Multiphoton Emission Enhancement from a Single Colloidal Quantum Dot Using SiO₂-Coated Silver Nanoparticles

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ABSTRACT: The enhancement of multiphoton emission from a single colloidal nanocrystal quantum dot (NQD) interacting with a plasmonic nanostructure was investigated using SiO₂-coated silver nanoparticles (Ag/SiO₂) as the plasmonic nanostructure. Using Ag/SiO₂ with five different SiO₂ shell thicknesses, we observed modification of the emission behavior depending on the distance between the NQD and silver nanoparticle (AgNP). The single-photon emission from a single NQD converted to multiphoton emission with a shortening of the emission lifetime as the NQD–AgNP distance decreased, whereas an increase and decrease in the emission intensity were observed. From the distance-dependent results, we concluded that the probability of multiphoton emission was increased by the quenching of the single-exciton state due to energy transfer from the NQD to the AgNP and that the emission intensity was modified by the enhancement of the excitation rate and quenching. These results indicate that the plasmonic nanostructure is very effective in controlling the emission photon statistics, that is, single- and multi-photon emission and the emission intensity from the single NQD, which is difficult to achieve in an NQD alone.

INTRODUCTION

Colloidal nanocrystal quantum dots (NQDs) are dispersible nanoscale emitters that are of great interest because of their potential applications in a wide range of optoelectronic devices1−10 and in biosensing.11−13 The emission photon statistics, that is, single-photon emission and multiphoton emission, from a single NQD is an important optical property obtained as a result of multie exciton dynamics, which can be explained as follows. When multiple excitons are simultaneously generated in a single NQD, multie exciton states (MX), such as the triexciton state (TX) or biexciton state (BX), are formed, depending on the number of generated excitons. In the emission process, the excitons decay from the TX or BX to the single-exciton state (SX) by emitting a single photon on a picosecond time scale. Then, the remaining single-exciton decays from the SX to the ground state (GS) by emitting a single photon on a nanosecond time scale.14 Thus, multiple photons can be emitted by this cascade emission. The obtained multiphoton emission can behave as an entangled photon pair, which is important for quantum information technologies.15 However, when multiple excitons are generated, nonradiative Auger recombination occurs. The excitons decay nonradiatively from the MX to the SX.16 Subsequently, the remaining single-exciton decays from the SX to the GS by emitting a single photon. Therefore, single-photon emission can be obtained via Auger recombination.17−20 Single-photon emission is also important for quantum information technologies. Generally, the emission photon statistics of an NQD are controlled by quantum confinement, which depends on the size, shape, and atomic composition of the NQDs themselves.

Recently, control of the photon statistics of NQDs using plasmonic nanostructures, that is, metallic nanostructures (MNSs), has received substantial attention. An increase in the probability of multiphoton emission through the interaction with MNS has been reported using various NQD–MNS systems.21−37 Two mechanisms have been proposed to explain the increase in multiphoton emission. One is the enhancement of the multiphoton emission rate by enhancement of the radiative rate. Because of this enhancement, a single NQD–MNS can emit multiple photons before the excitons are annihilated by Auger recombination, that is, the quantum yield of the MX emission (ΦMX) increases.21−25,27,30−34,36 The other mechanism is the quenching of the SX by the MNS, that is, a decrease in the quantum yield of the SX emission (ΦSX) rather than an actual increase in the ΦMX. This mechanism can be understood as follows: When the excitons are quenched by the MNS, due to energy or electron transfer, the quenching of the SX is more efficient than that of the MX because of the longer lifetime of the SX. Because of the decrease in ΦSX, the contribution of the MX emission increases. Consequently, the

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probability of the MX emission increases.\textsuperscript{28,37–40} Although these two mechanisms were proposed, the details are not yet fully understood.

