

Reusable Stamps for Printing Sub-100 nm Patterns of Functional Nanoparticles

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Printed electronics are ubiquitous in many devices such as photovoltaics, thin-film transistor (TFT) backplanes, radio frequency identifications (RFID), and touch-panel displays.^[1–3] The printing process has the advantage of reducing the fabrication cost, compared with conventional silicon-based processing, because the existing, expensive, patterning technologies are potentially expected to be replaced by the roll-to-roll process. It also has the benefit of employing various functional materials such as metal nanoparticles (NPs) and semiconductor nanocrystals, which are proven to be essential to photonic, electronic, and sensing devices.^[4–8] Although printed electronics are close to commercialization, there still exist some restrictions or limitations on realizing high-resolution patterns, such as sub-100 nm features, which are likely to replace the existing miniaturized semiconductor fabrication or nanoscaled heterojunction solar cell devices.

To date, there have been several reports on the unconventional printing methods such as contact or transfer printing of functional materials.^[9–16] It has been noted that the most important aspect for the printing technique is the stamp design because pattern resolution is significantly dependent upon the choice of stamp materials. In order to realize high-resolution patterns with a stamp, the stamp required some rigidity to overcome the lateral collapse of neighboring patterns, which is a serious problem for soft polydimethylsiloxane (PDMS) based stamps.^[17] Stamps should also have low surface energy to transfer ink materials to a target substrate. Furthermore, the stamp materials should not be swollen by the solvent for functional materials. In order to satisfy those requirements, there have been many complicated attempts,^[17–29] such as fabrication of rigiflex stamps followed by anti-adhesion surface treatments, or synthesis of stamp materials with special designs. After preparing a proper stamp with a complicated process, the feature must be uniformly coated with functional ink materials onto protruding parts of the stamps. In the case

of sub-100 nm patterning of NPs, we would spin-coat the NPs onto the stamp because of the need for control of the film consistency. Following spin-coating, the NPs in the protruding parts of the stamp are transferred to a target substrate, then the designed stamps should be reusable for the next round of NPs transfer. However, the NPs trapped in the recessed parts of the stamps are hard to remove, especially because some inorganic and metal NPs are not soluble in typical organic solvents, as shown in Figure S1 of the Supporting Information. Etching with strong acids is one possibility to remove the NPs; however, the stamps could be deformed or denatured due to these harsh processing conditions.

In this communication, we present an effective process for reusable stamps in high pattern resolution of functional NPs. A patterned stamp is cleaned by removing NPs in the recessed region of the patterns with a UV-curable adhesive before moving on to the next cycle of printing with the stamp. The process, which is applicable not only to organic stamps, but also to inorganic stamps such as silicon stamps which have expensive processing costs, allows the same stamp to be reused repeatedly for the NP patterning. We demonstrate high-resolution patterning by rigid stamps with a low surface energy, the repeated use of the reusable stamp for defining sub-100 nm scale features, and the formation of an RGB (red, green, blue) pattern by transferring quantum dots (QDs) for three colors with these stamps. This color patterning has been performed using just one color per stamp, and then by using one stamp for multiple colors.

Figure 1 shows scanning electron microscopy (SEM) images of stamps and transferred NPs on a target surface. We used a perfluoropolyether (PFPE) material which incorporates a tetra-crosslinking site in order to increase rigidity.^[25] Also, the fluorinated surface helps the stamps to have a low surface energy.^[25–29] After preparing a silicon master, fabricated by the conventional photolithography and dry etching process, the PFPE prepolymer, which is solid at room temperature, was heated to 60 °C for liquid-like behavior and was poured onto the silicon master. A thin, flexible, polyethylene terephthalate (PET) film was then pressed onto the liquid film as a supporting backplane. After crosslinking by ultraviolet (UV) exposure, the PFPE film was removed from the master with PET film, and was subsequently used as a stamp. For a pattern transfer, the PFPE stamp was spin-coated with NPs suspended in toluene. In this case, QD NPs are suspended in toluene (2 wt%). After evaporating the solvent at room temperature, the coated NPs were transferred by contact printing to a substrate

