

# Extended photoresponse of ZnO/CdS core/shell nanorods to solar radiation and related mechanisms



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## ABSTRACT

We report the study on the influences of shell thickness and core–shell structure on the optical properties of ZnO/CdS core/shell nanorods (NRs) for an elucidation of the mechanisms responsible for the extended photoresponse of ZnO/CdS core/shell NRs to solar radiation. Well aligned ZnO/CdS core/shell NRs were fabricated on indium tin oxide substrates using hydrothermally grown ZnO NRs as the cores and pulsed laser deposited CdS coatings as the shells. The sample structure was characterized by X-ray diffraction and Raman backscattering spectroscopy, revealing the wurtzite structure of both the ZnO cores and CdS shells, and the improvement in the structure after annealing. The optical properties were studied through optical transmittance, absorbance and photoluminescence measurements, showing the optical properties featured with type-II heterogeneous nanostructures constructed from ZnO and CdS. The results provide a support that the optical properties of the CdS covered ZnO NRs are attributed to the suppressed radiative recombination of photogenerated carriers due to the efficient spatial separation of electrons and holes in the nanosized ZnO–CdS heterostructures.

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## 1. Introduction

Semiconductor nanomaterials have become a subject of great scientific and technological interests because of the possibility of tailoring properties simply by varying their sizes, shapes and structures as well as by changing the surface atoms. Among various semiconductor nanomaterials, a variety of nanostructured II–VI semiconductors have been synthesized successfully and their properties have been studied extensively. With a wide direct band-gap of 3.37 eV and a large exciton binding energy of 60 meV as well as a high electron mobility of  $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [1,2], one-dimensional zinc oxide (ZnO) nanostructures including nanowires, nanorods (NRs) and nanoneedles are proposed as photoelectrodes for photovoltaic processes and photocatalysts for photocatalytic reactions due to their large surface areas, short diffusion lengths and high energy conversion efficiencies [3,4]. Because of its wide band-gap, however, ZnO itself cannot absorb and utilize visible light, hence has disadvantages when being used for applications in the visible region. An efficient approach to extend the spectral region of photoresponse and enhance the photocatalytic or

photovoltaic efficiency of ZnO-based devices is to sensitize the surface of nanostructured ZnO with photosensitizers such as narrower band-gap semiconductors, dye molecules, and metal nanoparticles. Depositing a thin coating of a narrower band-gap semiconductor outside nanosized ZnO provides an approach to permanently sensitize ZnO [2,5–8]. Meanwhile, the inorganic semiconductor coating can protect nanosized ZnO from surface degradation. Compared with organically sensitized ZnO, the core/shell structures constructed of ZnO cores and semiconductor shells have stable properties and can tolerate harsh conditions. For an efficient electron transfer from sensitizer to ZnO photoelectrode or photocatalyst and hole transfer from ZnO photoelectrode or photocatalyst to sensitizer and hence a suppressed recombination of photogenerated electrons and holes, in addition, both the conduction and valence bands of the sensitizer must be higher than the corresponding bands of ZnO, constructing a so-called type-II core/shell heterostructure [6,8]. Not only an extended photoresponse but also an improved charge separation, and hence an enhanced photovoltaic or photocatalytic efficiency can be expected in such heterostructures. Cadmium sulfide (CdS), another II–VI semiconductor with a direct band-gap of 2.4 eV and high optical absorbance in the region from violet to cyan [9–11], is considered to be one of the most suitable visible sensitizers for ZnO. Moreover, CdS has the same structure as ZnO and hence a good

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compatibility with ZnO. Therefore, CdS is one of the most excellent candidate shell materials to construct core/shell heterostructures with ZnO, including one-dimensional core/shell heterostructures [2,12,13] which are most promising for photovoltaic and photocatalytic applications.

We have recently fabricated CdS covered ZnO (ZnO/CdS) NRs by pulsed laser deposition (PLD) of thin CdS coating over hydrothermally grown ZnO NRs [14]. The nano-heterostructures constructed of ZnO cores and CdS shells exhibit an extended photo-response and increased optical absorption in the spectral region from ultraviolet (UV) to near infrared (IR). In the present work, we evaluated the influences of the thickness of CdS shells and the structure of ZnO cores and CdS shells on the optical properties of ZnO/CdS core/shell NRs. After the characterization of the structural and optical properties and the evaluation of the influences of shell thickness and sample structure, the mechanisms responsible for the optical properties of the heterostructured ZnO/CdS core/shell NRs were discussed.

## 2. Experimental details

### 2.1. Sample preparation

ZnO NRs were first grown on an indium tin oxide (ITO) substrate [15]. Prior to the growth of ZnO NRs, a dense nanocrystalline ZnO (NC-ZnO) film (~20 nm in thickness) was deposited on a cleaned ITO substrate by pulsed laser deposition. The NC-ZnO film served as a buffer layer for ZnO NRs to grow on the lattice-mismatched ITO substrate and a seed layer to guide the nucleation of ZnO and the growth of ZnO NRs. ZnO NRs were grown on the NC-ZnO seeded ITO substrate by hydrothermal reaction using a mixture of 0.04 M hexamethylenetetramine (HMT) and 0.04 M zinc nitrate hexahydrate  $[Zn(NO_3)_2 \cdot 6H_2O]$  resolved in 1 L de-ionized water as the hydrothermal precursor solution. The hydrothermal growth was performed at 90 °C in a thermostatic water bath for 6 h.

