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RESEARCH ARTICLE

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Facile Patterning of Hybrid CdSe Nanoparticle Films by Photoinduced Surface Defects

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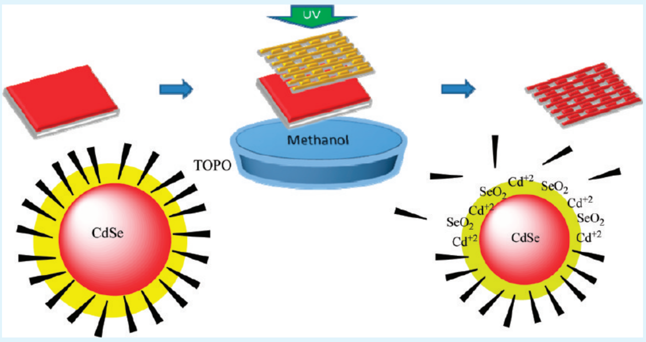
Supporting Information

ABSTRACT: The photopatterning of CdSe quantum dots (QDs) films is facilitated by preparing defect-rich QDs on selective sites on the film. A key step is UV irradiation in the presence of a polar solvent such as methanol in situ as a "developer" which readily dissolves trioctylphosphine oxide (TOPO) but not the QDs. This results in a dramatically reduced photopatterning time and irradiation intensity requirement. The optical property changes were examined by UV−vis and fluorescence spectroscopy. Furthermore, the photo-oxidized pattern of the CdSe QD film was readily observed by fluorescence microscopy. The chemical change due to attenuation of the P═O vibration of TOPO (due to its removal) could be detected by FT-IR imaging or FT-IR chemical mapping. Thus, the protocol is a simple yet effective way of patterning PL properties of QD films at much reduced exposure time compared to previously reported methods. It may find utility for a host of cell-based film assays and PL display device applications at various resolutions.



KEYWORDS: hybrid, CdSe, quantum dots, photobleaching, UV irradiation, micropatterning

INTRODUCTION

Organic−inorganic hybrid semiconducting quantum dots (QDs) have been of high interest in the past two decades for their size-dependent optical properties. Optoelectronically active organic ligand-capped semiconducting QDs are applicable in various fields such as light-emitting diodes,[1−5] photovoltaic cells,[6−9] and biosensors.[10−12] Furthermore, bulky organic ligands provide steric hindrance to the inorganic semiconductor core, stabilizing the QD colloidal system from spontaneous aggregation by delaying diffusion kinetics from the solution subphase to the surface of QDs. Also, the use of dendritic ligands modified with highly conjugated moieties could serve as energy donor or acceptor in the QD system. Our group have previously reported the use of conjugated polythiophene dendron ligands to coat semiconducting CdSe QDs through ligand exchange resulting in energy transfer properties from thiophene dendrons shell to the CdSe core.[13] Similarly, photoinduced excitons are possibly recombined or dissociated in peripheral electroactive Fréchet-type polybenzyl ether dendron-coated CdSe QDs by electrochemistry.[14] Such modification and post-treatment of hybrid QDs have received much attention for designing novel electro-optical device and sensor applications.[15]

Designing optically active films with 2D or 3D patterned features is significant for optical display device preparation. It is important to utilize the appropriate QDs that luminesce or induce charge transfer at the appropriate wavelength or photochemical condition resulting in patterned features. Several methods of film patterning have been reported recently.[16−19] Most commonly, 2D designed QD films have been prepared by directly applying the QD solutions onto prepatterned substrates by physical or chemical adsorption between peripheral organic ligands on the surface of QDs and a prepatterned or templated film. This allows for the QDs to settle or adsorb onto selective sites of the prepatterned frames that have been prepared by self-assembly,[19,20] photoresist lithography,[21,22] or stamping.[23] Otherwise, QDs have also been patterned chemically to specifically functionalized sites of the substrate by dip pen nanolithography,[24] constructive nanolithography[25] and photomasking.[26,27] Selectively organic-functionalized, prepatterned frames of the substrate interacts with capping ligands on the surface of QDs allowing them to bind to a prepatterned film more tightly.[24,28,29] Hybrid QDs can be charged by functionalizing capping ligands ionically on the surface of the metal cores. Electrostatic interaction between ionically charged QDs systems and ionically modified substrate allow for the preparation of well-organized and designed 2D QD films.[25,30,31]

