



Interfacial charge carrier dynamics of type-II semiconductor nanoheterostructures

Yi-Fang Lin, Yung-Jung Hsu*

Department of Materials Science and Engineering, National Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan, ROC

ARTICLE INFO

Article history:

Received 15 August 2012

Received in revised form 19 October 2012

Accepted 28 October 2012

Available online 7 November 2012

Keywords:

Type-II semiconductor nanoheterostructures
Charge separation
Photoconversion
Photocatalysis
CdS nanowires

ABSTRACT

Semiconductor nanoheterostructures with type-II band offset have exhibited unique optoelectronic properties that are beneficial to photoconversion applications. Debatable arguments however exist in the literature for interpreting the most enhanced photocatalytic performance of type-II semiconductor nanoheterostructures when an optimal content of the constituents is employed. In this work, time-resolved photoluminescence is used to investigate the interfacial charge carrier dynamics for CdSnO₃-decorated CdS nanowires, a prototype type-II nanoheterostructures system, with varying CdSnO₃ contents. Our results show that the CdSnO₃ content of 2.5 at% rendered CdS–CdSnO₃ NWs the most significant charge carrier separation, above which electron–hole recombination across CdS/CdSnO₃ interface mediated carrier transfer to compromise the overall charge separation efficiency. The carrier dynamics results are in good accordance with that of photoconversion performance evaluation in dye photodegradation, which assists in resolving the very critical but still controversial issue as to the factors causing the depressed photocatalytic efficiency of type-II nanoheterostructures when the constituent content exceeds the optimal value.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

With the inherently high degree of complexity, nanoheterostructures composed of two or more materials joined in unique architectures may exhibit superior synergetic properties that are difficult or impossible to acquire from their individual constituents. Of particular interest are the type-II semiconductor nanoheterostructures, where the relative band alignment of the constituents promotes effective charge separation to bring them desirable properties for photoconversion applications [1–14]. For example, with the decoration of Ag₂O nanoparticles, TiO₂ nanobelts displayed significantly enhanced photocatalytic activities under both ultraviolet and visible light illumination. This enhancement results from the staggered band offset between Ag₂O and TiO₂, which inhibits charge recombination to capture more charge carriers for participation in photocatalysis [8]. Besides, a five-fold increase in photoconversion efficiency was observed for TiO₂ nanotubes once they were coated with a thin layer of CdS. This improvement is due to the more negative conduction band of CdS, which ensures a quick electron transfer from CdS to TiO₂ and thus the facilitated collection of electrons [10]. Till now, various kinds of semiconductor nanoheterostructures with type-II band offset

have been proposed and fabricated to further the advancement of photoconversion technology.

To comprehend the factors dictating the photoconversion efficiency of type-II semiconductor nanoheterostructures, several research groups have focused on realizing the interfacial charge carrier dynamics using ultrafast laser spectroscopy techniques [15–20]. Primary results show that the difference in conduction band energy level between the two constituents of type-II nanoheterostructures determines the driving force for interfacial charge transfer and thereby governs the charge separation property. By enlarging this energy difference, type-II nanoheterostructures may exhibit significantly improved charge separation and performed better in photoconversion applications [18–20]. Besides the energy difference, the relative content of the constituents of nanoheterostructures affects the resultant photoconversion efficiency as well. It has been extensively observed that there exists an optimal content of each constituent for enhancing the photocatalytic efficiency of type-II semiconductor nanoheterostructures [21–30]. This phenomenon has often been ambiguously ascribed to issues like inhibited light absorption [21–24], structural effect [21,25,26], charge trapping [27,28], or even no apparent reasons [29,30]. Moreover, there are very few studies in the literature regarding the dependence of interfacial charge transfer on the relative content of the constituents for such nanoheterostructures, and their correlation with the resultant photoconversion efficiency has never been reported. Therefore, a quantitative study on this subject is crucial to both the fundamental

* Corresponding author. Tel.: +886 3 5712121x55317; fax: +886 3 5724724.
E-mail addresses: yhsu@cc.nctu.edu.tw, yhsu@mail.nctu.edu.tw (Y.-J. Hsu).

Table 1
Kinetic analysis of emission decay for pristine CdS and different CdS–CdSnO₃ NWs.

	$A_1/(A_1 + A_2)$ (%)	τ_1 (ns)	$A_2/(A_1 + A_2)$ (%)	τ_2 (ns)	k_{et} (s ⁻¹)
Pristine CdS	26.4	8.03	73.6	2.19	–
CdS–CdSnO ₃ , 1.25 at%	22.0	5.22	78.0	0.57	1.30×10^9
CdS–CdSnO ₃ , 2.5 at%	5.6	4.69	94.4	0.24	3.71×10^9
CdS–CdSnO ₃ , 5.0 at%	11.6	4.84	88.4	0.30	2.88×10^9
CdS–CdSnO ₃ , 10.0 at%	30.1	6.48	69.9	1.36	0.28×10^9

understanding and the practical applications for type-II semiconductor nanoheterostructures.

