

行政院國家科學委員會專題研究計畫 成果報告

非揮發記憶體用之高分子/核殼奈米顆粒奈米複合材料之合成與元件製備(3/3) 研究成果報告(完整版)

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行政院國家科學委員會補助專題研究計畫 ☒ 成果報告
☐ 期中進度報告

非揮發記憶體用之高分子/核殼奈米顆粒奈米複合材料之合
成與元件製備

計畫類別：☐ 個別型計畫 ☒ 整合型計畫

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計畫主持人：韋光華

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中 華 民 國 年 月 日

行政院國家科學委員會專題研究計畫成果報告

利用 core/Shell 結構之 CdSe@ZnSe 量子點與 P3HT 混合當作主動層，做成有機薄膜電晶體，成功地完成光學寫入與電子抹除之記憶體元件

An optical programming/electrical erasing memory device:
Organic thin film transistors incorporating core/shell
CdSe@ZnSe quantum dots and poly(3-hexylthiophene)

計畫編號：NSC 98-2218-E-009-003

執行期限：96 年 8 月 1 日至 99 年 7 月 31 日

計畫主持人：韋光華 交通大學材料系

共同主持人：許鈺宗、徐雍瑩 交通大學材料系

Abstract

An optical programming/electrical erasing memory device was fabricated by adopting organic thin film transistors incorporating core/shell CdSe@ZnSe quantum dots (QDs) and poly(3-hexylthiophene) (P3HT) as active layers. After illumination, the presence of quantum well-structured core/shell CdSe@ZnSe QDs within the P3HT film enhanced the maximum ON/OFF ratio substantially to 2700; this value was maintained for 8000 s without noticeable decay. The ON state current could be erased effectively when using a single pulse of the gate voltage (-10 V). This fabrication approach opens up the possibility of improving the memory performance of polymeric materials prepared at low cost using simple processes.

採用包覆核殼 CdSe@ZnSe 量子點(QDs)和 3-己烷噻吩(P3HT)為主動層之有機薄膜電晶體去製作光學寫入/電子抹除記憶體元件。照光後，在 P3HT 膜內存在有量子牆結構核殼 CdSe@ZnSe 量子點(QDs)強化 ON/OFF 比例達 2700;此值可維持達 8000 秒而沒有明顯衰退。當使用單一閘極電壓脈衝(-10 V)，這 ON 狀態電流可以有效地被抹除。此製作方式開啟改善高分子材料製備在簡單低價值製程過中之記憶體效果的可能性。

關鍵字：optical programming (光學寫入), electrical erasing(電子抹除), core/shell quantum dots (核殼量子點)

1. Introduction

The development of conjugated polymers for use in organic optoelectronic devices is an area of intense investigation. Several research groups have recently reported the photoresponse and memory functions of organic thin film transistors (OTFTs) ^[1-9]. One such early device took advantage of the illumination of poly(3-hexylthiophene)(P3HT) with light at a wavelength of 632.8 nm to create electric charges that were later trapped at the polymer – dielectric interface ^[1]; this system

featured an ON/OFF ratio of ca. 30 for the memory window at a gate voltage (V_{GS}) of 60 V under a light intensity of 70 mW/cm². This device exhibited a loss of 70% in its drain current and a short retention time after turning the light off. An alternative approach involves the use of conjugated polymers or quantum dots (QDs) as photosensitive materials along with carbon nanotube (CNT)-based field effect transistors for the fabrication of optoelectronic memory devices that function through optical programming and electrical erasing. One such

memory device featuring a CNT transistor coated with poly(3-octylthiophene) (P3OT) exhibited an ON/OFF ratio of ca. 103 after lasing at a wavelength of 457 nm at a value of V_{GS} of 4 V under a laser power of ca. 190 mW/cm². For this system, a several percentage loss of the ON state current occurred 40 s after the laser light was turned off^[2]. The same research group reported that for a similar device structure that exposed to a much higher laser power^[3], it showed an absence of current decay after light turn-off or there exist two regimes: one decaying and one non-volatile^[4]. Another optoelectronic memory device, comprising a conjugated polymer coating a CNT transistor irradiated with UV light at 365 nm, provided an ON/OFF ratio of ca. 4 at a value of V_{GS} of 4 V, but with a retention time of over 16 h^[5].

It appears that commercially viable TFT memory devices exhibiting high ON/OFF current ratios and long retention times (particularly when the gate voltage is turned off) are difficult to prepare. Approaches toward improving device performances while simplifying their fabrication processes are, therefore, necessary for the development and application of future commercial memory devices.

Bulk heterojunctions^[10], in which n-type (e.g., fullerene) and p-type (e.g., conjugated polymer) materials are intimately mixed on the nanometer scale to form interpenetrated networks, have been adopted recently to achieve efficient photoinduced charge generation and separation^[11,12]. On the other hand, semiconductor nanocrystal quantum dots (QDs) have also been used in such organic optoelectronic devices as solar cells^[13] and light-emitting diodes (LEDs)^[14]. Recently, the first bulk heterojunction photoresponsive OTFT memory device incorporating P3HT and CdSe QDs by our group was reported to have an ON/OFF ratio of ca. 102; because the CdSe QDs served as trap centers, the memory effect of the device was maintained for 1 h-even without a gating voltage^[15].

Type-I core/shell structured QDs, in which the conduction and valence bands of the shell material are higher and lower, respectively,

than the corresponding values of the core material, feature a quantum well structure that can confine both holes and electrons in the core^[16]. Hence, the quantum well structure of such QDs enhances their electroluminescence (EL) in LED applications^[17].

In this paper, we report bulk heterojunction polymer TFT memory devices exhibiting long retention times and high ON/OFF ratios that we fabricated using quantum well-structured QDs comprising CdSe cores and ZnSe shells (CdSe@ZnSe). To the best of our knowledge, this system is the first to employ a quantum well structure to enhance the memory effect of polymer TFTs.

2. Experimental Section

2.1. Materials

Regioregular poly(3-hexylthiophene) was obtained from Rieke Metals and used as received. Cadmium acetate dehydrate [Cd(OAc)₂ · 2H₂O] was obtained from Fisher Chemicals. Selenium (Se, 99.999%) and hexadecylamine (HDA, tech. 90%) were obtained from Aldrich. Trioctylphosphine oxide (TOPO, 98%), n-octylphosphonic acid (OPA, 98%), and trioctylphosphine (TOP, tech. 90%) were purchased from Alfa Aesar. Zinc stearate was obtained from J.T. Baker. The solvents heptane, toluene, methyl alcohol, and chloroform (HPLC-grade) were obtained from commercial sources. TOPO-capped CdSe and CdSe@ZnSe QDs were synthesized using a modification of a procedure reported previously^[18,19]. A mixture of Cd(OAc)₂ · 2H₂O (105 mg), HDA (1.39 g), OPA (225 mg), and TOPO (1.95 g) was heated in a 25-ml three-neck flask at 270 °C under an argon flow to obtain a colorless, clear solution. At this temperature, the Se solution (100 mg in 2.4 ml TOP) was injected rapidly. The growth temperature was maintained at 270 °C for 100 s and then the reaction mixture was cooled to room temperature. The CdSe QDs were collected as powders after their precipitation with MeOH. A colloidal solution of the CdSe QDs (ca. 20 mg) in heptane (4 ml) was heated in a 25-ml three-neck flask under an argon flow. After

addition of TOPO (2.5 mg) and HDA (1.5 mg), the mixture was heated at ca. 190 °C to completely remove the heptane. Zinc stearate (316 mg) was dissolved in toluene (2.5 ml) at ca. 60 °C. After cooling to room temperature, the resulting 0.2 M solution was mixed with TOP (2.5 ml) and Se (39.48 mg). This mixture was injected via syringe pump (0.085 ml/min) into the reaction flask containing the CdSe QDs at ca. 190 °C. After the addition was complete, the crystals were annealed at 190 °C for an additional 1 h. The CdSe@ZnSe QDs were collected as powders after their precipitation with MeOH.

2.2. Device fabrication and measurement

A solution of P3HT in CHCl_3 was blended with a solution of the QDs in CHCl_3 ; the P3HT/QD composite weight ratio was 1:0.1. The P3HT and P3HT/QD TFT devices were fabricated in a bottom-gate configuration. An n+ silicon wafer ($<0.005 \Omega \text{ cm}$) was used as the substrate and gate; 900-Å thermal SiO_2 (capacitance: 38.4 nF/cm^2) was the gate insulator; a photolithographically patterned Au/Cr layer (thickness: 600/50 Å) functioned as the source and drain electrodes ($W = 1000 \mu\text{m}$; $L = 10 \mu\text{m}$). Octadecyltrichlorosilane (OTS) was deposited by immersing the substrate in 1 mM heptane solution for 10 min; the substrates were rinsed with heptane and isopropanol, followed by drying with N_2 . The P3HT and P3HT/QD films (thickness: ca. 60 nm) were deposited through spin-coating and then they were annealed at 150 °C for 5 min inside a glove box under N_2 atmosphere. The samples were then transferred to a cryogenic probe station (VFTTP4, Lakeshore). The performance of each device was measured under vacuum ($<1 \times 10^{-5}$ torr) in the dark using a Hewlett – Packard 4156C semiconductor parameter analyzer. The devices were illuminated under vacuum using a tungsten halogen lamp (2.75 mW/cm^2).

2.3. Characterization

TEM images were obtained using an FEI Tecnai Spirit TWIN apparatus operated at 120

keV. For TEM analysis, the devices were placed into 1% HF solution; after the active layers had floated to the solution surface, they were transferred to the TEM grid. A Hitachi U-4100 spectrophotometer was used to obtain optical absorption spectroscopy in the UV – vis range; a Hitachi F-4500 FL spectrophotometer was employed to obtain photoluminescence spectra.

3. Results and Discussion

To discern the effect that the ligands on the QDs had on the performance of the memory devices, we investigated trioctylphosphine oxide (TOPO) as the ligand because TOPO-capped CdSe QDs feature large barriers that prevent electron tunneling into P3HT and better dispersion than pyridine-capped CdSe QDs in P3HT (see Fig. S1, Supplementary material).

Fig. 1a presents the UV–vis and photoluminescence (PL) spectra of CdSe and CdSe@ZnSe QDs that we prepared from the same concentrations in toluene. The first excitonic absorption peak of the CdSe QDs appeared at ca. 540 nm, suggesting an average particle size of ca. 2.85 nm^[20], which is consistent with the dimensions obtained from transmission electron microscopy (TEM) image analyses. The presence of the ZnSe shell caused a red shift in the absorption spectrum and enhanced the PL intensity.

Fig. 1b displays a schematic energy level diagram of the CdSe and ZnSe bulk materials, P3HT, and Au electrodes^[21,22]. Because the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of P3HT lie above the conduction band (CB) and valence band (VB) edges of the CdSe and ZnSe materials, respectively, the P3HT–ZnSe interface forms an offset band heterojunction; in contrast, the CdSe core and ZnSe shell form a type-I heterojunction. When illuminated, excitons were generated in the QDs and P3HT, charge separation occurred at the P3HT–QDs interface, and

then electrons and holes were transferred into the QDs and P3HT, respectively [23]. The work function of Au (5.1 eV) matched the HOMO of P3HT (4.9 eV); therefore, an Ohmic contact formed for hole injection, resulting in hole-only transport in the P3HT/QD TFTs.

Fig. 2a displays the transfer curves (drain-to-source voltage, $V_{DS} = -20$ V) of the P3HT-only and P3HT/QD (including CdSe and CdSe@ZnSe) bulk heterojunction TFTs in the dark and under white light (2.75 mW/cm^2). All of the devices exhibited the characteristic behavior of p-channel field-effect transistors. The hole mobility μ_h was obtained using the following equation [24]:

$$I_{DS} = W/2L\mu_h C(V_{GS} - V_{th})^2 \quad (1)$$

where V_{th} is the threshold voltage, W is the channel width, L is the channel length, C is the gate oxide capacitance per unit area, and V_{GS} is the gate voltage. In the saturation regime, the hole mobilities of the P3HT-only, P3HT/CdSe QD, and P3HT/CdSe@ZnSe QD devices were 4×10^{-4} , 8×10^{-4} , and $3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Since the HOMO of the P3HT is much higher than the VB of CdSe QDs, this energy difference constitutes a larger energy barrier that prevents holes transferring from P3HT to CdSe QDs [25]. Thus, incorporation of the CdSe and CdSe@ZnSe QDs into the P3HT enhanced the hole mobility of the devices slightly, owing to the fact that it is possible that the QDs reduced the density of traps in the polymer [the concentration of the QDs in the P3HT film was 10% (w/w)]. The hole mobility of each of these three composites was lower than that reported recently for pure P3HT (ca. 10^{-2} to $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [26]. Note, however, that several factors, such as the molecular weight of the P3HT, its methods of preparation and purification, the channel dimensions, and the substrate treatment conditions, can influence the characteristics of a TFT device. The values

of V_{th} of the P3HT-only, P3HT/CdSe QD, and P3HT/CdSe@ZnSe QD devices were 0.8, 3.4, and 3.8 V, respectively; i.e., those of the blended devices shifted to more-positive values, indicating the existence of a permanent electric field at the interface. The increase in the drain current of the polymer/QD blends under illumination resulted from accumulation of the majority carriers (holes) inside the active layer; these holes tended to drift toward the drain electrode, whereas the electrons will stay in the QDs or the insulator layer. It is well-known that the properties of the interface between the insulator and the semiconductor can critically influence the device performance. When the OTFT is illuminated, the electrons are attracted to the interface with the gate dielectric by a positive gate voltage; they are then trapped either in the dielectric layer or at the interface. Acceptor-like traps, when the traps are filled by electrons, leads to a positive threshold voltage. After turning the light off, electron detrapping under a negative gate bias indicates a returning to the initial state.

