

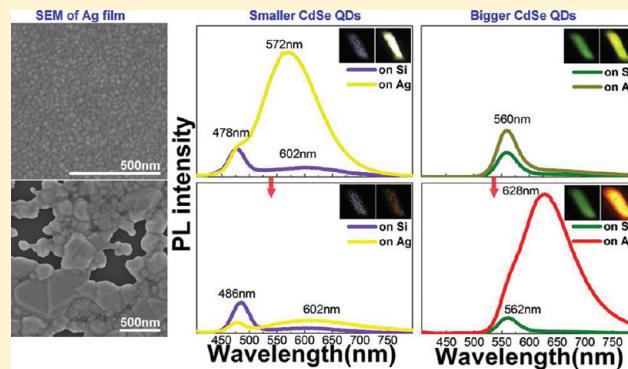
Plasmon-Enhanced Surface-State Emission of CdSe Quantum Dots and Its Application to Microscale Luminescence Patterns

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S Supporting Information

ABSTRACT: In this paper, we report distinct enhancement of surface-state emissions (SSEs) of colloidal CdSe quantum dots (QDs) via coupling to localized plasmons (LPs) in Ag nanostructures. The roles of oleic acid (OA) ligand on QDs in the formation of Ag nanostructures and in the intense enhancement of SSEs of CdSe QDs are explored. We find that OA ligand on CdSe QDs plays a critical role in modifying the morphology of the contacted Ag, which consequently impacts the coupling of QD emitters with LPs in Ag. A systematic study of size effect of QDs on coupling of SSEs with LPs shows that as-deposited small Ag particles favorably enhance the SSEs of small-size CdSe QDs. The OA ligand on QDs yields better Ag crystallinity and clear corners during the annealing process; therefore, it promotes reshaping of small Ag particles into larger ones, favorable to enhance the SSEs of large-size CdSe QDs. The annealed QDs/Ag hybrid structures are more stable than the unannealed ones due to the loss of the OA ligand in the heating process. The selective coupling of QD emitters with LPs in Ag nanostructures allows feasible realization of microscale fluorescent color patterns. The approach of OA-assisted modification of plasmonic properties of Ag nanostructures provides a new route to synthesizing bright luminescence materials and devices that use colloidal QDs.



1. INTRODUCTION

Colloidal semiconductor quantum dots (QDs) as fluorescent materials have attracted much attention in optoelectronics, biotechnology, and other basic researches because of their small sizes and high quantum yields. The large surface-to-volume ratio of colloidal QDs makes the surface states greatly impact the optoelectronic properties. To improve quantum yields of colloidal QDs, much effort has been made to suppress the surface states.¹ On the contrary, studies showed the surface states of colloidal QDs could be potentially applied in white light emitting diodes (LEDs) because their radiative surface state emissions (SSEs) are right in the visible light region and display broad emission bands.^{2–6} Colloidal CdSe QDs have been widely used as bright fluorescent emitters and may become an alternative candidate for the next generation of white LEDs. CdSe QDs generally exhibit two main emission peaks in the visible light region: band edge emission and SSE. Different fluorescent colors can be realized from one group of such QDs through modulating both the wavelength of emission and the intensity ratio of the two peaks, as the fluorescent colors of the emitters are determined by superposition of the two peaks. The band edge emission of CdSe QDs could be tuned via controlling the size and composition in the synthesis stage, while the SSEs at longer wavelength can be tuned by modifying the solution environment around QDs.^{5–8} D. Baker

and P. Kamat tuned SSE peaks and the intensity ratio of the band edge: SSE of CdSe QDs via altering 3-mecaptopropionic acid concentration to obtain different colors.⁶ However, the above chemical method is only able to change the fluorescent color of a whole bottle of colloidal QDs rather than selectively changing colors in designated area. Hu et al. realized physical methods of tuning the fluorescent colors of colloidal CdSe QDs by postsynthesis annealing and photoactivation (PA).⁷ Our study shows that the colors made by annealing and PA are clearly not rich but in low hue contrast. The reason is that the ultraviolet (UV) irradiation leads to a similar luminescent intensity change for both the band edge emission and SSE. To highlight hue contrast of the QDs fluorescent colors, one should find an effective way to adjust luminescent intensity ratios of the two peaks. Plasmon-exciton coupling in metal–semiconductor nanostructures could effectively enhance fluorescent intensity of emitters because these hybrid systems have novel features beyond single components.⁹ Localized plasmons (LPs) in metal–semiconductor nanostructures could influence the vicinal semiconductor emitters.^{10,11} In this paper, we present distinct enhancement of the SSEs of CdSe QDs via

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coupling the QD emitters with LPs excited on silver (Ag) nanostructures. It is found that the oleic acid (OA) ligand on the QDs plays a critical role in the intense luminescence enhancement of the CdSe QDs/Ag nanostructures, and annealing of the QDs/Ag hybrid systems greatly affects the features of SSEs. OA on the CdSe QDs modifies the morphology of Ag films and leads to the formation of metal crystals. With this new approach of OA reshaping Ag particles and consequent realization of intense luminescence enhancement, the luminescence colors of CdSe QD layers could be changed selectively, and microscale luminescence color patterns have been demonstrated.

2. EXPERIMENTAL SECTION

2.1. Materials. Cadmium oxide (CdO, 99.95%), selenium powder (Se, 99.999%), oleic acid (OA, 90%), 1-octadecane (ODE, 90%), tri-*n*-octyl phosphine (TOP, 90%), and polymethylmethacrylate (PMMA, average MW 350 000) powders were purchased from Alfa Aesar. Toluene, ethanol, and acetone were used as received.

2.2. Synthesis and Purification of CdSe QDs Capped with Oleic Acid. Three groups of OA-capped CdSe QDs of different sizes were used in this investigation. These groups are named #1QDs, #2QDs, and #3QDs with sizes from small to large. #1QDs have the shortest wavelength of band edge emission and were typically synthesized as follows: 0.2566 g (2 mmol) of CdO powder, 4 mL of OA, and 30 mL of ODE were loaded in a 50 mL three-neck flask. The mixture was heated to 300 °C under an argon atmosphere until a transparent Cd precursor was formed. Then the heater was removed to cool down the Cd precursor. When the temperature of the Cd precursor dropped to 170 °C, 2 mL of Se precursor stock solution TOP-Se (Se powders dissolved in TOP with 2 M concentration) was swiftly injected into the flask. Subsequently, the flask was cooled in an ice bath. The finished CdSe QD dispersed in ODE was yellowish. #2QDs and #3QDs have longer emission wavelengths and were synthesized similarly: the injection temperature for #2QDs and #3QDs was 240 and 250 °C, respectively, with the flask cooled naturally for #3QDs.

The synthesized QD solution was mixed with the same volume of hexane/methanol mixture to extract the remaining precursors in ODE phase. The ODE phase was then mixed with a double volume of ethanol and centrifuged at 4000 rpm. Finally, the precipitate was redispersed in toluene.

