Over 1000-Fold Enhancement of the Unidirectional Photoluminescence from a Microsphere-Cavity-Array-Array-Capped QD/PDMS Composite Film for Flexible Lighting and Displays

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The development of quantum dot (QD) composite films for lighting and displays is of great importance because of their exceptional mechanical flexibility, chemical stability, and optical tunability. Generally, QDs are attached to plasmonic nanostructures to enhance their photoluminescence (PL) emission. However, plasmonic QD composite films suffer from deteriorated inherent quantum yields and lower enhancement ratios due to variations in the refractive index and dielectricity in the composites. Herein, the use of a dielectric microsphere cavity is reported to realize over 1000-fold enhancement of the PL in CdSe/ZnS QD/polydimethylsiloxane films with a highly unidirectional emission angle of ≈9°. The field regulation by the optical whispering-gallery resonance and directional antenna effect at the microscale is revealed to interpret the PL enhancement mechanism. Additionally, the microsphere cavity allows for the enhancement of white-light emission in the RGB-QD hybrid composite film. The present work inspires a straightforward strategy for boosting the light efficiency in QD composite films, with promising applications in flexible lighting/display devices.

1. Introduction

Over the past decades, semiconductor quantum dots (QDs), especially binary II-VI compounds (e.g., CdSe), have been widely investigated and employed in light-emitting diodes, lasers, and biomarkers for displays and labeling[1–4] owing to their transparency, solution processability, broad absorption, high quantum yield (QY), tunable bandgap, and sharp emission spectrum.[5–9] In recent years, the development of flexible lighting/display devices has required the integration of luminescence materials on flexible substrates with the characteristics of luminescence properties and the capability to be stretched into arbitrary shapes.

A possible approach for this purpose is to incorporate QDs into a transparent composite film, in which the polymer matrix provides mechanical stretchability and chemical stabilization for the nanosized particles.[10–12] Unfortunately, assembling QDs into solid films from solvents generally results in agglomeration and complexation with polymer molecules, dramatically deteriorating the photoluminescence quantum yield (PLQY) due to nonradiative processes. The PL intensity of QDs embedded in a polymer matrix is acknowledged to be several times lower than that of colloidal QDs.[13–15] Moreover, the weakening of the out-coupling efficiency by the high refractive index polymer matrix further reduces the PL emission from the film.[16–18] These inherent drawbacks limit the development of QDs used in flexible devices for practical applications. The
regulation of the radiative properties of QDs was therefore investigated to meet this challenge.

Plasmonic metal nanostructures have demonstrated the capability to boost the PLQY through local enhancement of the incident optical field by modifying the radiative rate and increasing the out-coupling. A variety of metallic nanostructures, such as nanowires,[19] nanorods,[20,21] nanodiscs,[22] nanotriangular prisms,[23–26] nanoshells,[27,28] nanocubes,[29] nanocavities,[30,31] nanogrooves,[32] and nanopores[33] made of Au, Ag, Pt, etc., were employed. The enhancement ratios were in the range of 10–10^4 according to the specialized nanograting.[19–33] The complicated fabrication processes and great optical loss in plasmonic nanostructures lead to high manufacturing cost and energy consumption. Most importantly, the strategy of plasmonic enhancement using metallic nanostructures is highly sensitive to the geometry of the plasmonic nanostructure, resulting in either a large enhancement or quenching.[34,35] Therefore, improving the efficiency and stability of plasmonic enhancement is a major challenge for flexible nanodevices. The use of a photonic crystal structure with a designed bandgap is an alternative method for enhancing the PL emission by up to two orders of magnitude.[36–39] However, the problem of flexibility is not solved, and very few studies on the PL enhancement of QD/polymer composite films have been performed thus far. The narrow working spectral bands of plasmonic and photonic crystal nanostructures have restricted their applications in white-light lighting/display enhancement. A possible strategy to enhance the PL from a flexible multiple-QD composite film in the full visible band is therefore desirable.

