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# Controlled Placement of Colloidal Quantum Dots in Sub-15-nm Clusters

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**Abstract:** We demonstrated a technique to control the placement of 6-nm-diameter CdSe and 5-nm-diameter CdSe/CdZnS colloidal quantum dots (QDs) through electron-beam lithography. This QD-placement technique resulted in an average of three QDs in each cluster, and 87% of the templated sites were occupied by at least one QD. These QD clusters could be in close proximity to one another, with a minimum separation of 12 nm. Photoluminescence measurements of the fabricated QD clusters showed intermittent photoluminescence, which indicates that the QDs were optically active after the fabrication process. This optimized top-down lithographic process is a step towards the integration of individual QDs in optoelectronic and nano-optical systems.

**Keywords:** templated self-assembly, placement, electron-beam lithography, sub-10-nm, nanocrystals, colloidal quantum dots, CdSe, CdSe/CdZnS, photoluminescence, blinking.

## 1. Introduction

Semiconductor colloidal quantum dots (QDs) are important building blocks for nanoscience.[1] One key aspect of this system is the fine synthetic control of its electronic and optical properties.[1], [2] For convenience, many optical and electronic studies use a thin film of QDs deposited by spin casting, dip coating or drop casting. This ensemble configuration is extensively used to investigate the fundamental properties of QDs, such as band-gap engineering,[2] energy transfer,[3-5] and multi-exciton generation,[6] which are relevant to the future applications of QDs in solar cells[6] and light-emitting diodes.[7] However, properties such as exciton lifetime and photoluminescence intermittency are obscured by ensemble measurements and can be better understood at the single-QD or few-QD-cluster level.[2, 8] Most single-dot and cluster studies are performed on films spun from very dilute solutions, which results in a random distribution of quantum dots on a substrate. Some of these measurements would benefit immensely from accurate position control of sub-10-nm QDs, which has not previously been possible. Single-QD patterning is one of the challenges in designing a system that takes advantage of the single-dot properties of QDs.[9] In addition, systematic investigation of single QDs, dimers (clusters of two QDs), and trimers (clusters of three QDs) is limited by complex, or non-reproducible fabrication processes. Hence, placement of sub-10-nm QDs at desired positions is expected to be a powerful tool to quantitatively investigate this system.

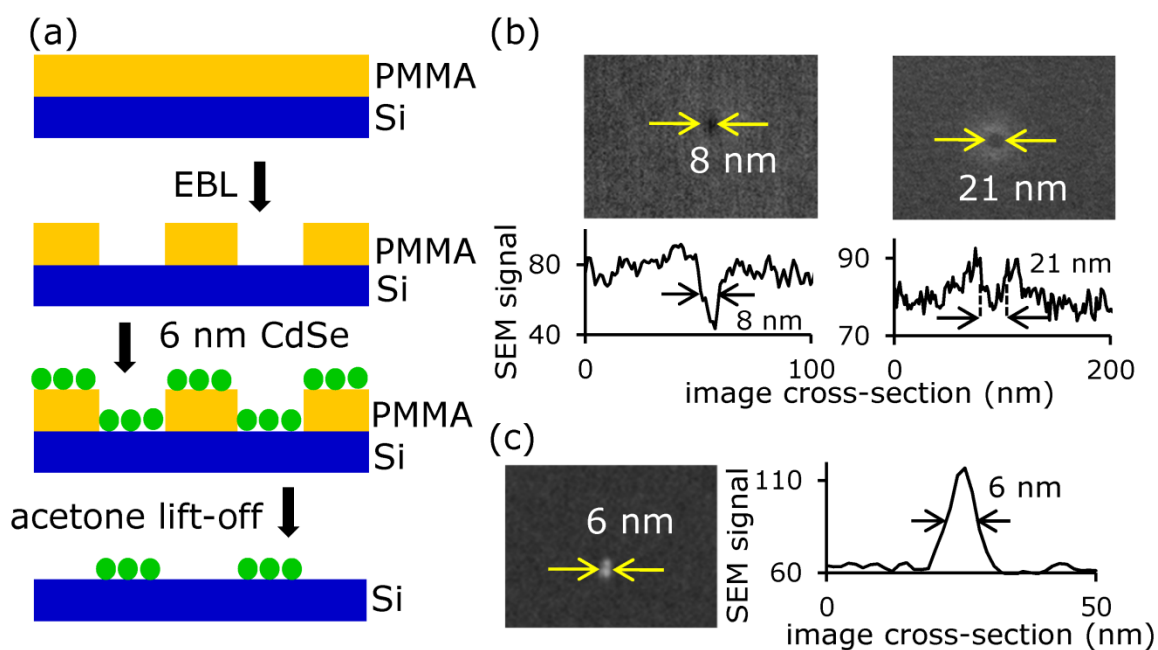
Previous reports have demonstrated template-directed self assembly of colloids at the 100-nm scale.[10-15] In the sub-100-nm scale, there are reports of template-directed placement of sub-20-nm-diameter clusters of gold colloidal QDs,[16-20] and sub-50-nm-diameter clusters of semiconductor colloidal QDs[15, 21-25] using electron-beam lithography, dip-pen lithography, scanning-probe lithography, and block-copolymer self assembly. However, for semiconductor QDs smaller than 10 nm in diameter, sub-20-nm patterning has not previously been possible and is crucial to permit placement of single QDs and small QD clusters.

