

Large-Area Multicolor Emissive Patterns of Quantum Dot–Polymer Films via Targeted Recovery of Emission Signature

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A facile one-step fabrication of large-area multicolored emissive photopatterns in mixed quantum dot-polymer films is demonstrated. This is in sharp contrast to the current photopatterning approaches that utilize only a single quantum dot (QD) component for single-color patterns. Strategies are presented that allow for either selective or collective modification of specific predetermined photoluminescent peaks of green and red QDs during photopattern development. These strategies yield novel patterns and allow for unprecedented control over how the color contrast of the photopattern evolves with continuous light illumination. These results clearly show that the evolution of the emission spectra of a multicolor mixed QD-polymer film can be readily tailored during pattern development, either by careful selection of the excitation wavelength or through combinations of controllably unstable and stable QDs with different recovery rates. Notably, these strategies are simple, fast, and robust, yielding high-resolution microscopic patterns over large areas (up to fractions of a cm²). Furthermore, the flexibility and capabilities of these strategies greatly expand the potential applications of multicolor emissive photopatterns, particularly in the areas of sensing, imaging, and lasing systems where it is important to exert delicate control over the intensity of selected colors within specific spatial regions.

inkjet printing,^[11] self-assembly,^[12] transfer printing,^[13] and template-based infiltration,^[14] with techniques like inkjet printing having the potential for large-scale patterning of nanostructures.^[15,16] However, typically material and manufacturing restrictions limit or prohibit large-scale physical patterning of nanoparticles and nanostructures. In contrast, techniques such as spectral photopatterning use light to intrinsically modify the emission of photoluminescent components. This procedure produces a photoluminescence (PL) pattern without adding or removing material, substantially reducing the complexity of the patterning procedure.

Quantum dot (QD) nanostructures are good candidates for such emissive photopatterning because they exhibit size-dependent absorption and emission that can be readily tuned over much of the visible spectrum due to the quantum confinement effect.^[17,18] This tunability makes it possible to develop photopatterns in the visible range with colors ranging from blue to red. Single-color photopatterning

has been demonstrated using a single type of quantum dot, with approaches including degradation of a photoluminescence quenching agent,^[19] photoactivation of QDs,^[20] photooxidation of QDs,^[21] and photoenhancement through the passivation of surface traps or photoionization.^[22] Recently, multicolor photopatterning was demonstrated using the blue-shift in emission that accompanies the photoactivation of QDs, but the color contrast (CC) required nearly two weeks to develop.^[20] These initial demonstrations hint at the potential of photopatterning by showing that high-contrast photoluminescence patterns can be developed.

However, using only a single active optical material component severely limits the spectral signature and practical utilities of a photopattern. Furthermore, restricting the photopattern system to one PL component prohibits the use of variations in QD emission dynamics (exhibited by QDs of different size and stability) to develop photopatterns that evolve in unique ways and display more complex multi-peak emission profiles. These restrictions severely hinder the potential of emissive photopatterning in the areas of sensing, LED lighting,^[23] displays,^[24] and labeling and imaging^[25] where the presence and control of multi-peak emission are highly advantageous.

1. Introduction

Patterning optical materials is often utilized to develop photonic systems for lasers,^[1–3] diffraction gratings,^[4] waveguides,^[5] and light-emitting diodes (LEDs).^[6,7] Typically, nanoscale and microscale patterning are achieved via physical or chemical modification of materials using a variety of techniques^[8] including optical and electron beam lithographies,^[9] capillary transfer lithography,^[10]

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The limitations encountered by single PL component photopattern systems can be overcome by using a mixture of emission components, opening up possibilities to create next-generation photopatterns that exhibit complex spectral profiles. To date, limited multicolor photopatterning has been demonstrated using a combination of QD and dye, with photobleaching of the dye providing the color contrast.^[26] However, pure QD mixtures are a more versatile alternative than the QD-dye mixture for a number of reasons. First, QDs exhibit size-dependent optical absorption and emission over the optical wavelength region.^[17,18] This feature provides flexibility in terms of color output. Second, the size-dependent absorption provides a route for selective or collective modification of specific QDs within the mixture via excitation wavelength since the recovery of emission is proportional to the absorbance at the excitation wavelength. For example, the difference of absorbance between red and green QDs at a specific wavelength leads to different recovery rates which can be used to tune color contrast. Finally, QDs can be synthesized to exhibit stable emission intensity or synthesized to display an increase, decrease, or shift in emission when exposed to light (dynamic emission behavior is often attributed to photoactivation,^[27] photoelectrification,^[28] or photoneutralization^[29]). The capability to engineer photoluminescence stability or instability into the QD provides a promising route for selective modification of the unstable QD color while the stable QD color remains unchanged.

Herein, we report how the dynamics of QD emission recovery can be exploited to control the development of multi-peak photoluminescence patterns in mixed QD-polymer films. These emissive patterns can span large areas (up to fractions

of a cm^2) and develop over relatively short time scales (often less than 1 h). Specifically, two general and robust strategies for fabricating photoluminescent photopatterns in mixed color QD films are demonstrated. These strategies stem from judicious consideration of factors such as development wavelength and the stability/instability of QD emission, which have been largely overlooked in previous photopatterning studies. The first strategy allows for the modification of multiple emissive bands concurrently (collective recovery), while the second strategy involves the modification of an individual emissive band (selective recovery) during the development process. Since the spectral signature controls the color appearance, these strategies allow for the fabrication of single or multicolor photopatterns depending upon the employed development strategy.

2. Results and Discussion

2.1. Photopatterning: General Strategy

Figure 1 depicts the general procedure for photopatterning the QD-polymer films. In this strategy, both decay and recovery of photoluminescence are utilized to fabricate the photopatterns. In the first step the QD-polymer film is deposited onto a wafer (step 1). The film is then exposed to light for approximately two minutes to reduce the QD emission to approximately its minimum value (step 2). A photomask that is opaque to the development light is then placed on the film to protect specific areas of the film from direct exposure to the development light (step 3). The sample is then exposed to light that causes the