To elucidate the mechanism, a single NQD–MNS system in which the spectral overlap and distance are fully controlled is ideal. When the localized surface plasmon resonance (LSPR) band of the MNS overlaps the absorption spectrum of the nearby emitter, the excitation rate of the emitter is enhanced by the electric field of the localized surface plasmon (LSP) generated on the MNS by incident light. When the LSPR band overlaps with the emission spectrum of the emitter, the relaxation process, that is, radiative and nonradiative processes, of the emitter is enhanced by the dipole–dipole interaction between the emitter and MNS.\textsuperscript{41–45} The enhancement factors strongly depend on the distance between the emitter and MNS. Although the relationship between the change in photon statistics and spectral overlap has often been discussed in the literature,\textsuperscript{22,24,25,31,36,46} few reports have examined the dependence of the change in photon statistics on distance.\textsuperscript{31,37} Coating the MNSs or NQDs with the dielectric material SiO\textsubscript{2} is an effective method for controlling the distance. Numerous studies have reported the modification of the PL intensity and lifetime of distance-controlled NQD–MNS systems using a SiO\textsubscript{2} shell.\textsuperscript{31,34,47–50} However, only one report has examined the relationship between the photon statistics and distance.\textsuperscript{31} In that work, the distance-dependent emission photon statistics was measured using SiO\textsubscript{2}-coated gold nanoparticles with 5 and 10 nm thick SiO\textsubscript{2} shells. To elucidate the mechanism of modification of the emission behavior of the NQDs using MNSs systematically, further experimental results using different NQD–MNS systems are required.

In this work, to elucidate the relationship between photon statistics and distance and the mechanism of enhancement of MX emission, SiO\textsubscript{2}-coated silver (Ag/SiO\textsubscript{2}) nanoparticles with five different SiO\textsubscript{2} shell thicknesses were used to control the distance between a single NQD and a silver nanoparticle (AgNP). A dielectric SiO\textsubscript{2} spacer with a controlled thickness provides a simple means of tuning the interactions between a NQD and AgNP. To control the distance using the SiO\textsubscript{2}-shell thickness, using a single Ag/SiO\textsubscript{2} nanoparticle and single NQD and following a previously reported atomic force microscopy (AFM) manipulation technique\textsuperscript{36} is ideal. However, the AFM manipulation of Ag/SiO\textsubscript{2} is hindered by the adsorption of Ag/SiO\textsubscript{2} onto the silicon AFM cantilever. Therefore, the emission photon statistics of single NQDs interacting with Ag/SiO\textsubscript{2} was detected for samples prepared by dispersing NQDs and Ag/SiO\textsubscript{2} nanoparticles on a coverslip by spin-coating.

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**RESULTS AND DISCUSSION**

Transmission electron microscopy (TEM) images of Ag/SiO\textsubscript{2} nanoparticles with different shell thicknesses and histograms of each shell thickness are shown in Figure 1. The core AgNPs were almost spherical, and the average diameter was 54 ± 2 nm (Figure 1f). The shell thicknesses were estimated as 5 ± 1, 7 ± 1, 15 ± 1, 24 ± 2, and 38 ± 2 nm from the TEM images. Figure 2 shows the absorption and PL spectra of the NQDs in toluene (a) and the extinction spectra of the prepared Ag/SiO\textsubscript{2} with different thicknesses (b). The LSPR band of the Ag/SiO\textsubscript{2} nanoparticles...
two isolated NQDs with Ag/SiO₂ particles with 5 nm thick shells (ε=1) exposed to an excitation laser at 405 nm with an intensity of 710 W/cm². The number of excitons generated in a single NQD by a single excitation pulse, (N), was estimated at 0.48 by taking into account the absorption cross-section of an NQD at 405 nm (1.1 x 10⁻¹⁴ cm²) and the number of photons in the single excitation pulse. The time trace of the PL intensity obtained from the reference NQD displayed 200 counts/ms and characteristic blinking behavior (Figure 4a). The low-intensity level of blinking results from the quenching of the exciton by the charged state of the NQD. The quenching process causes the short decay component of the PL decay curve. The PL decay curve shown in Figure 4b was fitted using a two-exponential function, \( I(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) \), where \( \alpha \) and \( \tau \) represent the normalized amplitude and PL lifetime, respectively, with lifetimes of \( \tau_1 = 0.8 \text{ ns} \) (\( \alpha_1 = 60.0\% \)) and \( \tau_2 = 18.1 \text{ ns} \) (\( \alpha_2 = 40.0\% \)). The short lifetime, \( \tau_1 = 0.8 \text{ ns} \), was obtained as a result of quenching of the exciton. In the photon correlation histogram (Figure 4c), the contribution of the center peak at a delay time of 0 ns was much lower than that of the other peaks at delay times of ±100 ns. The second-order correlation function, \( g^{(2)}(0) \), provides information about the emission photon statistics, that is, the probability of single-photon emission increases when \( g^{(2)}(0) \) is close to zero. In addition, the PL decay curve (Figure 4f) was fitted using a three-exponential function, \( I(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) + \alpha_3 \exp(-t/\tau_3) \), with three lifetimes of 0.3 ns (88.1%), 1.1 ns (12.7%), and 6.7 ns (1.9%). Because the lifetime of 0.3 ns was the same as the instrument response function (IRF), the actual lifetime is probably shorter. Shortening of the lifetime indicated that the relaxation process of the NQD was modified by Ag/SiO₂. In the photon correlation histogram (Figure 4g), the contribution of the center peak increased, and the \( g^{(2)}(0) \) value was estimated as 0.09 in Figure 4c, thus indicating that the reference NQD exhibited single-photon emission.