Fig. 2b present plots of the ratio I_{light}/I_{dark} versus V_{GS} . We obtained the ratio I_{light}/I_{dark} from the transfer curves of the drain current for samples either in the dark or irradiated under white light (2.75 mW/cm^2). The I_{light}/I_{dark} ratio depends on the gate bias for a given drain bias; it decreases as the gate bias is applied above or below the switch-on voltage. In the depletion regime, the maximum I_{light}/I_{dark} ratios for the P3HT-only, P3HT/CdSe, and P3HT/CdSe@ZnSe devices were 1.6×10^2 , 7.1×10^2 , and 2.7×10^3 , respectively; i.e., the photosensitivity of the P3HT/CdSe@ZnSe device was higher than that of the P3HT-only and P3HT/CdSe devices. Because the switch-on voltages, which were defined by the maximum I_{light}/I_{dark} ratios, for the P3HT/CdSe and P3HT/CdSe@ZnSe devices were 5.6 and 8 V, respectively (Fig. 2b), we chose to operate these two devices at a value of V_{GS} of 5 V for our subsequent time-response studies.

Fig. 3a displays the evolution of the normalized drain current for the P3HT/CdSe

and P3HT/CdSe@ZnSe devices at values of V_{DS} and V_{GS} of -20 and 5 V, respectively, after they were subject to a light of 2.75 mW/cm^2 with a duration of 100 s. At the onset of illumination, the drain current of both the P3HT/CdSe and P3HT/CdSe@ZnSe devices increased dramatically, and then dropped off to form plateaus when light is turned off. After the light had been turned off for 400 s, the drain current of the P3HT/CdSe@ZnSe device had decreased by 14%, compared with a corresponding loss of 60% for the P3HT/CdSe device. We suspect that the mechanism underlying this behaviors involved two relaxation processes: (i) rapid decay corresponding to the recombination of closely spaced charge carriers and (ii) slow decay resulting from the recombination of well-separated carriers ^[27] (Fig. 3b). The slow decay might be manifested by the fact that, in a heterojunction device, the spatially separated holes and electrons will move differently-the holes drifting toward the channel and then reaching the drain electrode, the electrons mostly confined in the QDs and at the P3HT-SiO₂ interface. After the light was turned off, the devices existed in a non-equilibrium state; some of the photogenerated holes presumably recombined with some residual electrons that were not confined in QDs, causing a reduction in the drain current, eventually reaching a metastable state. Because the coverage of the CdSe QDs surfaces by TOPO was only ca. 55% ^[21], the ZnSe shell layer between the CdSe core and the P3HT polymer in the P3HT/CdSe@ZnSe devices resulted in an additional tunneling barrier that prevented the electrons from tunneling back to P3HT, leading to a smaller decrease in the drain current and a larger retention time relative to those of the CdSe QDs devices, as indicated by the slope of the drain currents at 600 s.

Because low power consumption is an important feature for non-volatile memory applications, it is preferable to operate optoelectronic memory devices in the absence of a gate voltage. Fig. 3c displays

the evolution of the normalized drain currents at values of V_{DS} and V_{GS} of -20 and 0 V, respectively, for the devices subjected to a light of 2.75 mW/cm^2 with a duration of 100 s. After turning off the light, the P3HT/CdSe@ZnSe and P3HT/CdSe devices exhibited losses of 8 and 35%, respectively, of their ON state currents, with ON/OFF ratios of 36 and 1.5, respectively. Therefore, we conclude that Type-I heterojunction core/shell QDs are more suitable than homogenous QDs for memory applications both with and without applied gate voltages.

Fig. 4 presents TEM images of the CdSe and CdSe@ZnSe QDs dispersed in the P3HT matrix at a P3HT-to-QD weight ratio of 1:0.1. The bright appearance of the P3HT regions relative to dark QD regions in the contrast image was probably due to the large difference in their respective electron densities. The CdSe QDs were distributed rather homogeneously in the P3HT matrix; we suspect that the lower homogeneity of the P3HT/CdSe@ZnSe film was due to a loss of TOPO coverage during the growth of the shell. The TEM images in the insets to Fig. 4 reveal that the CdSe and CdSe@ZnSe QDs had average sizes of ca. 2.9 and 4.3 nm, respectively. The ZnSe shell thickness was ca. 0.7 nm, i.e., slightly larger than the critical penetration length of electrons (ca. 0.5 nm) ^[21].

To determine the optimal operating conditions, we fabricated 10 devices from three independently prepared P3HT/CdSe@ZnSe films; the optimal ON/OFF ratio was greater than 1000 at a value of V_{GS} of 10 V. Fig. 5 reveals that the P3HT/CdSe@ZnSe devices exhibited a high ON/OFF ratio of 2700 at a value of V_{GS} of 10 V-without any noticeable decay after the light had been turned off for 8000 s. This result indicates that incorporating core/shell QDs into a conjugated polymer significantly extends the lifetime of the memory states of the resulting polymer TFTs. Moreover, the inset to Fig. 5 also displays the dynamic responses of the optical programming and electrical erasing of the P3HT/CdSe@ZnSe device. The ON state current could be erased

effectively when using a single pulse of the gate voltage (-10 V) for a short duration (1 s). When this negative pulse gate bias was applied, the Fermi level of CdSe and ZnSe modulated up towards the conduction band, thereby reducing the barrier height. As a result of the decrease in the barrier height, electron jump back into the P3HT and recombine with hole. Thus, we suspect that the trapped electrons were induced by the electric field to move out of the QDs and recombine with the holes to reform the OFF state. Based on this protocol of operation, it was possible for us to program the P3HT/CdSe@ZnSe device optically and then erase it electrically.

4. Conclusions

In summary, we have examined the optoelectronic properties and memory effects of polymer TFTs incorporating P3HT/CdSe and P3HT/CdSe@ZnSe QDs as an active layer. After illumination, the presence of the quantum well-structured core/shell CdSe@ZnSe quantum dots in the P3HT film substantially enhanced the ON/OFF ratio to 2700, maintaining this value for 8000 s without noticeable decay. This fabrication approach opens up the possibility of improving the memory performance of polymeric materials prepared at low cost using simple processes.

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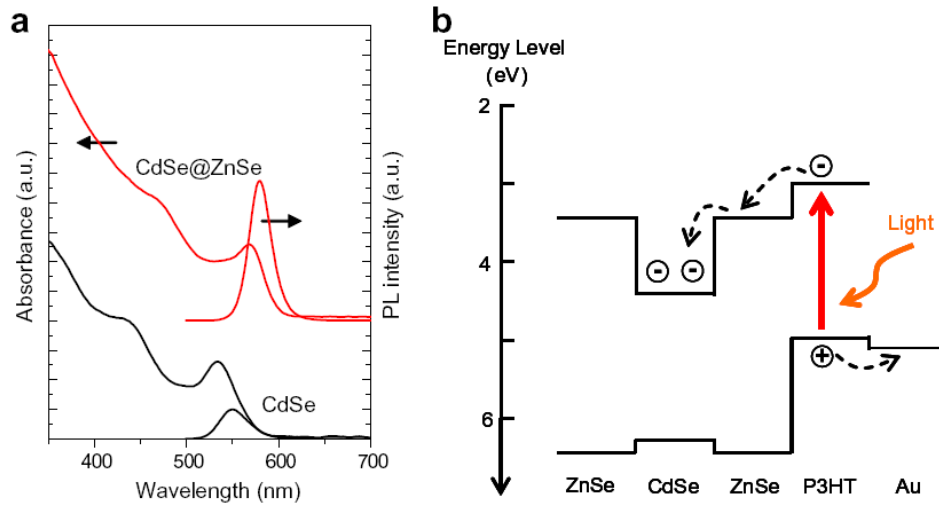


Figure 1. (a) Absorption and photoluminescence spectra of the CdSe and CdSe@ZnSe QDs. (b) Energy level diagram for the CdSe and ZnSe bulk materials, P3HT, and the electrode materials.

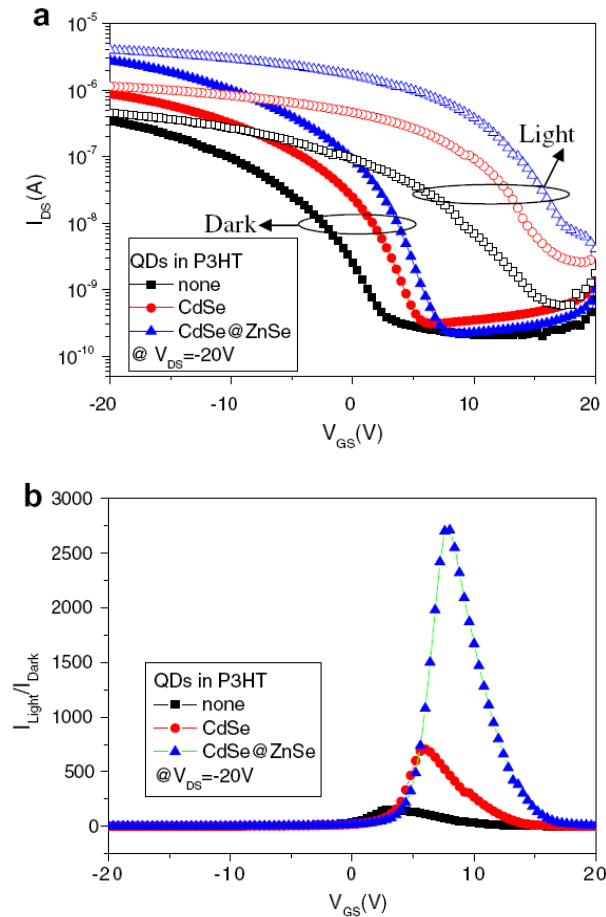


Figure 2. (a) Transfer characteristics ($V_{DS} = -20$ V) of TFTs incorporating P3HT-only, P3HT/CdSe, and P3HT/CdSe@ZnSe blend films and operated in the dark and under white light (2.75 mW/cm^2). (b) Relative I_{Light}/I_{Dark} ratios of the transfer characteristics of the drain current in the dark and under white light.

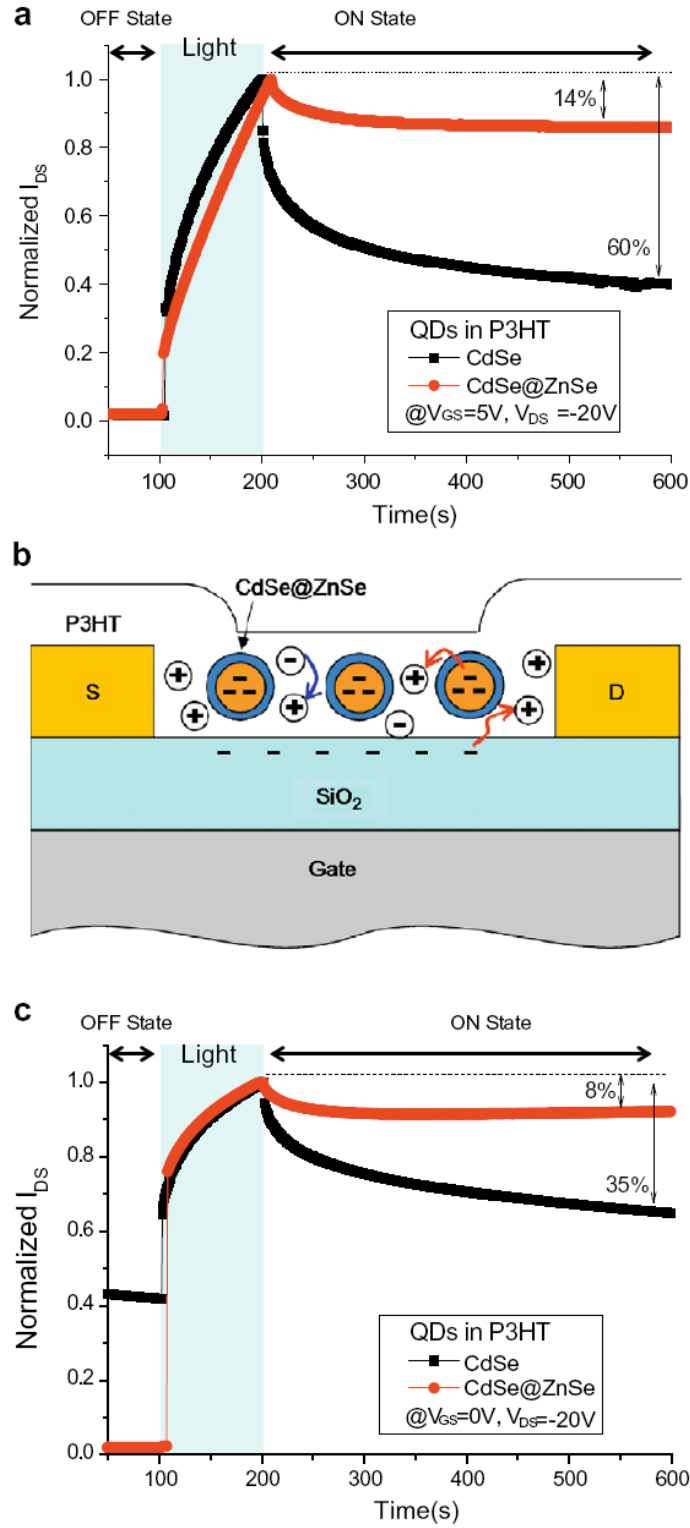


Figure 3. Time responses of the normalized drain currents of the P3HT/CdSe and P3HT/CdSe@ZnSe devices ($V_{DS} = -20\text{ V}$) illuminated by a light of 2.75 mW/cm^2 with a duration of 100 s at values of V_{GS} of (a) 5 and (c) 0 V. (b) Schematic representation of the relaxation processes within the bulk heterojunction P3HT/CdSe@ZnSe active layers in TFT devices. Red: slow decay process; blue: fast decay process. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