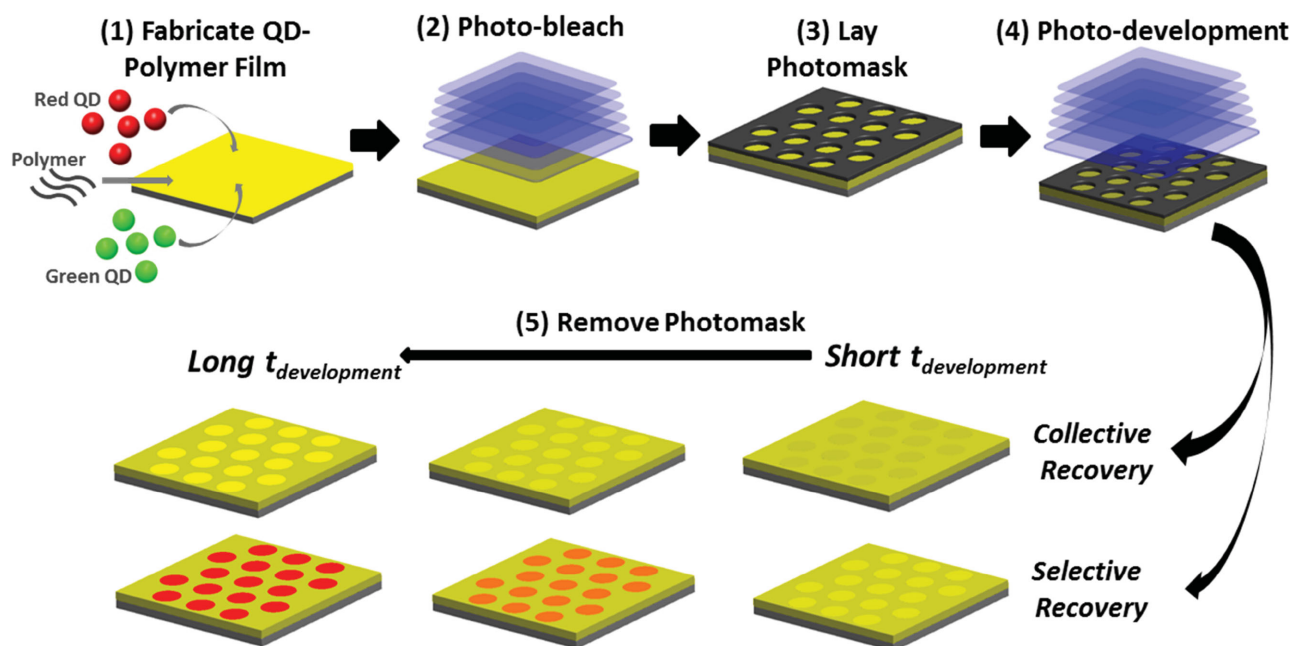


Figure 1. The utilization of both decay and recovery of emission to create photopatterns. 1) A mixture of polymer, red QD, and green QD are deposited onto a wafer. 2) The film is exposed to light to reduce the QD emission to approximately its minimum value. 3) A photomask that is opaque to the exposure light is then placed on the film to protect specific areas of the film from direct exposure to the development light. 4) The sample is then exposed to light causing the emission of the exposed areas of the film to recover. 5) The photomask is removed, yielding a non-physical photoluminescence photopattern. The color of the photopattern depends on the color of QDs and the approach (selective or collective recovery) used to develop the pattern.

emission in the unprotected areas of the film to recover (step 4) (Figure 1). The color appearance of the photopattern depends on the stability type of QDs and the wavelength of development light.

2.2. Film Characteristics: Physical and Optical

Two general types of core-shell Cd-based QDs were used to fabricate photopatterns: one type that maintains the emission intensity when exposed to light (stable QDs) and another type that exhibits a change in the emission intensity (reduction or increase) when exposed to light (unstable QDs). Stable emission was imparted to the stable QDs using a synthesis approach that yields an alloyed core-shell interface (i.e., CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y QD composition, see Experimental Section), which has been shown to render improved photostability.^[30] The improvement in photostability is attributed to a reduction in crystallographic lattice mismatch at the interface which reduces the lattice strain and in turn the number of defect sites.^[31] Furthermore, a smeared potential over the entire QD can suppress the Auger recombination processes, a common obstacle for stable, high quantum yield QDs.^[32,33] Unstable emission was engineered into the unstable QDs using a synthesis approach that imparts a sharp core-shell interface (i.e., CdSe/ZnS QD composition, see Experimental Section), which can yield a metastable energetic interface state that is susceptible to external factors such as temperature and light exposure.^[31]

The QD-polymer films studied here are composed of a mixture of red QDs (614 nm emission) and green QDs (512 or 541 nm emission) (Figure 2a and inset). The difference in emission positions are due to the degree of quantum confinement of the exciton, which is controlled by the size and composition of the QDs.^[17] Films with minimized agglomeration of the QDs in PMMA matrix were fabricated by utilizing hexadecylamine or butylamine as the primary ligand (small amounts of oleic acid still present), which interact favorably with PMMA and share a common solvent (i.e., toluene) with PMMA. Films typically had a thickness near 800 nm with a QD loading (volume fraction) of $\approx 3\%$. The ratio of red-to-green QDs for the unstable red-green QD-polymer films was $\approx 1:3$. The QD-polymer films with the mixture of unstable red and stable green QDs had a red-to-green ratio closer to (200:1) since the emission of the stable green QDs is much higher than the unstable red QDs. The films typically were smooth and uniform with minor surface depletions below 10 nm and occasional deeper (>100 nm) holes caused by solvent evaporation during drying (Figure S1, Supporting Information). The overall R_q surface microroughness was near 6 ± 2 nm over a $50 \mu\text{m}^2$ area, which confirms a smooth and uniform surface morphology.^[34] The films also exhibited uniform bright photoluminescence indicating the uniform distribution of QDs throughout the entire film (Figure S2, Supporting Information).

2.3. Emission Dynamics: Decay-to-Recovery Processes

The QDs exhibit an emission that can fluctuate in response to light exposure, where the rate and magnitude of emission

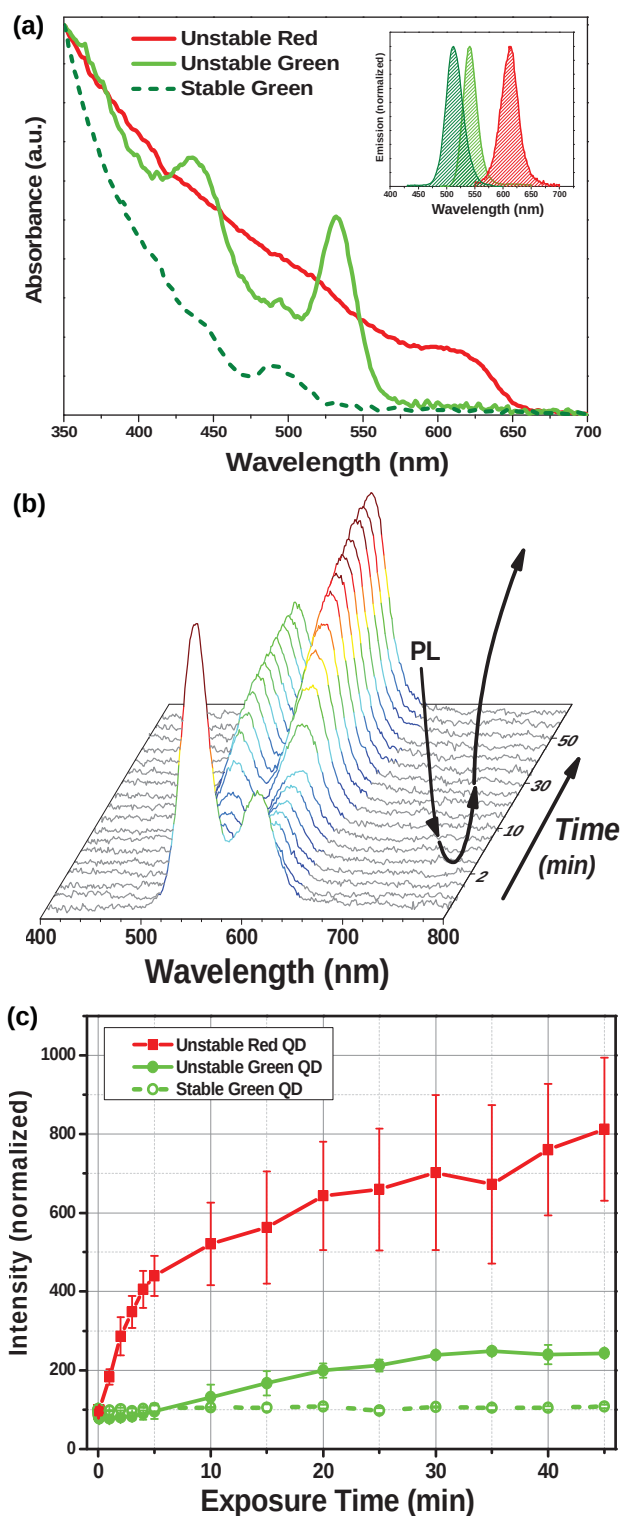


Figure 2. Photopatterning is performed on QD-polymer films with a mixture of green and red QDs that have a) different absorbance profiles and emission positions (inset). b) A waterfall plot of the PL shows the changes in intensity of unstable red and green QD photoluminescence that occurs over a period of 45 min of continuous light exposure. c) Gaussian fitting of the emission peaks provides information about how emission intensity evolves during continuous light exposure (normalized to the intensity at 0 min).

fluctuation depends on the wavelength of exposure light and whether the QD was synthesized to be stable or unstable under the excitation light. By carefully considering these parameters, it is possible to fabricate photopatterns with multiple emission peaks and to control the relative intensities of emission bands during the photopattern development process. Controlling the emission peaks can occur either through selective recovery of a specific band within the pattern (red emission increases, green emission does not) or through collective recovery of multiple bands within the pattern (red and green emission both increase). In order to effectively control the intensity of each emission band during photopattern development, it is necessary to understand how the emission changes in response to the wavelength of development light.

