Characterization of hot carrier cooling and multiple exciton generation dynamics in PbS QDs using an improved transient grating technique

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Abstract

Multiple exciton generation (MEG) dynamics in colloidal PbS quantum dots (QDs) characterized with an improved transient grating (TG) technique will be reported. Only one peak soon after optical absorption and a fast decay within 1 ps can be observed in the TG kinetics when the photon energy of the pump light $h\nu$ is smaller than $2.7E_g$ (E_g : band gap between LUMO and HOMO in the QDs), which corresponds to hot carrier cooling. When $h\nu$ is greater than $2.7E_g$, however, after the initial peak, the TG signal decreases first and soon increases, and then a new peak appears at about 2–3 ps. The initial peak and the new peak correspond to hot carriers at the higher excited state and MEG at the lowest excited state, respectively. By proposing a theoretical

model, we can calculate the hot carrier cooling time constant and MEG occurrence time constant quantitatively. When MEG does not happen for $h\nu$ smaller than $2.7E_g$, hot carrier cools with a time constant of 400 fs. When MEG occurs for $h\nu$ larger than $2.7E_g$, hot carrier cools with a time constant as small as 200 fs, while MEG occurs with a time constant of 600 fs. The detailed hot carrier cooling and MEG occurrence dynamics characterized in this work would shed light on the further understanding of MEG mechanism of various type of semiconductor QDs.

Key words: PbS, Quantum dots; Multiple exciton generation; Hot carrier cooling; Transient grating

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1. Introduction

Semiconductor quantum dots (QDs) have attracted increasing interest as potential light-harvesting materials in the application to cheap and highly efficient next generation solar cells because of the following unique properties [1–4]. First, the energy gaps of the QDs can be tuned by controlling their size, and thus the absorption spectra can be tuned to match the spectral distribution of sunlight. Secondly, semiconductor QDs have large extinction coefficients due to the quantum confinement effect. Thirdly, semiconductor QDs have the potential to generate multiple electron-hole pairs with one single photon absorption (multiple exciton generation: MEG) [1,4], which would lead to incident-photon-to-current (IPCE) efficiencies of over 100%. Therefore, Nozik and Hanna have theoretically predicted that the maximum thermodynamic efficiency for photovoltaic devices with a single sensitizer could be improved to as much as ~44% by employing semiconductor QDs [5]. Since QD-based solar cells could be made

very cheaply using simple chemical methods, they are expected to be a candidate of the promising next-generation cost-effective high efficiency solar cells [1–4].

Since the initial experimental evidence of efficient MEG in colloidal PbSe QDs was obtained by Schaller and Klimov [6], enhanced MEG has been observed in several types of semiconductor QDs such as PbS, CdSe, PbTe, InAs and Si at threshold photon energies of 2–3 times the HOMO-LUMO transition energy (E_g) of the QDs, based on transient absorption (TA) spectroscopy, time-resolved photoluminescence (TRPL) technique and **Time-resolved terahertz spectroscopy (TRTS)** [6–12]. In addition, more direct signatures of MEG were observed in PbS QD photodetectors, PbS QD-sensitized solar cells and PbSe QD-based heterojunction solar cells as the excitation photon energy exceeds 2.7 times E_g [13–15]. However, some reports questioned the reported higher MEG quantum yield (QY) in semiconductor QDs (e.g., PbSe QDs) and the existence of MEG in some cases (e.g., in CdSe QDs) [16,17]. To understand the phenomenon of MEG in QDs, further experimental and theoretical studies are necessary, including dynamics of MEG occurrence and the mechanism of MEG. The most common and useful methods used to characterize MEG in QDs are TA and TRPL techniques [1,7,11]. **TRTS, which measures the intraband photoinduced absorption, has also been employed to study MEG and provides complementary information** [12]. By measuring the transient absorption or transient luminescence kinetics between LUMO and HOMO in the QDs, the recombination dynamics of excitons in the lowest excited state can be monitored. The condition for these measurements is that the pump light intensity should be low enough such that less than one exciton is excited in each QD. Then, if MEG does not happen, the lifetime of a single exciton would be as long as nanoseconds and thus only a slow decay process due to single exciton relaxation with a lifetime as long as nanoseconds can be observed. However, if MEG happens after light absorption, then more than one exciton will be produced in one QD. Then an additional fast decay resulting from Auger recombination of the generated multiexcitons, accompanying with the slow decay due to single exciton relaxation, will be observed in the TA or TRPL

