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Supporting Information

for *Small,* DOI: 10.1002/smll.201801503

The Role of Liquid Ink Transport in the Direct Placement of Quantum Dot Emitters onto Sub-Micrometer Antennas by Dip-Pen Nanolithography

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SUPPORTING INFORMATION

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Three-Step Deposition Process using Dip-pen Nanolithography (DPN):
gQD deposition and associated AFM imaging were carried out using a DPN 5000 system (NanoInk, Skokie IL). Deposition of gQDs on silicon nanodisks was accomplished using a three-step process. The reading step was first performed to obtain the structural landscape of the silicon nanodisk array. The sample substrate and a microwell (ACST, Carlsbad, CA) or silicon wafer were first placed on a vibration isolation stage. An A-type AFM tip (ACST, Carlsbad CA) was used in contact mode-constant force under feedback where an area of the substrate was scanned to include a 10×10 array of silicon nanodisks. An outline of the A-type tip and substrate markers were traced onto a transparency that was overlaid onto an optical image visible on the computer monitor. The digital AFM image was captured and saved onto the sample stage map of the DPN 5000 software. The A-type AFM tip was withdrawn from the substrate and the vibration isolation stage was activated.

A new M-type AFM tip array (ACST, Carlsbad CA) was used for inking and deposition, where, first, all but one tip was removed from the array. The single M-tip was mounted onto the instrument leaving the sample undisturbed. The transparency including the markings was then re-aligned so that the position of new M-tip was aligned with the tip position on the transparency. Once the AFM tip was lowered to be within a few microns of the sample, the sample stage was moved so that the substrate marker on the stage was aligned with the marker on the transparency. This was to ensure that both AFM tips were in the same position for reading and writing.

To ink the M-type AFM tip using the dip-coating method, the microwell was filled with gQD ink using a micropipette and inking was carried out soon afterwards. We note that the ink remains liquid throughout even long DPN writing protocol, e.g., from 1 to 2 hours from initial dip-coating of tip to final writing steps. Ink "longevity" on the tip is likely due to several factors, including presence of surfactant molecules, e.g., oleic acid (QD bound and unbound), the QDs themselves (higher concentration inks dry out more slowly than lower concentration inks), the high humidity of the DPN chamber, and the microchannel of the tip. With respect to the latter, we do notice that ink left in the dipping well dries faster than ink on the tip, though addition of oleic acid extends ink lifetime in the well, even up to several days.

When scan coating was used to ink the M-type tip, the gQD ink was placed on the silicon wafer and allowed to dry for 20 minutes at 25 °C and 15% relative humidity (RH), to allow the formation of microdroplets. The M-type tip was then scanned over a 10 x 10 μm^2 area of ink microdroplets at 3 Hz.

To prepare for deposition, the digital AFM image of the silicon nanodisk landscape was marked with "spots" using the DPN 5000 software to allow the inked tip to deposit gQDs on top of each silicon nanodisk. Once the M-tip was inked, it was moved to the silicon nanodisk array, and after further alignment to ensure the M-tip and the substrate marker aligned well with the tip and marker on the transparency, gQD deposition was carried out in contact mode-constant height (no feedback) at 25 °C and 40-55% relative humidity.

An important aspect of this three-step process is that deposition does not have to be carried out under feedback, which is necessary when depositing "spots" as opposed to "lines" of ink, to

prevent lines of ink forming between silicon nanodisks. Additionally, this allows the working area to be as large as 2.5 x 2.5 cm^2, which enables the use of larger substrates containing many nanostructured-surface regions.