A dielectric optical microcavity is a novel photonic device with the ability to modify the optical field in the full spectral band. The photonic state density is increased, and the interaction between photons and molecules/excitons/electrons is boosted.[40,41] A dielectric microsphere cavity is the simplest plasmonic microcavity attracting considerable interest. A microsphere cavity supports whispering-gallery modes (WGMs) with an ultrahigh Q-factor up to 10^12 for single nanoparticle/molecule/ion (interactions) transduction,[42,43] optical frequency comb generation,[44] ultralow-threshold lasing,[45] etc. Moreover, a microsphere is a natural Mie scatterer and solid immersion lens, which can generate photonic nanojets beyond Abbe’s diffraction limit and confine the scattering within a small divergence solid angle.[46,47] The low absorption and high transmission of dielectric microspheres in the visible spectrum guarantees high efficiency in wide-band light regulation. Microcavities have been applied in super-resolution imaging,[48–50] fluorescence/Raman scattering enhancement,[51,52] nanopatterning,[53,54] etc. These cavities have become a versatile tool for optical field regulation in nanophotonics.

In this work, we report a hybrid structure composed of a monolayer of a dielectric microsphere cavity array to enhance the PL emission from a flexible QD composite film with different central wavelengths. Here, a microsphere cavity with a diameter of tens of micrometers is capped onto a QD/polymer composite film. The experimental and theoretical results reveal that the microsphere cavity not only boosts the PLQY via regulation of the optical field in the vicinity of the microsphere but also effectively confines the PL as a unidirectional emission. The microsphere cavity array enhances the white-light emission from an RGB-QD hybrid composite film by up to three orders of magnitude. The high chemical stability and isolated enhancement channel further demonstrate the feasibility of using microsphere cavities in flexible applications.

2. Results and Discussion

2.1. Synthesis of Microsphere-Cavity-Array (MCA)-Capped QD/ Polydimethylsiloxane (PDMS) Composite Films

Commercial CdSe/ZnS core–shell QDs with sizes of 9–11 nm were selected as the luminescence sources, with emission peaks at 454 (blue), 548 (green), and 647 nm (red). PDMS was chosen as the polymer matrix due to its high transparency in the visible band, chemical stability, nontoxicity, and flame resistance. Most importantly, PDMS is a versatile building block in silicon-based photonics and optoelectronics owing to its high adsorption and compatibility with silicon substrates. Figure 1a shows the general approach for the fabrication of a single-QD composite film (see the Experimental Section). Images of the PL emission of the QD/PDMS composite films excited by UV light are shown in Figure 1b. The film thicknesses were 6–120 µm to realize good flexibility along with homogenous emission, as shown in Figure 1c. The PLQY was reduced by 50%–80% when the QDs were embedded in the PDMS film due to the variation in the ambient refractive index and complexation with polymer molecules. The MCA capping procedure is illustrated in Figure 1d, where the diameters of the high refractive index microspheres are 22, 39.5, and 55 µm. The microspheres were first sprayed onto the film and mechanically pressed by 3M low-adhesive tape several times, through which a microsphere monolayer was formed by van der Waals and electrostatic forces, as shown in Figure 1d. Afterward, the hybrid film was heated to 80 °C to achieve mechanical adhesion for practical use. Figure 1e shows top and cross-section view images of a hexagonally close-packed MCA capped on a QD/PDMS composite film. Figure 1f shows fluorescence images of films covered with an MCA and a single microsphere. The strong PL emission from the microsphere cavity was achieved using a low pumping power that cannot excite the QDs in the composite film without microspheres.

2.2. PL Enhancement by Single Microsphere Cavity (MC) Capping of QDs/PDMS Composite Films

A single MC was first employed to quantitatively estimate the enhancement ratio, as schematically shown in Figure 2a. The laser beam was focused by a 10x objective with NA = 0.25 onto the centre of the microsphere to achieve the maximum enhancement ratio. The backward scattering configuration was used to collect and direct the PL emission into the spectrometer. Figure 2b shows the PL emission from the QD/PDMS composite films with/without the MC. The PL intensity was boosted by the MC by approximately two orders of magnitude. The effect of the QD/PDMS composite film thickness on the enhancement ratio of intensity (ERI) is demonstrated in Figure 2c, in which the film thickness ranges from 6 to 120 µm. The ERI increased.
as the film thickness decreased. Our previous study validated that a thin luminescent layer is beneficial for achieving a high ERI due to the strong confinement and low scattering of excitation and emission photons. Moreover, the evolution of the ERI with the microsphere diameter is shown in Figure 2d, in which 22-, 39.5-, and 55-µm-diameter MCs were selected and the film thickness was set to 6.3, 11.3, and 17.4 µm. The 6.3-µm-thick QD/PDMS composite film capped with the 55-µm-diameter MC achieved the maximum ERI of 106 ± 19.

