High-Q Microcavity Enhanced Optical Properties of CuInS$_2$/ZnS Colloidal Quantum Dots toward Non-Photodegradation

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ABSTRACT: We report on a temporal evolution of photoluminescence (PL) spectroscopy of CuInS$_2$/ZnS colloidal quantum dots (QDs) by drop-casting on SiO$_2$/Si substrates and high quality factor microdisks (MDs) under different atmospheric conditions. Fast PL decay, peak blue shift, and line width broadening due to photooxidation have been observed at low excitation power. With further increasing of the excitation power, the PL peak position shows a red shift and the line width becomes narrow, which is ascribed to the enhanced Förster resonant energy transfer between different QDs by photoinduced agglomeration. The oxygen plays an important role in optically induced PL decay, which is verified by a reduced photobleaching effect under vacuum. When the QDs are drop-casted on MDs, photooxidation and photobleaching are accelerated because the excitation efficiency is greatly enhanced with coupling the pumping laser with the cavity modes. However, when the emitted photons couple with cavity modes, a PL enhancement by more than 20 times is achieved because of the increased extraction efficiency and Purcell effects of MDs at room temperature (RT) and 35 times at 20 K. The photobleaching can be avoided with a small excitation power but with a strong PL intensity by taking advantage of high quality factor cavities. The highly efficient PL emission without photodegradation is very promising for using CuInS$_2$ QDs as highly efficient photon emitters at RT, where the photodegradation has always limited the practical applications of colloidal quantum dots.

KEYWORDS: CuInS$_2$ colloidal quantum dots, high quality factor, microcavity, photodegradation
optical cavities and plasmonic cavities by greatly suppressing the spontaneous emission lifetime. Strong coupling between an exciton in a QD and a photon in a high quality factor (Q) optical resonator has been reported recently when the exciton energy is resonant with the cavity mode. Among these microcavities, microdisks (MD) are relatively easy to fabricate and have a very high Q of whispering-gallery modes (WGMs). Due to the large size of the MDs, they provide a great opportunity to drop-cast QDs on MDs for investigating the enhancement of optical properties of colloidal QDs.

To couple the colloidal QDs with the MDs, QDs have been embedded inside the MD cavity to maximize the coupling strength due to the better field overlapping. However, this makes the fabrication processes of MDs much more complex and also limits the Q because of the nonuniformity of the MD layer. In fact, the QDs could couple efficiently the evanescent electric field of cavity modes when QDs are drop-cast on top of the cavities, which also enhances the optical properties of QDs. In this work, we report on the temporal evolution of the PL properties of colloidal CIS/ZnS QDs dispersed on SiO₂/Si substrates and MDs. The PL intensity of QDs on the edge of MDs is greatly enhanced by 20 times at room temperature (RT) and 35 times at 20 K because of the Purcell effect of MDs. It is found that the PL intensity of close-packed CIS/ZnS QDs initially decreases and then remains stable with CW laser illumination, which can be ascribed to photobleaching and photooxidation. The photoinduced degradation is investigated under air and vacuum atmospheric environments at different temperatures. We found that optically induced degradation can be avoided with a small excitation power by taking advantage of enhanced PL emission using MDs.

## RESULTS AND DISCUSSION

Figure 1 shows a schematic diagram of a conventional confocal micro-PL system for PL measurement of QDs on SiO₂/Si substrates and MDs (as shown in the inset). Figure 2a–c show wide-field PL images of CIS QDs on a MD by shining a pumping laser at different locations. During the PL mapping, the pumping laser was filtered out with a long-pass filter. When the pumping laser touches the edge of the MD, as shown in Figure 2a, the contacting part turns red due to the PL, while the opposite MD edge away from the laser spot remains dark. When the laser totally irradiates on the edge of a MD, the whole edge of the MD turns on, which is demonstrated in Figure 2b. This indicates that the pumping laser couples to the WGMs of the MD, which excites the QDs on the edge. Another possibility is that the emitted light from QDs also couples to the cavity modes. After the laser goes far away from the edge of the MD, the PL intensity becomes weak, as shown in Figure 2c. To illustrate the cavity modes of the MD, a two-dimensional finite-difference time-domain method was used to simulate the cavity modes. Figure 2d shows electric field magnitude distribution of a TE mode of about 669.75 nm, which is close to the center of the PL spectrum. The enlarged cavity mode distribution is shown in the inset of Figure 2d. It can be seen that the simulated field distribution on the edge of the MD corresponds well with the observed PL images.

