Spatially Selective Optical Tuning of Quantum Dot Thin Film Luminescence

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Quantum dots (QDs) have found numerous applications in areas ranging from optoelectronics (e.g., light sources and solar cells) to tags for use in biosensing. The ability to create spatially addressable platforms of QDs with selective optical properties would greatly enhance many of these applications.[1] Several approaches, including colloidal assembly, electrostatic deposition, covalent bonding, biorecognition, Langmuir−Blodgett, and self-assembly, have been used to position materials such as metal nanoparticles and QDs on a variety of substrates.[2] However, assembling different QDs on the same substrate with submicrometer resolution remains a significant challenge, as this first requires the synthesis of QDs with the desired optical properties and then a means of directing them to a desired location. This can be a relatively laborious and noneconomical process, requiring several experimental steps.[3] Recently, it has been shown that by using photooxidation, the effective "size" of QDs can be modified postsynthetically to tune their emission.[2e,4,5] However, solution phase processing of QDs by such photochemical reactions can often result in aggregation, yielding undesirable spectral broadening and inhomogeneity.[2e,4c,5b] Akin to these photochemical methods it has been reported that spatially selective photobrightening and photodarkening of QD thin films have been accomplished using optical microscopy by controlling laser intensity.[6] Combining optical lithographic patterning with postsynthetic photochemical modification, however, may yield a facile means of fabricating QD arrays with tunable optical and chemical characteristics, but such approaches remain largely unexplored.

Here we illustrate a "lithosynthesis" process in which a thin film of luminescent CdSe QDs can be patterned to create arrays of QDs with submicrometer spatial resolution and emission at different wavelengths, but all starting from a single material (Figure 1A). To demonstrate this, thin films of CdSe QDs (*ca.* 4 nm in diameter) capped with 16-mercaptohexadecanoic acid (16-MHA) were assembled *via* layer-by-layer deposition (*ca.* 2 layers) on surfaces such as glass and oxidized Si, in which a positively charged polymer (PDADMAC) links the QDs to the surface (see Supporting Information).[7] By rastering a focused Ar ion laser across the film with different rates at varying locations, selective photooxidation of the illuminated QDs occurs resulting in patterned arrays of QDs with different luminescence intensities and wavelengths (Figure 1B, C). Here, changes in both emission wavelength and intensity can be controlled with high spatial resolution depending on the laser power, illumination time, and, most importantly, the local chemical environment.

Upon laser illumination, the photoluminescence (PL) intensity of the CdSe initially increases up to 6-fold or even higher (photobrightening), followed by photodarkening, along with a concomitant blue shift in emission wavelength (see Supporting Information). The increase in photoluminescence intensity has been purported to result from several potential factors[8] including the decrease of surface trap sites and roughness under illumination,[5] desorption of physically bound molecules,[9] accumulation of
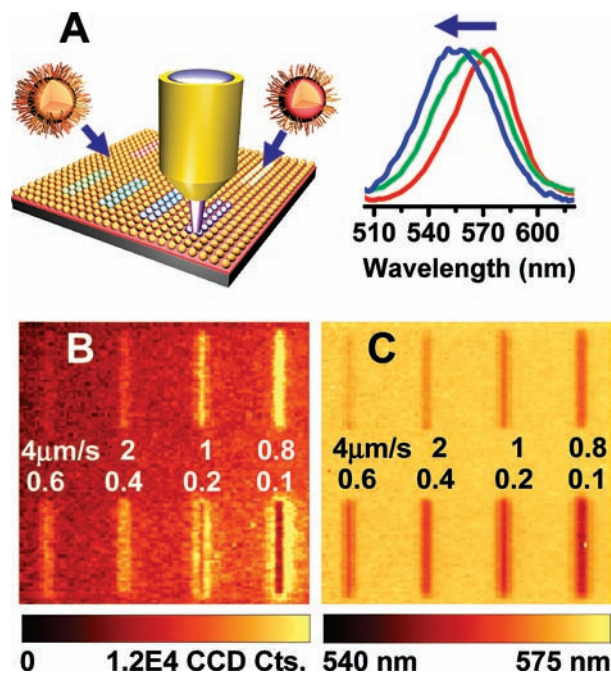

Figure 1. (A) Schematic diagram showing the phototuning of CdSe optical properties using a focused laser beam at 488 nm. (B) Photoluminescence image (30 μm × 30 μm) and (C) peak position image (30 μm × 30 μm) of patterned CdSe QDs. The intensity of QDs was selectively tuned by altering the laser scanning speed ranging from 0.1 μm/s to 4 μm/s. The fluorescence intensity of the lines increases at first and then decreases as the laser dwell time raises, while increased exposure time results in a continuous blue-shifting of the QD emission.

