

# The Patterning of Sub-500 nm Inorganic Structures for Hybrid Photovoltaic Applications

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## ABSTRACT

In this work, we have used the Pattern Replication in Non-wetting Templates (PRINT®) technique to pattern both titania and cadmium selenide (CdSe) quantum dots for potential application in hybrid photovoltaic devices. Titania lines have been replicated from an E-beam fabricated line grating master that consists of lines that are 60 nm in width, 100 nm in height, and spaced by 60 nm. Additionally we have extended the PRINT process to include the ability to pattern CdSe quantum dots. Patterns in this material have been generated using a master that consists of cylinders that are 200 nm in diameter and 200 nm in height. We have also demonstrated the ability to conformally coat these inorganic structures with a conjugated polymer film, indicating the possibility for these patterns to be used in hybrid photovoltaic devices.

**Keywords:** soft lithography, perfluoropolyether, titania, cadmium selenide, photovoltaics

## 1 INTRODUCTION

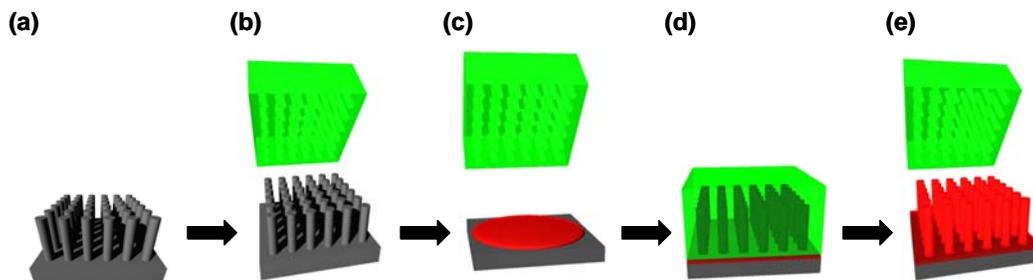
With global energy demands increasing yearly and current energy production dependent on a finite supply of fossil fuels, solar energy provides a sustainable energy alternative to traditional energy sources. Current approaches in the field of organic-based solar cells typically rely on blended films of donor and acceptor-type materials, such as conjugated polymers and PCBM respectively.<sup>1,2</sup> These methods result in the formation of a disordered bulk heterojunction (BHJ) morphology where it can be difficult to control the device architecture over large areas.<sup>3</sup> The imperfections in the film morphology of these devices often leads to poor charge separation and transport within the

device. Consequently, the overall efficiency of these devices is quite low.

In organic-based photovoltaic devices, 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 donor-acceptor interface. Studies have shown that 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 organic-based solar cells would consist of an interdigitated network of the donor and acceptor materials that is on the length scale of exciton diffusion. This geometry would allow for both an increase in the harvesting of excitons and charge transport within the device. Additionally, for efficient absorption of sunlight, the device needs to be 100 – 200 nm thick.<sup>4</sup>

Soft lithography offers a top-down fabrication method for obtaining the ideal device architecture just described. Typically this process uses polydimethylsiloxane (PDMS) as a low modulus mold material to pattern organic materials into continuous arrays.<sup>5</sup> The most commonly used PDMS is Sylgard 184, a commercially available elastomer with a surface energy of 22-25 dynes cm<sup>-1</sup>.<sup>6</sup> However, Rolland *et al.* have recently developed crosslinkable perfluoropolyethers (PFPEs) as a new mold material for soft lithography. PFPEs possess excellent solvent resistance and extremely low surface energies (8-10 dynes cm<sup>-1</sup>) and are thus well suited to patterning relevant materials for photovoltaic applications.<sup>7</sup>

Previously we have used the PRINT technique, a technology that utilizes PFPEs as a mold material, to pattern metal oxides for hybrid solar cells.<sup>8</sup> In this soft lithography method, shown in Figure 1, an elastomeric mold is generated from a liquid PFPE precursor. Once photochemically cured, the mold is released from the



**Figure 1.** Schematic illustration of the PRINT process: a) silicon master template; b) mold release from master template; c) embossing a liquid precursor; d) pattern transfer to the substrate; e) mold release from the embossed film.

master and used to pattern a liquid sol-gel at elevated pressure and temperature. Due to the chemical inertness and high gas permeability of the mold, a wide variety of sol-gel chemistries can be patterned into sub-500 nm structures. Additionally, the PRINT technique is an attractive method for solar cell production because of its amenability for scale-up to large area device fabrication.