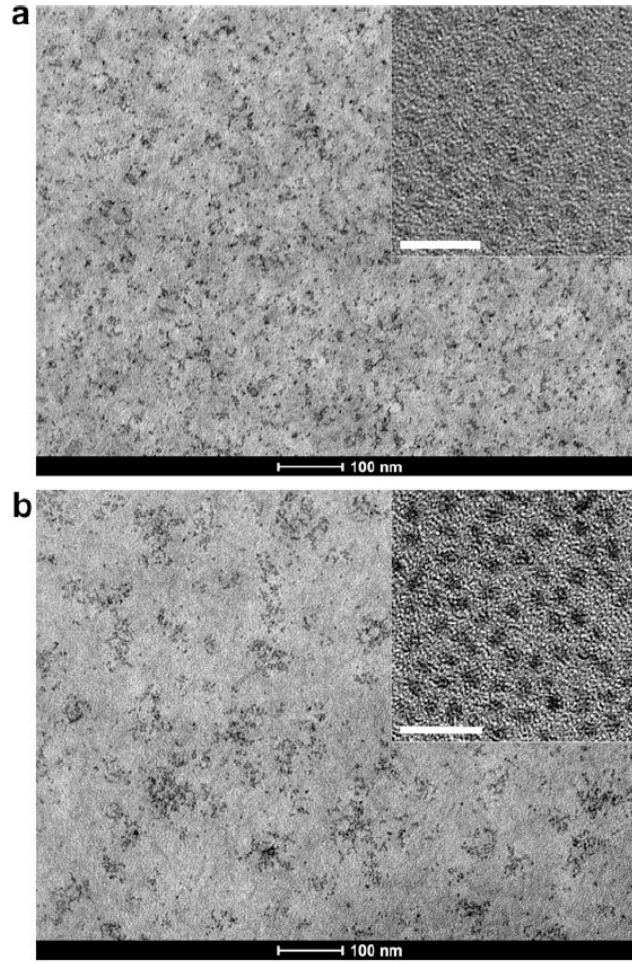


Figure 4. TEM images of (a) the CdSe QDs and (b) the CdSe@ZnSe QDs dispersed in the P3HT matrix. Insets: TEM images of the CdSe and CdSe@ZnSe QDs (scale bar: 20 nm).

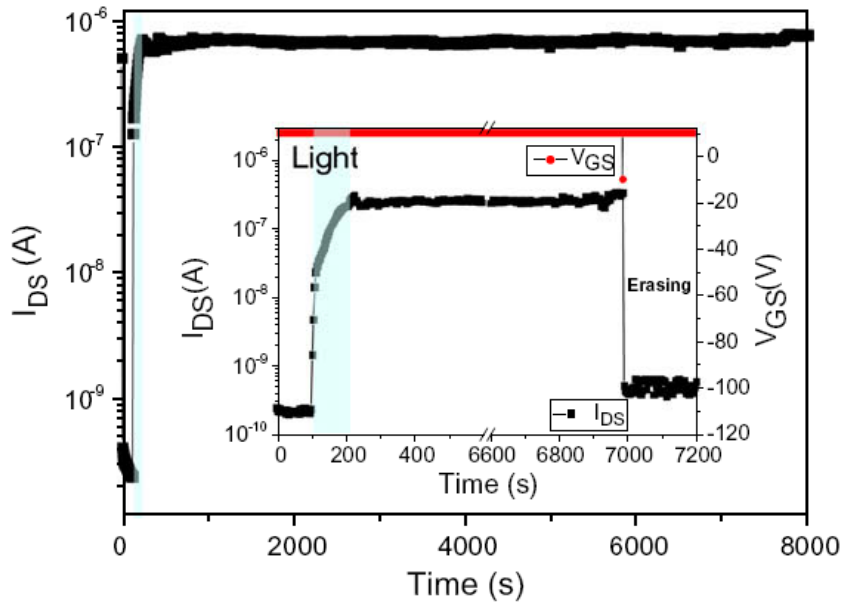


Figure 5. Time response of the value of I_{DS} of the P3HT/CdSe@ZnSe device at $V_{GS} = 10$ V and $V_{DS} = -20$ V illuminated by a light of 2.75 mW/cm^2 with a duration of 100 s. Inset: Time response of the P3HT/CdSe@ZnSe device after a negative gate voltage pulse ($V_{GS} = -10$ V) was applied at 7000 s to erase the memory.

行政院國家科學委員會專題研究計畫成果報告

P3HT/CdSe 量子點(Quantum dot)薄膜電晶體之光學反應與記憶體之效應

Photoresponses and memory effects in organic thin film transistors incorporating poly(3-hexylthiophene...)/CdSe quantum dots

計畫編號：NSC 98-2218-E-009-003

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計畫主持人：韋光華 交通大學材料系

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Abstract

This paper describes the optical responses and memory effects of poly(3-hexylthiophene) P3HT/CdSe quantum dot (QD) thin-film transistors (TFTs). TFTs incorporating P3HT/CdSe QD blends as the active layer exhibited higher photocurrents than did the corresponding P3HT-only devices because the heterojunction between P3HT and the CdSe QDs enhanced the separation of excitons. Moreover, the CdSe QDs served as trap centers so that the memory effect was maintained for several hours, even when the device was operated without a gating voltage. Here, we demonstrate the potential applicability of such P3HT/CdSe QD TFTs through repeated optical programming and electrical erasing.

此篇論文描述這 P3HT/CdSe 量子點薄膜電晶體之光學反應與記憶體效果。薄膜電晶體包覆有 P3HT/CdSe 量子點為主動層比僅有 P3HT 元件存在有較高的光電流，因為 P3HT 與 CdSe 量子點之間的異質界面強化這激子的分離。而且，即使當元件被操作在沒有閘極電壓下，這 CdSe 量子點可提供一個陷阱中心以便於記憶體效果可維持幾個小時。這裡我們證明這樣 P3HT/CdSe 量子點薄膜電晶體經由光學寫入/電子抹除潛在應用性。

關鍵字：optical responses (光學反應), memory effects (記憶體效應), quantum dots (量子點)

1. Introduction

During the past few years, a tremendous amount of effort has been devoted to studies of polymer-based optoelectronic devices. The use of polymer memory has several advantages, including ease of fabrication and low cost. Many research teams are actively pursuing polymer phototransistors, but few are focusing on memory effects in the polymer devices, especially for polymer devices operated using optical programming and electrical erasing. A simple optically writeable memory device incorporating poly(alkylthiophene) as the active layer has been proposed, with the optically induced charge being trapped at the

polymer-dielectric interface.¹ Carbon nanotube networks have also been coated with polymers to form optoelectronic memory devices that are written optically and read and erased electrically, but these blended polymer/carbon nanotube devices lost their memory capability because the carbon nanotubes separated from the substrate and because the nanotube bundles contained metallic nanotubes.² In polymer-based memory devices, the dynamic switch phenomenon depends strongly on the gate effect.³ The “on” state can be returned to the “off” state by removing the gate voltage.⁴ Unfortunately, the on states of these devices were not maintained for very long in the

absence of an applied gate voltage, which limits their potential use in commercial applications. In this paper, we describe poly(3-hexylthiophene) (P3HT)/CdSe quantum dot (QD) thin-film transistors (TFTs) that exhibit long retention times for their on states even in the absence of a gate voltage. This behavior differs significantly from that reported previously.

Composite films of CdSe QDs and P3HT have been widely used in photovoltaic devices⁵ in which exciton dissociation and charge separation occur at the interface between the CdSe QDs and P3HT. Based on this principle, the electrons become trapped in the CdSe QDs when the light is turned off. This behavior enhances the retention time of polymer-based phototransistors. In this paper, we demonstrate that hole-only transport occurs in P3HT/CdSe QD TFTs. The drain-source currents (I_{DS}) of both the P3HT and P3HT/CdSe TFTs increased by up to several orders of magnitude upon irradiation with light when operated in the depletion mode. After turning off the light, the current decayed to a metastable state, where it remained for several hours, when the devices were subjected to a positive or zero gate voltage.

Trioctylphosphine oxide (TOPO)-capped CdSe QDs were synthesized using a modification of a procedure reported previously.⁶ A solution of P3HT (Rieke Metals, used as received) in chloroform (5 mg/mL) was blended with a solution of CdSe QDs (diameter of 3.5 ± 0.5 nm). The P3HT and P3HT/CdSe TFT devices were fabricated in a bottom-gate configuration (Fig. 1). An n^+ -silicon wafer ($< 0.005 \Omega \text{ cm}$) was used as the substrate and gate. 900 Å thermal SiO_2 (capacitance of 38.4 nF/cm^2) was the gate insulator. It was hydrophobically modified using hexamethyldisilazane vapor. The source and drain fingerlike electrodes ($W=3000 \mu\text{m}$ and $L=10 \mu\text{m}$) were defined using standard photolithography. A bilayer of Au/Ti (thickness of $1000/100 \text{ Å}$) was thermally evaporated and then lifted off. The P3HT and P3HT/CdSe films (thickness of 100 nm) were deposited through spin coating. The density of CdSe QDs in the thin P3HT film is about $9.93 \times 10^{17} \text{ cm}^{-3}$.

The films were subsequently annealed at 150°C under N_2 for 5 min. The performance of each device was measured under vacuum ($< 1 \times 10^{-5}$ torr) in the dark using a Hewlett-Packard 4156C semiconductor parameter analyzer and a cryogenic probe station (VFTTP4, Lakeshore). The devices were illuminated under vacuum using a tungsten halogen lamp.

Figure 2 displays the transfer curves (drain-to-source voltage $V_{DS}=-20 \text{ V}$) of the P3HT-only and P3HT/CdSe QD blend TFTs in the dark and under a white light of 0.26 mW/cm^2 . Both the P3HT and P3HT/CdSe TFTs exhibit the characteristic behavior of p -channel field-effect transistors. Ambipolar-type TFTs based on blended donor- and acceptor-type materials have been reported previously.⁷ The work function of Au (5.1 eV) matched the highest occupied molecular orbital of P3HT (4.9 eV),⁸ forming an Ohmic contact for hole injection. The drain currents measured by sweeping gate voltage at $V_{DS}=20 \text{ V}$. We observed a weak electron current in the P3HT/CdSe and pure P3HT TFTs. The electron current remains weak even if higher positive gate voltages. Whereas Au strongly suppressed electron injection into CdSe [lowest unoccupied molecular orbital (LUMO): 4.3 eV]⁹ and P3HT (LUMO: 3.0 eV)⁸ because of a large mismatch between its work function and the LUMO band of CdSe and P3HT. In addition, the current in the P3HT/CdSe TFTs is about one order of magnitude larger than for the pure P3HT TFTs in the whole voltage range. Incorporation of CdSe QDs into the P3HT lightly enhances the hole mobility of the devices, it is possible that CdSe reduced the density of traps in the polymer.¹⁰

The inset of Fig. 2 displays phase images—obtained by AFM (Multimode, DI) in the tapping mode—of both the P3HT and P3HT/CdSe thin films. The P3HT/CdSe composite thin film had a rougher surface morphology (rms roughness of 3.6 nm) in comparison with that of the P3HT-only film (2.0 nm). The surface morphology of the film incorporating the CdSe QDs was rough because of CdSe aggregation. The contrast in the phase image of the film blend indicates phase

separation. The transmission electron microscopy image of the blend film (not shown here) revealed that the CdSe QDs had unexpectedly aggregated into clusters. To avoid aggregation of the CdSe QDs, a suitable ligand must be used to passivate the QDs to enhance the performance of the memory devices.

We observed photoconductivity and the photovoltaic effect in the active layer of the transistors upon illumination.¹¹ We attribute the significant increase in the drain current in the off state, when the device was being illuminated, to the enhancement of the drain current caused by the excitons in the polymer and nanocrystal. When illuminated, the excitons were generated in the CdSe QDs and P3HT. The electrons and holes eventually separated as a result of the electrical field. The drain currents of the P3HT/CdSe devices were larger than those of the P3HT-only devices because of the built-in field present at the P3HT-CdSe interface. The photoexcitation hole density within the thin film also contributed to the drain current and increased the threshold voltage to a large positive value.

Threshold voltages (V_{th}) were determined from the intercepts of the $\sqrt{I_{DS}}-V_{GS}$ plot. In general, the values of V_{th} of the blend P3HT/CdSe devices shifted to more-positive values, indicating the existence of a permanent electric field at the interface. The $I_{DS}-V_{GS}$ curve shifted toward a positive voltage under illumination. As shown in Fig. 2, the value of V_{th} of the P3HT/CdSe device shifted to 10.0 V (illuminated) from 4.2 V (darkness), i.e., $\Delta V_{th}=5.8$ V. In contrast, the value of ΔV_{th} of the P3HT-only device was ~ 1.9 V. The ΔV_{th} extracted from the backward sweep curve is more pronounced than that extracted from the forward sweep. For the forward sweep, when an initial negative gate voltage is applied, the trapped electrons in the P3HT/SiO₂ interface and CdSe QDs would easily detrap and recombine with the hole in P3HT, leading to a reduction in the carrier density. Whereas, the recombination process of electrons and holes in backward sweep took place in the region that is not concerned with the memory functionality.

