Extended photo-response of ZnO/CdS core/shell nanorods fabricated by hydrothermal reaction and pulsed laser deposition

Qin Yang,1,3 Yanli Li,1 Zhigao Hu,2 Zhihua Duan,2 Peipei Liang,1 Jian Sun,1 Ning Xu,1 and Jiada Wu1,*

1Department of Optical Science and Engineering, Fudan University, Shanghai 200433, China
2School of Information science & technology, East China Normal University, Shanghai 200241, China
3College of Science, Guizhou Minzu University, Guiyang 550025, China

Abstract: Heterogenous nanostructures shaped with CdS covered ZnO (ZnO/CdS) core/shell nanorods (NRs) are fabricated on indium-tin-oxide by pulsed laser deposition of CdS on hydrothermally grown ZnO NRs and characterized through morphology examination, structure characterization, photoluminescence and optical absorption measurements. Both the ZnO cores and the CdS shells are hexagonal wurtzite in structure. Compared with bare ZnO NRs, the fabricated ZnO/CdS core/shell NRs present an extended photo-response and have optical properties corresponding to the two excitonic band-gaps of ZnO and CdS as well as the effective band-gap formed between the conduction band minimum of ZnO and the valence band maximum of CdS.

©2014 Optical Society of America

OCIS codes: (160.4236) Nanomaterials; (160.4760) Optical properties; (300.1030) Absorption; (300.6280) Spectroscopy, fluorescence and luminescence; (310.1860) Deposition and fabrication.

References and links
1. Introduction

Nanosized heterostructures constructed of two or more semiconductors have attracted much attention because of their modified properties and improved performance compared with the constructing materials [1–4]. In this respect, nanostructured materials are superior to the bulk ones, since hetero-nanostructures can be constructed simply by surface modification or surface coating. ZnO is promising for various applications including photovoltaic processes and photocatalytic reactions [5]. Owing to its wide band-gap (3.37 eV), however, ZnO itself can only be used in the ultraviolet (UV) region. Therefore, ZnO has been proposed to form heterostructures with a narrower band-gap semiconductor to extend the spectral region of photo-response [1,2]. With a narrower band-gap (2.4 eV) and the same crystal structure [6,7], CdS has a good compatibility with ZnO and is an ideal material to sensitize ZnO and construct type-II heterostructures with ZnO [8,9]. The band alignment of ZnO-CdS heterostructures contributes to spatially separating electrons and holes and is favorable for photovoltaic and photocatalytic applications [1,2]. Using ZnO as the core material and CdS as the shell material, one-dimensional rod-like or wire-like ZnO-CdS in particular, is superior in both the surface-to-volume ratio for modifying the surface [10] and the lateral size for reducing the nonradiative recombination and carrier scattering loss [2,11]. An extended spectral region for light absorption and a suppressed loss of photogenerated carriers can be expected.

In this study, ZnO-CdS heterostructures in the form of CdS covered ZnO (ZnO/CdS) nanorods (NRs) constructed of wurtzite ZnO cores and wurtzite CdS shells were fabricated. After morphology examination and structure characterization, the optical properties of the ZnO/CdS core/shell NRs were studied through the measurements of photoluminescence (PL) and optical absorption and the discussion of the relevant mechanisms.

2. Experimental details

ZnO NRs were first grown on nanocrystalline ZnO seeded indium-tin-oxide (ITO) substrates by hydrothermal reaction at 90 °C in the precursor solution of 0.04 M hexamethylenetetramine (HMT) and 0.04 M zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] resolved in 1 L de-ionized water [12]. The grown ZnO NRs were served as the cores over which CdS coatings were deposited by pulsed laser deposition as the shells. The second harmonic of a Q-switched Nd: YAG laser (wavelength 532 nm, pulse duration 5 ns, repetition rate 10 Hz) was used to ablate a CdS target after being focused (spot size ~1.2 mm² and fluence ~2 J/cm²). The deposition of CdS coatings was performed in vacuum (~10⁻⁴ Pa) at room temperature for 20 min. The fabricated ZnO/CdS NRs were then annealed in a flowing N₂ atmosphere (~10⁻⁵ Pa) at temperatures up to 500 °C for 60 min. The morphologies of bare ZnO NRs and ZnO/CdS core/shell NRs were examined by field-emission scanning electron microscopy (FESEM, Hitachi S-4800). The sample structure was characterized by X-ray diffraction (XRD, Rigaku D/MAX 2550 VB/PC) and Raman scattering (Jobin-Yvon LabRAM-1B). With the excitation by a 325-nm He-Cd laser beam, room-temperature and low-temperature PL spectra were recorded by an intensified charge-coupled device (ICCD, iStar DH720, Andor) equipped on a 0.5 m spectrometer (SpectraPro-
500i, Acton). Absorption spectra were measured in the UV–near-infrared (near-IR) range using a Shimutsu UV3101PC Photo-Spectrometer.

