Luminescence Change of CdS and CdSe Quantum Dots on a Ag Film

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ABSTRACT: Enhanced luminescence of an emitter on a Ag film is usually ascribed to the resonant surface plasmons. In these studies, the solid cadmium sulfide (CdS) and cadmium selenide (CdSe) quantum dot/silver (QD/Ag) hybrids were prepared, and the luminescence characteristics of these QD/Ag hybrids were measured. It is found that the enhancement of the trap state emission (TSE) is related to the QD size. The TSE features of the annealed QD/Ag hybrids are insensitive to the morphology of the Ag film. We used the wet and dry methods to separate the QD and Ag components and found that the photoluminescence (PL) of the QD component was permanently changed rather than the surface plasmons. This doping method uses pure Ag as the Ag+ ion source. In this case, though the CdS and CdSe QD/Ag hybrids are the solid state, the cation exchange between Ag+ and Cd2+ ions can still occur on the QD surface. Even a small amount of Ag can efficiently influence the luminescence of the QDs embedded in the poly(methyl methacrylate) matrix. A hypothetical model was proposed to explain the PL modification of the QD/Ag hybrid with and without annealing. Using this dry method for doping, the transparent luminescence label can be prepared easily, and the doped QDs can be further doped with Ag+ dopants.

INTRODUCTION

Metal–semiconductor hybrid materials have unique photovoltaic properties resulting from the complementary properties of their composite materials.1,4 Several possible interactions between the two components can influence the final properties, such as the coupling of exciton-plasmons, the Schottky Junction, and chemical reactions between the components. The fluorescent material may emit enhanced luminescence when nearby a metal material, such as silver and gold. The plasmonic effect has been proposed to explain metal-enhancement phenomena.3,4

Quantum dots (QDs) are a kind of advanced fluorophores that are placed into the metal–semiconductor hybrid to research the metal-enhanced luminescence. Cadmium selenide (CdSe) and cadmium sulfide (CdS) are the most popular model QD systems because they have simple composition and remarkable luminescence in the visual range. Silver (Ag) is a versatile metal that can play several roles in the semiconductor–metal hybrid, including a plasmonic metal and reflection mirror. The Ag-enhanced luminescence is usually ascribed to the plasmonic effect because the Ag has excellent plasmonic properties. The focused electromagnetic field nearby the Ag nanostructure can influence the excitation and emission of the fluorophore. However, the chemical reaction between the metal and the QD is rarely discussed.2,5

QDs with dual emissions6–17 provide another way to tune luminescence beyond the traditional method.18,19 For a typical dual-color QD, besides the band edge emission (BEE), other emissions may originate from surface defect traps,6–8 shell traps,9 and the dopant-related trap levels.10–14 The Ag film can both enhance the emission of the nearby QDs and influence the distribution of the BEE and the trap state emission (TSE).15–17 We found that the CdS and CdSe QDs on the Ag film have enhanced TSE and that the TSE enhancement was related to the QD size and the annealing treatment;15–17 these methods thus provide the post-synthetic modification of QD emission. It seems that the Ag-enhanced TSE of II–VI QDs is a physical effect related to the resonant plasmonic enhancement.15–17 Under this explanation, the resonant plasmons in the Ag nanostructure altered the decay process of the excited QD that resulted in the enhancement of TSE.

Based on previous work about the optical properties of the II–VI QD/Ag hybrid, we have done much work to unveil the mechanism between the Ag nanostructure and II–VI QDs in the QD/Ag hybrid with enhanced TSE. Increasing numbers of experimental results convince us that the enhancement of the TSE is not the result of a plasmonic effect, but instead, it is the result of a doping effect. Herein, we discuss in detail the mechanism of the enhanced emission in CdSe and CdS QD/Ag hybrids.

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Supporting Information

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RESULTS AND DISCUSSION

Size-Dependent Enhancement of TSE of the QD/Ag Hybrid. Oleic acid (OA)-capped CdSe and CdS QDs with zinc-blende structures were used for researching the Ag-enhanced TSE. For each kind of QD, two batches of QD were prepared, one batch of small QDs and one of large size QDs. The BEEs for two CdS QD batches were 412 and 470 nm, while those for CdSe QD batches were 486 and 560 nm, respectively (Supporting Information, Figure S1). The mean sizes of the 412 and 470 nm CdS QDs are 3.1 and 4.0 nm, and those of the 486 and 560 nm CdSe QDs are 3.2 and 3.7 nm (Supporting Information, Figure S1). These QD batches were coated on the Ag/Si substrates to form the QD/Ag hybrid, respectively.