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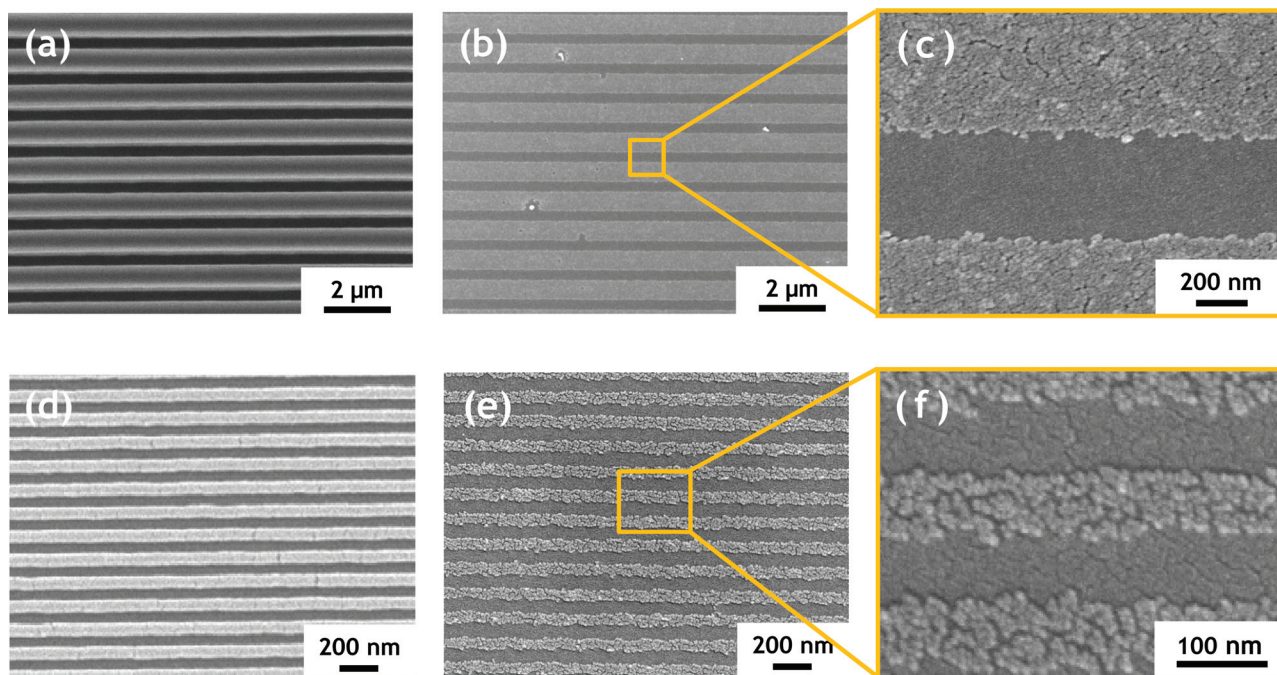


Figure 1. SEM images of PFPE stamps and QD arrays transferred onto substrates. a) An SEM image of a PFPE stamp with 400 nm wide lines separated by 200 nm spaces. b) An SEM image of a QD array transferred onto a PEDOT:PSS-coated substrate. Only QDs placed on the protruding area of the PFPE stamp are transferred. c) An amplified image of (b). d) An SEM image of a PFPE stamp with 60 nm wide lines separated by 60 nm spaces. e) An SEM image after the QD transfer with the PFPE stamp shown in (d). f) An enlarged SEM image of (e).

coated with poly(3,4-ethylenedioxythiophene)–polystyrene sulfonic acid (PEDOT:PSS). Due to the low surface energy of PFPE, facile release from the master template without destruction of features, along with efficient transfer of NP pattern onto the desired substrate, was achieved. It is noted that the silicon master could be used as a stamp as well.

Figure 1a is the SEM image of PFPE stamp with 400 nm wide protruding lines (1 μm high) separated by 200 nm wide spaces between the lines. As shown in Figure 1b, the QDs on the protruding parts of the PFPE stamp are transferred onto a PEDOT:PSS layer. Figure 1c shows the magnified image of Figure 1b. It is noted that if the pattern is formed by pressure, the pattern shape should be a negative of the stamp. In order to demonstrate patterning of sub-100 nm features with NPs, we additionally used a master with a line width of 60 nm. The replicated PFPE stamp has lines 60 nm wide without lateral collapse as shown in Figure 1d. The QDs on the protruding parts of the PFPE stamp are transferred successfully (Figure 1e). Figure 1f shows the magnified image of Figure 1e.