The increase in the value of the carrier density N^* in the active layer could be

estimated using the equation $N^*=C_i \Delta V_{th}/e$, where C_i is the capacitance per unit area of the dielectric layer, ΔV_{th} is the shift of the threshold voltage, and e is the elementary charge. The values of N^* of the P3HT/CdSe device and the P3HT-only device were $\sim 1.39 \times 10^{12} / \text{cm}^2$ and $\sim 4.53 \times 10^{11} / \text{cm}^2$, respectively, indicating that the P3HT/CdSe devices were more efficient at separating excitons, presumably because of the heterojunction at the P3HT-CdSe interface in the active layer.

Upon sweeping the voltage from positive to negative and then back to positive, we observed obvious hysteresis under illumination, but indistinct hysteresis in the dark (Fig. 2). This behavior was a consequence of the trapped charges present at the polymer-dielectric interface or in the dielectric material. The hysteresis for a P3HT device was typically less than 1.1 V. For the P3HT/CdSe devices, it was ~ 0.8 V. These similar values indicate a very small difference in their interface trap densities. The manifest hysteresis under illumination has also been observed in P3HT/PCBM phototransistors and organic capacitors.^{10,12} Apparent hysteresis occurred upon illumination as a result of an increased number of carriers in the active layer becoming easily trapped, either at the P3HT-SiO₂ interface or in SiO₂ itself. In the P3HT/CdSe devices, some of the carriers were trapped in the CdSe QDs, resulting in the reduced degree of hysteresis.

Hysteresis in the illuminated devices resulted from trapped electrons. When applied a positive gate voltage of 7.5 V (where the hysteresis is most pronounced in the Fig.2), Fig. 3(a) indicates that the current in the P3HT-only devices reached a metastable state after turning off the pulse light source (30 s). This behavior is consistent with previous observations.¹⁻³ Trapping of electrons in SiO₂ or at the P3HT-SiO₂ interface screened the back-gate potential, resulting in the metastable state. We attribute the slow current decay to bulk recombination, which is an indication of the slow nonexponential relaxation process inherent to polymer-based devices. After turning off the light source, the drain current decayed rapidly when the gate voltage was equal to zero. The current moved back to the

initial state in the P3HT devices after turning off the light (100 s). In the absence of a gate voltage, there was no external electrical field to induce the electrons; thus, the trapped electrons escaped from the trap centers (i.e., from the SiO₂ or the P3HT-SiO₂ interface) into the active layer, resulting in decay of the drain current in the P3HT devices.

Relative to the P3HT-only devices, the P3HT/CdSe devices displayed entirely different behavior, as shown in Fig.3(b). Under illumination, the electrons were trapped not only in SiO₂ and at the P3HT-SiO₂ interface but also in the CdSe QDs. After photoexcitation, the trapped electrons escaped from the trapping centers (SiO₂ or P3HT-SiO₂) after a few minutes. In contrast, the highly localized electrons inside the CdSe QDs had difficulty jumping back into the polymer. Also, the presence of TOPO on the surface of the CdSe QDs enhanced the trapping of electrons. This metastable state was maintained for several hours, even in the absence of a gate bias. The P3HT/CdSe devices exhibited higher I_{ON}/I_{OFF} ratios (>100) than did the P3HT-only devices (10). A large on/off ratio can also be achieved for the P3HT/CdSe and P3HT-only devices providing an appropriate gate voltage is applied. Our observations show that the on/off ratio of P3HT/CdSe TFTs is at least one order of magnitude larger than that the pure P3HT TFTs near the threshold voltage. Moreover, there is a much long retention time for the P3HT/CdSe devices than the P3HT-only devices in absence of a gate voltage. Although the P3HT/CdSe devices exhibited a memory effect in the absence of a gate voltage, their I_{ON}/I_{OFF} ratios were too low to meet the required memory window.

Upon illumination with white light (2.75 mW/cm²), the drain current of the P3HT/CdSe device rose from 1.5 to 415 nA (Fig. 4). After turning off the white light, the drain current dropped slowly and eventually settled at a metastable state of 260 nA. Moreover, this metastable state could be erased efficiently using a single pulse of a gate voltage for a short duration (−15 V, 100 ms). When this negative pulse gate bias was applied, trapped electrons quickly recombined with the majority carriers

from the trap centers. After applying the negative electrical field, the Fermi level of CdSe also modulated up toward the conduction band, reducing the built-in field and, hence, enhancing recombination. Based on this mode of operation, we could repeatedly program the P3HT/CdSe device optically and electrically erase it.

In summary, we have investigated the electrical and optical properties of polymer memory TFTs incorporating P3HT and P3HT/CdSe as active layers. Upon illumination, the P3HT/CdSe TFTs exhibited stronger carrier induction in the channel and greater electron trapping ability than did the P3HT-only devices. This phenomenon resulted in a relatively high I_{ON}/I_{OFF} ratio. After introducing the CdSe QDs as electron trap centers, the retention time of the metastable memory state of the P3HT/CdSe TFT improved in the absence of a gate voltage. We are currently optimizing the working point of V_{th} at values of V_{GS} near 0 V to maximize the photoresponse so that the memory window can be widened further. We are also investigating replacing the TOPO molecules with long alkyl chains to enhance the retention time.

We are grateful to the National Science Council (NSC-96-2218-E-009-011) and the MOE-ATU Program in Taiwan for financial support.

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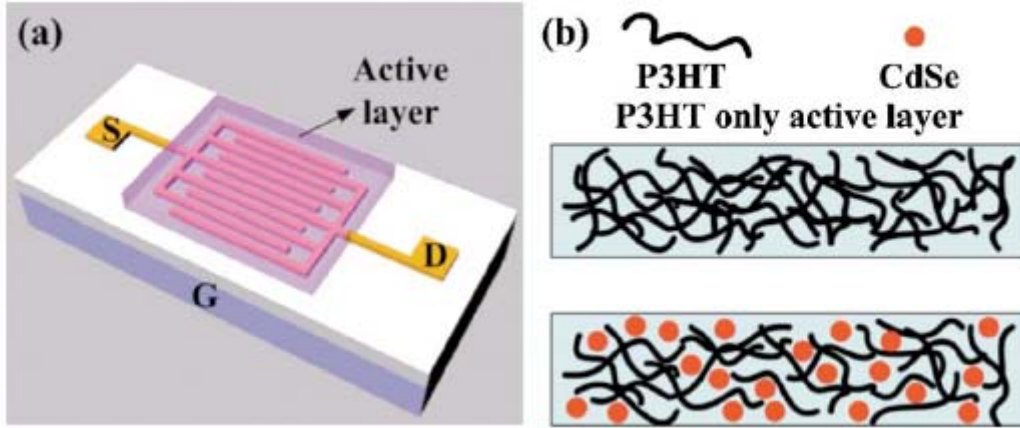


Figure 1. (Color online) Schemes of devices structure and organic active layers. (a) Schematic representation of the bottom-gate organic TFT configuration with an active polymer layer and interdigitated source and drain (S for source, D for drain; and G for gate). (b) Schematic representations of the P3HT-only and P3HT/CdSe blend films.

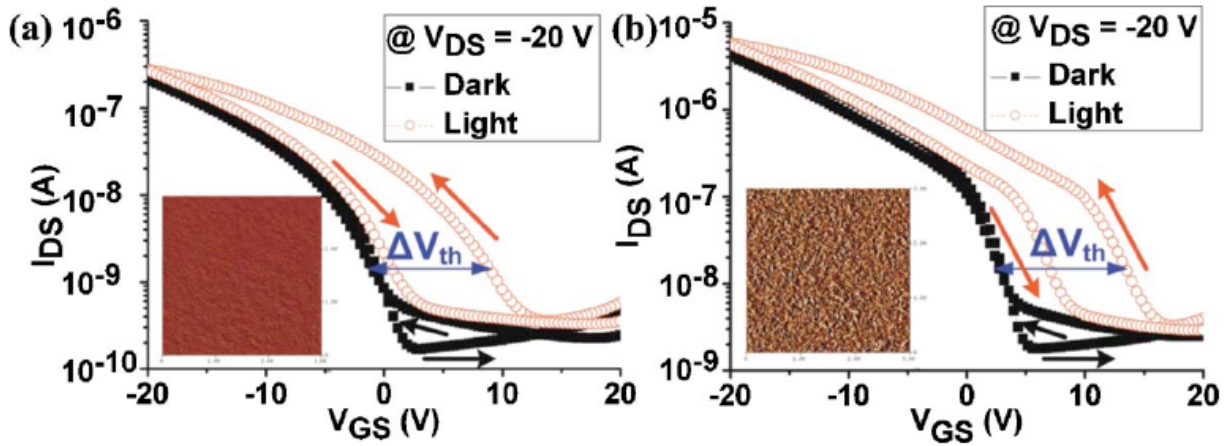


Figure 2. (Color online) Transfer characteristics obtained for the (a) P3HT-only and (b) P3HT/CdSe blend films (i) initially (in the dark) and (ii) under illumination. Under illumination, all of the devices displayed hysteresis. Transfer characteristics of the devices in the dark and under illumination (0.27 mW/cm^2) were measured at $V_{DS} = -20$ V. Inset: AFM phase images of P3HT films in the (a) absence and (b) presence of CdSe QDs. Image size was $3 \times 3 \text{ }\mu\text{m}$.

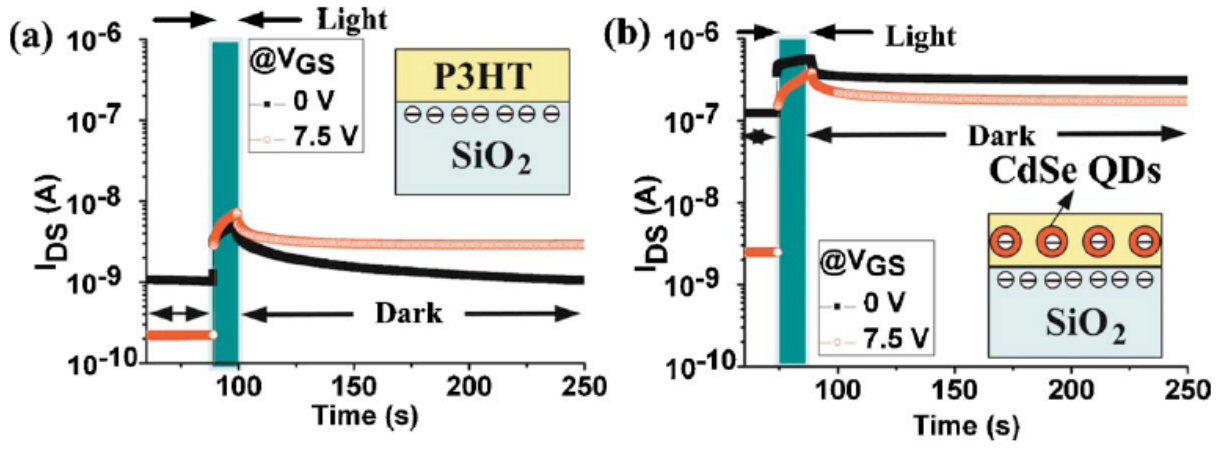


Figure 3. (Color online) Time responses of the drain current at $V_{GS}=7.5$ V and $V_{GS}=0$ V of the (a) P3HTonly and (b) P3HT/CdSe devices to a light pulse (2.75 mW/cm^2 , 30 s). Inset: Illustrations of the electron trap mechanisms for the (a) P3HT-only and (b) P3HT/CdSe devices.

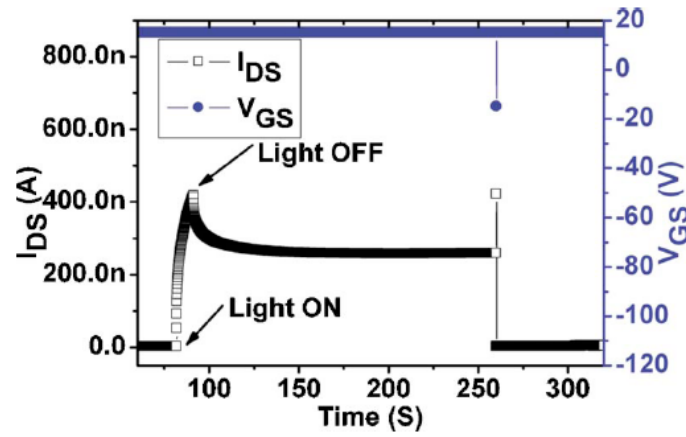


Figure 4. (Color online) Dynamic responses of the optical programming and electrical erasing of a typical P3HT/CdSe device. Light was turned on at $t=80$ s and turned off at $t=90$ s. A short (100 ms) negative gate voltage pulse was applied at $t=260$ s to erase the memory.

