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Manipulating charge transfer from core to shell in CdSe/CdS/Au heterojunction quantum dots

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Abstract

The photophysics of charge transfer and recombination mechanisms in a heterojunction structure of CdSe/CdS/Au quantum dots (QDs) are studied by temperature-dependent steady-state photoluminescence (PL) and time-resolved PL (TRPL). We manipulate the charge transfer from core to shell surface by varying the tunneling barrier height resulted from temperature variation, and the barrier width resulted from shell thickness variation. The charge transfer process, which can be described by a tunneling transmission model, is manifested by two competitive recombination processes, an intrinsic exciton emission and a trap emission in the near-infrared (NIR) range. Our study establishes the photophysics foundation for core/shell/metal application in photocatalyst and optoelectronics.

Keywords

time-resolved, steady state; photoluminescence; core/shell; tunneling; recombination

Quantum dots or nanorods decorated with metal nanoparticles such as gold (Au) and platinum (Pt) have considerable applications in photocatalysis^{1–9} and optoelectronics^{10–12} due to their novel properties such as high surface to volume ratio, hot carrier and carrier multiplication.^{13–16} Therefore, understanding the fundamental photophysics mechanisms including charge transfer and recombination processes in these systems is the foundation to tune their optical and electrical functionality. Very often, to reduce surface defect states and Auger recombination process as well, the core quantum dots are passivated with a shell to form a core/shell heterojunction structure.^{17–19} As a result, the shell quality plays a significant role in tuning charge transfer and recombination process.^{20,21} However, the study of influence of shell, which addresses the interplay between intrinsic excitons and shell-related surface states in trap-related core/shell/metal QD is currently lacking. This is due to the hard-detected or very weak surface state emission, originating from the strong quenching of metal domain on intrinsic emission in these systems.^{1,22} In addition to the shell property, the charge carrier recombination and transfer from core to shell surface also depends on the band offset between the core and shell that relies on temperature parameter. However, in surface state-related core/shell/metal QDs system, how do these two competing mechanisms vary with temperature still remains unclear.

In this report, to comprehensively understand the interplay between charge transfer and recombination mechanisms in CdSe/CdS/Au heterojunction nanocrystals, we study these systems with temperature-dependent steady-state PL and TRPL. We manipulate the charge transfer to shell surface by varying the tunneling barrier height resulted from temperature variation, and the barrier width resulted from shell thickness variation. These mechanisms are manifested by an intrinsic exciton emission and trap emission in the NIR range. These two competitive recombination processes can be described by a tunneling transmission model.

A. Temperature dependent steady-state PL

Four samples are synthesized with two different shell thickness (~6 MLs and 12 MLs) and detailed parameters are listed in Table 1. Preparation of core/shell only CdSe/CdS QDs can be seen as an excellent photophysics comparison with Au-decorated system to clearly examine the existence of surface traps. Absorption and emission spectra of CdSe/CdS QDs show the only main intrinsic exciton emission with narrow PL peaks (Figure S1). On the other hand, once Au nanoparticles grow on the shell surface, as demonstrated by Figure 1a and insets (TEM images) of Figure 1b, c, there appears a broad NIR emission for both shell thickness dots, in addition to the main intrinsic exciton emission. However, the NIR emission becomes weak with shell thickness increasing, while the PL peak shifts slightly on a scale of < 50 meV as demonstrated in Figure 1c. The main exciton emission still keeps narrow PL full width at half maximum (FWHM), which indicates that the core CdSe remains almost unaffected as the formation of QD-Au heterojunction.

To address the nature of the NIR emission, the temperature-dependent steady-state PL is demonstrated in Figure 2. First, it can be clearly seen that CdSe/CdS/Au QDs film emits NIR wavelength light while the feature of this NIR emission is not demonstrated in CdSe/CdS core/shell QD despite of variable temperature. Thus, the NIR emission does not

arise from the core/shell interfacial trap states due to the well passivation. Second, we preclude the possibility of metal-related transfer-recombination process where electron can initially transfer to Au particles and then go back to core to recombine with the holes, because the separated states takes long-live time on a scale of microsecond or hundreds of nanoseconds for charge annihilation with no emission.^{23,24} Third, the NIR emission energy is independent of material of metal particles, while same wavelength emission is also observed in CdSe/CdS/Pt heterojunction structure. (Figure S2) Therefore, we conclude that the NIR emission is attributed to the radiative surface states or trap states on the shell surface that form during the growth of metal (see Experimental details, Supporting information). In addition, the existence of metal on shell surface can potentially drive the photogenerated electron transfer to shell surface through shell thickness,²² facilitating trap emission occurrence.