When the size of the feature of the stamp such as 60 nm lines in Figure 1 is relatively small, the lines can collapse laterally or cling to one another unless the stamp material has a relatively high Young's modulus. The critical aspect ratio preventing lateral collapse has been shown to be determined by^[30]

$$\frac{h}{w} \left(\frac{8\gamma}{3E^*w} \right)^{1/4} \leq \sqrt{d/w} \quad (1)$$

where $E^* = E/(1-\nu^2) \approx 4E/3$ (ν is the Poisson's ratio of the material), h is the height of the feature, w is the width, E is

Young's modulus of the material, d is the distance between the lines, and γ is the surface energy of the stamp material.^[31] If the distance d is equal to the line width w , the equation can be rearranged to give

$$E \geq 2\gamma \frac{h/w}{w} \quad (2)$$

From the equation, the modulus for no lateral collapse can be calculated. The required modulus for 60 nm lines with an aspect ratio of 5 and a surface energy of 20 mN m^{-1} is 3.3 MPa. The PFPE replica stamp utilized in this study has a relatively high modulus (~ 160 MPa as shown in Figure S2, Supporting Information) and a low surface energy (17.7 mN m^{-1} by the Owen–Wendt method).^[32] Therefore, the stamp has the sufficient mechanical integrity to resist lateral collapse. When a silicon master is used as a stamp to transfer QDs, the feature size could be much smaller because of the high modulus of the inorganic master. It is noted that the theoretical approximation does not exactly define the resolution for sub-nanometer scale features because there exist many other factors that can influence the pattern transfer fidelity such as feature size, aspect ratio, pattern density, sidewall profile, and processing conditions.^[33]

The ability to control thickness of NPs on the PFPE stamp by varying the concentration of $\text{Cd}_{1-x}\text{Zn}_x\text{Se}_{1-y}\text{S}_y$ quantum dots in toluene is shown in **Figure 2**. When the concentration is 0.1 wt%, the printed patterns exhibit some porosity due to partial coverage by NPs, as shown in the atomic force microscopy (AFM) image in Figure 2a. However, as shown in Figure 2b for 1 wt% QD solution, QD coverage is more than

