Templated Placement of Colloidal Quantum Dots

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Semiconductor colloidal quantum dots (QDs) are electronically-quantized systems with promising applications in optoelectronic devices [1]. A key aspect of such systems is the fine control of optical transitions in the synthesis process [2]. For convenience, these QDs are predominantly used in thin-film arrangement, deposited by spin casting or dip coating. However, the investigation of single QDs, dimers (two QDs), and trimers (three QDs) is limited by complex and non-reproducible processes. Therefore, single-QD placement is one of the major challenges to both investigating and designing a system that takes advantage of individual properties of QDs [3]. Applications that may emerge by using this technique is the fabrication of single-photon emitters [3], excitonic circuits [4], and nano-optical devices. Previous reports [5, 6] demonstrated placement of sub-100-nm clusters of colloidal QDs. However, further investigation is necessary for the placement of single QDs smaller than 10 nm.

We will present a templated-self-assembly technique to control the position of individual QDs through electron-beam lithography (EBL), as shown in Figure 1a. The template size was minimized by using cold development [7] leading to minimum feature size of 5 nm. Figure 1b shows isolated QD clusters attached on the substrate. The novelty of this approach is in the combination of sub-10-nm EBL, optimized concentration of QD solution, and optimized resist thickness. This technique enables fabrication of QD clusters with an average of 3 QDs in each cluster, shown in Figure 1c. One figure of merit in this process is the pattern yield, which is the ratio of fabricated QD clusters to the patterned templates. The optimized pattern yield achieved was 87%. We compare the templating effect by modifying the surface chemistry of the QDs (i.e., by ligand exchange) and the substrate (i.e., by using a self assembled monolayer). In addition, we use 200-kV EBL to place QDs in close proximity due to higher resolution capabilities, as indicated in Figure 2.

To achieve highly luminescent QD patterns, we chose to use 5-nm-diameter core/shell dots of CdSe/CdZnS. We lithographically placed these QDs on SiO_2/Si substrate and performed confocal photoluminescence, in order to demonstrate the optical quality of the placed QDs, as shown in figure 3.

References: **[1]** A. P. Alivisatos, *Science* 271, 933 (1996); **[2]** S. A. Empedocles *et al.*, *Phys. Rev. Lett.* 77, 3873 (1996); **[3]** Lukas Novotny and Niek van Hulst· *Nat. Photon.*5, 83 (2011); **[4]** Alejandro Perdomo *et al., Appl. Phys. Lett.* 96, 093114 (2010); **[5]** S. Liu *et al.*, *Nano Lett.* 4,845 (2004); **[6]** J. A. Liddle *et al.*, *J. Vac. Sci. Technol. B* 22, 3409 (2004); **[7]** B. Cord *et al.*, *J. Vac. Sci. Technol. B* 25, 2013 (2007).