Examination of the emission spectra of the unstable red and unstable green QDs upon light exposure shows that the PL intensity exhibits large changes in intensity over a period of 45 min (Figure 2b). Fitting of the photoluminescence peaks for the three types of QDs used in this study (stable green alloyed $\text{CdSe/Cd}_{1-x}\text{Zn}_x\text{Se}_{1-y}\text{S}_y$, and unstable green and red CdSe/ZnS) shows that the dynamic behavior of emission involves two steps, where the first step is a quick decay within the first seconds/minutes of light exposure and the second step is a slower recovery of emission over a period of 45 min or more of light exposure (Figure 2c and Figure S3, Supporting Information). This behavior has been observed in QD systems exposed to low-humidity oxygen environments.^[35] The initial fast decay could be caused by the photooxidation of the diethylzinc precursor which is sensitive to oxygen. The recovery of emission for the unstable QDs is likely due to further photooxidation of the QD surface since the emission exhibits a blue-shift during the recovery period (11 nm for unstable green CdSe/ZnS QD and 3 nm for unstable red CdSe/ZnS QD) (Figure S4, Supporting Information).^[27,36] The stable green QDs display a small red-shift of emission (1–2 nm), which could result from annealing of the core-shell interface which reduces the quantum confinement by smearing the exciton wavefunction.^[30,37,38]

The rate of decay and recovery and the plateau recovery value depends on the type of QD (stable alloyed core-shell interface or unstable sharp core-shell interface). For example, when unstable green QDs are exposed to 470 nm 28 mW light they exhibit a rapid decay of $\approx 25\%$ followed by a recovery plateau value of $\approx 250\%$, whereas the unstable red QDs show values of 10% and 800%, respectively. The stable green QDs show modest fluctuations of intensity (10%) over the 45 min of exposure.

The difference in decay rates and recovery plateaus between red and green QDs is attributed to the differences in the number of defects in the QD, the amount of absorbance at the pumping wavelength, and the optical absorbance cross-sections. The unstable red QDs likely exhibit a larger recovery of PL than their green counterpart because they have higher absorbance than green QDs at any particular wavelength, which is due to their higher optical absorbance cross-section arising from their larger physical size.^[39] These effects cause the red QDs to absorb more photons than the green QDs, leading to an increased probability for PL recovery to occur.

2.4. Photopatterning Process and Characterization

The photopatterning process is exemplified by fabricating a GT photopattern on an unstable red-stable green QD-polymer film (Figure 3). The light used to develop the pattern ("development" light) was selected to fall within the absorbance range of both the red and green QDs (470 nm, 30.5 mW). Photoluminescence imaging shows a yellow emission pattern (exposed region) surrounded by a green region (protected region) (Figure 3a). The yellow color results from the recovery of red QD emission mixing with the stable green QD emission. The pattern corresponds closely in shape and size to the original photomask. Bright field imaging, dark field imaging, and AFM scanning of photopatterned films show no changes in film surface characteristics that could account for the observed PL patterns, indicating that these patterns are induced by intrinsic modification of the emission pathways in the QDs, not changes in the physical morphology of the film (Figure S5,S6,S7, Supporting Information).

Quantitative spectral evaluation of emission from different regions of the photopattern is provided by hyperspectral scanning, which tracks the intensity of specific red, green, and blue wavelengths over the sample, as noted by the circles in Figure 3b.^[40,41] The hyperspectral map shows a pattern with similar shape, size, and pattern to that observed via photoluminescence imaging. PL spectra collected from points inside and outside the photopatterned area confirms the increase in red emission due to the light exposure (Figure 3c).

2.5. Photopatterning: Collective Recovery and Selective Recovery

This work focuses on how the photopattern process can be altered to control how the spectral properties of the photopattern evolve during the development process (Figure 1, step 4). Specifically, we examine how to selectively recover a single color or collectively recover multiple colors in the photopattern. Since the ratio of emission bands controls the overall color, selective recovery and collective recovery can cause the color of the photopattern to evolve differently during the development process (Figure 1, step 5). For example, for a mixture of red and green QDs, collective recovery will increase the intensity but not change the color of the photopattern since the relative intensity between green and red emission remains nearly equal during the development. On the other hand, selective recovery of red QDs in a mixed red-green QD film produces a photopattern that becomes redder when developed.

2.5.1. Collective Recovery (C)

The first and most simple photopatterning method for QD-polymer films with a mixture of QDs is collective recovery. This strategy uses a mixture of unstable red and unstable green QDs (both QDs exhibit recovery of their emission) and a development wavelength that falls within the absorbance of each QD ($\lambda_{\text{devel}} < \lambda_{1s,\text{QD1,QD2}}$) where λ_{1s} represents the lowest energy transition. This strategy is useful when trying to develop a photopattern where the exposed region of the photopattern has