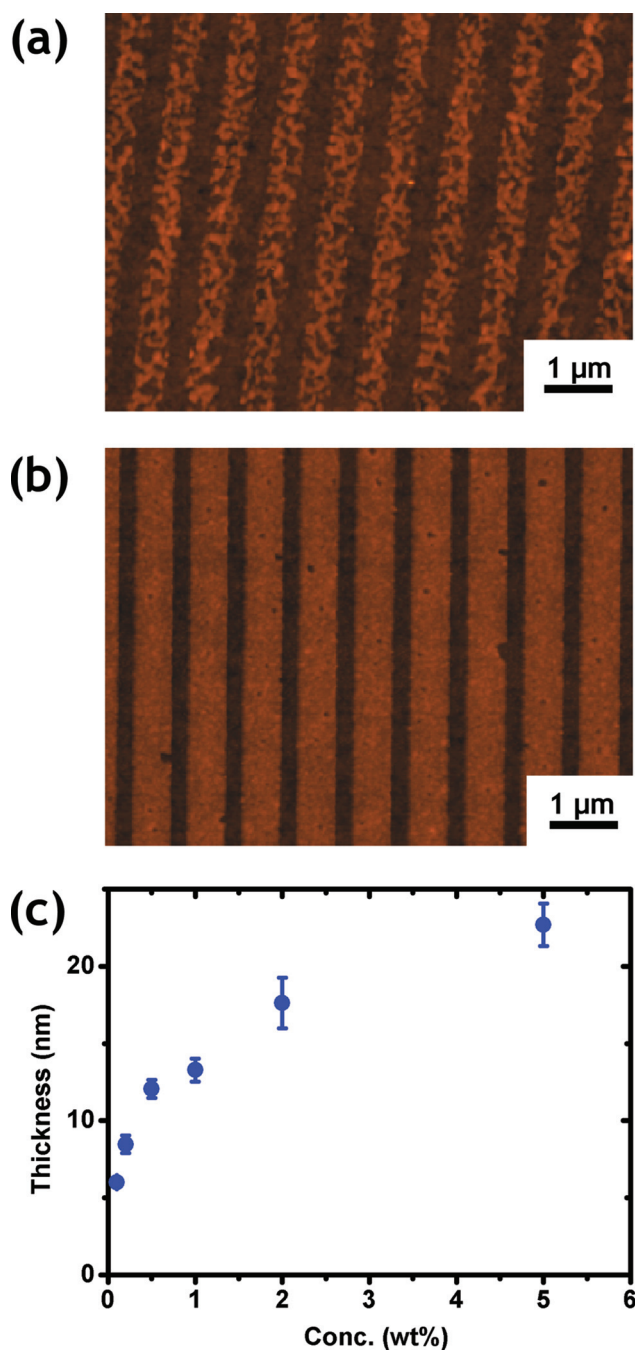


Figure 2. AFM images showing NP arrays on PEDOT:PSS-coated substrates when the concentration of QD in toluene is: a) 0.1 and b) 1 wt%. The bright areas are the QD-transferred areas. When QD concentration is 0.1 wt%, empty spots are clearly shown in the line shape patterns. c) Coated layer thickness as a function of QD solution concentration.

monolayer in all areas of the substrate. Figure 2c displays the average thickness of deposited QDs on the substrate as a function of concentration of QD solution. The thickness in this graph represents the average value of the deposited QD layer. In the case of 2 wt% QD solution, for instance, the thickness of the QD layer is approximately 18 nm.

Figure 3 shows a schematic illustration of the cleaning process for reusable stamps. The PFPE stamp replicated from

a silicon master is shown in Figure 3a, and the stamp spin-coated with NPs is depicted in Figure 3b. To transfer the particles (Figure 3c), the PFPE stamp coated with QDs was placed on a PEDOT:PSS-coated substrate, and then pressed against the substrate at ~ 400 kPa and 100 °C. There was no pattern formed on the substrate under the same conditions when the bare stamp without NPs was used, which indicates that no imprinting is involved in the transfer process. Figure 3d shows the substrate after the transfer. As illustrated in Figure 3e, the NPs in the recessed part of the stamp still remain in the stamp. These NPs are difficult to remove and become increasingly cumbersome as the feature size shrinks. For repeated high-resolution patterning of nanoparticles, however, their removal is a necessity. A commercialized UV-curable resin (Norland Optical Adhesive (NOA)) was used to remove the NPs from the PFPE stamp as shown in Figure 3f. Therefore, through these steps, transferred NP arrays on a substrate were fabricated by repeated transfers with a reusable PFPE stamp.

The fluorescence microscopy images, obtained during the cleaning process illustrated in Figure 1, are shown in **Figure 4**. Figure 4a shows the PFPE stamp that was spin-coated with QDs suspended in toluene. Figure 4b is the image of PEDOT:PSS-coated substrate after QD transfer. The used PFPE stamp after the QD transfer (Figure 4c) shows the mirror image of the QDs detached from the used stamp by UV-curable adhesive (Figure 4d). After the removal, the used stamp surface is devoid of QD as shown in the fluorescence microscopy image of Figure 4e. Figure 4f shows the failure of removing QDs in the recessed area of a used stamp even after several sonication steps in toluene.

An important aspect of the present study is that it is possible to transfer more than one kind of particle with a single reused stamp as shown in **Figure 5**. For the nanoscale, orthogonal pattern in Figure 5a, QDs are transferred in a line pattern (60 nm wide lines with 60 nm spacing) onto a substrate. After this first transfer of QDs, we cleaned the stamp with the detaching method and used the same stamp again to transfer the line pattern in the direction perpendicular to the original lines. The same demonstrations with a silicon master are shown in Figure S3 in the Supporting Information. Red (R) and green (G) lines, as shown by the fluorescence microscopy image in Figure 5b, were formed by first transferring red-emitting QDs onto a substrate, followed by the green-emitting QDs, using a single, reused stamp. The same procedure as in Figure 5a was followed to transfer the QDs and clean the stamp. Furthermore, it is possible to construct an RGB display by transferring red, green, and blue QDs onto a substrate. First, red-emitting QDs were deposited onto the substrate by the transfer process, and the used PFPE stamp was cleaned by the detaching process. Subsequently, green- and blue-emitting QDs were patterned by sequential transfer printings with manual alignment (Figure S4, Supporting Information). The display of RGB lines constructed with a single, reused stamp is shown in Figure 5c.