Photofabrication or photolithographic methods is an efficient technique for patterning hybrid CdSe QDs or CdSe/CdS core−shell QDs which require no further treatment of substrates (e.g., prepatterning). In the presence of oxygen, UV irradiation can oxidize the surface of CdSe QDs into cadmium cations and selenium oxides, and tunes the size-dependent

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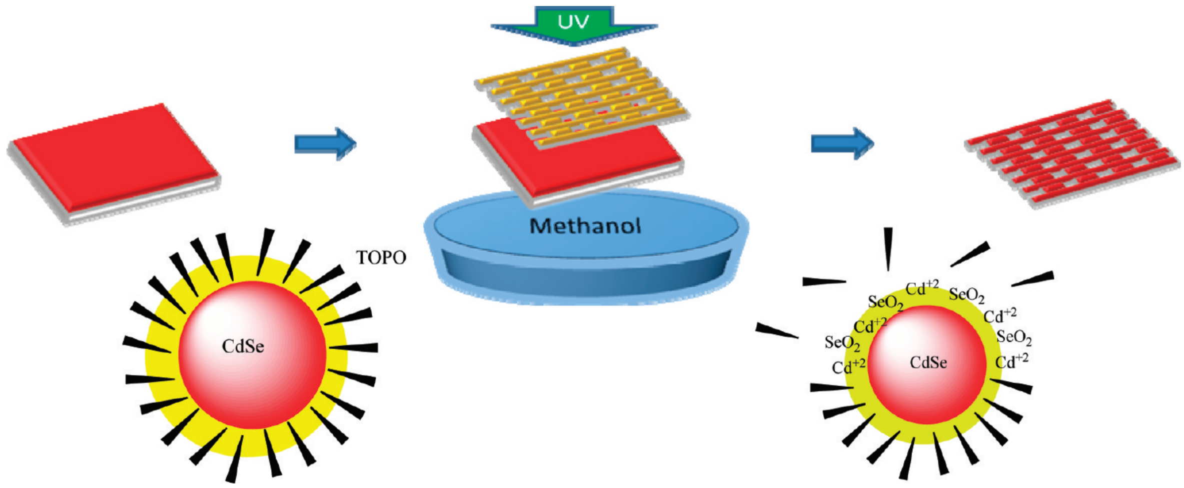
Scheme 1. **Schematic Method to Prepare Micropatterned CdSe-TOPO QD Films by Photo-Masked UV Irradiation in Methanol**



photoluminescence (PL) of CdSe QDs.[32−34] Not only does UV irradiation decrease the size of the QDs, it can also produce defect-rich surfaces. Trap states of the defect-rich QDs changes the band gap condition and provides an alternative relaxation pathway for quenching the PL of CdSe QDs. Therefore, it is possible to modify the optical distribution or excitation of QD films simply by UV irradiation through a patterned mask.[33] In practice, UV irradiation to tune fluorescence colors of solid-state QD films in the presence of air (or oxygen) has limited abilities and requires high laser or irradiation intensities. It has been reported that a laser power of 30 mW/cm^2 was needed for photobrightening and an even higher energy of 200 mW/cm^2 was needed for photodarkening.[32] A 12 h UV irradiation requirement for QDs patterned in solid state films has been reported.[33,34] Photopatterned QD films can be prepared by photoenhancement through rearrangement of the surfactant that is present for stabilizing the surface trap states.[35−38] Often the drawback is that it also destroys the optical properties of the semiconducting QDs completely.[32−34]

In this paper, we report the utilization of UV oxidation and photomasking method for the patterning of trioctylphosphine oxide (TOPO) capped CdSe QD films. We dramatically reduced the PL of the film simply by dipping the film in methanol solvent, which delivers oxygen efficiently to the surface of QDs, detaching the TOPO from the surface, and decomposing the CdSe QDs surface more readily into cadmium cations and selenium oxides as shown in Scheme 1. CdSe-TOPO drop cast film on glass substrate was simply masked with a TEM grid and were then dipped into methanol, irradiated by UV light and then dipped in methanol for 30 min. The unexposed regions were not photobleached and maintained the original optical properties of the CdSe QDs whereas the exposed areas were. This simple method should enable a safe and highly efficient protocol for preparing optoelectronically active patterned QD films for a host of applications including solid-state display devices, sensors, and photovoltaic cells.

