

## Direct Patterning of CdSe Quantum Dots into Sub-100 nm Structures

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Ordered, two-dimensional cadmium selenide (CdSe) arrays have been fabricated on indium-doped tin oxide (ITO) electrodes using the pattern replication in nonwetting templates (PRINT) process. CdSe quantum dots (QDs) with an average diameter of 2.7 nm and a pyridine surface ligand were used for patterning. The PRINT technique utilizes a perfluoropolyether (PFPE) elastomeric mold that is tolerant of most organic solvents, thus allowing solutions of CdSe QDs in 4-picoline to be used for patterning without significant deformation of the mold. Nanometer-scale diffraction gratings have been successfully replicated with CdSe QDs.

### Introduction

The assembly of colloidal QDs into large area, organized arrays can be used in a variety of applications including photonics,<sup>1</sup> light-emitting devices,<sup>2</sup> and hybrid organic/inorganic solar cells.<sup>3</sup> Recently, progress has been made toward the fabrication of photovoltaic (PV) devices using a blend of CdSe QDs in a conjugated polymer matrix. These devices are typically fabricated by spin-casting a solution of QDs and a conjugated polymer onto an electrode. In these systems, light absorption by the conjugated polymer generates an excited state known as an exciton. In order to obtain a charge separated state, the exciton must first diffuse to the polymer–QD interface. An exciton can diffuse 5–15 nm in conjugated polymer films before recombining.<sup>4</sup> Due to these constraints, the ideal device architecture for these solar cells would consist of an interdigitated network of the donor and acceptor materials with dimensions that are on the length scale of exciton diffusion. Electron transfer to the QD network follows charge separation; however, the overall efficiency of such devices remains low due to limited electron extraction through the QD network.<sup>5,6</sup>

Efficient electron extraction depends on reaching a percolation threshold such that long-range connectivity exists between individual QDs within the polymer film. By employing rod-shaped or tetrapod QDs, instead of spherical QDs, this threshold is more easily attained. Sun and co-workers have demonstrated that, once a percolation pathway has been created, an increase in electron transport perpendicular to the plane of the polymer film is observed, which leads to a measurable improvement in device performance.<sup>7,8</sup> Additionally, hyperbranched nanocrystals have been incorporated into PV devices to improve electron extraction.

This approach creates a percolation pathway within the polymer film as each CdSe particle extends from the bottom to the top electrode; however, the performance of these devices is limited by the inability of the conjugated polymer film to penetrate into the dense branches of the nanocrystals.<sup>9</sup> Another improvement in device performance was achieved by exchanging the surface ligand of the as-synthesized QDs, usually tri-*n*-octylphosphine oxide (TOPO), with pyridine. Replacement of TOPO is important because the long alkyl chain of the TOPO ligand can significantly decrease solar cell efficiencies by suppressing charge transfer between particles.<sup>10</sup> In an attempt to improve the dispersion of CdSe QDs in the polymer film, more sophisticated approaches have also been taken. For example, Liu and co-workers altered the end group functionality of a poly(thiophene) conjugated polymer so that rod-shaped CdSe-pyridine QDs were significantly more dispersed in the polymer film.<sup>11</sup> In another example, Sudeep and co-workers grafted an oligo(phenylene vinylene) ligand to CdSe QDs in order to achieve better dispersion in the neat phenylene vinylene polymer film.<sup>12</sup>

A variety of self-assembly techniques have been employed to fabricate ordered arrays of QDs. Water-soluble poly(ethylene oxide) (PEO) functionalized CdSe nanorods will organize themselves in the pores or channels of a diblock copolymer template; however, these arrays are not ideal for electronic applications due to the presence of both the insulating PEO surface ligands and the block copolymer film.<sup>13</sup> CdSe QDs have also been incorporated into breath figures, a technique based on the phenomenon of water condensing into well-ordered arrays of droplets on a polymer film.<sup>14</sup> This methodology generates thin films of QD patterns that are suitable for use in separation membrane and site-specific catalysis applications.

