



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

Tsung-Wei Zeng^a, I-Shuo Liu^a, Kuo-Tung Huang^a, Hsueh-Chung Liao^a, Chih-Tao Chien^a, Daniel Kwan-Pang Wong^b, Chun-Wei Chen^a, Jih-Jen Wu^b, Yang-Fang Chen^c, Wei-Fang Su^{a,*}

^a Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan

^b Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

^c Department of Physics, National Taiwan University, Taipei, Taiwan

ARTICLE INFO

Article history:

Received 25 August 2010

Accepted 1 March 2011

Available online 8 March 2011

Keywords:

Quantum dot

Nanocolumn

Linker

Heterostructure

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.

© 2011 Elsevier Inc. All rights reserved.

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 TiO₂ 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/TiO₂ 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

* Corresponding author. Fax: +886 2 33664078.

E-mail address: suwf@ntu.edu.tw (W.-F. Su).

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 TiO₂ 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 N₂/O₂ 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 cm²) 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 cm²) 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 cm² 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

Download English Version:

<https://daneshyari.com/en/article/608577>

Download Persian Version:

<https://daneshyari.com/article/608577>

[Daneshyari.com](https://daneshyari.com)