Light programmable materials interfacing bacterial biofilm

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The main vision of the work is a development of chemical reaction networks for energy transferring reactions to have light initiated spatiotemporal ion [1], molecular concentration gradients [2] in the system based on photocatalytic reaction of water splitting [3], formation of reactive oxygen species (ROS) [4] and other possible ones depending on chemicals presented in the system to make new materials flexible in terms of delivery of different amounts and types of chemicals [5] and ions [6] to actuate soft matter [7], cells [8] and biofilms [9]. The topic is promising for a new live-inspired generation of "smart" materials for biofilm study where we aim to localize gradient of different molecules, ions at certain sectors with sectors communication to amplify or inhibit signal of one another. Control of molecules, ion (e.g. proton, sodium, potassium) gradient is suggested by assembly on semiconductor surface soft matter, e.g. pH responsive polyelectrolytes layer-by-layer (LbL) assembly, lipid bilayers and system of synthetic ionic channels. Our concept is illustrated in Fig. 1 has three main advantages. 1) The range of nanoblocks used to assemble these coatings is very broad, their structural response upon changes in pH and ionic strength can be enormous, synthetic ionic channels and host-guest molecular chemistry are also possible. 2) Photo-response of semiconductor particles can be tailored via their composition and surface properties. This provides a materials class, which can generate reactive oxygen species (ROS) in significant concentrations upon irradiation, which consequently induces a local change of pH (ΔpH). 3) Biofilms can be locally chemically reprogrammed by higher concentration of ions, e.g., H^+ or K^+, which would result in synchronization of material photoreactions (PM) and biofilm (B) growth or a chemical input to a biofilm dissociation.

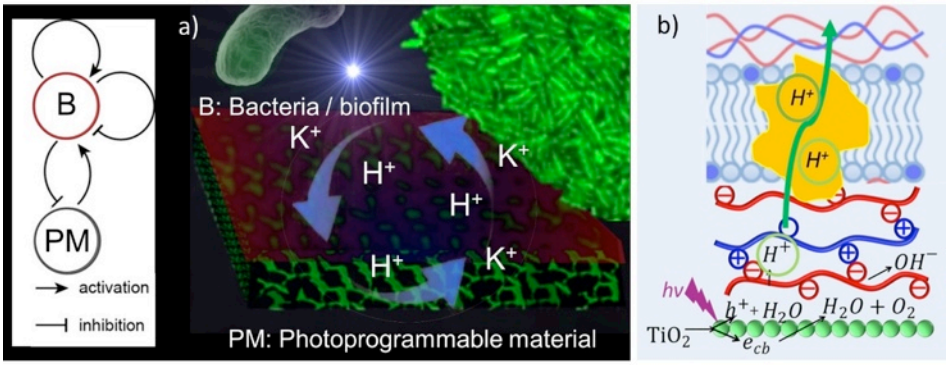

Fig.1: a) Schematic depiction of a photo-responsive material (PM) for programming of bacteria / biofilm (B) in a cascade of photo- or bio-reactions via their activation or inhibition. b) Electromagnetic irradiation leads to the production of reactive oxygen species (ROS) and a local change of pH (ΔpH) [1], release of ions will be regulated by proper surface nanoarchitecturing.

As surface for "photoproton" pumping anodized titania layer can be used [3]. The change of the surface pH was studied in detail *in situ* with the scanning ion-selective electrode technique (SIET) (Fig. 2) [3]: "Light-induced proton pumping with a semiconductor with a vision for photoproton lateral separation and robust manipulation". For pH 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 the localization of the effect. We apply SIET to map the activity and migration of H^+ ions over the TiO_2 surface. SIET is a unique technique available for measuring *in situ* changes in ion concentrations locally in space and following the dynamics of the processes in time. The main advantage of this unique method is that it allows measurements of local pH changes near the surface without any pH-sensitive markers, which may potentially themselves affect the photoreactions in the system. Maps of the pH are collected for pristine TiO_2 before illumination (Fig. 2a), during illumination (Fig. 2b), after 20 min after switching off the illumination, and during 40 min of

relaxation (Fig. 2c). It is seen from the presented proton distribution maps that, under irradiation, the reaction of the generation of protons is observed. Thus it is possible to couple light and pH and we know how to "read" the system in time and see processes under local illumination.

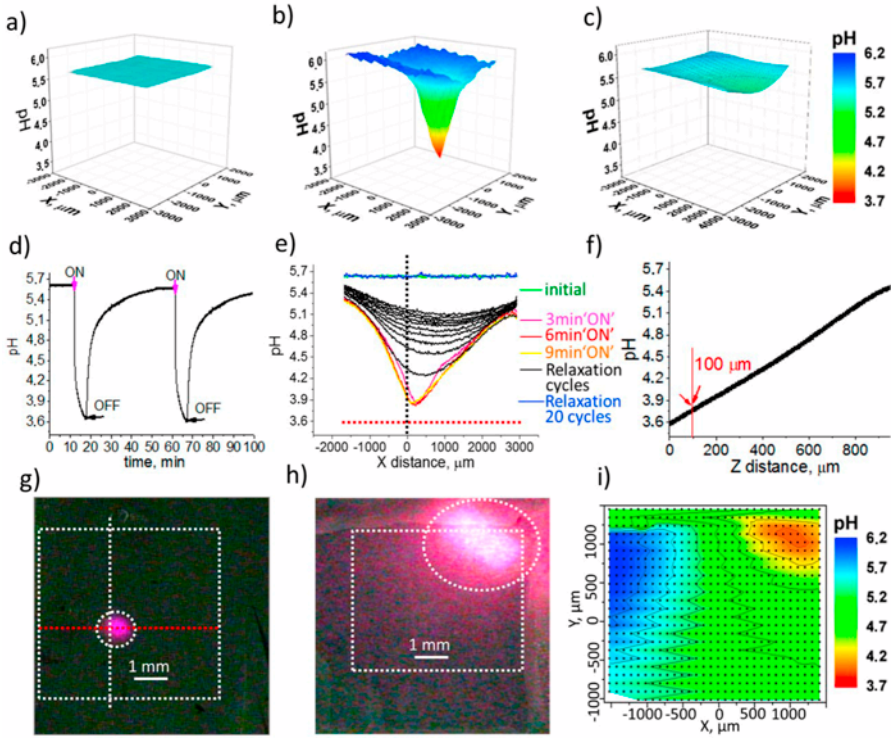

Fig. 2 Copyright from [3]: Light-induced variable pH gradient and proton pumping. Maps obtained by the in situ scanning ion-selective electrode technique (SIET) to analyze local pH gradients generated on nanostructured TiO_2: a) before irradiation, b) during local irradiation, and c) after irradiation (20 min of relaxation). d) pH measurement inside an irradiation spot (shown in panel g) and single-spot time-evolution measurements on a titania layer after switching on and switching off the light. e) Local pH measurements in a line (shown in panel g in red) before, during, and after irradiation (maximum coincides with the position of the irradiation spot, the time of measurement of each line was 3 min). f) pH in the Z direction during illumination inside the irradiated spot. g) X−Y dashed lines shown in the optical image of the surface and the location of the focused irradiation spot on TiO_2 described above (panels a−e) mapped in panels a−c. h) X−Y optical image with defocused light to show the flexibility of the method to change the intensity of illumination and its location and effect on the pH gradient of the surface with corresponding i) pH map with color-pointed pH areas.

The results have a significant impact for future studies on the application of such composite films in a broad range of areas such as defouling surfaces medicine, bioscience and even chemical computing and information processing.

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