EXPERIMENTAL SECTION

All chemicals were purchased from Aldrich Chemical Co. and were used directly without further purification. Solvents for the synthesis of CdSe QDs were bubbled with nitrogen gas prior to use. The other solvents for UV irradiation were used directly without further degassing, except for the degassed methanol for the photomasked-UV irradiation experiment without oxygen. Nitrogen gas was bubbled about 4 h in a closed system. UV−vis spectra were recorded using Agilent 8453 Spectrometer. Fluorescence spectra were obtained using a Perkin-Elmer LS45 luminescence spectrometer. FT-IR spectra were obtained on a Digilab FTS 7000 (now Agilent) equipped with HgCdTe detector at a range from 4000 to 700 cm^{-1}. FT-IR imaging were obtained on a Digilab FTS 7000 (now Agilent) equipped with a step-scan spectrometer and UAM 600 IR microscope. The FT-IR images were obtained using 32 × 32 focal plain array (FPA) detector, covering a sample area of 704 × 704 μm^2 in reflection mode. All images were taken with 8 cm^{-1} spectral resolution. The IR images were collected by 128 scans. All images were plotted using Win-IR Pro 3.4. X-ray photoelectron spectroscopy (XPS) data was collected using a Physical Electronics 5700 instrument with photoelectrons generated by the nonmonochromatic Al Kα irradiation (1486.6 eV). Photoelectrons were obtained at a takeoff angle of 45° using a hemispherical analyzer. Hemispherical analyzer operated with an energy resolution setting of 11.75 eV in the fixed retard ratio mode. Cu 2p3/2 and Ag 3d5/2 lines were used to calibrate the binding energy scale prior to any measurement. Charge neutralization was applied through the irradiated area cobombardment with an electron beam and used the nonmonochromated Al Kα source. C 1s peak is set at a binding energy of 284.6 (0.2 eV). Fluorescence microscope images were captured using a 20× objective lens on an Olympus BX61 (BX61TRF) epifluorescent motorized microscope, resulting in a combined 200× magnification of images. Images were collected by fluorescence under BH2-RFL-T3 fluorescence burner and motorized fluorescence filter turret with CY3 and DAPI filter sets. The fluorescence microscope image was captured with a Hamamatsu C4742−96-G04 monochrome camera. The images were collected using Quad-Processor Power PC G5 Apple with software of Si Slide Book v. 4.2 from Intelligent Imaging Innovations, Inc.

Preparation of CdSe QD Capped with TOPO or Trioctylphosphine Oxide. The preparation of CdSe QDs capped with TOPO followed a published method.[13] CdO, TOPO, octadecylamine-(ODA), and n-hexylphosphonic acid (HPA) mixture was first heated to 270−320 °C followed by adding the Se/trioctylphosphine(TOP) mixture. The red solution was washed with methanol several times to remove free TOPO until no TOPO was detected in the UV spectrum of

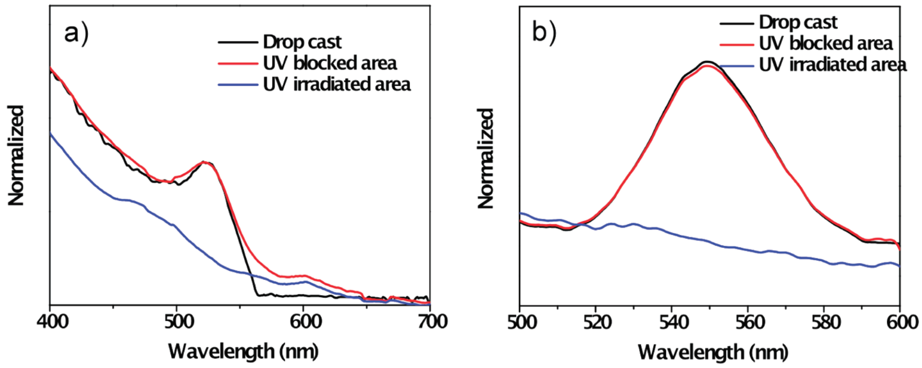


Figure 1. (a) Absorption and (b) emission spectra of the covered and uncovered CdSe-TOPO film in methanol after 30 min UV irradiation.

