quality in ZnO sample is good.

Schematic diagram of energy levels of CdSe with respect to ZnO is shown in Fig. 6. The size quantization of quantum dots can affect both the conduction band and the valence band. Varying the conducting band potential of CdSe quantum dot will increase the conducting band difference between ZnO nanocolumns and CdSe quantum dots. Additionally, introduce the interfacial linker can create an additional energy offset between energy levels of CdSe and ZnO, thus leads to differed charge injection rate.

The PL spectra of CdSe quantum dots coated ZnO nanocolumns are shown in Fig. 7. The concentrations of CdSe quantum dots on ZnO nanocolumns by different linkers are similar which can be determined from Cd amounts in XPS data. The ZnO-none-CdSe

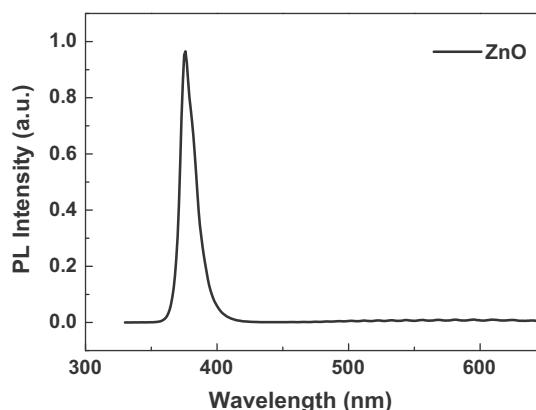


Fig. 5. Room temperature PL spectrum of a ZnO nanocolumn film.

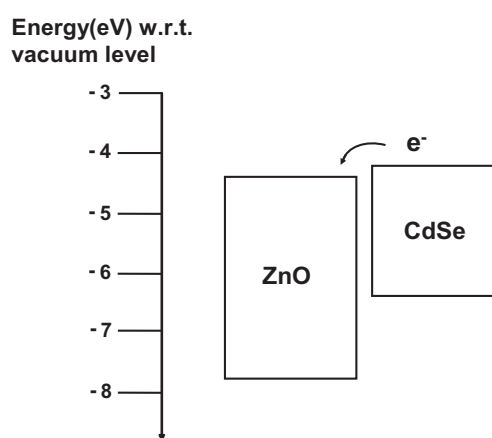


Fig. 6. Schematic energy level diagram for CdSe quantum dots with ZnO nanocolumns.

sample is prepared by spin coating CdSe quantum dot solution (the same concentration, 1% by wt., which is used in ZnO-APS-CdSe and ZnO-APhS-CdSe samples) on ZnO nanocolumn film. The concentrations of Cd from XPS data of the samples have shown that CdSe, ZnO-none-CdSe, ZnO-APS-CdSe, and ZnO-APhS-CdSe are 4.12%, 4.22%, 3.80%, and 4.17%, respectively. From the result, we can assume the concentrations of Cd are similar in the four samples. The PL intensity from the wavelength of 450 nm to 600 nm comes from the CdSe quantum dot emission, and the defect band emission of ZnO nanocolumns is negligible. Compared with TOPO

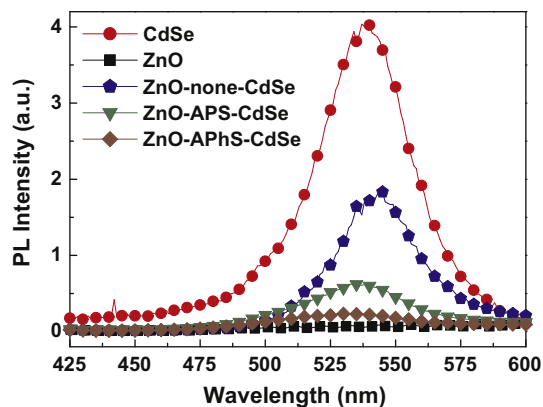


Fig. 7. PL spectra of heterostructures of CdSe quantum dots with ZnO nanocolumns as compared to CdSe quantum dot film or ZnO nanocolumn film.

capped CdSe quantum dots, we can find an obvious PL quenching in the samples of CdSe quantum dots with ZnO nanocolumns. The results indicated that ZnO/CdSe interface charge separation takes place as light irradiated CdSe quantum dots.

PL intensity of ZnO-none-CdSe sample is larger than those of ZnO-APS-CdSe and ZnO-ApHS-CdSe. This indicates that the existence of the linker can improve the charge transfer at the interface between CdSe quantum dots and ZnO nanocolumns due to good adhesion of CdSe or increased charge injection rate due to the introduced molecular linker. CdSe quantum dots without linkage cannot adhere well on the bare ZnO nanocolumns and may incline to form larger aggregation; the charge separation efficiency from these CdSe dots to ZnO nanocolumns is lowered as a result. We can also find the PL quenching efficiency of the ZnO-ApHS-CdSe is higher than that of ZnO-APS-CdSe. The aromatic ring in the linker of ZnO-ApHS-CdSe offers an effective route for electron transferring from CdSe quantum dots [29].