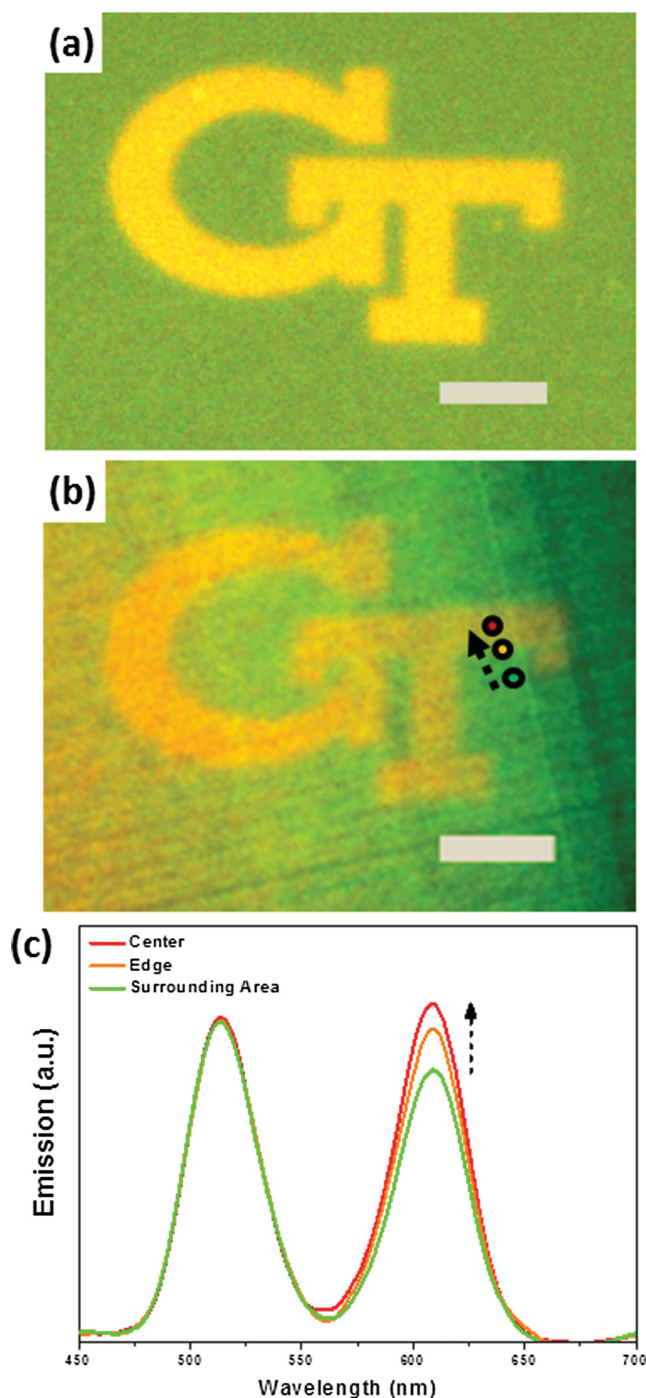


Figure 3. The development of a photopattern in a QD-polymer film (20 min, 470 nm and 30.5 mW) is monitored via PL imaging and hyperspectral mapping. a) PL imaging and b) hyperspectral scanning clearly show the presence of a photopattern made on a stable green-unstable red QD-polymer film, which corresponds closely in shape and size to the photomask. Areas of the film exposed to development light exhibit stronger emission and a more yellow color than areas of the pattern not exposed to development light. c) PL spectra were collected from three regions (green, yellow, and red circles from (b) to quantitatively evaluate the emission from different areas of the pattern. The results confirm the recovery of only red emission. All scale bars are 50 μm .

a higher intensity but similar spectral signature (color) to the protected region of the film. In other words, the exposed and protected regions maintain the same relative intensity between emission peaks (i.e., green vs red) but both increase for the duration of pattern development.

Collective recovery was demonstrated by developing the photopattern with 350 nm light at 2.5 mW, which significantly exceeds the bandgap energy of both the green and red QDs, and provides near-equal recovery of the red and green emission intensity during early development (Figure 4a). The similar recovery rate for the red and green QDs is likely due to the generation of hot excitons (a result of the high energy development light). Hot excitons have a higher probability of entering a surface trap state than a lower energy exciton,^[42] and therefore potentially initiate the recovery mechanism. Additional factors that determine the relative rate of recovery between the red and green QDs include the amount of light absorbed by each QD, which depends on the absorbance profile of each QD and the relative concentration of each QD in the film. The photopattern closely corresponds in shape and size to the photomask and covers a surface area of many 100 μm (Figures S8,S9, Supporting Information). In addition, the size of the pattern repeat unit is 5–10 times smaller than those from previous studies that used a nonlaser exposure source, demonstrating an excellent pattern resolution.^[27]

As the photopattern develops, both the unstable red and unstable green QDs experience a recovery of emission in the regions exposed to light. Photoluminescence imaging and hyperspectral scanning show that longer exposure times lead to more recovery, yielding photopatterns with greater intensity contrast (Figure 4b,c). PL imaging over a large area suggests uniformity of the photopattern over areas approaching mm^2 (Figure 4d). Spectra from the exposed and protected regions of the photopattern are selected from the hyperspectral scan during the course of development, revealing that the exposed regions exhibit more intense emission than the protected regions, and that the emission increases with longer development times (Figure 4e). Gaussian peak fitting (and normalization) of the red and green emission peaks from the exposed and protected regions of the pattern confirms these observations and shows that the photoluminescence recovery is similar for both colors (Figure 4f). It is worth mentioning that the protected regions also exhibit PL recovery, which is due to proximity effects during pattern development (i.e., the development light enters the protected regions). The proximity effect reduces pattern contrast and is an ongoing challenge in photopatterning.

Collective or selective recovery can be verified by tracking the intensity of red emission and green emission separately using a hyperspectral scan. For example, hyperspectral tracking of both the red and green peaks shows a clear photopattern that appears yellow due to the combination of red and green intensity (Figure 5a). However, a pattern is also present when tracking either the red PL peak only or the green PL peak only (Figure 5b,c). The presence of a pattern for both the red and green emission peaks indicates that the photopattern is a result of collective recovery (i.e., recovery of both colors).

Differences in color between the exposed regions and protected regions of the photopattern can be evaluated by

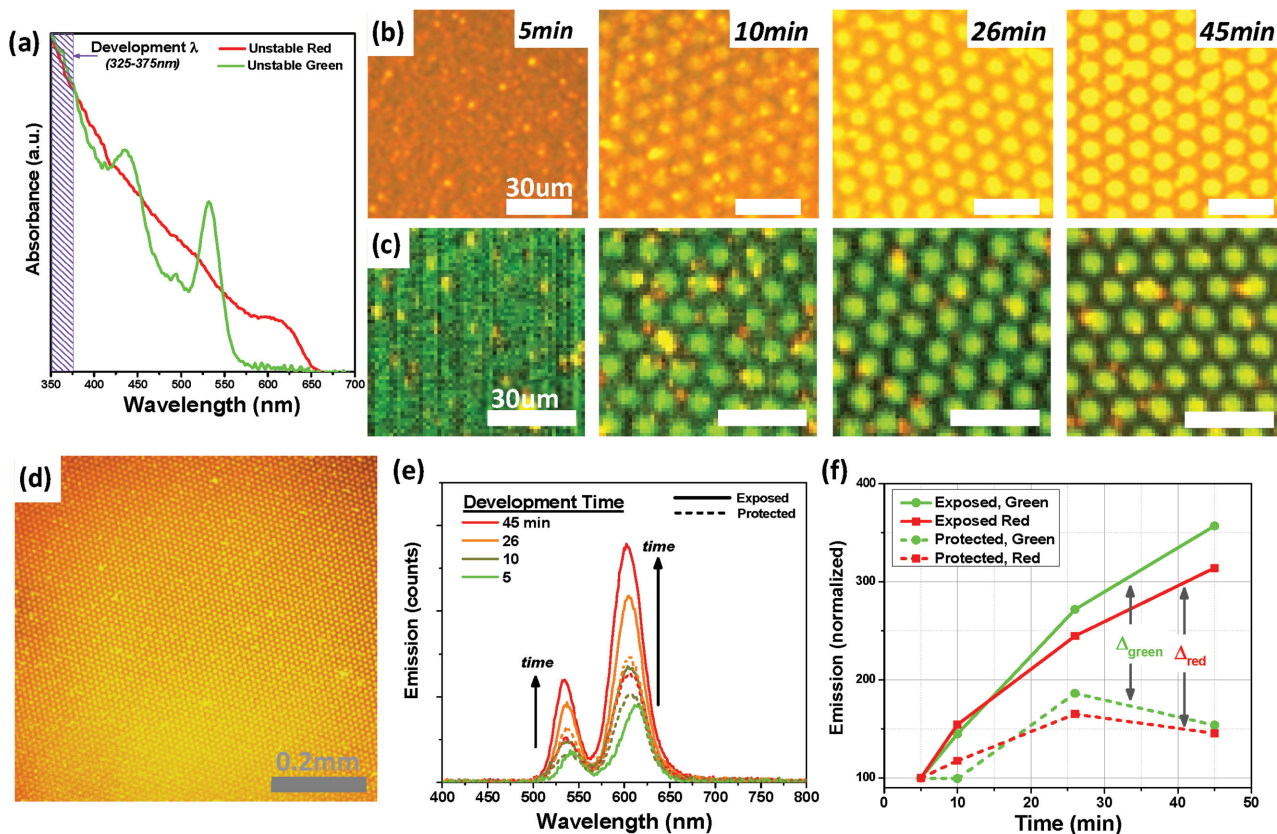


Figure 4. Collective recovery via near-equal recovery rates method (C): Unstable red and unstable green QDs are used to develop a photopattern where both emission peaks recover at a similar rate (i.e., green vs red) for the duration of pattern development. a) Near-equal recovery was achieved by developing the pattern with high energy light of 350 nm and 2.5 mW ($\lambda_{\text{development}} \ll \lambda_{1s,\text{green}}$ and $\lambda_{1s,\text{red}}$) (absorbance normalized at 350 nm for clarity). b) PL imaging and c) hyperspectral scanning show that longer exposure times lead to more recovery, yielding photopatterns with greater intensity contrast (all scale bars are 30 μm). PL imaging of the pattern (d) demonstrating the large-area uniformity of the pattern. PL spectra from the (e) exposed and protected regions of the film show that the exposed regions have higher intensity than the protected regions. f) Peak fitting (normalized) shows a near equal increase in emission for the red and green emission peaks.