To get detailed spectral information, the PL spectra were mapped by moving the objective in a step of 1.5 μm. Figure 3a and c show the PL mapping of the QDs of a quarter of an area of the MD at RT and 20 K. The red annulus similar to the edge of the MD shows an enhancement of the PL, which is induced by the cavity modes of the MD. The PL spectra from the edge of the MD and from outside the MD are shown in Figure 3b and d. The integrated PL intensity on the edge of the MD (black dashed line) is enhanced by 20 times compared with that of the QDs outside the MD (red solid line) at RT, and an enhancement of 35 times was observed at 20 K. In general, MDs with a large diameter of around 150 μm have a high density of WGMs and the mode separations are very small (less than 0.1 nm). Such a small mode separation is less than our spectrometer resolution of about 0.1 nm. Therefore, we cannot resolve the different modes of the MD as before. Normally, the cavity modes in different wavelengths could have different quality factors, which results in a different enhancement in the PL spectrum range of the QDs. However, the inset of Figure 3b shows the normalized PL spectra of different positions, which are in the exact same line shape. This verifies that the cavity enhances the PL emission with the same degree for the emission wavelength range of CIS QDs.

As a comparison, SiO₂/Si wafers have been used as substrates to drop-cast QDs for optical spectroscopy measurement. Figure 4a and b describe the temporal evolution of PL spectra of close-packed CIS/ZnS QD solids on a SiO₂/Si substrate with an excitation power of about 300 μW in air and under vacuum, respectively. The PL spectra are clearly affected by the laser irradiation time and the environment. In air, the PL intensity initially decreases rapidly and then gradually stabilizes, as shown in Figure 4a. The overall PL intensity reduces to around 10% with an irradiation time of 3000 s. It is well known that the decreasing PL intensity of colloidal QDs is due to the photooxidation and the photobleaching. To separate photooxidation and photobleaching effects, a similar PL measurement was performed under vacuum as shown in Figure 4b. It can be seen that the PL intensity decreases in a slower manner compared with that in air. Without considering the photooxidation, the PL decay as a function of time is due to the photobleaching. The photobleaching can be explained by the fact that optically induced damage of oleylamine (OLA) introduces defect states at the surface of CIS/ZnS QDs, resulting in nonradiative channels in the recombination.

To further show the photooxidation-induced PL decay behavior, the time evolution of normalized PL intensity with
different excitation powers under air and vacuum is shown in Figure 4c and d, respectively. In general, the higher the excitation power, the faster the decay of the PL intensity both in air and under vacuum. For the sample exposed in air, the PL decay rate increases with increasing the excitation power up to 120 μW and then saturates, but the decay rate in the vacuum

Figure 2. Wide-field PL images of CIS QDs on a MD by moving the pumping laser spot crossing the edge of the MD close to the edge (a), on the edge (b), and away from the edge (c). The pumping laser was filtered when the images were captured. (d) Magnitude of the electric field distribution of a cavity mode at 669.75 nm of the MD, which was simulated by a finite-difference time-domain method with the following parameters: r = 75 μm, n_{SiO2} = 1.456, mesh = 25 nm. The inset shows an enlarged pattern of the mode distribution.

Figure 3. (a and c) PL mapping of CIS/ZnS QDs on MDs with a scanning area of 80 × 80 μm². The color bars are in log scale. (b and d) Typical PL spectra of close-packed CIS QD solids at RT and at 20 K. The black dashed lines are the PL spectra of QDs on the edge of the MD, and the red solid lines are PL spectra collected far away from the MD. The inset in (b) shows the normalized PL spectra of QDs.
increases monotonically. At a fixed value of excitation power, the PL intensity in air decreases faster than that under vacuum, as discussed above. For example, at an excitation power of 300 μW, the PL intensity drops more than 80% in the first 400 s and continues to drop with a slower rate within the rest of the measuring time. While under vacuum, the PL intensity decreases by around 30% after 400 s, and no clear saturation can be observed within the measurement time of about 3000 s.

