Non-destructive dispersion of quantum dots into gases

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Abstract. We report on our experimental results for the nondestructive dispersion of CdSe/ZnS core-shell quantum dots and ZnS-AgInS₂ solid solution quantum dots into buffer gases by using a nebulizer. By monitoring scattering light from droplets and fluorescence from quantum dots, we discuss the evaporation and loss of the droplet and the fluorescence quenching of the quantum dot after the evaporation.

1. Introduction

A semiconductor quantum dot (QD) is one of nanoparticles attracting a great deal of interest in many fields. Since its electronic structure and spectral property are strongly influenced with their size and environment[2], more precise size control of the QD is considered to be one of key factors involved in its future applications for efficient opt-electronic devices. The aim of our study is to carry out the size-separation of the QDs in gases, which have low viscosity and high thermal diffusivity, by optical means. In liquid helium, the optical size-separation has been successfully demonstrated for CuCl QDs created by laser ablation.[3] Since a typical viscosity value for a gas at normal temperature is close to the one for the liquid helium, a similar manipulation would be expected to be possible in a buffer gas. The use of the buffer gas enables us to control temperature more widely and reduce the influence of convection and foam in addition to relative ease of an experimental setup. For realizing similar optical separation for a variety of chemically synthesized QDs at normal temperature, we are developing an experimental approach for their non-destructive dispersion into buffer gases.

In this paper, we report our recent experimental results for the dispersion and isolation of CdSe/ZnS core-shell QDs[4] and (Ag In)ₓZn₂(1-x)S₂ solid solution (ZAIS) QDs[5] into buffer gases of dry nitrogen by using droplets generated with nebulizers.

2. Experimental setup

To non-destructively introduce quantum dots into buffer gases, we constructed the experimental apparatus using a mesh-type nebulizer (Omron NE-U) with a PZT oscillator (Fig.1). The CdSe/ZnS QDs and ZAIS QDs were dissolved, respectively, in diethyl ether and hexane (the typical QD number...
density of the solution was approximately $10^{13} - 10^{14}$/ml, and each solution (0.5 ml) was injected into a gas cell (~100 ml) by using the nebulizer. The CdSe/ZnS QDs used in the experiment are commercial products from Sigma-Aldrich Co.. Their diameter is approximately 6.3 nm, and the peak wavelength of the fluorescence spectrum is approximately 630 nm. The ZAIS QDs are chemically synthesized and characterized in Nagoya University, and their diameter is nearly 5 nm. In this experiment, we used two types of ZAIS QDs with the ratio $x = 0.3$ and 0.7, whose absorption and emission spectra are different from each other; the peak wavelengths of their fluorescence spectra are 570 nm and 630 nm, respectively (532 nm excitation). Nominal diameter of the generated droplet is around 5 μm, and the typical number of QDs included in a single droplet is estimated to be 100-1000. To isolate QDs in the buffer gas, we enhanced the evaporation of the solvent from the droplet by two means; the heating of the gas cell (~320K) and the cold trapping of solvent vapor with liquid nitrogen.

3. Results and discussions

The generation and evaporation of the droplet were monitored by observing the scattering intensity of the probe laser beam (628 nm, 10mW). The observed time dependence of the scattering intensity is shown in Fig.2. From this figure, it is found that almost all the visible droplets were lost in nearly 1 min. Possible causes of this loss are considered to be the falling by gravity, the sticking on the cell wall through the diffusion, and the evaporation. To prevent the former two loss processes, we applied the CO$_2$ laser heating (~10 W/20 mm$^2$) to the droplets. As a result, it was confirmed that the evaporation was successfully enhanced and almost all the droplets evaporated less than 30 s as see in Fig.2.

Figure 1. Experimental apparatus for the non-destructive dispersion of quantum dots into a dry nitrogen buffer gas.

Figure 2. Decrease of the laser scattering intensity with and without the CO$_2$ laser heating.
The fluorescence from the QDs was monitored with a CCD monochromator. The wavelength of the excitation laser is 532 nm, and the intensity is typically 1.4 W/7 mm². Figure 3(a) shows the time dependence of the fluorescence spectrum observed in the case of the CdSe/ZnS QD. Just after the droplet generation relatively high fluorescence was observed due to the QDs in the droplets. However, the fluorescence intensity gradually decreased in approximately 1 min. This decay rate is similar to the one observed in the scattering intensity, and fluorescence from the isolated QD was not observed apparently. The observed fluorescence decay is considered to be caused from the loss of the QDs due to the falling and sticking of the droplets as seen in the scattering measurement.

To observe the fluorescence from the isolated QD, we enhanced the evaporation of the droplet by the CO₂ laser heating during the fluorescence measurement. Figure 3(b) shows the change of the fluorescence intensity after the CO₂ laser heating. As seen in this figure the fluorescence intensity sharply decreases as the droplets evaporate. This result suggests the occurrence of the strong fluorescence quenching due to the evaporation of the droplet.

Since the exciton in the CdSe is weakly binding, it is well known that the change of the QD surface considerably affects the emission efficiency.[6] In contrast, in the case of the ZAIS QD, the emission quantum efficiency is expected to be less sensitive to its surface change, since the photon emission is...
caused by the defect localized in the QD. However, the fluorescence observed from the ZAIS QD ($x = 0.7$) showed the same strong quenching to the CdSe/ZnS QD (Fig. 4). On the other hand, in the case of the ZAIS QD ($x = 0.3$), which was optically excited under the condition of the red-side far-wing excitation (Fig. 5), the fluorescence decay rate was apparently lower. This fact indicates that the thermal relaxation after the optical excitation should play an important role in the fluorescence quenching. The slight recovery of the fluorescence intensity around 120 s is due to the fluctuation of the QD number density and photo detector noise.

Finally, to reduce the influence of impurity contamination on the emission efficiency, we also tried to decrease the size of the droplet. We newly constructed an experimental apparatus with a cluster generator by using a metal mesh rotor (Corona Co. CNR-400B). The typical cluster size is in the range of 10 to 100 nm in the case of H$_2$O clusters. From the scattering measurement it was confirmed that the almost all the visible clusters evaporates in approximately 30 s, which indicates that the generated clusters are smaller than the previous droplets. However, the similar fluorescence quenching was observed for both ZAIS QDs ($x = 0.3$ and $0.7$) even after 30 s from the generation of the clusters.

4. Conclusion

The CdSe/ZnS QDs and ZAIS QDs ($x = 0.3$ and $0.7$) were nondestructively dispersed in a dry nitrogen buffer gas by using micro-droplets and nano-clusters. Evaporation behavior of the droplet and clusters were monitored by measuring scattering and fluorescence. The enhancement of the evaporation by the CO$_2$ laser heating was demonstrated successfully. From the fluorescence measurement, it was found that the fluorescence from the QD was strongly quenched after the evaporation of the droplets and clusters. The difference in the fluorescence decay rate between QDs suggests that the thermal relaxation after the optical excitation is one of possible causes of the fluorescence quenching.

5. Acknowledgement

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