Supporting Information Available

 Lengthy experimental details. (2) XPS figure of C 1s peak for bare and lactoferrin-immobilized surfaces

(1) Polymer thin films were deposited by spin coating of the commercial solution (Accuglass T-12B Honeywell) onto monopolished monocristalline silicon wafers. To evaluate the SFE properties, given by the sum of the dispersive Lifshitz van der Waals (LW) and the polar Lewis acid base (AB) components, the Chaudary-Good-van Oss method was applied, with the measurements of contact angle of three probe liquids [van Oss, C.J. *Coll. Surf. B: Biointerf.* **1995**, *5*, 91-110]. Radiofrequency plasma treatments (PlasmaSolution, 13.53 MHz source, O₂ gas flow at 99.95% of purity, 100 Pa of pressure, exposure time of 60 s) to convert as deposited low-energy surfaces (35 ± 5 mJ/m², corresponding to water static contact angle WCA=90°±2°) into high-energy surfaces (63 ± 3 mJ/m², exhibiting very hydrophilic character, i.e., WCA<5°) [C. Satriano, G. Marletta and B. Kasemo, *Surf. Interface Anal.*, 2008, **40**, 649]. As deposited hydrophobic surfaces showed a dominant dispersive character (LW component about 94% of the total SFE), while the plasma-treated hydrophilic ones exhibited a significant contribution from the polar term (AB component about 65% of the total SFE), due to amphiphilic acid-base surface properties induces by the oxygen plasma treatment.

For the preparation of HYL-np (or HYB-np) two facing hydrophobic (or hydrophilic) squared samples of about 1 cm² of area were placed in an aqueous colloidal dispersion (1% wt) of carboxylated-polystyrene (PS-COO⁻, Polyscience) or polystyrene added with Triton surfactant (PS, Sigma). The diameters of the employed nanoparticles were respectively of 209 nm, 362 and 489 nm for PS-COO⁻, while 202 nm and 400 nm for PS. After 1hr of immersion in the colloidal suspension the two polymer samples were separated and placed vertically in a vial in order to allow a slow dewetting-driven self assembly of the colloidal particles. The homogeneity and the hexagonal closely packing of the colloidal assembly was checked by AFM (Nanoscope IIIA, Veeco Instr.) in tapping mode in air with standard silicon nitride tip. After this, a volume of 50 µl of PHMS solution was

dispensed at the edge of each sample to wick into the interstices of the closely packed PS-COO⁻ or PS particles. After 24 hrs the colloidal particles were easily removed by sonication for 15 minutes in methanol/water (3/1 v/v) solution. In the case of PS particles, the sonication step was preceded by 1 minute of oxygen plasma in order to transform the casted hydrophobic film into hydrophilic one.

(2)

Figure 1-Supporting information. XPS peaks of carbon for: (a) HYB, (b) HYL, (c) HYB + Lf and (d) HYL + Lf . The assignment of components obtained by peak fitting analysis is showed.

