Positioning and Immobilization of Individual Quantum Dots with Nanoscale Precision

Chad Ropp,† Zachary Cummins,‡ Roland Probst,† Sijia Qin,§ John T. Fourkas,*,§,† Benjamin Shapiro,*† and Edo Waks*,†,⊥,‡

†Department of Electrical and Computer Engineering, ‡Fischell Department of Bioengineering, §Department of Chemistry and Biochemistry, †Institute for Physical Science and Technology, †Institute for Research in Electronics and Applied Physics, and #Joint Quantum Institute, University of Maryland, College Park, Maryland 20742, United States

ABSTRACT We demonstrate a technique for the precise immobilization of nanoscale objects at accurate positions on two-dimensional surfaces. We have developed a water-based photoresist that causes nanostructures such as colloidal quantum dots to segregate to a thin layer at surfaces. By combining this material with electroosmotic feedback control, we demonstrate the ability to position selected, individual quantum dots at specific locations and to immobilize them with 150 nm precision via localized UV exposure.

KEYWORDS Quantum dots, deterministic assembly, electroosmotic flow, feedback control

The ability to place nanoscopic objects at precise locations on patterned or prepared surfaces is essential for a broad range of device applications. One important example is the positioning of quantum dots (QDs) in nanophotonic structures such as cavities1−3 and waveguides4 for single-photon generation,5−7 quantum dot lasers,8 or nonlinear optical devices.9 Another example is the nanoscale positioning of metallic and dielectric particles on prepared metamaterial surfaces to engineer nanoscopic electronic circuits.10 The majority of these applications exploit optically resonant interactions that require the nanoscopic particles to have the correct spectral properties. For these applications, it is essential to have a technique that can preselect the particles with the correct spectral properties and place them at the correct locations on a surface.

The positioning of preselected particles with nanometric precision is an extremely difficult task with few good solutions. Optical tweezers are a widely utilized technique for nanometer scale particle manipulation.11,12 However, optical gradient forces scale with particle volume, making it difficult to trap nanoscopic objects.13 In addition, these traps also do not ensure single particle manipulation since they are nonspecific and will acquire multiple particles over time.12 Other techniques that make use of mechanical manipulators have also been used to push, pull, and place individual metal and dielectric nanoparticles on a variety of surfaces.14−17

In this paper, we demonstrate a broadly applicable method for positioning and immobilization of nanoparticles in precise locations on a surface. This method takes advantage of electroosmotic flow control (EOFC), a technique that we have recently demonstrated for the accurate, nanoscale positioning of nanoparticles.18 In EOFC, particle positioning is achieved by controlling the flow of the surrounding fluid and feedback is used for the continuous correction of the position of a chosen nanoparticle. Previous demonstrations of flow control have achieved manipulation of micrometer-sized particles with micrometer precision,19−21 random capture of nanoparticles with nanometric holding accuracy,22−24 and more recently manipulation of nanoparticles with nanometric precision.18

A major limitation of EOFC to date has been that actuation of individual particles can only be achieved in two of three dimensions, since fluid flow occurs only along the directions that lie parallel to the fluid channels. Thus, a particle that is being manipulated on the bottom surface of the device is free to diffuse out of plane, making it difficult to place the particle on a prepatterned surface. Another important limitation is that all particles in the device are subject to flow. Therefore, once a desired particle has been positioned, it is not possible to manipulate a second particle without disturbing the position of the first one.

Here, we demonstrate a method that overcomes both of these difficulties. The specific nanoparticles that we manipulate are colloidal cadmium selenide quantum dots (QDs). Single QDs are generally difficult to manipulate due to their small sizes and sensitivity to their physical environment. However, QDs are exceptionally interesting for nanophotonics and quantum optics applications in which they can serve as bright sources of single photons. QDs also play an important role in biological applications as tags and markers.25 To achieve manipulation and immobilization of individual QDs along a surface we have developed a water-based, negative-tone photoresist that causes QDs to be localized within a thin sheath along the surfaces of a microfluidic channel. When using this photoresist, EOFC of the nanoparticles occurs effectively in two dimensions at the surface of interest. After the QD has been delivered to a desired
location by EOFC, a brief exposure to ultraviolet light polymerizes the surrounding fluid to immobilize the QD. Once a selected QD has been immobilized, manipulation of subsequent QDs will not affect its position. This technique makes possible the sequential, high-precision positioning and immobilization of a large number of selected nanoparticles on a 2D surface.