examining the color contrast (CC), where CC at a specific time (t) is defined as follows

$$CC(t) = |\Delta_{\text{green}} - \Delta_{\text{red}}| \left(\Delta_{\text{color}} = I_{\text{norm}}^{\text{exposed}} - I_{\text{norm}}^{\text{protected}} \right) \quad (1)$$

Small color contrast values indicate that the red and green QDs in the exposed region of the film underwent a similar amount of recovery, which means that the exposed region will have a similar color to the protected region of the film (since the ratio between red and green intensity does not change). In contrast, large CC values imply that the red and green QDs experienced a different amount of recovery in the exposed region of the film, suggesting that the exposed region will have a different color than the protected region of the film due to the change in the ratio between red and green intensity. These statements are summarized below, assuming equal red and green intensity initially:

$$\text{Small CC} \rightarrow \text{Color}_{\text{exposed}} \sim \text{Color}_{\text{protected}} \rightarrow \text{single color pattern} \quad (2)$$

$$\text{Large CC} \rightarrow \text{Color}_{\text{exposed}} \neq \text{Color}_{\text{protected}} \rightarrow \text{multicolor pattern} \quad (3)$$

For the present example of collective patterning, the average CC during the course of pattern development is 16% (zero min

value excluded). The maximum color contrast is 34% at 45 min of development (Figure S10, Supporting Information). Photopatterning was also performed using the 470 nm development light at 28 mW, and showed similar results in terms of collective recovery and the pattern contrast (Figures S11,S12; Supporting Information).

2.5.2. Selective Recovery via Development Wavelength (S1)

Selective recovery is useful when trying to develop a photopattern with different colors in exposed and protected regions (high color contrast). The first method for selective recovery (S1: Selective recovery via development wavelength) uses a mixture of QDs that are both unstable and development light that only the low energy bandgap QD can absorb ($\lambda_{1s,\text{high energy}} < \lambda_{\text{development}} < \lambda_{1s,\text{low energy}}$). The low energy bandgap component in this example is the unstable red-emitting QD, so the wavelength of the development light is selected to satisfy $\lambda_{1s,\text{green}} < \lambda_{\text{development}} < \lambda_{1s,\text{red}}$. This type of development causes the emission of only the low energy bandgap QD to recover while the emission of the high energy bandgap QD remains constant.

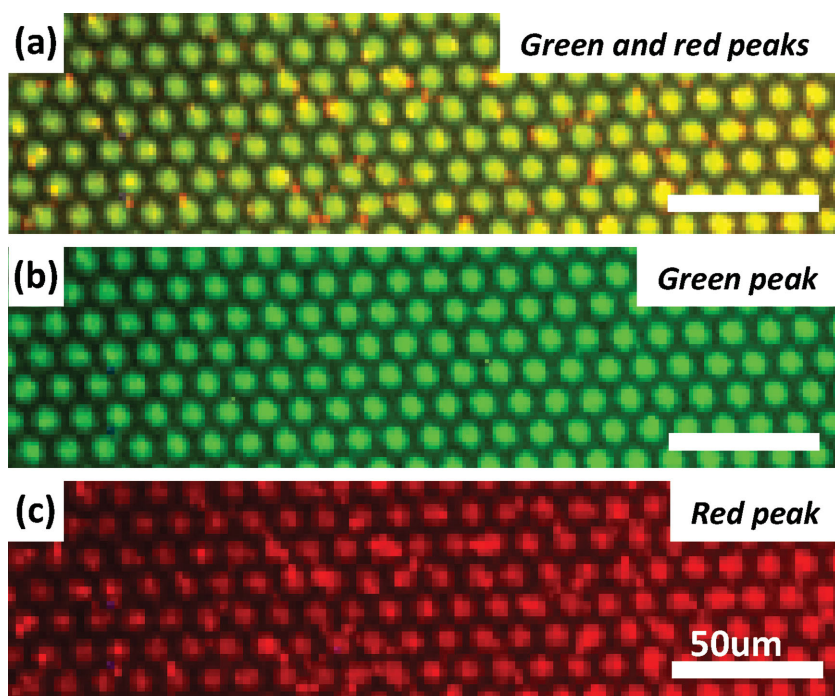


Figure 5. A multicolor photopattern fabricated using collective recovery. The unstable red and unstable green QDs are used to develop a photopattern where both emission peaks recover for the duration of pattern development. Collective recovery is confirmed using hyperspectral scans by tracking the intensity of a) both the red and green PL peaks, b) only the red PL peak, and c) only the green PL peak intensity. All scans show a clear photopattern on the QD-polymer film, indicating that the overall photopattern is due to collective recovery of both the red and green QDs. All scale bars are 50 μm .

To demonstrate this selective recovery method, unstable green and unstable red QDs were deposited into a film and developed using 580 nm light at 17 mW, which satisfies the condition $\lambda_{1s,\text{green}} < \lambda_{\text{development}} < \lambda_{1s,\text{red}}$ so that only the red QDs absorb the development light and exhibit PL recovery (Figure 6a). Photoluminescence imaging and hyperspectral characterization show that the contrast of the film increases and the color of the exposed regions become more orange over 153 min of development (Figure S13, Supporting Information). Hyperspectral characterization of the photopattern shows that selective recovery of red QD emission occurs with very little recovery of green emission (Figure 6b). In this example of patterning, the average color contrast between red and green recovery is 46% (not including the zero minute mark), with a maximum color contrast of 54% occurring after 25 min of development (Figure S13e, Supporting Information). Selective recovery is confirmed by hyperspectral maps that clearly show that the red QDs are patterned while the green QDs are not patterned, proving that the photopattern is due only to the recovery of red emission (Figure 6c).

The efficiency of this strategy depends largely on the difference in absorbance positions between the unstable components. Using optical components that have similar λ_{1s} positions (for example, orange QDs with red QDs) could lead to a nonzero amount of absorption by the high energy QD, which will result in collective recovery instead of selective recovery. Collective recovery can be avoided by increasing the difference

in λ_{1s} position between the two components (for example, using red QDs with blue QDs), which minimizes absorbance by the high energy QD and provides a larger region of appropriate development wavelengths to achieve selective recovery. Taking these steps can improve color contrast and the ability to develop a multicolored photopattern. However, developing the pattern with redder wavelengths tends to slow the PL recovery, and thus more time is required for recovery to occur. The increase in the required development time can lead to more pronounced proximity effects of the development light into the protected regions of the film due to small variations in mask position, which reduces intensity contrast. These competing effects need to be considered when utilizing this technique.