Figure 1 displays the photoluminescence (PL) spectra of the CdSe QD hybrid with and without annealing treatment.

For each kind of QD, a size-dependent enhancement of the TSE with and without annealing of the QD/Ag hybrid was evident. We described this finding in our previous works.\textsuperscript{15,17} For the 412 nm CdS QDs, the unannealed QD/Ag hybrid presents a clearly enhanced TSE at 526 nm and a suppressed BEE. Annealing quenched the PL of the QD/Ag hybrid, and the distribution of the two peaks of the QD/Ag hybrid returns to a line shape similar to the colloidal states of 412 nm CdS QDs (Figure 1a). For the 470 nm CdS QDs on Ag, compared to the QD/Si sample, the TSE (610 nm) of the unannealed QD/Ag sample is enhanced about 14 times (Figure 1d). Annealing treatment further enhanced the TSE of the QD/Ag hybrid such that the TSE (602 nm) dominates the PL spectra. The PL of the annealed 470 nm CdS/Ag is similar to the PL of the unannealed 412 nm CdS QD/Ag.

The CdSe QD/Ag hybrids also show the analogous size-dependent properties compared with those of the CdS QD/Ag hybrids. For both CdS and CdSe QDs with small size, unannealed QD/Ag have the dominant TSE. The TSE lifetime of the unannealed QD/Ag is longer than that of the bare QD (Figure 1b,h). Annealing quenched the PL of the QD/Ag hybrid, thereby the TSE lifetime of the annealed QD/Ag is shorter than that of the bare QD (Figure 1b,h). For the large size QDs, the QD/Ag hybrids have the enhanced and long-decaying TSE compared to the bare QD (Figure 1e,k). Annealing further elevates the PL intensity and the lifetime of TSE of QD/Ag (Figure 1e,k).

This size-dependent enhancement of TSE is also reflected in the chromaticity chart in Figure 1c,f,i,l. Comparing Figure 1c,i, the CIE coordinates of the unannealed QD/Ag PL spectrum are near the edge of the chart. This is due to the dominant TSE on Ag (Figure 1a,g). Annealing quenched the TSE of the QD/Ag (Figure 1a,e) and shifted the CIE coordinates of PL on Ag moving toward the coordinates of QD PL. In contrast, for the large QDs (470 nm CdS and 560 nm CdSe QDs), annealing enhanced the TSE on Ag intensely such that the CIE coordinates of the QD/Ag PL spectrum move away from the coordinates of QD PL (Figure 1f,l).

In our previously published studies,\textsuperscript{15–17} we considered that the localized plasmons influence the final emission characteristics of the QD/Ag hybrid. However, when the experimental data of CdS and CdSe QDs are listed together (Figure 1), two confusing facts are clear. One is that the Ag film enhances the TSEs of CdS and CdSe QDs at different wavelengths instead of a special wavelength consistent between the two. It seems that the peak of Ag-enhanced TSE (on Ag) is usually close to the TSE of bare QDs (on Si). Different compositions and sizes of QDs result in different enhancement effects on the same Ag film. The second confusing fact is that the enhanced TSE always exhibits a longer lifetime than that of the bare QDs, while the custom plasmon-enhanced PL corresponds to the shorter lifetime.

The Unitary PL Character of QD/Ag Hybrids Induced By Annealing Treatment. Besides the size-dependent enhancement of the TSE, another interesting phenomenon is that the TSE QDs show no preference for Ag films with varied initial morphology. The PL characteristics of 560 nm CdSe QDs on Ag films with different thicknesses and morphologies were investigated. Ag films with four different surface morphologies were prepared (Figure 2). (1) The as-deposited 6 nm Ag film. (2) The as-deposited 60 nm Ag film. (3) A 60 nm Ag film stored in ambient air for several months. (4) The Ag island film generated by annealing the as-deposited Ag film (thickness 60 nm) at 180 °C. The scanning electron microscopy (SEM) images of Ag nanostructures described above are listed on the left in Figure 2b,d,f,h. The 6 nm Ag film has a discrete surface composed of myriad Ag islands (size ~20 nm), whereas the 60 nm Ag film has a continuous surface consisting of small Ag particles or grains (~30 nm). For the 60 nm Ag film, one piece was stored in air for several months; the color of the film became brown from sulfurization (Supporting Information, Figure S3). Compared to the fresh 60 nm Ag, the sulfurized Ag film has a rough surface (Figure 2f).

