

**Analytical and Bioanalytical Chemistry**

**Electronic Supplementary Material**

**Design and microfabrication of a miniature fiber optic probe with integrated lenses and mirrors for Raman and fluorescence measurements**

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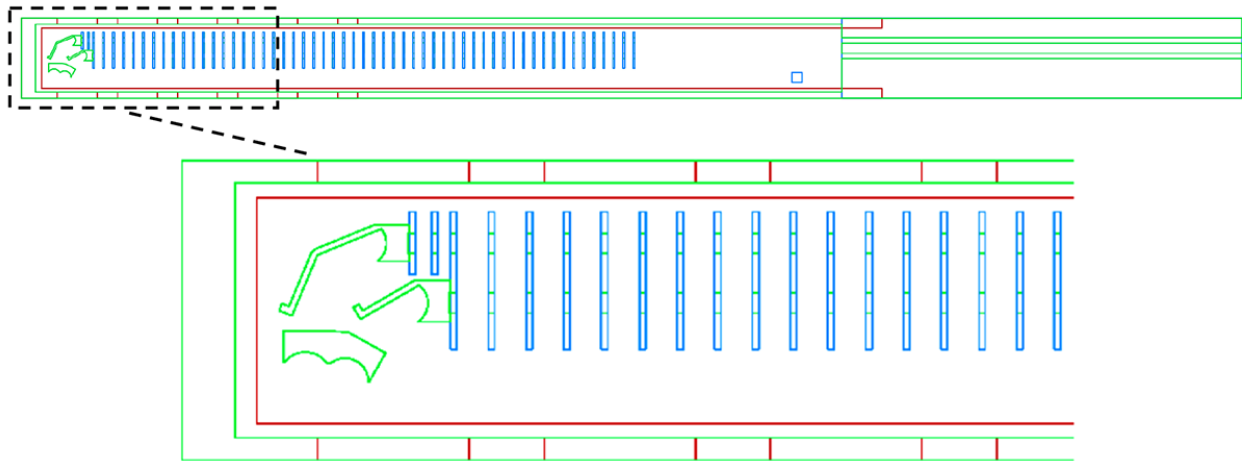
**Fig. S2** Schematic summarizing fabrication process of probe

**Fig. S3** Refractive index of PDMS

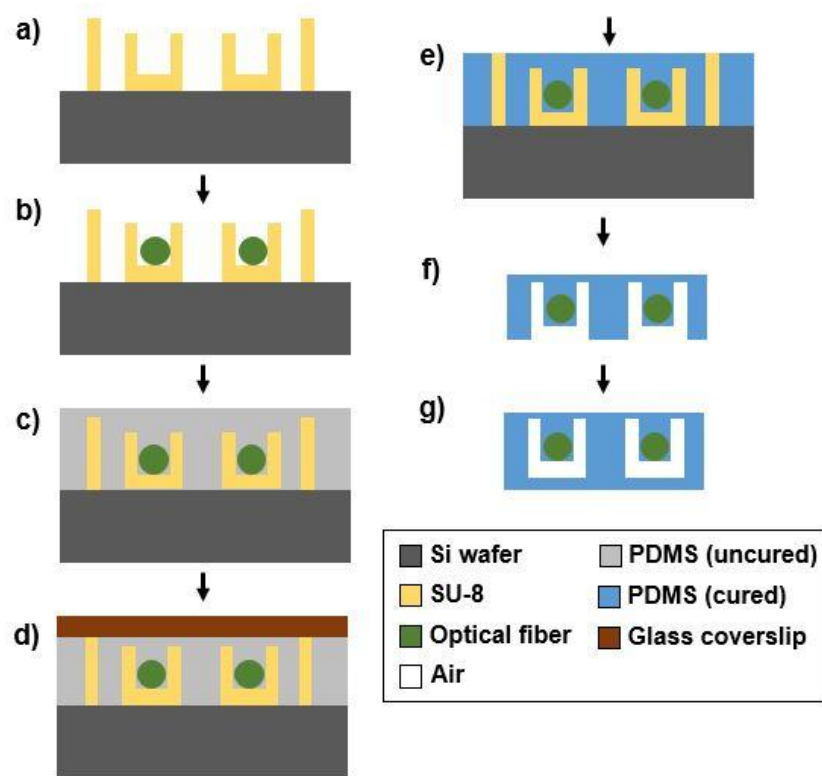
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**Table S1** Summary of specific conditions for fabrication of SU-8 master mold