This letter presents a simple and effective patterning technique to control the position of individual QDs by using sub-10-nm electron-beam lithography (EBL). We show that the placed QDs are luminescent and present intermittent photoluminescence (PL), known as blinking, which indicates the presence of single QDs.[3-5] Applications that may emerge through the use of this technique are the fabrication of single-photon emitters,[9, 26] excitonic circuits,[27-29] and a large variety of nano-optical devices.[30, 31]

## **2. Results and Discussion**

The fabrication process for QD placement is illustrated in Figure 1. A poly(methylmethacrylate) (PMMA) resist was spin coated on a silicon substrate to a thickness of 40 nm, and baked at 200°C for 2 minutes on a hotplate. Then, a design with single-pixel exposures (doses from 10 to 200 fC/dot) and 10- to 20-nm-diameter areal exposures (doses from 400 to 4,000  $\mu\text{C}/\text{cm}^2$ ) were exposed on PMMA by EBL. This exposure was used to obtain an array of templates, PMMA holes, with varying diameters. EBL was carried out at an electron energy of 30 keV on a Raith 150 EBL system (see

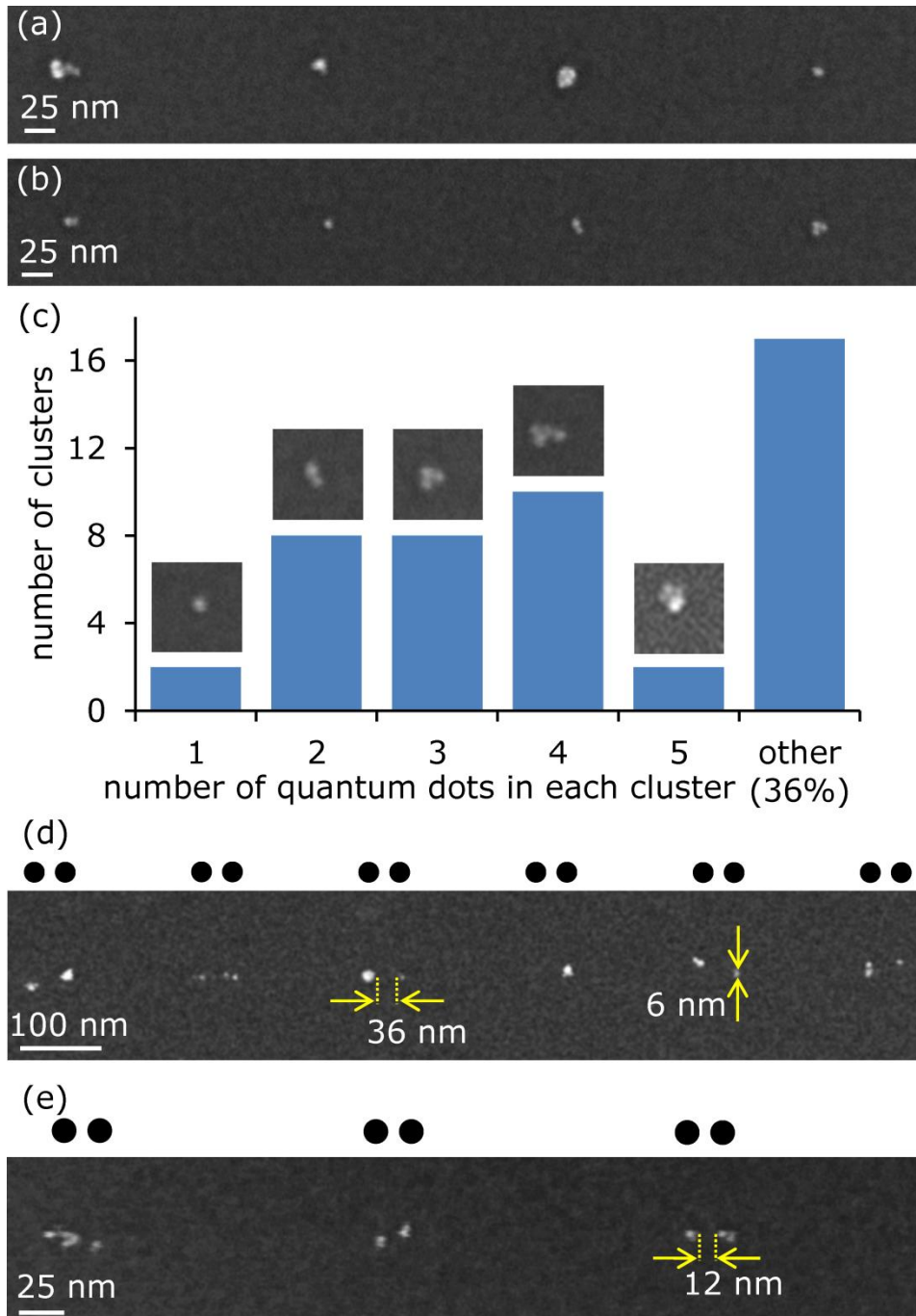
details in Appendix). The QD deposition was carried out at a relative humidity lower than 38%. In particular, working in a nitrogen glove box improved QD assembly uniformity[24]. The QD solution (6-nm-diameter CdSe or 5-nm-diameter CdSe/CdZnS) was spin cast or drop cast on top of the PMMA templates, and the remaining resist was removed by dissolution in acetone for 3 min. This process resulted in QD clusters attached to the substrate. Figure 1b shows the patterned PMMA with templates from 8 to 21 nm in diameter. The placed QDs were analyzed in a Zeiss scanning electron microscope (SEM), as shown in Figure 1c.