2.3. Optical WGM-Enhanced PL Emission in the MC

Although the mechanisms of microsphere-enhanced fluorescence were theoretically proposed in previous studies, the lack of experimental evidence has led to a limited understanding of the light manipulation by an MC in PL enhancement, especially for the QD/PDMS composite film. According to our pilot work, the contribution of focusing via the microsphere was negligible, as the intensity of the surface defect state-related PL emission was linear with the excitation intensity, different from the excitonic behavior in semiconductors. Therefore, the other two enhancement channels, i.e., the optical WGMs and the directional antenna effect, were sophisticatedly studied.

To observe the WGMs in the MC capped on the QD/PDMS composite film, a high objective (20×, NA 0.4) was employed to focus the excitation laser onto the edge of the MC to realize the maximum coupling efficiency in free space. Figure 3a demonstrates the typical WGMs of PL emission regulated by the microsphere diameter. The free spectral ranges (FSR) were measured in the PL spectra and followed a linear function of $1/D$ (microsphere diameter), as shown in Figure 3b. The microsphere diameters calculated using $\text{FSR} = (\lambda/2n\pi)^2$, where $n$ is the refractive index of the microsphere and $\lambda$ is the wavelength,
were 23, 39, and 55 µm, in good agreement with the manufacturer provided values. Figure 3c shows the Q-factors estimated by $\frac{\lambda}{\Delta\lambda}$, where $\Delta\lambda$ is the full width at half maximum (FWHM) of the emission peak of the WGM in Figure 3a. The Q-factor increased with increasing MC diameter due to the reduction in the radiative loss. The maximum Q-factor was ≈1500 for the 55-µm-diameter MC capped on the QD/PDMS composite film. The internal quantum efficiency is well acknowledged to be modulated by Purcell’s effect of optical WGMs, through which the spontaneous emission is enhanced.[41,60] The ERI due to WGMs, $\text{ERI}_{\text{WGM}}$, is therefore approximated by

$$\text{ERI}_{\text{WGM}} = \frac{3}{4\pi^2} \left(\frac{\lambda}{n}\right)^2 \left(\frac{Q}{V}\right)$$

where $Q$ and $V$ are the quality factor and mode volume of the MC, respectively. A numerical simulation of optical WGMs was performed. The numerically calculated Q-factor variation with the MC diameter was consistent with the experimental measurement, as shown in Figure 3c. An increased MC diameter linearly improved the Q-factor, thereby achieving a higher ERI in PL emission according to Equation (1). The theoretical prediction showed good agreement with the experimental result shown in Figure 2d. Figure 3d demonstrates the typical WGMs in an MC, where the evanescent waves are in the vicinity of the microsphere edge and boost the interaction with QDs in the PDMS film, leading to PL enhancement.

### 2.4. Directional Antenna Effect of the MCA for Realizing Unidirectional PL Emission

In addition to improving the internal quantum efficiency of QDs via optical WGMs, application of the directional antenna effect of the microsphere is a simple approach to further enhance the PL emission by increasing the collection efficiency, acting as a highly unidirectional solid immersion lens. To reveal the directional emission property, the angle-resolved PL (AR-PL) spectra were captured as shown in Figure 4a, where the excitation laser was perpendicularly incident on the MCA-capped QD/PDMS composite film, whereas the angle of the detector was varied. The intensity of the PL emission was highly
anisotropic and decreased with increasing detection angle, $\beta$. The inset of Figure 4a demonstrates the UV-illuminated QD/PDMS composite film with a patterned MCA. The brightness when facing the film surface was significantly higher than that when the tilt angle was greater than 30°. Figure 4b shows the normalized polar emission patterns from the composite films with/without an MCA. The PL emission intensity was isotropic for the bare film, whereas the unidirectional property appeared after capping with the MCA. The majority of the emission energy was confined within ±4.5°. The experimental AR-PL intensities were acquired as shown in Figure 4c. The corresponding $\text{ERI}_{\text{antenna}}$ due to the unidirectional emission can therefore be calculated by