行政院國家科學委員會專題研究計畫成果報告

Au-CdS 核殼奈米晶體其介面載子傳輸動力學研究 Interfacial Charge Carrier Dynamics in Core-Shell Au-CdS Nanocrystals

計畫編號：NSC 98-2218-E-009-003

執行期限：96 年 8 月 1 日至 99 年 7 月 31 日

計畫主持人：韋光華 交通大學材料系

共同主持人：許鈺宗、徐雍瑩 交通大學材料系

Abstract

The interfacial charge carrier dynamics for core-shell Au-CdS nanocrystals with various shell thicknesses were investigated and presented. Due to the difference in band structures between Au and CdS, a pronounced photoinduced charge separation took place at the interface of Au and CdS, resulting in the electron-charged Au core and the hole-enriched CdS shell. The electron-charging of Au core in Au-CdS nanocrystals was revealed with the corresponding XPS analysis and photocurrent measurement. Time-resolved PL spectra were measured to quantitatively analyze the electron transfer event between CdS shell and Au core for Au-CdS nanocrystals. An increase in the electron-transfer rate constant was observed for Au-CdS nanocrystals with increasing shell thickness, probably due to the less pronounced electron-hole interaction of thicker CdS, which enabled a fuller extent of participation of photoexcited electrons in the charge separation process. On the other hand, the hole-enriched CdS shell of Au-CdS nanocrystals upon light illumination was characterized with a photocatalytic process. The photocatalytic activity of Au-CdS nanocrystals was found to increase with increasing shell thickness, attributable to the greater capability of light absorption achieved by the extensive growth of CdS shell. The correlation of photocatalytic activity with the shell thickness of Au-CdS nanocrystals corresponded well with that of electron-transfer rate constant. As compared to the relevant commercial products like N-doped P-25 TiO₂ and CdS powders, the as-synthesized Au-CdS nanocrystals exhibited superior photocatalytic performance under visible light illumination, demonstrating their potential as an effective visible-light-driven photocatalyst. Furthermore, the result of performance evaluation under natural sunlight shows that the present Au-CdS nanocrystals can be used as highly efficient photocatalysts which may practically harvest energy from sunlight.

此研究主題為探討不同殼層厚度的金-硫化鎘(Au-CdS)核殼奈米晶體其界面間載子傳輸的動力學。由於硫化鎘與金其能帶結構上的差異，可有效地將光激發所產生的電子侷限於金奈米粒子中，而電洞則會相對的累積於硫化鎘殼層材料。電子儲存在金核層的現象係利用 X 光光電子能譜儀(XPS)與光電流(Photocurrent)量測設備來解析。另一方面，我們係利用時間解析螢光光譜儀(Time-resolved PL spectra)來定義分析出硫化鎘與金界面間電子傳輸現象，其電子傳輸速率常數(electron-transfer rate constant)隨著硫化鎘殼層厚度的增加而增加，推測可能的原因為於較厚的硫化鎘殼層情況下，其界面間電子電洞對交互作用較不明顯。另一方面，光激發程序所產生與累積在硫化鎘殼層材料中的大量電洞也進一步利用於光催化系統中。於實驗中可得到其光催化活性隨著硫化鎘殼層厚度的增加而增加，其原因可歸屬於其成長較厚的硫化鎘殼層具有較佳的光吸收能力，其光催化活性與其界面間電子傳輸速率常數也可得到相呼應的現象。相較於氮-參雜的 P-25 TiO₂ 粒子與其硫化鎘商用品的比較下，Au-CdS 核殼奈米晶體於可見光的光催化系統中同樣展現出過人優秀的催化活性，

此結果也展現其材料具有潛力可發展於可見光催化的系統中。此外，於利用自然太陽光的結果，Au-CdS 核殼奈米晶體則也具有潛力應用作為太陽能轉化作為高效率的光催化材料。

關鍵字：charge carrier dynamics (載子動力學), core-shell nanocrystals (核殼奈米晶體), charge separation (載子分離), photocatalysis (光催化)

1. Introduction

Modulation of charge carrier dynamics for semiconductors is important to the development of light-energy conversion systems.¹ In general, the fast recombination of charge carriers in semiconductors would diminish the resulting photoelectric conversion efficiency. To effectively gain energy from light, the photoexcited electrons and holes of semiconductors must be separated to suppress the direct recombination of them. Previous studies have shown that charge separation of semiconductors can be essentially promoted through the introduction of suitable electron acceptors, such as metals,² carbon derivatives,³ and other semiconductors with appropriate band structures.⁴ By adopting these composite systems, a significant enhancement in the photoconversion efficiency can be attained. For example, CdSe quantum dots can show 2-3 orders of magnitude improvement in photocurrent generation once they were capped with a molecular shell of C₆₀.^{3a} This is due to the sufficiently positive reduction potential of C₆₀, which ensured a quick electron transfer from excited CdSe to C₆₀ and thus the successful collection of electrons. Besides, with the attachment of CdS nanoparticles, ZnO nanowires exhibited enhanced photocatalytic activities.^{4b} This enhancement resulted from the band offsets between CdS and ZnO, which may retard charge recombination to capture more charge carriers for participation in photocatalysis.

Photocatalysis is a valuable approach to practically utilize the solar power. In the last two decades, much research effort has been expanded to develop semiconductor photocatalysts because of their capability of converting light energy into chemical energy. Among the various composite systems, metal/semiconductor combination is of particular interest to photocatalytic applications.^{2,5} For metal/semiconductor composites, the presence of

metal-semiconductor interface may induce effective charge separation to favour the subsequent photocatalysis. The most commonly used semiconductor photocatalysts have been metal oxides like TiO₂, which exhibits ultraviolet absorption ability only due to its large bandgap energy. Many efforts have thus been made to modify TiO₂ such that it can absorb visible light to carry out photocatalytic reactions. For example, through the doping of suitable elements, an additional electronic level can be created and located in the energy gap of TiO₂, extending its light absorption range from ultraviolet to visible regions.⁶ In addition to the doped TiO₂ photocatalysts, many other semiconductors that possess suitable bandgap energies are found to show fascinating photocatalytic activities upon sunlight illumination.⁷ CdS is one of the most popular visible-light-driven photocatalysts since it has a bandgap energy of 2.5 eV that corresponds well with the visible light. Furthermore, its conduction band at relatively negative potential (-1.0 versus NHE)⁸ offers CdS good photocatalytic activities. Till now, many structural forms of CdS including nanoparticles,⁹ hollow nanospheres,¹⁰ porous nanocrystals,¹¹ nanowires,¹² nanotubes,¹³ and nanocomposites¹⁴ have been proven effective in relevant photocatalytic processes.

We previously showed that core-shell Au-CdS nanocrystals exhibited pronounced charge carrier separation upon light illumination.¹⁵ For Au-CdS nanocrystals, Au core can serve as an effective electron scavenger for CdS shell due to its lower Fermi energetic level (+0.5V versus NHE) than the conduction band of CdS (-1.0V versus NHE).⁸ Consequently, the photoexcited electrons in CdS shell would preferentially transfer to Au core, leaving positively-charged holes in CdS domain to achieve charge carrier separation. In this work, we explored the interfacial charge carrier dynamics for Au-CdS nanocrystals with various shell thicknesses. By probing the

emission lifetime of CdS, the electron transfer event between CdS shell and Au core for Au-CdS nanocrystals was quantitatively analyzed. A higher electron-transfer rate constant was observed for Au-CdS nanocrystals with thicker CdS shell, probably due to the less pronounced electron-hole interaction of thicker CdS that enabled a fuller extent of participation of photoexcited electrons in the charge separation process. On the other hand, the hole-enriched CdS shell of Au-CdS nanocrystals upon light illumination was characterized with a photocatalytic process. The photocatalytic activity of Au-CdS nanocrystals was found to increase with increasing shell thickness, attributable to the greater capability of light absorption achieved by the extensive growth of CdS shell. As compared to the relevant commercial products like N-doped P-25 TiO₂ and CdS powders, the as-synthesized Au-CdS nanocrystals exhibited superior photocatalytic performance under visible light illumination, demonstrating their potential as an efficient visible-light-driven photocatalyst. Furthermore, the photocatalytic performance under natural sunlight was also examined, and the result shows that the present Au-CdS nanocrystals can be used as highly efficient photocatalysts which may practically harvest energy from sunlight.

2. Experimental Section

Chemicals. All chemicals were analytic grade reagents and used without further purification. Special attention should be paid when dealing with the hazardous cadmium source and the highly poisonous potassium cyanide (KCN).

Preparation of Au-CdS Nanocrystals. The detailed synthetic approach and relevant characterizations of Au-CdS nanocrystals used here can be found in our previous work.¹⁵ Briefly, Au colloids and *L*-cysteine-Cd²⁺ complexes (Cys/Cd) with a suitable molar ratio were mixed and allowed for hydrothermal reaction at 130°C for 6 h. The product (Au-CdS nanocrystals) was then centrifuged and washed with distilled water and ethanol to remove remaining ions. By increasing the volumes of Cys/Cd mixed with Au colloids, Au-CdS nanocrystals with increasing shell thickness can

be obtained. In this work, Au-CdS nanocrystals with three different shell thicknesses (9.0, 14.0 and 18.6 nm) were prepared and compared. The shell thickness of Au-CdS nanocrystals was determined by examining dozens of nanocrystals from the low-magnification TEM image. A number-averaged value was then calculated and represented.

Preparation of CdS Counterpart Nanocrystals. CdS counterpart nanocrystals were prepared by treating Au-CdS nanocrystals with 0.1 M KCN solution, resulting in the removal of Au core and the preservation of CdS shell (hollow structures).

Preparation of N-doped P-25 TiO₂. N-doped P-25 TiO₂ was prepared by annealing Degussa P-25 TiO₂ powder (1130 mg) in the mixed atmosphere of Ar (200 sccm) and NH₃ (10 sccm) at 500°C for 2 h.¹⁶ The *x* value of the product (TiO_{2-x}N_x) was about 0.28 as estimated from the XPS measurement.

Photocurrent Measurement. Photocurrent measurement for Au-CdS nanocrystals was conducted in a photoelectrochemical system under white light irradiation (xenon lamp, 250 W, with a light intensity of 100 mW/cm²). Spin-coated film of Au-CdS nanocrystals on fluorine-doped tin oxide (FTO) substrate was used as the photoanode in the three-electrode cell which consisted of Pt counter electrode, Ag/AgCl reference electrode, and 0.1 M Na₂S redox couple.

Photoluminescence Lifetime Measurement. Time-resolved photoluminescence (PL) spectra were measured using a home-built single photon counting system. GaN diode laser (408 nm) with the pulse duration of 50 ps was used as the excitation source. The signals collected at the excitonic emission of CdS ($\lambda = 495$ nm) were dispersed with a grating spectrometer, detected by a high-speed photomultiplier tube, and then correlated using a single photon counting card. The emission decay data were analyzed with the biexponential kinetics in which two decay components were derived. The lifetimes (τ_1 and τ_2), preexponential factors (A_1 and A_2), and intensity-average lifetime ($\langle\tau\rangle$) for Au-CdS nanocrystals and the corresponding CdS counterparts were determined and summarized in Table 1.

Photocatalytic Activity Measurement. The photocatalytic activity of Au-CdS nanocrystals was evaluated by the photodegradation of rhodamine B (RhB, $C_{28}H_{31}N_2O_3Cl$) under visible light illumination. A quartz tube with a capacity of 30 mL was used as the photoreactor vessel. The optical system used for photocatalytic reaction consisted of a xenon lamp (500 W, with a light intensity of 175 mW/cm^2) and a bandpass filter (with the bandwidth of 400-700 nm) that ensured the irradiation in visible range. All the photocatalysis experiments were conducted at room temperature in air. Four kinds of photocatalysts including N-doped P-25 TiO_2 , commercial CdS powders (Aldrich-Sigma, with the particle size of 10-20 nm), CdS counterpart and Au-CdS nanocrystals were used and compared in the photodegradation of RhB. Typically, 5.4 mg of photocatalyst was added into 18 mL of RhB aqueous solution ($1.0 \times 10^{-5} \text{ M}$) in the photoreactor vessel. Prior to irradiation, the suspension was stirred in the dark for 30 min to reach the adsorption equilibrium of RhB with photocatalyst. At certain time intervals of irradiation, 1.5 mL of the reaction solution was withdrawn and centrifuged to remove photocatalyst particles. The filtrates were analyzed with a UV-Visible spectrophotometer to measure the concentration variation of RhB through recording the corresponding absorbance of the characteristic peak at 553 nm. Furthermore, photodegradation of RhB ($1.0 \times 10^{-5} \text{ M}$) under natural sunlight by using Au-CdS nanocrystals (5.4 mg) as photocatalyst was also examined.

Characterizations. The morphology and dimensions of Au-CdS nanocrystals were examined with a high-resolution TEM (HRTEM, JEOL JEM-3000) operated at 300 kV. X-ray photoelectron spectroscopy (XPS) data were recorded with a VG Scientific Microlab 350 electron spectrometer using $Mg \text{ K}\alpha$ ($h\nu = 1253.6 \text{ eV}$) as X-ray source under a base pressure of $1.0 \times 10^{-9} \text{ Torr}$. The spectrum resolution of XPS was 0.1 eV, and the pass energy for survey and fine scans was 40 eV. All the binding energies were calibrated by C 1s at 284.6 eV. Photocurrent signals were recorded with a Keithley 2400 semiconductor analyzer.

UV-Visible spectra were collected using a Hitachi 3900H at room temperature under ambient atmosphere.

