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Photon antibunching in enhanced photoluminescence of a single CdSe/ZnS nanocrystal by silver nanostructures

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ABSTRACT

The photon antibunching behavior in the photoluminescence (PL) of single CdSe/ZnS semiconductor nanocrystals (NCs) interacting with the localized surface plasmon resonance (LSPR) of Ag nanostructure was investigated using fs-pulsed laser excitation at two excitation wavelengths. The time traces of the PL intensity, the PL decay curves, and the photon correlations of single NCs on a rough Ag film and on a coverslip were measured simultaneously, and an increase in the PL intensity accompanied by shortening of the PL lifetime was observed for the single NCs on the rough Ag film. The enhancement factor of the PL intensity depended on the excitation wavelength. Nearly all of the single NCs with enhanced PL exhibited photon antibunching behavior independent of the enhancement factor. Based on the enhanced radiative- and nonradiative-decay rates estimated from the experimental data, the mechanism of the photon antibunching behavior was considered as follows. To exhibit the photon antibunching behavior, the nonradiative Auger recombination between the generated excitons in a single NC is important. When the radiative- and the nonradiative-decay rates enhanced by the LSPR are faster than the Auger recombination rate, the probability of photon antibunching decreases. However, such fast radiative- and the nonradiative decay rates were not observed for single NCs interacting with the LSPR of the rough Ag film in this work. Therefore, the PL intensity from a single NC can be increased while maintaining the photon antibunching behavior. Our findings assist in the creation of effective single-photon sources and provide important information on the emission properties of an NC coupled with the plasmon of a metal nanostructure.

1. Introduction

Over the past two decades, colloidal semiconductor nanocrystals (NCs) have been studied extensively because of their potential for use in optoelectronic applications [1–5] and biolabeling [6–11]. One interesting optical property of single NCs is their single-photon emission behavior at room temperature [12–17]. Single-photon sources capable of emitting only one photon at any point in time have been extensively investigated for use in quantum information processing. In this context, NCs are good candidates because of their flexible controllability of photon energy, large absorption cross-section, and superior photostability. One effective approach for increasing the efficiency of the single-photon emission from single NCs is coupling with the localized surface plasmon resonance (LSPR) of metal nanostructures. There are numerous reports regarding the emission behavior of fluorophores, including NCs [18–29], coupled with LSPR. As a result of the LSPR, an increase in the photoluminescence (PL) intensity is accompanied by a shortening of the PL lifetime, suppression of the PL blinking behavior (on-off behavior of PL intensity), and improvement of the photostability. Application of these effects is expected to create a single-photon source that emits single photons with high frequency. Thus, the investigation of the single-photon emission behavior, i.e., photon antibunching behavior, of fluorophores coupled with LSPR is extremely important.

Recently, we have investigated the photon antibunching behavior of a single NC coupled with LSPR of silver nanoparticles (AgNPs) in details employing ps-, and fs-pulsed laser excitations [30,31]. By measuring photon correlation in the enhanced PL of single CdSe/ZnS core/shell NCs coupled with LSPR of AgNP, we revealed that the probability of photon antibunching decreased when the PL lifetime was shortened to less than 500 ps (time resolution of the instrumental set-up) by coupling with LSPR. This result was interpreted as follows. A single NC itself exhibits photon antibunching, even when multiple excitons are generated in a single NC by an intense single excitation pulse because an exciton decays non-radiatively by the Auger recombination between the excitons, resulting in one exciton [12–15]. The timescale of the

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Auger recombination depends on the size of the NC. The recombination occurred within 100 ps for the NC used (core radius: 2.6 nm) [32]. However, in the case of single NCs interacting with LSPR, the radiative rate enhanced by the LSPR competed with the Auger recombination which is the exciton–exciton annihilation process and the key mechanism for the photon antibunching observed for NCs. Therefore, the single NC with a short lifetime (i.e., the radiative decay rate was faster than the Auger recombination process) exhibited a decrease in antibunching behavior. Yuan et al. also reported antibunching behavior of a single CdSe/ZnS NC coupled with the LSPR of a silver nanoprism [26]. However, they reported that the antibunching behavior was observed even when the PL was enhanced by the LSPR, although the relationship between the antibunching behavior and the lifetime was not described.

To elucidate the antibunching behavior of the fluorophore coupled with LSPR, additional experimental data are required. Therefore, in this work, photon antibunching behavior of single CdSe/ZnS NCs coupled with the LSPR of rough Ag film is investigated using fs-pulsed laser at two excitation wavelengths. In general, the LSPR alters both the excitation and emission properties of nearby fluorophores. The excitation rate of the fluorophore is enhanced by the electromagnetic field of LSPR induced by the incident laser. In the emission process, the radiative decay rate of the fluorophore increases, that is, the quantum yield of the fluorophore increases because of an increase in the local electromagnetic density of the states induced by the metal nanostructures. In addition, the non-radiative decay rate also increases because of energy transfer to the metal nanostructures that occurs when the distance between fluorophore and metal nanostructures is small. The influence of the excitation and the emission processes on the emission properties of the NC coupled with the LSPR may be estimated by measuring the excitation wavelength dependence. When the excitation process is mainly modified by the LSPR, the change of the emission properties can be observed depending on the excitation wavelength. On the other hand, when the emission process is mainly modified by the LSPR, the emission properties of the NCs do not change depending on the excitation wavelengths [33].