2.3. Preparations of Samples and Characterization. Silicon wafers were successively cleaned in acetone, ethanol, and deionized water by sonication. Next, half of a Si wafer was coated with a 60 nm Ag film by thermal evaporation. The thickness of Ag films was controlled by a crystal monitor. The CdSe QD/toluene solution was then spin-coated on the Si wafer. Each wafer was cleaved into two pieces along the direction perpendicular to the boundary between the areas with Ag and without Ag. One cleaved piece was kept as a reference sample, while the other was annealed in air at 150 °C in an oven for 30 min. Figure 1 illustrates the preparation steps of QDs/Ag/Si and QDs/Si nanostructures.

The photoluminescence (PL) spectra of both the areas with and without Ag were measured. Steady PL and lifetime measurements were made by an Edinburgh FLS920 system with the excitation line of 325 nm from a xenon lamp (for PL) and a hydrogen lamp (for lifetime).

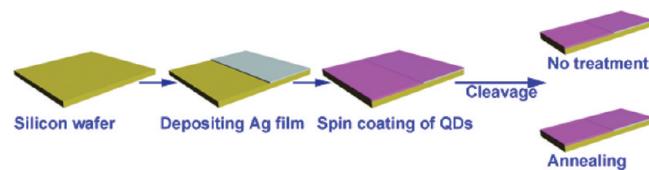


Figure 1. Schematic diagrams for the fabrication of the QDs/Ag/Si and QDs/Si nanostructures.

3. RESULTS AND DISCUSSION

3.1. Size Effect of QDs on Coupling with Plasmons in Ag Nanostructures. The three groups of OA-capped CdSe QDs (#1, #2, and #3) were characterized by steady PL. The PL spectra in Figure 2 show that band edge emissions are centered

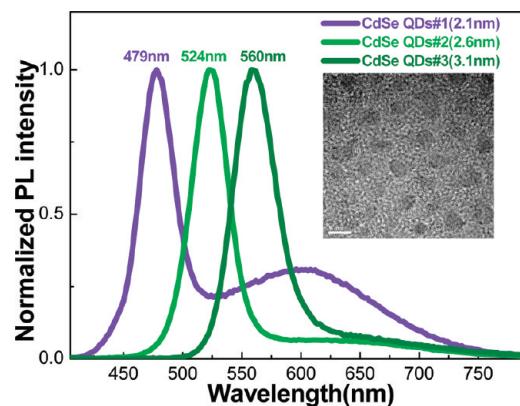


Figure 2. PL spectra of the three groups of CdSe QDs. The average sizes of the QDs are 2.1, 2.6, and 3.1 nm for #1, #2, and #3 QDs, respectively. A transmission electron microscope (TEM) image of the #3QDs is given in the inset.

at 479, 524, and 560 nm, respectively. The average sizes in diameter of QDs are calculated from the band edge emissions.¹² The PL spectrum of the smallest QDs (#1) shows the most intense SSE spanning nearly the whole visible band (centered at ~600 nm) as the smallest QDs have the largest surface/volume ratio, whereas the other two groups have relatively weak SSEs located at 602 and 646 nm, respectively. Evidently, a larger surface/volume ratio related to smaller QDs presents a higher density of surface states that lead to an enhanced SSE.^{13,14}

Figure 3 shows the PL spectra for the QD hybrid samples in which the QD layers (~50 nm) were spin coated only once. The left column of Figure 3 shows the PL spectra of the three groups of QDs on the Si area and Ag/Si area without annealing treatment, while the right column shows the PL spectra of the annealed ones. Accordingly, Figure 4 shows the PL spectra of the hybrid samples with thicker QD layers (~100 nm) fabricated by three-time spin coating. As demonstrated in Figure 3, the emissions from the area of QDs/Ag/Si are remarkably different from those from the QDs/Si area for all three groups of QDs. In Figures 3a and 3c, the SSEs of both #1 and #2 QDs on the Ag/Si area display distinct intensity enhancement compared to those of the QD/Si area (more than 10 times of the peak heights), whereas the intensities of band edge emissions rarely change. For #1QDs, the peak of the enhanced SSE from the QD/Ag/Si area locates at 572 nm that has an evident blue shift in reference to the SSE from the QD/Si area (~600 nm). The SSE peak intensity is about 4 times

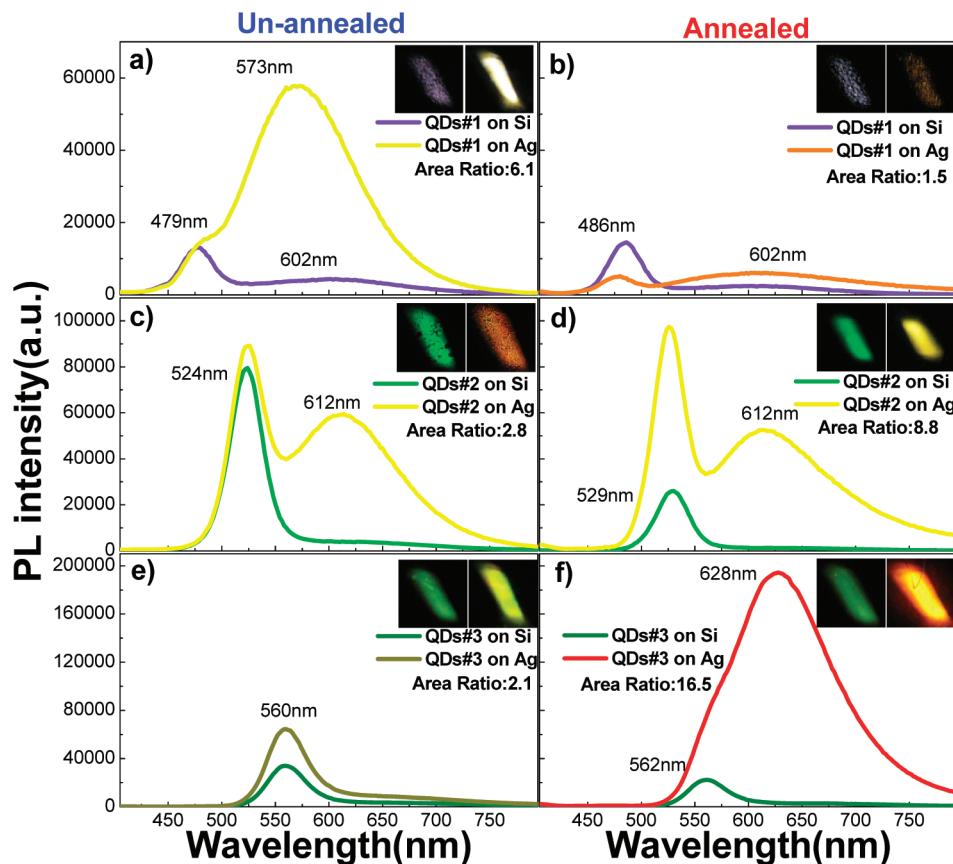


Figure 3. PL spectra of the unannealed (left) and annealed (right) CdSe QD hybrid samples. Each row corresponds to one of the three groups of QDs (#1, #2, and #3 from top to bottom).

higher than the band edge emission peak intensity such that the SSE dominates the luminescence color of the QD/Ag/Si area (yellow). For #2QDs, the enhanced SSE peak locates at 612 nm as shown in Figure 3c. In Figure 3e, the PL peak intensity of the QD/Ag/Si area is twice that of the QD/Si area, while SSE changes little.