3. Results and discussion

3.1 Morphology and structure

Figure 1(a) shows the FESEM images of the hydrothermally grown ZnO NRs, indicating that the bare ZnO NRs grew nearly oriented with their axes perpendicular to the substrate and are almost shaped with hexagonal prisms having an average diameter of 90 nm and length of 2 um. Figure 1(b) shows that the ZnO NRs are uniformly covered with CdS from bottom to top, forming ZnO/CdS core/shell NRs. The CdS covered ZnO NRs exhibit increased diameters and rough surfaces compared with the bare ZnO NRs. After annealing, no obvious changes in the morphology were observed.

![Fig. 1. FESEM images of bare ZnO NRs (a) and ZnO/CdS core/shell NRs (b).](image)

Figure 2 shows the XRD patterns taken from the bare ZnO NRs and the ZnO/CdS core/shell NRs. For the bare ZnO NRs, a strong diffraction peaking at 2θ = 34.42° with a full width at half-maximum (FWHM) of 0.11° dominates the XRD pattern. This peak is indexed to the (002) diffraction of wurtzite ZnO (JCPDS: 36-1451). Besides those diffracted from the ITO substrate (marked with *), three prominent peaks and three weak ones are resolved. They can be indexed to the (101), (102), (103), (100), (110) and (112) diffractions of wurtzite ZnO, respectively. For the ZnO/CdS core/shell NRs, additional diffractions appear including a broad one at 2θ = 26.65° (FWHM = 0.56°) and two weak ones. They are attributed to the (002), (101) and (110) diffractions of wurtzite CdS (JCPDS: 41-1049). Therefore, the fabricated ZnO/CdS core/shell NRs are composed of wurtzite ZnO cores and wurtzite CdS shells. After annealing, the diffractions from CdS become stronger and an additional peak corresponding to the (100) plane of wurtzite CdS appears, indicating an improvement in the crystal structure due to the annealing treatment.

Figure 3(a) shows the Raman spectra of the bare ZnO NRs and the as-fabricated ZnO/CdS core/shell NRs. A prominent peak at 98 cm\(^{-1}\) and a weak one at ~436 cm\(^{-1}\) are recognized in the Raman spectrum of the bare ZnO NRs (spectrum 1 and the inset). They correspond to the low- and high-frequency branches of the non-polar optical phonon modes [E\(_2\) (Low) and E\(_2\) (high)] of ZnO [13,14]. After the deposition of CdS, the Raman spectrum is dominated by a strong peak at 299 cm\(^{-1}\) and a weak one around 598 cm\(^{-1}\) (spectrum 2). They correspond to the first-order longitudinal optical (1LO) mode of wurtzite CdS and its 2-phonon scattering processes (2LO) [15]. The Raman measurements confirm the hexagonal wurtzite structure of the ZnO cores and the CdS shells. For the annealed ZnO/CdS core/shell NRs, the featureless background in the Raman spectra decreases significantly, as shown in Fig. 3(b), also confirming the improvement in the structure after annealing.
3.2. Photoluminescence

With 325-nm light excitation, the bare ZnO NRs emit a luminescence including a strong and narrow UV peak at ~384 nm (FWHM = 15 nm) and a broad band in the green-yellow region, as shown in Fig. 4(a). The UV emission is attributed to the near-band-edge (NBE) emission from ZnO [16], while the visible emission is related to the defects in ZnO such as oxygen vacancies [17]. For the ZnO/CdS core/shell NRs, the intensity of the luminescence is greatly reduced, especially the UV NBE emission whose intensity decreases to about 0.7% of that of the bare ZnO NRs. One of the main contributions to the reduction in the measured luminescence is the suppression of radiative recombination of photogenerated electrons and holes in the heterostructures composed of ZnO and CdS [2,10], since the staggered energy band alignment in a type-II hetero-nanostructure is favorable for spatially separating electrons and holes. However, the defect-related nonradiative recombination process and the absorption of the exciting photons in the laser beam and the emitted photons of UV emission from the ZnO cores by the CdS shells could also result in the reduction in the measured UV luminescence [2,10]. To clarify the mechanisms responsible for the reduction in the luminescence, the ZnO/CdS core/shell NRs were annealed in a flowing N\textsubscript{2} atmosphere (~10\textsuperscript{5} Pa) for 60 min and then submitted to PL measurement. The inset of Fig. 4(a) shows that for the sample annealed at 300 °C, the ZnO UV emission is enhanced, which is due to the
improvement in the ZnO structure after annealing [12]. When the annealing temperature increases to 500 °C, however, the intensity of this UV emission decreases nearly to that of the as-prepared sample. Considering the increase of UV emission from the ZnO cores after annealing, the reduction of the measured ZnO UV emission due to the CdS shells is more significant for the annealed sample than for the as-fabricated sample. Besides the structure of ZnO cores, the interfaces between ZnO and CdS as well as the structure of the CdS shells were improved during the annealing process. The improvement in the ZnO and CdS structures and the ZnO/CdS interfaces facilitates the transfer of both electrons and holes in the ZnO cores and the CdS shells as well as across the interfaces between ZnO and CdS, and hence enhances the separation of electrons and holes, resulting in the suppression in the radiative recombination of photogenerated carriers. The significant reduction in the measured luminescence of the annealed ZnO/CdS core/shell NRs should be mainly attributed to the suppression of radiative recombination due to the enhanced charge separation, rather than the defect-related nonradiative recombination process or the absorption by the CdS shells.