**Figure 1.** Overview of the fabrication process for placing QDs. (a) Schematics of the fabrication process: PMMA was spin-coated to a thickness of 40 nm on Si, followed by EBL; Then, 6-nm-diameter CdSe QDs were spin-coated or drop cast; Finally the PMMA lift off was done with acetone, leaving clusters of CdSe QDs. (b) Top: scanning-electron micrographs of PMMA templates with 8 nm (minimum feature size used) and 21 nm diameters. Bottom: SEM image cross-section across the PMMA templates. (c) Left: SEM of a patterned CdSe QD cluster (dimer). Right: SEM cross-section over one CdSe QD, with full-width at half maximum of 6 nm.

In order to minimize the number of QDs in each cluster and increase the patterning yield, defined here as the percentage of the templated sites that were occupied by at least one QD, the QD solution concentration, the QD solution purification[2], the resist thickness, and the feature size were systematically optimized (see details in the Supplementary Information). We found that 1-2 layers of QDs were obtained by spin casting a 2- $\mu$ M QD solution or by drop casting a 2-4  $\mu$ M solution of QDs (as determined by the absorption at 350 nm).[32] We maximized the QD adhesion on the substrate by purifying the QDs three times [33] (see details in Supplementary Information) to reduce the number of ligands on the QD surface and to reduce the number of free ligands in solution. To achieve the smallest QD clusters, the EBL development was optimized to obtain the smallest templates. PMMA development was done at 7°C [20, 34] for 30 s in 3:1 (isopropyl alcohol: methyl isobutyl ketone), without any subsequent rinse, and blow dried with a nitrogen gun for 1 min. The resist thickness was also minimized to 12 nm to decrease the number of QDs that could fit inside each template hole in the resist.

Figure 2 shows the results of the optimized process, achieved by using 12-nm-thick PMMA as the mask, a development temperature of 7°C, and a 2- $\mu$ M QD concentration. We achieved placement of a few QDs in each cluster for the smallest templates, as shown in Figure 2b. We also observed a few QDs present outside the patterned area; we suspect that these QDs were re-deposited during the lift-off process (see details in Supplementary Information).



