Electronic Supplementary Material (ESI) for Sensors & Diagnostics.

Supplementary Information

Cavity Enhanced Lab on Fiber Optrode for Ultra-sensitive pH Monitoring

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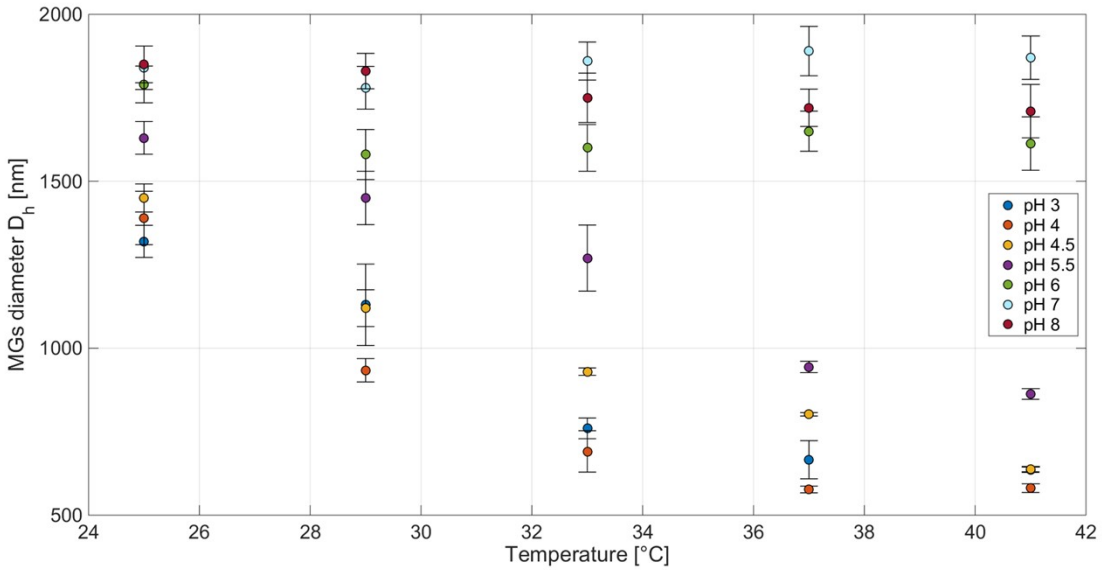
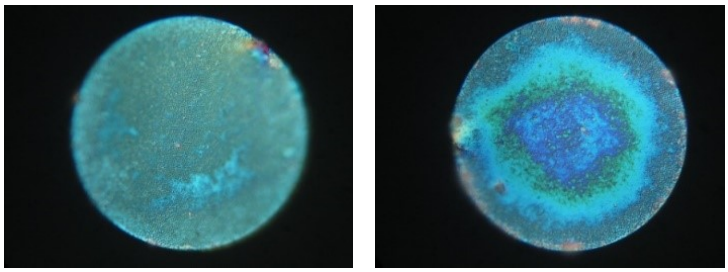
S1. DLS (Dynamic light scattering) measurements

The microgel (MG) particle size have been analyzed by means of DLS (Dynamic light scattering) measurements. To further characterize the pH effect, we measured the MGs diameter as a function of temperature (ranging from 25°C to 41°C) at various pH values. Below the pKa value the acidic groups are in the protonated form and have little or no effect on the volume phase transition temperature (VPTT). Above the pKa, the (acrilic acid) AAc moiety is deprotonated and has a significant effect on the size and the MGs volume phase transition temperature due to the hydrophilic nature of the anion, columbic repulsion and osmotic swelling [1]. As expected, at high pH (from pH 6), no phase transition occurs however, because in these conditions MGs are less temperature responsive and the pH effect is dominant in increasing their size [2].

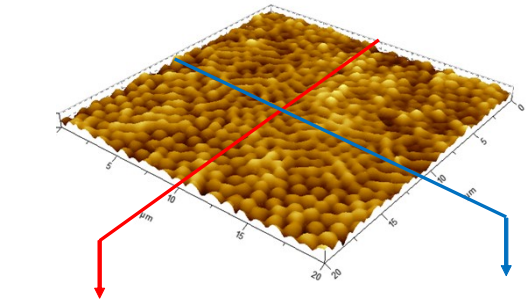


S2. Morphological analysis of the MG film deposited onto the fiber tip (before the second gold deposition)

The figure below shows the optical microscopy images taken after the first (on the left) and the second (on the right) deposition step (dipping). It is evident that the single deposition step gives rise to MG layer that appears uniform above the whole fiber tip. The second deposition step allows to reach a thicker MG layer, at the expense of the extension of the uniform area.

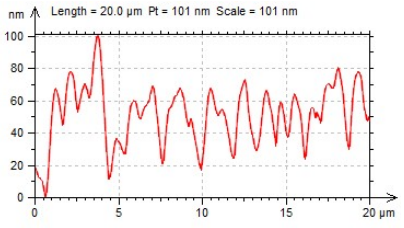


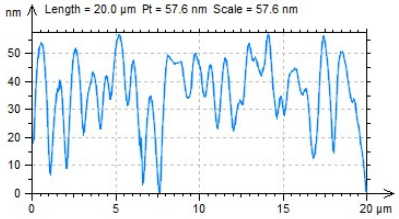
Below we report an additional analysis of the atomic force microscopy (AFM) data compliant with the standard ISO 25178 for the roughness characterization, containing detailed information about the roughness and uniformity of the MG layer.



ISO 25178
Height Parameters

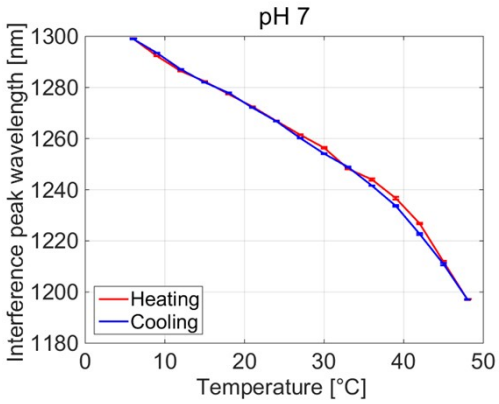
Sq	16.0	nm
Ssk	-0.154	
Sku	3.08	
Sp	57.9	nm
Sv	72.0	nm
Sz	130	nm
Sa	12.7	nm





S3. Thermal characterizations and Sensor Hysteresis

The probe was immersed in an Eppendorf tube containing a solution at pH 7 whose temperature was changed from 6 °C to 48 °C by (and vice versa) exploiting a customized holder integrating Peltier cells. The results of this thermal characterization are reported in the figure below.



The red and blue curves refer to the heating and cooling dynamics respectively. It can be noticed that the heating and cooling curves are essentially superimposed.

References

[1] Fernandez-Nieves, A., Fernandez-Barbero, A., Vincent, B., de la Nieves, F.J., 2000, ***Macromolecules*** , 33, 2114–2118.

[2] Kawasaki, H., Sasaki, S., Maeda, H., 1997, ***J. Phys. Chem. B*** 101, 5089–5093.