Representative results for the two single NQDs with Ag/SiO₂ are shown in Figure 4e–l. For the single NQD shown in Figure 4e–h, the PL intensity increased compared to that of the reference. The time trace of the PL intensity displayed 480 counts/ms and a reduction of the low-intensity levels (Figure 4e), which has also been observed in previous reports using AgNP and gold nanoparticles (AuNPs) as MSNs. The PL decay curve (Figure 4f) was fitted using a three-exponential function, \( I(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) + \alpha_3 \exp(-t/\tau_3) \), with three lifetimes of 0.3 ns (88.4%), 1.4 ns (12.7%), and 6.7 ns (1.9%). Because the lifetime of 0.3 ns was the same as the instrument response function (IRF), the actual lifetime is probably shorter. Shortening of the lifetime indicated that the relaxation process of the NQD was modified by Ag/SiO₂. In the photon correlation histogram (Figure 4g), the contribution of the center peak increased, and the \( g^{(2)}(0) \) value was estimated as 0.81. This result indicates that the probability of multiphoton emission increased compared to that of the reference, shown in Figure 4c.

For the single NQD shown in Figure 4i–l, the PL intensity decreased to 28 counts/ms with shortening of the PL lifetime. As the background count under this experimental condition was 0.3 counts/ms, the single NQD exhibited a low PL intensity. By fitting the PL decay curve (Figure 4j), three lifetimes were obtained: 0.3 ns (88.1%), 1.1 ns (10.4%), and 4.3 ns (1.4%). From Figure 4k, the \( g^{(2)}(0) \) value was estimated as 0.99, thus indicating that the probability of multiphoton...
emission was increased, similar to that for the single NQD shown in Figure 4g. In Figure 4h, l, no clear change in the PL spectra was observed compared with the reference (Figure 4d). Although the peak wavelengths of the spectra were different from those of the reference, the difference was within the spectral distribution of the individual NQDs. Because of the small shift in the BX and TX emission spectra compared with the SX emission spectrum, distinguishing the multiphoton emission spectrum from the SX emission spectrum at room temperature is difficult. Although we considered the spectral change with respect to the full width at half-maximum, no significant change was observed. The observed increase in the $g^{(2)}(0)$ value was attributed to the change in the PL behavior of the NQD because neither emission nor background
scattering from Ag/SiO₂ was observed in Figure 4h,l. The above emission behavior, that is, a reduction in the blinking and increase in the probability of multiphoton emission with shortening of the lifetime, was identical to our previous results, and the increase in the probability of multiphoton emission was also identical to that noted in prior reports.

The above results are only representative examples obtained from single NQDs with and without Ag/SiO₂ dispersed on a coverslip. As we have reported recently, the direct observation of changes in the emission behavior with the approach of an MNS provides meaningful results, even if the results are obtained from a few individual NQDs. However, in single NQD measurements, such as those shown in the present work, statistical data compiled from all results obtained from a large number of single NQDs was important to elucidate the essential emission behavior because the emission behavior of individual NQDs and NQD–Ag/SiO₂ interactions have broad heterogeneity. For example, in the sample, both aggregated and isolated Ag/SiO₂ were observed, as shown in Figure 3. Thus, the NQD–Ag/SiO₂ interaction strongly depends on each NQD–Ag/SiO₂ pair. In addition, the NQD–Ag/SiO₂ distance was not controlled in the sample. Therefore, we discuss the emission behavior of single NQDs on the basis of the statistical data in the following section.