The 560 nm CdSe QDs were coated on these substrates and the same measurement was performed. Our previous work indicated that the QD layer can etch the Ag film and that annealing can accelerate the etching process (Supporting Information, Figure S3).\textsuperscript{15,17} For the annealed QD/Ag hybrid, the QD layer was washed in toluene and the remaining Ag film can be observed. The SEM images show that the annealing
QD/Ag hybrid enhanced the TSE due to the fact that Ag have excellent plasmonic properties. Based on the current data, are sensitive to the micromorphology of the metal. The doped QDs always have the characteristic emission of the dopant impurity. The Ag⁺ doping process may occur in the structure (Figure 1j). The QDs separated from the Ag film retained the PL features from when they were on the Ag substrate.

Figure 3. (a) Demonstration of the wet method for detaching the 560 nm CdSe QDs and Ag film. First, the 560 nm CdSe QD dispersion was dropped on the Ag/Si substrate. After the QD dispersion dried, the QD/Ag/Si sample was cleaved into two parts. The upper part was not treated and the lower part was annealed at 150 °C for 30 min. Then, these two parts were immersed in toluene to collect the QDs. The photographs were taken under ambient light and 365 nm UV light. (b) PL and absorption spectra of 560 nm CdSe QDs (with and without annealing) detached from the Ag film (the PL and absorption spectra of the 560 nm CdSe QD dispersion with no treatment is displayed for reference). The photographs of the 560 nm CdSe QD dispersion, the 560 nm CdSe QDs detached from unannealed and annealed QD/Ag parts were taken under ambient light (upper part of the inset) and 365 nm UV light (lower part of the inset). (c) Time-resolved decay PL curves corresponding to the PL spectra in (b). The colors of the decay curves are coherent with the PL curves in (b).

The 560 nm CdSe QDs dispersed in toluene were dropped on the 60 nm Ag film and dried naturally. Under 365 nm UV light, the dried QDs, which are attached at the edge of the substrate, have weak red emission, whereas the liquid dispersed QDs have green emission. Once the QD layer was dry, the sample was cleaved into two parts and one part was annealed. The annealed QD/Ag piece exhibits red emission under UV light (as mentioned above). Next, the two pieces were soaked in toluene to collect the QDs. Figure 3b shows that the PL features of the QDs are similar to the corresponding QD/Ag structure (Figure 1j). The QDs separated from the Ag film retained the PL features from when they were on the Ag film. This means that the QD PL changed permanently, even after the QDs were separated from the QD/Ag hybrid. This confirms that the Ag⁺ dopants cause the change of the PL and the doping can occur at room temperature without extra heating. The PL properties depend on the chemical composition of the QD/Ag hybrid rather than the physical properties of the Ag film. The absorption spectra of the doped QDs is similar to that of the nontreated QDs (Figure 3b).

Proof of the Doping Hypothesis: Detaching the QDs and Ag Film. For the phosphor-metal hybrid with plasmon-enhanced PL, the physical interaction between the phosphor and the metal modifies the PL properties of the hybrid. In other words, if the phosphor material was separated from the metal, the enhanced emission should change back to its original state. Consequently, we tried two methods to detach the QD component and the Ag film to verify the reversibility of the QD emission.

For the first method, the QD/Ag structures with and without annealing were soaked in toluene to dissolve the QD layer. The QD layer would be dissolved in toluene and the Ag film still attached on the Si substrate. This wet method transferred the solid QD layer to the liquid phase, resulting in the separation of the QD and Ag film. The experimental processes are presented in Figure 3a.
Ag has a prolonged lifetime, which is consistent with the natural characteristics of the dopant.\textsuperscript{10,11}

The Ag/Cd ratio of the doped QDs separated from the Ag film can be measured by inductively coupled plasma mass spectroscopy (ICP-MS). For these four QD batches stated above, the Ag/Cd ratios of the doped QDs form the QD/Ag samples with and without annealing are listed below. Two distinct features can be seen in Table 1. The first one is that the annealing increased the Ag/Cd ratio of the doped QDs, which indicates that annealing can improve the doping process in this QD/Ag system. The second feature is that the QDs with the small size (410 nm CdS and 486 nm CdSe) have a bigger Ag/Cd ratio than the large QDs (470 nm CdS and 560 nm CdSe). The Ag/Cd ratio of the doped 470 nm CdSe without annealing is 0.77%, which is bigger than that of the doped 560 nm CdSe QDs with annealing. For the doped CdS QDs, the same is true.