Similarly, time-dependent PL measurement has been performed on the edge of MDs where the PL emission is greatly enhanced, as shown in Figure 5, at different atmospheric environments (air or vacuum) and different temperatures (RT or 20 K). Comparing with Figure 4c for QDs exposed in air, a similar PL decay is observed at high excitation power. For instance, the PL intensity under an excitation power of 150 μW drops to 80% after exposure of about 200 s in air and then stabilizes. In vacuum or under low temperature as shown in...
quantum information processing.46 with a high excitation power on the edge of the MD with a laser wavelength at 532 nm. When the excitation laser illuminates the emission range of QDs from 550 to 850 nm and the excitation wavelength range including both the emission wavelength and the QD diameter, the cavity modes cover a broad range of QDs from 550 to 850 nm and the excitation wavelength at 532 nm. When the excitation laser illuminates with a high excitation power on the edge of the MD with a laser spot of 1–2 μm in diameter, photoluminescence can be observed from the QDs on the edge of the whole MD, as shown in Figure 2a. This confirms that the pumping laser couples to the modes in the cavity and circulating in the cavity, which excites all the QDs on the edge of the MD. Additionally, the emitted photons from QDs under the illuminating spot coupling with the WGMs of the MD are extracted more efficiently, resulting in an enhanced emission.

Another reason for the enhanced emission is the Purcell effect, where the QDs couple with the cavity modes in a weakly coupling regime.59 In this case, the spontaneous emission rate is enhanced by suppressing the luminescence lifetime of the QDs, which enhances the PL efficiency. Here, no clear increase was observed in the slope of the emission intensity versus the excitation intensity, which is due to the amplified spontaneous emission. This might be caused by the enhancement of photooxidation, photobleaching, and the Auger effect with increasing pumping power. With a reduced lifetime of the QDs, the fast Auger process (around 100 ps) could also be suppressed, resulting in an increased biexciton emission in the QDs.45 This needs to be confirmed with further measurement using ultrafast time-resolved PL measurement. Nevertheless, excitation power can be greatly reduced to achieve the same emission intensity with QDs on the edge of MDs, compared with that on SiO2/Si substrates. The excitation power can be reduced from 7.5 μW to 0.75 μW to achieve a luminescence intensity of 1 million counts/s with QDs on the MDs, as shown in Figure 5d. It can be seen that the rates of the photooxidation and photobleaching are greatly reduced because of the smaller excitation power in the vacuum at RT. One striking observation is that photoinduced degradation almost disappears with a small excitation power, while a relatively high emission intensity is obtained with an excitation power of 0.01 μW on MDs under vacuum at RT. The integrated PL intensity decreased only by 2.1% within the measurement time, as shown by inverted blue triangles in Figure 5d, which still can be improved. But for QDs on SiO2/Si substrates, an optically induced PL intensity decrease by 6.3% is observed for similar PL intensity since it requires a pumping power of 1 μW (green triangles in Figure 5d). No PL degradation under vacuum makes CIS/ZnS QDs very promising for high efficiency photon emission for quantum information processing.

