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Low-pressure/environmental electron and photoelectron techniques; a new age for a merged biointerface analysis.

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Surface and interface bio-analytical systems can be categorized, as well as surface modification and biofunctionalization processes, into wet and gas phase (mostly vacuum) operating techniques. While wet and gas phase biofunctionalization routes have coexisted and are even used in sequential processes, the use of traditional vacuum analytical techniques has been severely criticized due to modification of natural thermodynamic conditions and potential sample damage. This has not fully excluded the use of electron microscopies (EMs) and photoelectron spectroscopy (XPS) in the analysis of biointerfaces, but has created controversies by comparison with information provided by wet analytical processes. That is the reason why, many biointerface analysis studies using mechanical, electrochemical or optical transduction of biomolecular sorption do not provide additional EM or XPS evidence of the interface. The advantage of some of these techniques (such as the Quartz crystal microbalance or surface plasmon resonance) is the possibility to monitor the kinetics of modification of the biointerface. Nevertheless, these techniques monitor exclusively the addition of new matter (as added mass or added index of refraction) and leave a margin of uncertainty (depending on the considered protocol) on the matter actually adsorbed on the surface. New technological advances, mainly electron selective pinholes enabling pressure gradients, have allowed the development of so called environmental electron microscopies (envEM) and environmental photoelectron spectroscopies (envXPS). These new advancements demonstrate that, even if analyses do not take place at atmospheric conditions, the analyzed biological samples keep a hydration layer as the most significant physicochemical trace of their pristine state upon analysis. The control of thermodynamic conditions in envEMs (particular case of a wet scanning transmission EM) allows for instance a recording of water adsorption isotherms from the contrast change induced by a water adsorption progressing at increasing relative humidity. In the case of envXPS, the presence of a water layer is evidenced by a trace component in the O1s core level, assigned to water in the vapor phase. From these seeding fundamental results, we provide several examples of how envEMs and envXPS have already complemented applied biointerface structures in the therapeutic and diagnostics field. These studies suggest that the gap to make compatible the results of the analysis of biointerfaces by wet and vacuum techniques is shortening and may open a new age for a fully merged biointerface analysis.

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