Alternative Three-Step Deposition Process using DPN:
In addition, in experiments that utilized a dipped-tip (rather than a raster-scanned tip) an alternative process was employed that is faster and more amenable to large-scale depositions. Here, a single M-type tip was used for both imaging and writing. Using the alignment feature of the DPN software, the coordination of a scanned area of interest was saved. A transparency is not needed in this case, as the DPN stage is not moved since tips are not switched. The tip is then inked by the dipping method, bled of excess ink, and brought back to the saved scanned area of interest. A very quick scan is then initialized (typical scan rate: $\geq$4 Hz) in order to find a feature that was in the saved image, but not one to be used for writing. Once found, this quick scan is immediately stopped, and the tip aligned to the saved position within nm precision. Finally, the writing process is executed on the antenna structures present in the saved image from step one. One drawback for this approach is that scanning with an inked tip can lead to contamination of the substrate area of interest. This issue is largely avoided by (a) using a quick scan to minimize ink deposition during scanning, (b) picking features to be scanned with the inked tip that are not features targeted for deposition and (c) ensuring that scanned features are sufficiently far from target features ("sufficiently" is defined by specific substrate and ink conditions.

Photoluminescence for gQDs Deposited on Nanoantennas: Photoluminescence images of gQD-loaded and empty nanopillars on transparent substrates were obtained using an inverted, sample-scanned confocal microscope setup for time-correlated single-photon counting. gQD photoluminescence was both excited (at 437 nm) and collected through a x60, 0.7 numerical aperture objective (LUCPLFLN, Olympus). Sample emission was filtered through a long-pass excitation dichroic mirror (450 DCLP, Omega Optical) and a 488 nm long-pass filter (488RE, Semrock) and detected using a single-photon counting silicon avalanche photodiode operating in Geiger mode (SPCM-AQR, PerkinElmer)

Supplementary Figures

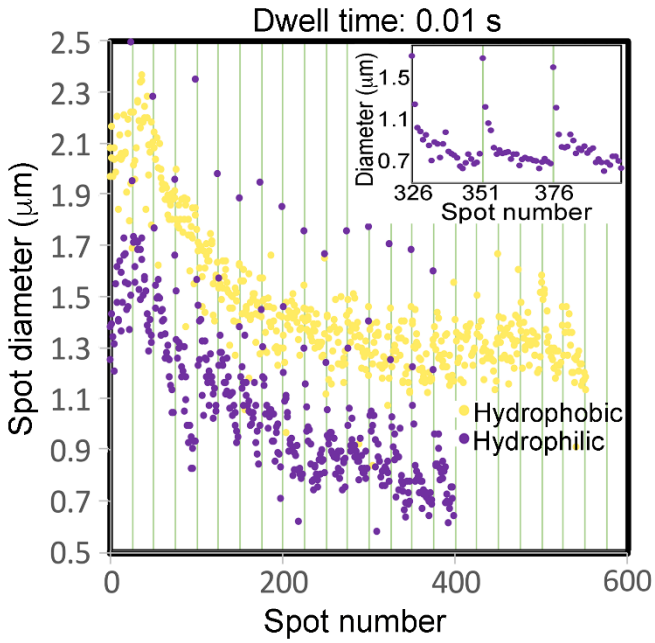

Figure S1. Trajectories of spot diameters for extended printing of the QD-*o*-DCB nanocrystal liquid ink with spot number for a 0.01 s dwell time on either a hydrophilic or a hydrophobic substrate. Inset: spot size spiking in first spots of each array for spots on hydrophilic substrate.