The PL decay of CIS/ZnS QDs can be fitted by a biexponential form as $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$.50 Two time constants, $\tau_1$ and $\tau_2$, can be extracted by the fitting PL decay in Figures 4 and 5. Figure 6 summarizes the time constants of the decay of integrated PL intensity as a function of excitation power with continuous irradiation. The fast decay constant $\tau_1$ is in the range of 10 to 160 s, but $\tau_2$ varies in the range of 300 to 3700 s. At RT, both $\tau_1$ and $\tau_2$ in air are much smaller than those under vacuum, which means that oxygen in the air induces mainly the photooxidation and photobleaching as reported before.6 As mentioned before, the PL decays faster with increasing the excitation power. Here, the required excitation power on the MDs is much smaller than that on SiO2/Si substrates, where it has similar decay rates. This is due to the fact that the pumping laser is coupled to the cavity modes, which enhances the excitation efficiency and accelerates the photooxidation process in CIS QDs. It should be noticed by contrast that photoinduced degradation is surprisingly small with a low excitation power, which gives a very long decay time constant $\tau_2$. The time constants of PL decay of the sample at 20 K are much smaller than those under vacuum at RT, but are larger than those in air. This could be due to the fact that the OLA ligands are more easily damaged by the laser at low temperature, resulting in a faster PL decay.

Under a continuous illumination with a pumping laser, temporal evolution of the peak position and line width of PL spectra is very useful to understand the mechanism of photoinduced degradation.6,54 The variations of PL peak position and the full width at half-maximum (fwhm) as a function of irradiation time are depicted in Figure 7 and Figure 8, respectively. Figure 7a represents the PL peak shifting of QDs on the edge of an MD under different excitation power in air. Since the photodegradation here is an irreversible process for QDs, the laser spot was moved to different places for each measurement when the excitation power was changed. It can be seen that the starting peak position has a blue shift with an increase in the excitation power because of the state filling as reported before.7 At a low excitation power up to 7.5 μW, the peak position shows a quick blue shift first and then becomes...
stabilized as a function of exposure time. As the excitation power is further increased, the peak starts with a quick blue shift (less than 10 s) and then a slow red shift. In the end, when the excitation power is more than 120 μW, only a red shift can be observed within the time resolution in our measurement.

Because of the power-induced broadening, the line width of PL spectra increases generally with increasing excitation power without considering the time evolution, as shown in Figure 8a. In order to see the clear change of the PL spectra, we define \( \Delta \lambda \) and \( \Delta \text{fwhm} \) as the difference between the first spectrum and the rest of the spectra of the central emission peak.51 The \( \Delta \lambda \) and \( \Delta \text{fwhm} \) as a function of excitation time with different pumping powers are shown in Figure 7b–f and Figure 8b–f, respectively. The PL blue shifts at a low excitation power exposed in air can be explained by photooxidation. During the illumination exposed in air, the surface of CIS QDs is oxidized when oxygen diffuses through the passivating layer of ZnS, which reduces the average sizes and broadens the size distribution of QDs.22 The reduced sizes of QDs induce a blue shift because of the increased quantum confinement, which is similar to the results of CdSe/ZnS QDs.4 The broadened size distribution induces a line width increase of the PL spectra, as shown in Figure 8b for the low excitation power cases of less than 30 μW.

One possible reason for the red shift could be the thermal expansion of QDs because of the increased sample temperature at a high excitation power. However, a surprising phenomenon is that the line width decreases with excitation power over 120 μW, as shown in Figure 8a and b. The red shift and the line width narrowing at high excitation power cannot be simply attributed to thermal expansion. Additionally, the line width narrowing with increasing pumping power could be due to the enhanced coupling between QDs and MDs, similar to a lasering effect. But it can also be excluded that enhanced spontaneous emission should not be necessarily coming along with a red shift. Therefore, we ascribe the red shift with line width narrowing to the agglomeration of QDs induced by high-intensity laser illumination. Because of the laser-induced OLA ligand damage, the average distances between QDs are reduced after the agglomeration. The reduced average distance enhances the Förster resonant energy transfer (FRET) between different QDs. The enhanced FRET from small QDs to large ones gives a red shift and a narrowed line width of the PL spectrum. Similar results on both the blue shift and red shift can be observed for the QDs on SiO2/Si substrates, which are not as strong as the cases on the MDs, as shown in Figure 7c and Figure 8c. Although no line width narrowing can be observed of the QDs on SiO2/Si substrates, the line width broadening slows down when the excitation power is more than 150 μW (green triangles in Figure 8c). This strengthens the claim that MDs accelerate the photooxidation with a high excitation power.