\[
\text{ERI}_{\text{antenna}} = \frac{\int_{2\pi[1-\cos^{-1}(\text{NA})]} I_{\text{MCA}}(\theta) \, d\Omega \times \int_{2\pi[1-\cos^{-1}(\text{NA})]} I_{\text{bare}}(\theta) \, d\Omega}{\int_{2\pi[1-\cos^{-1}(\text{NA})]} I_{\text{MCA}}(\theta) \, d\Omega}
\]

where $I_{\text{MCA}}(\beta)$ and $I_{\text{bare}}(\beta)$ are the angle-dependent emission intensities with/without the MCA. The calculated $\text{ERI}_{\text{antenna}}$ values were 24-, 36-, and 52-fold for the 22-, 39.5-, and 55-μm-diameter MCAs, respectively.

To validate the PL emission within a narrow divergence angle, the directional antenna effect of the microsphere was numerically simulated as shown in Figure 4d. The PL emission was collected and confined by the microsphere, realizing directional emission. The numerical far-field emission patterns further confirmed that a larger microsphere was beneficial for directing the PL emission due to the higher equivalent NA of the microsphere lens. The theoretical $\text{ERI}_{\text{antenna}}$ can therefore be estimated by

\[
\text{ERI}_{\text{antenna}} = \frac{\int_{2\pi[1-\cos^{-1}(\text{NA})]} |E_{\text{MCA}}(\theta)|^2 \, d\Omega}{\int_{2\pi[1-\cos^{-1}(\text{NA})]} |E_{\text{bare}}(\theta)|^2 \, d\Omega}
\]

where $|E_{\text{MCA}}(\beta)|$ and $|E_{\text{bare}}(\beta)|$ are the angular vectors of the electric fields with/without the MCA in the far field. The calculated $\text{ERI}_{\text{antenna}}$ values were 24-, 40-, and 51-fold for the 22-, 39.5-, and 55-μm-diameter microspheres, in good agreement with the experimental results mentioned above.

To further reveal the contribution of unidirectional emission to PL enhancement, the effect of the objective NA on the total ERI was investigated as shown in the inset of Figure 4e. The total ERI was increased with objective NA reduction due to the highly directional emission achieved via 55-μm-diameter MCA capping of the QD/PDMS composite film. The maximum ERI was up to 1400-fold under the objective NA of 0.08, as shown in Figure 4e, where the unidirectional confinement contributes an

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**Figure 3.** Optical WGMs in an MC capped on a QD/PDMS composite film for PL enhancement. a) Spectra of WGM-regulated PL emission. b) Experimental and theoretical evolution of FSR with MC diameter. c) Experimental and numerical Q-factors of the MCs with various diameters. d) Electrical field of PL emission trapped in an MC for the WGMs.
ERI of ≈50. Therefore, the enhancement ratio from the Purcell's effect of optical WGMs can be estimated to be 1400/50 ≈ 28-fold. Under the optimized configuration, the ERIs for blue- and green-QD/PDMS composite films were also obtained, which were 420- and 2900-fold, respectively, as shown in Figure 4f,g. The distinctive ERIs from the red-QD/PDMS composite film...
was attributed to the different emission wavelengths resulting in variation of the optical WGMs and the directional antenna effect. The MCA produced an ERI of more than two orders of magnitude for the QD/PDMS composite film.