The band edge emission of the #1QD/Si structure shows a slight red-shift from 479 to 486 nm after annealing, which is ascribed to the coupling of the adjacent QDs resulting from annealing.⁷ Red shifts of 8 nm (#1QDs), 5 nm (#2QDs), and 2 nm (#3QDs) were observed in the annealed samples. The decrease of a red shift with increasing size indicates that smaller QDs have stronger coupling between adjacent QDs after annealing. This could be explained in terms of chemical potential at the synthesis stage because the QDs with smaller sizes have higher surface energy so that they have stronger coupling in the annealing process. For #1QDs, after annealing treatment the emissions on the QD/Ag/Si area are clearly quenched in comparison to the emissions of the QD/Si area as shown in Figure 3b. Figure 3d shows that the emissions of the #2QD/Ag/Si area change seldom after annealing. A spectrum area ratio (defined as the ratio of the integrated PL intensity of QD/Ag/Si to that of QD/Si) changes from 2.8 to 8.8 after annealing due to a quench of band edge emission from the QD/Si area. Figure 3f shows the most intensely enhanced SSE from the #3QD/Ag/Si area after annealing, and the spectrum area ratio reaches 16.5. As seen in Figure 3, there is an apparent discipline from top to bottom for the SSEs of all the QD/Ag/Si samples: an opposite intensity variation trend of the SSE intensities before (left) and after (right) annealing, i.e., before

annealing SSE intensity decreases as QD size increases, whereas the trend reverses after annealing. It indicates annealing can enhance the SSE of large-size QDs (#3) more easily than that of the small-size ones.

3.2. Thickness of QD Layers on Coupling with Ag Nanostructures. Figure 4 shows the PL spectra of the samples with thick QDs layers which display PL spectra similar to the thin ones shown in Figure 3. For the unannealed thick samples (left column in Figure 4), all three groups of QD/Ag/Si samples have evidently enhanced SSEs compared to those of QD/Si. Figure 4c shows that the SSE of the #2QD/Ag/Si is enhanced more intensely than that shown in Figure 3c; i.e., the intensity of SSE of #2QDs is much higher than that of band edge emission. Here the ratio of the SSE intensity of QDs/Ag/Si to the band edge emission intensity of QDs/Si is defined as the relative intensity of SSEs, called peak ratio for short hereinafter.

The peak ratios and spectra area ratios (called area ratios for short) are plotted in Figure 5. Figure 5a corresponds to Figure 3, while Figure 5b corresponds to Figure 4. For the two sets of samples, similar ratio changes with size increase of QDs are observed in Figure 5, i.e., the monotonic decrease of the peak ratio and area ratio for the unannealed samples and the monotonic increase of the peak ratio and area ratio for the annealed samples. The coherence of the ratios within the two sets of samples is due to the fact that the area ratio is dominated by the broad SSE rather than the band edge emission. It is seen that the SSE of the unannealed small-size QDs is enhanced more notably, but annealing treatment reverses this tendency (the purple line and blue line in Figure 5 have opposite trends).

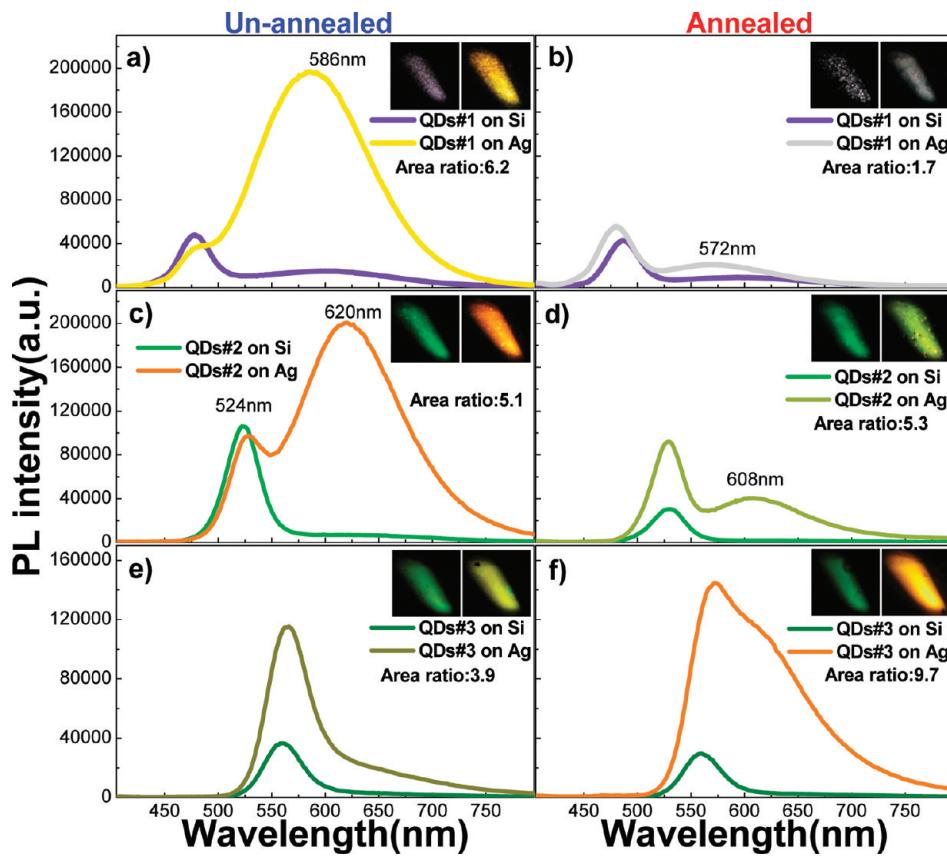


Figure 4. PL spectra of the unannealed (left) and annealed (right) thick CdSe QD hybrid samples that were spin coated three times.

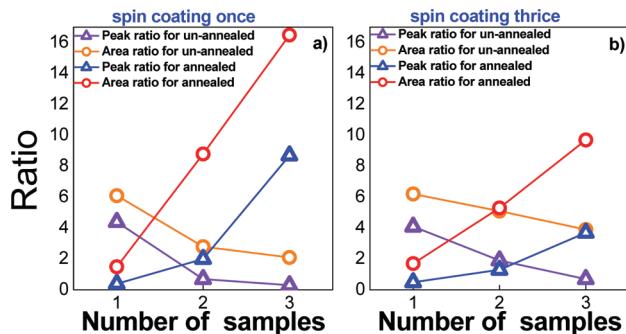


Figure 5. Peak ratios and area ratios obtained from thin QD layer samples shown in Figure 3 and thick QD layer samples shown in Figure 4. The annealed thin QD layer samples demonstrate the higher peak ratios and area ratios than those of thick ones.