2.5.3. Selective Recovery via Stable–Unstable Mixtures (S2)

The second method for selective recovery photopatterning (S2: Selective recovery via a stable–unstable mixture) utilizes a mixture of a stable QD and an unstable QD. The only requirement for $\lambda_{\text{development}}$ is that it falls within the absorbance region of the unstable QDs ($\lambda_{\text{development}} < \lambda_{1s,\text{unstable}}$). In this process, only the emission from the unstable

QD recovers when exposed to light, resulting in an increase in the intensity difference between the emission of the stable and unstable QDs. This approach is useful when trying to develop a photopattern with very high color contrast. The advantage of this selective recovery strategy over the previous selective recovery strategy (S1) is that there is less restriction on the wavelength that can be used to develop the pattern. In this case, higher energy light can be used for pattern development, which increases the PL recovery rate, and reduces proximity effects caused by small fluctuations in the mask position.

To demonstrate this method, stable green QDs and unstable red QDs were deposited into a film and developed with 350 nm light at 2.5 mW, which satisfies the condition of $\lambda_{\text{development}} < \lambda_{1s,\text{unstable}}$ (Figure 7a). Photoluminescence imaging and hyperspectral characterization reveal that the contrast of the film increases and the color of the exposed regions become more orange over 86 min of development (Figure S14, Supporting Information). The orange color is due to the recovery of red emission (with no corresponding recovery of green emission observed) (Figure 7b). Hyperspectral scanning of specific peaks clearly shows that the photopattern results from the recovery of only red emission, a clear indication of selective recovery (Figure 7c). In this patterning process, the average color contrast is 211% (not including the zero minute mark) with a maximum color contrast of 346% emerging after 49 min of development (Figure S14e, Supporting Information). Obviously, the color contrast provided by this patterning method is

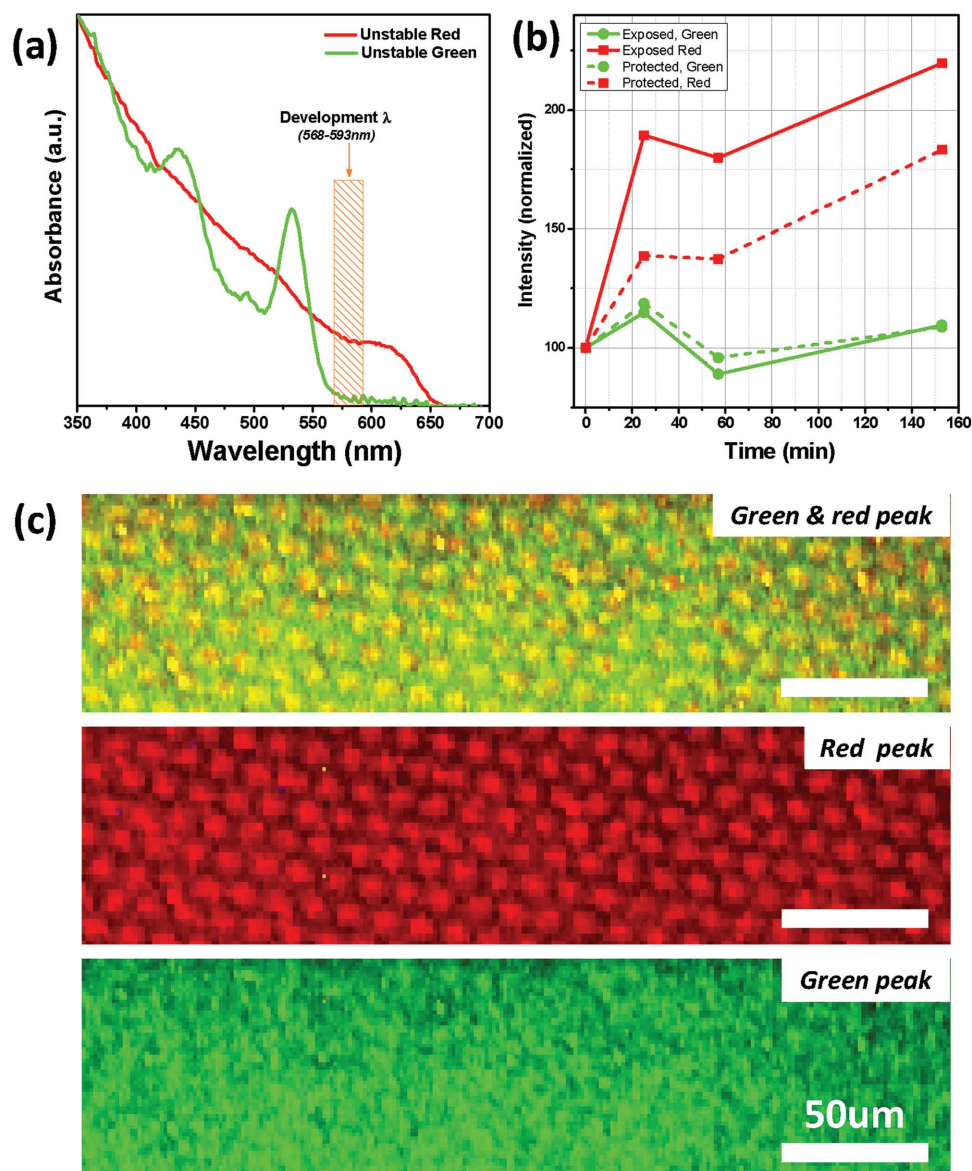


Figure 6. Selective recovery via development wavelength method (S1): Unstable red and unstable green QDs are used to develop a photopattern where a specific emission peak is recovered while the other remains constant for the duration of pattern development. a) Unequal emission recovery was achieved by developing the pattern with light that only the red QDs can absorb strongly, in this case 580 nm and 17 mW ($\lambda_{1s, \text{green}} < \lambda_{\text{development}} < \lambda_{1s, \text{red}}$) (absorbance normalized at 350 nm for clarity). b) Peak fitting of emission from the exposed and protected regions of the film shows that red emission increases while green emission remains nearly constant. Hyperspectral scans of c) both red and green, only red, and only green emission shows selective recovery of only the red QDs. All scale bars are 50 μm .

significantly higher than the collective recovery method. The effectiveness and flexibility of this method depends on the degree of PL stability of the stable QD, and can be compromised at high excitation intensities.

2.5.4. Comparison of Photopatterning Strategies and Methods

Two general strategies were introduced for developing photopatterns (selective recovery and collective recovery) which provide the platform to develop single-color or multi-color photopatterns. These strategies offer flexibility during pattern

development depending on the type of system being patterned. Each method has advantages and disadvantages in terms of the required exposure wavelength and the required types of QDs (stable or unstable). The requirements and characteristics of each method for a mixture of red and green QDs are summarized in Table 1.

