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## Supporting Information

## Fiber-cap biosensors for SERS analysis of liquid samples



Figure S1. UV-vis absorbance spectrum of bare PDMS showing poor absorbance in the visible range.



Figure S2. AFM images of the top surface of PDMS caps after releasing from the mold.

Few isolated holes and some weak strips are present, probably they are the replica of the tool's footprint on the mold surface. (see fig S2).



Figure S3. Mean dimensions of hydrodynamic diameters of different populations of citrate-capped (a) gold nanospheres, (b) gold nanostars, and (C) CTAB-capped gold nanorods calculated by DLS analysis.



Figure S4. UV-Vis absorption spectrum of MPTMS-silanised PDMS flat surfaces after 12h incubation with NRs solution prepared at pH 7 (green line) and pH 11 (blue line).



Figure S5. Static contact angles of water on bare PDMS (a), air plasma-treated PDMS (b), APTES-modifies (c) and MPTMS-modified (d) PDMS. Ultrapure water was used as probe liquid. The contact angles were measured at room temperature by drop technique determining the contact angle based on both the circle and elliptic fitting with ImageJ dedicated plugin. Droplets of  $5 \div 10 \mu$ l were gently dispersed on the surfaces and measurements were repeated thrice and results were averaged.



Figure S6. To verify the repeatability of optimized NPs deposition processes, UV-vis spectra were acquired on different NSts-decorated (a) and NRs-decorated (b) PDMS substrates. Optical density mean values and relative standard deviations were considered as indication of process repeatability.



Figure S7. UV-vis spectra of NSts-decorated (a) and NRs-decorated (b) PDMS substrates acquired before and after incubation (from 1 minute till 30 minutes) with PBS buffer solution used for Aβ protein dilution.





Figure S9. Raman spectra of the  $A\beta$  peptide and the buffer used for the protein dilution acquired with nanostars (a) and nanorods (b) decorated samples with and without biofunctionalization with the Anti-A $\beta$ . No consistent Raman signals ascribable to antibody could be clearly detected as the main peaks observed for Anti-A $\beta$  conjugated samples were at 1089 cm<sup>-1</sup>, 1282 cm<sup>-1</sup> and 1438 cm<sup>-1</sup> almost overlapping with the main peaks assigned to PDMS. Moreover, no significative differences were observed respect to the spectra acquired against the buffer solution with PDMS decorated with NPs but without biofunctionalization except for the small increase in signal intensity in the region of Amide I (1600 cm<sup>-1</sup> – 1800 cm<sup>-1</sup>) and Amide III (1200 cm<sup>-1</sup> – 1300 cm<sup>-1</sup>) that could derive from the main structure of the antibody.