kinetics [1,9,11]. Thus the signature of MEG is the fast decay dynamics with lifetimes in the range between 10 ps and 100 ps appearing in the TA or TRPL kinetics. However, in these TA and TRPL kinetics, only carrier dynamics for times longer than 3–5 ps after optical absorption were usually utilized [1,9,11], by which time hot carrier cooling and MEG are complete [1,9,11]. But the dynamics of MEG occurrence (such as at what time MEG starts), which happens as fast as less than a few picoseconds, were not be observed clearly by using the TA, TRPL and TRTS kinetics. Figure 1 shows the schematic illustration of MEG generation and characterization using the TA method.

Figure 1. Schematic illustration of MEG generation and characterization using the transient absorption (TA) method.

To study the dynamics of MEG occurrence, we have proposed an improved transient grating (TG) technique [18–28] as a new technique to characterize MEG dynamics and applied it to PbS QDs which were used as a model material. The TG technique is one kind of photothermal methods and the transient refractive index change of samples due to pulsed light absorption is measured. Compared to the conventional TG technique, the improved TG technique features a simple optical setup and highly

sensitive detection [18–28]. The principle of the improved TG technique has been explained in detail in the previous papers [18–28] and is only described briefly here. A pump beam is incident on the transmission grating and the spatial intensity profile of the pump beam has an interference pattern in the vicinity of the other side of the transmission grating. When a sample is brought near the transmission-grating surface, it can be excited by the optical interference pattern. The refractive index of the sample changes according to the intensity profile of the pump light and the induced refractive index profile functions as a different type of transiently generated grating. When the probe beam is incident in a manner similar to that of the pump beam, it is diffracted both by the transmission grating (called a reference light) and the transiently generated grating in the sample (called a signal light). In principle, the two diffractions progress along the same direction; therefore, these two diffractions interfere, which is detected by a detector positioned at a visible diffraction spot of the reference beam. We have succeeded in observation on the dynamics of MEG, including the start and complete of MEG, together with a hot exciton relaxation dynamics in PbS QDs [24]. In addition, the relaxation dynamics of the generated multiple excitons to a single exciton in the QDs through Auger recombination could be clarified clearly. Recently, we have applied the TG technique to study hot carrier cooling and MEG in alloy $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ colloidal QDs [26]. The TG measurements revealed a composition x dependent multiple exciton generation process which competes with phonon mediated carrier cooling to deplete the initial hot carrier population. The interplay between these two mechanisms is strongly dependent on the electron effective mass which in these alloys has a marked composition dependence and may be considerably lower than the hole effective mass. For a composition $x = 0.52$, we found a maximum carrier multiplication quantum yield of 199% with pump photon energy 3 times the bandgap energy, E_g , whilst the threshold energy is calculated to be just $2.15E_g$. These results indicate that alloy $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ QDs are promising materials for solar cell application or LED [26].

In this paper, we will quantitatively calculate the time constants of hot carrier cooling time and MEG occurrence in PbS QDs from the ultrafast TG kinetics within a few ps by proposing a theoretical model for the first time. We find that the photoexcited carrier relaxation processes including hot carrier cooling changed clearly when $h\nu$ increases from less than $2.7E_g$ to larger than $2.7E_g$, and MEG occurs for $h\nu$ is larger than $2.7E_g$.