Table 1. Ag/Cd Ratio of the QDs Separated from the Ag Film

| Ag/Cd ratio          | W/O annealing (%) | with annealing (%) |
|----------------------|-------------------|--------------------|
| 410 nm CdS/Ag        | 1.75              | 3.16               |
| 470 nm CdS/Ag        | 0.14              | 0.23               |
| 486 nm CdSe/Ag       | 0.77              | 3.1                |
| 560 nm CdSe/Ag       | 0.09              | 0.42               |

Another method to separate QD and Ag was inspired by the original way to obtain the monolayer graphite. For this method, the poly(methyl methacrylate) (PMMA)-QD layer was coated on a transparent quartz plate and then the Ag film was deposited on the PMMA-QD layer by thermal evaporation. Compared to the QD layer, the PMMA-QD layer adhered well to the quartz plate. In addition, the PMMA-QD layer is harder than the QD layer. The Ag/PMMA-QD/quartz sample was then annealed at 150 °C for 30 min. Finally, part of the Ag film was removed using scotch tape. It was found that the adhesion strength of the Ag film coating to the PMMA layer was not good. Most part of the Ag film adhering to the scotch tape can be easily peeled off and the PMMA-QD layer still attached on the quartz plate. The final sample has three regions; region I, PMMA-QD/quartz; region II, Ag/PMMA-QD/quartz; and region III, PMMA-QD/quartz separated from the Ag film.

The PL was measured from the back of the quartz substrate. PL features of the PMMA-QD/quartz and Ag/PMMA-QD/quartz (560 nm CdSe) area are similar to the QD/Si and QD/Ag hybrids, as stated above (Figure 2c). The PL spectrum of PMMA-QD separated from the Ag film (region III) is similar to that of region II. This further proves that the doping occurs in the PMMA-QD/Ag hybrid. In Figure 3b, the photoluminescence excitation spectra (PLE) of the enhanced TSE on region II and III have a similar shape except for around 320 nm. The peak at 540 nm of PLE spectra is related to the excitation of the band edge. The PLE spectrum on region II has a pit at 320 nm, whereas the PLE spectrum on region III does not have this pit. This pit at 320 nm corresponds to the interband transition of Ag bulk.\textsuperscript{20} Thus, the excitation light near 320 nm tends to penetrate the PMMA-QD/Ag structure while excitation light at other wavelengths is reflected by the Ag film. This results in the relative low excitation efficiency near the 320 nm.

Figure 4. (a) Dry method for detaching the QD and Ag film. (b) PL and PLE spectra of the three regions of the PMMA-QD (560 nm CdSe QDs) sample. (c) Decay PL curves correspond to the spectra in (b). (d) Depositing Ag on the PMMA-QD film (560 nm CdSe QDs) with a hollow mask to prepare the luminescence patterns. Before and after the annealing treatment, the photographs were taken under ambient light and UV light, respectively. Top, 60 nm Ag was deposited on the PMMA-QD film (560 nm CdSe QDs), and the treatment is the same as that in (a). Middle and bottom, less than 1 nm Ag was deposited on the PMMA-CdSe QD (560 nm CdSe QDs) and PMMA-CdS QD (470 nm CdS QDs) film.

The thick Ag film often cannot be peeled clean (Top row of Figure 4d). This effect would influence the transparency of the sample. The leakage of Ag vapor around the hollow area is hard to see in ambient light, but after annealing, the limited amount of Ag can still dope the PMMA-QD to form a red halo under UV light. We further evaporated a very small amount of Ag (less than 1 nm) on the PMMA-QD film covered with a hollow mask (second and third rows of Figure 4d). Under ambient light, the sample is as transparent as the single PMMA-QD film. However, under UV light the area deposited with Ag has a different luminescence color.