In summary, we have presented a cleaning process of used stamps for repeated, high-resolution patterning of

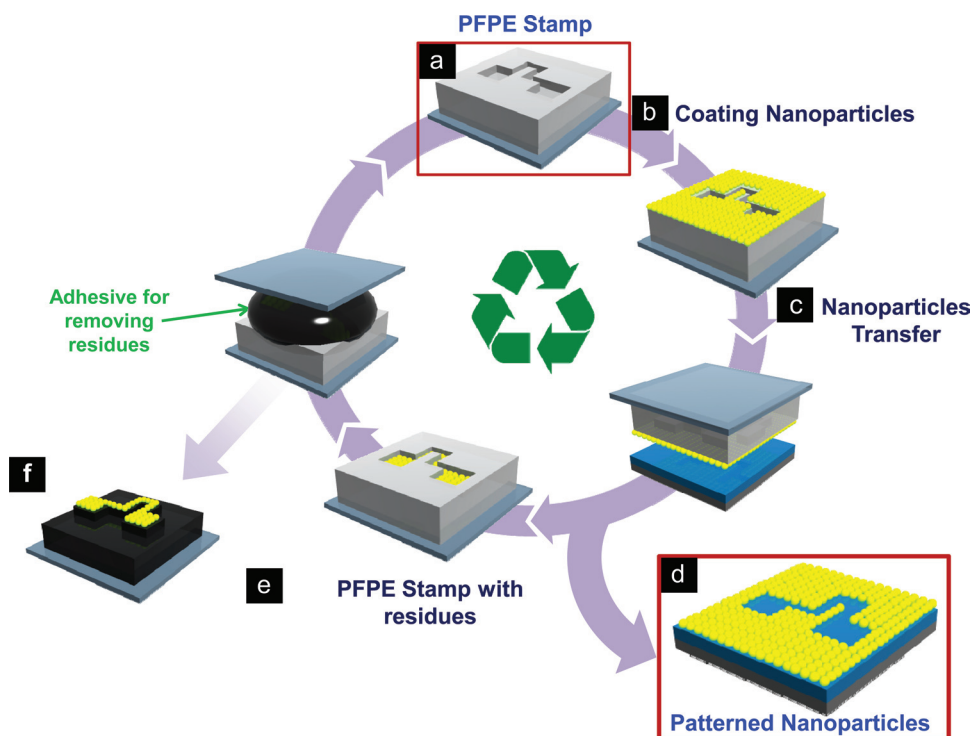


Figure 3. A schematic illustration of the cleaning process for reusable stamps. a) A PFPE stamp with desired feature size and patterns. b) Top of the stamp following spin-coating with NPs. c) NP transfer process with proper pressure and heat. d) Transferred NP patterns on a substrate. e) A PFPE stamp with residues in the recessed area of the stamp. f) Removal of NPs in the recessed area of the stamp with a commercialized UV-curable resin.

NPs. The process, which is applicable not only to organic stamps, but also to inorganic stamps such as silicon wafer stamps, allows the same stamp to be reclaimed, and

repeatedly reused for NP patterning. The NP patterning demonstrated here was in the sub-100 nm range (60 nm wide lines), which has never been reached before. The