Comparison of Figure 5a with 5b indicates that the thickness of QD layers influences the enhancement strength of SSEs for both unannealed and annealed samples. Greater intensity enhancements of SSEs are observed in Figures 4c and 4e than that in Figures 3c and 3e. However, after annealing, the enhancements of SSEs of QD/Ag/Si shown in Figure 4d and 4f are smaller than those shown in Figure 3d and 3f. This indicates that an as-deposited thick QD layer avails to the coupling of SSE with Ag, but after annealing the SSE of a thin QD layer has relatively higher enhancement effect than the thick one.

To analyze the underlying mechanisms of the intense enhancement of SSE by annealing of QD/Ag/Si, #3QD was used for further study because #3QD/Ag/Si shows the most significant enhancement of SSE after annealing within the three groups of QDs. #3QD/toluene solution was directly dropped

on a piece of Ag-coated silicon wafer, and then the piece was annealed. The digital photographs were taken before and after annealing under visible light and 405 nm purple light illumination, respectively. Figures 6a and 6c show photographs under indoor light illumination, while Figures 6b and 6d are ones under purple light illumination. It is clearly seen from Figures 6b and 6d that after annealing the luminescence color of the QDs changes from green to red, and the color of the thin part is redder and brighter than that of the thick part. This phenomenon is consistent with the results of PL measurements shown in Figure 5: after annealing the thin #3QD layer samples have more intense SSE enhancement than the thick ones.

3.3. Oleic Acid Role in the Formation of Ag Nanostructures and Intense SSE Enhancement of QDs. It is known that annealing decreases the density of ligand around QDs, quenches the light emission of QDs, and causes a red shift of QD emission peaks.⁷ We find here that annealing of the QD/Ag/Si hybrid structures clearly changes the surface morphology of the underneath Ag films and the contact between QDs and Ag. The possible variation of both QDs and Ag layers by annealing is illustrated in Figure 7a. Figures 7b~7d show the scanning electron microscope (SEM) images of the Ag films in three different states. An as-deposited Ag film shown in Figure 7b is composed of a myriad of dense Ag particles with sizes of ~50 nm. The change of Ag surface morphology caused by annealing of the QD/Ag/Si hybrid structures can be revealed by removal of the QD layer using toluene or chloroform. As shown in Figure 7c, after annealing the dense Ag particles became bigger (>100 nm), and some of them display crystal facets and clear corners. X-ray diffraction (XRD) characterization observed a significant increase of

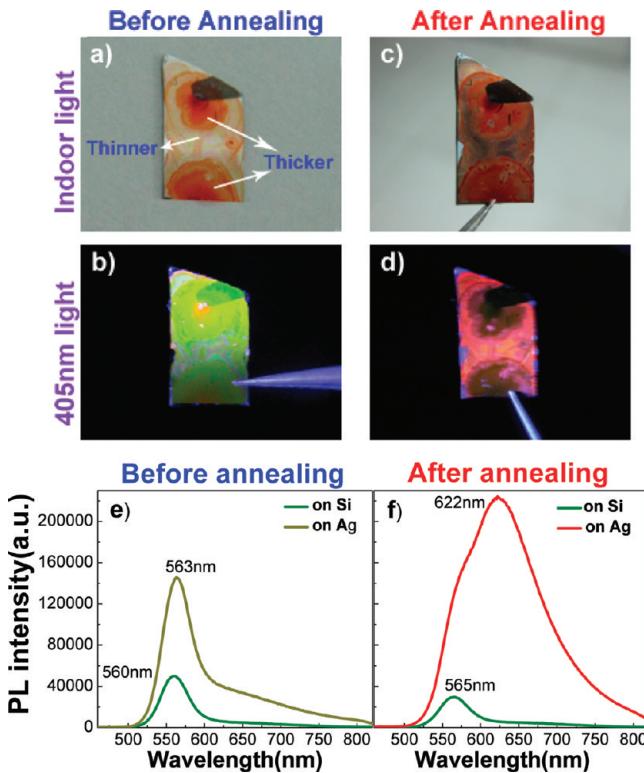


Figure 6. Digital photographs of the ununiformly distributed #3QD/Ag/Si before and after annealing under indoor light (a, c) and 405 nm purple light (b, d) illumination and comparison of the PL spectra of the sample before and after annealing (e, f). The SSE intensity of the annealed QD/Ag/Si is hugely enhanced.

diffraction intensity of the Ag(111) peak after annealing Ag films in OA ambient (Supporting Information). However, annealing a bare Ag/Si sample in air leads to the well-known island morphology shown in Figure 7d, i.e., water-drop-like individual Ag islands with smooth boundaries, called the dewetting phenomenon.¹⁵ The dewetting caused by large-scale diffusion of Ag atoms on substrate surfaces has been well studied.^{15–19} The different dewetting phenomenon observed in the annealed QD/Ag/Si in reference to the Ag/Si annealed in air is ascribed to the influence by a second material (OA capped QDs) on the Ag surface; i.e., the placement of a QD layer on Ag inevitably alters the surface diffusion process. It appears that the QD layer inhibits the dewetting phenomenon while allowing grain growth. The realized different Ag morphology possibly changes the interaction of QD emitters with LPs in Ag nanostructures.

The evident change of Ag surface morphology caused by annealing of QD/Ag/Si and intense SSE enhancement of the annealed QD/Ag/Si hybrid structures indicates that the modification of Ag films in the annealing process may play a critical role in the enhancement of SSE of QDs. To verify this hypothesis, we did the following experiments: a #3QD layer was coated on a transparent quartz chip and annealed at 150 °C for 30 min. Subsequently, a Ag film was deposited on the #3QDs layer. Figure 8a shows the schematic diagram of the process in which the emissions were measured from the quartz substrate side. The measured PL in Figure 8b illustrates that there is no evident enhancement of the SSE of the annealed #3QDs layer on as-deposited Ag film. Therefore, we can conclude that the modification of the Ag films in the annealing

