Modulation and Improvement on Separation of Photoinduced Charge Carriers in CdS-Metal Nanoheterostructures

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We demonstrate the feasibility of modulating and improving the separation of photoinduced charge carriers of CdS—M nanoheterostructures through partial replacement of S with two group 16 elements of larger atomic size, Se and Te. With the incorporation of Se or Te into the CdS nanowires (NWs), the defect states of the CdS NWs were effectively passivated, enabling a fuller extent of participation of the photoinduced electrons in the charge separation process, thus resulting in a more pronounced photoluminescence quenching and photocurrent depression for the $CdS_{1-x}Se_x$ and $CdS_{1-x}Te_x$ NWs. The present study provides a facile way of improving the photocatalytic efficiency of CdS through the improvement in retarding the recombination of photoinduced charge carriers.

Introduction

Semiconductor or metal-based nanoheterostructures have drawn much and continuing research attention in recent years for their possible improvement in certain optical and electronic functionalities.1 Particularly, great progress has been made in creating nanoheterostructures from semiconductor and metal nanocrystals.² These nanoheterostructures have been proven useful in a wide range of applications, such as biolabels,³ chemical sensors, 4 nonvolatile memory devices, 5 photochemical solar cells, 6 low-temperature carbon monoxide oxidation, 7 and photodriven hydrogen production.8 Among them, nanoheterostructures composed of semiconductor and metal nanocrystals are of particular interest to photocatalytic applications. 9 In general, photocatalytic efficiency is limited by the fast recombination of photogenerated charge carriers. To boost photocatalytic performance, charge carrier recombination has to be suppressed so that the photoinduced charge carriers can participate in the photocatalytic reaction. In semiconductor-metal nanoheterostructures, the presence of the semiconductor-metal interface may promote effective charge carrier transfers to favor charge carrier separation and subsequent photocatalysis.¹⁰

CdS is one of the most attractive photocatalysts because of its suitable band gap (2.5 eV), corresponding well with the spectrum of sunlight. Its valence band at relatively negative potential offers CdS good photocatalytic activities. ¹¹ Furthermore, the photoluminescence (PL) property of CdS has been explored for sensing toward a number of ionic species ¹² and biomolecules. ¹³ We previously showed that ethylenediamine (EN)-capped CdS nanowires (NWs) can selectively detect Ag⁺ and Cu²⁺ among 12 biologically relevant metal ions. ^{12d} When the EN-capped CdS NWs were put in contact with Ag⁺ or Cu²⁺, spontaneous reduction of Ag⁺ or Cu²⁺ led to the production of Ag or Cu nanoparticles on the NW surface, forming CdS—Ag or CdS—Cu nanoheterostructures. The sensing was realized

through the drastic PL quenching achieved with the effective electron transfer toward the metal domain. The pronounced charge transfer from CdS toward metals was also revealed in the core—shell Au—CdS nanocrystals. ¹⁴ The result of our previous work ^{12d} stimulates further interest to investigate the possibility of modulating the separation of photoinduced charge carriers in semiconductor—metal nanoheterostructures. In this paper, we report a novel method for creation of nanoheterostructures consisting of CdE (E = S, $S_{1-x}Se_x$, $S_{1-x}Te_x$) NWs coated with Ag or Cu nanoparticles. The partial replacement of S with other group 16 elements of larger atomic size, Se and Te, proves to be an effective way of modulating and improving the separation of photoinduced charge carriers for the CdE—M (M = Ag, Cu) nanoheterostructures.

Experimental Methods

Nanowire Synthesis. All chemicals used were analytical grade reagents and used without further purification. The synthesis of CdS NWs was conducted in a solvothermal process. Briefly, Cd(NO₃)₂•4H₂O (1.85 g, 0.006 mol), sulfur powder (0.19 g, 0.006 mol), and ethylenediamine (EN, 100 mL) were mixed for a solvothermal reaction at 180 °C for 24 h. The product (CdS NWs) was then centrifuged and washed with distilled water and ethanol to remove remaining ions. For the synthesis of CdS_{1-x}Se_x NWs, Cd(NO₃)₂·4H₂O (1.85 g, 0.006 mol), sulfur powder (0.16 g, 0.005 mol), selenium powder (0.079 g, 0.001 mol), and ethylenediamine (EN, 100 mL) were used as the starting materials, followed by the same procedure performed in the synthesis of CdS NWs. As to the fabrication of $CdS_{1-x}Te_x$ NWs, $Cd(NO_3)_2 \cdot 4H_2O$ (1.85 g, 0.006 mol), sulfur powder (0.16 g, 0.005 mol), and tellurium powder (0.128 g, 0.001 mol) were used as the cadmium and chalcogen sources, respectively, followed by the same procedure performed in the synthesis of CdS NWs. These products were then dried at 100 °C in vacuum for later use.