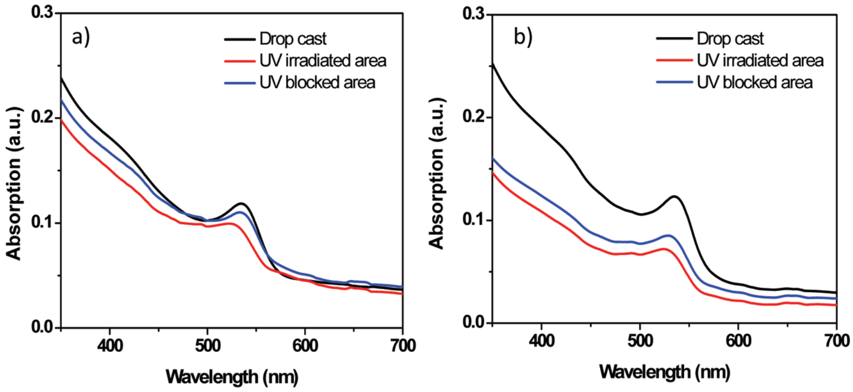


Figure 2. Absorption spectrum of CdSe-TOPO NC films exposed to UV light in (a) water, (b) hexane.

the sample. The precipitated red powder was dissolved in chloroform and stored.

Preparation of CdSe QD Film. CdSe QD films were prepared by drop-casting on glass substrates. The solution was drop-cast on the cleaned glass slides and then dried in the air. The glass slides were prepared by rigorous sonication in a Fisher sonicating solution and with water for 10 min, followed by immersion of the slides in piranha solution (30:70 = 30% H_2O_2:98% H_2SO_4) for 45 min, carefully washed with deionized water several times and dried. The average thickness of the film with this method ranged from 200 to 500 nm, depending on the number repeated drops.

Patterning of the CdSe QD Film. The CdSe QD films were UV irradiated with a typical UV irradiation lamp (Spectroline, ENF-280C) under a long wavelength UV (365 nm) with a power density of 470 μW/cm^2 for different times in air and in the methanol solvent. Micropatterned films were prepared by photomasked UV irradiation through the TEM grid (Gold, 300 Mesh) on top of the film that was immediately dipped in methanol prior to irradiation.

RESULT AND DISCUSSION

Absorbance and Emission Spectral Properties. When the film was exposed to UV light, the maximum absorption peak at 527 nm attributed to the CdSe QDs, was slightly blue-shifted in solution and solid state, which indicates that the CdSe-TOPO QDs have been etched (See the Supporting Information, S2). However, the absorption peaks have not disappeared by UV treatment, though the intensity of the bands decreased with increasing irradiation time. The absorption peak of the CdSe-TOPO QDs in the solid state was slightly blue-shifted from 527 to 522 nm even after 8 h of UV irradiation while QDs in chloroform was blue-shifted from 527 to 519 nm in an hour, which indicates the QDs' stability against phototreatment as compared to their solution state. In fact, UV irradiation etched CdSe-TOPO QDs more efficiently in solution state than in a solid-state (dry) film. Oxygen is one of the most important requirements for photobleaching and photo-oxidation of CdSe QDs, which proceed by attacking selenium sites and detaching selenium oxides.[38,39] On the other hand, the rearrangement of organic capping ligands stabilizes trap states and often results to photoenhancement. Therefore, TOPO-capped CdSe QDs-drop cast film was stored in nondegassed methanol for subsequent photobleaching. Methanol was also used for removing detached TOPO to prevent the stabilization of the trap states and the delivery of oxygen.

To demonstrate micropatterning, the reticulated structure of the TEM grid (gold, 300 mesh) was used as a photomask to cover the film and block UV penetration selectively. The frame of the TEM grid has 20 μm features and consequently patterned films have 20 μm wide optically activated reticulated areas by simple irradiation. The TEM grid covered area (UV blocked area) of the film retained initial absorption and emission peaks of the QDs at 527 and 549 nm, respectively (Figure 1, black). Upon UV irradiation, the absorption peak exhibited by the film through the TEM grid at 527 nm was blue-shifted to about 50 nm (Figure 1a, red) and the intensity decreased dramatically. Moreover, the emission peak at 549 nm was quenched quickly (30 min) after UV irradiation in the presence of methanol (Figure 1b, red). Interestingly, this study revealed that in the presence of methanol as a "developer" this saves time and power for revealing the pattern after irradiation. The irradiation time resulting in a remarkable decrease in emission intensity took only 30 min, which is much shorter as compared to the usual 12 h UV irradiation requirement for patterning in solid state films.[33,34]