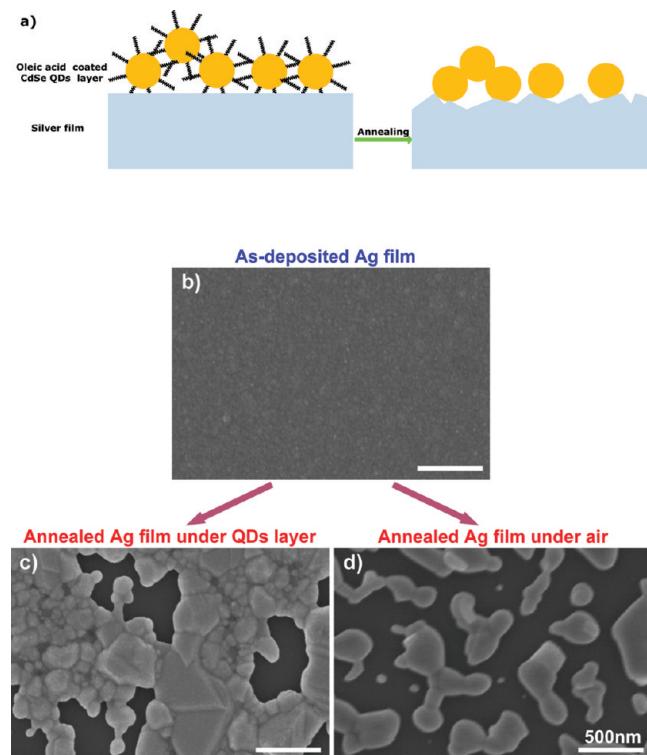


Figure 7. (a) Schematic diagram of the changes of a QD layer and the underneath Ag film by annealing. (b) SEM image of the surface of an as-deposited Ag/Si film. (c) SEM image of the surface of Ag after annealing of #3QDs/Ag/Si. (d) SEM image of the surface of bare Ag/Si after annealing in air.

of QD/Ag/Si hybrid structures is a key factor for the enhancement of SSEs of CdSe QDs.

The significant difference in morphologies between the annealed QD/Ag/Si and Ag/Si structures (Figure 7) and consequently the much variation in enhancements of SSEs (Figures 3f and 8b) indicate that the existence of a QD layer on Ag in the annealing process is a key factor to cause these great changes. It is known that the main components in the QD layer are OA-capped CdSe QDs with a small fraction of residual toluene. The residual toluene on the Ag surface volatilizes quickly at room temperature and should be excluded as a modifier of Ag. On the other hand, OA as a surfactant or etchant could affect the morphology of nanomaterials.^{20–22} Thus, we presume that the OA ligand on CdSe QDs modifies the Ag films in the annealing. To verify this hypothesis, we performed the following test: a piece of Ag/Si samples was annealed in OA at 150 °C for 30 min and was then cleaned with toluene to remove the residual OA on the surface of Ag. The morphology of the Ag film was inspected by both SEM (Figures 9a and b) and a digital camera (Figures 9c and d). Afterward, the modified Ag film was coated with a #3QD layer for PL characterization as plotted in Figure 9e.

The SEM images shown in Figures 9a and 9b demonstrate that the annealed OA–Ag/Si surface is remarkably different from the unannealed sample. Interestingly, the morphology of the annealed Ag film in Figure 9b is very similar to that in Figure 7c: the sizes of Ag particles become larger, and their shapes are irregular. Here we can picture the morphology evolution of Ag films by annealing with OA: as temperature increased, a myriad of tiny Ag particles (Figure 9a) began to merge by diffusion of Ag atoms, while the OA etchant

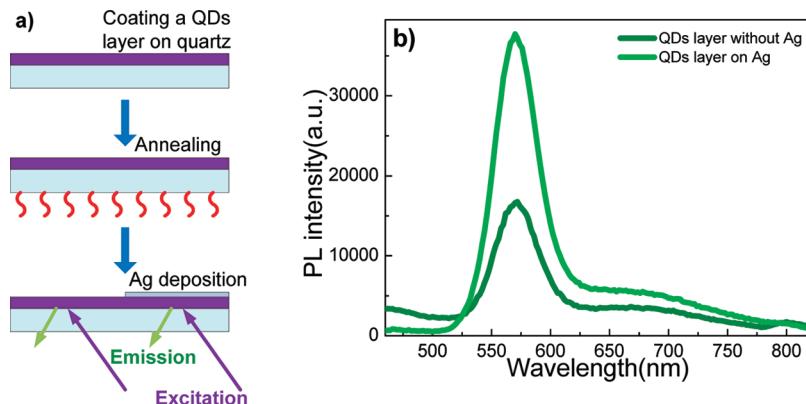


Figure 8. (a) Schematic diagram of the preparation for a Ag/#3QD/Si hybrid structure. (b) Comparison of PL spectra measured from the Ag/#3QD/Si area and #3QD/Si area.

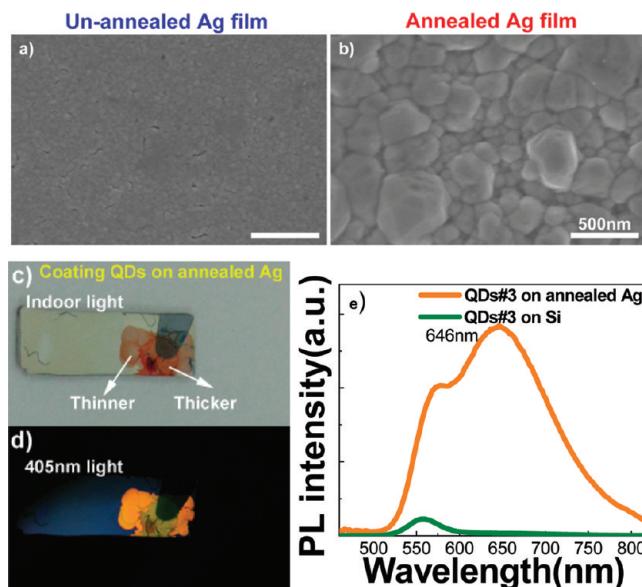


Figure 9. (a, b) SEM images of the Ag films without annealing and after annealing with OA. (c, d) Digital photographs of the Ag film coated with a #3QD layer under visible light and 405 nm purple light. (e) Comparison of PL spectra of #3QD layers on Si and on the annealed Ag/Si film.

interacted with the surface of Ag by selective etching, which led to the formation of large Ag particles with irregular shapes and improved crystallinity.

As observed in Figure 9d, the #3QD on the annealed OA–Ag/Si structure emits primarily orange light in a thickness-dependent manner; i.e., the thick part of the #3QD layer emits green-yellow light rather than orange light from the thin part (see Figures 9c and 9d). The brighter orange color of the thin part also indicates that the SSE of a thin QD layer is enhanced more intensely than that of a thick QD layer. Therefore, we conclude that the OA ligand on CdSe QDs plays a critical role in modifying the Ag morphology during annealing and consequently impacts the coupling of QD emitters with LPs in Ag nanostructures as observed in Figures 3f and 4f. Further, OA as a sort of ligand on CdSe QDs provides rich surface states and a broad radiative SSE, which is favorable to the coupling of SSE with LPs in Ag nanostructures.