In order to apply this technique to hybrid solar cells, we patterned disordered, sub-100 nm titania features and tested PV devices with these patterns.<sup>9</sup> The patterned titania/polymer devices showed a two-fold improvement in power conversion efficiency (PCE) when compared to flat titania/polymer devices. However, the overall PCE of 0.61% was still much lower than literature reports for organic BHJ solar cells comprised of PCBM/polymer. We believe that using a master template with smaller feature sizes and a higher degree of order could lead to an improvement in efficiency. Additionally, employing a materials system comprised of quantum dots and a conjugated polymer could lead to higher device efficiencies.

In this work, we explore the possibility of using E-beam fabricated line gratings as master templates for patterning titania. Additionally, we extend the PRINT process to include the patterning of CdSe quantum dots into arrays of sub-500 nm features.

## 2 EXPERIMENTAL

### 2.1 Mold Fabrication

A liquid PFPE precursor solution comprised of 1.0 kg mol<sup>-1</sup> PFPE  $\alpha,\Omega$ -functionalized dimethacrylate and the photoinitiator 2,2-diethoxyacetophenone was poured over a patterned master template. The liquid precursor was then crosslinked using UV photoirradiation ( $\lambda = 365$  nm) for 3 min under a constant nitrogen purge. The fully cured PFPE elastomeric mold was then released from the master template.

### 2.2 Titania sol gel synthesis and patterning

A stable TiO<sub>2</sub> sol was prepared by chelating the inorganic titanium precursor titanium tetrakis(*n*-butyloxyde), Ti(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>, with acetylacetone. This solution was diluted with 2-propanol before adding acetic acid. Solvent removal from this system was performed at 110°C and a xerogel was formed. This amorphous solid was calcined at 450°C to obtain the anatase form of TiO<sub>2</sub>. The molar ratios of the titanium precursor, chelating ligand, and catalyst were 7:16.2:1 respectively.

Titania patterns were embossed following the steps outlined in Figure 1. The liquid sol-gel precursors were drop-cast onto a relevant substrate and a PFPE mold was pressed into the sol and held at constant pressure. The sample was held at an elevated temperature in order to undergo the sol-gel transition via solvent removal. After sufficient time for

solvent evaporation, the low surface energy mold was peeled off the substrate, leaving an embossed xerogel film.

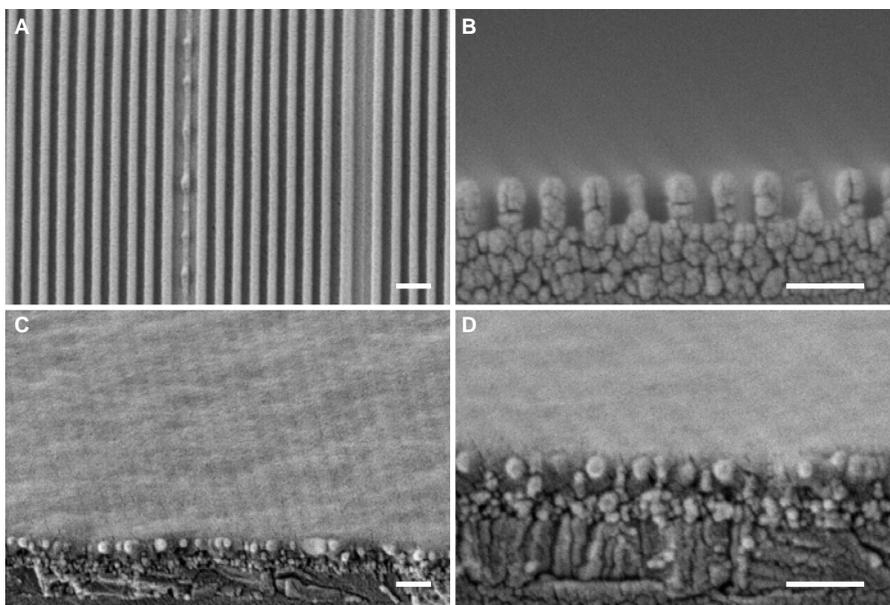
### 2.3 CdSe quantum dot synthesis and patterning