During the process of thermal evaporation, some Ag clusters can enter into the shallow place of the PMMA-QD layer. This increase the contact between Ag and QDs. Some Ag\textsuperscript{+} ions at the interface between the Ag and PMMA-QD layer can diffuse into the PMMA-QD layer to dope the QDs. To dope the QDs embedded in PMMA, the diffusion of Ag\textsuperscript{+} ions in the PMMA-QD layer is important. The thickness of the PMMA-QD layer will influence the diffusion of Ag\textsuperscript{+} ions and the doping process.
PMMA-560 nm CdSe QD layers with four thicknesses were coated on the 60 nm Ag substrate. The thicknesses of the three thinner PMMA-QD layers were 93.8, 131.3, and 187.5 nm, respectively. The thickest PMMA-QD layer was prepared by dropping the PMMA-QD dispersion on the substrate. The thickest PMMA-QD layer was too rough to measure its thickness by an ellipsometer. Then these four samples were annealed at 150 °C for 30 min. The PL spectra of these annealed PMMA-QD/Ag samples are displayed in Figure 5a.

![Figure 5](image-url)

**Figure 5.** (a) PL spectra normalized at BEE of the annealed PMMA-QD/Ag samples (560 nm CdSe QDs) with varied PMMA-QD thickness (PL of the annealed undoped PMMA-QD layer is displayed for reference). (b) Decay PL curves corresponding to the dopant PL in (a). (c) PL spectra of the annealed PMMA-QD/PMMA/Ag and PMMA-QD/PMMA-OA/Ag structure (560 nm CdSe QDs were used). The PL of PMMA-QD layer on Si was displayed by a dashed line for reference. (d) Schematic for explaining the diffusion of Ag⁺ ions in the PMMA-QD/PMMA/Ag and PMMA-QD/PMMA-OA/Ag structures for doping the QDs embedded in PMMA.

For the three thinner samples, the dopant PL area of the PMMA-QD layer increases with the increase of the thickness. The decay curves in Figure 5b show that the relatively strong dopant PL corresponds to a longer lifetime. This indicated that increasing the thickness of the PMMA-QD layer within a certain range can optimize the doping process. The thickest PMMA-QD layer/Ag sample had the weakest dopant PL, which indicated that it is difficult for Ag⁺ ions to diffuse far enough to reach the surface of the thick PMMA-QD layer. Our previous studies indicated that the oleic acid (OA) in the QD (or PMMA-QD) layer can etch the Ag film to fabricate Ag⁺ ions for doping the QDs. PMMA-QD/Ag layer, in this case, plays dual roles of the dopant receptor and the etchant to Ag. The thinner PMMA-QD layer facilitates the diffusion of Ag⁺ ions, but the thicker PMMA-QD layer with more amount of QDs can etch the Ag film to create adequate Ag⁺ ions. These two competitive mechanisms show that the PMMA-QD layer with a moderate thickness has an optimized doping effect. The gradient of Ag⁺ ions along the thickness direction results in the gradual doping along the thickness direction. This causes that the 187.5 nm PMMA-QD layer has a red-shifted and broader dopant PL than the 131.3 nm PMMA-QD layer. Here, a sample with the PMMA-QD/PMMA/Ag structure was prepared by successively coating a PMMA (~80 nm) and a PMMA-QD layer (~200 nm) on the 60 nm Ag substrate. The PMMA layer was inserted between the Ag film and PMMA-QD layer for isolating the PMMA-QD and Ag film. This mid PMMA layer can not only inhibit the etching of the Ag film by residual OA in the PMMA-QD layer but also may hinder the diffusion of Ag⁺ ions toward the PMMA-QD layer. In line with expectations, the annealed PMMA-QD/PMMA/Ag sample has a weak dopant PL. Another PMMA-QD/PMMA/Ag sample with OA-doped PMMA mid layer was prepared for comparison. Figure 5c shows that the annealed PMMA-QD/PMMA-OA/Ag sample has a distinct dopant PL, which indicates that the OA in the mid layer can etch the Ag film to produce Ag⁺ ions and these Ag⁺ ions can cross the mid layer to doping the QDs in the annealing process.

**The Role of Annealing and the Mechanism of Ag Doping.** For the QD/Ag hybrid, in this case, annealing plays an interesting role to change the dopant PL characteristics. The features of dopant PL mainly depend on the concentration and position of the dopants.10−14,21−24 Annealing may create more Ag⁺ in the environment, improve the diffusion of Ag⁺ dopants to QD, and restructure the QD surface. Some PL features of the QD/hybrid such as the size effect and the blue shift of TSE can be explained with the Ag-doping process.

