Photocatalytic reactions on TiO_2 for light switching of pH sensitive polymers

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Materials, in particular polymers, which respond to external stimuli are of great current scientific interest due to their wide applications [1-2]:

- addressable microsamplers and microdispensers well-compatible with laboratory-on-chip;
- self-healing dynamic materials;
- stimuli-trigged nanocapsule arrays and membranes;
- 'smart' supports for growing cells and tissues;
- drug delivery;
- (bio-)sensors.

Among the broad range of external triggers for structural changes of polymers (temperature, pH, ionic strength, electric field, light, …), light is probably the most attractive stimulus, since it is convenient to apply and localize, light intensity and energy can be varied over a broad range.

Our research aims at the development of light-sensitive composites of TiO_2 and polymers for the fundamental understanding of their response behavior. Instead of using light-sensitive polymers, which are limited in number and limited in terms of their response, we use photoactive TiO_2 layers as mediator to induce local pH changes, which is the internal trigger for pH-sensitive polymers. Fortunately the range of pH-sensitive polymers is extremely broad including polyelectrolytes, biopolymers, hydrogels and copolymer micelles. Two types of systems are in our focus: 1) Layer-by-Layer (LbL) assembly of polymers multilayer on TiO_2 (Fig. 1) layer; and 2) polymers with incorporated TiO_2 nanoparticles (Fig. 2).

Multilayer polymer films can be fabricated by LbL assembly of pH-responsive polymers on a photo-catalytic semiconductor layer. In a highly synergistic manner light activates the release of ions (H^+ and OH^-) into the polymer matrix which responds locally in terms of swelling or deswelling due to these changes in pH. Consequently the properties of the overall film are altered in a cascade like fashion. Example of the chosen multilayer system to regulate cell behavior on the surface is shown in Fig.1. The test system consists of the following multilayers: glass or Ti – substrate; TiO_2 photosensitive layer; pH sensitive micelles and polyacrylic acid (PAA) – dynamic pH sensitive layer. LbL formed biocompatible interfaces can regulate the adhesion and the dynamics of proteins, peptides, lipids, polysaccharides, cells, etc. as well as tissue growth in both, space and time, by using electromagnetic irradiation. Experiments with pre-osteoblast *MC3T3* cells after 6 days cultivation show significant changes of the cell density before and after irradiation (Fig. 1) due to changes of the properties of dynamic layer. Thus before irradiation the cell density on the dynamic coating on glass and on the dynamic layers -TiO_2 coating is approximately the same (ca. 500 and 500 cells/mm^2), but after irradiation the cell density on the hydrogel-TiO_2 side decreases by 1.5 times while the cell density on the hydrogel-glass increases. In Fig. 2 one sees how cells migrate from the hydrogel-TiO_2-side to the hydrogel-glass side. As it was mentioned above a TiO_2 film under UV-irradiation activates the pH-sensitive dynamic layers, which leads to an increase of their thickness, whereas the thickness of the polymer layers on the glass side remains the same, because it couldn't be activated without the TiO_2 film.

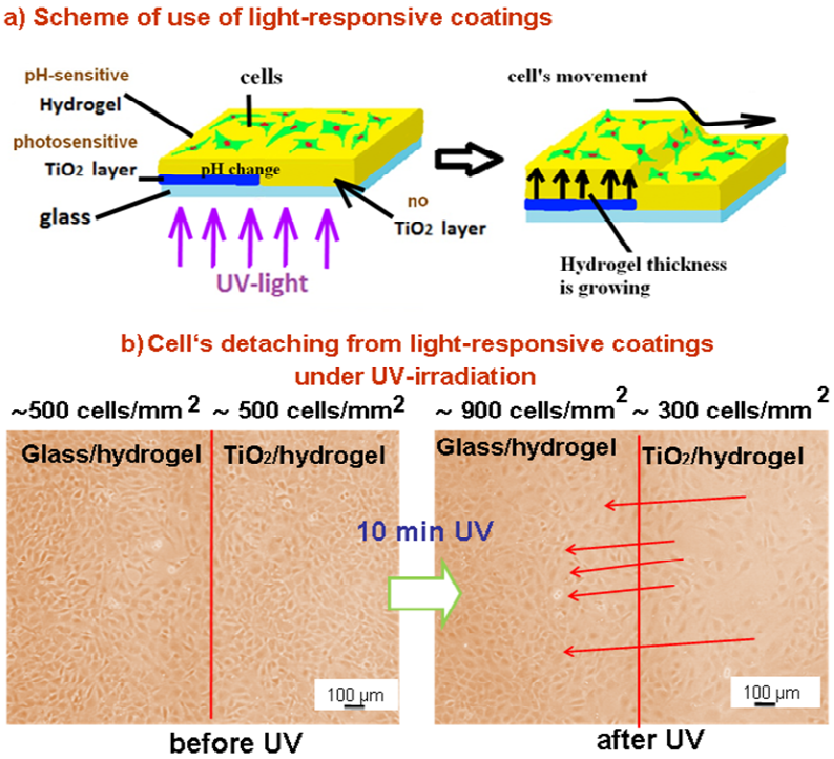

Fig. 1 a *–Scheme of use of light-responsive coatings based on mesoporous TiO_2 films and pH-responsive hydrogels; b –the cells detaching from light-responsive coatings under UV-irradiation.*

Light-healing cellulose based hydrogel was developed for 3D organ-printing devices. To heal cellulose hydrogel TiO_2 nanoparticles were introduced in its composition. The hydrogel healing is shown in Fig. 2.

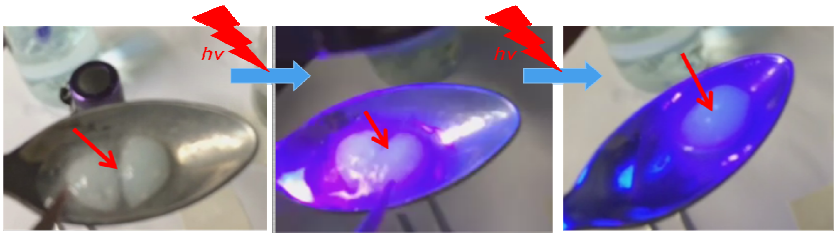

Fig. 2 Light-healing of cellulose hydrogel under irradiation due to photocatalytic reaction and local pH-changes on introduced into hydrogel titania nanoparticles. The light-healing zone is shown with arrows.

In all in our research we analysis the light-pH coupled composite TiO_2-polymer system response mechanism on different length and time scales. The photo-mechanical cyclic changes, namely film thickness and roughness, the degree of swelling and morphological changes are in focus. Furthermore, photo-chemical changes are investigated. These comprise the diffusion of reactive oxygen species (ROS) and ions (H^+ and OH^-) in time and space as well as polymers degradation. The photo-mechanical and photo-chemical effects are studied before, during and after irradiation with a special focus on the relaxation of the polymers.

[1] Skorb, E.V., Volkova, A., Andreeva, D.V. (2015): Current Organic Chem., DOI: 10.2174/138527281
[2] Skorb, E.V., Möhwald, H. (2013): Adv. Mater., 36, 5029-5043.