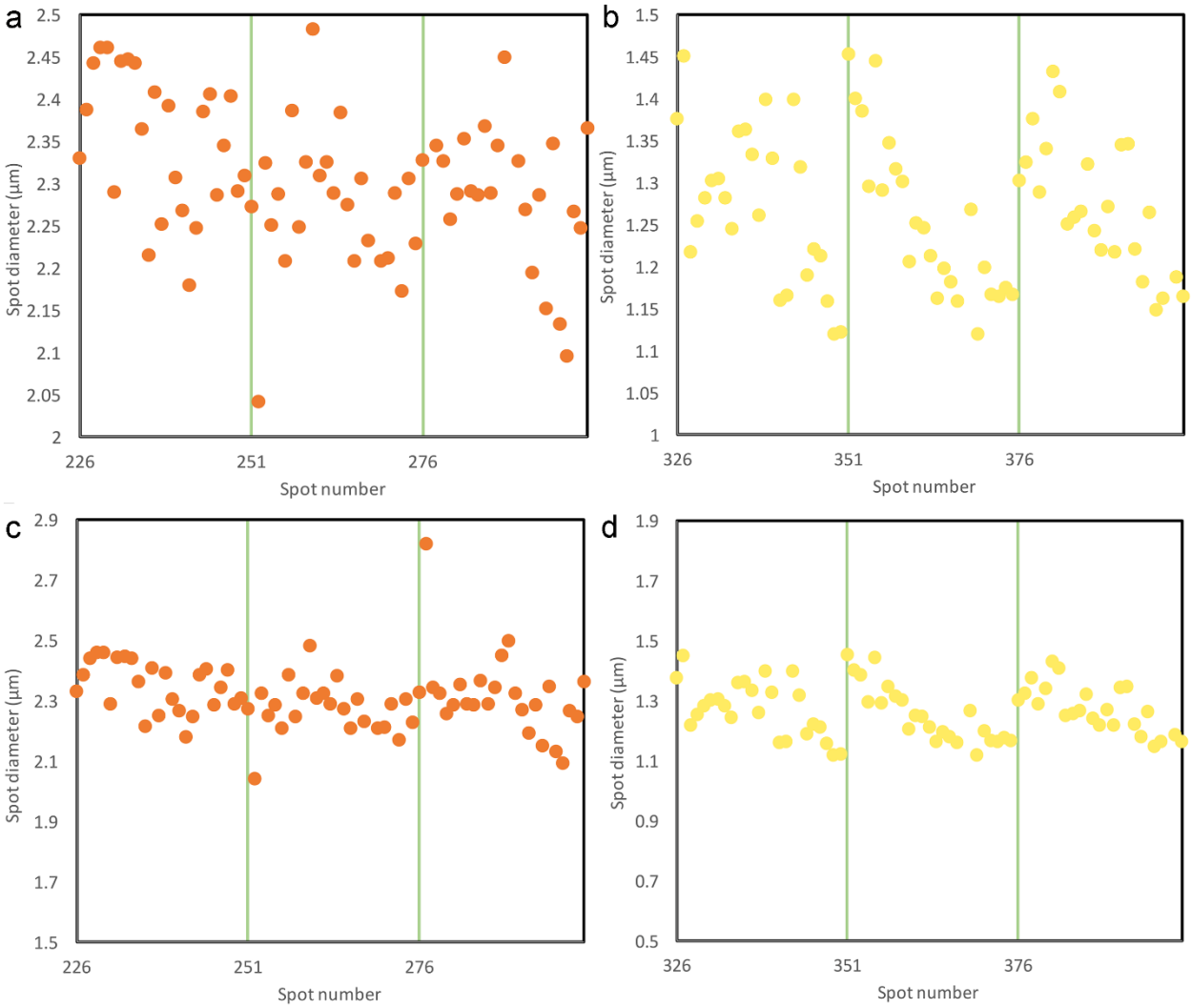

Figure S2. Spot-size trends for arrays written on hydrophobic substrates. (a) and (c) correspond to a 2 s dwell time and (b) and (d) to a 0.01 s dwell time. Close-up of several arrays in each case reveals random (2 s dwell time) or diminished size-spiking (0.01 s dwell time) obtained by writing protocol executed on this type of substrate that is in contrast to writing conducted on a hydrophilic substrate.