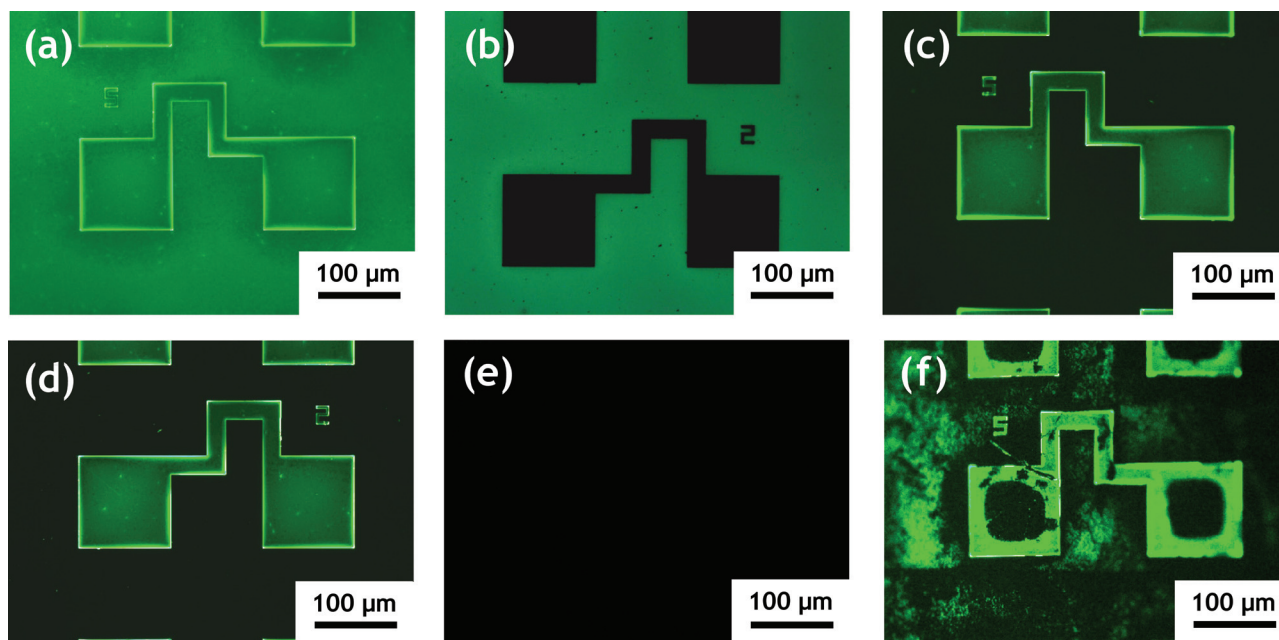


Figure 4. Fluorescence microscopy images obtained during the cleaning process for a reusable stamp. a) A fluorescence microscopy image after coating QDs on a prepared PFPE stamp. b) An image of a QD-transferred, PEDOT:PSS-coated substrate. The green area is the QD-transferred area. c) An image of the PFPE stamp after QD transfer to the substrate. The green area represents the QDs left in the recessed region of the stamp after QD transfer. d) An image of a UV-cured adhesive film containing QDs after their removal from the PFPE stamp. e) A used stamp surface without residual QDs. f) An image of a PFPE stamp obtained after sonication only. Note that a large amount of QDs still remain on the stamp even after ultrasonication.