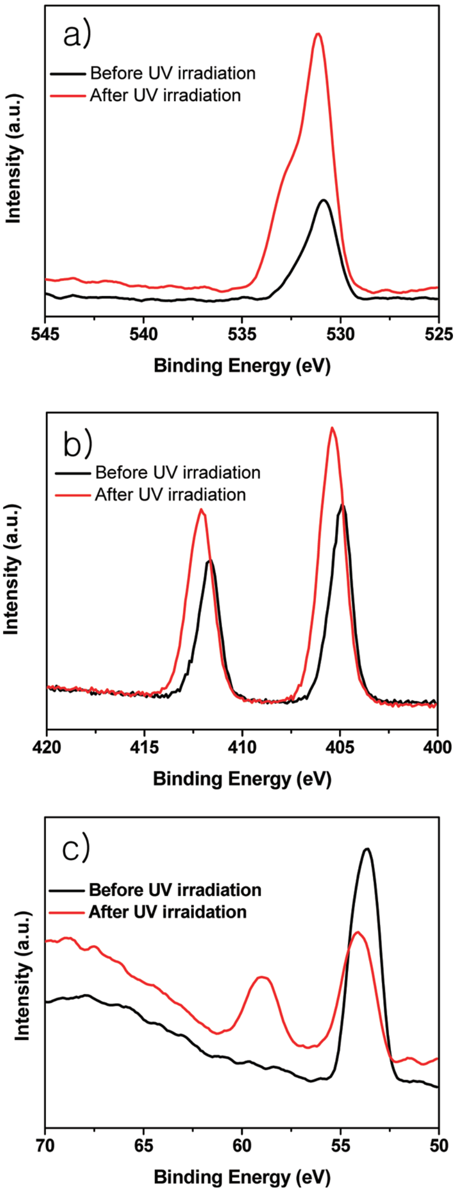


Figure 3. XPS spectrum of (a) O1s, (b) Cd3d5, (c) Se3d before and after UV irradiation.

It has been reported that a laser power density of 30 mW/cm^2 was even needed for photobrightening and an even higher power density of 200 mW/cm^2 was needed for photodarkening.[32] In contrast, we have shown that the methanol treatment with UV irradiation only requires 30 min irradiation time to oxidize the QDs. Consequently, the methanol treatment facilitates photodarkening and also allows for less power, only requires 470 μW/cm^2 for photodarkening CdSe-TOPO QD films. According to other reports, a light power density of 4.7 mW/cm^2 for irradiation requires a longer time, up to 72 h, for completion.[33,34]

Applying methanol is thus essential to allow shorter UV irradiation time for photooxidation and photobleaching CdSe QDs. Although an 8 h UV irradiation shifted the absorption peak of CdSe-TOPO QDs in a solid-state dry film slightly (5 nm shift, see Supporting Information, S2), the absorption peak of CdSe-TOPO QDs was blue-shifted by 64 nm after UV irradiation when the film was stored in methanol (Figure 1) at a shorter time of 30 min. Other solvents, such as water, hexane, acetone, and tetrahydrofuran, were also used for the films during UV irradiation. Due to the lower solubility of the ligand or polarity of the solvents, however, absorption and emission bands of the films were changed little under the same UV irradiation with these solvents even up to 2 h. This was 4 times longer than the UV exposure time required compared to methanol. The polarity of water (dielectric constant) is 80, which is larger than methanol (33). Yet, water is not a good solvent. The film exposed to UV light in water exhibited a slight blue-shift of the absorption peak only after 2 h UV irradiation which still indicates photooxidation, but not enough for the photobleaching the QDs. A nonpolar solvent such as hexane is neither a good solvent for both ligand and QD core. The oxygen solubility in hexane is even less than that of water or methanol,[40] thus the photooxidation and photobleaching were not efficient in hexane (Figure 2). This could be attributed to a faster nonpolar oxygen delivery to QDs in polar methanol than in nonpolar hexane. Because both UV irradiated and UV blocked CdSe films immersed in hexane demonstrated decreased absorbance, this observation could be attributed to desorption of TOPO capped CdSe QDs into the hexane. Although the absorbance of both films was decreased, the decreased ratio of both CdSe films was similar. In addition, there was no significant blue shift detected. This could be explained by a decrease in the concentration of QDs instead of the degradation

