

Photochemical Behavior of Type-II Semiconductor Heterodimers

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(Received 04 June 2013; published online 31 August 2013)

Type-II semiconductor heterodimers with a staggered alignment of band edges at the heterointerface can promote spatial charge separation of the electron and hole in different parts of the heterodimer for photocatalytic and photovoltaic applications. In this paper, the two kinds of CdS-based type-II semiconductor heterodimers were successfully synthesized. Type-II CdS-CdTe heterodimers without any defects exhibited clear photo-induced electron transfer, whereas CdS-Cu₃₁S₁₆ heterodimers showed dominant consumption of photogenerated carries via vacancy-induced decay processes.

Keywords: Photochemical behavior, Charge separation, Semiconductor, Type-II alignment, Heterodimer.

PACS numbers: 61.46.Df, 64.75.Qr, 78.67.Bf

1. INTRODUCTION

Heterostructured nanoparticles (NPs), in which two or more distinct inorganic materials are connected together, are expected to provide new ways to manipulate wave functions, plasmon resonances, and spin. In semiconductor heterodimers, the choice of semiconductor materials allows control of the manner of confinement of the electron and hole wave functions in NPs. Type-II heterostructured NPs with a staggered alignment of band edges at the heterointerface can promote spatial charge separation of the electron and hole in different parts of the heterodimer for photocatalytic and photovoltaic applications.

2. CdS-CdTe HETERODIMERS

CdTe is one of the ideal absorbing layers for solar cells, because it has a direct band gap of 1.5 eV almost perfectly matched to the solar spectrum. Type-II CdS-CdTe based solar cells, which have a simple heterojunction design, that is, *p*-type CdTe matched with *n*-type CdS, have reached an efficiency of 16.5%. Recently, we have investigated the formation and spatial charge separation efficiency of nanoscale CdS-CdTe heterodimers with epitaxial heterointerfaces.

Semiconductor heterodimers can be synthesized by partial transformation of NPs into heterostructures as well as seed-mediated approach [1-3]. Several studies have demonstrated that partial ion exchange reactions of ionic semiconductor NPs are effective for selective synthesis of semiconductor heterostructures [4]. Because smaller ionic crystals have a larger surface-to-volume ratio and enhanced reactivity, ionic NPs exhibit unusually high ion exchange rates relative to the bulk form. Cation exchange reactions in metal chalcogenide NPs have been studied extensively, although few examples of anion exchange reactions of ionic NPs have been reported [5]. Increased understanding of anion exchange reactions will allow the range of structure control of ionic NPs to be extended. The choice of materials is also important for control of the morphologies of the resulting heterostructures because the strain between the already formed phases (seeds) and newly grown phases induces spontaneous phase segregation during the ion exchange

reaction. Here we report a novel anion exchange reaction of ionic CdS NPs with tri-*n*-octylphosphine telluride (TOP = Te) to form CdS/CdTe heterodimers. 6)

The thermodynamically stable phases of CdS and CdTe crystals are wurtzite (*w*) and zinc blende (*zb*), respectively, and large strain at the heterointerface should induce spontaneous phase segregation. The anion exchange reaction proceeded smoothly to give anisotropically phase-segregated CdS-CdTe heterodimers with one heterointerface as an intermediate during formation of the completely exchanged product, CdTe NPs. Spontaneous formation of CdS-CdTe heterodimers took place because of the strain relaxation of the different crystallographic orientations of the *w*-CdS and *zb*-CdTe phases. As shown in Fig. 1, atomic-resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) observations revealed that the heterointerface was *w*-CdS (0001)/*zb*-CdTe (111). Transient absorption spectroscopy demonstrated that photoinduced onedirectional charge separation occurred in CdS-CdTe heterodimers because of the type-II band-edge alignment with one heterointerface (Fig. 2).