While under vacuum, both a blue shift and a red shift still can be observed with increasing excitation power on SiO2/Si substrates and on MDs, as shown in Figure 7d and e. The photooxidation-induced blue shift can be ascribed to the absorption of oxygen on the QDs’ surface under vacuum. The overall peak changes on both the blue shift and red shift are much less than those in air. In particular, a red shift is only about 3 nm with QDs on MDs under vacuum, compared with a 10 nm shift in air. This confirms that oxygen in the air is a key issue in photooxidation and photobleaching. No line width narrowing has been observed, as shown in Figure 8d and e. It
should be emphasized that the PL peak shift and line width broadening can be negligible for QDs on MDs under vacuum with a small excitation power, for instance, 0.37 μW in Figures 7d and 8d. Figure 7f shows the PL peak shifts of QDs on the edge of MDs at 20 K as a function of time with different excitation powers, which are much less than those at RT (Figure 7b and d). As the excitation power increases up to 60 μW, the blue shifts become stronger, but get weaker with a further increase of excitation power. This can be explained in a similar way to the case under vacuum. The line widths do not change very much at 20 K (Figure 8f). In contrast to the case under vacuum at RT, the ligands of QDs are more easily damaged, resulting in faster photobleaching at 20 K. However, no strong red shift can be resolved even with a high excitation power, which shows that the QDs do not aggregate very much at low temperature.

To achieve a high fluorescence intensity, it is necessary to increase the pumping laser power. While due to the photooxidation and photobleaching, the PL intensity of CIS QDs drop-casted on SiO2/Si substrates decreases because of the low collection efficiency within the irradiation time both in air and under vacuum. This can be solved by drop-casting QDs on MDs under vacuum, where the photodegradation can be avoided with a low excitation power because of the Purcell effect and the enhanced collection efficiency. Thus, a proper surface protection of CIS QDs on MDs could be used to obtain enhanced PL emission without photodegradation.

**CONCLUSIONS**

In summary, the temporal evolution of PL properties of CIS/ZnS QDs has been systematically investigated by drop-casting QDs on SiO2/Si substrates and MDs in different atmospheric conditions. In air, strong photodegradation has been observed because of the photooxidation and photobleaching accompanying a PL peak blue shift and line width broadening at low excitation power. With a further increase in the excitation power, the PL spectra have shown a red shift and narrowing line width. This is due to the fact that the photoinduced ligand damage induces the agglomeration of QDs, which enhances FRET between different QDs. The enhanced FRET gives a red shift and a reduced line width. All these photobleaching effects are reduced under vacuum, which shows that oxygen plays an important role in the optically induced PL decay. When the QDs are drop-casted on MDs, the pumping laser and emitted photon energy couple with the cavity modes of the MDs. When the pumping laser couples with leaky modes in the MDs, the excitation efficiency is greatly enhanced, which accelerates photobleaching. When the QDs couple with cavity modes, however, the extraction efficiency is greatly improved because of the Purcell effect, resulting in a PL enhancement by 20 times at RT and by 35 times at 20 K. By taking advantages of enhanced PL extraction efficiency, photobleaching can be avoided with a small excitation power but with a relatively high PL intensity. Since photodegradation has been one of the major obstacles for using colloidal QDs in many applications, the highly efficient PL emission without photodegradation is very promising for utilizing CIS QDs as highly efficient photon emitters at RT. This paves a new way for CIS QDs to implement single-photon emission at RT for quantum information processing, instead of InAs QDs working at cryogenic temperature.49,52
METHODOLOGY