A schematic of the microfluidic device used in our experiments is shown in Figure 1a. The device is composed of a pair of microfluidic channels formed between a glass coverslip and a molded block of polydimethylsiloxane (PDMS). The control region resides at the intersection of the two channels and has a width of 100 μm and a height of 5 μm. The microfluidic channels are filled with a mixture of QDs (Invitrogen Qtracker PEG CdSe/ZnS 655 nm) suspended in an aqueous photoresist we have developed. The photoresist is composed of a water-soluble multifunctional acrylic monomer, a radical photoinitiator, and a rheology modifier used to increase fluid viscosity. A detailed description of the resist is provided in the Supporting Information. When exposed to UV light, the photoresist will cross-link in the exposed area to form a small polymerized region that can be used to encapsulate and immobilize a QD. The monomer is added at a concentration near its solubility limit, which causes the QDs to segregate to the surfaces of the device, as shown and discussed in detail in the Supporting Information. Four electrodes are immersed in the fluid reservoirs, providing the voltages necessary for EOFC. These electrodes can actuate the buffer to flow in any of the four cardinal directions parallel to the glass substrate.

Figure 1b shows a diagram of the experimental setup, which consists of an inverted confocal microscope that images the QDs onto a CCD camera operating at a 10 Hz frame rate. QDs are illuminated with a 532 nm laser at 100 W/cm². Individual QDs are tracked in real time by the imaging system. Subpixel averaging, based on a centroid estimate, is used to determine the position of a QD to a precision that is much better than the diffraction limit of the optical system (see Figure S1 in the Supporting Information). Once the position of a QD is determined, a control algorithm applies voltages to the four electrodes to actuate the correcting electroosmotic flow. The control algorithm applies the voltages needed to move the QD from its current location toward the target location via a continuous control loop, quickly driving the position error down to a limit set by the imaging accuracy and particle diffusion between control updates.

Figure 2 shows how QDs that have been pushed to the surfaces of the device can be manipulated along the surface by electroosmotic actuation. The chosen QD is selected by our control software and moved toward the specified location, as shown in Figure 2a–c. We observe a strong blinking...
behavior, which is evidence that we are indeed manipulating single QDs (definitive proof that we are manipulating single QDs is obtained by performing photon antibunching measurements, as discussed in the Supporting Information). The control algorithm performs actuation only when the QD is in the luminescent state, as determined by a threshold value for its observed intensity. Once the QD is at the target position, the area containing the QD is irradiated by a 375 nm laser beam that is centered on the target position to achieve local cross-linking of the photoresist. The UV laser is focused to a spot size of 2\( \mu \)m with an intensity of 500 W/cm\(^2\). A shutter is triggered automatically to expose with UV light for 400 ms (Figure 2d) once the QD is determined to be within 80 nm of the target position. Figure 2e,f shows successive camera frames obtained after the QD was immobilized. A voltage was applied on the north electrode to create electroosmotic actuation in the south direction. As can be seen from these two frames, the immobilized QD remains at the same position while the surrounding QDs move with the flow.

The ability to position and immobilize nanoparticles opens up the possibility for assembling complex patterns of preselected QDs. As an example, we created a 3\( \times \)3 square lattice array of QDs with 5\( \mu \)m separation between adjacent lattice sites. A single QD was first positioned and immobilized at a desired location near the center of the control area. A piezo stage was then used to move the sample to the next location in the array, where the next QD was subsequently positioned. A video of the array being assembled is available in the Supporting Information. Figure 3a shows the resulting 3\( \times \)3 array. This image is an average of four consecutive frames, each with a 500 ms exposure time, and is displayed on an intensity-log scale. The leftmost QD in the middle row emitted less brightly than the others during this exposure period, and so it appears dimmer in the image. The entire array was monitored over a period of 15 s and subpixel averaging was used to measure the position of every QD during frames in which they were in the luminescent state (Figure 3b). Figure 3c shows a zoomed-in plot of the measured positions for one of the QDs. These measured positions are all well localized. We note that there is a slight asymmetry between the variance in the x and y directions of the measured positions. This asymmetry is attributed to a small drift of the piezo stage over the measurement time.