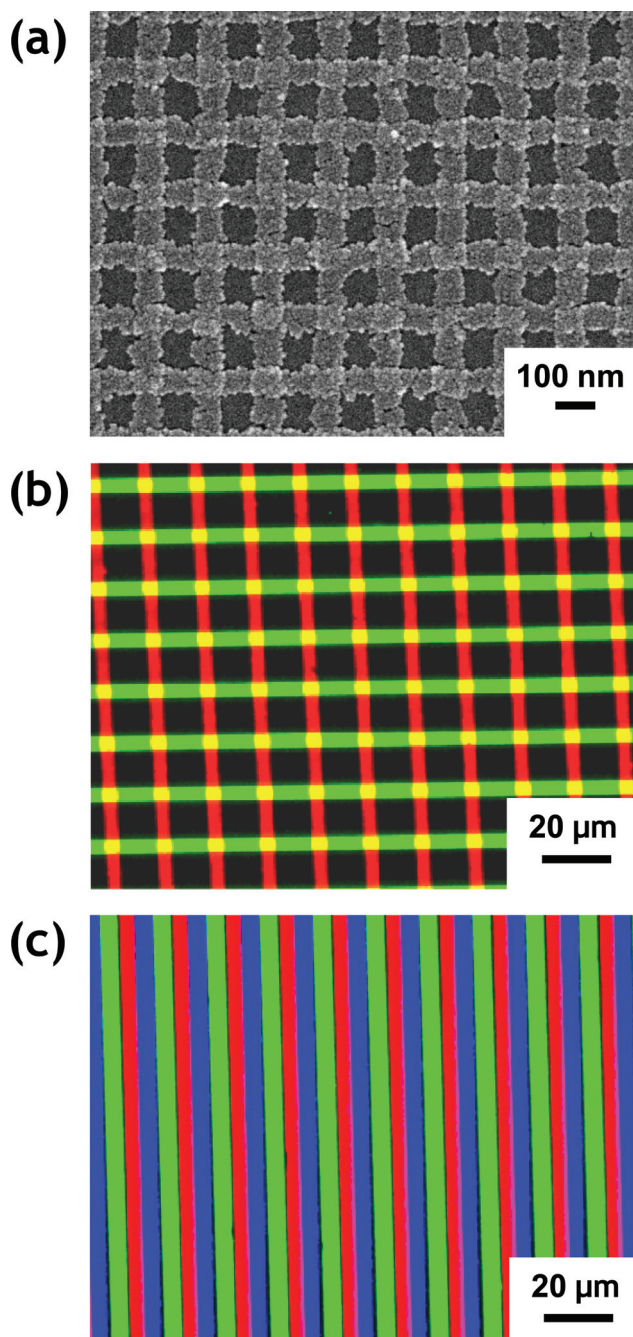


Figure 5. a) An SEM image of criss-crossing stripes (60 nm wide with 60 nm spacing) of QDs obtained by transferring QDs twice onto a PEDOT:PSS-coated substrate with a single, reused stamp. b) A fluorescence microscopy image of orthogonally transferred QD arrays with red and green emissions on PEDOT:PSS-coated substrate. c) A fluorescence microscopy image of directionally transferred RGB QD arrays on a PEDOT:PSS-coated substrate.

same technique makes facile sub-100 nm patterning possible through the proper choice of stamp material. The ability to transfer many different NPs with a single, reused stamp, as demonstrated here, for the realization of an RGB display, must be valuable in fabricating various devices such as light-emitting diodes, solar cells, thin-film transistors, and displays.

Experimental Section

PFPE Stamp Fabrication: We prepared PFPE stamps by blending PFPE precursor (5101x, Solvay Solexis Inc.) with 4 wt% photoinitiator (Darocur 1173, Ciba). The PFPE resin utilized is in solid state at room temperature (melting point: ~ 35 °C). Thus, the material is heated up to around 60 °C and is blended with the photoinitiator. By using this UV-crosslinkable PFPE material, we fabricated the silicon master by the conventional photolithography and dry etching process. After drop-casting the precursor onto the master and placing a PET film as a backplane on top of the PFPE precursor, the stamp was exposed to UV light (~ 2 mW cm $^{-2}$, 365 nm) to crosslink the PFPE stamp for the nanoparticle transfer procedure. After detaching the stamp from the master at a rate of ~ 20 mm s $^{-1}$, the stamp was fully cured under UV light (~ 15 mW cm $^{-2}$, 365 nm, 30 min).

QD Synthesis: The QDs utilized in this study were synthesized by the process discussed in previous works.^[33,34] The green and red QDs in this study have a core/shell structure (Cd $_{1-x}$ Zn $_x$ Se $_{1-y}$ S $_y$) with composition gradients, which relieve the lattice mismatch between the CdSe core and the ZnS shells. The emission wavelengths of the QDs are produced by changing the relative amounts of Cd, Zn, Se, and S. With a higher concentration of cadmium, the core is larger and the peak shift results from the change in the core size of the QDs. The blue QDs were synthesized by introducing sulfur precursors into the mixed solution of cadmium oleate and zinc oleate. The emission wavelength of Cd $_{1-x}$ Zn $_x$ S/ZnS core/shell nanostructures was finely tuned from violet (415 nm) to blue (461 nm) by adjusting the amount of sulfur precursors in the first injection (sulfur in 1-octadecene), thus changing the actual cadmium content ratio in the alloyed Cd $_{1-x}$ Zn $_x$ S.

Transfer Printing with Cleaning Process: We spin-coated QDs suspended in toluene onto the prepared PFPE stamp (3000 rpm, 30 s). After evaporating the solvent at room temperature, the QDs on the protruding parts of the stamp were transferred to the PEDOT:PSS (coating thickness of ~ 50 nm) layer on the silicon master. In the transfer process, the use of appropriate pressure and heat (~ 400 kPa, 100 °C for 10 min) make it easier to transfer the particles to the desired position. After transferring the QDs, we detached the residual QDs in the recessed area of the used PFPE stamp with a conventional, UV-curable adhesive (NOA-73, Norland), which was peeled off the stamp after curing with UV light at ~ 2 mW cm $^{-2}$ for 5 min. This cleaning procedure allows the reuse of the PFPE stamp for NP transfer processes. As shown in Figure 5, we can transfer various nanoparticles onto a substrate in multi-step processes to produce, e.g., the RGB multicolor pattern, using only a single, reused stamp.

Measurements: The patterns generated were examined by scanning electron microscopy (SEM, XL30FEG) and atomic force microscopy (AFM, NS3A). The average height of NP patterns on the substrate was obtained by the image analyzer software (Gwyddion). We measured the height of these patterns in 5 different areas, and their average values, as well as the standard deviations, are reported.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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