The assumption that the OA ligand on CdSe QDs as an etchant modifies the Ag films is further confirmed by the

observations of morphology change and corresponding PL spectra of the #3QD/Ag/Si hybrid structures at different storage periods. The #3QD/Ag/Si samples were stored at room temperature. As shown in Figure 10, after 6 months

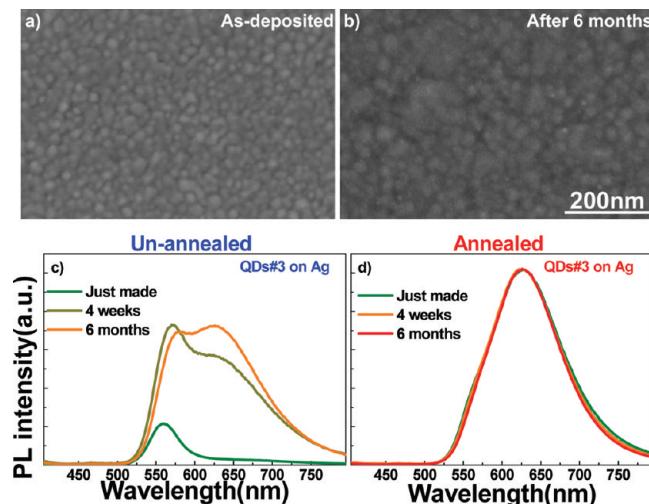


Figure 10. SEM images of the Ag films covered with a #3QD layer: as-deposited (a); after 6 months (b); and PL spectra measured at different storage periods for an unannealed #3QD/Ag/Si sample (c) and an annealed #3QDs/Ag/Si sample (d).

neighboring grains of Ag merged, and the surface became blurred in comparison to the as-deposited one. Consequently, PL spectra of the unannealed #3QD/Ag/Si sample also changed evidently with time lapse. However, the PL spectra measured at three different stages for the annealed sample (Figure 10d) rarely changed because OA evaporated during the annealing process. These results verified that OA on QDs modifies Ag films by anisotropic etching even at room temperature.

3.4. Coupling Mechanism of LPs in Ag Nanostructures with QD Emitters and Intense Enhancement of SSE. The observation of intense enhancement of SSEs in Figure 3 can be explained by the resonant coupling of CdSe QDs with LPs in Ag nanostructures. Here, the resonance between surface states of CdSe QDs and the LPs in Ag nanostructures possibly enhances the radiative decay rates of SSEs. As concluded in Section 3.3, OA modifies the Ag films mainly through selectively etching the Ag surface and forming irregular Ag

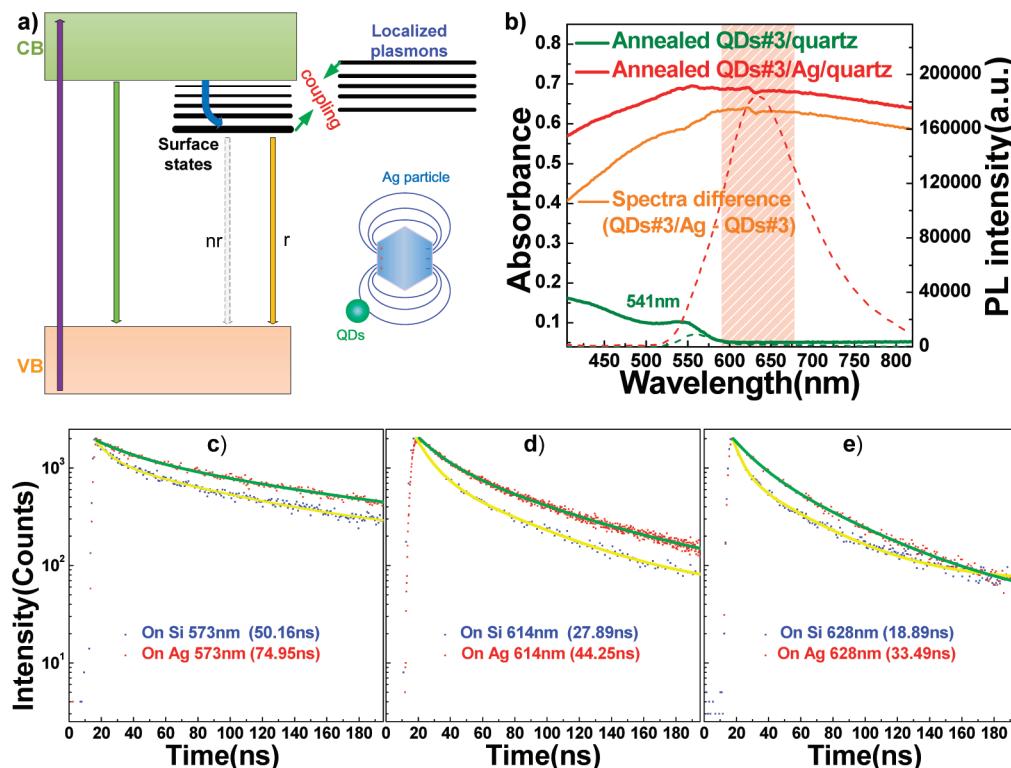


Figure 11. (a) Jablonsky diagram of the CdSe QDs with surface states and the energy levels of LPs in Ag nanostructures. (b) The absorption spectra (bold real lines) and PL intensity spectra (dotted lines) of the annealed samples. The difference spectrum ($\text{QD}\#3/\text{Ag}$ minus QDs spectra) is also plotted out. (c), (d), and (e) PL decay spectra of the enhanced SSEs on Ag for the three groups corresponding to Figure 3a, d, and f, respectively.

nanostructures with clear corners. It is known that local electric field, which influences plasmonic coupling, is much greater around corners than that at other places.^{23,24} Therefore the interaction between the QD emitters and LPs is greatly modulated through these intensive local fields in the Ag nanostructures. XRD (Supporting Information) shows that the Ag films annealed in OA have better crystallinity favorable for the #3QD SSE enhancement. Figure 11a depicts the resonance between the emissions of QDs and those of LPs in the Ag nanostructures. Surface states on CdSe QDs are usually thought to be an essential path for nonradiative relaxation.¹ As illustrated in Figure 11a, large quantities of conduction-band electrons relax to the valence band via nonradiative decay routes related to the surface states, thus we can only observe weak SSEs (through radiative decay routes) from the as-synthesized QDs as shown in Figure 1. LP coupling greatly intensifies the radiative decay rate related to surface states: by fast extracting the occupied surface states to the valence band, LP coupling induces fast conduction-band electron transfer to the surface states, which leads to the evident enhancement of SSEs. The intensely enhanced SSEs observed in the QD/Ag/Si hybrid structures are similar to that of the acceptors in resonance energy transfer (RET) systems.²⁵

Measurement of absorption spectra for the #3QD/Ag hybrid structures reveals the resonance (or correlation) of the plasmon frequencies with the light frequencies corresponding to the enhanced SSEs. To measure the extinction spectra of the QD/Ag/Si samples, we deposited thin Ag films (15 nm) on transparent quartz substrates. Figure 11b shows the absorption spectra (bold solid lines) and PL spectra (dotted lines) of the annealed #3QD/Ag/quartz and #3QD/quartz samples. A difference spectrum (the intensity of absorption spectrum for