2. Experimental

In the improved TG technique used for studying the ultrafast carrier dynamics of semiconductor QDs, the laser source was a titanium/sapphire laser (CPA-2010, Clark-MXR Inc.) with a wavelength of 775 nm, a repetition rate of 1 kHz, and a pulse width of 150 fs [18–28]. The light was separated into two parts. One part was used as a probe pulse. The other was used to pump an optical parametric amplifier (OPA) (a TOAPS from Quantronix) to generate light pulses with a wavelength tunable from 290 nm to 3 μm . The probe pulse wavelength was 775 nm. It has been confirmed that the changes in the real and imaginary parts of the refractive index in a sample can be selectively detected by controlling the distance between the transmission grating and the sample [24,29]. In this experiment, nitrobenzene was used as a reference sample to determine the sample positions for selectively detecting changes in the real part of the complex refractive index due to excitation by UV pump light. Nitrobenzene is well known for use as a thermal reference material because all the energy absorbed by it is released in the form of heat within 1 ns [24,29]. Thus, the sample position for selective detection of the real part of the refractive index change was determined from when the maximum TG signal for nitrobenzene was obtained, at a longer time such as 3 ns. Similarly, a Sunset Yellow solution was used as a reference sample to determine the position for selective detection of the change in the real part of the complex refractive index for visible light excitation.

As a model material, PbS colloidal QDs obtained from Evident Technologies were used as samples. The PbS QD surface were passivated with oleic acid ligands. Figure 2 shows the HRTEM images of PbS QDs. The average size of the PbS QDs used in this study was 3.2 nm, and they had an optical absorption peak at 990 nm, corresponding to a band gap energy, E_g , of 1.25 eV. For the TG measurements, the PbS QD solution was put into a 1-mm quartz cell. Only the TG signals resulting from changes in the real part of the complex refractive index in PbS QDs will be shown and discussed in this study. The pump pulse wavelength was varied from 290 nm ($h\nu$: $3.42E_g$) to 520 nm ($h\nu$: $1.9E_g$) and the probe pulse wavelength was 775 nm. The solution was stirred during all TG measurements.

Figure 2. High-resolution transmission electron microscopy (HRTEM) images of PbS QDs.

3. Results and discussion

For studying MEG in QDs using the TG measurements, the pump light intensity of each wavelength used should be low enough so that less than one exciton would be excited in each QD. Thus, we first measured the pump light intensity dependence of the TG kinetics over a time scale as long as 400 ps and confirmed that the waveforms of the TG kinetics overlap each other very well when they are normalized for each pump wavelength from 290 nm ($h\nu/E_g$: 3.42) to 520 nm ($h\nu/E_g$: 1.9) for different light intensity [24], which means that the relaxation time constants are independent of the pump light intensity. For example, for the wavelength of 520 nm ($h\nu$: $1.9E_g$), MEG should not occur at this wavelength since the photon energy of $1.9E_g$ is less than 2 times E_g [1,6–11]. In fact, we found that only single excitation with lifetimes as long as nanoseconds were excited and no ‘many-body’ recombination (such as Auger) processes occurred under these experimental conditions. This also consistent with the small initial average number of excitons per QD, $\langle N_0 \rangle$, which was calculated to be less than 0.1 for the highest pump intensity [24,30]. Similarly the $\langle N_0 \rangle$ for other pump light wavelength was also very small less than 0.1–0.15. For photon energies larger than $2.7 E_g$, however, an increase in the peak intensity and the appearance of a fast decay component (with a lifetime of ~ 30 ps determined by fitting with a biexponential function) for times less than 100 ps was clearly observed, while the TG kinetics overlap each other quite well for times longer than 150 ps. Since considerably less than one exciton was excited in one QD under our experimental conditions as mentioned above, the initial increase in the TG signal intensity with increasing photon energy and the appearance of the fast decay was believed to be the occurrence of MEG (Figure 3). The fast decay process corresponds to Auger recombination of generated biexcitons due to MEG, while the slow process corresponds to single exciton relaxation after the completion of the Auger recombination of biexcitons [24]. Our results are in good agreement with the experimental results obtained by the TA technique [1,6,9,11] for the longer time scale measurements up to 400 ps.

Figure 3. A comparison of the TG kinetics of the PbS QDs normalized at 400 ps for two different wavelengths of 520 nm ($h\nu: 1.9E_g$) and 290 nm ($h\nu: 3.42E_g$) [24].