Preparation of NW Suspensions. For the purpose of PL measurements, NWs of CdS, CdS_{1-x}Se_x, or CdS_{1-x}Te_x (0.01 g) were dispersed in ethanol (120 mL) to serve as the stock solution (5.8 \times 10⁻⁴ M). As for the preparation of NW films, NWs of

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CdS, CdS_{1-x}Se_x, or CdS_{1-x}Te_x (0.003 g) were dispersed in ethanol (0.3 mL) to make more concentrated NW suspensions.

Preparation of Metal Ion Solutions. AgNO₃ and CuCl₂ were used as the Ag⁺ and Cu²⁺ sources, respectively. Proper amounts of these metal salts were dissolved in water (18.3 M Ω ·cm) to prepare the various metal ion solutions at desired concentrations.

Preparation of NW Films for Electrical Measurements. NW films, well adhered to Si substrates, were prepared by dripping NW suspensions of a sufficient amount onto Si wafers $(0.4 \text{ cm} \times 0.4 \text{ cm})$, followed by a heat treatment at 70 °C for 20 min to remove the solvent.

Characterizations. The morphology and dimensions of the products were examined with a field emission scanning electron microscope (FESEM, Hitachi S-4700). The crystallographic structure of the samples was investigated with a high-resolution TEM (HRTEM, JEOL JEM-3000) operated at 300 kV. The compositional information was obtained with an energydispersive spectrometer (EDS), an accessory of the HRTEM (JEM-3000), and an X-ray photoelectron spectroscope (XPS, VG Scientific, Microlab 350). For photoluminescence (PL) spectroscopy, a Hitachi F-4500 equipped with a xenon lamp (150 W) was used. The excitation wavelength was set at 400 nm. All of the emission spectra were obtained at 25 °C under ambient atmosphere. Electrical measurements for the NW films were conducted under white light illumination (halogen lamp, 150 W) via a Keithley 236 semiconductor parameter analyzer by contacting the film surface with two measuring microprobes. The distance between the two microprobes was around 0.1 cm. The intensity of the white light was about 1.3 mW/cm². Besides, no significant IR drop was observed due to the small size of the samples (0.16 cm² for Si substrates) used in the measurement.

Results and Discussion

First, NWs of CdS, CdS_{1-x}Se_x, and CdS_{1-x}Te_x were prepared from a solvothermal process by using Cd(NO₃)₂·4H₂O as the Cd source; S, Se, and Te powders as the matching chalcogen sources; and EN as the solvent and capping reagent. As shown in Figure 1, NWs of CdS, $CdS_{1-x}Se_x$, and $CdS_{1-x}Te_x$ of about 30 nm in diameter were successfully prepared. The values of x determined from the TEM-EDS analyses were about 0.1 and 0.05 for the $CdS_{1-x}Se_x$ and $CdS_{1-x}Te_x$ NWs, respectively. Figure 1b,d,f shows the HRTEM images of these NWs, confirming the solid-solution nature instead of core-shell structure of the NWs. Interlayer spacings of 0.67, 0.68, and 0.68 nm were observed in the axial direction for the CdS, $CdS_{1-x}Se_x$, and $CdS_{1-x}Te_x$ NWs, respectively, in agreement with the d spacing of their (0001) lattice planes determined from the corresponding XRD analyses shown in Figure 2. For CdS NWs, the diffraction peak located at the 2θ value of 26.5° corresponds well to the (0002) planes with a d spacing of 0.336 nm. For $CdS_{1-x}Se_x$ and $CdS_{1-x}Te_x$ NW samples, the diffraction peak located at the 2θ value of 26.3° gave an interplanar spacing of 0.339 nm for the (0002) planes, consistent with the HRTEM observation shown in Figure 1. The slight expansion of the lattice in doped samples, indicated by the slight left shift of the diffraction peak location, as illustrated in the inset of Figure 2, was due to the partial replacement of S with Se or Te atoms, which are of larger atomic size. Upon addition of Ag+ with a moderate concentration, 400 µM, a large quantity of nanoparticles with a size of 10-20 nm was found produced on the NW surfaces, as evident from Figure 3a-c. The TEM-EDS data shown in the insets of Figure 3 reveal that these nanoparticles were Ag. The X-ray photoelectron spectra presented in Figure 3d further confirm the existence of metallic Ag (with the binding energies of 368.1

