

Light controlled processes at semiconductor / polyelectrolyte interfaces

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Processes at the interface of inorganic solids and polymers are of utmost importance to understand their properties, and polyelectrolyte multilayers are very suitable for their study, as they can be manipulated at will between glassy, rubbery and hydrogel or organogel. The processes at inorganic / polyelectrolyte interfaces mimics a large variety of natural processes such as stimuli response behavior, self-healing, actuation, sensing, transport and delivery, pH-buffering.

We suggest to investigate the system, photo-catalytically triggered local pH changes in titania / polyelectrolyte Layer-by-Layer assembled (LbL) interfaces, to serve understanding of mimicking nature as a novel design strategy for inorganic / polymer interfaces. We thus answer the following key questions.

- (a) How can the photogeneration of charges in titania be used to change the properties of adjacent soft matter? The question contains topics as photon absorption, carrier generation, chemical conversion into a pH gradient, lifetimes and polymer stability.

Sub-questions then are

- (b) the dependence on LbL architecture,
- (c) the specificity for TiO_2 as semiconductor, effectiveness of doping, duration and intensity of irradiation.

The objective, light triggered local pH changes in inorganic/ polyelectrolyte interfaces for LbL activation, is illustrated in Fig. 1. The light-response of semiconductors can be tailored by the composition and surface properties of the semiconductor. This provides a materials class which can induce a local change of pH (ΔpH) for reversible actuation of LbL assemblies without degradation by the generated reactive oxygen species (ROS).

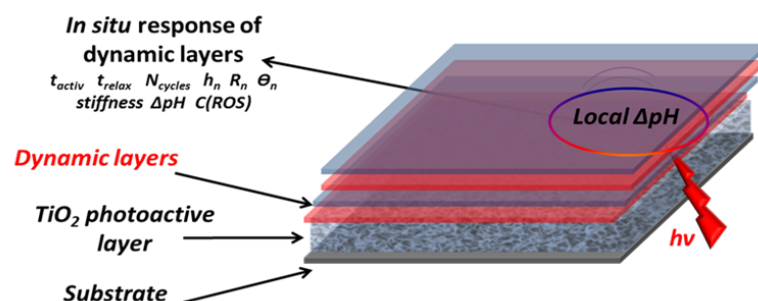
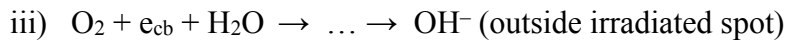
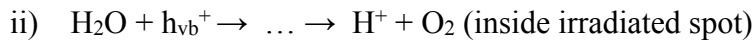
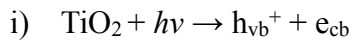


Fig.1: Schematic depiction of a photo-responsive composite film made of semiconductor titania surface with a polyelectrolyte film assembled on it. Electromagnetic irradiation leads to the production of reactive oxygen species (ROS)

and a local change of pH (ΔpH), which affects the composite film in terms of film thickness, roughness and local morphology.

For pH sensitive modulation with light it is important to understand, how photoinitiated processes on TiO_2 result in the transformation of light into a pH change, including localization of the effect. We apply the *in situ* ion-selective microelectrode technique (SIET) for mapping of the activity and migration of H^+ ions over TiO_2 surface with a LbL assembly of a weak positively charged polyelectrolyte (PEI, polyethylenimine), and a strong negatively charged one (PSS, polystyrene sulfonate): $TiO_2/(PEI/PSS)_2$. The proton distribution suggest that under irradiation in the center preferably the reaction of the generation of protons is occurs, the OH^- are also seen in the areas around the irradiation spot.



Interesting is that the drastically different character of the pH relaxation on TiO_2 vs. $TiO_2/(PEI/PSS)_2$. The polyelectrolytes apparently have a strong influence on charge carrier transformation into H^+ and are a proton storage.

Although more quantitative studies are needed, it is already now clear, that there is great prospect of conversion of energy of electromagnetic irradiation into pH gradients enabling also spatial regulation by localization of the irradiation spot.