

**SUBPICOSECOND UP-CONVERSION
MEASUREMENTS OF PHOTOLUMINESCENCE
OF THIOGLYCEROL-CAPPED CADMIUM
SULFIDE NANOPARTICLES
COLLOIDAL SOLUTIONS**

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1. Introduction

For understanding the primary photochemical events of semiconductor particles and further improving their efficiency as a photocatalyst, it is very important to study the behavior of the carrier generated immediately after the photoexcitation of the particles. So far we have discussed the behavior of the carriers on the thiol-capped CdS nanoparticles from the results of the measurement of their subpicosecond time-resolved transient absorption spectra [1]. In the present study, we also discussed the behavior of the photogenerated carriers on thiol-capped CdS nanoparticles from the results of the measurement of their subpicosecond time-resolved photoluminescence (PL) by the up-conversion method. The results suggested that the photogenerated electron was transferred considerably to oxygen adsorbed on the surface of thiol-capped CdS nanoparticles within the duration time of the excitation pulse.

2. Experimental

Thioglycerol-capped CdS nanoparticles (TG-CdS) were synthesized by the pyrolysis of thiourea in the presence of cadmium acetate and 1-thioglycerol. Their colloidal solutions were prepared by dispersing the nanoparticles in either water or DMF. The core size of their particles estimated from the absorption spectra of their colloidal solutions was ca. 2.5 nm. Subpicosecond time-resolved PL measurements were carried out by up-conversion method. The excitation pulse was the second harmonic pulse ($\lambda_{\max}=396$ nm) of the fundamental pulse ($\lambda_{\max}=792$ nm) from a cw self mode-locked Ti:Sapphire laser (MIRA, 76 MHz, 170 fs FWHM). The fundamental pulse was used as a gate pulse. The sum frequency signal generated in a BBO crystal by mixing PL of the sample and a gate pulse was detected by a photomultiplier tube and a gated photon counter after passing through a monochromator. These sum frequency measurements were carried out while the arrival time of a gate pulse to the BBO crystal was changed in order to obtain the time profile of PL of samples. A quartz flow cell with 1 mm-path length was used for the measurements.

3. Results and Discussion

The time profiles for PL of TG-CdS in water and in DMF could be fitted by sum of two exponentials for a time region of 30 ps in a wavelength range of 470 to 550 nm examined (Fig.1). Namely, PL consists of a fast decay component with a time constant (τ_1) of several ps and a slow one with a time constant (τ_2) of few tens to a hundred ps. Both τ_1 and τ_2 for TG-CdS in water were smaller than those for TG-CdS in DMF. In both solvents, both time constants increased with increasing the wavelength at which PL was observed. And further ratio of the slow decay component also increased with increasing the wavelength. Furthermore, effects of dissolved oxygen on decay dynamics for PL (at 490 and 550 nm) of TG-CdS were investigated in water and in DMF by use of their colloidal solutions which were bubbled Ar or O₂ gasses. For TG-CdS in water, the intensity of PL immediately after the excitation enhanced

remarkably by bubbling Ar gas, and its decay became faster. However, the effect of Ar gas bubbling for TG-CdS in DMF was not observed virtually (Fig. 2). These results may be explained well by the fact that adsorption of dissolved oxygen onto the surface of TG-CdS nanoparticles occurs easily in water compared with in DMF and consequently the effect of bubbling of Ar gas appears distinctively for the dynamics for PL of TG-CdS in water. The results also suggest that the transfer of the photo-generated electrons to oxygen adsorbed on the particles is an ultrafast process which can compete with the recombination of electrons and holes immediately after the pulse excitation.

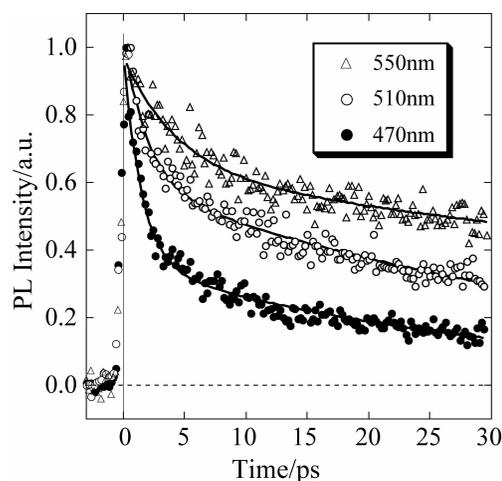


Fig.1 Wavelength dependence of time profiles for photoluminescence of TG-CdS in DMF.

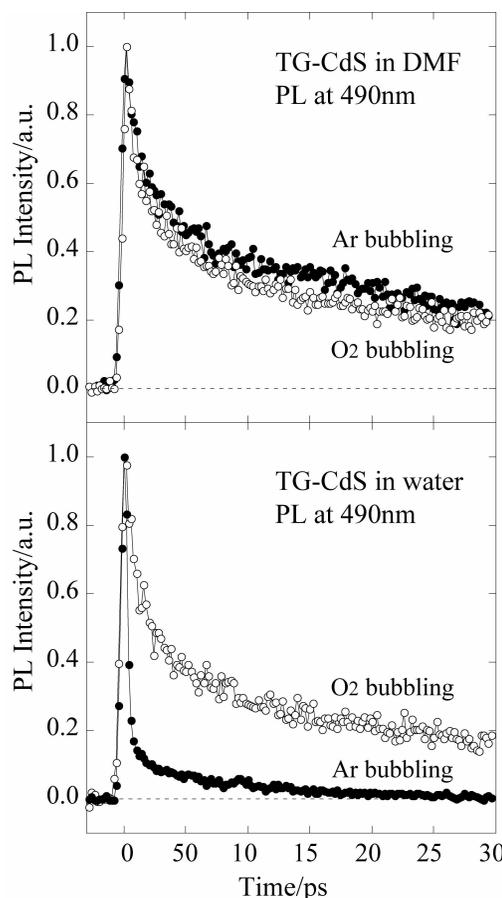


Fig.2 Time profiles for photoluminescence of TG-CdS under various conditions.

Ref.[1] T. Uchihara et al., J. Photochem. & Photobiol. A: Chem., 161 (2004) 227; 141 (2001) 193; 121 (1999)199.