On-chip electrochemical detection of CdS quantum dots using normal and multiple recycling flow through modes

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Supporting Information

1. PDMS Fabrication process.

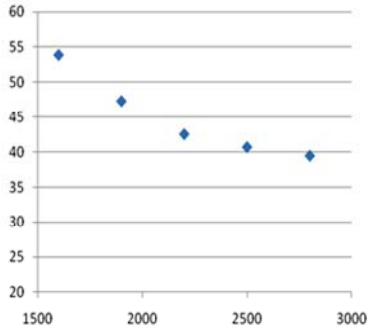
1.1. Design and simulation

The mask was designed with the desirable features, through a CAD (computer assisted design) program (AUTOCAD, CSIC license), which were transferred to an acceptable-resolution transparency (polyester or acetate sheet; minimum resolution of 3600dpi).

1.2. Microfabrication

SU-8 deposition on silicon wafer

Spin-coating has to be performed in a clean-room environment or under laminar hood to avoid dust. SU8 (5-6 ml of SU8 polymer) was poured onto the silicon wafer fixed by vacuum application.
The plate is spun in at least two stages which may be programmed according to the desired micro channel thickness. During the first stage the plate is spun at a low to moderate speed (500-1000rpm; *optimum*: 500rpm for 20seconds for a motive thickness of 50µm and 500rpm for 20seconds for a motive thickness of 100µm). The final thickness of the coating is then determined and controlled during the second stage by spinning the coating at a higher speed (1500-300rpm; *optimum*: 2000rpm for 50seconds for a motive thickness of 50µm and 1000rpm for 50 seconds for a motive thickness of 100µm) to constant acceleration of 300rpm/sec^2 (see Figure 1)



Rotation Speed (RPM)	Thickness (µm)
2800	39,43
2500	40,66
2200	42,52
1900	47,32
1600	53,93

Figure 1. Influence of spinning speed using the SU-8 photoresist. Conditions: Initial distribution during 90 sec at 1000rpm. Preheating during 40 min at 95ºC; cooling to environment temperature during 20sec and post heating process of 25min at 95ºC.

Optimized parameters were obtained by controlling, step by step, the effect of each parameter in the microfabrication process. Controls were based on the evaluation of shape and thickness of the final pattern by using characterization techniques such as SEM, profilometry and confocal laser scanning microscopy (CLSM).
Profilometry studies were performed directly onto the master to evaluate the motive without being modified. The used of a profilometer was convenient for the thickness features, less than 65µm, but for higher thicknesses, CLSM studies on reflection mode must be carried out.

Pre-baking times

Were optimized for a range time of 10 to 60 minutes (by intervals of 10 minutes) and temperature range from 65ºC to 95ºC (by intervals of 10ºC). The best condition of temperatures and times were 95ºC during 40min.

Exposure times

Were also optimized, as for the two different motives manufactured. Exposure times less than 20 seconds were considered underexposed. According to the Table 1, the recommended exposure time was selected to be 60 seconds due to the lower standard deviation of the channel height (the channel width is independent of the exposure time).

Exposure time (s)	Channel width (µm)	Standard deviation of the channel height
5	100	6.26%
10	100	0.27%
15	100	0.29%
20	100	0.15%
25	100	0.10%
60	100	0.06%

Table 1. Height and width effect at different exposition times. Conditions: UV Intensity: 7.9 mW/cm2. Pre-heating during 40 minutes at 95ºC and post-heating during 25minutes at 95ºC.

Post-baking times

Was optimized for interval times from 1 to 25 minutes. For the first range of time interval studies the structures were formed according to the design but for higher intervals of times undesirable zones were polymerized making more complicated the posterior development process. In conclusion, the optimum post-baking time was of 25 minutes (see Table 2).

Post-baking time (min)	Channel width (µ)	Standard deviation of the Channel height
0	N/A	N/A
2	102	1.14%
4	100	0.42%
6	100	0.32%
8	102	0.21%
10	100	0.02%
15	100	0.04%
20	100	0.04%
25	100	0.02%
30	100	0.02%
45	100	0.02%

Table 2 . Post-heating time optimization. Conditions: UV intensity: 7.9 mW/cm2; Pre-heating during 40 min at 95ºC; Post-heating during 25 min at 95 °C.