electrons in the organic surroundings,[6,10] or the oxidation and desorption of the capping reagent.[11] It is well-known that many of the colloidal QD capping ligands are efficient quenchers and 16-MHA capped CdSe has a lower quantum yield than TOPO capped CdSe (*ca.* 1% vs 30%).[11c] Under illumination, the thiol capping ligands can be removed by their photocatalytic oxidation to disulfide,[11a] along with the formation of more complicated oxidized sulfur species, as determined by X-ray photoelectron spectroscopy (see Supporting Information). Thus, by starting with QDs capped with 16-MHA, their removal by local photooxidation results in a dramatic increase in photoluminescence at the exposed regions of the film. Importantly, this process can be reversed, affording the ability to create patterns with not only variable wavelengths but also variable intensities, controllable through readsorption of the same or other ligands following photooxidation. The enhanced emission can be quenched back by immersing the patterned QD film in a 16-MHA solution, which can then be "rewritten" by laser lithography at the same region several times (Figure 2). Following long-term or intense photooxidation however, the PL intensity rapidly declines to less than 6% of the initial intensity. We have
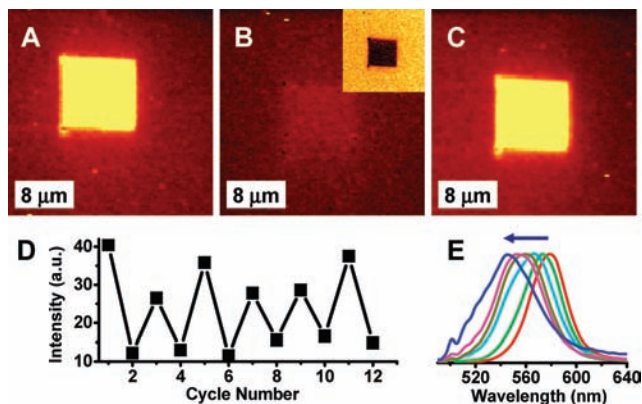
Figure 2. Demonstration of reversible surface modification of QDs. A square is patterned onto the CdSe QD film (A) where the QDs are partially oxidized and capping groups partially removed. (B) The sample is then immersed in a 16-MHA solution for 5 min. Inset shows the wavelength channel of the same region ($\Delta\lambda \approx 5$ nm bright to dark). (C) The surface is then repatterned in the same location. (D) This process can be repeated many times with minimal relative signal loss. During these cycles, the QD emission peak is continuously blue-shifted (E).

probed what environmental conditions may be employed to ameliorate this effect by using microfluidic arrays to compare changes in PL under several different oxidizing environments at the same time on the same samples (see Supporting Information). By carrying out local photooxidation in the presence of 16-MHA/ethanol, the emission could be readily blue-shifted equivalent amounts to that in air (*ca.* 40−50 nm), but with the QDs retaining significantly higher luminescence (*ca.* 30 times greater) than those patterned in air.

Beyond simply shifting the luminescence, the photooxidized QDs show an increased propensity to bind new molecules relative to the background film, enabling a facile approach for spatially selective QD surface modification. This approach has some advantages compared to regular deep UV, UV-ozone, or other ligand exchange surface modification methods. First, visible light may be used with little to no damage to either the supporting QDs or loading target molecules. Second, by employing lithography, modification of the QD films can be spatially localized. As such, this simple patterning approach to ligand replacement offers a facile method for selective modification of immobilized QDs, as compared to functionalization in solution, where long ligand exchange and separation times can be required and aggregation can often occur.[3b] We have explored this by selectively binding a porphyrin with a pentanethiol tether (see Supporting Information). As shown in Figure 3C, after binding of porphyrins to the patterned regions of the QD film, significant quenching of the QD luminescence was observed. This can be attributed to fluorescence resonance energy transfer (FRET) and/or charge transfer between the QDs and porphyrin.[12]

In summary, upon visible light illumination, the capping ligands of the QDs are photocatalytically oxidized along with the QDs themselves allowing for the selective modification of their local optical properties (emission intensity and wavelength). This method should be broadly applicable to other QD materials and has many distinct advantages for creating patterned arrays of QDs with different optical properties. This includes needing only a single starting material and the ability to fabricate these structures using typical photolithographic techniques, affording ready industrial scale-up. The patterns can be created with high densities on any surface with appropriate modification, making them useful for
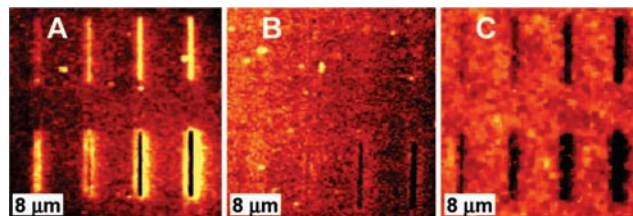

Figure 3. Photoluminescence intensity images of (A) a control sample patterned in air with the same raster rates as those in Figure 1 and then soaked in CH_2Cl_2; (B) another control sample that had been immersed in 16-MHA solution; and (C) a sample that had been immersed in porphyrin thiol solution (CdSe emission channel). It is shown that both 16-MHA and the porphyrin can be inserted into the CdSe films, which suggests a facile way for selective modification of immobilized CdSe QDs in the photopatterned regions.

creating display or sensing platforms. Moreover, the patterned structures can also be "erased" or modified by the selective addition of new surface ligands multiple times, allowing the optical properties of the films to be reconfigurable.