It is notable that previous photopatterning studies demonstrated significant limits of resolution and photoluminescence pattern contrast and were important steps in the early development of photopatterning. However, our work offers an important advancement in the photopatterning process by examining how mixtures of QDs of different emission and various

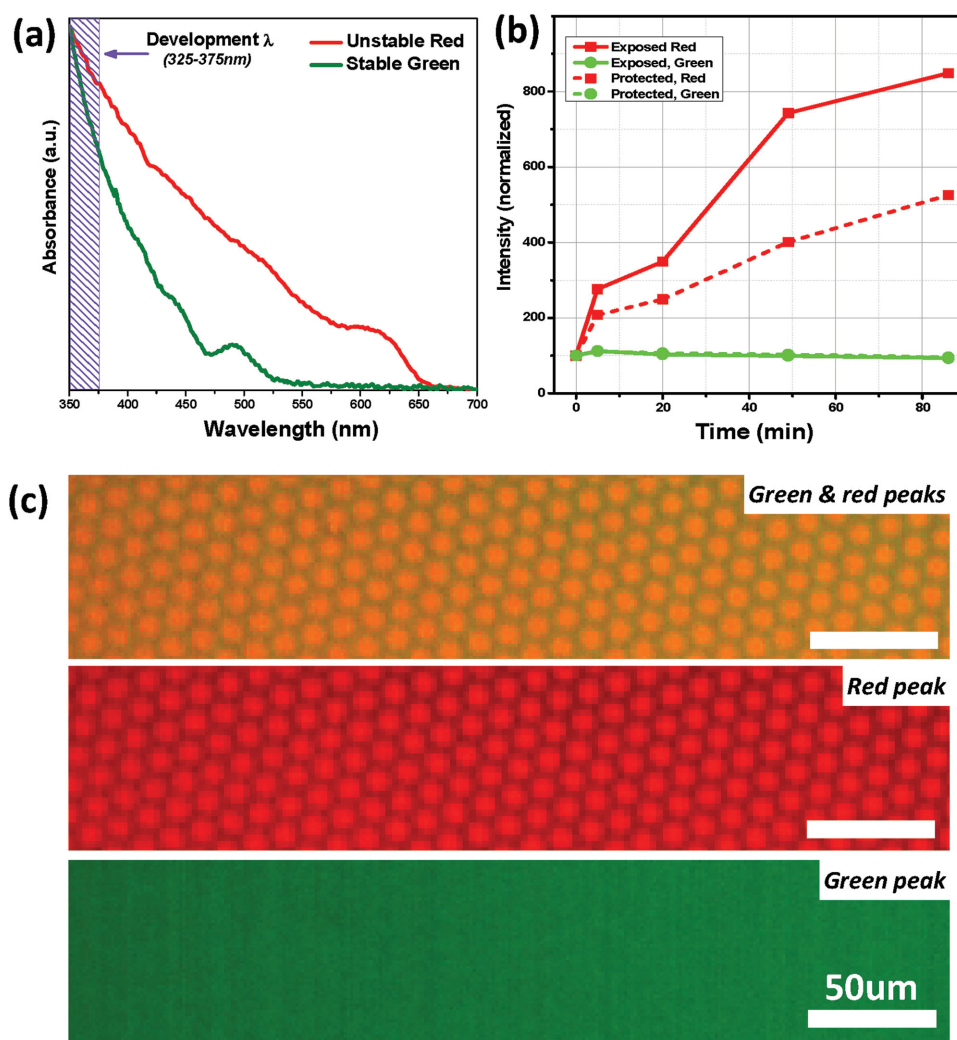


Figure 7. Selective recovery via stable-unstable mixtures method (S2): Stable green and unstable red QDs are used to perform selective recovery photopatterning where only the emission of the unstable red QDs recovers. $\lambda_{\text{development}}$ is selected so that it can be absorbed by the unstable QDs ($\lambda_{\text{development}} < \lambda_{1s, \text{unstable}}$). In this case, a) this requirement is satisfied by using light of 350 nm (2.5 mW) which falls within the absorbance of the unstable red QDs (absorbance normalized at 350 nm for clarity). b) Peak fitting of emission from the exposed and protected regions of the film shows that the red emission increases while the green emission remains nearly constant. Hyperspectral scans of c) both red and green, only red, and only green emission shows selective recovery of only the red QDs. All scale bars are 50 μm .

development approaches can be implemented to provide unprecedented control over the development of single-color or multicolor photopatterns. The potential of the strategies and methods explored in this work is much broader than the few examples shown here. Simple extensions include using QDs with emission other than red and green, increasing the number of QD colors in the mixture, and capitalizing on more complex combinations of stable and unstable QDs. In addition, these photopatterning strategies can be employed with any optical

nanostructures or chemicals that exhibit changes in their PL when exposed to light. Furthermore, there exist many combinations of selective recovery and collective recovery that could potentially lead to photopatterns that are more complex than any presented in this work.

Weakened photopatterns were found still to be visible four months after fabrication; however, they experienced a significant reduction of emission intensity and poor pattern contrast, as well as a shift in color due to degradation of the QDs

Table 1. Summary of the requirements and characteristics of the collective and selective photopatterning strategies.

Method	Recovery	QD stability type	Development λ	Color Contrast
C	Collective ($\uparrow$ green and red PL)	Unstable QDs (<i>Near-equal recovery rates</i>)	$\lambda_{\text{devel}} < \lambda_{1s, \text{green}}$ and $\lambda_{1s, \text{red}}$	Low (single color)
S1	Selective ($\uparrow$ red PL)	Unstable QDs	$\lambda_{1s, \text{green}} < \lambda_{\text{devel}} < \lambda_{1s, \text{red}}$	Medium (multicolor)
S2	Selective ($\uparrow$ red PL)	Unstable QD + stable QD	$\lambda_{\text{devel}} < \lambda_{1s, \text{unstable red}}$	High (multicolor)

(Figure S15, Supporting Information). Improving the optical stability of the photopatterns should be addressed in future studies through careful consideration of the chemical composition of the components.

3. Conclusions

In summary, we report simple yet robust photopatterning strategies that use mixtures of different QDs and judicious implementation of the development wavelength to produce high-resolution multicolor photopatterns with tunable color appearance. The collective and selective recovery strategies are easy to implement, applicable to a large variety of QD systems, and yield complex multiplex emission profiles, representing a significant departure from previous single-component photopatterning studies. Finally, these patterns have periodic shapes preprogrammed by the photomask, extend over large areas, and exhibit high-resolution features smaller than those previously reported that used a traditional noncoherence excitation source.

Such photopatterning strategies may find particular potential in the area of parity-time photonic systems, which exhibit interesting properties such as unidirectional invisibility^[43,44] and optical isolation.^[45] However, the design of parity-time materials and devices requires transitions from optical gain to loss with minimal refractive index contrast.^[46] Meeting these requirements using conventional lithography techniques can be challenging since they introduce refractive index contrasts. Photopatterning can produce optical contrast without introducing refractive index contrast because it works by intrinsically modifying the optical efficiency of the QD film without physically adding or removing material. Furthermore, the flexibility and capability of these strategies enable them to be potentially useful for a rich variety of additional systems for use in sensing, imaging, and lighting where delicate control over emission strength for specific colors is important. Finally, this work may open up possibilities for combining emissive photopatterning with physical patterning to craft next generation photonic systems that exhibit exceptionally complex spatial and spectral emission profiles that are not achievable via either patterning technique individually.

4. Experimental Section

Chemicals and Materials: Cadmium oxide, tri-*n*-octylphosphine (TOP, 90%), and selenium powder, were obtained from Sigma Aldrich. 1-tetradecylphosphonic acid (TDPA, 98%), tri-*n*-octylphosphine oxide (TOPO, 90%), diethylzinc (15 weight% in hexane), and hexane were obtained from Alfa Aesar. 1-Octadecene (90%), hexadecylamine (90%), butylamine (98%), oleic acid (97%), and bis(trimethylsilyl) sulfide (95%) were obtained from TCI. Poly(methyl methacrylate) (PMMA) (MW = 120 000) was obtained from Sigma Aldrich. Toluene was obtained from BDH Chemicals. All chemicals were used as received.

Synthesis of Unstable Green and Red CdSe/ZnS QDs: Green-emitting CdSe QDs were synthesized following a literature procedure.^[47] Specifically, 50 mg of CdO, 300 mg of TDPA, and 4 g of TOPO were placed in a three-neck flask. The mixture was heated to 120 °C and degassed for 1 h. Subsequently, the temperature was increased to 290 °C under Ar. After the solution became transparent and clear, 1 mL of 1 M

Se/TBP solution was swiftly injected to initiate nucleation and growth. CdSe QDs were allowed to grow at 290 °C for 10 s. The heating mantle was then removed to stop the reaction. When the temperature reached 70 °C, 5 mL of hexane was added to the solution.