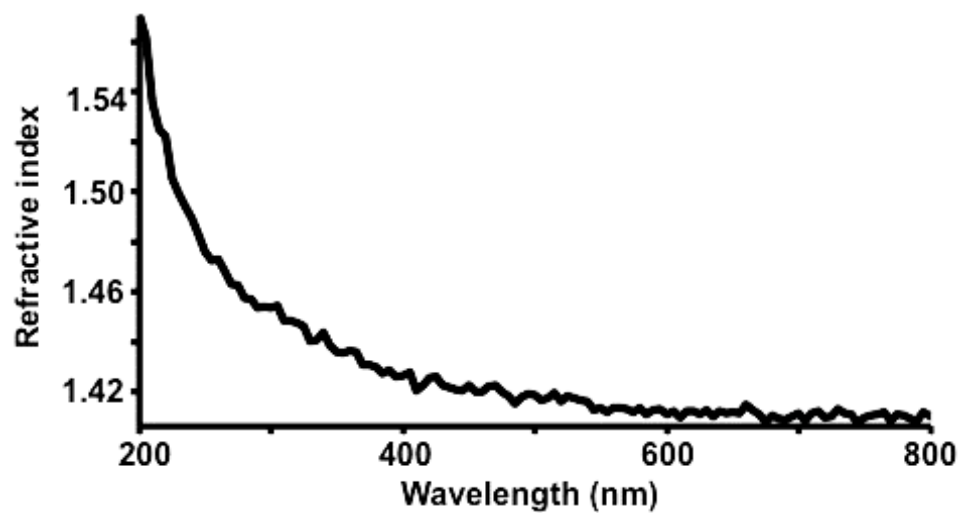
**Table S2** Comparison of fiber optic based microfluidic detection systems



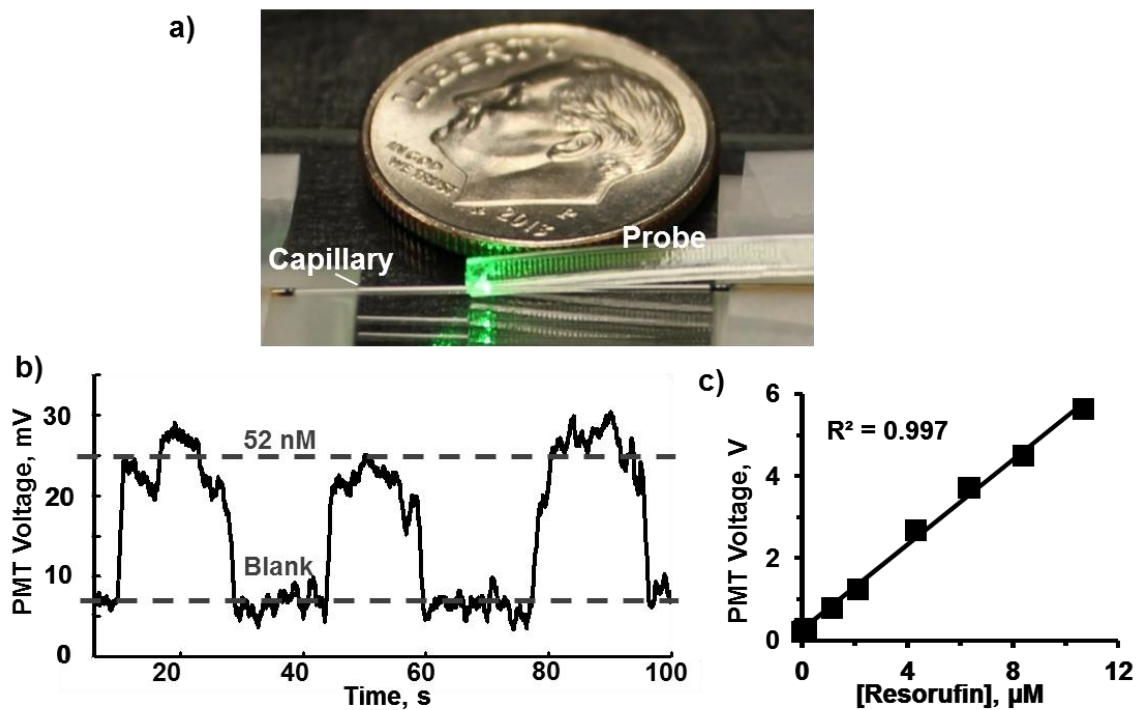
**Fig. S1** AutoCAD design of a representative probe (side-firing), showing layouts of 3 lithographic masks. The first lithographic layer (blue) includes the skids for lifting optical fibers from the mold. The second layer (green) consists of the posts for holding optical fibers, and optical components at fiber tips. The third layer (red) includes a bounding box, used as the outer edge of the probe



