

pH-Switched Adsorption of Cytochrome c to Self-Assembled Monolayers on Gold Surfaces and Nanoparticles

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Understanding nanoparticle-biomacromolecule interactions is important in the design of nanotechnology-based biosensors, diagnostic agents and novel materials. In this context, monolayer-capped gold nanoparticles (**AuNP**) provide a suitable scaffold for developing biomarker platforms due to their unique optical properties, robustness, and high surface areas [1,2]. In this work, the adsorption characteristics of horse heart cytochrome c (**HCC**) onto mercaptoundecanoic acid (**MUA**)-capped AuNP and also on self-assembled monolayers of MUA on gold surfaces were studied by quartz crystal microbalance, atomic force microscopy, UV-visible spectroscopy and ζ -potential.

To follow the formation of bionano-conjugates of HCC on citrate-capped AuNP; or on MUA-capped AuNP, a previously developed method based on ζ -potential measurements was used [3]. Analysis of the obtained Langmuir isotherms allowed concluding that HCC adsorption to AuNP is thermodynamically favored in the presence of a MUA capping in relation to citrate capping (Figure 1). UV-visible data on both types of bionano-conjugates show aggregation as a function of the solution pH, inducing a shift of the AuNP plasmon band corresponding to a red-to-blue color change in the solution. Both bionano-conjugates aggregate at around pH 6.2, whereas citrate- or MUA-capped AuNPs pH values correspondent to the pKa value of the capping species. These aggregation results were confirmed by ζ -potential determinations.

Quartz crystal microbalance provided quantitative information regarding the adsorption of HCC onto a bare gold surface and a MUA self-assembled monolayer on gold. Results of experiments carried out with this pseudo-two dimensional system at pH 7.4 and 4.5 showed an increase in protein adsorption at the higher pH. This increase is threefold higher when a MUA self-assembled monolayer is present, comparatively with the bare surface. Atomic force microscopy studies of this system in solution provided images showing the distribution of individual protein molecules adsorbed onto the surfaces (Figure 2).

In conclusion, the interaction of HCC with MUA-capped nanoparticles and surfaces is mainly of an electrostatic nature, and pH can be used as an adsorption modulator, with a “switching” pH value for protein adsorption.

References:

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- [2] You, C.-C.; Verma, A.; Rotello, V. M. *Soft Matter*, **2** (2006) 190.
- [3] Gomes, I.; Santos, N. C.; Oliveira, L. M. A.; Quintas, A.; Eaton, P.; Pereira, E.; Franco, R. *Journal of Physical Chemistry C*, **112** (2008) 16340.

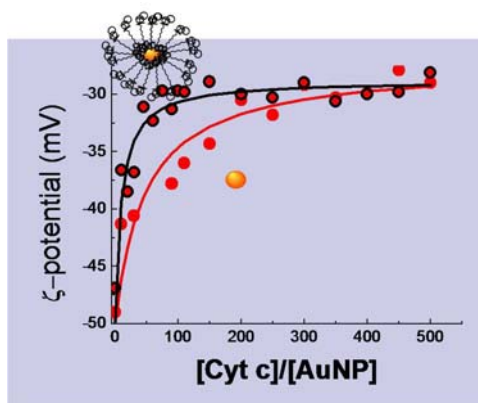


Figure 1 – Cytochrome c adsorption to citrate- and MUA-capped AuNPs as determined by ζ -potential

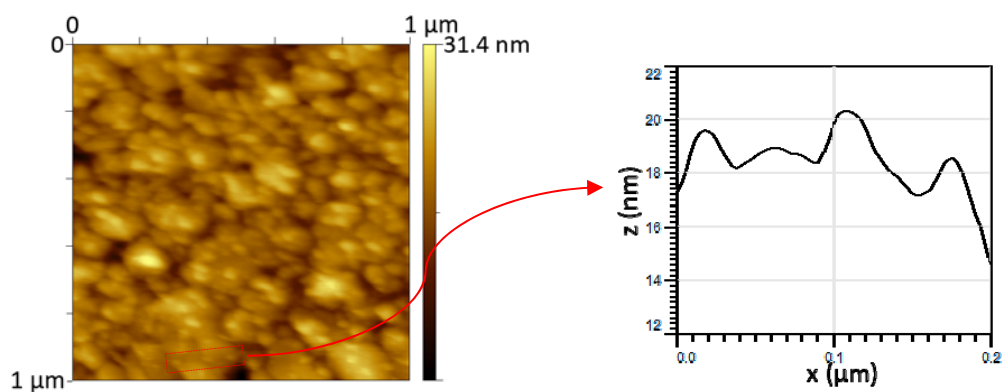


Figure 2 – Atomic Force Microscopy of a gold crystal surface with Cytochrome c deposited over a MUA self-assembled monolayer (pH 7.4; in buffer). The marked region is shown in the height profile, indicating 3 adsorbed protein molecules.