The small QD on the Ag film show enhanced PL while annealing favors the enhancement of QDs with a bigger size. Previous studies proposed that the Ag⁺ can penetrate into the interstitial positions,13,21 substitute the surface Cd atoms,10,22,23 or attach to the Se atom.24 The substitutional Ag⁺ ions were considered to be the origin of the dopant PL.10 The Cd/Se and Cd/S ratios of the QDs stated above were semiqualitatively measured by energy-dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS) (Table 2). The smaller QDs have a larger Cd/chalcogenide ratio, which benefits the exchange between Ag⁺ and Cd²⁺.25 Additionally, the high surface to volume ratio makes the small QD sensitive to surface doping. The surface of small QDs tends to absorb enough dopants at room temperature, thereby the QD/Ag hybrids have an evident TSE peak (Figure 1a,g). The QD surface may adsorb excess dopants beyond the optimal concentration in the annealing process. This introduces extra defect states that act as nonradiative centers. Therefore, the annealed QD/Ag, including small QDs, has decreased TSE with a shorter lifetime. As the energy transfer from the band edge to trap defect increases, the BEE lifetime of the annealed QD/Ag decreases (Figure 1b,h).

For the large QDs on the Ag film, the surface doping can occur at room temperature such that the QD/Ag has enhanced TSE compared with the bare QD (Figures 1−3). Annealing improves doping with Ag⁺ ions to achieve the optimal amount and position of Ag⁺ ions in the QD. Therefore, the annealed QD/Ag has increased TSE. This explains the size-dependent enhancement of TSE in Figure 1.

The proper or excess dopants will result in the enhancement or quenching of PL. Moreover, the OA in the QD layer can...
etch the Ag film and provide an adequate quantity of Ag⁺ ions surrounding the QDs. In Figure 2, the same QD layer is deposited on Ag films with varied morphology, thus inducing varying amounts of Ag⁺ ions. This results in the different initial PL characters. Annealing promptly optimizes the concentration and position of Ag⁺ dopants that result in uniform PL characters (Figure 2). We also found that depositing the ZnS shell on the core QDs (such as the CdZnS and CdSe QDs) can block the exchange between Ag⁺ and Cd²⁺ ions. For the QD/Ag hybrid with CdZnS/ZnS or CdSe/ZnS QDs, almost no significant enhancement of the TSE was observed (Supporting Information, Figure S5).

Previous literature indicates that the increasing dopant concentration results in the red shift of the dopant PL. In our experience, the TSE peak of the annealed QD/Ag hybrid usually have shorter wavelengths than those of the unannealed one (Figure 1). In the coordinate system with energy as the horizontal axis, the PL spectrum of the QD/Ag hybrid can be well fitted with two Gaussian bands including the BEE and TSE (shown in Figure 6). The as-prepared 470 nm CdS/Ag hybrid has the TSE at 2.07 eV with a blue shift of 0.04 eV. The TSE of the as-prepared 470 nm CdS/Ag hybrid located at 1.94 eV, whereas the TSEs of the 4 months aged and annealed CdSe/Ag hybrid are located at 1.91 and 1.94 eV, respectively.

Annealing or aging treatments may improve the diffusion of Ag⁺ ions in QD. The surface Ag⁺ dopants may move toward the interior by lattice diffusion during the annealing course. This interior doping may result in the blue shift of the dopant TSE because the interior ligand field is different from that on the surface. The Ag⁺ dopant in CdSe QD has been considered as the hole trap state for the carriers. A hypothetical model in Figure 6c is proposed to explain the phenomenon stated above. In our case, surface doping can occur at room temperature (Figures 1–3). Annealing tends to transfer the surface dopants to the interior of the QD. In the annealing or aging process, some Ag⁺ ions diffuse inside the QD such that the interior dopant levels become shallow due to the change of the ligand field around the dopants. The surface doping also occurs in the annealing or aging process. The dominant interior doping will cause the blue shift of TSE. Otherwise, if the dopants gather on the QD surface, the energy levels of dopants become tight. This can induce the carriers to relax to the deeper levels and therefore causes the PL peak to shift to the longer wavelength. For supporting this statement, two QD/Ag hybrid samples (470 nm CdS and 560 nm CdSe QDs) were annealed in a vacuum for comparison. In Figure 6a,b, it can be seen that annealing the CdS/Ag and CdSe/Ag hybrids in a vacuum causes the evident red shift of TSE (1.97 and 1.79 eV). The ligands on the QD surface will escape when the QDs are heated in a vacuum. The QD surface lacking protection tends to attach Ag⁺ dopants, resulting in dominant surface doping. This results in the evident red shift of the TSE peak.