3. Results and Discussion

First, core-shell nanocrystals of Au-CdS were prepared in a hydrothermal process by using the pre-synthesized Au colloids and Cys/Cd complexes as the starting materials. The formation of Au-CdS nanocrystals involved the binding of Cys/Cd complexes toward Au nanoparticles, followed by the decomposition of Cys/Cd in the hydrothermal reaction and the subsequent growth of CdS onto the surfaces of Au. By suitably modulating the experimental parameters such as the volumes of Cys/Cd added, a controllable shell thickness of Au-CdS nanocrystals can be achieved. In this work, Au-CdS nanocrystals with three different shell thicknesses (9.0, 14.0 and 18.6 nm) were prepared and compared. The present Au-CdS nanocrystals provide an ideal platform to study the interfacial charge carrier dynamics for metal-semiconductor core-shell heterostructures. Due to the difference in band structures between Au and CdS, a pronounced photoinduced charge separation took place at the interface of Au and CdS, resulting in the electron-charged Au core and the hole-enriched CdS shell. The electron-charging of Au core in Au-CdS nanocrystals can be revealed with the corresponding XPS analysis and photocurrent measurement. As shown by the XPS spectra of Figure 1(a), a binding energy of 84.1 eV of Au $4f_{7/2}$ peak was found for pure Au colloid sample, which is in good agreement with the value of bulk metallic Au.¹⁷ However, a negative binding energy shift of around 0.5 eV of Au $4f_{7/2}$ peak was observed for Au-CdS nanocrystals, indicating a significant difference in electronic structures between Au and CdS and a strong electronic interaction therein.¹⁸ Similar phenomenon was ever reported in Au-SnO₂ core-shell nanocrystal system, in which the binding energy shift of Au 4f was attributed to the effective electron transfer from SnO₂ to Au.¹⁹ Here we ascribed the negative binding energy shift of Au 4f observed in Au-CdS nanocrystals to the electron-charging of Au core that resulted from the occurrence of

charge separation. To further elucidate the effect of Au on the charge separation of CdS for the present core-shell nanocrystals, we compared the photocurrent response of Au-CdS nanocrystal and CdS counterpart electrodes by inserting them in a photoelectrochemical cell. Note that CdS counterpart was composed of CdS hollow structures, which were prepared by dissolving the Au core of Au-CdS nanocrystals.¹⁵ Figure 1(b) depicts the photocurrent generation for Au-CdS nanocrystal and CdS counterpart electrodes subjected to the white light irradiation. Both electrodes showed prompt response to the on/off cycles of light illumination, demonstrating the effective charge transfer and successful electron collection for the samples within the photoelectrochemical cell. More importantly, Au-CdS nanocrystals exhibited lower photocurrents than CdS counterpart upon light irradiation. We believed that the significant electron transfer from CdS shell to Au core accounted for such an evident photocurrent depression found in Au-CdS nanocrystals.

If the observed photocurrent depression as well as the XPS binding energy shift for Au-CdS nanocrystals indeed involved the electron transfer from CdS to Au, we should be able to reveal this event in the excitonic emission decay profile of CdS. Figure 2 represents the time-resolved PL spectra for two Au-CdS samples with different shell thicknesses. The emission decay data were analyzed with biexponential kinetics in which two decay components were derived. For Au-CdS nanocrystals with the shell thickness of 14.0 nm, emission lifetimes of both components were shorter than those of the corresponding CdS counterpart ($\tau_1=0.40$ ns, $\tau_2=2.95$ ns for Au-CdS versus $\tau_1=0.53$ ns, $\tau_2=2.98$ ns for CdS counterpart). The intensity-average lifetime was then calculated to make an overall comparison of the emission decay behaviour.²⁰ The difference in the average emission lifetime between Au-CdS ($\langle\tau\rangle = 0.57$ ns) and CdS counterpart ($\langle\tau\rangle = 1.06$ ns) indicates the emergence of a nonradiative pathway from the interaction between CdS and Au. This proposition can be

confirmed by the emission quenching of CdS observed for Au-CdS sample.¹⁵ Such difference became more noticeable as the shell thickness of Au-CdS nanocrystals further increased to 18.6 nm ($\langle\tau\rangle = 0.48$ ns for Au-CdS versus $\langle\tau\rangle = 1.51$ ns for CdS counterpart), inferring a much more significant electronic interaction between CdS and Au. If electron transfer from CdS to Au was the predominant process that dictated the emission quenching of CdS, we can then estimate the electron-transfer rate constant (k_{et}) of Au-CdS nanocrystals from the emission lifetime data by the following equation:

$$k_{et} = \frac{1}{\langle\tau\rangle}(\text{Au} - \text{CdS}) - \frac{1}{\langle\tau\rangle}(\text{CdS})$$

Using the lifetime values listed in Table 1, we obtained the electron-transfer rate constants as 0.36×10^9 , 0.51×10^9 , and 1.42×10^9 s⁻¹ for Au-CdS nanocrystals with the shell thickness of 9.0, 14.0 and 18.6 nm, respectively.

It should be noted that the electron-transfer rate constant of Au-CdS nanocrystals increased with increasing shell thickness. The less pronounced interaction between electrons and holes in the thicker CdS shell may contribute to such an increase in electron-transfer rate constant for Au-CdS nanocrystals with increasing shell thickness. We noticed that the emission lifetimes of the three CdS counterpart samples were substantially different, with CdS of larger characteristic size (thickness) showing longer emission lifetime, as can be seen in Table 1. This size-dependent correlation of exciton lifetime has been widely reported for CdS nanocrystals.²¹ It is generally believed that the significant interaction between electrons and holes, which is due to the confinement of electrons and holes in a particle of reduced size, may induce additional pathways for nonradiative recombination.²² A shortened exciton lifetime would consequently be observed for CdS nanocrystals with reduced size. The electron-hole interaction in small particles is related to the trapping of excitons by the abundant surface states that may further act as alternative sites for nonradiative charge recombination.²³ For the present Au-CdS

nanocrystals, it is reasonable to presume a less pronounced electron-hole interaction for Au-CdS with thicker CdS shell since they possessed a larger characteristic size of CdS and thus a less amount of surface states. Such less pronounced electron-hole interaction in fewer surface states prohibited charge carriers from being consumed in nonradiative recombination, which further enabled a fuller extent of participation of photoexcited electrons in the charge separation process. Accordingly, an increase in the electron-transfer rate constant was observed for Au-CdS nanocrystals with increasing shell thickness.

Since Au-CdS nanocrystals exhibited pronounced charge separation upon light illumination, it is worth studying the potential application that this property may bring. Owing to the effective electron transfer from CdS shell to Au core, photogenerated holes with an abundant amount were existent in CdS shell and would transfer to the surfaces of Au-CdS nanocrystals. These highly reactive holes could oxidize water to produce hydroxyl radicals that can further decompose organic pollutants through an oxidation process. A spectacular capability of photocatalytic oxidation is therefore expected at the surfaces of Au-CdS nanocrystals. A series of photocatalysis experiments were performed in this work to investigate the photocatalytic properties of the as-synthesized Au-CdS nanocrystals. RhB, a typical dye that can be decomposed by hydroxyl radicals,²⁴ was used as the test pollutant to monitor the photocatalytic oxidation progress for Au-CdS nanocrystals. The time-dependent UV-visible spectra of RhB solutions under visible light illumination in the presence of Au-CdS nanocrystals with a shell thickness of 14.0 nm were first shown in Figure 3(a). It can be seen that the intensity of the characteristic absorption peak at 553 nm decreased dramatically with the irradiation time. Besides, a concomitant blue shift in the absorption maximum was observed after the solution was irradiated for 20 min. It is well known that the photodegradation of RhB undergoes two competitive processes.²⁵ One is the destruction of dye chromogen, which is characteristic of the loss of absorbance at 553

nm. The other is the N-demethylation reaction that produces a series of N-demethylated intermediates, accompanied by a blue shift in the absorption maximum from 553 to 498 nm. In the current case, RhB concentration was determined by referring to the absorbance of the characteristic peak at 553 nm. To quantitatively understand the reaction kinetics of RhB photodegradation for our samples, we analyzed the normalized concentration of RhB (C/C_0) as a function of irradiation time. As shown in the inset of Figure 3(a), an exponential decay of RhB concentration with the irradiation time was evident for Au-CdS nanocrystal photocatalyst. The photodegradation process was then fit to pseudo-first-order reaction, in which the value of the apparent rate constant (k_{RhB}) is equal to the slope of the fitting line according to the following expression:²⁶

$\ln(C/C_0) = -k_{RhB} t$, where C_0 and C are the concentrations of RhB at initial and at a certain irradiation time t , respectively.

For Au-CdS nanocrystals with a shell thickness of 14.0 nm, k_{RhB} is found to be 0.026 min^{-1} . The mechanism for RhB photodegradation by using Au-CdS nanocrystal photocatalyst can be described by the following four pathways:



Under visible light illumination, charge separation occurred within Au-CdS nanocrystals, resulting in an electron-charged Au core and a hole-enriched CdS shell (1). Subsequently, the photogenerated holes transferred to the surfaces of nanocrystals and reacted with water to produce hydroxyl radicals (2). RhB molecules were then decomposed by hydroxyl radicals through an oxidation process (3). Once the photogenerated holes were depleted in photocatalysis, Au-CdS nanocrystals underwent a Fermi level

equilibration due to the accumulation of photoexcited electrons.²⁷ Note that experiments of RhB photodegradation were conducted in air. The exposure to air during the operation of photocatalysis can discharge the accumulating electrons of Au-CdS nanocrystals to the dissolved oxygen,^{5a,28} which resulted in a neutralized state of nanocrystals that are allowed for further photoexcitation (4).

The photocatalytic performance of Au-CdS nanocrystals with three various shell thicknesses was then compared in Figure 3(b). It should be noted that experiment in the absence of photocatalyst showed almost no RhB photodegradation, implying that the self-photolysis of RhB is negligible under visible light illumination. For Au-CdS nanocrystals with a shell thickness of 9.0 nm, about 50% of RhB was degraded after 40 min of irradiation. A higher extent of RhB photodegradation to around 70% at the same irradiation time was achieved when using Au-CdS nanocrystals with a thicker shell of 14.0 nm. For Au-CdS nanocrystals with the shell thickness of 18.6 nm, RhB was almost completely decomposed after 40 min of irradiation. From the above observations, we concluded that the photocatalytic activity of Au-CdS nanocrystals was enhanced with increasing shell thickness. This is mainly a result of the extensive growth of CdS shell in Au-CdS nanocrystals. With increasing shell thickness, a raised ratio in the amount of CdS to Au was attained, leading to a greater capability of light absorption for Au-CdS nanocrystals and thus the generation of more charge carriers. This argument can be verified by the fact that the excitonic absorption of CdS for Au-CdS nanocrystals turned significant with increasing shell thickness.¹⁵ Consequently, a higher amount of photoexcited charge carriers was expected for Au-CdS nanocrystals with larger shell thickness, which in turn promoted the resulting photocatalytic efficiency toward RhB photodegradation. It is worth noting that the increase in photocatalytic activity of Au-CdS nanocrystals with the increasing shell

thickness corresponded well with the result of electron-transfer rate constant variation, which could be realized by the causal relation between electron transfer and hole generation. As the shell thickness of Au-CdS nanocrystals increased, more and more photoexcited electrons transferred from CdS shell to Au core, simultaneously leaving photogenerated holes of an increased amount in CdS shell. The rise in the number of photogenerated holes further led to the enhancement in the resulting photocatalytic performance as observed. For more clarity on this relation, we depicted the correlations of electron-transfer rate constant (k_{et}) and rate constant of RhB photodegradation (k_{RhB}) with the shell thickness of Au-CdS nanocrystals in Figure 4.

Further comparative experiments were conducted to demonstrate the superior photocatalytic performance for the present Au-CdS nanocrystals. Four kinds of photocatalysts including N-doped P-25 TiO₂, commercial CdS powders, CdS counterpart and Au-CdS nanocrystals were used in the photodegradation of RhB under the same experimental conditions. The comparative results were shown in Figures 5(a), from which several points can be observed. First, as compared to the relevant commercial products like N-doped P-25 TiO₂ and CdS powders, Au-CdS nanocrystals exhibited superior photocatalytic performance under visible light illumination, demonstrating their potential as an efficient visible-light-driven photocatalyst in relevant redox reactions. Second, Au-CdS nanocrystals performed better toward RhB photodegradation than CdS counterpart, which can be accounted for by the pronounced charge separation that occurred at the interface of Au and CdS. This demonstration addresses the benefit of the present metal-semiconductor core-shell nanocrystals to photocatalytic applications. To further explore the applicability of the as-synthesized Au-CdS nanocrystals in a more practical situation, their photocatalytic performance under natural sunlight was also evaluated. As illustrated in Figure 5(b), after exposure to 150 min of daytime sunlight, 90% of RhB was degraded by using Au-CdS nanocrystals, accompanied with

an evident decoloration of the resultant solution. This result shows that the present Au-CdS nanocrystals can be used as highly efficient photocatalysts which may practically harvest energy from sunlight. As a final note, the as-prepared Au-CdS nanocrystals did not suffer significant photocorrosive oxidation as deduced from the XPS data. In Figure 5(c), both Cd and S XPS spectra of Au-CdS sample exhibit signals corresponding to the bulk CdS with the binding energies of 404.8, 411.6 and 161.8 eV for Cd 3d_{5/2}, Cd 3d_{3/2} and S 2p core levels, respectively.²⁹ For the S 2p XPS spectrum, note that no sulphate-related peak at around 168.4 eV, which originated from the photocorrosive oxidation of CdS with oxygen and water,³⁰ was observed. The absence of sulfate-related peak in S 2p spectrum indicates that the present Au-CdS nanocrystals exhibited considerably high stability in air, which is important to the durability performance during their use as photocatalysts.

