行政院國家科學委員會專題研究計畫 期中進度報告

複合半導體奈米基材；基理的探索以及尖端應用的研究 (1/3)

期中進度報告(精簡版)

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共 同 主 持 人：季昀、何佳安、楊家銘

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行政院國家科學委員會補助專題研究計畫 期中進度報告

複合半導體奈米基材；基理的探索以及尖端應用的研究(1/3)
Composite Semiconductor Nanomaterials; Probing Fundamentals and Avant-garde Applications.

計畫類別：□ 個別型計畫　　☑ 整合型計畫
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計畫主持人：周必泰 Chou, Pi-Tai
共同主持人：季昀、楊家銘、何佳安 Chi, Yun、Yang, Chia-Min、Ho, Ja-An Annie
計畫參與人員：

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一、中英文摘要

我們在這三年的計畫提出有關奈米基材，尤其是半導體量子點的光物理化學性質以及應用的研究。在基理方面，我們將結合飛秒雷射系統（包含螢光合頻以及瞬態吸收光譜）來積極探討 II-VI（或 III-V）族量子點的線性以及非線性光學性質，並進一步研究其電子和電洞的緩解機制，包含了粒徑, 溫度等效應。我們在這方面的研究最大優勢仍在於我們在合成方面已建立了非常成功的建制，尤其是在 Type II P/N 半導體量子點的合成研究上。我們也根據基理的發展定下五個執行的子計畫，但我們再次強調這五個計畫是一體的，將由總主持人策劃平行進行，但又間接具互補的功能，五個執行計畫如下：

一、我們將仔細研究探討 II-VI 量子點其單光子以及雙光子吸收的最基本原理。

二、我們將利用飛秒快速偵測系統來探測 Type II 量子點的電子與電洞的緩解機制，這方面的研究將對下個主題利用 Type II 量子點或量子棒做太陽能電池的基理有透徹的解析。

三、我們將立足於基理，利用 II-VI 半導體奈米基材來探討太陽能電池的可行性，並著重於元件的製作與改良。

四、我們將利用不同的奈米發光基材，經化學修飾後應用於生化相關的辨識，偵測以及治療上。

五、我們也將積極開發不同於 II-VI 及 III-V 族方面的奈米發光基材，其基本訴求將立足於較不具生理毒性以及具相當彈性的化學修飾能力。

最後，基於過去的成功經驗，我們相信我們可以在三年之內完成這些計畫。

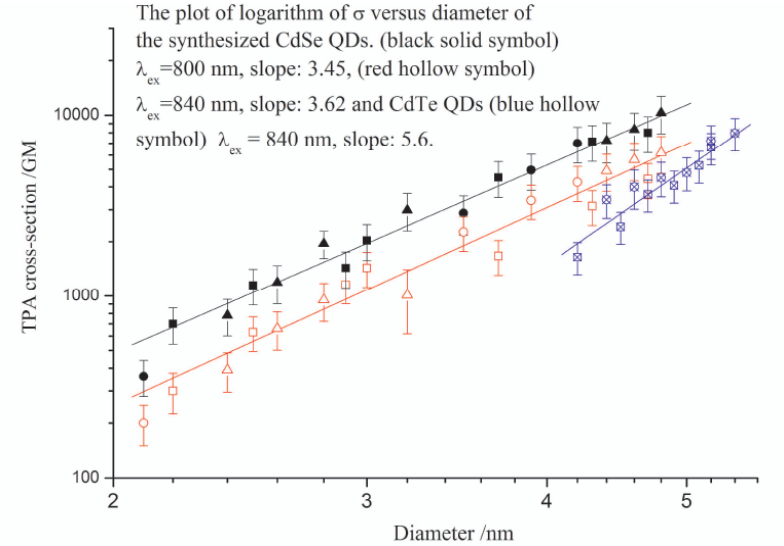
We propose to probe the corresponding linear and nonlinear photophysical behaviors of composite semiconductor quantum dots (QDs) based on various femtosecond techniques, as well as to explore cutting-edge applications. Our advantages are surely lying in the insurance of QDs quality, chemical functionality as well as state-of-the-art experimental set up. Four main projects will be carried out in parallel but tightly linked through the fundamental basis, including:

1. **One-photon and two photon absorption (TPA) properties of II-VI QDs.**
2. **Early relaxation dynamics of type II QDs**
3. **Energy related applications, particularly on the solar energy conversion.**
4. **Biomedical related application based on type II QDs**
5. **Silicon Based Quantum QDs in the biomedical application.**
6.