The model stated above indicates that annealing can not only improve the doping process (cation exchange) on the QD surface but also transfer the surface dopants to the interior of the QDs. For further supporting this conjecture, we intentionally prepared the Ag-doped 470 nm CdS QDs (surface-doped Ag: CdS QDs) with an easy wet method (Experimental Section) and observed the change of the dopant PL after the annealing treatment (150 °C, 30 min). Figure 7 shows the PL spectra of the 470 nm Ag: CdS QDs on the Si substrate with and without annealing treatment. Compared with the undoped 470 nm CdS QDs, the as-prepared Ag: CdS QDs have a dopant PL peak located at 616 nm. With annealing treatment, the dopant PL peak of the Ag: CdS QDs became stronger slightly and shifted to 602 nm (Figure 7a). The dopant PL lifetime of the annealed Ag: CdS QD/Si structure (34.5 ns) is shorter than that of the unannealed one (40.2 ns). Figure 7c shows that coating the Ag: CdS QDs on the Ag film will further dope the Ag: CdS QDs due to the increased dopant PL and Ag/Cd ratio. Annealing the Ag: CdS QD/Ag hybrid can further enhance the dopant PL and cause the blue shift of dopant PL (602 nm). The dopant PL lifetime of the annealed Ag: CdS QD/Ag structure (43.9 ns) is shorter than that of the unannealed one (48.3 ns). For the case in Figure 7a, the dopant concentration will not increase during the annealing process because the external source of Ag⁺ ions is not taken into account (Figure 7e shows that the Ag/Cd ratio decreased after the annealing). Therefore, the diffusion of the Ag⁺ dopants in QDs should be the main cause of the blue shift (616–602 nm) of the dopant PL. Ag⁺ dopants may diffuse to the interior or exterior of the QDs in the annealing process (Figure 7e). If inward diffusion is not considered, the outward diffusion of Ag⁺ ions will decrease the dopant concentration that will cause the decrease in dopant PL (Figure 7c shows that increasing the dopants in the Ag: CdS QDs causes the
enhancement of dopant PL and vice versa). In summary, the inward diffusion of Ag$^+$ dopants caused the blue shift of the dopant PL. The interior doping benefits the enhancement of dopant PL (Figure 7a,c) that corresponds to the bigger radiative recombination rate and the decreased PL lifetime (Figure 7b,d). In contrast, the surface doping will cause the red shift of the dopant PL. The wet method for doping at room temperature (Supporting Information, Figure S4) may mainly cause the surface doping.

For the undoped QD/Ag hybrid, the surface and interior doping may coexist during the annealing process, thereby the competition mechanism between the surface and interior doping will influence the PL characters.

## CONCLUSIONS

For the solid QD/Ag hybrid with enhanced TSE, the QD component was separated from Ag but the enhanced TSE remained. We conclude that the Ag-enhanced TSE of CdSe and CdS QDs is ascribed to the doping process. This proves a way to identify whether other selective enhancements of PL come from the plasmonic resonance.

The residual OA in the QD layer can etch the Ag film to produce appreciable Ag$^+$ ions around the QDs. The high ratio of the surface area to the bulk renders the small CdSe and CdS QDs sensitive to the surface doping. Meanwhile, the Cd-rich surface of the small QD benefits the cation exchange between Ag$^+$ and Cd$^{2+}$ ions. These two factors result in the unannealed small QD/Ag hybrid to exhibit a dominant TSE. In the annealing process, the excess Ag$^+$ ions dope the small QDs to produce extra defects as nonradiative centers, which quench the PL.

The dopant PL can be modified by tuning the concentration and position of the dopants. Annealing the QD/Ag hybrid in air at the proper temperature can improve the diffusion of the surface Ag$^+$ dopant into the QD, consequently modifying the ligand field around the dopants. The interior doping can cause the dopant level to shift shallower, resulting in a blue shift of the TSE. Conversely, annealing the hybrid in a vacuum can cause the surface doping to be dominant, thereby causing a red shift of the TSE. The above-stated methods provide an effective way to dope the solid CdSe and CdS QD film (or QD-PMMA hybrid) at a designed area. The traditional method for postsynthetic Ag$^+$ doping employs the Ag source in the liquid phase, thereby the doping course will introduce unexpected organic impurities into the surroundings of the reaction. The dry method presented herein differs from the typical wet method in that it uses pure solid silver as the Ag source. This dry doping method can further dope the doped QDs such as Ag:CdS QDs to modify the PL properties.