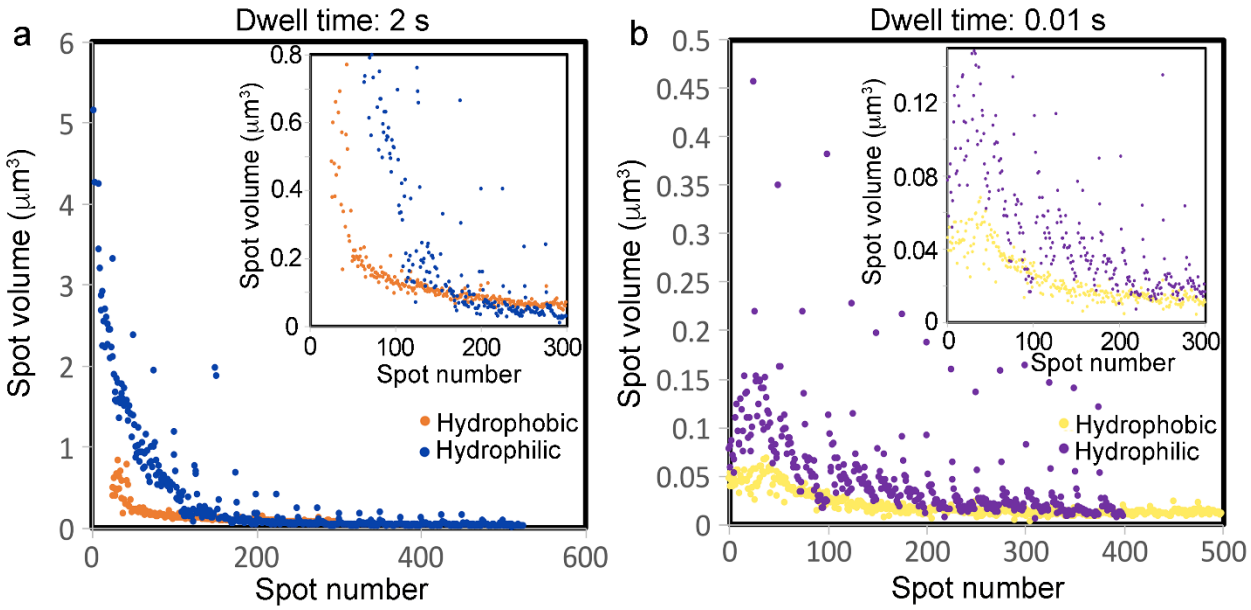

Figure S3. Trajectories of spot volumes for extended printing of the QD-*o*-DCB nanocrystal liquid ink with spot number for two different dwell times and on either a hydrophilic or a hydrophobic substrate. (a) Spot volume decay for a long dwell time of 2 s. Inset: close-up of rapid-decay regime revealing substrate differences. (b) Spot volume decay for a short dwell time of 0.01 s. Inset: close-up of rapid-decay regime revealing substrate differences.

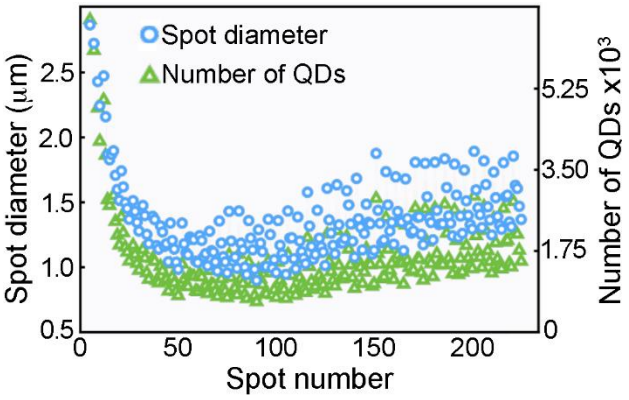

Figure S4. Trajectories for spot size and number of QDs per spot versus spot number for modified long-term writing protocol that includes pause between columns within arrays and use of smaller QDs that suspend in *o*-DCB without significant self-association.

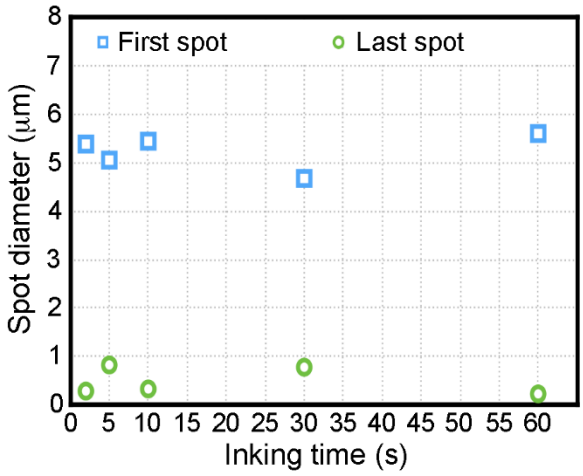

Figure S5. Spot sizes for the first (blue) and last (green) spots in array 1 written for a series of short tip inking times.