The CIS/ZnS QDs were synthesized by thermolysis with a mixture solution of copper(I) acetate, indium acetate, and oleylamine as ligands in a high boiling point solvent at 240 °C. The details of the synthesis process can be found in our previous reports.5–3 The CIS/ZnS core/shell QDs have diameters of about 2–5 nm and exhibit a tunable PL emission wavelength range from 500 to 900 nm.5–2 The CIS QD powder was dissolved in toluene assisted by ultrasonic vibration, then drop-casted on a SiO2/Si substrate or a silica MD.5–2 After the toluene was evaporated, the close-packed QD solids were formed.5–4 Steady-state PL spectra were measured by a conventional confocal micro-PL system, as shown in Figure 1. The CIS QD samples were placed in a coldfinger cryostat with an optical window for PL measurement, with which the sample temperature can be tuned from 20 K to RT. An excitation laser with a wavelength of 532 nm was focused on the samples by using a large numerical aperture objective with a spot size around 1–2 μm in diameter. The objective is mounted on a two-dimensional PZT-controlled stage for spatial mapping. The excitation laser power was measured after the objective above the samples. The fluorescence from CIS/ZnS QDs was collected by the same objective and then dispersed through a 0.55 m spectrometer. The PL spectrum was measured by a charge-coupled device camera cooled with liquid nitrogen. The inset of Figure 1 shows a scanning electron microscope (SEM) image of the cross section of a silica MD. The diameter of the MD is around 150 μm, which is marked in Figure 1. The WGMs are confined at the edge of the MD, which induces high quality factors. The quality factors in the wavelength range of QDs are about 106, by a transmission measurement using a tunable semiconductor laser around 635 nm.5–2