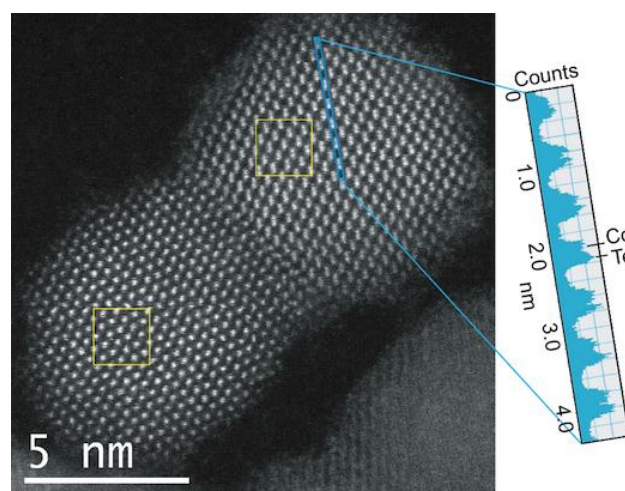


Fig. 1 – Atomic-resolution HAADF-STEM image of a single CdS-CdTe heterodimer (from ref. 3)

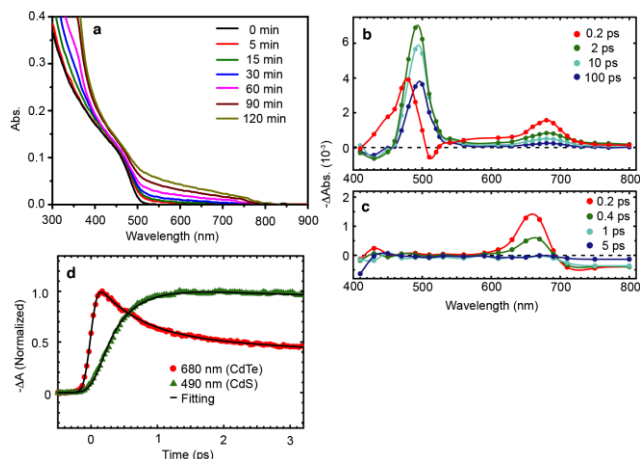


Fig. 2 – (a) Temporal evolution of UV-vis-NIR absorption spectra during the anion exchange reaction of *w*-CdS with TOP = Te. (b, c) Transient absorption spectra of (b) CdS-CdTe heterodimers and (c) the mixed *w*-CdS and *zb*-CdTe NPs ($\lambda_{pump} = 600$ nm). (d) Kinetics of CdTe and CdS state-filling signals in (b) during the first 3 ps after photoexcitation (from ref. 3)

3. CdS-Cu_{2-x}S HETERODIMERS

The type-II thin film solar cell consisting of Cu₂S and CdS films was developed more than 50 years ago, where the Cu₂S film with a band gap of 1.21 eV absorbs almost all the solar energy and the photoexcited electrons are transferred into the conduction band of the CdS film. The recent progress in the synthetic techniques of nanoscale inorganic materials turns the spotlight again onto the type-II semiconductor solar cells. One of the important issues to overcome the performance of photoelectric conversion devices is to suppress the recombination of photogenerated electrons and holes. Because the exciton lifetime greatly affects the recombination, let's see how the exciton lifetime in light-absorbing phase (Cu_{2-x}S) affects the spatial charge separation in CdS-Cu_{2-x}S ($x > 0$) heterodimer.

In 2011, Han et al. successfully synthesized disk-shaped heterodimers consisting of monoclinic Cu_{1.94}S and *w*-CdS by the partial cation exchange of preformed hexagonal-shaped Cu_{1.94}S nanodisks (41.7 ± 3.3 nm in diameter and 15.9 ± 1.0 nm in thickness) with Cd precursor [7]. The carrier dynamics of the CdS-Cu_{1.94}S nanodisks using ultrafast laser spectroscopy revealed that the carrier separation is based on a donor-acceptor charge transfer and that an ultrafast electron transfer takes place from Cu_{1.94}S phase to CdS phase with a charge transfer rate of 0.80 ps.