CdSe nanoparticles were synthesized via a CdO based route, similar to the method published by Qu and Peng.<sup>10</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 turned 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 nanoparticle growth. The solution was allowed to cool to room temperature and 20 mL of chloroform was added to precipitate out the CdSe nanocrystals. 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 nanocrystals 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 nanocrystals were dissolved in anhydrous pyridine at 10 mg/mL and sonicated overnight at 75°C. The resulting insoluble portion was discarded and the CdSe nanocrystals were precipitated with hexanes and recovered via centrifugation. The surface ligand exchange reaction was repeated in order to ensure surface coverage with pyridine. The nanocrystals were characterized with UV-Vis absorption data, FT-IR spectroscopy data, and HRTEM before and after ligand exchange.

CdSe patterns were generated by starting with a 0.17 mg/ $\mu$ L solution of the CdSe-pyridine nanocrystals in 4-picoline. A Mayer rod was used to draw a film from the CdSe solution on an ITO coated glass slide. A PFPE mold was 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.

### 2.4 Conjugated polymer film deposition

Polymer films were deposited over the patterned inorganic structures from a 1 weight percent solution of poly (3-hexylthiophene), P3HT, in dichlorobenzene. The polymer solution was spun cast at 1000 rpm for 60 sec to obtain the appropriate film thickness. A melt infiltration was performed at 185°C for 5 min to promote conformal coating of the inorganic structures with the polymer film.



**Figure 2.** SEM micrographs depicting: (a) and (b) anatase TiO<sub>2</sub> patterns replicated from a 60 x 100 nm line grating master; (c) and (d) TiO<sub>2</sub> line patterns covered with a film of P3HT. All scale bars are 200 nm.

### 3 RESULTS AND DISCUSSION

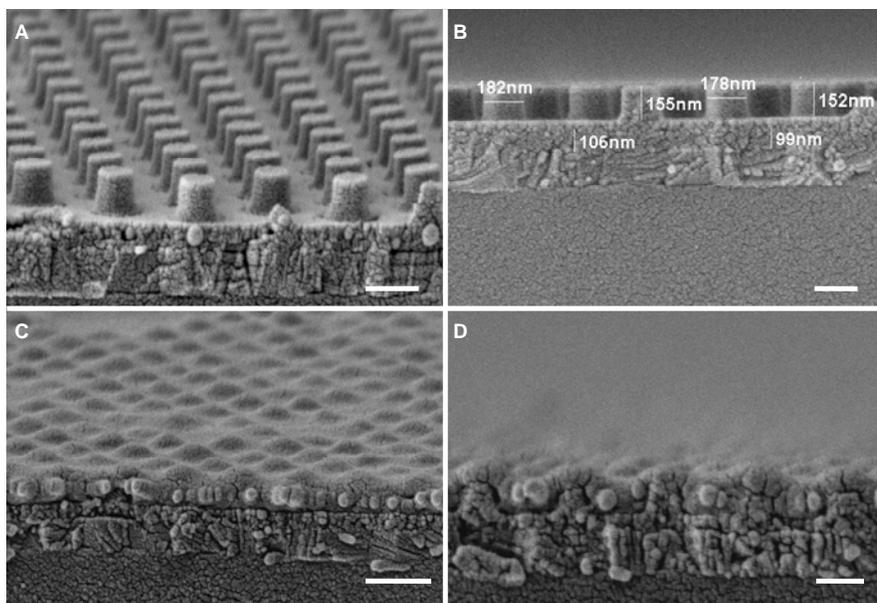
The ideal device architecture for a BHJ solar cell consists of an interdigitated network of two materials with different electron affinities, on the length scale of the exciton diffusion length. This geometry increases the likelihood of (1) charge separation and (2) charge transport. Based on HOMO/LUMO levels, many inorganic materials, including metal oxides and semiconducting quantum dots, are electronically compatible with conjugated polymers for solar cell applications.<sup>11,12</sup> However, simple blends of these materials do not easily form an interconnected network of the inorganic component in the polymer film. Such a percolation pathway is necessary for electron transport through the inorganic material to the electrode. The PRINT technique offers a top-down fabrication route to enable the formation of inorganic domains that provide a direct pathway for electron transport.