For clarifying the ultrafast carrier dynamics, including the expected occurrence of MEG, and carrier cooling from the higher excited states to the lowest excited state, we were especially interested in the initial TG kinetics over a short time scale obtained with a higher temporal resolution for different pump light wavelengths. Figure 4 shows the TG kinetics for pump light wavelengths decreasing from 520 nm to 290 nm, i.e., the photon energy increases from $1.9E_g$ to $2.70E_g$ (a) and from $2.72E_g$ to $3.42E_g$ (b) [24]. Very clearly, a significant change in the initial TG kinetics arises when the photon energy became larger than $2.70E_g$. In the case of photon energy less than $2.70E_g$, a fast decay process with a time constant of less than 1 ps, which corresponds to hot carrier cooling, and a subsequent slow decay process which corresponds to a single exciton relaxation between LUMO and HOMO. On the other hand, in the case of photon energy larger than $2.70E_g$, the TG signal decreases due to hot carrier cooling after the first peak (related to hot carrier states), and then soon increases again and finally a new peak appears at around 2–3

ps. The second peak intensity increases as the excitation photon energy increases. So in this case, along with hot carrier cooling within a few hundred femtoseconds, MEG also happens within a few hundred femtoseconds, resulting in a saturated exciton density in the lowest excited state at around 2–3 ps [24].

Figure 4. Normalized TG kinetics (a) for pump light wavelengths from 520 nm ($\hbar\nu$: $1.9E_g$) to 370 nm ($\hbar\nu$: $2.70E_g$) and (b) for pump light wavelengths from 365 nm ($\hbar\nu$: $2.72E_g$) to 290 nm ($\hbar\nu$: $3.42E_g$), where the TG signals are normalized at the initial peaks [24].

Here, we propose a model to analyze the ultrafast TG kinetics (Figure 5) and to determine the hot carrier cooling time constant from higher excited states to the lowest excited states and the exciton

generation time constant for the lowest excited states. As shown in Figure 5, the hot carrier density at higher excited state is assumed to be $N_1(t)$ and the carrier density at the lowest excited state is assumed to be $N_2(t)$ for time t after optical excitation.

Figure 5. Schematic illustration of the theoretical model for analyzing the ultrafast TG kinetics within a few ps. $N_1(t)$ and $N_2(t)$ are the hot carrier density at higher excited state and the carrier density in the lowest excited state, respectively.

As discussed in detail in our earlier papers [24,26], the TG signal Y is proportional to the refractive index change $\Delta n_{\text{carrier}}(t)$ of the sample due to photoexcited carriers in the timescale of a few ps [24,26].

$$Y \propto \Delta n_{\text{carrier}}(t) \quad (1)$$

In general, $\Delta n(t)$ is dependent on the excited state of the carriers, the probe light frequency and the carrier density $N(t)$. Thus Y can be approximately expressed as follows [24,26,31–33]:

$$\Delta n_{\text{carrier}}(t) \propto A_1 N_1(t) + A_2 N_2(t) \quad (2)$$

where $N_1(t)$ and $N_2(t)$ are the hot carrier densities at higher excited state and at the lowest excited state, respectively. A_1 and A_2 are constants related to the probe light frequency, ω , and the excited state, E_i , of the carriers. Since the probe beam frequency is a constant, ω_0 here (only one probe light wavelength of 775 nm was used), A_1 and A_2 are only dependent on the initial higher excited state and the lowest excited state respectively. By assuming that (1) N_1 decreases exponentially with time after the pulsed pump light excitation; (2) N_2 increases with time and became maximum up to 2–3 ps and then (3) N_2 decreases due to exciton relaxation at the lowest excited state such as recombination between LUMO and HOMO levels for time larger than 3 ps. Then we assume TG signal Y can be expressed by the following equation for the timescale less than 3 ps, in which the first and second term reflects the above (1) and (2) processes, respectively:

$$Y = B_1 e^{-t/t_1} + B_2 (1 - e^{-t/t_2}) \quad (\text{for time} \leq 3 \text{ ps}) \quad (3)$$

where t_1 and t_2 are hot carrier relaxation time constant from higher excited states and generation time constant of carrier at the lowest excited state, respectively. B_1 is a constant proportional to initial hot carrier density at higher excited states and B_2 is a constant proportional to the largest carrier density at the lowest excited state for time of 2–3 ps. Then we fitted each TG kinetics measured under different pump wavelength using Eq. (3) for the timescale of about 3 ps and found that they could be fitted very well as shown in Figure 6. The fitting results of the parameters t_1 , t_2 , B_1 and B_2 for each pump wavelength are shown in Table 1. Figure 7 shows the dependence of hot carrier cooling time constant t_1 at the initial higher excited state and carrier generation time constant t_2 at the lowest excited state on $h\nu/E_g$. It is very interesting that hot carrier cooling time constant t_1 is the same as the carrier generation time constant at the lowest excited state t_2 for $h\nu/E_g < 2.7$, i.e., 400 fs. This result indicates that the hot carrier relaxation