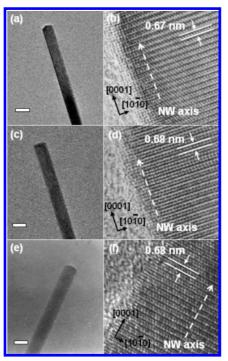


Figure 1. TEM images of (a) CdS, (c) CdS_{1-x}Se_x, and (e) CdS_{1-x}Te_x NWs. Their corresponding HRTEM images are shown in (b), (d), and (f), respectively. The scale bar is 30 nm.

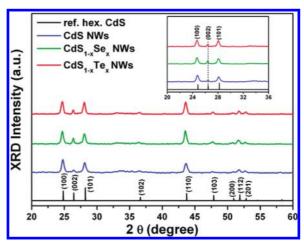


Figure 2. XRD patterns of CdS, $CdS_{1-x}Se_x$, and $CdS_{1-x}Te_x$ NWs compared with that of the reference hexagonal CdS (JCPDS no. 06-0314).

and 374.0, corresponding to the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks, respectively)¹⁵ for these three Ag⁺-treated samples. Similar phenomena were observed for the Cu²⁺-treated NWs. Cu nanoparticles of 5-20 nm in size were found to form on the surfaces of the host NWs upon addition of Cu²⁺. Consequently, the nanoheterostructures of CdE-M, consisting of CdE NWs coated with M nanoparticles, were successfully produced.

The formation mechanism of Ag or Cu nanoparticles on the surfaces of the CdS NWs has been discussed in our previous work. 12d Briefly, the EN thin layer present at the surfaces of the CdS NWs coordinated and subsequently reduced the metal ions to the corresponding metal elements. Interestingly, the CdS NWs were found to be an indispensable initiator for the reduction of Ag⁺ and Cu²⁺ with EN. Evidently, for the present work, a minor replacement of S with Se or Te did not alter the role played by the CdE NWs as a reduction initiator. To investigate the effect of Se or Te incorporation on the separation of photoinduced charge carriers in the CdE-M nanohetero-

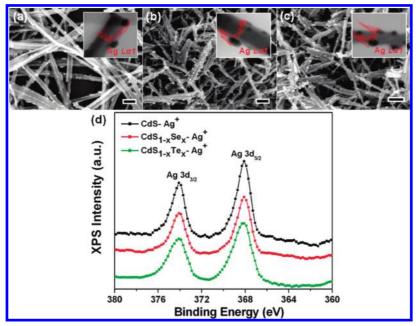


Figure 3. SEM images of (a) CdS, (b) CdS_{1-x}Se_x, and (c) CdS_{1-x}Te_x NWs after addition of 400 μ M Ag⁺. The scale bar is 200 nm. The insets show the corresponding TEM-EDS line-scan results.

structures, we collected the PL spectra of the CdE NW suspensions after addition of Ag⁺ or Cu²⁺ with increasing concentrations. Upon addition of Ag⁺ or Cu²⁺, there will be formed CdE–M nanoheterostructures that enhance the separation of photoinduced charge carriers and thus quench the PL emissions. Higher concentrations of metal ion lead to the formation of larger metal nanoparticles and thus a greater extent of PL quenching.¹⁶