## EXPERIMENTAL SECTION

**Chemicals.** Selenium powder (Se, 99.999%), cadmium oxide (CdO, 99.95%), 1-octadecane (ODE, 90%), oleic acid (OA, 90%), tri-n-octyl phosphine (TOP, 90%), and poly(methyl methacrylate) (PMMA, average MW 350 000) were purchased from Sigma-Aldrich. Tributylphosphine (TBP, 95%), sulfur powder (99.99%), and oleylamine (80−90%) were purchased form Aladdin-reagent. Solvents such as toluene, ethanol, and acetone were used as received.

**Preparation of CdS and CdSe QDs.** For CdS QDs with an emission peak at 412 nm, 2 mmol CdO powder, 3 mL OA, and 30 mL ODE were loaded in a three-necked flask. The flask was heated to 300 °C under an argon atmosphere until a transparent Cd precursor was formed. The heat was then removed and 1 mL TBPS solution (S powder dissolved in TBP with 3 M concentration) was injected into the flask, after which the flask was cooled immediately. For 486 nm CdSe QDs, the Cd precursor was prepared as above, and 2 mL
TOPSe (selenium dissolved in TOP with 2 M concentration) was injected into the flask at 170 °C, after which the flask was cooled immediately. The QD product was precipitated through centrifugation. The precipitate was dispersed in toluene. The wavelength of the QDs can be tuned by mainly varying the injection temperature and the reaction time. The details were stated in previous papers. 15−17

Preparation of the QD/Ag Hybrid Sample. The method was described in our previous papers. 15−17 Briefly, the clean Si wafer was cut into square pieces. Half of the polished Si surface was coated with a 60 nm Ag film by thermal evaporation. The QDs dispersed in toluene were coated on the Si wafer with a spin coater. Then the sample was cut into two pieces along the direction perpendicular to the boundary between the areas with Ag and without Ag. One piece was kept as a reference sample and the other one was annealed in air at 150 °C for 30 min.

Preparation of the PMMA-QD Film. The PMMA powders were added to the QD dispersion with a 3% weight concentration. The PMMA-QDs/toluene blend was placed until the PMMA powders were dissolved completely. The blend can be coated on the Si wafer or quartz glass to form the blend film. For preparing the PMMA-QD/PMMA/Ag sample, the PMMA dissolved in toluene (3% weight concentration) was first coated on the 60 nm Ag film, and then the PMMA-QD blend was coated on the dried PMMA layer. For preparing the PMMA-QD/PMMA/Ag sample with the OA-doped PMMA mid layer, the OA-doped PMMA solution (0.3 mL OA was added into 9 mL PMMA solution) was coated on the Ag film first and then the PMMA-QD blend was coated again.

Preparation of the Ag:CdS QDs with Wet Method. AgNO₃ (6 mmol) was dissolved in a mixture of 24 mL toluene and 6 mL oleylamine, and then the mixture was diluted with toluene to reach the Ag concentration of 10⁻² M. With the help of ICP-MS, the 470 nm CdS QDs were dispersed in toluene with the Cd concentration of 4 × 10⁻² M.

The Ag-doped CdS QD dispersion was prepared by mixing the Ag precursor and 470 nm CdS QD dispersion with the Ag/Cd ratio of 1:50. Then, the doped QDs were precipitated through centrifugation. The precipitate was dispersed in toluene.

Measurement and Equipment. PL spectra were measured using an Edinburgh FL5920 PL system. The steady PL spectra were measured with the excitation of a 325 nm line of a Xe lamp. Time-resolved PL (TRPL) was measured using an Edinburgh FLS920 PL system. The steady PL spectra were measured with the excitation of a 325 nm line of a Xe lamp. Time-resolved PL (TRPL) was measured using an Edinburgh FLS920 PL system.

The basic characterization for the four batches of QDs (PL and absorption spectra, XRD, TEM images); detailed description of the PL characters of the QD/Ag hybrids with and without annealing; photographs of samples for describing the etched Ag film under a QD layer and the QD/Ag hybrids with varied Ag film morphology; doping experiment on 412 and 470 nm CdS QDs with a wet method; the test of the QD/Ag hybrid with CdSe/ZnS core/shell QDs (with 560 nm CdSe core)

# ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01096.
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