Positions for each of the nine QDs were determined by averaging over each data set. We determined the vision accuracy of the subpixel averaging, based on the standard deviation of measured positions for each QD, to be 14 nm (8 nm) in the x (y) directions. To obtain a measure of the relative in-plane positioning precision for QD immobilization, we fit our data to an ideal 5\( \mu \)m grid by translating and rotating the data and optimizing the average distance between the two. When optimized, the average error in distance was measured to be 127 nm, which is our precision in reproducing the array on the surface.

A single image of the encapsulated QDs after channel removal is shown in Figure 3c on an intensity-log scale. All of the polymerized regions remained adhered to the slide surface, and several of the QDs (shown circled in red) can be seen clearly emitting at the correct locations even after channel removal. The remaining QDs were in a dark state during this particular frame. At other camera frames, these QDs became luminescent while some of the other QDs became dark. The data in Figure 3 demonstrate that devices can be assembled in a fluidic environment and then used once the channels have
been removed. We note that a degradation in emission brightness of the QDs is observed after channel removal. The cause of this emission degradation is not fully understood but may be due to oxidation during assembly and cleaning. Methods for reducing this contamination using oxygen scavengers have been investigated previously and could serve to reduce QD degradation significantly.\(^{28}\) We also note that the polymerized regions shown in Figure 3d are on the order of 2–3 \(\mu\)m in diameter. Such large polymerized regions are not suitable for applications requiring close packing of many nanoscopic particles. These spot sizes could be reduced with improved focusing of the UV beam and could potentially be made much smaller (sub 100 nm diameter) using multiphoton absorption polymerization.\(^{29,30}\)

To measure the distance of the immobilized QDs from the surface, we exploited the fact that a small fraction of QDs adhere to the surface naturally in the course of an experiment. These adhered QDs serve as reference points that enable us to determine the position of the glass surface. We positioned and immobilized three QDs in a 20 \(\times\) 20 \(\mu\)m area that contained three naturally adhered QDs. This small region was chosen to minimize systematic errors in depth measurements due to nonuniformity of the surface and to spherical aberrations in the microscope. The distance between the objective lens and the surface was then varied by moving the piezo stage in and out of focus in steps of 200 nm. Both the immobilized and naturally adhered QDs were imaged for many frames at each position and the sizes of the diffraction spots were tabulated using the variances of the QD image. For every QD, a median diffraction spot size was calculated at each position and the data were fit to a beam divergence function of the form\(^{31}\)

\[
w(z) = w_0 \sqrt{1 + \left(\frac{z - z_0}{z_R}\right)^2}
\]

where \(w\) represents the width of the diffraction spot as a function of focus position \(z\). The minimal diffraction spot size denoted by \(w_0\) is located at the vertical position \(z_0\). The Rayleigh range of the diverging spot is \(z_R\). A plot of the diffraction spot size, in pixels, of one of the encapsulated QDs as a function of focal depth is shown in Figure 4a. The
fit was used to determine the location of the minimal diffraction spot (and hence the in-focus position of the QD) from the fitting parameter $z_0$. This procedure was carried out for the remainder of the QDs, and the results are shown in Figure 4b. The vertical positions of the naturally adhered QDs are shown in black and those of the immobilized QDs are shown in red. We denote the average position of the naturally adhered QDs as $z_0$, the location of the glass surface. The position of this surface was determined with a standard deviation of 80 nm. The average position of the three encapsulated QDs is given by $35 \pm 38$ nm. The uncertainty in the vertical measurements of both the adhered and encapsulated QDs is likely caused by vision noise in our imaging setup, QD blinking, and the inherent roughness of the slide cover. The accuracy of the measurement could be improved significantly by using better methods for measuring the out-of-plane position of the QDs based on cylindrical lenses or a double helix point spread function.

