Electronic Supplementary Information

Selective dual-side functionalization of hollow SiO$_2$ micropillar arrays for biotechnological applications

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**Fig. S1.** Cross-view SEM micrograph of a 150 μm-thick macroporous silicon. Zoomed images at different depths display uniform pores in diameter and smooth wall surfaces. Scale bar: 10 μm.
**Fig. S2.** Dark-field TEM images of A) a single broken micropillar showing a uniform SiO$_2$ wall and a hollow structure; B) a detail of the micropillar tip
Fig. S3. Schematic representation of the GTA reaction onto APTES. A) Partial dehydration of the primary amine into a secondary amine; B) complete dehydration of the secondary amine into an imine group.
Fig. S4. Second derivative FT-IR spectra of a nanoporous sample after functionalization with APTES (green line) and subsequent GTA docking (pink line). The minimum at 1506 cm\(^{-1}\) falls in the region of the secondary amine secondary amine $\delta$NH (1490-1580 cm\(^{-1}\)), whereas the minimum at 1656 cm\(^{-1}\) is in the region of $\nu$N=C(1660-1675 cm\(^{-1}\)). Assuming these assignments are correct, this implies there is equilibrium in the GTA docking on APTES between the partially and completely dehydrated forms.
**Fig. S5.** FT-IR spectra of a nanoporous sample freshly etched (H-terminated, blue line), after oxidation (OH-terminated, black line) and after MPTMS functionalization (SH-terminated, orange line).
**Fig. S6.** FT-IR spectra of a nanoporous sample freshly etched (H-terminated, blue line), after oxidation (OH-terminated, black line) and after MPMS functionalization (NH$_2$-terminated, pink line).