For CdSe/CdSe core/shell structure, the behaviors of peak energy, PL intensity, and FWHM dependence with temperature are well understood by the interaction between exciton and phonon.^{25–27} In general, as Figure 2 a,b indicated, the peak energy decreases with temperature increasing, reflecting a reduction of energy bandgap, which is due to the effect of exciton-phonon coupling and lattice deformation potential.²⁶ Change in peak energy can match the empirical Varshni relation.²⁸ (Eq. S1, Table S1) Decreased PL intensity with increased temperature results from the enhancement of nonradiative recombination such as surface carrier trapping and multiple longitudinal-optical phonon assisted thermal escape from dots.^{29,30} The thermal activation energy can be extracted by an Arrhenius relation from the PL intensity dependence on temperature. (Eq. S2, Table S2)

In contrast to core/shell only, the heterojunction structure of core/shell/Au QDs demonstrates more characteristics due to different recombination mechanisms, as illustrated in Figure 2c, d. At low temperature, trap emission peak for 6 ML shell system has stronger intensity than that of the main exciton emission, indicating there are more photogenerated electrons can tunnel from core to shell surface for the radiative trap recombination. On the other hand, the peak intensity decreases as the shell thickness is increased to 12 ML, suggesting stronger electron diminution in longer tunneling distance. As the temperature further increases, the trap peak intensity decreases faster than the excitonic emission and eventually vanishes despite of shell thickness at the temperature of 400 K. Therefore, this highly suggests that trap emission intensity and electron tunneling probability strongly depend on temperature and shell thickness. As demonstrated by insets in Figure 2c, d, the main exciton emission peak for 6 ML and 12 ML structures have a similar dependence on temperature with the core/shell only system, while the trap emission peak wavelength is almost temperature independent. This indicates that the trap energy levels shift along with the conduction band or the valence band. In particular, over the temperature range, the maximum shift of trap emission peak is ~ 6.1 meV (~18.0 meV) for 6 ML shell system (12 ML shell system), significantly smaller than that of the exciton emission ~111.97 meV (~94.69 meV) for 6 ML shell system (12 ML shell system), as shown by the insets in Figure 2c, d. We attribute the high intensity of trap emission at low temperature to the reduced core/shell interface band offset that leads to a higher electron tunneling probability. The decreased intensity for thicker shell CdSe/CdS/Au is because of the reduced electron-hole overlapping. In addition, shell thickness and temperature dependence of FWHM is also

calculated for two systems, suggesting that the thicker (12 MLs) shell and higher temperature can result in more broadened FWHM due to the more lattice-mismatching-induced defects and stronger exciton-phonon coupling respectively. (Figure S3,4)

Therefore, the recombination and charge transfer mechanisms can be described by the band diagram in Figure 3a to indicate how we manipulate the charge transfer and recombination mechanisms. Upon photoexcitation, photoexcited carriers thermalize to the conduction band edge of the core, followed by either intrinsic exciton emission, or transfer to the Au nanoparticles, or transfer to the surface states by trap emission. Figure 3b shows that the ratio of the integrated PL intensity of trap emission (A_{trap}) and exciton emission (A_{exc}) initially decreases and then gradually increase with increased temperature for both thickness shell, similar with the trend of PL peak intensity ratio of $I_{\text{trap}}/I_{\text{exc}}$ (Figure S5). This is due to the band offset reduction since the band gap of CdSe increase with temperature increasing.³² The ratio of $A_{\text{trap}}/A_{\text{exc}}$ can be described by a classic exponential relation with a tunneling rate:

$$\sim \exp(-\alpha L \sqrt{KT}), \quad \text{Eq. 1}$$

where L is the shell thickness, K is the Boltzmann constant, T is the temperature, and the α is the fitting parameter. Assuming initial electron energy close to zero due to band edge thermalization, for temperature region <320 K, both curves can be fitted by Eq. 1. The ratio of $A_{\text{trap}}/A_{\text{exc}}$ for 6 ML sample exhibits a drastic drop (from 6.22 to 1.68) while slightly change (from 1.35 to 1.21) is present for 12 ML sample, which reveals that the shell thickness has a dominant effect on charge transfer process compared to the temperature. For temperature region >320 K, where the initial energy values dominate, both curves show increasing tendencies on a roughly same magnitude. It indicates that over the high temperature region, the dominant effect on electron transfer is from the change in temperature rather than shell thickness. This reveals that higher temperature offers electron larger thermal energy, facilitating photogenerated electrons transfer to shell surface irrespective of shell thickness.

B. Temperature dependent TRPL

The charge transfer and recombination mechanisms indicated by Figure 3a are further qualitatively supported by the TRPL results using a biexponential or triexponential fitting for average lifetime for the main excitonic emission, as shown in Figure 4 and Figure S6. Clearly, the earlier lifetime of CdSe/CdS/Au significantly reduces to be less than 0.2 ns, (faster than our instrument resolution of 0.2 ns) in contrast to the longer exciton lifetimes of CdSe/CdS structure for both shell thickness structures.