On the basis of the measurements shown in Figure 4, the correlations between \( g^{(2)}(0) \) and the PL intensity and between \( g^{(2)}(0) \) and the average lifetime detected from single NQDs are shown in Figures 5 and 6, respectively. The values obtained from the single NQDs with Ag/SiO₂ shown in Figure 4 are marked by blue circles in Figures 5b and 6b. Each correlation was built from more than 100 single NQD measurements. The decay curves detected from the reference NQDs were fitted by single- or two-exponential functions, whereas the decay curves of the single NQDs with Ag/SiO₂ were fitted using two- or three-exponential functions. The average lifetime was calculated as follows: \( \alpha_1 \times \tau_1 + \alpha_2 \times \tau_2 + \alpha_3 \times \tau_3 \). In the case of the reference NQDs, the PL intensity and average lifetime were distributed in a range of 80–400 counts/ms and 2–23 ns, respectively (Figures 5a and 6a). Nearly all single NQDs exhibited \( g^{(2)}(0) \) values of less than 0.2, thus indicating that the single NQDs emitted single photons. These results represent the typical emission behavior of the single NQDs and were used as a reference. The distributions of the reference values are indicated by green squares in each correlation.

The single NQDs with Ag/SiO₂ exhibited large distributions of the correlations compared with the reference NQD. Among the single NQDs with Ag/SiO₂ with 5 nm thick shells (Figures 5b and 6b), a large number of single NQDs exhibited higher \( g^{(2)}(0) \) values than those of the reference. The single NQDs with higher \( g^{(2)}(0) \) values exhibited large distributions of PL intensity, in the range of 25–600 counts/ms (Figure 5b). However, single NQDs with a higher intensity than that of the reference (greater than 400 counts/ms) were rare, whereas the number of single NQDs with a lower intensity than that of the reference increased, as confirmed by the histogram of PL intensities shown in Figure 5b. As shown in Figure 6b, the single NQDs with higher \( g^{(2)}(0) \) values exhibited shorter average lifetimes compared to those of the reference, and the average lifetime decreased with increasing \( g^{(2)}(0) \) values. These
changes in emission behavior were caused by the interaction with Ag/SiO$_2$. However, single NQDs with nearly identical $g^{(2)}(0)$ values and average lifetimes to those of the reference were observed and are surrounded by green squares in Figures 5b and 6b. These NQDs probably did not interact with Ag/SiO$_2$ because these data were obtained from samples prepared by just dispersing the NQDs and Ag/SiO$_2$ on the coverslip by spin-coating. The contribution of the NQDs with higher $g^{(2)}(0)$ values and shorter lifetimes decreased with increasing shell thickness. In the case of the single NQDs with Ag/SiO$_2$ with 7 nm thick shells, the contribution of the NQDs with $g^{(2)}(0)$ greater than 0.8 slightly decreased in the $g^{(2)}(0)$ histograms shown in Figures 5c and 6c. The contribution of the high $g^{(2)}(0)$ further decreased with increasing shell thickness, that is, for 15 nm thick shells (Figures 5d and 6d) and 24 nm thick shells (Figures 5e and 6e), and most of the NQDs exhibited the same $g^{(2)}(0)$ and average lifetime as those of the reference for 38 nm thick shells (Figures 5f and 6f). These results clearly indicated that the increase in $g^{(2)}(0)$, that is, the increase in the probability of multiphoton emission, is strongly dependent on the NQD–AgNP distance. We are convinced that the emission behaviors shown here were obtained from single NQDs because of the following reasons: (1) Using the same concentration of an NQD-dispersed solution, most NQDs were isolated in the case of the reference sample (Figures 5a and 6a). (2) In the case of NQDs with Ag/SiO$_2$ with SiO$_2$ shell thicknesses of 24 and 38 nm, most NQDs exhibited the emission behavior of single NQDs, that is, low $g^{(2)}(0)$ values, as shown in Figures 6e,f and 7e,f, using the same concentration of an NQD-dispersed solution. (3) We checked the emission behavior by changing the concentration and measured the emission behavior at quite a low concentration. (4) In Figure 6b, a clear correlation between the average lifetime and $g^{(2)}(0)$ value was observed, that is, an NQD with a lower average lifetime exhibited a higher $g^{(2)}(0)$ value. Actually, it was reported that this type of correlation was observed even in the case of the aggregate of NQDs. However, if the correlation shown in Figure 6b was caused by the aggregate, the correlation should not show distance dependence as shown in Figure 6. Therefore, the correlation was due to the interaction with Ag/SiO$_2$.