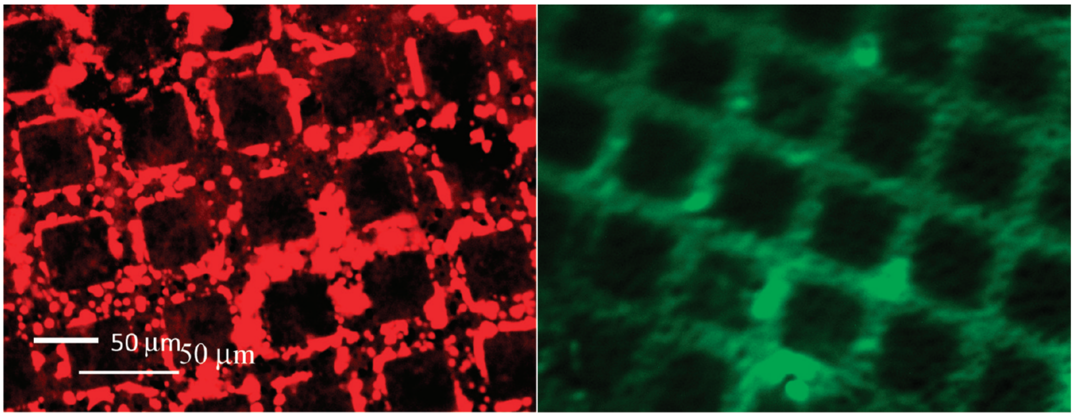


Figure 4. (a) Fluorescence microscope images that were excited at (a) 350 nm and (b) 540 nm patterned with a 50 μm grid scale.

of QDs. A large blue shift of the absorption peak of CdSe QDs was also observed in acetone whose polarity (21) is closer to methanol (See the Supporting Information, S3a) but still took a longer time to decay.

XPS Characterization. The surface binding energy of the UV patterned film was examined by XPS analysis. The CdSe-TOPO QDs film has oxygen atoms which are contained only in the phosphine oxide moiety before photooxidation and photobleaching. As discussed previously, CdSe QDs decomposed into cadmium cations and selenium oxides by photooxidation. After UV irradiation, from XPS analysis, it was apparent that the intensities of C and P atoms, which are the constituent components of TOPO, were decreased and the intensity of O was increased (see the Supporting Information, S4).[37] The intensity of C was decreased from 18.4 to 10.4% and that of P was decreased from 4.5% to 3.6% after UV irradiation. O 1s binding energy was slightly shifted from 530.8 to 531.1 eV after UV treatment in methanol and showed a shoulder around 532.7 eV. Although 530 eV is attributed to Se-related oxides and 540 eV is attributed to Cd-related oxides, a peak shift to higher binding energy and shoulder appearance indicate that the CdSe QDs has higher Cd/Se ratio.[41] This phenomenon indicates that the QDs have become more Cd rich after photooxidation. The Cd binding energy was shifted slightly without changing the patterns after UV irradiation but this observation is not conclusive to assert Cd oxidation.[37] However, the binding energy of Se splits into two, at 54.0 and 58.9 eV, indicating SeO_2 formation after UV irradiation, though only one peak was observed from Se3d due to the CdSe QDs before the UV irradiation (Figure 3).[37] Abe et al. reported the selenium oxide peak to be around 14% in photobrightening state, and 42% in photodarkening state.[37] Similarly, the selenium oxide peak (58.9 eV) was about 48% in this system. The Cd to Se ratio on the surface of QDs increased by about 1.9 times after UV irradiation which indicates that the QD surface becomes Cd rich. Therefore, the UV irradiated area of CdSe-TOPO films is Cd rich and almost half of the selenium is oxidized, though the TEM grid covered area kept the original Cd to Se ratio of the TOPO-capped CdSe QDs and no selenium was oxidized.