2.5. White-Light PL Emission and Flexibility of a Multi-QD/PDMS Composite Film Enhanced by a Patterned MCA

The broadband response of the MCA was beneficial for enhancing white-light emission. Trichrome QDs, including red (647 nm), green (548 nm), and blue (454 nm), were mixed and sealed in a PDMS film, as shown in the insert picture of Figure 5a. Considering the various ERIs of the QDs, the concentration ratio was set as 1:5:60 for the red, green, and blue QDs, to achieve white-light emission after MCA enhancement. Figure 5a shows the original and enhanced PL emission spectra in the visible band achieved by capping a 55-µm-diameter MCA. The chromaticity values moved from (0.23, 0.23) to (0.32, 0.39). The three emission peaks were simultaneously enhanced by 163-, 500-, and 1078-fold for the blue, green, and red colors, respectively. The difference in the ERIs was attributed to the emission re-absorption and resonant energy transfer from the wide bandgap QDs to the narrow ones, i.e., from blue QDs to green/red QDs and from green QDs to red QDs. Figure 5b presents photographs of a UV-illuminated trichrome QD-mixed composite film capped with MCAs patterned in four letters, for which bright unidirectional white-light emission was achieved.
An alternative white-light emission structure is presented in the insert picture of Figure 5c. The layer-by-layer (LBL) film structure weakened the interaction between different QDs. The concentration ratio in the LBL structure was set as 20:17:1 for red, green, and blue QDs. The thickness of each layer was fixed at 6 μm. Figure 5c illustrates the PL spectra of the LBL QD/PDMS composite films with/without 55-μm-diameter MCA capping and the corresponding chromaticity values. The ERIs were 3-, 12-, and 410-fold for the red, green, and blue QDs, respectively. The low ERIs for the green- and red-QD films were due to the two films being away from the focal point of the microsphere bottom (>6 μm), through which the contributions of the optical WGMs and directional antenna effect to PL enhancement were reduced. The chromaticity values of the PL emission without and with the MCA were (0.52, 0.47) and (0.31, 0.36), respectively, where the enhanced PL emission color was close to white light, as shown in Figure 5d. Compared with the abovementioned mixed QD/PDMS composite film, the color of the PL emission before MCA capping was tuned more easily due to the weakened interaction between different QDs. However, the maximum ERI was only achieved for the top QD/PDMS composite film contacting the MCA.

Considering the isolated enhancement unit and the high stiffness of the dielectric microsphere, the major advantage of the MCA-capped QD/PDMS composite film should be its high flexibility. Figure 5e,f shows the flexibility of the patterned MCA-capped QD/PDMS composite film adhered on the skin of a human’s finger. The MCA demonstrated the ability for giant PL enhancement on the curved surface and a significant unidirectional emission property. This array will be applied to a flexible luminescence device in the future for highly efficient unidirectional lighting/displays.

3. Conclusion
We have reported a straightforward and cost-effective strategy to boost and direct PL emission from a QD/PDMS composite film by applying a dielectric MCA. The PL enhancement ratio is up to three orders of magnitude, with a highly unidirectional emission angle of ≈9°. The contributions of the optical WGMs and directional antenna effect to the PL enhancement owing to Purcell’s effect and optical confinement have been experimentally and theoretically validated. The isolated unit of the MCA enhancer demonstrates the ability for PL enhancement in flexible QD/PDMS composite films. The low absorption of the MCA in the full visible spectrum is beneficial for achieving a giant enhancement in the bright white-light emission from the QD/PDMS composite film. The MCA holds promise as a full-color luminescence enhancer superior to the plasmonic nanostructure in QD-based flexible nanophotonic devices for energy-saving and highly directional lighting/displays.

4. Experimental Section

Synthesis of Color-Tunable QD/PDMS Composite Films: The synthesis procedure included the following steps: (1) Commercial CdSe/ZnS core–shell QDs with emission peaks at 647/548/454 nm and QYs of 50%/75%/70%, respectively, purchased from Suzhou Xingshuo Nanotech Co., Ltd., were diluted to a concentration of 5 mg mL⁻¹ in toluene. The solutions were ultrasonically dispersed for 5 min to prevent aggregation and sedimentation. (2) The PDMS Sylgard 184, purchased from Dow Corning, was mixed and stirred with the curing agent at a ratio of 10:1 by weight to obtain the PDMS colloidal solution. (3) The QD solution and the PDMS colloidal solution were mixed in a ratio of 1:6 and mechanically stirred for 10 min to obtain a homogeneous dispersion. (4) The mixed solution was placed in a vacuum chamber to remove the bubbles. (5) A glass substrate (40 mm × 40 mm × 0.5 mm) was ultrasonically cleaned in acetone, ethanol and deionized water for 5 min each. Then, the QD/PDMS colloidal solution was spin-coated onto the glass substrate at a rotation speed of 1000–8000 rpm for 40 s, where the film thickness was controlled by the rotation speed of the spin-coater. (6) The QD/PDMS colloidal solution coated on the glass substrate was baked at 80 °C for 10 min on a plate heater for solidification. (7) The QD/PDMS composite film was peeled off. The synthesis of LBL QDs/PDMS composite films was similar to the above procedure. Red-, green-, and blue-QD/PDMS composite films were bottom-up-prepared layer by layer using a concentration ratio of 20:17:1, achieving a multilayer structure as shown in Figure 5b.