The PL responses of CdS, $CdS_{1-x}Se_x$, and $CdS_{1-x}Te_x$ NWs toward the addition of Ag⁺ at six increasing concentrations were first investigated and shown in Figure 4. Here, the PL spectrum of the ion-free NW sample was taken as the control. For the CdS NWs, the intensity of the excitonic emission at $\lambda = 508$ nm decreased with increasing Ag⁺ concentration, as expected. Similar trends in PL quenching were observed for the $CdS_{1-x}Se_x$ and $CdS_{1-x}Te_x$ NWs. As shown in Figure 4b,c, the monotonic decay of the excitonic emission intensity at $\lambda = 535$ and 517 nm for $CdS_{1-x}Se_x$ and $CdS_{1-x}Te_x$, respectively, again demonstrated the successful charge carrier separation during the bandto-band recombination process. Note that the excitonic emissions of the doped CdS NWs red shifted as compared with that of the CdS NWs, reflecting the corresponding band gap shrinkage from the doping. This drastic PL quenching phenomenon was also observed for the Cu2+-treated samples (data not shown here). Note that the metal nanoparticles formed in situ on the NW surfaces can serve as an effective electron scavenger for the NWs. The Fermi levels of both Ag and Cu are located at around +0.15 V versus NHE (normal hydrogen electrode), 17a lower in energy states than the conduction bands of bulk CdS (-1.0 V versus NHE), ^{17b} CdSe (-0.3 V versus NHE), ^{17c} and CdTe (-0.7 V versus NHE)^{17d} crystals. Consequently, the photoinduced free electrons of these cadmium chalcogenide NWs would transfer to the metal domain, leading to depletion of free electrons in the NW domain and subsequent suppression of the excitonic emission.

The intensities of the excitonic emission of these NWs as a function of the Ag⁺ and Cu²⁺ concentrations were plotted in Figure 5 to more clearly display the effect of Se or Te incorporation on the charge carrier separation. First, we note that, for all cases, the PL intensity drops sharply and then tends

to level off with increasing metal ion concentrations. For the case of CdS, the curves start to level off at the ion concentration of 800 μ M. The PL decreasing trend for the cases of CdS_{1-x}Se_x and $CdS_{1-x}Te_x$, however, persists even at the much higher ion concentrations of 2000 μ M. In addition, the extent of PL quenching, as compared with the control sample, for the cases of $CdS_{1-x}Se_x$ (91% with Ag^+ addition and 73% with Cu^{2+} addition at the ion concentration of 2000 μ M) and CdS_{1-x}Te_x (93% and 75%) was significantly larger than that achieved in the CdS case (78% and 49%). These two observations indicate that the quenching effect is more pronounced in the $CdS_{1-x}Se_x-M$ and $CdS_{1-x}Te_x-M$ than in the CdS-M nanoheterostructures. It is thus concluded that the separation of photoinduced charge carriers is improved with partial replacement of S with Se or Te. In addition, the effect of Te incorporation is the most pronounced one among the three investigated cases.

To further elucidate the effect of the dopant (Se and Te) incorporation on the charge carrier separation in the CdS-M NWs, we compared the electrical behaviors of films, fabricated from the plain and doped CdS NWs, under illumination. Figure 6 shows the current-voltage (I-V) curves of four NW films, CdS, CdS $-Ag^+$, CdS $_{1-x}Te_x$, and CdS $_{1-x}Te_x-Ag^+$, measured under white light illumination. There are several points to be observed from the figure. First, the white light stimulated photocurrents produced from the plain CdS NW film were larger than those from the Te-doped CdS NW films. This is mainly a result of the dimension difference between the two kinds of NWs. Although both have a diameter of 30 nm, the plain CdS NWs were much longer in length, $5-10 \mu m$, than the Te-doped CdS NWs, $0.6-1 \mu m$. The films fabricated from the Te-doped CdS NWs will contain many more inter-NW contacts than the plain CdS NWs. These inter-NW contacts will retard the electron transfer, leading to smaller photocurrents. Second, the photocurrents of the CdS NW films were dramatically depressed if the CdS NWs were treated with Ag⁺ (\sim 300 μ M) to form the CdS-Ag nanoheterostructure. The significant electron transfer from the CdS NWs into the attached Ag nanoparticles accounted for such a drastic photocurrent depression. Similar depression phenomena were observed for the Te-doped CdS NW films upon