**Figure 2.** Scanning-electron micrographs of (a, b) 6-nm-diameter CdSe QDs and (d, e) 5-nm-diameter CdSe/CdZnS. The fabrication was optimized to minimize the number of QDs in each cluster. (a) QD clusters were fabricated using templates with 15-20 nm diameter. (b) QD clusters were fabricated using templates with 8-15 nm diameter; these were the smallest clusters fabricated. (c) Histogram of the number of QDs in each cluster *versus* the number of clusters, using the smallest fabricated templates. We analyzed

54 sites designed for QD clusters. The QDs were counted from the SEM micrographs. Representative SEM images were added to the histogram. The top of (d) and (e) shows the designed templates with ~12 nm diameters for placing QDs in close proximity to one another, with gaps of ~36 nm in (d) and ~12 nm in (e). The bottom of (d) and (e) shows SEM micrograph of clusters of QDs composed of 5-nm-diameter CdSe/CdZnS (core/shell).

In order to quantify the statistical distribution of this process, a histogram of the fabricated structures in Figure 2b is shown in Figure 2c. The QDs in each cluster were counted from SEM micrographs. The pattern yield (percentage of the templated sites occupied by at least one QD) was 87%. An average of three QDs in each site was observed. For this average value, only clusters with an identifiable number of QDs (64% of total) were considered. QD clusters with undetermined number of QDs were 36%. From these undetermined clusters, 24% (8% of total) had area smaller than 12×12 nm (2×2 dots), so they were expected to have less than 5 QDs in each cluster. 76% of the undetermined clusters (27% of total) had area larger than 12×12 nm, so they were expected to have more than 5 QDs in each cluster. The difficulty in counting QDs is due to the SEM resolution limits, residues of PMMA and solvents (i.e., acetone, hexane) from the fabrication process, and possible QD vertical stacking.

This technique allows QDs to be placed with the accuracy and resolution of EBL. Figure 2d shows placement of pairs of QD clusters with ~36 nm separation. We also defined the dimer placement yield, which is the percentage of two adjacent templated sites occupied by at least one QD in each site. The dimer placement had 55% yield (the placement yield of each QD cluster was 78%). Figure 2e shows placement of pairs of QD clusters with ~12 nm separation. The dimer placement here had a 36% yield (the



placement yield of each QD cluster was 66%). We hypothesize that the placement yield was significantly smaller for 12-nm gaps due to two factors: (1) reduced template uniformity; and (2) the template size was close to the hydrodynamic radius of the QDs (~10 nm).