1.3. PDMS molding

In order to decrease the time of the degasification of the PDMS after the mixture between the oligomer and crosslinking agent, a vacuum desiccator was used during 1minute by three repetitions (optimized conditions). The PDMS curing time was optimized for a time intervals of 1 to 4 hours (by intervals of 30 minutes) at PDMS curing temperature (65ºC). The minimal time required to solidify the PDMS was 2 hours.

1.4. Device bonding

A hybrid platform with PDMS and polycarbonate as a substrate was developed. In order to achieve a well adhesion between these materials was necessary to do a previous surface treatment by immersion of the polycarbonate substrate into 3-Aminopropyltriethoxysilane (APTES) solution after plasma treatment, in order to functionalize the surface with amino groups. In parallel, the PDMS part was activated by using plasma cleaner and finally the integration was completed. The optimization was performed by changing the concentration of the APTES at 1% and 2%, and also changing the incubation time 0.5, 1 and 1.5 hrs. Finally, the optimal conditions were: For polycarbonate: plasma treatment during 1min, after immersion in 2% v/v APTES/mQ water; In the same time, PDMS channel is treat also with plasma, and finally both surfaces are put in contact for irreversible bonding. In order to verify the behavior of adhesion, a fluidic test was carried out by using syringe pump to introduce fluid into the channel at different flows, and for sure operation, the suggested maximum flow to introduce is 150µL/min without leakages.

2. Other electrochemical measurements.

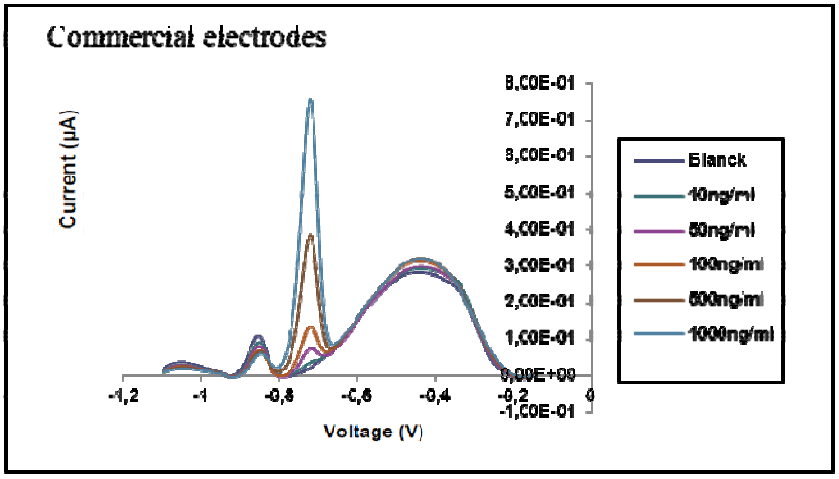


Figure 2. Current peaks at different concentrations by using mercury based screen printed electrodes.