Fig. 4. (a) Room-temperature PL spectra of ZnO NRs and ZnO/CdS NRs (the inset shows PL spectra of as-fabricated and annealed ZnO/CdS NRs); (b) PL spectra of as-fabricated ZnO/CdS NRs taken at 300 K and reduced temperatures.

It is worthwhile noticing that although significantly reduced, the visible luminescence of the ZnO/CdS core/shell NRs, whether annealed or not, has an obvious red-shift compared with that of the bare ZnO NRs. This broad visible luminescence should include the NBE emission from CdS, the defect-related emissions from ZnO and CdS as well as the emission attributed to the radiative recombination of the electrons in the conduction band minimum of ZnO with the holes in the valence band maximum of CdS [2]. Such a multi-band emission suggests that the ZnO/CdS core/shell NRs have a photo-response region much broader than the bare ZnO NRs.

Figure 4(b) illustrates the PL spectra of the as-fabricated ZnO/CdS core/shell NRs at reduced temperatures and compares them with the room-temperature PL spectrum. The intensity of the UV emission increases significantly with an obvious blue shift and a much narrower width (FWHM ~5 nm at 10 K) as the temperature decreases. This can be explained in terms of the freeze-out of phonons and quenching of nonradiative recombination processes in ZnO at low temperatures [12,16]. The strong UV emission in the low-temperature PL also suggests that the absorption by the CdS coatings contributes little to the reduction in the measured room-temperature PL spectra of the ZnO/CdS core/shell NRs. With the decrease in temperature, in addition, the intensity of the broad visible luminescence also increases. Especially, a prominent emission band centered near 516 nm appears at low temperatures. This band corresponds to the NBE emission from CdS. The appearance of this emission and the increase of the wide visible luminescence can also be attributed to the quenching of nonradiative recombination in the sample at low temperatures.
3.3 Optical absorption

Figure 5 shows that the bare ZnO NRs present a clear absorption edge near 380 nm corresponding to the excitonic band-gap of ZnO [5,16]. After being covered by CdS shells, the sample exhibits increased optical absorption in the visible to near-IR region and shows a second absorption edge near 510 nm corresponding to the excitonic band-gap of CdS [6,7,17]. Furthermore, additional absorption is found extending below the CdS band-gap into the near-IR, which could arise from an interfacial transition coupling a hole state in the CdS shell with an electron state in the ZnO core, i.e. the transition corresponding to the so-called effective band-gap formed between the conduction band minimum of ZnO and the valence band maximum of CdS [2,10]. The spectral extension of the optical absorption is consistent with the red-shift of the visible luminescence from the CdS covered ZnO NRs. As a result, the ZnO/CdS core/shell NRs have a much broader absorption region than the bare ZnO NRs due to the band alignment in the heterostructures constructed of ZnO and CdS. For the annealed samples, in addition, the absorption decreases with increasing annealing temperature because of the improved structure, providing another evidence for the explanation that the reduction in the measured luminescence results mainly from the suppressed radiative recombination of photogenerated carriers, rather than the absorption of the exciting photons and the emitted photons by the CdS shells. The ZnO NRs covered with CdS shells therefore exhibit an enhanced charge separation and an extended photo-response compared with the bare ZnO NRs. The increased optical absorption and the extended photo-response region are expected to improve the utilization efficiency of solar energy and most favorable for photocatalytic reactions and photovoltaic processes.

4. Conclusions

Heterogeneous nanostructures in the form of aligned ZnO/CdS core/shell NRs have been fabricated on ITO substrates by pulsed laser deposition of CdS coatings on hydrothermally grown ZnO NRs. The fabricated hetero-nanostructures are constructed of wurtzite ZnO nanorod cores and wurtzite CdS shells. The photoluminescence from ZnO cores is significantly quenched by the CdS shells mainly because of the suppressed radiative recombination of photogenerated electrons and holes due to the enhanced charge separation in the hetero-nanostructures. The ZnO/CdS core/shell NRs exhibit increased optical absorption and an extended photo-response region compared with the bare ZnO NRs and present optical properties corresponding to the two excitonic band-gaps of wurtzite ZnO and wurtzite CdS as well as the effective band-gap formed between the conduction band minimum of ZnO and the valence band maximum of CdS.
Acknowledgments

This work is supported by the National Basic Research Program of China (2012CB934303) and the National Natural Science Foundation of China (11275051). Acknowledgment is also made to the Research Fund for the Doctoral Program of Higher Education of China (20110071110020).