Enhancements of the excitation rate and radiative rate can be considered to be part of the mechanism of increase of the PL intensity, whereas the decrease in the PL intensity is caused by enhancement of the nonradiative rate (quenching). Enhancements of the radiative and nonradiative rates result in shortening of the lifetime. Therefore, the observed increase in PL intensity with increasing $g^{(2)}(0)$ and shortening of the lifetime can be explained by the enhancement of the radiative rate or by a combination of enhancement of the excitation rate and nonradiative rate. Similarly, the decrease in PL intensity with increasing $g^{(2)}(0)$ and shortening of the lifetime can be explained by the enhancement of the nonradiative rate. As shown in Figure 2, the LSPR band of the isolated Ag/SiO$_2$ nanoparticles overlaps with the absorption and PL spectra of the NQD, although the spectral overlap between the LSPR and PL bands was smaller than the spectral overlap of the LSPR band with the absorption band, and the LSPR band was generated by 405 nm excitation. Thus, the combination of enhancement of the excitation rate and nonradiative rate is probably a more predominant mechanism of increase of the PL intensity. The AFM image revealed aggregation of some of the Ag/SiO$_2$ nanoparticles (Figure 3). The LSPR band of metallic nanoparticles is known to be red-shifted by interactions between metallic nanoparticles. In our sample, such aggregates should display a red-shifted LSPR band, depending on the condition of the aggregates, that is, the number of Ag/SiO$_2$ particles and the distance between the particles. Thus, for these aggregates, the spectral overlap between the LSPR and PL bands increased, whereas the spectral overlap between the LSPR and absorption bands decreased. This effect was probably responsible for the decrease in PL intensity due to the increase in the enhancement of the nonradiative rate and the decrease in the enhancement of the excitation rate. Unfortunately, our instrumental setup did not allow assignment of the LSPR bands of individual Ag/SiO$_2$ nanoparticles. However, the increase in the $g^{(2)}(0)$ values was attributed to the enhancement of the relaxation process. We discuss the distance-dependent results below to elucidate the mechanism.

Figure 7 shows the enhancement factors of the PL intensity ($I_p/I_{ref}$) (a), and $g^{(2)}(0)$ value ($g^{(2)}(0)_p/g^{(2)}(0)_ref$) (b) depending on the shell thickness. The subscripts “p” and “ref” refer to the NQDs with Ag/SiO$_2$ and reference NQDs, respectively. $I_p$ and $g^{(2)}(0)_p$ were estimated as the average values from the NQDs that exhibited higher $g^{(2)}(0)$ values compared to those of the reference (outside the green square in Figures 5 and 6). $I_{ref}$ and $g^{(2)}(0)_ref$ were estimated as the average (black solid square), minimum (red solid circle), and maximum (blue solid triangle) values.
squares in Figures 5 and 6, to eliminate the NQDs that did not interact with Ag/SiO₂. The following three combinations of values of \( I_{\text{ref}} \) and \( g^{(2)}(0)_{\text{ref}} \) were used: first, the average of all values, \( I_{\text{ref ave}} = 216 \text{ counts/ms, } g^{(2)}(0)_{\text{ref ave}} = 0.095 \); second, the minimum value, \( I_{\text{ref min}} = 77 \text{ counts/ms, } g^{(2)}(0)_{\text{ref min}} = 0.052 \); and third, the maximum value, \( I_{\text{ref max}} = 400 \text{ counts/ms, } g^{(2)}(0)_{\text{ref max}} = 0.206 \). Using these three combinations, the enhancement factors were estimated. The values of the enhancement factors for PL intensity shown in Figure 7a increased with decreasing shell thickness, and the enhancement factor reached the maximum value at a shell thickness of 7 nm for each of the three combinations of values. Then, the value decreased for the particles with 5 nm thick shells. In the case of \( g^{(2)}(0) \), the enhancement factor increased with decreasing shell thickness (Figure 7b). This result indicates that the probability of multiphoton emission is enhanced with decreasing distance.