Supporting Information Available: Sample preparation and patterning, TEM and XPS of the CdSe films, and microfluidic test patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Lundstrom, T.; Schoenfeld, W.; Lee, H.; Petroff, P. M. *Science* **1999**, *286*, 2312–2314. (b) Coe, S.; Woo, W.-K.; Bawendi, M.; Bulović, V. *Nature* **2002**, *420*, 800–803. (c) Craig, N. J.; Taylor, J. M.; Lester, E. A.; Marcus, C. M.; Hanson, M. P.; Gossard, A. C. *Science* **2004**, *304*, 565–567. (d) Sapsford, K. E.; Pons, T.; Medintz, I. L.; Mattoussi, H. *Sensors* **2006**, *6*, 925–953. (e) Borisov, S. M.; Wolfbeis, O. S. *Chem. Rev.* **2008**, *108*, 423–461.

(2) (a) Chen, J.; Liao, W.-S.; Chen, X.; Yang, T.; Wark, S. E.; Son, D. H.; Batteas, J. D.; Cremer, P. S. *ACS Nano* **2009**, *3*, 173–180. (b) Jaffar, S.; Nam, K. T.; Khademhosseini, A.; Xing, J.; Langer, R. S.; Belcher, A. M. *Nano Lett.* **2004**, *4*, 1421–1425. (c) Rabani, E.; Reichman, D. R.; Geissler, P. L.; Brus, L. E. *Nature* **2003**, *426*, 271–274. (d) Bigioni, T. P.; Lin, X.-M.; Nguyen, T. T.; Corwin, E. I.; Witten, T. A.; Jaeger, H. M. *Nat. Mater.* **2006**, *5*, 265–270. (e) Wang, Y.; Tang, Z.; Correa-Duarte, M. A.; Liz-Marzán, L. M.; Kotov, N. A. *J. Am. Chem. Soc.* **2003**, *125*, 2830–2831.

(3) (a) Bruchez; Jr, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013–2016. (b) Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Mattoussi, H. *Nat. Mater.* **2005**, *4*, 435–446.

(4) (a) Bowen Katari, J. E.; Colvin, V. L.; Alivisatos, A. P. *J. Phys. Chem.* **1994**, *98*, 4109–4117. (b) Wang, X.; Zhang, J.; Nazzal, A.; Xiao, M. *Appl. Phys. Lett.* **2003**, *83*, 162–164. (c) Torimoto, T.; Murakami, S.-Y.; Sakuraoka, M.; Iwasaki, K.; Okazaki, K.-I.; Shibayama, T.; Ohtani, B. *J. Phys. Chem. B* **2006**, *110*, 13314–13318. (d) Galian, R. E.; de la Guardia, M.; Pérez-Prieto, J. *J. Am. Chem. Soc.* **2009**, *131*, 892–893. (e) Liu, L.; Peng, Q.; Li, Y. *Inorg. Chem.* **2008**, *47*, 3182–3187.

(5) (a) van Sark, W. G. J. H. M.; Frederix, P. L. T. M.; Bol, A. A.; Gerritsen, H. C.; Meijerink, A. *ChemPhysChem* **2002**, *3*, 871–879. (b) Derfus, A. M.; Chan, W. C. W.; Bhatia, S. N. *Nano Lett.* **2004**, *4*, 11–18. (c) Zimnitsky, D.; Jiang, C.; Xu, J.; Lin, Z.; Tsukruk, V. V. *Langmuir* **2007**, *23*, 4509–4515.

(6) Uematsu, T.; Kimura, J.; Yamaguchi, Y. *Nanotechnology* **2004**, *15*, 822–827.

(7) Decher, G. *Science* **1997**, *277*, 1232–1237.

(8) Carrillo-Carrión, C.; Cárdenas, S.; Simonet, B. M.; Valcárcel, M. *Chem. Commun.* **2009**, 5214–5226.

(9) Nazzal, A. Y.; Qu, L.; Peng, X.; Xiao, M. *Nano Lett.* **2003**, *3*, 819–822.

(10) Uematsu, T.; Maenosono, S.; Yamaguchi, Y. *J. Phys. Chem. B* **2005**, *109*, 8613–8618.

(11) (a) Aldana, J.; Wang, Y. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 8844–8850. (b) Aldana, J.; Lavelle, N.; Wang, Y.; Peng, X. *J. Am. Chem. Soc.* **2005**, *127*, 2496–2504. (c) Munro, A. M.; Plante, I. J.-L.; Ng, M. S.; Ginger, D. S. *J. Phys. Chem. C* **2007**, *111*, 6220–6227.

(12) (a) Medintz, I. L.; Mattoussi, H. *Phys. Chem. Chem. Phys.* **2009**, *11*, 17–45. (b) Zenkevich, E.; Cichos, F.; Shulga, A.; Petrov, E. P.; Blaudeck, T.; von Borczyskowski, C. *J. Phys. Chem. B* **2005**, *109*, 8679–8692.

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