The kinetics of the interactions between CdSe and ZnO is gathered by the emission decay spectra using a 375 nm pulse laser as the excitation source. The emission intensity possesses a multi-exponential decay (Fig. 8). The explanation for the origin of multi-exponential emission decay of metal chalcogenides has been assigned due to influence of the trapping sites within the nanocrystal [29]. The obtained spectra are analyzed using bi-exponential decay kinetics which can be expressed by the following equation.

$$F(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \quad (1)$$

The CdSe, it posses a life time of 7.77 ns ( $a_1 = 0.45$ ) and 1.41 ns ( $a_2 = 0.50$ ), respectively. The emission life times ( $\tau_1$  and  $\tau_2$ ) decrease for the other samples. Among these samples, the emission life time of ZnO-ApHS-CdSe has shown the most significant decrease. For the charge separation at the interfaces between ZnO and CdSe quantum dots, this result reflects that the charge transfer at ZnO-ApHS-CdSe occurs faster than ZnO-none-CdSe and ZnO-APS-CdSe. Photogenerated charge carriers are transferred from CdSe to linker-ZnO through the aromatic ring preferably. In order to compare the emission life time among the samples, we have determined their average life time in the following by the following equation.

$$t = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \quad (2)$$

We have derived the average life time of each sample in the following by substituting the values of  $a_1$ ,  $a_2$ ,  $\tau_1$ , and  $\tau_2$  in Eq. (2). The obtained results are summarized in Table 1. The emission life time among these samples is in the ascending order as: ZnO-ApHS-CdSe (4.55 ns) < ZnO-APS-CdSe (6.01 ns) < ZnO-none-CdSe (6.67 ns) <

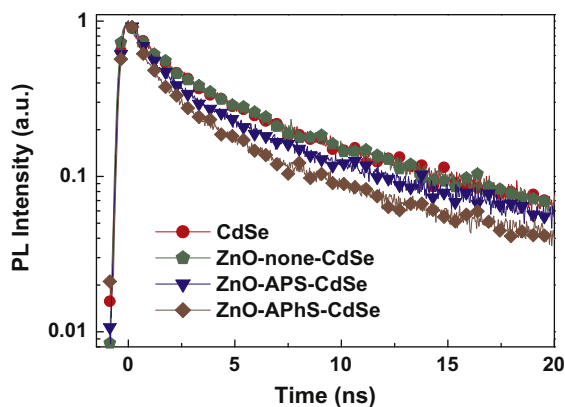


Fig. 8. PL lifetime decay heterostructures of CdSe quantum dots with ZnO nanocolumns as compared to CdSe quantum dot film.

Table 1  
Emission lifetime of CdSe quantum dots coated ZnO nanocolumns.

Sample	$\tau_1$ ( $a_1$ ) [ns]	$\tau_2$ ( $a_2$ ) [ns]	Avg. lifetime, [ns]
CdSe	7.77(0.45)	1.41(0.50)	6.70
ZnO-none-CdSe	7.69(0.46)	1.40(0.49)	6.67
ZnO-APS-CdSe	7.22(0.38)	1.18(0.58)	6.01
ZnO-ApHS-CdSe	5.61(0.35)	0.90(0.63)	4.55

CdSe (6.70 ns). The observed decrease in the PL intensity and emission life time corresponds to the mechanism of charge transfer which is critically depending on the presence of linkage and on the type of linker molecule. The sequence of the charge separation rate among the samples is then in the reversed order of their emission life time.

In the ZnO-linker-CdSe system, the bifunctional linker might contribute to the PL quenching. In previous studies, the CdSe quantum dot PL quenching induced by surface adsorbed molecule has been reported [13,29]. The ionization potential and electron affinity of interfacial layer of bifunctional linker are dependent on the structure of single molecule and the arrangement and packing of the molecules at the interface. The electronic properties of the interfacial layer can influence the electron transfer between the two semiconductors. This needs a detailed study in the future work.

In a related paper, the study on photovoltaic device photocurrent indicates that the photoanode of ZnO-ApHS-CdSe possesses higher photocurrent as compared to ZnO-APS-CdSe[22]. The increased number of charge collected under illumination reflects the improved charge transfer from CdSe to ZnO in ZnO-ApHS-CdSe. As the PL study in this paper is integrated with the photocurrent result, it is more convincing to speculate that more significant PL quenching in ZnO-ApHS-CdSe reflecting more efficient charge transfer at interface from CdSe to ZnO as compared to ZnO-APS-CdSe here.

#### 4. Conclusions

We have successfully bound CdSe quantum dots to ZnO nanocolumns through either aliphatic APS or aromatic ApHS bifunctional linkers. The exciton life time of either ZnO-APS-CdSe or ZnO-ApHS-CdSe is shorter than that of ZnO-none-CdSe reflecting that the photogenerated electrons in CdSe are more effectively scavenged with the usage of the linkers. The exciton life time of ZnO-ApHS-CdSe is shorter than that of ZnO-APS-CdSe, which reveals the photogenerated electrons in CdSe transferred through aromatic linker with higher efficiency. The usage of proper linker at the interface can facilitate tuning the charge transfer rate leads to improved optical and electronic properties of ZnO-linker-CdSe heterostructure of D/A for photovoltaic device applications.

