

## Electronic Supplementary Information

# Selective dual-side functionalization of hollow SiO<sub>2</sub> micropillar arrays for biotechnological applications

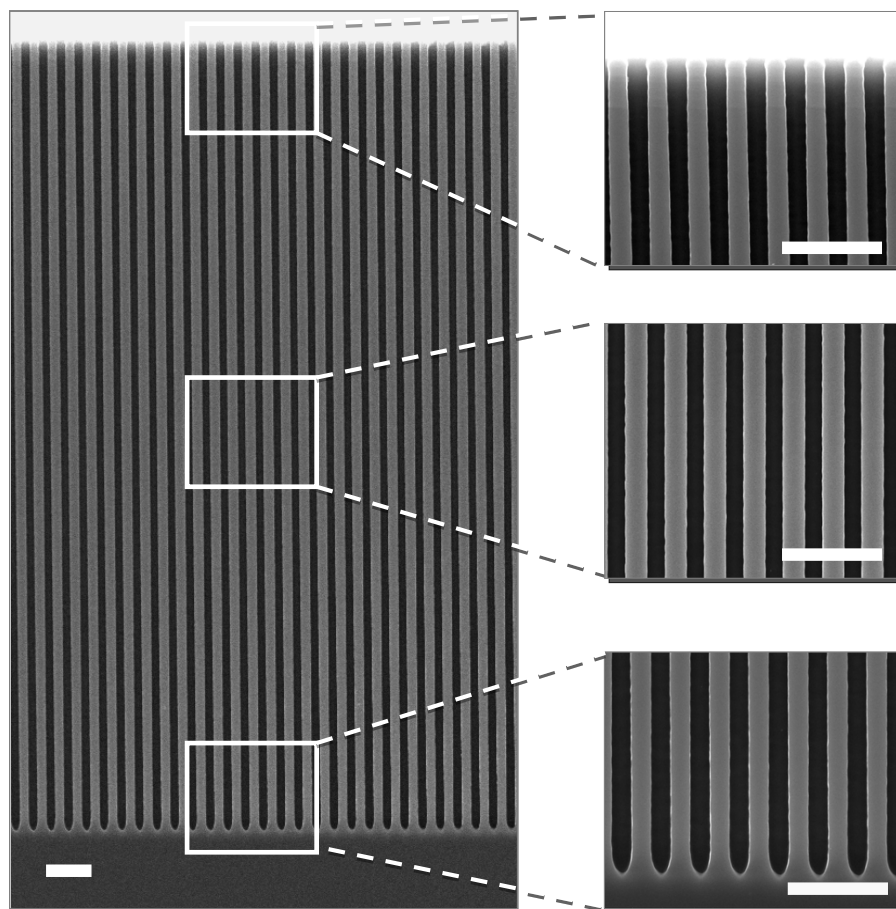
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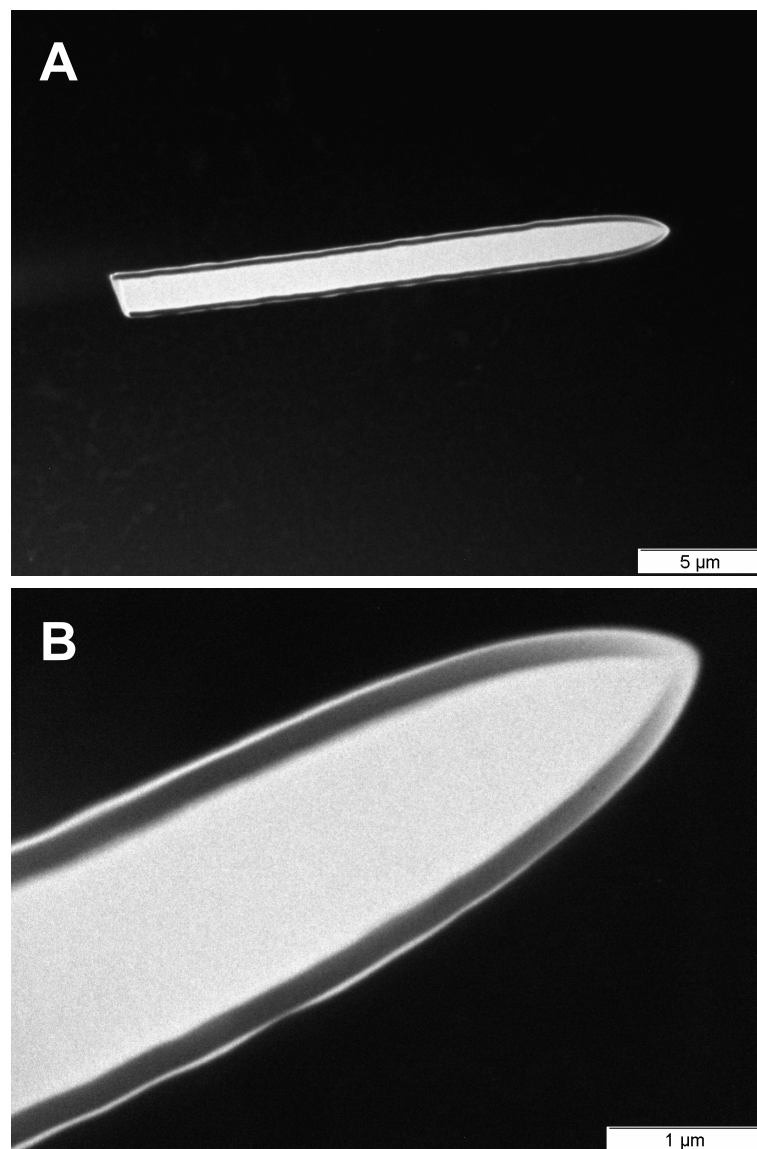
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Rovira i Virgili, Avda Països Catalans 26, 43007 Tarragona (Spain).