QD#3/Ag/quartz minus that for QD/quartz) is also plotted in a thin solid line. The difference spectrum reflects, to some extent, the extinction coefficient of the Ag film by revealing the interaction between QDs and Ag. The annealing process changes the extinction spectrum obviously: A broad peak appears at ~ 620 nm, close to the enhanced SSE peak (630 nm), in the annealed sample, whereas the extinction coefficient monotonically increases as wavelength rises for the samples without annealing. The close correlation of LP frequencies measured by absorption with the light frequencies of SSEs measured by PL also agrees with the results obtained by other experimental and theoretical investigations.^{10,26}

The resonance between the SSEs of QDs and LPs in Ag nanostructures is further verified by our time-resolved PL (TRPL) measurement. The TRPL spectra were measured at the SSE peaks as marked in Figure 3a, d, and f. The PL decay spectra are shown in Figures 11c, d, and e corresponding to the enhanced SSEs in Figures 3a, d, and f, respectively. The decay spectra are well fitted with two exponential functions (see Supporting Information). The fitted lifetime parameters are listed in Table 1. The PL decay spectra demonstrate that the plasmon-enhanced SSEs from the QD/Ag hybrid structures exhibit much longer lifetimes than the reference SSEs from QD/Si, similar to the increases in acceptor QDs' exciton lifetimes in RET systems.^{27–29} Evident increases of the SSE lifetimes observed in the QD/Ag hybrid structures indicate a possible effective energy transfer from the conduction band to surface states and suppression of nonradiative decay routes related to surface states by LP coupling.

The phenomenon of intense enhancement of SSEs in the QD/Ag hybrid structures observed in Figure 3 can then be explicitly explained: As-deposited Ag films composed of a

Table 1. Decay Lifetime Parameters Corresponding to Figures 11c, d, and e

	enhanced SSE peaks	τ_1 (ns)	τ_2 (ns)	A_1 (ns)	A_2 (ns)	$\langle \tau \rangle$ (ns)
#1QDs	573 nm on Si	9.88	81.67	43.89	56.11	50.16
	573 nm on Ag	9.93	89.86	18.65	81.35	74.95
#2QDs	612 nm on Si	10.25	54.19	59.85	40.15	27.89
	612 nm on Ag	15.24	66.48	43.38	56.62	44.25
#3QDs	628 nm on Si	5.97	38.69	60.50	39.50	18.89
	628 nm on Ag	14.65	50.17	46.97	53.03	33.49

myriad of tiny Ag particles are favorable for the SSE enhancement of smaller QDs (#1 and #2). OA in QD layers modifies Ag films by anisotropic etching that is reinforced by annealing. Hence, the annealed Ag films consisting of larger Ag crystals are favorable for the SSE enhancement of larger QDs (#3); i.e., the dominant plasmon modes in the Ag film red-shifted to ~ 630 nm. The red-shifted plasmon modes and the intensive local electric field in Ag nanostructures make strong resonance of the surface states of #3QDs with LPs in Ag such that the surface states are extracted significantly through radiative decay routes. The observed size-selective PL enhancements in Figure 3 also agree with the previous theoretical and experimental reports;^{30–32} i.e., an increase of Ag particle sizes leads to red-shifts of resonant wavelength of PL.

The QD–LP coupling model in Figure 11a can also explain the PL quenching phenomenon in Figure 3b. The dominant plasmon modes observed in absorption spectra are at ~ 630 nm, while the SSE peak of #1QD/Ag is at ~ 600 nm; i.e., a wide separation (~ 30 nm) between the LP modes and the SSE peak suppresses the SSE intensity by energy transfer from the surface states to crystal lattices rather than to the plasmon modes. As shown in Figure 3, the SSE peak of #2QDs locates between those of #1 and #3QDs; consequently, the SSE intensity of #2QDs is between the hugely enhanced #3QDs and the quenched #1QDs.

PMMA–QD composites were also tested to substitute bare CdSe QDs. Similar to the bare QD layers, PMMA–QD composites can also modify the morphology of underneath Ag films by annealing, leading to the PL spectra of the PMMA–QD/Ag composites similar to those in Figure 3 (Supporting Information). However, the addition of the PMMA matrix defers OA etching on Ag films due to dilution of OA in the PMMA–QD composites; thus, the PL of the PMMA–#1QD is not notably quenched after annealing (Supporting Information).

3.5. Microscale Fluorescent Color Patterns Fabricated by Coupling of QD Emitters with LPs. Using the new approach of strongly coupled QD–LP nanostructures, microscale fluorescent color patterns are produced via altering the luminescence of CdSe QDs in designated microscale areas. Figure 12a illustrates the fabrication of microscale luminescence patterns, in which PMMA–QD composites were used as emitters. Similar to a bare QD layer, PMMA–QD composites can also modify the morphology of underneath Ag films in its annealing process (Supporting Information). With the standard lithography technology, patterned photoresist on Ag can effectively separate the contact of the PMMA–QD layer to the Ag film at designated areas. Thus, in the annealing process the Ag film is selectively modified in the areas to which the QDs adhere. Figure 12b shows the realized microscale fluorescent color patterns by using standard photolithography.

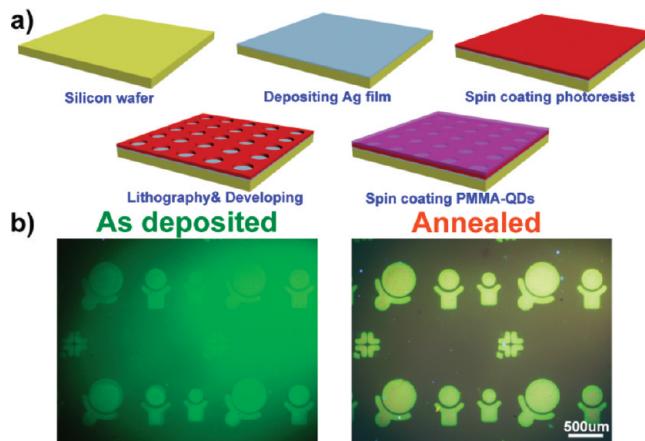


Figure 12. Microscale fluorescent color patterns of PMMA–QD produced by LP coupling. The fabrication procedure (a) and realized microscale fluorescent color patterns (b).

The luminescence of QDs is remarkably enhanced on the modified Ag areas, making the patterned areas different from the background area. The bright microscale fluorescent patterns are the outcome of the coupling of QD emitters with LPs on Ag nanostructures intensified by OA etching, whereas the interception of LP coupling by insertion of an insulating layer leads to dark colors (background area). The realized colorful fluorescent patterns state clearly that the selective coupling of CdSe QD–LP makes it possible to tune fluorescence colors in microscale.