To consider the enhancement mechanism, the dependence of the relative change in the enhancement factor of PL intensity on distance is important. Novotny et al. have investigated the distance-dependent PL intensity of a single organic molecule using a AuNP attached to the end of a pointed optical fiber and have also reported the distance-dependent enhancement factor of PL intensity, which was similar to our result.⁵⁸,⁵⁹ Using theoretical analysis, Novotny et al. clearly demonstrated that the change in the PL intensity as a function of distance can be interpreted as arising from a combination of enhancement of the excitation rate by the LSP of the AuNP and quenching of the PL by resonance energy transfer from the single molecule to the AuNP.⁵⁹ These reports support the interpretation of our results primarily by the same mechanism, that is, a combination of enhancement of the excitation rate and quenching. Both the enhancement of the excitation rate and quenching increase with decreasing distance. As a result, enhancement of the PL intensity reaches a maximal value and then decreases at shorter distances. Enhancement of the radiative rate is a possible mechanism for the increase in the PL intensity. An increase in the PL intensity due to enhancement of the radiative rate has been observed previously.⁶⁰ However, in the case of enhancement of the radiative rate, the PL intensity should increase with decreasing distance, even at 5 nm. Therefore, our results in this work can be interpreted as arising from a combination of enhancement of the excitation rate and nonradiative rate. Because of this enhancement of the nonradiative rate, that is, the decrease in \( \Phi_{\text{SR}} \) by Ag/SiO₂ as the proposed mechanism, the probability of multiphoton emission increased. Because the efficiency of quenching increases with decreasing distance, the \( g^{(2)}(0) \) values increased with decreasing distance.

To confirm the influence of excitation rate enhancement by Ag/SiO₂ and, in particular, to obtain distance-dependent electric field enhancement, a numerical simulation of Ag/SiO₂ particles with different shell thicknesses was conducted (details in the Supporting Information (SI)).⁶⁰,⁶¹ The diameter of the AgNP was fixed as 54 nm, which was estimated as an average value from the TEM observation, and the shell thickness was varied to be 5, 7, 15, 24, and 38 nm. Figure 8a shows the distribution of the electric field enhancement of a Ag/SiO₂ particle with a 15 nm thick shell, as an example, obtained by the simulation for illumination at a wavelength similar to that of the excitation laser (405 nm) with the z-direction of the electric field. Electric field enhancement was defined as \( I = \frac{|E|^2}{|E_0|^2} \), where \( E \) and \( E_0 \) are the electric field intensity on Ag/SiO₂ and the light source, respectively. Field enhancement can be observed at the surface of the SiO₂ shell. Figure 8b shows the electric field enhancement of 405 nm light at the surface of an SiO₂ shell with different thicknesses. The field enhancement decreased with increasing shell thickness, and the values at 24 and 34 nm were quite low (7.4 at 24 nm and 0.2 at 34 nm), thus indicating that field enhancement cannot be expected at 34 nm. This result is in good agreement with the experimental results shown in Figures 5 and 7, in which the PL intensity was not modified for the shell thickness of 38 nm.

## CONCLUSIONS

In this work, we observed modification of the emission behavior depending on the distance between NQDs and AgNPs using Ag/SiO₂ nanoparticles with different SiO₂ thicknesses to elucidate the mechanism of modification of the emission photon statistics. To eliminate the heterogeneity of each single NQD–Ag/SiO₂, statistical results compiled from more than 100 single NQD measurements were used. The probability of multiphoton emission increased with decreasing lifetime as the distance decreased. In addition, the PL intensity increased and then decreased with decreasing distance. We determined that the modification of the emission behavior was primarily caused by the combination of excitation rate enhancement and nonradiative rate enhancement (quenching). Thus, the PL intensity was increased because of the excitation rate enhancement induced by the LSP of the AgNPs and the probability of multiphoton emission was increased by the quenching of SX induced by the resonance energy transfer from the NQD to the AgNP. Numerical calculation of the Ag/SiO₂ supported the excitation rate enhancement. In fact, the PL
intensity did not increase, as expected from the numerical calculation, because of the quenching of SX.