A 2D simulation has been performed to calculate the mode distribution for a microdisk with a radius of 75 μm using the finite-difference time-domain method. A refractive index of 1.456 was used, which should be suitable for the emission wavelength range of CIS QDs, from 600 to 800 nm. A magnetic dipole (corresponding to the TE mode) at 563 THz with a pulse width of 3.5 fs was put 74.2 μm away from the center. The simulation region is a square with a side length of 160 μm, and the mesh is 25 nm in both the x and y directions. A mode position at 669.75 nm has been selected to calculate the electromagnetic field distribution, which is close to the peak position of PL emission from QDs, as shown in Figure 2d.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Klimov, V. I.; McBranch, D. W. Femtosecond 1P-to-1S electron relaxation in strongly confined semiconductor nanocrystals. Phys. Rev. Lett. 1998, 80, 4028–4031.
(2) Klimov, V. I.; Mikhailovsky, A. A.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. Quantization of multiparticle Auger rates in semiconductor quantum dots. Science 2000, 287, 1011–1013.
(3) Guo, W.; Li, J.; Wang, Y.; Peng, X. Luminescent CdSe/CdS core/shell nanocrystals in dendron boxes: Superior chemical, photochemical and thermal stability. J. Am. Chem. Soc. 2003, 125, 3901–3909.
(4) van Sark, W.; Frederix, P.; Van den Heuvel, D.; Gerritsen, H.; Bol, A.; van Lingen, J.; Donega, C.; Meijerink, A. Photooxidation and photobleaching of single CdSe/ZnS quantum dots probed by room-temperature time-resolved spectroscopy. J. Phys. Chem. B 2001, 105, 8281–8284.
(5) Nazabal, A.; Wang, X.; Qu, L.; Yu, W.; Wang, Y.; Peng, X.; Xiao, M. Environmental effects on photoluminescence of highly luminescent CdSe and CdSe/ZnS core/shell nanocrystals in polymer thin films. J. Phys. Chem. B 2004, 108, 5507–5515.
(6) Chen, B.; Zhong, H.; Zhang, W.; Tan, Z.; Li, Y.; Yu, C.; Zhai, T.; Bando, Y.; Yang, S.; Zou, B. Highly emissive and color-tunable CuInS2-based colloidal semiconductor nanocrystals: Off-stoichiometry effects and improved electroluminescence performance. Adv. Funct. Mater. 2012, 22, 2081–2088.
(7) Li, Q.; Zhai, L.; Zou, C.; Huang, X.; Zhang, L.; Yang, Y.; Chen, X.; Huang, S. Wurtzite CuInS2 and CuInxGa1−xS2 nanoribbons: Synthesis, optical and photoelectric properties. Nanoscale 2013, 5, 1638–1648.
(8) Akdas, T.; Walter, J.; Segets, D.; Distaso, M.; Winter, B.; Birjadar, B.; Speicker, E.; Peukert, W. Investigation of the size-property relationship in CuInS2 quantum dots. Nanoscale 2015, 7, 18105–18118.
(9) Sun, Y.; Qian, C.; Peng, K.; Bai, Z.; Tang, J.; Zhao, Y.; Wu, S.; Ali, H.; Song, F.; Zhong, H.; et al. Recombination processes in CuInS2/ ZnS nanocrystals during steady-state photoluminescence. Appl. Phys. Lett. 2016, 108, 041106.
(10) Shabaev, A.; Mehli, M. J.; Efros, A. L. Energy band structure of CuInS2 and optical spectra of CuInS2 nanocrystals. Phys. Rev. B. Condens. Matter Mater. Phys. 2015, 92, 035431.
(11) Pan, Z.; Mora-Sero, I.; Shen, Q.; Zhang, H.; Li, Y.; Zhao, K.; Wang, J.; Zhong, X.; Bisquert, J. High efficiency quantum dot solar cells. J. Am. Chem. Soc. 2014, 136, 9203–9210.
(12) Zhao, K.; Pan, Z.; Mora-Sero, I.; Canovas, E.; Wang, H.; Song, Y.; Gong, X.; Wang, J.; Bonn, M.; Bisquert, J.; et al. Boosting power conversion efficiencies of quantum-dot-sensitized solar cells beyond 8% by recombination control. J. Am. Chem. Soc. 2015, 137, 5602–5609.
(13) Knowles, K. E.; Hartstein, K. H.; Kilburn, T. B.; Marchioro, A.; Nelsen, H. D.; Whitham, P. J.; Gamelin, D. R. Luminescent colloidal semiconductor nanocrystals containing copper: Synthesis, photophysics, and applications. Chem. Rev. 2016, 116, 10820.
(14) Li, L.; Pandey, A.; Werder, D. J.; Khanal, B. P.; Pietryga, J. M.; Klimov, V. I. Efficient synthesis of highly luminescent copper indium sulphide-based core/shell nanocrystals with surprisingly long-lived emission. J. Am. Chem. Soc. 2011, 133, 1176–1179.
(15) Leach, A. D. P.; Macdonald, J. E. Optoelectronic properties of CuInS2 nanocrystals and their origin. J. Phys. Chem. Lett. 2016, 7, 572–583.
(16) Whitham, P. J.; Marchioro, A.; Knowles, K. E.; Kilburn, T. B.; Reid, P. J.; Gamelin, D. R. Single-particle photoluminescence spectra, blinking, and delayed luminescence of colloidal CuInS2 nanocrystals. J. Phys. Chem. C 2016, 120, 17136–17142.
(17) Berends, A. C.; Rabouw, F. T.; Spoer, F. C. M.; Bladt, E.; Grozema, F. C.; Houtepen, A. J.; Siebbeles, L. D. A.; de Mello Donegá, C. Radiative and nonradiative recombination in CuInS2 nanocrystals.
and CuInS$_2$-based core/shell nanocrystals. J. Phys. Chem. Lett. 2016, 7, 3503−3509.

(11) Knowles, K. E.; Nelson, H. D.; Kilburn, T. B.; Gamelin, D. R. Singlet-triplet splittings in the luminescent excited states of colloidal Cu$_2$-CdSe, Cu$_2$-InP, and CuInS$_2$ nanocrystals: charge-transfer reconfigurations and self-trapped excitons. J. Am. Chem. Soc. 2015, 137, 13138−13147.

(12) Zhong, H.; Bai, Z.; Zou, B. Tuning the luminescence properties of colloidal I-III-VI semiconductor nanocrystals for optoelectronics and biotechnology applications. J. Phys. Chem. Lett. 2012, 3, 3167−3175.

(13) Shi, A.; Wang, X.; Meng, X.; Liu, X.; Li, H.; Zhao, J. Temperature-dependent photoluminescence of CuInS$_2$ quantum dots. J. Lumin. 2012, 132, 1819−1823.

(14) Omata, T.; Nose, K.; Kurimoto, K.; Kita, M. Electronic transition responsible for size-dependent photoluminescence of colloidal I-III-VI semiconductor nanocrystals. ACS Photonics 2015, 2, 6867−6872.