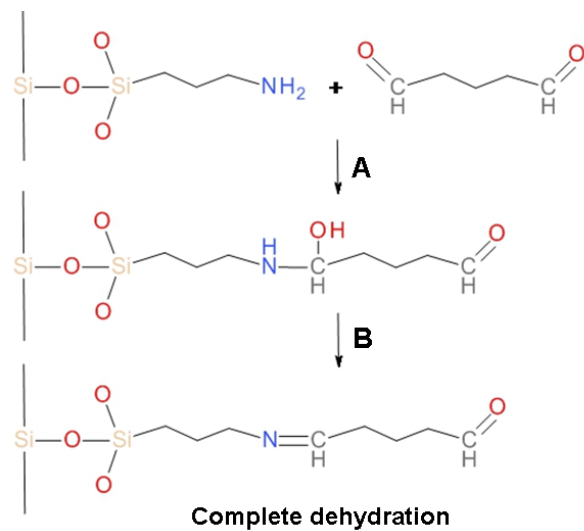
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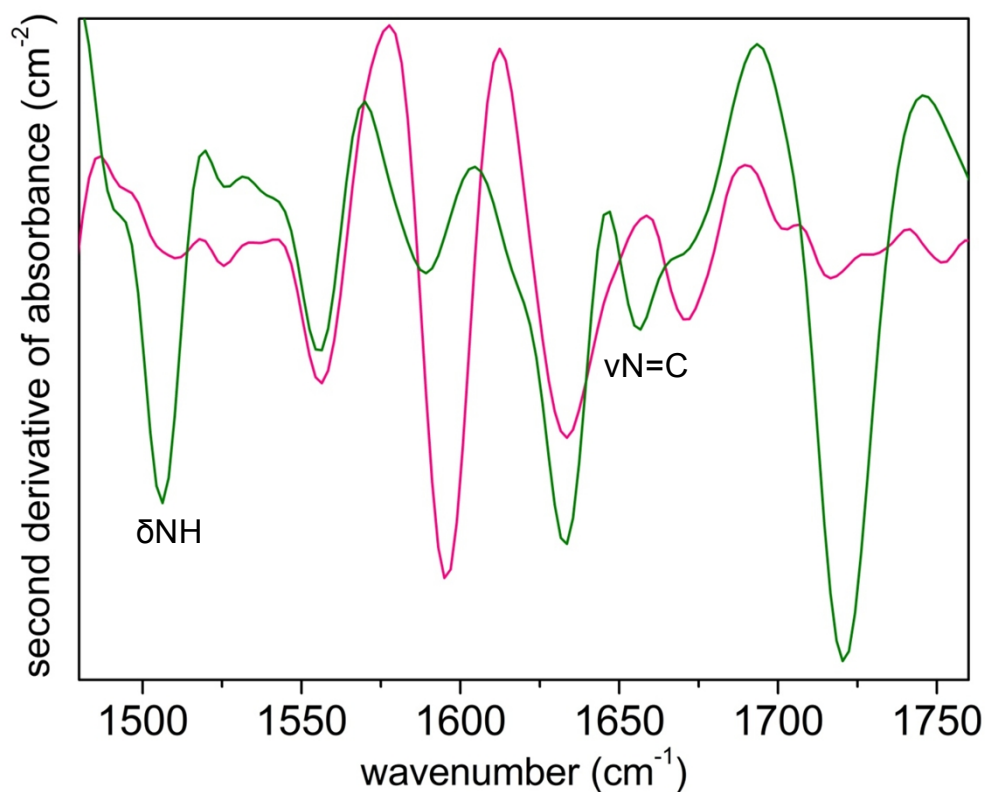
**Fig. S1.** Cross-view SEM micrograph of a 150  $\mu\text{m}$ -thick macroporous silicon. Zoomed images at different depths display uniform pores in diameter and smooth wall surfaces. Scale bar: 10  $\mu\text{m}$ .