4. CONCLUSIONS

In conclusion, a distinct enhancement of the SSE of colloidal CdSe QDs capped with OA is realized via coupling to LPs in Ag nanostructures. The role of OA ligand in the formation of Ag nanostructures and the intense enhancement of SSE of QDs are explored. It is found that the OA ligand on CdSe QDs plays a critical role in modifying or reshaping the Ag morphology and consequently impacts the coupling of QD emitters with LPs. The study of the effects of QD size and thickness of QD layers on coupling with Ag nanostructures shows the as-deposited small Ag particles are favorable to enhance the SSE of small-size CdSe QDs. The OA on CdSe QDs promotes reshaping of small Ag particles into larger and nonuniform ones with better crystallinity and clear corners in the annealing process which is favorable for the enhancement of the SSE of large-size CdSe QDs. The annealed QD/Ag hybrid structures are more stable than the unannealed ones due to the loss of OA in the heating process. The selective coupling of QD emitters with LPs in Ag nanostructures allows feasible realization of microscale fluorescent color patterns. The new approach of OA-assisted modification of plasmonic properties in Ag nanostructures is compatible with other tuning technologies for light emitters, such as photoactivation, and provides a way to precisely tune the light-emitting materials and devices that use colloidal QDs.

ASSOCIATED CONTENT

S Supporting Information

Preparation of QD–PMMA/Ag/Si hybrid structures; the results of plasmonic coupling with a blend of PMMA–CdSe QDs; time-resolved PL spectra of LP-enhanced SSE in PMMA–#3QDs/Ag/Si; comparison of X-ray diffraction of the as-deposited Ag film and the Ag nanoparticles annealed in air and

in OA ambient; analysis of the typical time-resolved PL spectra corresponding to the quenched and enhanced spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1996**, *100*, 468–471.
- (2) Bowers, M. J.; McBride, J. R.; Rosenthal, S. J. *J. Am. Chem. Soc.* **2005**, *127*, 15378–15379.
- (3) Chen, H. S.; Wang, S. J.; Lo, C. J.; Chi, J. Y. *Appl. Phys. Lett.* **2005**, *86*, 131905.
- (4) Sapra, S.; Mayilo, S.; Klar, T. A.; Rogach, A. L.; Feldmann, J. *Adv. Mater.* **2007**, *19*, 569–572.
- (5) Nizamoglu, S.; Mutlugun, E.; Akyuz, O.; Perkgoz, N. K.; Demir, H. V.; Liebscher, L.; Sapra, S.; Gaponik, N.; Eychmüller, A. *New J. Phys.* **2008**, *10*, 023026.
- (6) Baker, D. R.; Kamat, P. V. *Langmuir* **2010**, *26*, 11272–11276.
- (7) Hu, L.; Wu, H.; Du, L.; Ge, H.; Chen, X.; Dai, N. *Nanotechnology* **2011**, *22*, 125202.
- (8) Kalyuzhny, G.; Murray, R. W. *J. Phys. Chem. B* **2005**, *109*, 7012–7021.
- (9) Achermann, M. *J. Phys. Chem. Lett.* **2010**, *1*, 2837–2843.
- (10) Pompa, P. P.; Martiradonna, L.; Torre, A. D.; Sala, F. D.; Manna, L.; De Vittorio, M.; Calabi, F.; Cingolani, R.; Rinaldi, R. *Nat. Nanotechnol.* **2006**, *1*, 126–130.
- (11) Ming, T.; Chen, H.; Jiang, R.; Li, Q.; Wang, J. *J. Phys. Chem. Lett.* **2011**, *191*–202.
- (12) Wu, D.; Kordesch, M. E.; Van Patten, P. G. *Chem. Mater.* **2005**, *17*, 6436–6441.
- (13) Bullen, C. R.; Mulvaney, P. *Nano Lett.* **2004**, *4*, 2303–2307.
- (14) Park, J.; Lee, K. H.; Galloway, J. F.; Searson, P. C. *J. Phys. Chem. C* **2008**, *112*, 17849–17854.
- (15) Chatain, D.; Chabert, F.; Ghetta, V.; Fouletier, J. *J. Am. Ceram. Soc.* **1994**, *77*, 197–201.
- (16) Ye, J.; Thompson, C. V. *Adv. Mater.* **2011**, *23*, 1567–1571.
- (17) Giermann, A. L.; Thompson, C. V. *Appl. Phys. Lett.* **2005**, *86*, 121903.
- (18) Suzuki, Y.; Ojima, Y.; Fukui, Y.; Fazyia, H.; Sagisaka, K. *Thin Solid Films* **2007**, *515*, 3073–3078.
- (19) Chao, W.-H.; Wu, R.-J.; Tsai, C.-S.; Wu, T.-B. *J. Appl. Phys.* **2010**, *107*, 013101.
- (20) Mohamed, M. B.; AbouZeid, K. M.; Abdelsayed, V.; Aljarash, A. A.; El-Shall, M. S. *ACS Nano* **2010**, *4*, 2766–2772.
- (21) Muñoz-Hernández, G.; Escobedo-Morales, A.; Pal, U. *Cryst. Growth. Des.* **2008**, *9*, 297–300.
- (22) Han, X.-G.; Jiang, Y.-Q.; Xie, S.-F.; Kuang, Q.; Zhou, X.; Cai, D.-P.; Xie, Z.-X.; Zheng, L.-S. *J. Phys. Chem. C* **2010**, *114*, 10114–10118.
- (23) Zhou, F.; Li, Z.-Y.; Liu, Y.; Xia, Y. *J. Phys. Chem. C* **2008**, *112*, 20233–20240.
- (24) Mulvihill, M. J.; Ling, X. Y.; Henzie, J.; Yang, P. *J. Am. Chem. Soc.* **2010**, *132*, 268–274.
- (25) Sadhu, S.; Haldar, K. K.; Patra, A. *J. Phys. Chem. C* **2010**, *114*, 3891–3897.
- (26) Fedutik, Y.; Temnov, V. V.; Schöps, O.; Woggon, U.; Artemyev, M. V. *Phys. Rev. Lett.* **2007**, *99*, 136802.
- (27) Komarala, V. K.; Bradley, A. L.; Rakovich, Y. P.; Byrne, S. J.; Gun'ko, Y. K.; Rogach, A. L. *Appl. Phys. Lett.* **2008**, *93*, 123102.
- (28) Wang, C.-H.; Chen, C.-W.; Wei, C.-M.; Chen, Y.-F.; Lai, C.-W.; Ho, M.-L.; Chou, P.-T. *J. Phys. Chem. C* **2009**, *113*, 15548–15552.
- (29) Wang, C. H.; Chen, C. W.; Chen, Y. T.; Wei, C. M.; Chen, Y. F.; Lai, C. W.; Ho, M. L.; Chou, P. T.; Hofmann, M. *Appl. Phys. Lett.* **2010**, *96*, 071906.
- (30) Kumbhar, A. S.; Kinnan, M. K.; Chumanov, G. *J. Am. Chem. Soc.* **2005**, *127*, 12444–12445.
- (31) Aslan, K.; Leonenko, Z.; Lakowicz, J.; Geddes, C. *J. Fluoresc.* **2005**, *15*, 643–654.
- (32) Zhang, Q.; Li, W.; Moran, C.; Zeng, J.; Chen, J.; Wen, L.-P.; Xia, Y. *J. Am. Chem. Soc.* **2010**, *132*, 11372–11378.