Recently, we have synthesized type-II CdS-Cu₃₁S₁₆ heterodimers (8.3 ± 1.2 nm long and 6.6 ± 0.9 nm wide) by the in-situ seeded growth of the Cu₃₁S₁₆ phase selectively on preformed hexagonal CdS NPs (Fig. 3), [8] as observed in the PdS_x-Co₉S₈ system, [1, 2] in order to investigate the charge separation behavior dependent on copper vacancies of the Cu_{2-x}S phase ($x = 0.0625$ for Cu₃₁S₁₆). The interfacial lattice plane was determined to be hexagonal CdS (100) plane. The HRTEM image also reveals that the (110) planes of the hexagonal CdS phases are aligned parallel to the (046) planes of the monoclinic Cu₃₁S₁₆ phases, both of which are perpendicular to the heterointerfaces.

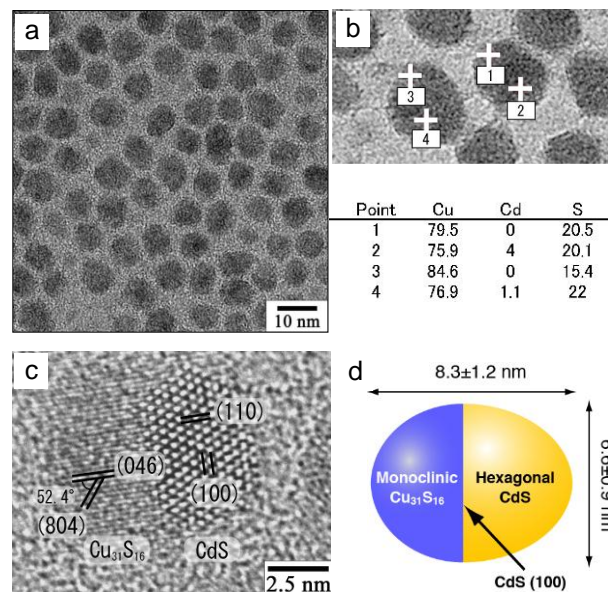


Fig. 3 – (a) TEM image, (b) nano-spot EDX results, (c) HRTEM image and (d) schematic of the CdS-Cu₃₁S₁₆ heterodimer (from ref. 8)

The transient absorption measurement of the CdS-Cu₃₁S₁₆ heterodimers was conducted using the fs-laser flash photolysis to clarify their exciton lifetime. The exciton lifetime of the Cu₃₁S₁₆ NPs (0.4 ± 0.1 ps) was significantly short compared with the previously reported value for the Cu_{1.94}S nanodisks and the Cu₂S NPs [7]. The photogenerated exciton in Cu₃₁S₁₆ NPs is quickly consumed through the Auger type charge recombination and/or energy transfer to localized surface plasmon. The exciton lifetime of the Cu₃₁S₁₆ phase in CdS-Cu₃₁S₁₆ heterodimer was similar to that of the Cu₃₁S₁₆ NPs (0.3 ± 0.1 ps), indicating that the photogenerated excitons were dominantly consumed via vacancy-induced decay processes (*i.e.*, Auger type charge recombination and/or energy transfer to localized surface plasmon) in the identical Cu₃₁S₁₆ phase rather than the electron transfer to the CdS phases. Considering that the CdS-Cu_{1.94}S nanodisks exhibited an electron transfer from Cu_{1.94}S to CdS, it is a quite interesting and important feature that slightly more copper vacancies in the Cu₃₁S₁₆ phase of heterodimer suppressed the electron transfer from Cu₃₁S₁₆ to CdS.

4. CONCLUSIONS

The two kinds of CdS-based type-II semiconductor heterodimers were successfully synthesized. Type-II CdS-CdTe heterodimers without any defects exhibited clear photo-induced electron transfer, whereas CdS-Cu₃₁S₁₆ heterodimers showed dominant consumption of photogenerated carries via vacancy-induced decay processes.

ACKNOWLEDGEMENTS

This work was supported by JSPS and METI.

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