4. Conclusions

In conclusion, the interfacial charge carrier dynamics for core-shell Au-CdS nanocrystals with various shell thicknesses were investigated and presented. Due to the difference in band structures between Au and CdS, a pronounced photoinduced charge separation took place at the interface of Au and CdS, resulting in the electron-charged Au core and the hole-enriched CdS shell. The electron-charging of Au core in Au-CdS nanocrystals was revealed with the corresponding XPS analysis and photocurrent measurement. Time-resolved PL data showed that a higher electron-transfer rate constant was observed for Au-CdS nanocrystals with thicker CdS shell. On the other hand, the hole-enriched CdS shell of Au-CdS nanocrystals upon light illumination was characterized with a photocatalytic process. The photocatalytic activity of Au-CdS nanocrystals was found to increase with increasing shell thickness, consistent with the result of electron-transfer rate constant variation. The current Au-CdS nanocrystals may find promising photocatalytic applications, especially in the

photooxidative decomposition of various organic pollutants such as aldehydes³¹ and chlorinated hydrocarbons.³² The present study also gives rise to a new class of highly efficient metal/semiconductor hybrid photocatalysts which may effectively utilize the solar power.

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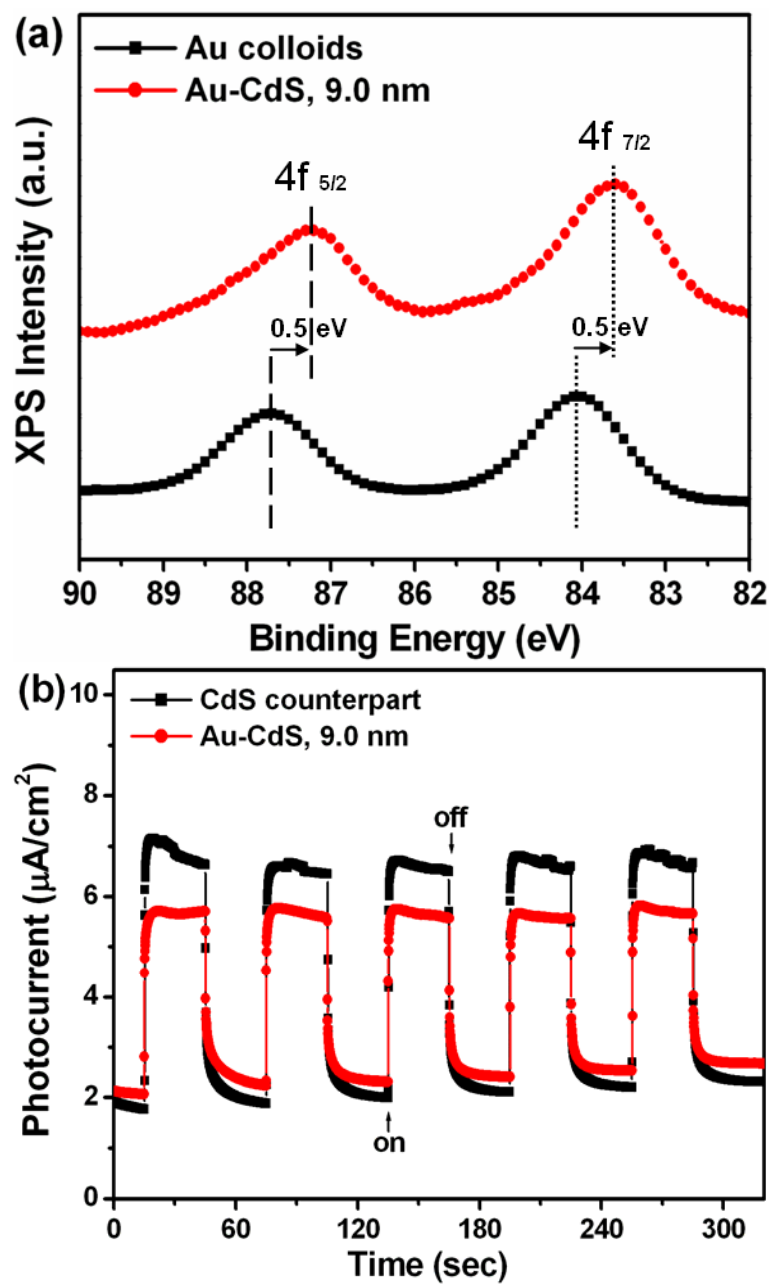


Figure 1. (a) XPS spectra of Au 4f for Au colloids and Au-CdS nanocrystals. (b) Photocurrent response of Au-CdS nanocrystal and CdS counterpart electrodes to on/off cycles of light illumination. The shell thickness of Au-CdS nanocrystals is 9.0 nm.

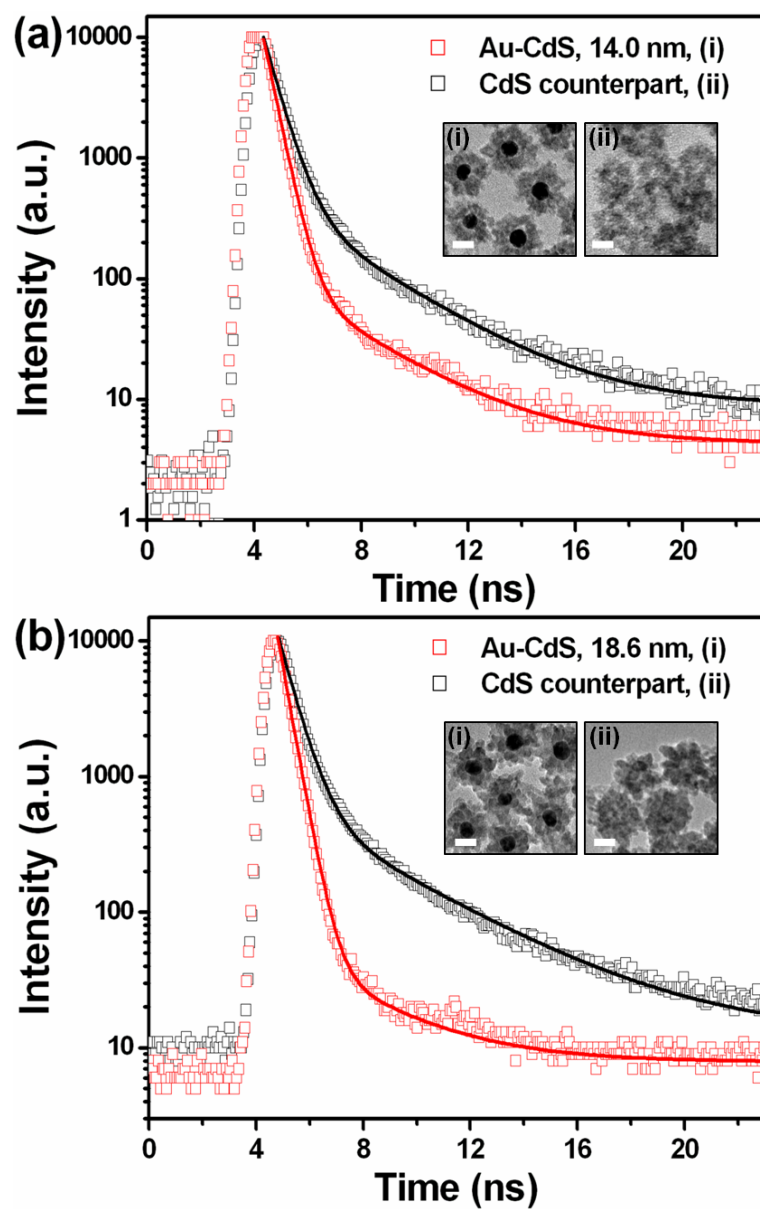


Figure 2. Time-resolved PL spectra of Au-CdS nanocrystals and CdS counterpart with the shell thickness of (a) 14.0 nm, and (b) 18.6 nm. The fitting results (solid curves) were also included for comparison. Insets show the corresponding TEM images and the scale bar is 20 nm.

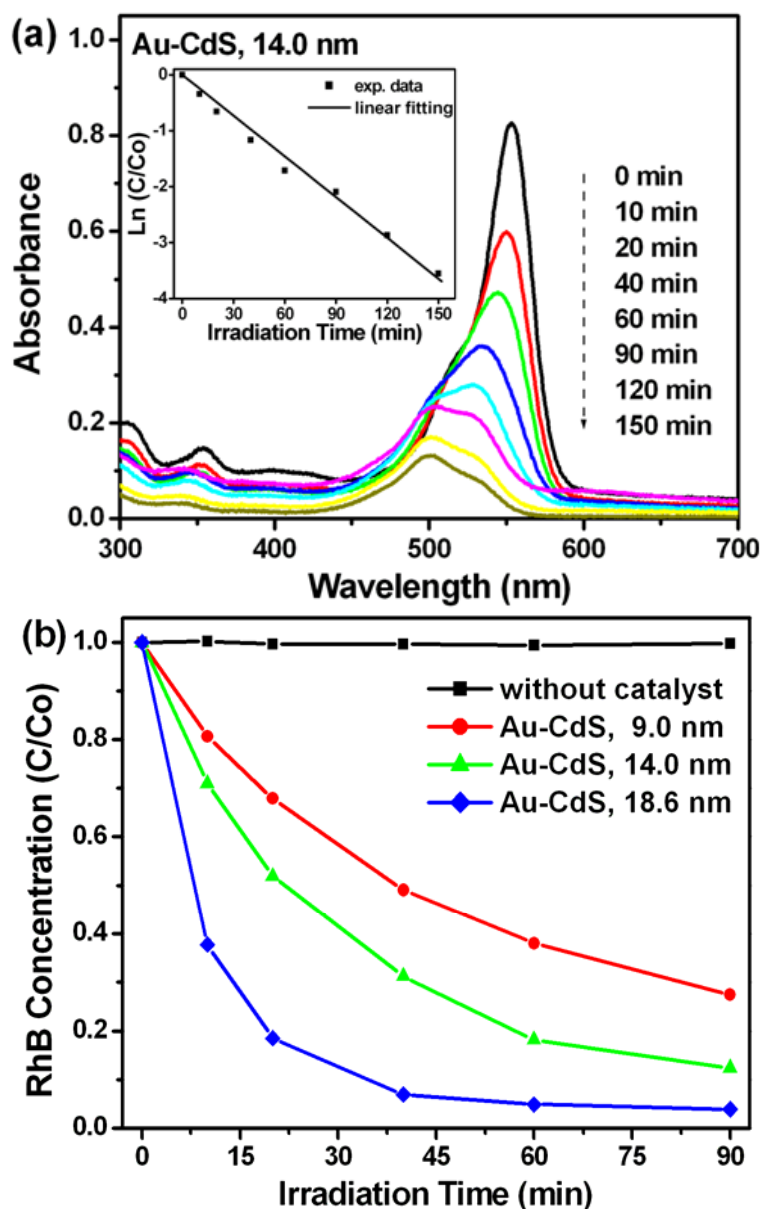


Figure 3. (a) Absorption spectra of RhB solutions under different irradiation times by using Au-CdS nanocrystals with the shell thickness of 14.0 nm. Inset shows the $\ln(C/C_0)$ versus irradiation time plot with the fitting result included. (b) C/C_0 versus irradiation time plots for RhB photodegradation without any catalyst and in the presence of Au-CdS nanocrystals with various shell thickness.

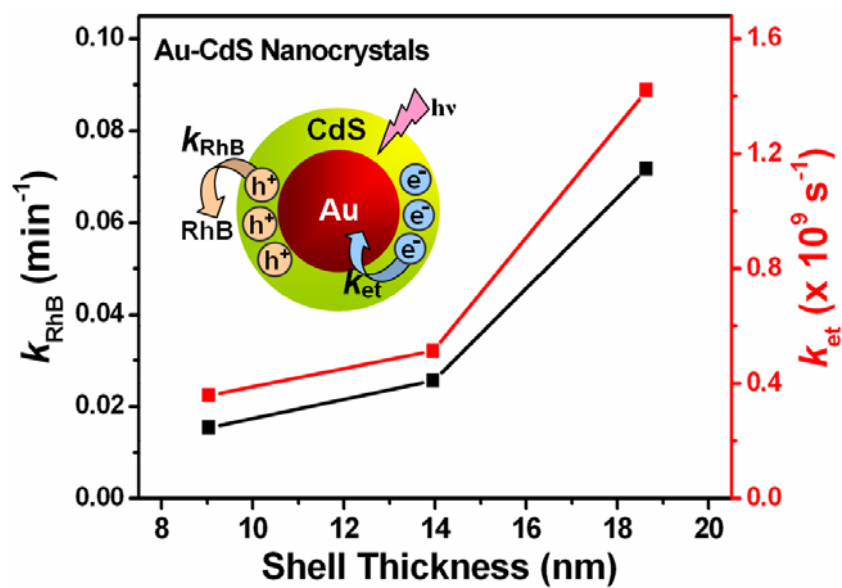


Figure 4. Correlations of electron-transfer rate constant (k_{et}) and rate constant of RhB photodegradation (k_{RhB}) with the shell thickness of Au-CdS nanocrystals.