Fluorescence Imaging. The films were photobleached after UV irradiation in the presence of methanol. Similarly, it was observed that the UV irradiated areas of the film have little PL while the UV blocked area retained strong emission. The image of the optically patterned film by photobleaching was collected by fluorescence microscopy. Emission was not observed on the square area that was UV irradiated area whereas the UV blocked areas emitted light (Figure 4) with excitation at two wavelenghts. The images were collected when the patterned films were excited at 350 and 540 nm. UV irradiated area exhibited dark square (50 μm × 50 μm), and UV blocked area by covered by TEM grid performs bright linear frame (20 μm width) with the original optical property of CdSe-TOPO QDs. The patterned image has good enough resolution to be seen in a fluorescence microscope. This phenomenon is opposite to the previous reports which showed stronger emission from the UV irradiated square part of the QD films (photoenhancement) than the emission from the UV blocked linear frame area in the air.[33] This is perhaps a consequence of the much longer time needed to photobleach films and the photoenhancement occurring at a shorter time compared to photobleaching, in which case, the UV-irradiated square area exhibited stronger emission than the TEM grid covered linear frame.[37] In this case, however, the UV irradiated and UV blocked area absorb and emit light in the same region and the difference between UV irradiated and UV blocked areas in emission intensity at the two excitation wavelengths is evident.

FT-IR Spectroscopy and Imaging. Surface defects on the surface of CdSe QDs due to the Cd cations and Se anions vacancies provide trap states in the band gap and allow for alternative nonradiative relaxation of the excitons, degrading the optical properties of the CdSe QDs.[36,42] Passivating the surface traps with higher band gap materials, e.g., ZnS,[43−45] or organic materials, such as TOPO, alkyl amines, and polymers,[35−38] increases the PL quantum yield and intensity. In CdSe-TOPO QDs, TOPO is attached to the QDs through Cd−O bond.[46] However, it has been reported that TOPO migrates from Cd site to Se site when CdSe QDs are in a photodarkening state by UV irradiation.[37] Therefore, the CdSe QDs system can be photobleached by migrating TOPO from the Cd site to Se site and detaching TOPO from the surface of the QDs to prevent passivating surface traps with UV irradiation in methanol. The absence of TOPO on the UV irradiated CdSe QDs area was observed by FT-IR imaging.

TOPO-capped CdSe QDs have a P=O moiety, which can be observed at 1200 cm^{-1} in solid state in the IR spectrum (Figure 5. c. solid line). However, photooxidation by UV irradiation in methanol detached TOPO from the surface of the QDs. Photodetached TOPO ligands would be dissolved and washed away by methanol. Absence of the peak at 1200 cm^{-1} indicates that TOPO ligands have been removed after photolithography (Figure 5c dotted line). The 2D structure of the photopatterned film can be detected by IR imaging based on P=O vibration of TOPO. The disappearance of peak after UV irradiation could be mapped by IR imaging as shown in Figure 5a. The 2D image scanned at 1200 cm^{-1} wavenumber shows the difference between UV treated area and TEM grid covered area. The intensity of the peak at 1200 cm^{-1} has significantly decreased and the intensity gap appeared in 2D and 3D images became clearly visible. The red frame area exhibits strong intensity of the peak and blue square area indicates no or little detection of the P=O vibration. The TEM grid has 50 μm × 50 μm size square and 20 μm width frame. TOPO on the surface of CdSe QDs under 20 μm width frame is unaffected by photooxidation and the 20 μm width frame area had a high intensity of P=O in 2D and 3D images. The IR images were collected in a 352 μm × 352 μm region. Although the failure of passivating surface traps with TOPO results in photodarkening, the square area where no TOPO was detected is photobleached area, so that the IR image showed a similar pattern to the fluorescence image. The image was clear enough to distinguish the patterned image in the micrometer scale and exhibited similar 2D grid pattern to the fluorescence image. What is also interesting is the difference in sharpness of area and grid dimension correspondence between the chemical mapping and fluorescence imaging in Figure 4, which reveals that the observed emission features are narrower compared to the actual functional group distribution in the pattern as observed by chemical mapping. This also explains the requirement of methanol application for photobleaching CdSe QDs. Methanol dissolves TOPO and removes the detached TOPO from the surface of CdSe QDs. Further optimization of patterning parameters for a higher resolution should possible.