To demonstrate that this positioning technique can deliver a QD to a marked location on a surface, we deposited a low concentration of a different species of QDs emitting at an average wavelength of 705 nm (Invitrogen Qtracker PEG CdSe/ZnS 705 nm) onto a dry slide cover. These QDs, which remain adhered to the glass surface after filling the channels, served as targets. The channels were filled with the same 655 nm emitting QDs used in previous experiments. The two species of QDs can be distinguished visually by using bandpass filters centered at 655 and 710 nm, respectively, in front of the imaging camera. We measured the emission spectra of the two types of QDs using a grating spectrometer (Acton SP 2758 with a resolution of 0.06 nm). Figure 5a shows the measured emission spectra of bulk samples of both types of QD. Additionally, overlaid in Figure 5a are the transmission spectra of the bandpass filters, demonstrating that they can be used for selective visualization of the two different types of QDs.

Individual 705 nm emitting QDs served as stationary targets for the positioning and immobilization of 655 nm emitting QDs. Target QDs whose emission does not bleed through the 655 nm filter were chosen so that the tracker would not get confused between the two QD types while performing the positioning. Nine 655 nm QDs were immobilized on top of nine chosen 705 nm QD targets, and the positions of all of them were then measured using...
subpixel averaging. In Figure 5b, the red dot at the origin marks the 705 nm target position for all nine pairs; the blue dots show the measured relative displacements of the nine placed and immobilized 655 nm QDs. The average distance between an immobilized QD and its target was calculated to be 155 nm. An overlapped diffraction image of one of the placed and immobilized 655 nm QDs (blue) versus its 705 nm target QD (red) is shown in Figure 5c with an asterisk labeling their inferred centroid positions.

A unique feature of our positioning and immobilization technique is that it enables us to characterize QDs before they are immobilized. Thus, QDs with desired spectral properties can be preselected and delivered to specific locations on a device. As a demonstration of this capability, we fabricated a 3 × 3 array of QDs with different specified colors at each point (Figure 6a). To construct this complex structure, we injected a mixture of both the 655 nm emitting and the 705 nm emitting QDs. By alternating between filters after each immobilization step, we assembled a 3 × 3 array of color selected QDs in a checkerboard pattern. A video demonstrating how this technique is able to differentiate between the two types of QDs for immobilization is available for viewing in the Supporting Information.

Figure 6b,c shows the final assembled array as seen through the 710 and the 655 nm filters, respectively. The picture in Figure 6b was acquired in one image frame with a 500 ms exposure time, while the picture in Figure 6c was acquired from an average of many minutes of frames with 500 ms exposure times each in order to visualize all five of the QDs, which were never in the luminescent state simultaneously. The QDs that are expected to be seen based on the filter used are circled in each picture. With the 710 nm filter in place only the correct QDs are visible. However, the top-middle QD from the 705 nm batch is clearly visible through the 655 nm filter (Figure 6c), due to the fact that the 705 nm QDs have more inhomogeneous spectral broadening than do the 655 nm QDs (as seen in the spectra in Figure 5a). Therefore, a QD from the 705 nm sample is more likely to partially overlap with the passband of the 655 nm filter.

In conclusion we have demonstrated a method for positioning and immobilization of preselected nanoparticles along a two-dimensional surface. These results were achieved by combining high precision tracking and feedback control with the development of a water-based photosensitizer that restricts QDs to a thin sheath near the surface of a microfluidic channel. Here we have demonstrated the positioning of colloidal quantum dots, but the technique is general and can be employed with any nanoscopic particle that can be visualized. It is also potentially amenable to use with virtually any substrate that is compatible with water. This technique is a powerful new approach for the precision, high-yield assembly of complex nanostructures that combines the advantages of bottom-up and top-down nanofabrication.

Acknowledgment. This work was supported by a DARPA Defense Science Office grant (Grant W31P4Q0910013). E.W. acknowledges funding support from a National Science Foundation CAREER award (grant number ECCS-0846494), the Physics Frontier Center at the Joint Quantum Institute, and the Office of Naval Research Applied Electromagnetics Center.

Supporting Information Available. Subpixel accuracy, photosensitizing chemistry, and autocorrelations of immobilized quantum dots. Also, movies showing the assembly of the 3 × 3 array corresponding to Figure 3 in the text and the technique of color discrimination are available. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