Fabrication of MC/MCA-Capped QD/PDMS Composite Film Structures: The refractive index of the high refractive index microsphere purchased from Microsphere-Nanospheres was 1.95 in the visible band. The microsphere was composed of BaTiO3, BaO, TiO2, SiO2, and Li2O with a specific ratio. A single MC was directly formed on the film by drop coating.[49] The monolayered MCA capping was performed as follows: (1) The dried microspheres were mechanically sprayed on the film. The microspheres were adhered onto the film surface by electrostatic and van der Waals forces. (2) The microspheres unattached to the film surface were removed by pressing 3M low-adhesive tape on the surface and peeling it off. (3) The above step was repeated several times until a monolayer microsphere array was formed, as shown in Figure 1. The patterned MCA capping followed the abovementioned procedure, and a mask with the letters B, J, U, and T was applied on the QD/PDMS composite film before spraying microspheres.

Acquisition of PL Spectra: The PL spectra were measured by a house-made micro-PL spectroscopy. A continuous-wave (CW) laser beam at 409 nm with an excitation power of 0.1 µW was focused onto a single MC by a 10x objective (Olympus, NA 0.25) and onto an MCA by a 3x objective (Thorlabs, NA 0.08). The backward scattering configuration was employed, in which the PL emission was collected by the same objective, filtered by an edge filter and directed into a spectrometer (Horiba iHR550) for spectral analysis. The integration time for signal acquisition was set in the range of 0.05–5 s. The AR-PL spectra were measured by an angle-resolved spectral analyzer (IdeaOptics R1, China). The raw beam of a 409 nm CW laser with a diameter of 7 mm was used as the excitation source, for which the power arriving at the sample surface was 10 mW. The increment of the detection angle from 0° to 90° was set to 1°.

Microscopic Imaging and Film Thickness Measurement: The optical images of the microsphere array in Figure 1e were captured by a scanning laser confocal microscope (Olympus LEX-OLS-3100) for top view and by a scanning electron microscope (FEI Quanta 650) for cross-section view. Fluorescence microscopy images were acquired by an Olympus BX-51 under reflection mode, where a 100 W mercury lamp filtered by a low-pass filter to realize UV illumination was used as the excitation source. The thickness of the QD/PDMS composite film was measured by a stylus profilometer (Veeco Dektak 150).

CIE Chromaticity Values of the PL Spectrum: The CIE chromaticity values of the PL spectrum for the RGB-QD/PDMS composite film were calculated by multiplying the emission spectra by the standard color matching functions (CIE standard 1964). The tristimulus values (X, Y, and Z) were obtained by integrating the calculated values over the entire visible spectrum. The CIE chromaticity values (x, y) were thereby calculated as follows[61]

\[
\begin{align*}
    x &= \frac{X}{X + Y + Z} \\
    y &= \frac{Y}{X + Y + Z}
\end{align*}
\]
Numerical Simulation: Numerical simulation of the electromagnetic field was performed by a finite element method (FEM) algorithm using COMSOL Multiphysics (licensed by COMSOL Co., Ltd.). The electric field distribution and far-field emission pattern could be numerically simulated for analysis. A 2D model was developed to understand the optical WGMs and directional antenna effect of the microsphere on the PL enhancement. The refractive indexes of the PDMS film and microspheres were set as 1.41 and 1.95, respectively. Perfectly matched layers and periodic boundary conditions were applied to the model. Mode analysis was used to simulate the WGMs in the MC. For the directional antenna effect, an electrical dipole was located at the microsphere bottom to understand the manipulation of light scattered by the MC. The experiment involving human subject has been performed with the full, informed consent of the volunteer, who is also the first author of the manuscript.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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