3. Valves proposal for peristaltic integrated pump.

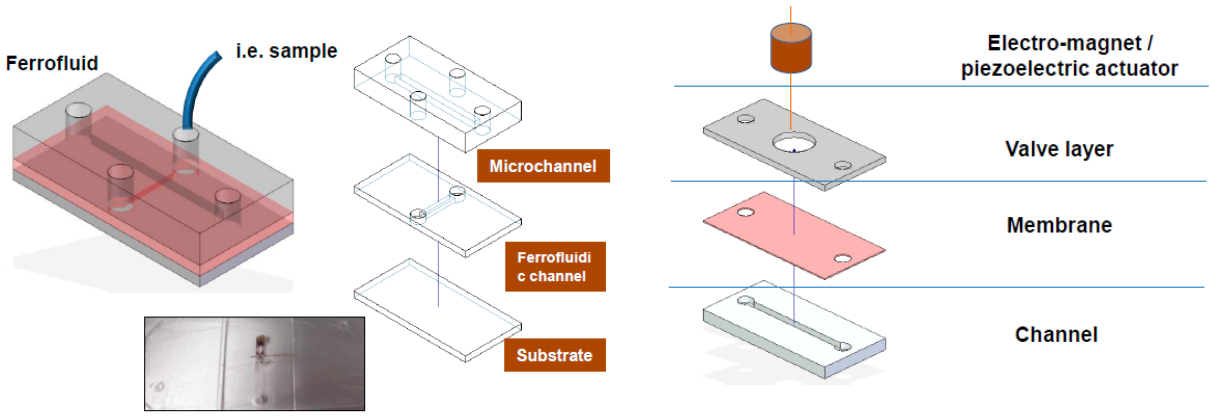
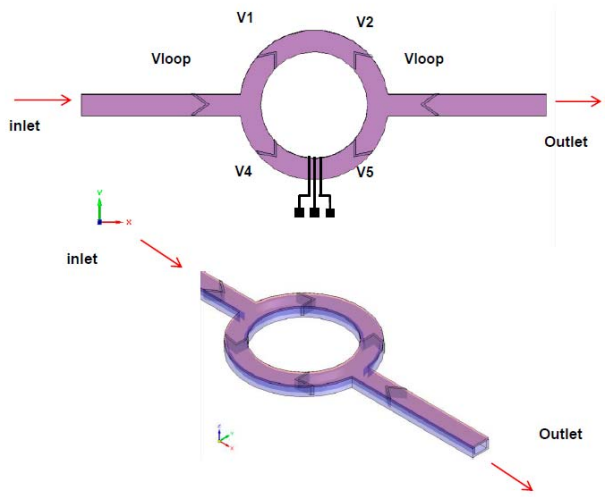


Figure 3. Valve designs for integrated peristaltic pump. Pneumatic actuated valve (a) and electromagnic actuated valve (b).



Steps	Vloop_i	V1	V2	V4	V5	Vloop_o
1	0	0	0	0	0	1
2	1	1	0	0	0	1
3	1	0	1	0	0	1
4	1	0	0	1	0	1
5	1	0	0	0	1	1
6	0	0	0	0	0	0

Figure 4. Sequential control of peristaltic pump (preliminary design)

4. Mixer design for QDs bioconjugation.

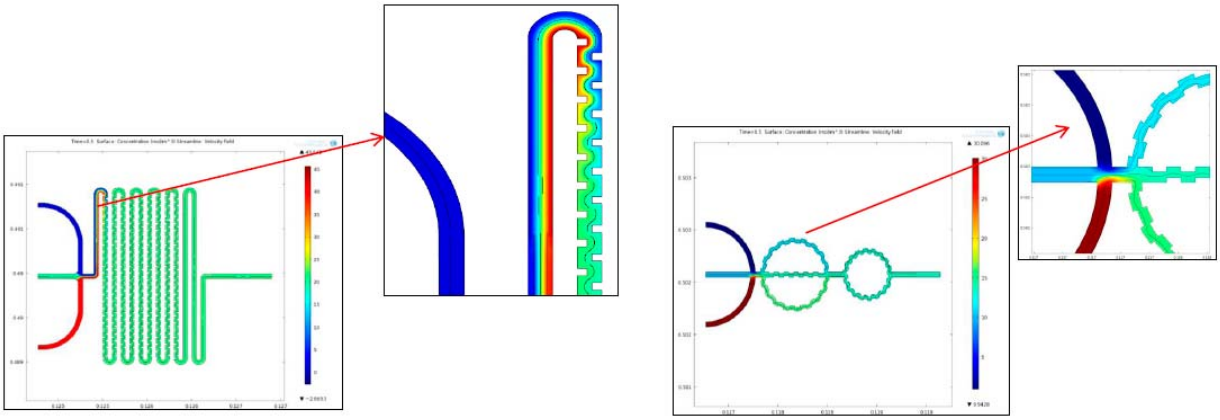


Figure 5. Micromixer simulations by using COMSOL Multiphysics (laminar flow and transport of diluited species models)