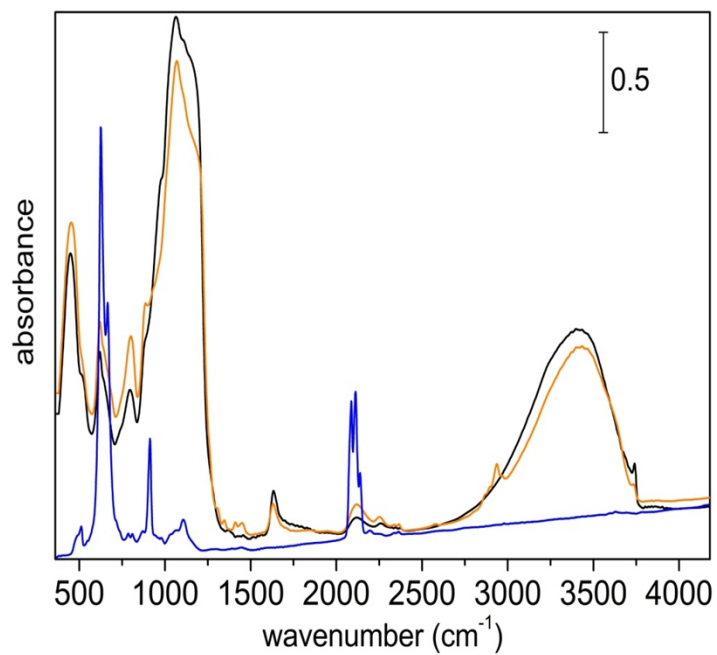
**Fig. S2.** Dark-field TEM images of A) a single broken micropillar, showing a uniform SiO<sub>2</sub> wall and a hollow structure; B) a detail of the micropillar tip



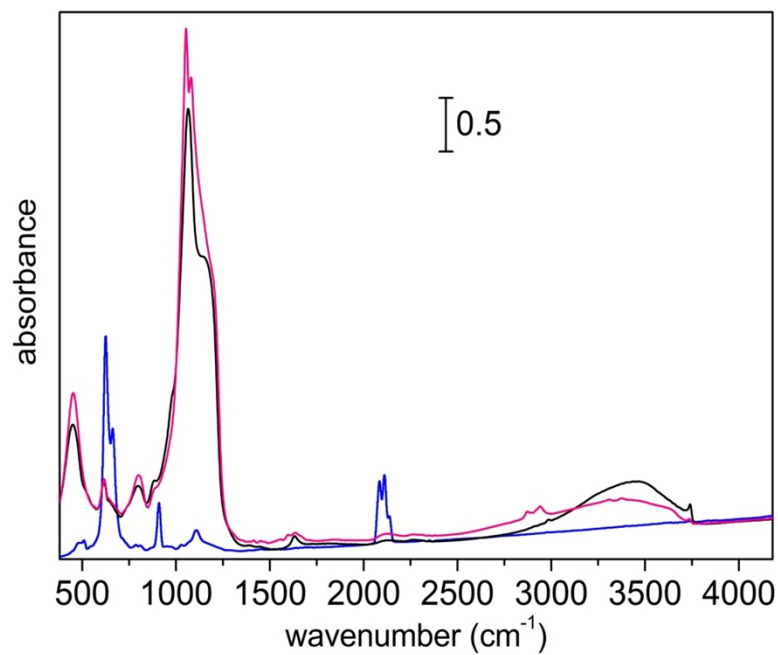
**Fig. S3.** Schematic representation of the GTA reaction onto APTES. A) Partial dehydration of the primary amine into a secondary amine; B) complete dehydration of the secondary amine into an imine group.



**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<sup>-1</sup> falls in the region of the secondary amine secondary amine  $\delta$ NH (1490-1580 cm<sup>-1</sup>), whereas the minimum at 1656 cm<sup>-1</sup> is in the region of  $\nu$ N=C(1660-1675 cm<sup>-1</sup>). 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<sub>2</sub>-terminated, pink line).