**Fig. S2** Illustration of microfabrication process for optical detection probe. The SU-8 mold was created on a silicon wafer by lithographic process and its surface was silanized for ease of PDMS release (a). A pair of optical fibers were inserted into the SU-8 skid-and-post mold structures (b) and a small volume of PDMS prepolymer was poured into the mold (c). A glass coverslip was pressed firmly into the contact with the upper surface of the SU-8 mold; hence, the thickness of the probe was defined by the height of the mold (d). The silicon wafer/SU-8 mold/PDMS/glass assembly was placed in an oven at 95 °C for 45 min to cure PDMS. A glass coverslip was then removed (e) and the probe was released by peeling of PDMS from the SU-8 mold (f). The probe was bonded with a cover layer of ~ 100 μm thick PDMS to prevent dusts and/or solvents from entering air gaps (g)



**Fig. S3** Refractive index of PDMS, Sylgard 184, from 200 to 800 nm. The PDMS was cured at 95 °C for 45 min












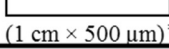
**Fig. S4** Probe detection on a glass capillary. a) Image of the probe on the 150  $\mu\text{m}$  inner diameter x 360  $\mu\text{m}$  outer diameter capillary. b) Trace of 52 nM resorufin switching with a blank. c) Calibration curve of 0.05 to 10  $\mu\text{M}$  resorufin, resulting in detection limit of 6 nM after 249 point boxcar smooth, acquisition rate of 250 samples/sec

**Table S1** Summary of specific conditions for soft-bake, exposure, and post-exposure bake processes. The baking processes were two-step processes, with 65 °C followed by 95 °C. The exposure energy was 17 mW/cm<sup>2</sup>

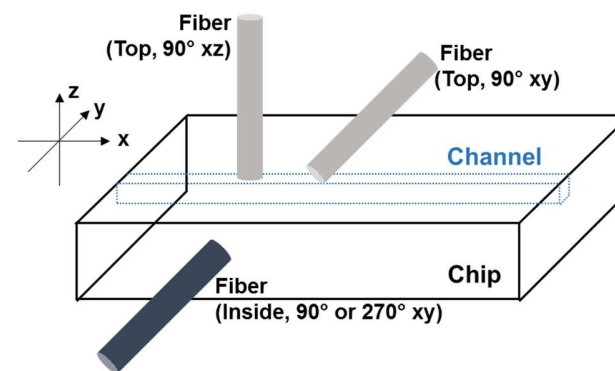
	Thickness	Soft bake		Exposure	Post-exposure bake	
		65°C	95°C		65°C	95°C
1	110 μm	5 min	20 min	18 s	5 min	10 min
2*	2 × 150 μm	2 × 5 min	2 × 30 min	28 s	5 min	23 min
3	110 μm	5 min	20 min	34 s	5 min	29 min

\*Layer 2 is 300 μm thick, created by spin-coating twice of 150 μm thick photoresist layer. The 300 μm thick layer was then exposed at once.