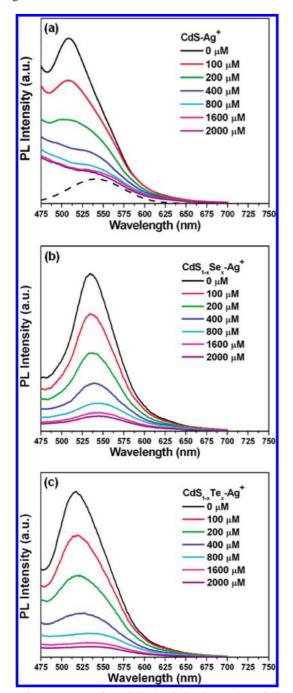


Figure 4. PL spectra of (a) CdS, (b) CdS_{1-x}Se_x, and (c) CdS_{1-x}Te_x NW suspensions upon addition of Ag⁺ at six increasing concentrations. The dashed line in (a) revealed the defect-level emission band derived from the peak deconvolution.

the Ag⁺ treatment. Third, the extent of photocurrent depression caused by the formation of metal nanoparticles was found to be more pronounced for the doped CdS NW films. For example, after the Ag⁺ treatment, a 73% decrease in photocurrent, measured at an applied voltage of 5 V, was observed for the plain CdS NW film, whereas a larger drop of 92% was found for the Te-doped CdS NW film at the same condition. These observations, together with those of the PL quenching, demonstrate that significant improvements on the separation of photoinduced charge carriers in CdS-M nanoheterostructures can be achieved through partial replacement of S with Se or Te.

A possible explanation for the enhanced performance in the separation of photoinduced charge carriers for the $CdS_{1-x}Se_x-M$

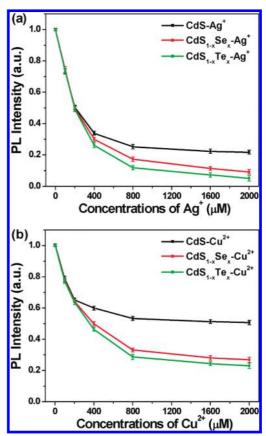


Figure 5. Intensities of excitonic emission of CdS, $CdS_{1-x}Se_x$, and CdS_{1-x}Te_x NW suspensions after addition of metal ions at different concentrations: (a) Ag⁺-treated samples and (b) Cu²⁺-treated samples.

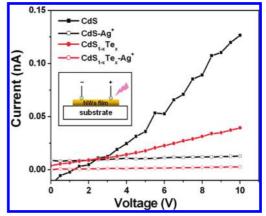


Figure 6. I-V curves of NW films of CdS, CdS-Ag⁺, CdS_{1-x}Te_x, and $CdS_{1-x}Te_x-Ag^+$ measured under white light illumination. The inset shows a schematic diagram for the I-V measurement system.

and $CdS_{1-x}Te_x$ -M nanoheterostructures is proposed as follows. For the CdS NWs, a shallow defect emission was involved in the carrier recombination process, which can be observed from the PL peak deconvolution of Figure 4a. This defect-level emission band became increasingly more dominant with increasing Ag⁺ concentrations, implying that a significant amount of photoinduced electrons was directed to this defect state for subsequent recombination, instead of being transferred to the Ag domain to suppress the electron-hole recombination. Through the incorporation of Se or Te into the CdS NWs, these defect states were effectively passivated, as can be inferred from the absence of longer wavelength emission bands in Figure 4b,c. The elimination of the shallow defect levels enables a fuller

extent of participation of the photoinduced electrons in the charge separation process, thus resulting in a more pronounced PL quenching and photocurrent depression for the $CdS_{1-x}Se_x$ and $CdS_{1-x}Te_x$ samples. In addition, the valence electrons of Se and Te atoms are located at outer shells farther away from the atomic nuclei and are thus less bound to the nuclei as compared with those of S atoms. During the recombination process, the excited electrons in the $CdS_{1-x}Se_x$ and $CdS_{1-x}Te_x$ NWs are more likely to depart from the binding atomic nuclei and move into the metal domains, leading to more effective charge carrier separation. As a result, the charge carrier separation can be effectively modulated and improved with the replacement of S with Se or Te in the CdS NWs.

Conclusions

In conclusion, we have successfully prepared CdE-M (E = S, $S_{1-x}Se_x$, $S_{1-x}Te_x$; M = Ag, Cu) nanoheterostructures and demonstrated the feasibility of modulating and improving the separation of photoinduced charge carriers of the CdS-M nanoheterostructure through partial replacement of S with two group 16 elements of large atomic size, Se and Te. The present study provides a facile way of improving the photocatalytic efficiency of CdS through the improvement in retarding the recombination of photoinduced charge carriers.

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