As results, the mechanism of modification of the emission behavior in this work was similar to that in the previous report, in which a silver-coated AFM tip was used as the plasmonic nanostructure. Although the obtained results were similar, the present results are important to confirm the generality of the mechanism because we could obtain similar results using different plasmonic nanostructures. The present results also support the validity of the reported mechanism and indicate that the emission behavior of NQDs can be modified using plasmonic nanostructures by controlling the enhancement effects of the plasmonic nanostructure and the distance between the NQDs and nanostructure.

**EXPERIMENTAL SECTION**

Monodisperse and well-defined AgNPs were prepared by the reduction of AgCl colloids with ascorbic acid. Details are provided in the SI. The prepared spherical AgNPs were coated with a dielectric SiO$_2$ shell (Ag/SiO$_2$) of five different thicknesses by a modified Stöber method (details in the SI). The SiO$_2$ shell acts as a rigid, chemically inert, and electrically insulating spacer between the NQDs and AgNPs. The NQD–Ag/SiO$_2$ sample was prepared by first spin-coating an Ag/SiO$_2$-dispersed ethanol solution onto a clean coverslip and then spin-coating a toluene solution of commercially available CdSe/ZnS core/shell NQDs (PL maximum wavelength: 605 nm; Invitrogen) onto the coverslip. To control the distance between the NQD and AgNP, adsorption and binding of the NQD onto Ag/SiO$_2$ using chemistry are favored methods. However, because these procedures damage the NQD surface and induce a low PL intensity, the samples in the present work were prepared by a simple spin-coating technique. The distance between the NQD and Ag/SiO$_2$ was not controlled in the sample. However, the minimum distance should be identical to the shell thickness. A reference sample composed of only isolated NQDs was prepared by spin-coating the NQD solution onto a clean coverslip. AFM topography images of the samples were obtained using an AFM (JPK Instruments, NanoWizard II) mounted on the microscope stage.

The emission behaviors of the isolated NQDs were measured with a Hanbury-Brown and Twiss type photon correlation setup in combination with picosecond-pulsed laser excitation at 405 nm (10.0 MHz, 90 ps full width at half-maximum) under a sample-scanning confocal microscope. Briefly, the excitation laser was focused on the single NQD by an objective lens (NA 1.4; Olympus) and the photons emitted from the NQD were collected by a same objective lens and passed through a filter (LP02-514RU; Semrock). Subsequently, half of the photons were detected with a spectrometer (SpectraPro2358; Acton Research Corporation) with a cooled CCD camera (PIXIS400B Princeton Instruments). The remaining half of the photons passed through a band-pass filter (FF01-607/36; Semrock) and were detected by two avalanche photodiode (APD) single-photon-counting modules (SPCM-AQR-14; PerkinElmer). A short-pass filter (ASAH1 SPECTRA, SIX780) was put in front of one of two APDs to cut the near-infrared photons emitted from the APD accompanying the detection of the PL photons. The signals from the two APDs were connected via a router to a time-correlated single-photon counting board (SPC-630; Becker & Hickl) for Hanbury-Brown and Twiss type photon correlation and lifetime measurements. By analyzing the obtained data with software designed in our laboratory, time traces of PL intensity, PL decay curves, and photon correlation histograms were simultaneously obtained for the single NQDs. The time-resolution of the lifetime measurement (IRF) was approximately 0.3 ns. All measurements were performed at room temperature under ambient conditions.

**ASSOCIATED CONTENT**

® Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00520.

Fabrication of SiO$_2$-coated silver nanoparticles (Ag/SiO$_2$); numerical simulation of the Ag/SiO$_2$ (PDF)

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Notes

The authors declare no competing financial interest.

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