**Table S-2.** Comparison of microfluidic optical detection systems. A detection system typically includes light source, optical fibers/waveguides, and detector. Discrepancy of limits of detection (LOD) could be due to several variables, such as excitation and emission wavelengths, quality of light source and detector, types of filters, alignment and efficiency of waveguides, light pathways, and detection volume.

Ref#	LOD	Analyte <sup>a</sup>	Chip material	Integrated		Light source	Fiber 1 <sup>b</sup> arrangement <sup>‡</sup>	Channel dimension	Fiber 2 <sup>c</sup> arrangement <sup>‡</sup>	Detector
				Lens	Mirror					
*	6 nM	Resorufin	Glass capillary	✓	✓	Laser, 543 nm	Top, 0° - 360° xy	 (150 μm I.D. × 360 μm O.D.)	Same as Fiber 1	Filter w/ PMT
	100 nM	Resorufin	PDMS	✓	✓	Laser, 543 nm	<i>same as above</i>	 (100 μm × 60 μm)	<i>same as above</i>	<i>same as above</i>
	11 nM	Fluorescein	Glass	✓	✓	Laser, 473 nm	<i>same as above</i>	 (80 μm × 25 μm)	<i>same as above</i>	<i>same as above</i>
38	25 nM	Fluorescein	PDMS	✗	✗	LED, 494 nm w/ Filter	Inside, 90° or 270° xy	 (50 μm × 50 μm)	No Fiber 2	Filter w/ μAvalanche-photodiode
39	44 pM <sup>†</sup>	Near-IR dye (NN382)	PMMA	✗	✗	Laser, 750 nm	Inside, 60° xy	 (150 μm × 75 μm)	Inside, 240° xy	Avalanche-photodiode
25	17 μM	FITC-labelled albumin	PDMS	✓	✗	White lamp w/ Filter	Inside, 90° xy	 (50 μm × 130 μm)	Inside, 270° xy	Spectrophotometer
37	21 nM	Rhodamine 6G	PDMS	✓	✗	Laser, 532 nm	No Fiber 1	 (50 μm × 125 μm)	Top, 90° xz	Filter w/ Spectrometer
52	120 nM	Fluorescein	PDMS	✗	✗	LED, 475 nm w/ Filter	No Fiber 1	 (110 μm × 40 μm)	Inside, 90° or 270° xy	Filter w/ PMT
53	50 nM	Fluorescein	Glass	✗	✗	Laser, 473 nm	Inside, 90° or 270° xy	 (100 μm × 25 μm)	No Fiber 2	Filter w/ PMT
54	200 nM	Fluorescein	PDMS	✗	✗	LED, 470 nm w/ Filter	Inside, 180° xz	 (1 cm × 500 μm) <sup>‡</sup>	Same as Fiber 1	Filter w/ Photodiode

<sup>‡</sup> Arrangement of optical fibers for on-chip detection



a. Excitation and emission wavelength of the analytes listed in the above table:

- Resorufin (570 nm/ 585 nm)
- FITC/Fluorescein (490 nm/ 520 nm)
- NN 382 (780 nm/ 800 nm)
- Rhodamine 6G (526 nm/ 555 nm)

b. Fiber 1 = waveguide from light source to sample

c. Fiber 2 = waveguide from sample to detector

\* The microfabricated probe reported herein

<sup>†</sup> The LOD was determined using  $S/N = 2$ . The low LOD was achieved using direct contact of the optical fiber with a sample

<sup>‡</sup> Not drawn to scale