The PRINT process depends on the fabrication of master templates for pattern replication. In order to obtain master templates with feature sizes below 100 nm, non-traditional lithography techniques must be employed. In previous efforts, Nano-Sphere Lithography (NSL) has been utilized to fabricate a master template consisting of disordered pillars that are 20-50 nm in diameter and 100 nm in height.<sup>9</sup> Lines grating master templates with a greater degree of order have recently been fabricated using electron beam instrumentation at Oak Ridge National Laboratories. The lines are 60 nm in width, 100 nm in depth, and spaced by 60 nm. The patterned area covers 1 cm<sup>2</sup>, which is a significantly larger area than typical E-beam patterned substrates. This surface area coverage was obtained by using a longer write time.

PFPE molds were made from this line grating master template and then used to pattern a titania sol gel. The resulting amorphous xerogel was then calcined at 450°C in order to obtain the anatase form of TiO<sub>2</sub>. The resulting patterns are shown in Figure 2. From the cross sectional image, it appears the titania lines closely replicated the original master template dimensions. These patterns could potentially be used for photovoltaic applications and to demonstrate this utility, we have successfully coated the titania lines with P3HT, a conjugated polymer commonly used in the photovoltaics field. As shown in Figure 2, the polymer film conformally coats the titania lines.

A major milestone for BHJ photovoltaics is to achieve device efficiencies of  $\geq 10\%$ .<sup>4</sup> However, literature reports for titania-polymer solar cells typically report efficiencies below 1%.<sup>12</sup> It is believed that device performance is limited by intrinsic trapping states in the titania; therefore, improved device performances will require the use of alternative inorganic materials. One commonly used material is semiconducting quantum dots, most notably cadmium selenide. Literature reports have established that blends of cadmium selenide with a conjugated polymer produce photovoltaic efficiencies near 3%.<sup>13</sup>

The PRINT technique offers an alternate route to achieve a percolation pathway of CdSe nanocrystals within a polymer film. In order to demonstrate the capability of the PRINT process, we have developed a technique for patterning CdSe quantum dots. Quantum dots were synthesized following the procedure developed by Qu and Peng that utilizes CdO as the starting material.<sup>10</sup> Additionally, a surface ligand exchange was performed to replace TOPO ligands with pyridine. This methodology has been established as a technique to increase device performance by improving charge transport between



**Figure 3.** SEM micrographs depicting: (a) and (b) 200 x 200 nm patterned arrays of CdSe quantum dots; (c) and (d) CdSe patterns coated with a film of P3HT. All scale bars are 200 nm.

nanocrystals. In order to pattern the CdSe, a film was cast on an ITO electrode from a solution of CdSe in 4-picoline. Initially, patterns were generated using a PFPE mold of a master template consisting of cylinders that were 200 nm in diameter and 200 nm in height. The resulting features are shown in Figure 3. To demonstrate the potential application of these patterns for photovoltaic devices, a P3HT polymer film has been deposited over the features. As shown in the cross sectional SEM, the film deposition process does not degrade the shape of the CdSe patterns and results in the even coverage of the features.

#### 4 CONCLUSIONS

The PRINT technique, a soft lithography process that employs PFPE molds for pattern replication, has been extended to include patterning sub-100 nm line gratings in titania and sub-200 nm cylinders in CdSe quantum dots. These inorganic materials can be utilized as electron accepting materials in BHJ photovoltaics. Additionally, we have demonstrated our ability to cover these inorganic patterns with conjugated polymers, further indicating the potential for this process to be used for device fabrication. Future work will include patterning CdSe quantum dots on the sub-100 nm length scale and subsequent device fabrication and testing of these patterns.

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