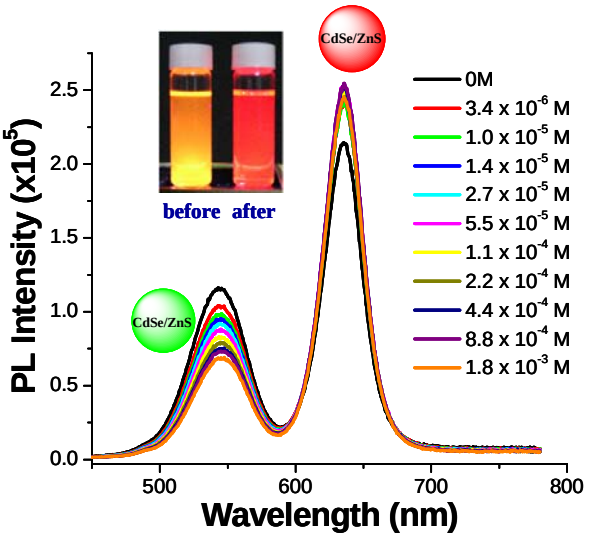
We believe that our recent achievements and gains on the relevant research fields surely warrant substantial credit in fulfilling the aims within a span of three years.

二、報告內容

2a. We have successfully tuned CdSe (CdTe) quantum dots (QDs) sizes and consequently measured their corresponding two-photon absorption (TPA) cross section in a systematic manner. As the size (diameter) of the quantum dots increased, the TPA cross section was found to be empirically 3.5 ± 0.5 and 5.6 ± 0.7 power of CdSe and CdTe QDs diameters, respectively. We tentatively rationalized the results on theoretical levels of two-photon excitation properties in a system incorporating exciton and defects. (*Small*, **2006**, *2(11)*, 1308-1313)