The exciton lifetime τ can be described by the following relation:

$$\tau = \frac{1}{K_{\text{rad}}} + \frac{1}{K_{\text{trap}}} + \frac{1}{K_{\text{Au}}}, \quad \text{Eq. 2}$$

where K_{rad} is the radiative rate, K_{trap} is the charge transfer rate to trap states, and K_{Au} is the transfer rate to Au. Therefore, the sharp decline of lifetime is due to significantly increasing

charge transfer rate because most photogenerated electrons transfer to the nonradiative Au domain, resulting from the large driving force from potential difference between QD conduction band edge and Au Femi level. This is consistent with the ~ 2 order magnitude decrease of exciton emission compared with that of core/shell system, as shown in Figure S7. In particular, as shown in Figure 4 insets for CdSe/CdS QDs (without Au), the lifetime at excitonic peak for both 6 ML and 12 ML shell CdSe/CdS QDs near-linearly increases with temperature increasing from 80 K to 320 K, which is consistent with the results of other groups.^{25–27} Prolonged PL lifetime can be due to the decreased nonradiative recombination rate at higher temperature.³² Meanwhile, excitons of 12 ML shell QDs have a longer lifetime (85.88 ns to 255.97 ns) than that (24.04 ns to 41.49 ns) of 6 ML shell QDs over the temperature range. The highly increased lifetime in thicker shell QDs (or called giant QDs) can be attributed to the reduced electron-hole spatial overlapping within the thicker shell, largely extending the recombination time between electron and hole.³⁴ Contrary to the increased exciton lifetime of CdSe/CdS with temperature, the lifetime of CdSe/CdS/Au exhibits a decreased trend. This is most likely because, at higher temperatures electrons with higher thermal energy would prefer to transfer to Au region despite of the shell thickness. As a result, the dominated transfer rate K_{Au} increases with temperature increasing and the overall exciton lifetime therefore decreases.

In conclusion, we manipulate the electron transfer to shell surface by varying the tunneling barrier height resulted from temperature variation, and the tunneling barrier width resulted from shell thickness variation, which is demonstrated by an intrinsic exciton emission and trap emission in the near-infrared range. These charge transfer and recombination mechanisms can be described by a tunneling model. Our study reveals a clear understanding of charge transfer mechanisms in trap-related emission and provides a rational pathway of manipulating the electron tunneling with shell thickness and temperature in their photocatalysis and optoelectronics applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

a) The schematic core/shell/Au heterojunction structure. b) Absorption and emission spectra of CdSe/CdS/Au with 6 monolayers (MLs) shell (b) and 12 MLs shell (c) in hexane solution. The emission spectra are normalized at 560 nm excitation wavelength. The insets show the corresponding transmission electron microscopy (TEM) images with scale bar of 20 nm.

Figure 2.

Normalized temperature-dependent emission for 6 ML shell CdSe/CdS (a), 12 ML shell CdSe/CdS (b), 6 ML shell CdSe/CdS/Au (c) and 12 ML shell CdSe/CdS/Au (d), in temperature range from 80 K to 440 K with a step size of 40 K. Inset (a) and (b) show the temperature dependence of PL peak energy and intensity. Inset (c) and (d) show the temperature dependence of PL peak energy for excitonic emission and trap emission. All PL spectra are taken at the excitation wavelength of 560 nm.

Figure 3.

(a) Schematic band diagram of core/shell/Au heterojunction structure at room temperature.

The right panel indicates the band diagram shift due to the variation of temperature and thickness. (b) The dependence of area ratio (A_{trap}/A_{exc}) of integrated PL emission with temperature. The solid lines are the fitting curve according to Eq.1.

Figure 4.

(a) Normalized temperature-dependent TRPL at excitonic emission peak for 6 ML shell CdSe/CdS without Au (abbreviated w/o Au) and CdSe/CdS/Au with Au (abbreviated w Au) in the temperature range from 80 K to 320 K. (b) Same measurement for 12 ML. The insets show the corresponding average decay lifetimes for CdSe/CdS without Au or with Au.

Table 1.

Detail parameters of two shell thickness structures of CdSe/CdS and CdSe/CdS/Au QDs. These parameters include the core diameter (d_{core}), the shell thickness (T_{shell}), the intrinsic band gap (E_{g}), and the surface state (trap state) related peak energy (E_{trap}) for QD-Au at room temperature. The diameter of Au nanoparticle is 2 nm.

	Shell	d_{core} (nm)	T_{shell} (nm)	E_{g} (eV)	E_{trap} (eV)
QD	6 ML	4.2	2.6	1.911	\
	12 ML	4.2	5.4	1.876	\
QD-Au	6 ML	4.2	2.6	1.938	1.351
	12 ML	4.2	5.4	1.925	1.392