## **Electronic Supporting Information (ESI)**

## Wash-free magnetic immunoassay of the PSA cancer marker using SERS spectroscopy and droplet microfluidics

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**Movie S1.** Isolation process of magnetic immunocomplexes (left) and the droplet fission process (right). This movie demonstrates the real-time tracking of individual droplets before and after the droplet fission.

**Fig. S1.** (a) Schematic of experimental setup comprising the microdrplet chip, Raman instrument and two syringe pumps. (b) Optical arrangement for focusing the laser on the capture area of the channel.

Fig. S2. Variation of droplet generation frequency as a function of  $Q_{ratio}$ .

**Fig. S3.** (a) SERS spectra of supernatant droplets (concentration of PSA marker = 200 ng/mL) for different  $Q_{ratio}$  values at the position indicated in the photograph. (b) Variation of the SERS intensity at 1612 cm<sup>-1</sup> as a function of  $Q_{ratio}$ . Error bars indicate the standard deviation of three measurements.





Movie S1

## (a)







Figure S1



Figure S2



Figure S3

Flow rate conditions	R <sub>oil</sub> (μl/min)	R <sub>water</sub> (μl/min)	$Q_{ratio} = R_{Water}/R_{Oil}$
А	3	1.05	0.35
В	3	2.1	0.7
С	3	3	1
D	3	4.05	1.35
E	3	5.1	1.7
F	3	6	2
G	3	7.5	2.5
Н	3	9	3
I	3	10.5	3.5

## Table S1. Flow rate conditions for droplet generation. Frequencies were optimized for SERS detection.