from higher excited state to the lowest excited state is the only one physical process for carrier generating at the lowest excited state under that condition of $h\nu/E_g < 2.7$, and the hot carrier cooling time constant was as fast as 400 fs. However, for $h\nu/E_g > 2.7$, t_1 decreases to be 200 fs, while t_2 increases up to 600 fs. This result demonstrates that besides hot carrier relaxation from higher excited state to the lowest excited state, another physical process also occurs for the creation of carriers at the lowest excited state. It can be considered as follows: when electrons in the PbS QDs are excited to higher excited states by a photon with an energy $h\nu$ larger than $2.7E_g$, then the hot carriers can give their energies to electrons in the ground states very quickly with a time constant of 200 fs, and the electrons in the ground state are excited and finally arrive at the lowest excited states with a time constant of 600 fs. This is the MEG phenomena. It is worth noting that B_2 increases with $h\nu$ increasing under the condition of $h\nu/E_g > 2.7$, which indicates that carrier density of the lowest excited states increases as the energy of the excitation photon increases. This result also confirms that MEG occurs under the condition of $h\nu > 2.7E_g$.

Figure 6. TG kinetics and theoretical fitting results using Eq. (3) for timescale up to about 3 ps, where (a) the pump light wavelength was changed from 370 nm to 520 nm and (b) the pump light wavelength was changed from 290 nm to 365 nm.

Table 1. Fitting results of the parameters t_1 , t_2 , B_1 and B_2 for the TG kinetics in a timescale of 3 ps using Eq. (3). λ and $h\nu$ are the wavelength and photon energy of the pump light, respectively. $h\nu/E_g$ is the ratio of $h\nu$ to the band gap E_g of the QDs.

λ (nm)	$h\nu$ (eV)	$h\nu/E_g$	t_1 (ps)	t_2 (ps)	B_1	B_2
290	4.28	3.42	0.2	0.6	1.1	1.6
350	3.54	2.83	0.2	0.5	1.1	1.5
355	3.49	2.79	0.2	0.5	1.1	1.2
362	3.42	2.74	0.3	0.6	1.0	0.8
365	3.40	2.72	0.3	0.4	1.0	0.7
370	3.35	2.68	0.4	0.4	1.0	0.7
400	3.1	2.48	0.4	0.4	1.0	0.8
520	2.38	1.90	0.4	0.4	1.0	0.9

Figure 7. Dependence of hot carrier cooling time constant t_1 at the initial higher excited state and carrier generation time constant t_2 at the lowest excited state on the $h\nu/E_g$.

4. Conclusions

We have characterized hot carrier cooling and MEG occurrence dynamics in PbS QDs using an improved TG technique. By proposing a theoretical model, we could quantitatively analyze the time constant of hot carrier cooling from higher excited states and the time constant of carrier creation at the lowest excited states. For the first time, our results clearly revealed that there is a significant change in the physical processes of photoexcited carrier relaxation in the QDs when the photon energy $h\nu$ of pump light changed from smaller than $2.7E_g$ to larger than $2.7E_g$. For $h\nu/E_g < 2.7$, hot carrier cooling from higher excited states to the lowest excited states is the only physical process for carrier creation at the lowest excited state with a time constant as fast as 400 fs and no MEG happens under this condition. For $h\nu/E_g > 2.7$, however, both hot carrier cooling and MEG simultaneously occur. As a result, the carrier density at the lowest excited state

increases and reaches a maximum with a time constant of 600 fs. We demonstrated that the TG technique is very helpful as a characterization method for photoexcited carrier relaxation in semiconductor QDs. The detailed hot carrier cooling and MEG occurrence dynamics characterized in this work would shed light on the further understanding of MEG mechanism of semiconductor QDs.

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Graphical abstract

With MEG