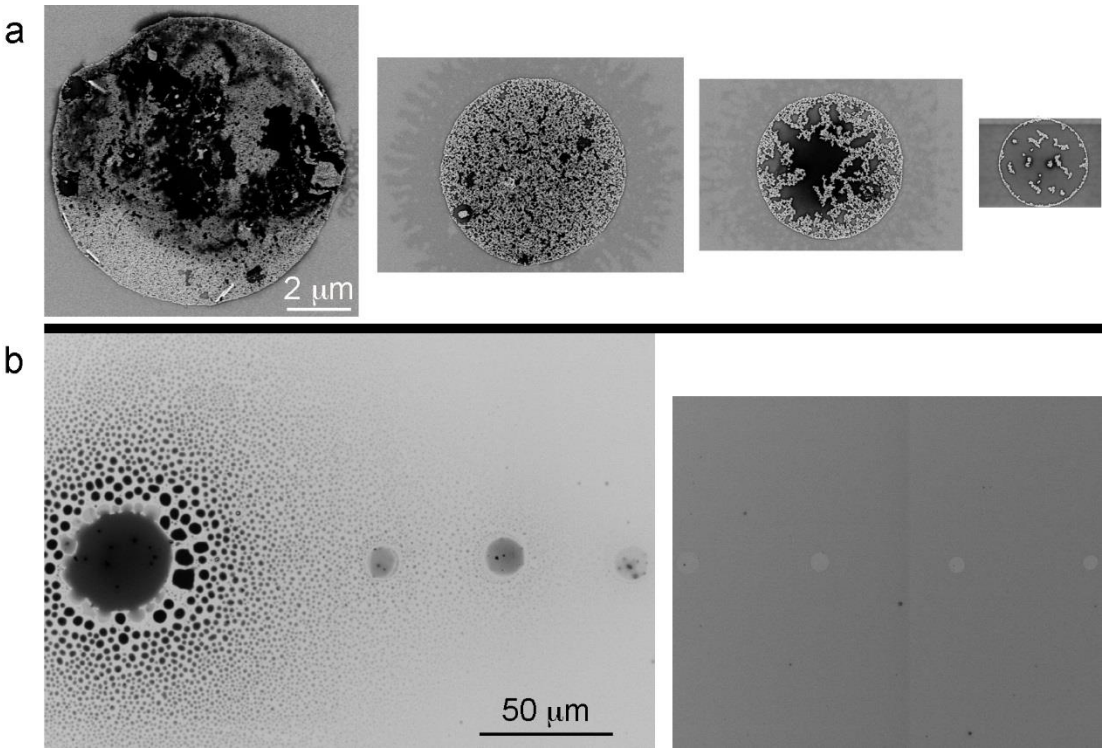

Figure S6. Bleed spots compared for nanocrystal inks comprising differently sized QDs. (a) 1st, 3rd, 5th and 10th bleed spots deposited using larger-QD inks (~15 nm diameter QDs; spot sizes are 9.2, 5.8, 4.6 and 2.8 μm, respectively). QDs dominate early spots, with QD numbers diminishing in later spots. (b) 8 bleed spots in order left-to-right deposited using smaller-QD inks (~10 nm diameter QDs). Based on contrast analysis – spots are dark if organic solvent dominates deposition and light if QDs are present in large numbers – early spots (1-4) comprise predominantly solvent, while in later spots (5-8) QDs fill spot areas. Spots range in size from ~40 μm (1st spot) to 15 μm (3rd spot) and 8.5 μm (5th spot). In summary: if nanocrystal-solvent suspensions are stable (b), the initial bleed spots are large and lacking QDs – *or QDs are effectively masked by a large spot solvent volume*. Also in this case, later bleed spots show QDs filling spot areas created by solvent. In contrast, if nanocrystal-solvent suspensions are less stable (a), initial bleed spots are relatively smaller, and QDs are clearly present in large numbers in the solvent spots, with numbers and coverage substantially diminishing over even moderate bleeds of ~8-10 spots.