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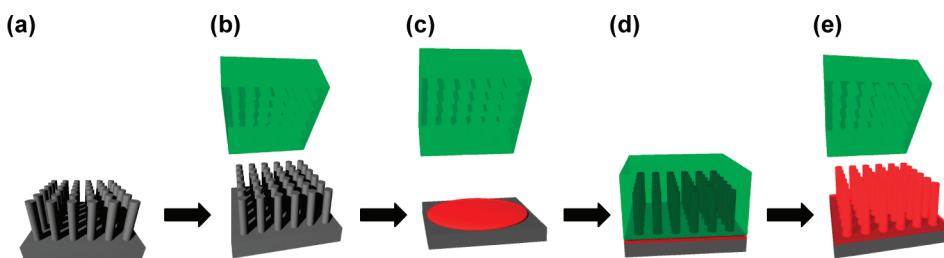
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**Scheme 1. Illustration of the PRINT Technique**

The assembly of QDs can also be achieved using top-down fabrication methods including Langmuir–Blodgett or microcontact printing. The Langmuir–Blodgett technique produces QD monolayers using an extremely low throughput process that is not amenable to the large-scale fabrication required for PV applications.<sup>15</sup> Microcontact printing utilizes a poly(dimethylsiloxane) (PDMS) stamp for molding and offers a more attractive methodology for fabricating solar cells based on the high speed and spatial resolution inherent to the process.<sup>16,17</sup> Unfortunately, microcontact printing suffers from swelling and deformation of the PDMS stamp in the presence of many common organic solvents including hexanes, xylenes, toluene, chloroform, and benzene.<sup>18</sup> In order to use these PDMS stamps for printing solutions of QDs, the mold is typically treated with an organic compound, such as Parylene-C, so that the surface is compatible with the QD solution. These chemical compatibility issues can increase the complexity of the printing process and also place limitations on the solvent system that can be used, thus restricting the nature of the surface ligand on the QDs. Recently, PDMS molds have been employed to generate CdSe QD patterns with dimensions of 150 nm or more, but these examples lack high spatial resolution.<sup>19,20</sup>

Cross-linkable PFPEs are a new class of mold material that can outperform PDMS in certain imprint lithography and micro-molding techniques.<sup>21,22</sup> PFPEs possess high solvent resistance and low surface energies ( $8\text{--}10 \text{ dyn cm}^{-1}$ ) and are thus well-suited to patterning a wide variety of materials. Previously, we have demonstrated the utility of PFPEs for molding metal oxide sol–gels for hybrid solar cells using the PRINT technique.<sup>23</sup> A general illustration for the process is shown in Scheme 1, depicting (a) the silicon master template, (b) mold release from the master template, (c) embossing a liquid precursor, (d) pattern transfer to the substrate, and (e) mold release from the embossed film. Herein, through the use of the PRINT technique and PFPEs, we present for the first time the fabrication of sub-100 nm patterned arrays of CdSe QDs using the PRINT process. These QDs possess pyridine surface ligands, making them attractive for use in solar cells.

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## Experimental Section

Chemicals were obtained from commercial sources and used as received. SEM images were obtained with a Hitachi S-4700 instrument. Fluorescence images were obtained with a Zeiss Axioskop 2MAT incident light microscope fitted with an AxiCam MRM digital camera.

**Mold Fabrication.** A liquid PFPE precursor solution comprising 1.5 kg/mol PFPE  $\alpha,\omega$ -functionalized dimethacrylate and the photoinitiator 2,2-diethoxyacetophenone was poured over a patterned master template. The liquid precursor was then cross-linked using UV photoirradiation ( $\lambda = 365 \text{ nm}$ ) for 3 min under a constant nitrogen purge. The fully cured PFPE elastomeric mold was then released from the master template.

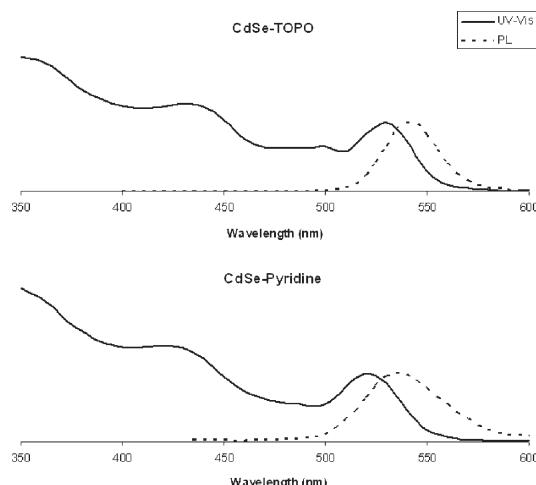
**CdSe QD Synthesis and Surface Ligand Exchange Reaction.** CdSe QDs were synthesized via a CdO-based route, similar to the method published by Qu and Peng.<sup>24</sup> CdO (0.064 g, 0.50 mmol), stearic acid (0.57 g, 2.0 mmol), hexadecylamine (HDA) (5.0 g), and tri-*n*-octylphosphine oxide (TOPO) (5.0 g) were combined in a reaction vessel and heated to 320 °C under argon. Once this mixture became clear, a solution of selenium (0.395 g, 5.0 mmol) in tributylphosphine (1.20 g) and octyldecylamine (4.0 g) was rapidly injected into the flask. An immediate color change from clear to deep red occurred, and the solution was held at 270 °C for 2 min to allow for QD growth. The solution was allowed to cool to room temperature and 20 mL of chloroform was added. This solution was held at 4 °C overnight in order to separate the CdSe from the excess ligand in solution. The resulting insoluble portion was discarded, and the CdSe QDs were precipitated with acetone and recovered via centrifugation. This step was repeated twice. The resulting orange-red precipitate was dissolved in hexanes and centrifuged to remove any remaining excess ligands. A surface ligand exchange was performed to replace the TOPO/HDA ligands with pyridine. The dried CdSe QDs were dissolved in anhydrous pyridine at 10 mg/mL and sonicated overnight at 75 °C. The resulting insoluble portion was discarded, and the CdSe QDs were precipitated with hexanes and recovered via centrifugation. The surface ligand exchange reaction was repeated in order to ensure surface coverage with pyridine. The QDs were characterized with UV–vis absorption data, FT-IR spectroscopy data, and HRTEM before and after ligand exchange.