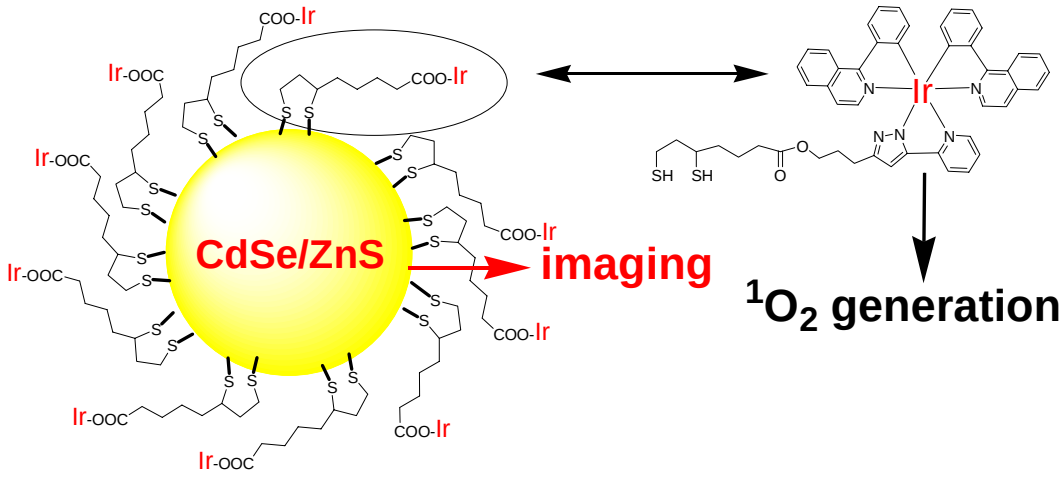


2b. Based on the syntheses of highly emissive, water-soluble CdSe/ZnS core/shell QDs capped by dihydrolipoic acid, we have successfully designed a sensitive fluorogenic sensor to probe the Hg^{2+} ion in both aqueous solution and heterogeneous solid film. The Hg^{2+} selectivity is very high, with negligible interference from most metal ions listed in EPA. As low as 10^{-7} M Hg^{2+} can be promptly detected. Furthermore, based on 15-Crown-5 functionalized CdSe/ZnS QDs, we have synthesized a novel fluorogenic sensor to probe the K^+ ion in H_2O. Recognition of K^+ can be achieved via K^+ bridging dual color QDs, so that the Förster type of energy transfer is operative (see Scheme 1). The K^+ selectivity is very high, with negligible interference from most metal ions. As low as 10^{-6} M of K^+ can be promptly detected via a ratiometric change of the dual emission. (*Chem. Commun.*, **2006**, 263-265.)



Scheme 1. The fluorescence titration of dual QDs with the addition of various $KClO_4$ in \H_2O (pH~ 7.0)

6c.W e have ingeneously designed an Ir-CdSe/ZnS system, in which the interplay between CdSe/ZnS QDs and [(piq)2Ir(L_2)] chromophores is negligible. The system possesses a bifunctional property in that CdSe/ZnS QDs and [(piq)2Ir(L2)] act as an imaging center and a $^1O_2$ sensitizing agent, respectively. For Ir-CdSe/ZnS in aerated MeOH, the quantum yield of the 590 nm CdSe/ZnS emission was determined to be 0.4, which is sufficiently high for application in imaging. ([*Chem. Commun.*, **2006**, 615 -617)



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3a. We have demonstrated for the first time a comprehensive investigation into the size-dependent TPA cross section of II-VI QDs. As the size (diameter) of QDs increased, the TPA cross section was found to be empirically proportional to the 3.5 ± 0.5 and 5.6 ± 0.7 power of sizes of CdSe and CdTe, respectively. Both experimental and theoretical approaches render a clue to the mechanisms of two-photon excitation and corresponding types of transition models as well as provide the feasibility to quantitatively probe TPA cross sections for CdSe and CdTe QDs. We thus believe that the correlation of TPA with respect to CdSe or CdTe is a valuable effort to characterize and measure the two-photon cross-section of colloidal quantum dots. This subject should gain importance as these materials are being increasingly used for two-photon fluorescence bio-microscopy.

3b. For project 2**b**, we have demonstrated that CdSe/ZnS QDs modified with 15-crown-5 in water exhibit excellent selectivity toward K^+. Signal transduction can be achieved through the energy transfer takes place between dual color QDs, resulting in a ratiometric change of dual emission intensity and hence the emission color. Taking the intensity ratio of 1.8 for 635 nm versus 545 nm emission in the K^+ free soluton and that of 2.2 in 3.4×10^{-6} M K^+ solution, the ratiomatric fluorescence is easily differentiated, the result of which concludes the K^+ detection limit to be on the order of 10^{-6} M. We thus present a conceptual design of 15-crown-5 functionalized CdSe/ZnS QDs and applied dual color energy transfer as a general detection scheme to probe K^+ in H_2O. This recognition scheme should spark a broad spectrum of interest due to its great versatility and flexibility.

3c. As the practical application of project 2**c**, specific target agents can be designed and co-anchored with [(piq)2Ir(L_2)] ligand to CdSe/ZnS, among which a potential candidate should be folic acid because it binds to a receptor that several kinds of cancer cells produce in unusually large amounts. The resulting system is expected to be water soluble as well as to possess a three-in-one property, namely specific targeting, imaging, and $^1O_2$ generation, which would greatly expand the usefulness of photodynamic therapy.

As for the fundamental and applications of II-VI and III-V zero and one-dimensional nanomaterials, we believe, there are still numerous relevant territories remain unexplored. In view of fundamental, our focus on the femtosecond relaxation dynamics of type II QDs is believed to be seminal and their associated mechanisms such as the Auger-like process is of extreme importance due to its future application of the harvesting sun light. In view of applications, the exploitation of QDs, integrated with singlet oxygen sensitizer and cancer cell-targeted substrate, has been carried out through the collaboration with a team form NTU

medical school. We are confident that future biomedical application involving the integrated QDs be fruitful. We are also applying for a patent dealing with such a technique and intend to issue the transfer of technology once patent is granted.