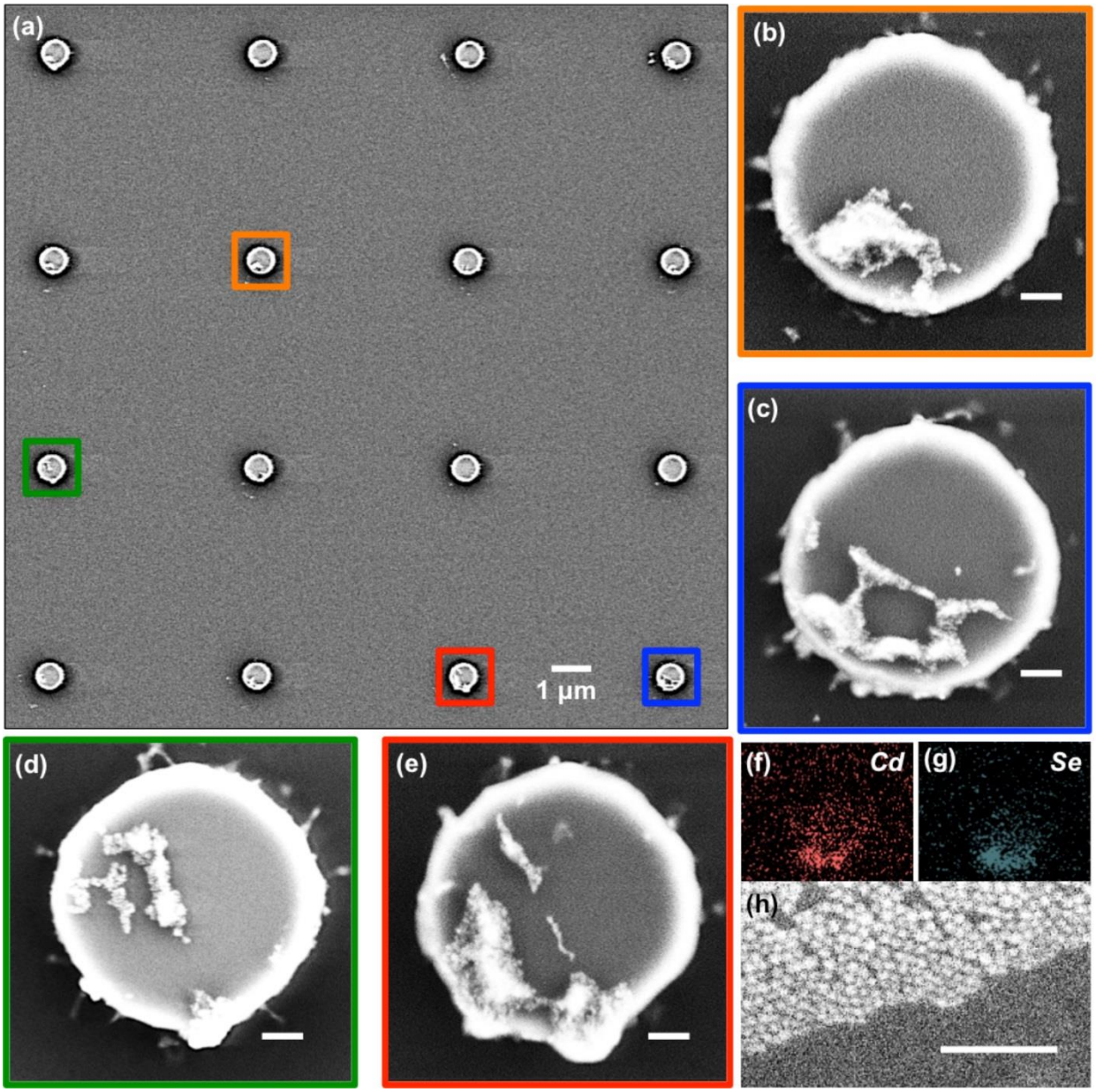

Figure S7. Experimental results of DPN where the AFM tip was coated using the scan-coating method. (a) Large area SEM image of InP-5CdSe-3CdS gQDs deposited on silicon nanodisk array where g-QDs are present only on top of each nanodisk. (b) - (e) Higher magnification SEM images of four randomly selected nanodisks. Energy dispersive spectroscopy (EDS) elemental maps for (f) Cd and (g) Se of one nanodisk. (h) High magnification SEM micrograph of as-synthesized InP-5CdSe-3CdS gQDs. All un-marked scale bars are 100 nm.