The grown ZnO NRs, used as the cores, were transferred to a vacuum chamber and fixed on a rotating platform for the

deposition of CdS coatings as the shells. The second harmonic of a Q-switched Nd:YAG laser was used to ablate a CdS target. The focused pulsed laser beam (wavelength 532 nm, pulse duration 5 ns, and repetition rate 10 Hz) with a spot size of ~1.2 mm<sup>2</sup> was incident on the target surface at an angle of 45°. The laser fluence on the target surface was about 2 J/cm<sup>2</sup>. The CdS coatings were deposited at a base pressure of ~10<sup>-4</sup> Pa at room temperature. The variation in the thickness of CdS shells was achieved by varying the deposition time of CdS coatings. In this work, ZnO/CdS core/shell NRs with different shell thickness were obtained by depositing CdS coatings outside ZnO nanorods with varied times of 10, 20 and 30 min. In order to examine the effects of post-fabrication annealing and to elucidate the mechanisms responsible for the optical properties, the sample with 20-min deposit of CdS outside ZnO NRs was annealed at 500 °C in a flowing N<sub>2</sub> atmosphere (~10<sup>5</sup> Pa) for 1 h.

In this paper, the sample of bare ZnO NRs without CdS shells is referred to as sample 1, the samples of as-fabricated ZnO/CdS core/shell NRs with 10-, 20- and 30-min deposit of CdS coatings as samples 2, 3 and 4, respectively, and the sample of annealed ZnO/CdS core/shell NRs with 20-min deposit of CdS coatings as sample 5.

### 2.2. Sample characterization

The sample morphologies were examined by field emission scanning electron microscopy (FESEM) with a Hitachi S-4800 microscope. The crystal structures of ZnO and CdS were examined by X-ray diffraction (XRD) with a Rigaku D/MAX 2550 VB/PC X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation ( $\lambda=0.15406$  nm). The sample structures were also characterized through the analysis of vibrational modes based on Raman backscattering measurements which were performed with a Jobin Yvon HR-Evolution confocal micro-Raman spectrometer using 325-nm He–Cd laser beam and 632.8-nm He–Ne laser beam as the exciting sources. The optical properties were studied by measuring the optical transmittance and optical absorbance of the fabricated ZnO/CdS core/shell NRs using a Perkin–Elmer Lambda 950 UV–visible–NIR spectrophotometer and comparing them with those of the bare ZnO NRs. The photoluminescence (PL) was measured by exciting

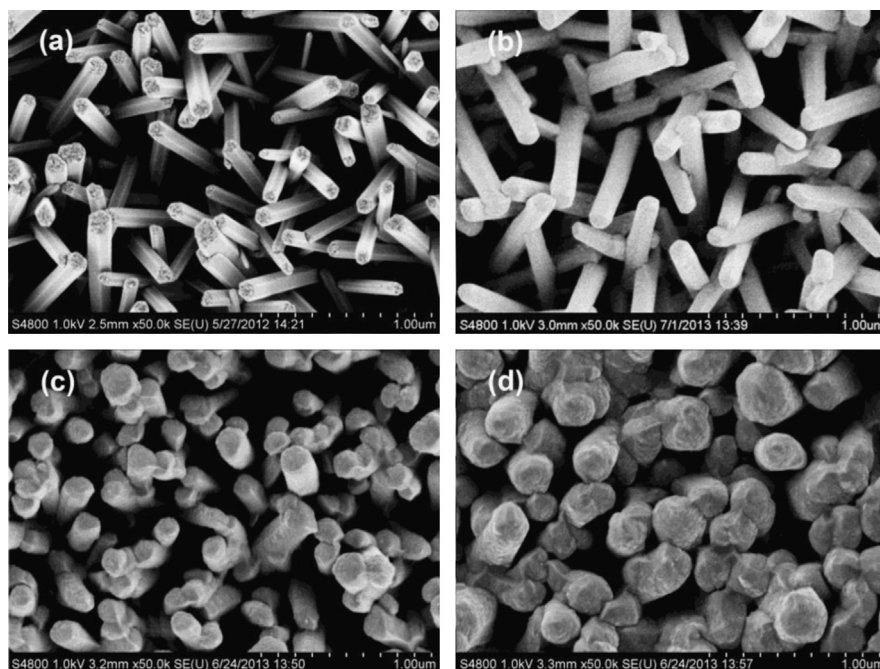


Fig. 1. FESEM images of bare ZnO NRs (a) and ZnO/CdS core/shell NRs with 10-min (b), 20-min (c) and 30-min (d) deposit of CdS.

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