2. Experimental

CdSe/ZnS core/shell NCs (Invitrogen, PL maximum wavelength: 605 nm) were used in this work. The rough Ag film was prepared on a clean coverslip by thermal evaporation under vacuum conditions. An atomic force microscopy (AFM) image of the prepared rough Ag film is shown in Fig. 1(a). The surface of the rough Ag film is composed of random nanostructures with valleys of approximately 10–50 nm in depth. Thus, the plasmon resonance band and the magnitude of the electromagnetic field of the plasmon are expected to strongly depend on the position of the NC on the surface of the rough Ag film, although the absorption and the transmittance spectra were not able to be measured because of the thick Ag film. The sample was prepared by spin-coating (3000 rpm, 90 s) a chloroform solution containing 0.5 wt% poly(methyl methacrylate) (PMMA) and approximately 10^{-11} mol/L of the NCs on the rough Ag film. A representation of the sample is shown in Fig. 1(b). Isolated NCs exist in the PMMA thin film on the rough Ag film. As a control sample, the same chloroform solution was spin-coated on a clean coverslip. The thickness of the PMMA film in the control sample was approximately 30 nm as determined by an AFM measurement. Although it was difficult to estimate the exact thickness of the PMMA film on the rough Ag film because of the roughness of the Ag film, the thickness of the PMMA film on the rough Ag film assumed to be the same as that on the coverslip, but with some heterogeneity. Therefore, the distance between the NCs and the Ag is within 30 nm; however, further control of the distance between the NCs and the Ag was not achieved in this sample. In this sample, a remarkable quenching of the PL from the single NCs was not observed, so we chose this thickness of the PMMA film. When a thinner PMMA film (a half of the present thickness) was used, the pronounced PL quenching was observed.

The PL properties of the isolated NCs were measured by a Hanbury–Brown and Twiss-type photon correlation set-up in combination with an fs-pulsed laser excitation at 405 and 488 nm (8.0 MHz, 200 fs FWHM) under a sample-scanning confocal microscope. The excitation laser was focused on the single NC by an objective lens (NA 0.95, Nikon), and the photons emitted from the NC were collected by the same objective lens and passed through a confocal pinhole, a long-pass filter (LP02-514RU, Semrock), and a band-pass filter (FF01-607/36, Semrock) suitable for the PL band of the NC. Then the photons were split into two paths by a 50/50 non-polarizing beam splitter and detected by two avalanche single-photon counting modules (APD, SPCM-AQR-14, PerkinElmer). The signals from the two APDs were connected via a router to a time-correlated single-photon counting board (SPC-630, Becker & Hickl) for the photon correlation measurement. The excitation laser-triggered time-correlated single-photon counting technique was also simultaneously used to measure the PL lifetime. By analyzing the obtained data using software designed in our laboratory, time traces of the PL intensity, the PL decay curve, and the photon correlation histogram were obtained simultaneously for the single NCs. The time-resolution of the lifetime measurement (i.e., instrument response function, irf) was approximately 0.5 ns. All of the measurements were performed at room temperature under ambient conditions.

3. Results and discussion

Fig. 2 shows typical results for the time traces of the PL intensity [(a) and (b)], the PL decay curves on a semi-logarithmic scale [(c) and (d)] and the photon correlation histograms [(e) and (f)] obtained from the single NCs in PMMA on a coverslip [(a), (c), and (e)] and on the rough Ag film [(b), (d), and (f)] using an excitation laser at 488 nm with 210 W/cm^2 power. The number of excitons generated in a single NC by a single excitation pulse was estimated to be 0.43, by taking into account the absorption cross-section of the NC at 488 nm (6.6×10^{-15} cm^2) and the number of photons in the single excitation pulse. The PL intensity obtained from the single NC on a coverslip (Fig. 2(a)) was found to be as high as 15 counts/ms, whereas the intensity increased as high as 120 counts/ms for the single NC on the rough Ag film. The increase in the PL intensity from the NCs on the Ag film indicated PL enhancement by LSPR. The PL lifetimes obtained by analyzing the decay curves were 14.4 and 8.3 ns for the NCs on the coverslip and on the Ag film, respectively. That is, the lifetime of the enhanced PL is shorter than the normal lifetime of the NC. The enhanced PL behaviors accompanied by shortening of the lifetime are similar to those reported for NCs with metal nanostructures [18–29].

We have evaluated photon antibunching behavior from the photon correlation histograms (Fig. 2(e) and (f)). In the photon correlation histograms, the probability of antibunching (i.e., single-photon emission) increases with a decrease in the detection events at a 0 ns delay time ($\tau = 0$) compared to the detection events at other delay times (τ). In Fig. 2(e) and (f), the detection events at $\tau = 0$ are quite low compared to those at the other delay times, which indicates that the PL from both NCs exhibited photon antibunching. Therefore, the photon antibunching was observed for the enhanced PL of the NC on the Ag film. The second-order correlation function, $g^{(2)}(0)$, is typically used to evaluate the photon correlation