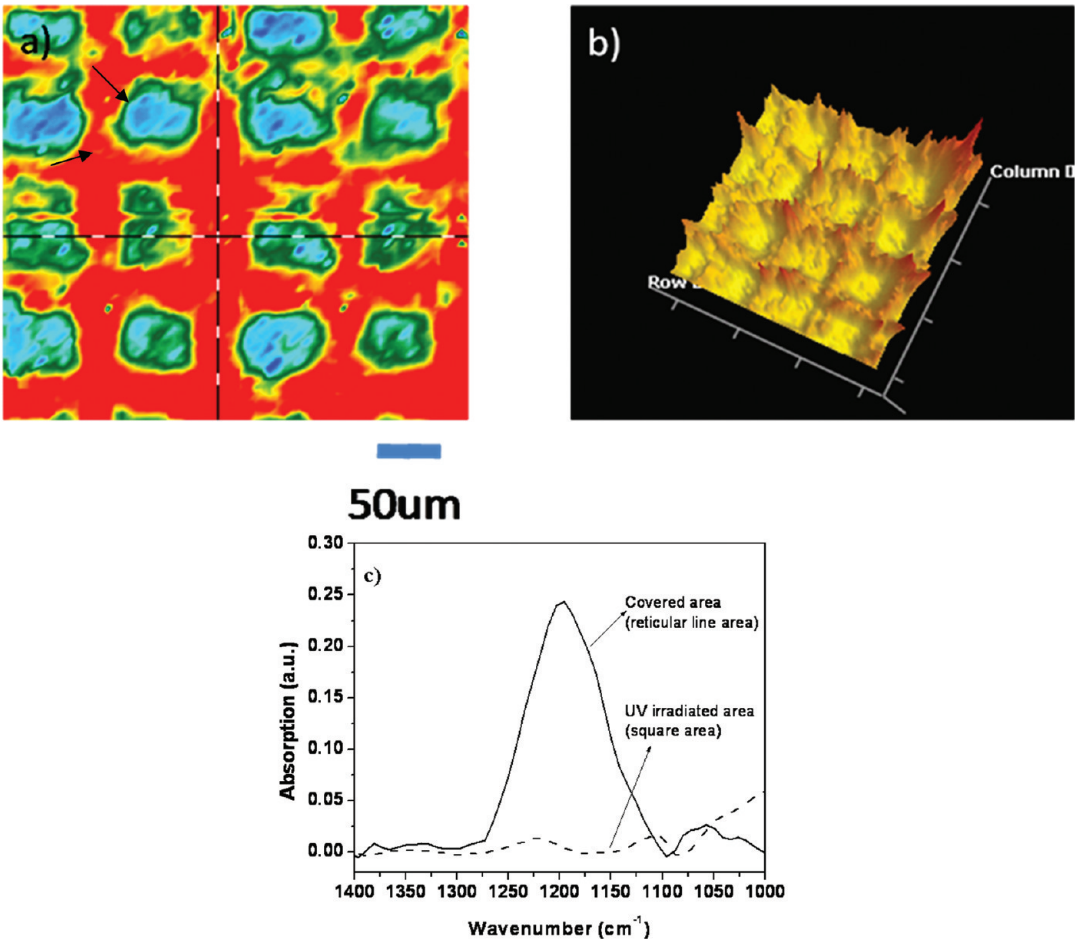


Figure 5. FT-IR image of patterned CdSe-TOPO QD film in (a) 2D with red-high intensity and blue-low intensity for the TOPO moeity, (b) 3D relief image, and (c) FT-IR spectrum of TEM grid covered area and UV irradiated area, which are extracted from the indicated points in a.

CONCLUSION

In this paper, a facile method was demonstrated for patterning CdSe-TOPO QD films by UV irradiation through a photomask in the presence of methanol. The film, which absorbs light maximal at 527 nm and emits around 549 nm, was photobleached in methanol. Control films with other solvents did not oxidize the films as effectively at a short time compared to methanol. Patterns prepared with the TEM grid had 20 μm wide optically active rectangular areas and 50 μm × 50 μm optically inactive square areas consistent with the TEM mask original dimensions. Oxygen binding energy shifts and the Cd and Se binding energies change as examined by XPS confirmed the oxidation of CdSe core into Cd cations and selenium oxides upon UV exposure. The emission features of micropatterning were examined with fluorescence microscopy and the chemical pattern by IR imaging. Fluorescence microscopy revealed that the covered frame area emitted strong light while the UV irradiated area did not. Similarly, the photomask covered area exhibited strong intensity of P═O vibration, but the UV irradiated area did not by IR imaging. This method could be an alternative procedure to prepare patterned QD films at higher resolutions without further postchemical or physical treatment and at much shorter irradiation times. Further studies are underway on these directions.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details of synthesis, characterization, Absorbance and emission spectrum of other cations are reported. This material is available free of charge via the web at http://pubs.acs.org.This material is available free of charge via the Internet at http://pubs.acs.org.

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