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#### References

- [1] S. Flink, F.C.J.M. van Veggel, D.N. Reinhoudt, Adv. Mater. 12 (2000) 1315.
- [2] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holmes, Nature 347 (1990) 539.
- [3] W.U. Huynh, J.J. Dittmer, A.P. Alivisatos, Science 29 (2002) 2425.
- [4] R. Zhu, C.Y. Jiang, B. Liu, S. Ramakrishna, Adv. Mater. 21 (2009) 994.
- [5] Y.Y. Lin, T.H. Chu, S.S. Li, C.H. Chuang, C.H. Chang, W.F. Su, C.P. Chang, M.W. Chu, C.W. Chen, J. Am. Chem. Soc. 131 (2009) 3644.
- [6] J. Bouclé, S. Chyla, M.S.P. Shaffer, J.R. Durrant, D.D.C. Bradley, J. Nelson, Adv. Funct. Mater. 18 (2008) 622.

- [7] I. Mora-Seró, S. Giménez, T. Moehl, F. Fabregat-Santiago, T. Lana-Villareal, R. Gómez, J. Bisquert, *Nanotechnology* 19 (2008) 424007.
- [8] K.S. Leschkies, P. Divakar, J. Basu, E. Enache-Pommer, J.E. Boercker, C.B. Carter, U.R. Kortshagen, D.J. Norris, E.S. Aydil, *Nano Lett* 7 (2007) 1793.
- [9] I. Robel, V. Subramanian, M. Kuno, P.V. Kamat, *J. Am. Chem. Soc.* 128 (2006) 2385.
- [10] T. López-Luque, A. Wolcott, L.P. Xu, S. Chen, Z. Wen, J. Li, E. De la Rosa, J.Z. Zhang, *J. Phys. Chem. C* 112 (2008) 1282.
- [11] I. Mora-Seró, J. Bisquert, *J. Phys. Chem. Lett.* 1 (2010) 3046.
- [12] D.F. Watson, *J. Phys. Chem. Lett.* 1 (2010) 2299.
- [13] D.R. Baker, P.V. Kamat, *Langmuir* 26 (2010) 11272.
- [14] R.S. Dibble, D.F. Watson, *J. Phys. Chem. C* 113 (2009) 3139.
- [15] M. Wu, P. Mukherjee, D.N. Lamont, D.H. Waldeck, *J. Phys. Chem. C* 114 (2010) 5751.
- [16] G. Gotesman, R. Naaman, *J. Phys. Lett.* 1 (2010) 594.
- [17] P. Ravirajan, A.M. Peiro, M.K. Nazeeruddin, M. Graetzel, D.D.C. Bradley, J.R. Durrant, J.J. Nelson, *J. Phys. Chem. B* 110 (2006) 7635.
- [18] S. Giménez, T. Lana-Villareal, R. Gómez, S. Agouram, V. Muñoz-Sanjosé, I. Mora-Seró, *J. Appl. Phys.* 108 (2010) 064310.
- [19] J.J. Wu, D.K.P. Wong, *Adv. Mater.* 19 (2007) 2015.
- [20] Y.Y. Lin, C.W. Chen, J. Chang, T.Y. Lin, I.S. Liu, W.F. Su, *Nanotechnology* 17 (2006) 1260.
- [21] J.Y. Kim, F.E. Osterloh, *J. Am. Chem. Soc.* 127 (2005) 10152.
- [22] T.W. Zeng, I.S. Liu, F.C. Hsu, K.T. Huang, H.C. Liao, W.F. Su, *Opt. Express* 18 (2010) A357.
- [23] J.E. Bowen Katari, V.L. Colvin, A.P. Alivisatos, *J. Phys. Chem.* 98 (1994) 4109.
- [24] X.Q. Wei, B.Y. Man, M. Liu, C.S. Xue, H.Z. Zhuang, C. Yang, *Physica B* 388 (2007) 145.
- [25] T.L. Barr, *J. Vac. Sci. Technol. A* 9 (1991) 1793.
- [26] Y. Chen, D.M. Bagnall, H.J. Koh, K.T. Park, K. Hiraga, Z. Zhu, T. Yao, *J. Appl. Phys.* 84 (1998) 3912.
- [27] K. Vanheusden, W.L. Warren, C.H. Seager, D.K. Tallant, J.A. Voigt, B.E. Gnade, *J. Appl. Phys.* 79 (1996) 7983.
- [28] M.H. Huang, Y. Wu, H. Feick, N. Tran, E. Webber, P. Yang, *Adv. Mater.* 13 (2001) 113.
- [29] I.S. Liu, H.H. Lo, C.T. Chien, Y.Y. Lin, C.W. Chen, Y.F. Chen, W.F. Su, S.C. Liou, *J. Mater. Chem.* 18 (2008) 675.