**CdSe Patterning Procedures.** CdSe patterns were generated by starting with a 15 w/w solution of the CdSe-pyridine QDs in 4-picoline. A #14 Mayer rod was used to draw a film from the CdSe solution on an ITO-coated glass slide. A previously patterned PFPE mold was then pressed into the film. After heating the substrate and mold for 10 min at 85 °C, the mold was peeled off the substrate, leaving an embossed film.

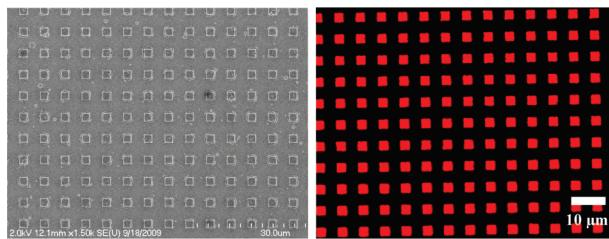
## Results and Discussion

The UV–vis and photoluminescence spectra of the CdSe-TOPO and CdSe-pyridine QDs in solution are shown in Figure 1. The size of the QDs can be calculated on the basis of the first

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**Figure 1.** UV-vis and photoluminescence spectra (PL) of CdSe-TOPO and CdSe-pyridine in solution.

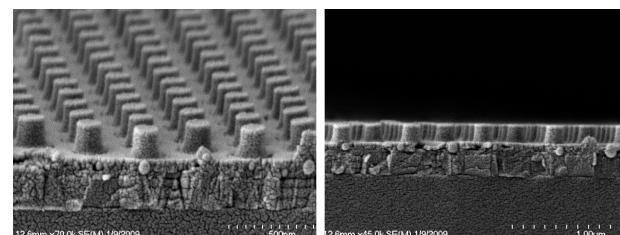


**Figure 2.** SEM and fluorescence images of patterned CdSe QDs using a  $3\text{ }\mu\text{m} \times 3\text{ }\mu\text{m} \times 0.75\text{ }\mu\text{m}$  mold.

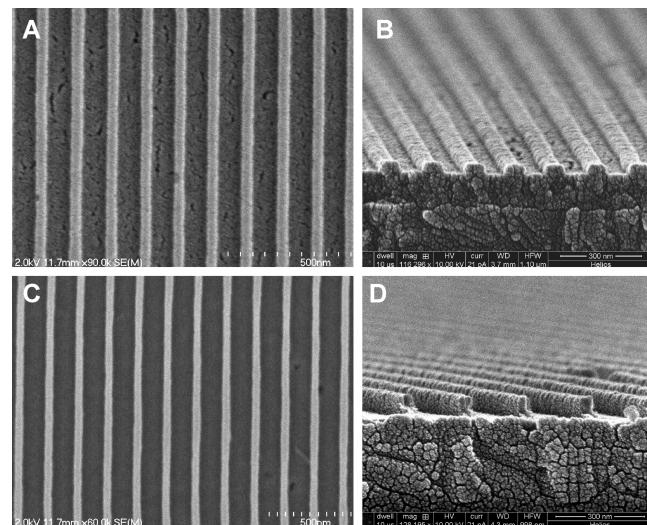
absorption peak wavelength.<sup>25</sup> The peak position of the CdSe-TOPO QDs is 530 nm, indicating an average QD diameter of 2.7 nm. As shown in Figure 1, the surface ligand exchange reaction does not significantly affect the first absorption peak position.