Red emitting CdSe core QDs were synthesized using a slightly modified reported procedure.^[48,49] Specifically, 1 mmol of CdO and 5 mL of oleic acid were placed in a three-neck flask. The mixture was heated to 150 °C and degassed for 1 h. Subsequently, 15 mL of 1-octadecene was added to the solution and the temperature was increased to 300 °C under Ar. When the solution became transparent and clear, 0.2 mL of 1 M Se/TOP solution was injected to initiate nucleation and growth. CdSe QDs were allowed to grow at 300 °C for 5 min and the heating mantle was removed to stop the reaction. 5 mL of hexane was added to the solution once the temperature reached 70 °C.

The ZnS shell for the unstable CdSe/ZnS core/shell QDs were synthesized following a procedure reported in literature.^[50] Briefly, 2 g of TOPO and 1 g of hexadecylamine were placed in a three-neck flask and degassed at 120 °C for 1 h. Subsequently, 5 mL of CdSe core QDs were added and the temperature was increased to 220 °C under Ar. Then, precursor solution (0.15 mL of diethylzinc and 0.05 mL of bis(trimethylsilyl) sulfide in 1 mL of trioctylphosphine) was injected dropwise to the vigorously stirring reaction mixture. The reaction proceeded for 30 min to allow the growth of the ZnS shell. Finally, the heating mantle was removed to stop reaction. 5 mL of hexane was added to the solution once the temperature reached 70 °C.

Synthesis of Stable Green Gradient CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y QDs: Stable green gradient CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y QDs were synthesized by modifying a reported method.^[51,52] Briefly, 0.2 mmol of CdO, 4 mmol of Zn(acetate)₂, 5 mL of oleic acid, and 15 mL of 1-octadecene were placed in three-neck flask and degassed at 150 °C for 1 h. The reaction was heated to 300 °C under Ar. At the elevated temperature (300 °C), 1 mmol of Se and 4 mmol of S in 2 mL of TOP were rapidly injected into the reaction vessel. The reaction was allowed to proceed at 300 °C for 10 min and then the heating mantle was removed to stop reaction. 5 mL of hexane was added to the solution once the temperature reached 70 °C. A ligand exchange with either butylamine or hexadecylamine was performed to improve the solubility of QDS in PMMA.

Sample Preparation: QD-polymer films of thickness 840 nm (± 120 nm) were prepared by spin-casting a QD-polymer mixture at 2000 rpm for 1.5 min. Films typically had a QD-loading (volume fraction) of $\approx 3\%$ ($\pm 1\%$), which was estimated via fitting of refractive indices derived from ellipsometry data with the Bruggeman model.^[53] The QD-polymer mixture was made by mixing a QD toluene solution with a 10%–12% PMMA toluene solution, and then vortexing. Equal parts QD solution and polymer solution were used. The concentration of the stock unstable CdSe/ZnS QD solutions was $\approx 50 \times 10^{-6}$ M, while the concentration of the stock stable CdSe/Cd_{1-x}Zn_xSe_{1-y}S_y QD solution was $\approx 1 \times 10^{-6}$ M. The ratio of red-to-green QDs for the unstable red-green QD-polymer films was generally close 1:3 as estimated from initial solution concentrations. The unstable red-stable green QD-polymer films had a red-green ratio closer to 200:1 since the emission of the stable green QDs is much higher than the unstable red QDs. Films were deposited on silicon with a 292 nm surface layer of SiO₂.

Photomasks: The GT photomask (Photo Sciences Inc.) was made of an opaque chrome pattern on a quartz substrate. The photomask was a G2000HA circular mesh (G2000HA-Cu) TEM grid from Electron Microscopy Sciences. The TEM grid was designed to have a pitch of 12.5 μ m, holes with a diameter of 6.5 μ m, and bars of 6 μ m.

Photopattern Development: Photopatterning development involved two exposure steps, each utilizing a 10 $\times$ objective (NA: 0.30). For the first step, the film (without the mask) was exposed to 450–490 nm light with a power ranging from 30.5 to 39.5 mW, or 325–375 nm light with a power of 2.5 mW to bleach the film to near its minimum value (≈ 2 min of exposure). For the second exposure step, the film with the mask was exposed to either UV light (325–375 nm), a blue bandpass filter (450–490 nm), or a yellow bandpass filter (568–593 nm) depending on the type of photopattern development. The light source was a 120 W Hg vapor short arc lamp (X-cite series, 120Q, Lumen Dynamics).

Characterization: UV–vis extinction spectra of nanostructures (QDs) in solution (quartz cuvette) from 350–750 nm (1 nm intervals) were collected using a Shimadzu UV–vis-2450 spectrometer with D2 and tungsten lamps offering a wavelength range of 300–1100 nm. The QD extinction spectra were corrected against the pure solvent background and the same quartz cuvette. Photoluminescence spectra of QDs in solution were collected using a Shimadzu fluorescent RF-5301PC spectrofluorophotometer. QD molar concentration was approximated using the Beer–Lambert law and extinction cross-sections of core CdSe QDs.^[54]

Photoluminescence images were collected using a Dagexcel-M Digital Firewire camera (cooled) and a 10× objective (NA: 0.30). All photoluminescence imaging was performed using photoluminescence excitation from a blue bandpass filter (450–490 nm) with a dichroic mirror that reflects optical wavelengths below 495 nm and with a longpass emission filter that passes optical wavelengths above 500 nm. The light source was a 120 W Hg vapor short arc lamp (X-cite series, 120Q, Lumen Dynamics).

Photoluminescence from QD-polymer films were collected from hyperspectral datacubes. Hyperspectral datacubes which were collected using a CytoViva Hyperspectral imaging system utilizing a diffraction grating spectrophotometer with a spectral range of 400–1000 nm and a spectral resolution of 2.8 nm. A 10× objective (NA: 0.30) was used to scan the surface with scans of 696×59 lines with an automated stage (10 nm step size scan resolution). A 0.3–1.0 second exposure time (per line) was used. Hyperspectral scans were performed using either the blue bandpass filter (450–490 nm) excitation setup or UV light (325–375 nm) excitation setup already mentioned. The light source was the 120 W Hg vapor short arc lamp, X-cite series, 120Q, Lumen Dynamics. 120–250 spectra were collected and averaged from the exposed and protected regions of the photopatterns from the hyperspectral maps to provide data on the development of the photopattern under the various development conditions over the period of development. Hyperspectral images were constructed from the data cube by the tracking three wavelength bands (red, green, and blue). The red and green emission bands were centered at the position of the red and green emission peaks, while the blue emission was centered at a default position with 400–460 nm. Hyperspectral images were smoothed with a Savitzky–Golay filter to reduce noise. Noise from the blue region was also reduced during filtering.

The thickness of the QD-polymer films was measured using a spectroscopic ellipsometer (Woollam, model M2000) with a wavelength range of 245–1000 nm and a rotating compensator configuration. Film thickness was determined by applying a cauchy model to the 600–1000 nm (near-transparent) region of the optical spectrum.

AFM images were collected using a Dimension Icon AFM microscope (Bruker) in tapping mode according to the usual procedure.^[55] MikroMasch pyramidal silicon tips were used with a height of 15 μm , a cantilever length of 150 μm , and a spring constant of 7 N m^{-1} . Scans had a size of 50 by 50 μm with a scan rate of 0.3–0.8 Hz.

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