(15) Manner, V. W.; Koposov, A. Y.; Szymanski, P.; Klimov, V. I.; Sykora, M. Role of solvent-oxygen ion pairs in photooxidation of CdSe nanocrystal quantum dots. ACS Nano 2012, 6, 2371−2377.

(16) Zhang, A.; Dong, C.; Li, L.; Yin, J.; Liu, H.; Huang, X.; Ren, J. Non-blinking (Zn)CuInS$_2$/ZnS quantum dots prepared by in situ interfacial alloying approach. Sci. Rep. 2015, 5, 15227.

(17) Vahala, K. Optical microcavities. Nature 2003, 424, 839−846.

(18) 'Tang, J.; Geng, W.; Xu, X. Quantum interference induced photon blockade in a coupled single quantum dot-cavity system. Sci. Rep. 2015, 5, 9252.

(19) Zhang, Y.; Komarala, V. K.; Rodriguez, C.; Xiao, M. Controlling fluorescence intermittency of a single colloidal CdSe/ZnS quantum dot in a half cavity. Phys. Rev. B: Condens. Matter Mater. Phys. 2008, 78, 241301.

(20) Yang, J.; Heo, J.; Zhu, T.; Xu, J.; Topolancik, J.; Vollmer, F.; Ilic, R.; Bhattacharya, P. Enhanced photoluminescence from embedded PbSe colloidal quantum dots in silicon-based random photonic crystal microcavities. Appl. Phys. Lett. 2008, 92, 261110.

(21) Kahl, M.; Thomay, T.; Kohlhe, V.; Beha, K.; Merlein, J.; Hagner, M.; Halm, A.; Ziegler, J.; Nann, T.; Fedutik, Y.; et al. Colloidal quantum dots in all-dielectric high-Q pillar microcavities. Nano Lett. 2007, 7, 2897−2900.

(22) Gupta, S.; Waks, E. Spontaneous emission enhancement and saturable absorption of colloidal quantum dots coupled to photonic crystal cavity. Opt. Express 2013, 21, 29612−29619.

(23) Pattantyus-Abraham, A. G.; Qiao, H.; Shan, J.; Abel, K. A.; Gupta, S.; Waks, E. Spontaneous emission enhancement and biexciton emission above 300K from SnO$_2$ quantum dots. J. Appl. Phys. 2010, 107, 10469.

(24) Xu, X.; Williams, D.; Cleaver, J. Electrically pumped single-photon sources in lateral p-i-n junctions. Appl. Phys. Lett. 2004, 85, 3238.

(25) Wang, X.; Zhang, J.; Nazzal, A.; Xiao, M. Photo-oxidation-enhanced coupling in densely packed CdSe quantum-dot films. Appl. Phys. Lett. 2003, 83, 162.

(26) Pankiewicz, C.; de Assis, P.; Cabral, P.; Chaves, C.; de Araujo, E.; Paniago, R.; Guimaraes, P. Characterization of the dynamics of photoluminescence degradation in aqueous CdTe/CdS core-shell quantum dots. J. Fluoresc. 2015, 25, 1389−1395.

(27) Xu, X. L.; Toft, I.; Phillips, R. T.; Mar, J.; Hammura, K.; Williams, D. A. Plug and play single-photon sources. Appl. Phys. Lett. 2007, 90, 061103.

(28) Bao, Z.; Ji, W.; Han, D.; Chen, L.; Chen, B.; Shen, H.; Zou, B.; Zhong, H. Hydroxyl-terminated CaIn$_2$S$_3$ based quantum dots: Toward efficient and bright light emitting diodes. Chem. Mater. 2016, 28, 1085−1091.

(29) Pan, S. S.; Li, F. D.; Liu, Q. W.; Xu, S. C.; Luo, Y. Y.; Li, G. H. Strong localization induced anomalous temperature dependence exciton emission above 300K from SnO$_2$ quantum dots. J. Appl. Phys. 2015, 117, 173101.