In order to generate a patterned array of QDs, a film was cast on an ITO electrode using a Mayer rod and a solution of CdSe QDs in 4-picoline. A patterned PFPE mold was then placed on top of this liquid film, and the solvent was evaporated at an elevated temperature. Following the evaporation step, the mold was easily removed from the embossed CdSe film. Prior to use, the PFPE mold is completely transparent and colorless, and it remains this way even after patterning the distinctively red solution of CdSe QDs in 4-picoline. This observation indicates that there is minimal absorption of the QD solution by the mold. The ease of this patterning technique is due to the chemical inertness, high gas permeability, and low surface energy of the PFPE mold. As the 4-picoline solvent evaporates through the mold, the remaining solution becomes increasingly concentrated with QDs. This concentrated solution fills the mold cavities due to capillary action. The fidelity of the resulting pattern of QDs depends on the original solution concentration and the rate of solvent evaporation. A solution with a QD concentration that is too low will incompletely fill the mold cavities and result in undersized or hollow features. SEM micrographs that depict this patterning result are available in Supporting Information.

The PRINT process enables pattern replication on both the micrometer and nanometer length scale. Figure 2 shows an SEM image and fluorescence pattern of embossed CdSe QDs on an ITO electrode. Figure 3 demonstrates a pattern where a cylindrical mold with a diameter of 200 nm and a height of 200 nm and a



**Figure 3.** SEM images of patterned CdSe QDs using a  $200\text{ nm} \times 200\text{ nm}$  cylindrical mold.



**Figure 4.** SEM images of patterned CdSe QDs from a diffraction grating with (A) and (B) a 150 nm pitch and 45 nm height and (C) and (D) a 180 nm pitch and 90 nm height.

solution of CdSe-pyridine in 4-picoline were employed. In order to demonstrate the inertness of the PFPE mold, we have also patterned CdSe-TOPO QDs in both *o*-xylene and diethylbenzene solvents. The fidelity of the resulting patterns is similar to the results in Figure 3, and SEM micrographs of these patterns have been included in Supporting Information. For the pattern in Figure 3, the film was embossed on a  $6.25\text{ cm}^2$  ITO electrode and consisted of cylinders that were approximately 150 nm in diameter and 150 nm in height. The reduction in feature size compared to the original mold dimensions indicates incomplete filling of the mold cavities. However, this process can be optimized by changing either the weight percent of the CdSe QD solution or the dimensions of the mold cavities. The patterns shown in Figure 4 were generated from a mold of a diffraction grating that has a 150 nm pitch and is 45 nm in height (Figure 4A,B) and one with a 180 nm pitch that is 90 nm in height (Figure 4C,D) but with the same solution concentration as in Figure 3. The feature dimensions of these patterns, all sub-100 nm, accurately reflect the original master template. It should be noted that the SEM micrographs in Figure 4 show surface texture that is from the metal sputtered on the sample for imaging purposes and does not arise from aggregates of the CdSe QDs. Additionally, we have replicated a master template that consists of randomly ordered silicon posts with dimensions as small as 30 nm, and SEM micrographs of these patterns are in Supporting Information.

Patterned QD arrays generated using the PRINT process are fairly robust. We have demonstrated the integrity of the features by sonicating the patterned arrays in  $\text{H}_2\text{O}$  for 20 min. After this

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time period, the samples were dried with nitrogen and examined using SEM. The postsonication features maintained the overall pattern quality, as shown by SEM images in the Supporting Information. Note that the patterned CdSe-pyridine QDs retain their respective surface ligand, as evidenced by dissolution of the patterned film after sonication in pyridine.

### Conclusions

We have demonstrated successful patterning of CdSe QDs on a sub-100 nm length scale using the PRINT technique. Additionally, due to the chemical inertness of the PFPE molds, we have not been limited in our choice of surface ligands or solvents for the QD solutions. As a result, the patterned QD arrays have the potential to be used in a variety of electronic applications where charge transport between QDs will not be impeded by the surface ligand. Furthermore, the PRINT process is amenable to high throughput fabrication techniques such as roll-to-roll processes. This technology would thus enable the facile production of large-scale solar cells, an important benchmark for the photovoltaics

field. In the future, we plan to fabricate and test hybrid solar cells using these sub-100 nm CdSe patterns.

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**Supporting Information Available:** SEM micrographs of various patterning results. This material is available free of charge via the Internet at <http://pubs.acs.org>.