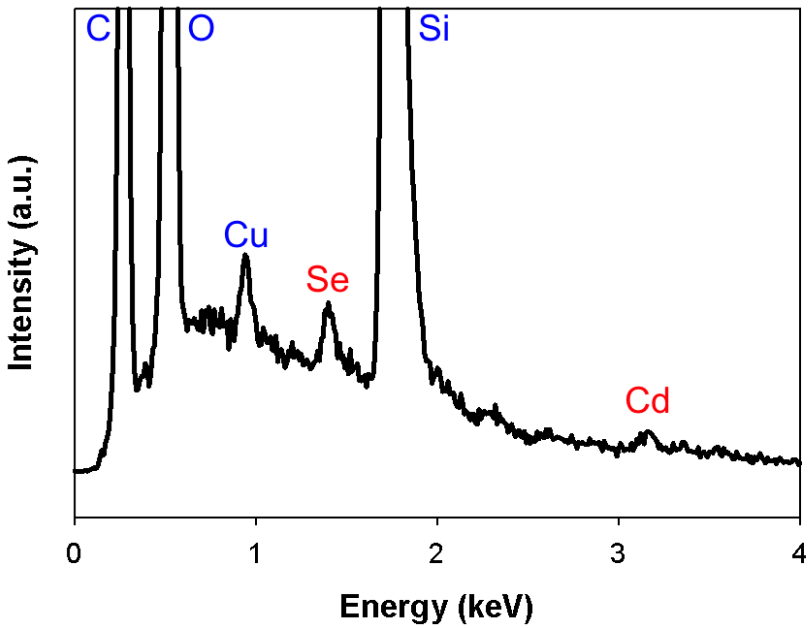

Figure S8. EDS spectrum of InP-5CdSe-3CdS gQDs that were deposited on a silicon nanodisk. The EDS signal for Cu is from the copper tape that was used to fasten the substrate to the SEM sample holder.

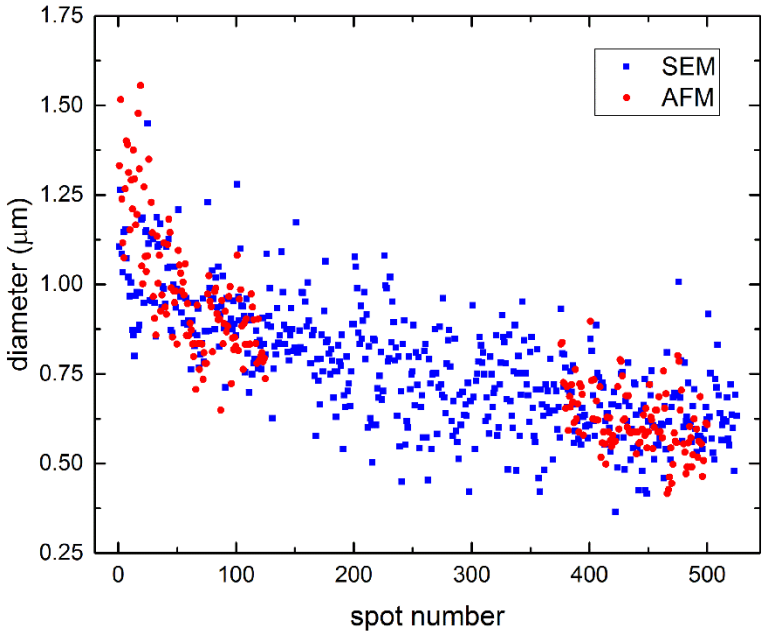

Figure S9. Comparison of spot sizes obtained using either AFM or SEM to image the same array series. Overlap of results obtained by respective image analyses demonstrates that either imaging technique can be employed with similar results. Gwyddion or ImageJ imaging processing programs were used to measure spot diameters.