In this work, we presented a prototype type-II semiconductor nanoheterostructures system by combining CdS and CdSnO₃ into a single hybrid. The samples were prepared by depositing CdSnO₃ nanocrystals on the surface of CdS nanowires (denoted as CdS–CdSnO₃ NWs) in the solvothermal reaction. For CdS–CdSnO₃ NWs, the surface-attached CdSnO₃ can serve as an effective electron scavenger for CdS due to its lower conduction band potential (+0.9 V vs. NHE) than that of CdS (–0.5 V vs. NHE) [31,32]. Consequently, the photoexcited electrons of CdS NWs would preferentially transfer to CdSnO₃ nanocrystals, leaving photogenerated holes at CdS domain to achieve charge carrier separation. Time-resolved photoluminescence (PL) measurements were conducted to explore the interfacial charge carrier dynamics for the as-prepared CdS–CdSnO₃ NWs. By probing the emission lifetime of CdS, the electron transfer event between CdS and CdSnO₃ for CdS–CdSnO₃ NWs and its dependence on CdSnO₃ content were quantitatively analyzed. A CdSnO₃ content of 2.5 at% was found to render CdS–CdSnO₃ NWs the most significant charge carrier separation, above which electron–hole recombination across interface mediated carrier transfer to compromise the overall charge separation efficiency. This consequence is in good agreement with the result of photoconversion performance evaluation in dye photodegradation, which helps to resolve debatable arguments about the factors causing the depressed photocatalytic efficiency of type-II semiconductor nanoheterostructures when the constituent content exceeds the optimal value.

2. Experimental

2.1. Chemicals

All chemicals were analytic-grade and used without further purification. Special attention should be paid when dealing with the hazardous Cd source.

2.2. NWs syntheses

The syntheses of pristine CdS and CdS–CdSnO₃ NWs were conducted in a solvothermal process [33]. For the preparation of CdS NWs, Cd(NO₃)₂·4H₂O (1.54 g, 0.005 mol) and sulfur powder (0.32 g, 0.01 mol) were mixed with ethylenediamine (80 mL) in the flask. The solution was then transferred to a Teflon-lined stainless steel autoclave (with a capacity of 100 mL) for solvothermal reaction at 180 °C for 24 h. The resulting yellow solid product (CdS NWs) was centrifuged, and washed with distilled water and ethanol to remove remaining ions. With the addition of SnCl₂·2H₂O (11.28 mg, 0.05 mmol) and NaOH (0.02 mL, 5 M) in the solvothermal reaction, growth of CdS NWs was accompanied by the deposition of CdSnO₃ nanocrystals, resulting in the formation of CdS–CdSnO₃ NWs. In this work, various concentrations of SnCl₂·2H₂O (0.00625, 0.0125, 0.025, 0.05 mmol) added in the reaction solution were employed to produce CdS–CdSnO₃ NWs with different CdSnO₃ contents (1.25, 2.5, 5.0, 10.0 at%, respectively). For comparison purpose, pure CdSnO₃ nanocrystals were also prepared.

2.3. PL lifetime measurement

Time-resolved PL spectra were measured using a home-built single photon counting system (Horiba Jobin Yvon) which delivers an instrument response function down to 25 ps FWHM. GaN diode laser ($\lambda = 375$ nm) was used as the excitation source. The signals collected at the excitonic emission of CdS ($\lambda_{em} = 502$ nm) were dispersed with a grating spectrometer, detected by a high-speed photomultiplier tube, and then correlated using a single photon counting card. Upon laser excitation, the photoexcited electrons of CdS were injected into CdSnO₃ due to the higher conduction band potential of CdS (–0.5 V vs. NHE) than that of CdSnO₃ (+0.9 V vs. NHE), which leads to a significant quenching on the emission of CdS. By comparing the emission decay profiles between CdS and CdS–CdSnO₃, the electron transfer from CdS to CdSnO₃ can be quantitatively deduced. It should be noted that CdSnO₃ did not exhibit PL emission around 500 nm, with which the emission decay of CdS at 502 nm was not interfered and its variation with the presence of CdSnO₃ can be precisely interpreted. The emission decay data were analyzed and fitted with biexponential kinetics model which generates two lifetime values, τ_1 and τ_2 , and the corresponding amplitudes, A_1 and A_2 . All the fitting results were summarized in Table 1. The value of goodness (χ^2) of the fitting was in the range of 1.00–1.06, indicating a good fit to the experimental data.

2.4. Photodegradation experiment

The photodegradation experiment on CdS–CdSnO₃ NWs was carried out by using rhodamine B (RhB) as the probe molecule under visible light illumination. A quartz tube with a capacity of 30 mL was used as the photoreactor vessel. The optical system used for photodegradation consisted of a xenon lamp (500 W, with a light intensity of 175 mW/cm²) and a bandpass filter (with the bandwidth of 400–700 nm) that allowed the irradiation in visible range. Six kinds of samples including pristine CdS NWs, four CdS–CdSnO₃ NWs, and pure CdSnO₃ nanocrystals were compared in the photodegradation of RhB. Typically, a fixed amount of sample (3 mg) was added into RhB aqueous solution (15 mL, 1.0×10^{-5} M) in the photoreactor vessel. Prior to irradiation, the suspension was aerated and stirred in the dark for 30 min to reach the adsorption equilibrium between RhB and sample. Dye adsorption capability of the sample was then evaluated by measuring the RhB concentration change after the adsorption equilibrium. At certain time intervals of irradiation, 1.5 mL of the reaction solution was withdrawn and centrifuged to remove sample 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 554 nm. Furthermore, photodegradation of RhB (1.0×10^{-5} M) under natural sunlight by using CdS–CdSnO₃ NWs (3 mg) was also tested.

2.5. Characterizations

The morphology and dimensions of the samples were examined with a field-emission scanning electron microscope (SEM, JEOL, JSM-6500F) and a high-resolution transmission electron

Download English Version:

<https://daneshyari.com/en/article/45819>

Download Persian Version:

<https://daneshyari.com/article/45819>

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