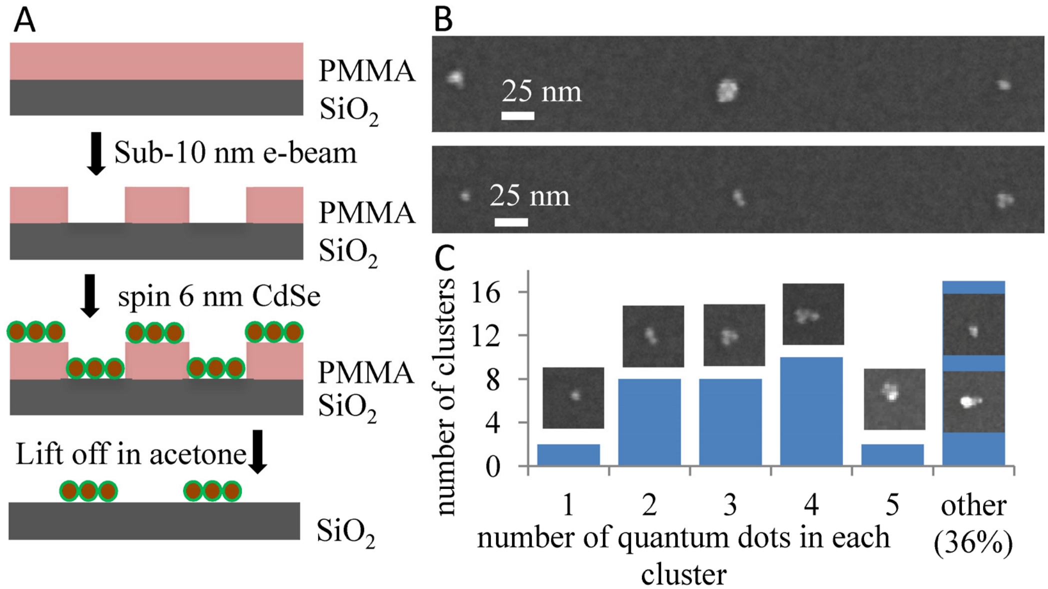

Figure 1. (A) Fabrication process of templated QDs. PMMA was spin coated to a thickness of 12 nm on SiO_2, followed by 30-kV EBL and development at 6°C in 3:1 isopropanol:methyl isobutyl ketone. Then, 6 nm of CdSe QDs were spin casted. The PMMA lift off was done with acetone, leaving small clusters of CdSe QDs. (B) shows scanning-electron micrographs of templated QDs (6-nm-diameter CdSe). The solution concentration was 2 μM. (C) Histogram of the number of QDs in each cluster *versus* the number of clusters, for the smallest fabricated templates. We analyzed 54 clusters of QDs, and the QDs were counted by using high-resolution SEM micrographs. On the inset of every histogram bar is presented one illustrative SEM image used.

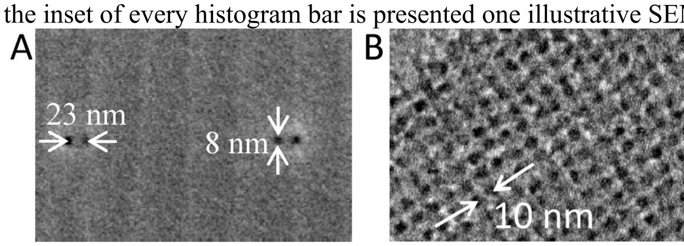

Figure 2. (A) Scanning-electron micrograph of two adjacent PMMA holes with 23 nm pitch, exposed with the same EBL process above at 30 kV. The minimum feature size was 7 ± 1 nm, and the dose was 5fC/dot. (B) Bright field transmission electron micrograph of 10-nm-pitch dot array of HSQ, exposed at 200 kV and developed with salty development. The minimum feature size was 5.6 ± 1.2 nm. The HSQ thickness was 20 nm and it was on top of a 50-nm-thick Si_3N_4 membrane. The dose was 9 fC/dot. The 200-kV EBL technique will lead to closer placement of QDs.

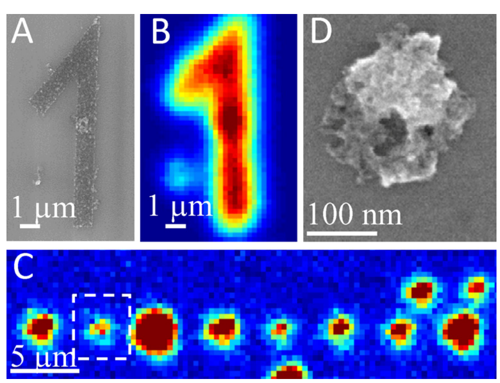

Figure 3. (A) is a scanning electron micrograph and (B) a confocal photoluminescence (PL) map of a large area pattern of CdSe/CdZnS QDs with 5 nm diameter. The peak of emission wavelength was 576 nm. (C) is a confocal PL of 200 nm clusters of QDs with 5 μm periodicity. The indicated square area on C is a representative structure that was imaged in the SEM and is shown on (D). PL of smaller QD clusters fabricated by this technique is currently under investigation.