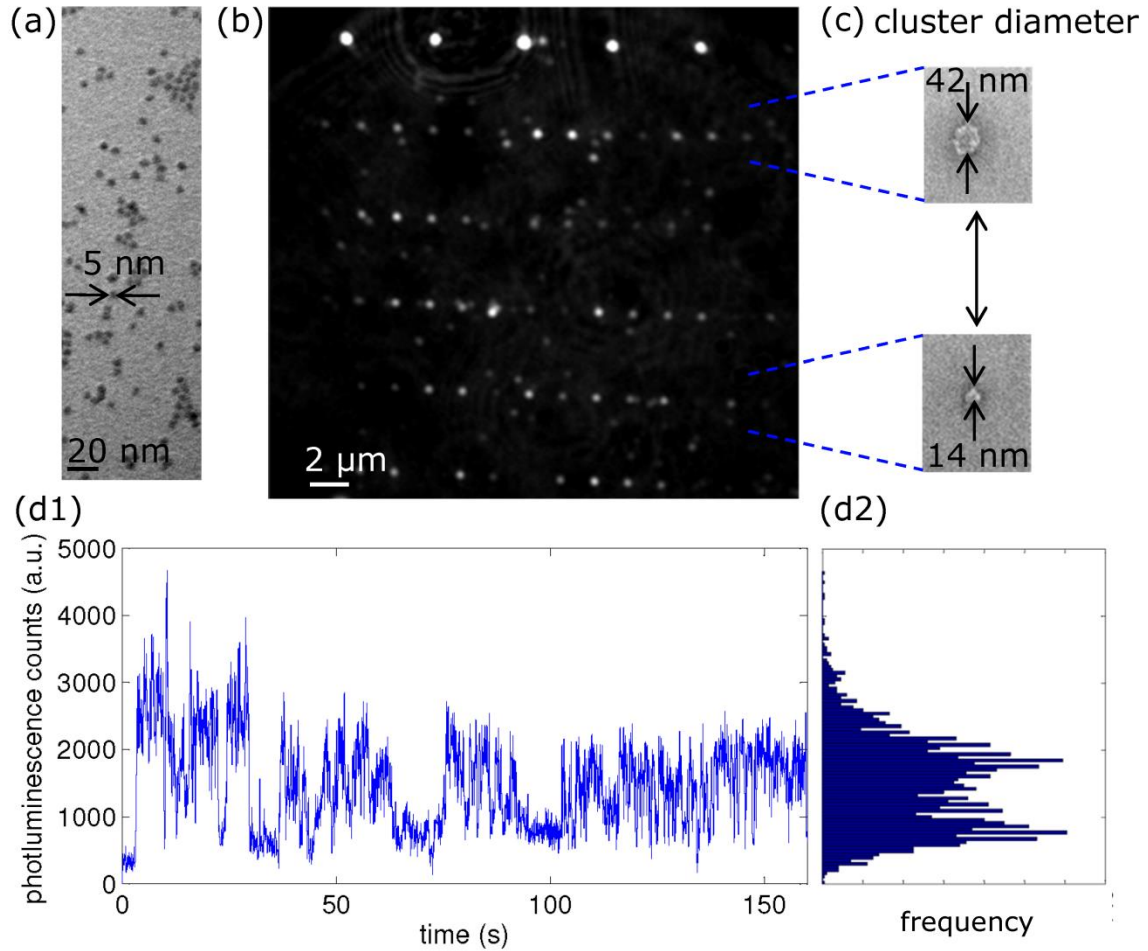
We hypothesize that the variation in the number of QDs placed in each site came in part by a non-chemical-equilibrium deposition of the hydrophobic QDs on the hydrophilic SiO<sub>2</sub> substrate. Because of this non-equilibrium, during solvent drying the QDs were forced to being deposited on the SiO<sub>2</sub> surface. Nevertheless, this process presented high resolution and simplicity, not requiring a pre-treatment of the substrate.

For the application of patterned QDs in excitonic or nano-optical devices, optical characterization is required. We investigated the resilience of the photoluminescence (PL) following the patterning process. By generating small QD clusters, we expected to be able to observe intermittent PL, i.e., “blinking”.<sup>[35]</sup>

The CdSe QDs (or core QDs) are not ideal for spectroscopic techniques that require high quantum yield because numerous non-radiative pathways are available in these QDs. For this reason, we used core/shell dots (CdSe/CdZnS) to maximize the PL signal. We generated samples using CdSe/CdZnS core/shell (5-nm diameter, synthesis method described in Appendix) QDs deposited on 300-nm-thick SiO<sub>2</sub> on a silicon substrate. The sample fabrication follows the same procedure previously described. We stored the samples in a nitrogen glove box before the PL measurements to prevent any QD oxidation.

The samples were observed with wide-field and confocal scanning microscopy, as shown in Figure 3. Figure 3a shows a TEM micrograph of the 5-nm CdSe/CdZnS QDs

used for optical characterization. In Figure 3b, the QD clusters were placed in a rectangular grid with  $2\ \mu\text{m} \times 5\ \mu\text{m}$  spacing to easily resolve their position in the PL microscope. We obtained significant PL signal of the QD patterns, with  $\sim 10$  to 200-nm dimensions. We also observed a few QDs present outside the patterned area. These QDs may have moved and re-deposited during the lift-off process. The top row in Figure 3b had 200-nm-QD clusters with constant PL. The PL signal was also constant for micrometer size clusters. The two lower rows of QDs in Figure 3b are made of QD clusters from  $\sim 10$  to 20 nm. We chose one QD cluster at the bottom row ( $\sim 15$  nm diameter) and measured the PL time trace for 160 s, as shown in Figure 3d1. We notice significant PL intermittency. This behavior was also observed for sub-40-nm QD clusters. Figure 3d2 is the histogram of the PL counts. This PL intermittency shows that we generated small enough QD clusters so that we can resolve PL fluctuation caused by QD blinking; thus, the placed QD clusters may be used for further experiments and applications.