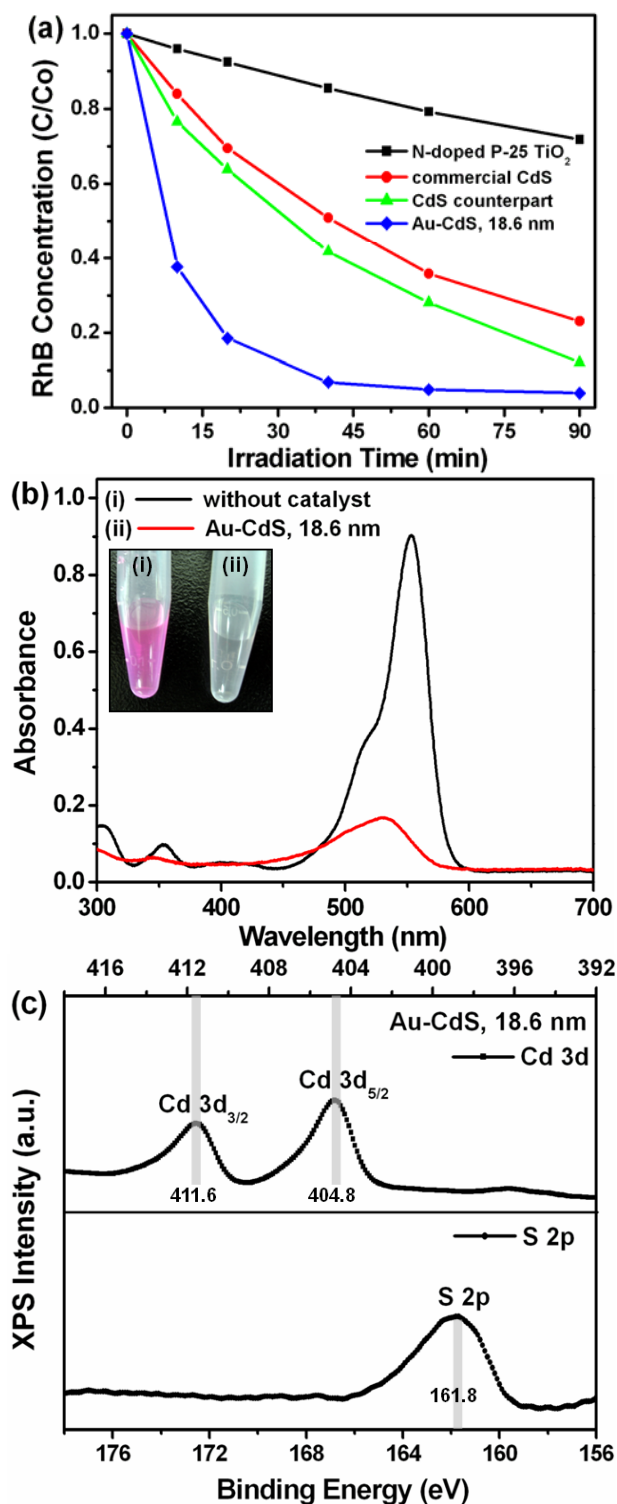


Figure 5. (a) C/C_0 versus irradiation time plots for RhB photodegradation in the presence of different photocatalysts. (b) Absorption spectra of RhB solutions after exposure of 150 min of daytime sunlight without any catalyst and in the presence of Au-CdS nanocrystals with the shell thickness of 18.6 nm. Insets show the corresponding solution color. (c) XPS spectra of Cd 3d and S 2p for Au-CdS nanocrystals with the shell thickness of 18.6 nm.

Table 1. Kinetic analysis of emission decay for Au-CdS nanocrystals with various shell thicknesses and their corresponding CdS counterparts.

entry	A_1	τ_1 (ns)	A_2	τ_2 (ns)	$\langle\tau\rangle$ (ns)	$k_{\text{et}}(\text{s}^{-1})$
Au-CdS, 9.0 nm	9843.3	0.37	60.9	2.58	0.46	0.36×10^9
CdS counterpart	11532.9	0.41	102.0	2.91	0.56	
Au-CdS, 14.0 nm	11539.6	0.40	110.7	2.95	0.57	0.51×10^9
CdS counterpart	9512.3	0.53	464.4	2.98	1.06	
Au-CdS, 18.6 nm	10633.5	0.39	49.4	2.99	0.48	1.42×10^9
CdS counterpart	9873.0	0.58	599.0	3.82	1.51	

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

☒ 達成目標

☐ 未達成目標（請說明，以 100 字為限）

☐ 實驗失敗

☐ 因故實驗中斷

☐ 其他原因

說明：

2. 研究成果在學術期刊發表或申請專利等情形：

論文：☒ 已發表 ☐ 未發表之文稿 ☐ 撰寫中 ☐ 無

專利：☐ 已獲得 ☐ 申請中 ☐ 無

技轉：☐ 已技轉 ☐ 洽談中 ☐ 無

其他：（以 100 字為限）

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以 500 字為限）

本計畫之主軸係非揮發性之記憶體元件製作為基礎，首先以光反應層材料為導電高分子(P3HT)並混入量子點(CdSe)，由實驗得知含有量子點材料的元件具有較高的光反應性及具有記憶體效應，即當移除光源後電子會因為被量子點捕捉而形成記憶效應，並且此結果在不需要外加電壓時量子點的電子捕捉時間也可以維持數小時之久，最後量子點中的電子可再被外加電壓給移除，此部分對於記憶體元件的應用有極大之貢獻，該成果發表於 Appl. Phys.Lett. 92, 143105, 2008. (SCI; IF:3.596)，刊出後立即被 Asia Materials 選為 Highlight 文章(請參考網址：<http://www.natureasia.com/asia-materials/highlight.php?id=124>)，並被選入刊於 Virtual Journal of Nanoscale Science & Technology, April 21, 2008 issue。隨後我們利用量子井核殼結構(Quantum well core-shell structure)之 CdSe@ZnSe 大幅改善記憶體的記錄時間及 ON/OFF ratio，在照光後，其存在有 CdSe@ZnSe 量子點之 P3HT 薄膜，強化其最大 ON/OFF 比例達 2700，其值可維持 8000 秒而不衰退。其 ON 狀態之電流，可利用單一脈衝之柵極電壓-10V 去有效地抹除。此重大突破使光記憶體元件的應用更具價值，並發表於 Organics Electronics, 10 (2009) 769-774 (SCI;IF:3.879)。另外地，本計畫中，我們也將

Poly(styrene-*b*-4-vinylpyridine)自組裝塊式高分子薄膜材料應用在非揮發性記憶體上，製備元件結構分別為 Al/PS-*b*-P4VP/Al 和 ITO/ PS-*b*-P4VP /Al 的三明治元件結構，分析後發現 Al/ PS-*b*-P4VP /Al 和 ITO/ PS-*b*-P4VP /Al 的傳導機制並不完全相同，但主要都是由導線機制(filament mechanism)主導。然而 ITO/ PS-*b*-P4VP /Al 元件，有較佳之元件特性(例如：On/Off 最高可以達到 10^6 ，寫入和抹除的時間可達到微秒)。其中，寫入(write)與抹除(erase)電壓分別為-0.5V 與 0.75V，電子的遲滯時間也可以維持數小時之久。此記憶體元件可再被外加電壓達到移除寫入之信號，此部分對於記憶體元件的應用有極大之貢獻，該成果發表於(Appl. Phys.Lett. 93, 203303, 2008. SCI；IF:3.596)。此些論文發表代表我們已達成預期的研究成果，並且成功發揚非揮發性記憶體元件之製作概念，相信這對於製程整合並架設光電記憶體、電阻式記憶體、金屬/半導體核殼異質介面元件量測系統之進展，有相當助益。最後地，本計畫也製備 Au-CdS 核殼奈米晶體，此由金屬與半導體所組成之異質結構，因其所具有之高效率載子分離特性，可廣泛應用於光觸媒分解有機分子、光催化氫氣生產、太陽能光電電池以及電子儲存記憶原件等。金屬奈米顆粒在此複合結構中乃扮演著電子捕捉者的角色，當半導體材料經照光而激發出電子電洞對時，由於能帶結構的相對關係，電子會從半導體端轉移至金屬端，此時半導體端成為電子施體而帶有大量的電洞，而金屬端則扮演電子捕捉者角色而帶有大量自由電子，此正負載子的分離經導出系統後，可分別應用於上述相關用途，尤其是核心 Au 所捕捉的大量電子，則可使奈米晶體於不同電場作用下展現不同電性狀態，故此 Au-CdS 奈米晶體亦可作為記憶體原件中之主動層材料。我們成功地藉由時間解析螢光光譜(time-resoled fluorescence spectroscopy)，來量測載子之生命週期與其於介面間的傳輸速率，此類資訊可作為判斷 Au-CdS 奈米晶體用於儲存電子效果好壞的依據；更重要地，我們可藉由瞭解介面間之載子動力學，來推論影響此 Au-CdS 奈米晶體之記憶體儲存效果的主要因素為何，如此便可對症下藥設計出最適化之材料配對與合成製程，以期能獲得具有最佳之電子儲存效率的結構。自 2007 年 8 月開始執行此計畫至今，共有 4 篇與計畫主題相關之期刊論文發表，此 4 篇論文均發表於國際知名期刊中，分別為 *Appl. Catal. B-Environ.* (2010, 97, 389-397. SCI IF=5.252)、*Langmuir* (2010, 26, 5918-5925. SCI IF=3.898)、*J. Phys. Chem. C* (2010, 114, 11414-11420)與 *Chem. Mater.* (2008, 20, 7204-7206. SCI IF=5.368)。此些論文發表代表我們已達成預期的研究成果，並且成功將我們的研究概念傳遞與發揚，相信這對於非揮發性記憶體原件之進展，乃有相當助益。

出席國際學術會議心得報告

計畫編號	NSC 98-2218-E-009-003-
計畫名稱	非揮發記憶體用之高分子/核殼奈米顆粒奈米複合材料之合成與元件製備 (3 /3)
出國人員姓名 服務機關及職稱	韋光華 交通大學 材料系 教授
會議時間地點	September 25-27, 2010, 中國大陸青島
會議名稱	第十一屆國際材聯亞洲材料大會

本人參加 99 年 9 月 26 日至 28 日於青島舉行之第十一屆亞洲材料大會，並擔任太陽能電池這個 session 之 chair。

本人於 9 月 25 日早上由台北出發抵達香港後及轉機前往青島。抵達青島流亭國際機場及前往青島國際會展中心如家酒店住宿。

9 月 26 日於青島國際會展中心舉辦之大會，上午共有五個 plenary speakers 包括台灣之清華大學陳力俊校長。本人之演講為邀請演講，講題為高分子太陽能電池排在下午之第一場。報告完後，並與大陸材料協會會談明年於台灣舉行之亞洲材料大會事宜。

隔天 9 月 27 日上午主持了一個 session，因為隔天 9 月 28 日本人必須授課，中午隨即前往機場搭機返台。

國科會補助計畫衍生研發成果推廣資料表

日期:2010/11/16

國科會補助計畫	計畫名稱：非揮發記憶體用之高分子/核殼奈米顆粒奈米複合材料之合成與元件製備(3/3)	
	計畫主持人：韋光華	
	計畫編號：98-2218-E-009-003-	學門領域：軟性電子跨領域專案計畫
無研發成果推廣資料		

98 年度專題研究計畫研究成果彙整表

計畫主持人：韋光華			計畫編號：98-2218-E-009-003-				
計畫名稱：非揮發記憶體用之高分子/核殼奈米顆粒奈米複合材料之合成與元件製備(3/3)							
成果項目			量化			單位	備註（質化說明：如數個計畫共同成果、成果列為該期刊之封面故事...等）
			實際已達成數（被接受或已發表）	預期總達成數(含實際已達成數)	本計畫實際貢獻百分比		
國內	論文著作	期刊論文	0	0	100%	篇	
		研究報告/技術報告	0	0	100%		
		研討會論文	0	0	100%		
		專書	0	0	100%		
	專利	申請中件數	9	9	100%	件	
		已獲得件數	5	5	100%		
	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
	參與計畫人力（本國籍）	碩士生	1	1	100%	人次	
		博士生	3	3	100%		
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		
國外	論文著作	期刊論文	35	35	100%	篇	
		研究報告/技術報告	0	0	100%		
		研討會論文	0	0	100%		
		專書	0	0	100%	章/本	
	專利	申請中件數	6	6	100%	件	
		已獲得件數	1	0	100%		
	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
	參與計畫人力（外國籍）	碩士生	0	0	100%	人次	
		博士生	0	0	100%		
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		

其他成果 (無法以量化表達之成果如辦理學術活動、獲得獎項、重要國際合作、研究成果國際影響力及其他協助產業技術發展之具體效益事項等，請以文字敘述填列。)	無。
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	成果項目	量化	名稱或內容性質簡述
科 教 處 計 畫 加 填 項 目	測驗工具(含質性與量性)	0	
	課程/模組	0	
	電腦及網路系統或工具	0	
	教材	0	
	舉辦之活動/競賽	0	
	研討會/工作坊	0	
	電子報、網站	0	
	計畫成果推廣之參與（閱聽）人數	0	

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

☒ 達成目標

☐ 未達成目標（請說明，以 100 字為限）

☐ 實驗失敗

☐ 因故實驗中斷

☐ 其他原因

說明：

2. 研究成果在學術期刊發表或申請專利等情形：

論文：☒ 已發表 ☐ 未發表之文稿 ☐ 撰寫中 ☐ 無

專利：☐ 已獲得 ☐ 申請中 ☒ 無

技轉：☐ 已技轉 ☐ 洽談中 ☒ 無

其他：（以 100 字為限）

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以 500 字為限）

本成果研究可促進有機非揮發性記憶體及隨機讀取記憶體的發展，預期可以協助有機記憶體的研究發展，本研究執行成果也已顯示出利用量子點，可以進一步改善有機記憶體的特性；又因量子點對光特性的作用，可進一步發展成『光記憶體元件』或『光讀取記憶體元件』。此創有機記憶體發展領域結合量子點發展之先驅。