**Figure 3.** (a) Transmission electron micrograph of CdSe/CdZnS core/shell QDs randomly deposited on a carbon membrane, with average diameter of 5 nm used for optical characterization. (b) Wide-field photoluminescence image of CdSe/CdZnS QD clusters placed in a rectangular array of  $2\ \mu\text{m} \times 5\ \mu\text{m}$ . The peak of emission wavelength was 576 nm. (c) SEM of QD clusters that are ~10 nm to 42 nm in diameter (the top bright clusters in (b) are 200-nm markers of QDs). (d1) Photoluminescence time trace of one QD cluster. The time trace shows intermittent luminescence (blinking). (d2) PL intensity *versus* frequency. The PL intensity presented a bi modal distribution, indicating blinking.

### 3. Conclusion

In summary, we demonstrated a technique to control the placement of few-QD clusters through EBL. This QD placement allows QD clusters of one to five QDs to be fabricated.

The process was developed by optimizing QD solution, resist thickness, and template size. One figure of merit in this process is the pattern yield, defined here as the percentage of templated sites occupied by at least one QD. A pattern yield of 87% was achieved with an average of three QDs in each cluster. We performed PL of the fabricated QD clusters, showing that the QDs are optically active after the fabrication process, presenting blinking in the photoluminescence. This optimized top-down lithographic process is a step towards the integration of individual QDs in optoelectronic systems.

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#### **4. Appendix**

Here we describe the experimental methods used in this article.

#### 4.1 Synthesis of CdSe( $Zn_xCd_{1-x}S$ ) core(shell) QDs

CdSe cores were synthesized according to previously reported procedures.[33, 36] Overcoating with an alloyed shell was carried out via modifications to previously reported procedures.[37] Briefly, CdSe cores precipitated from the growth solution by the addition of methanol were redispersed in hexane and injected into a degassed solution of 6 g of 99% trioctylphosphine oxide (TOPO) and 0.4 g *n*-hexylphosphonic acid. After removing the hexane under reduced pressure at 50°C, the flask was back-filled with dry N<sub>2</sub> and the temperature increased to 170°C before adding 0.25 mL of decylamine and stirring for 30 min. Precursor solutions of diethylzinc (ZnEt<sub>2</sub>), dimethylcadmium (CdMe<sub>2</sub>), and hexamethyldisilathiane [(TMS)<sub>2</sub>S] were prepared by dissolving the appropriate amounts of each in 4 mL of TOP and loading them into two separate syringes for metal and sulfur under an inert atmosphere. The molar quantity of ZnEt<sub>2</sub> required to achieve the desired shell thickness (typically 5 monolayers) was calculated according to the methods of Leatherdale.[32] For an alloyed shell, an appropriate mole fraction ZnEt<sub>2</sub> was replaced by CdMe<sub>2</sub>. A 1.5-fold molar excess of (TMS)<sub>2</sub>S was used. The precursor solutions were injected simultaneously into the 170°C bath at a rate of 4 mL/h. The QDs were stored in the growth solution under ambient conditions and centrifuged once more before use.

#### 4.2. Electron-beam Lithography (EBL)

EBL was carried out at an electron energy of 30 keV on a Raith 150 EBL system with a thermal-field-emitter source operating at 1800 K (~ 0.5 eV energy spread), a 20 μm aperture, 50 μm field size, a working distance of 6 mm and a beam current of 150 pA.

#### 4.3. Scanning electron microscopy

The colloidal quantum dots were placed on Si and 300-nm-thick SiO<sub>2</sub> on Si substrates (using the described fabrication method), and imaged in a thermal-field-emitter source Zeiss scanning electron microscope (the same used for lithography) at 10 keV, using in-lens secondary-electron detector, with electron-beam current of ~ 250 pA, and 6 mm working distance. No contrast enhancement techniques (such as metal deposition) were used.

#### *4.4. Transmission electron microscopy*

The TEM sample was prepared by dropping a dilute hexane solution of QDs onto a TEM grid (Ted Pella, Ultrathin Carbon Type-A, 400 mesh, Copper) resting on filter paper. TEM imaging was performed on a JEOL 200CX in bright field mode, with an accelerating voltage of 120 kV onto a 1.3Mpix AMT digital camera. Only standard condenser and objective apertures were used.

#### *4.5. Optical characterization*

The samples were observed with wide-field and confocal scanning microscopy using an air microscope objective (100×, 0.7 NA) and a 514-nm CW argon ion laser for excitation. The collected emission was detected by an avalanche-photodiode-based single-photon detector. The background from the laser was removed using a 514-nm filter.

**Supporting Information Available:** Detailed optimization of the fabrication process (Figures S1-S3).

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