Light-Induced Water Splitting Causes High-Amplitude Oscillation of pH-Sensitive Layer-by-Layer Assemblies on TiO₂

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Abstract: We introduce a simple concept of a light induced pH change, followed by high amplitude manipulation of the mechanical properties of an adjacent polymer film. Irradiation of a titania surface is known to cause water splitting, and this can be used to reduce the environmental pH to pH 4. The mechanical modulus of an adjacent pH sensitive polymer film can thus be changed by more than an order of magnitude. The changes can be localized, maintained for hours and repeated without material destruction.

The use of light as an external stimulus to modulate polymer systems has great potential in biosciences, medicine, and tissue engineering, owing to the possibility to irradiate micron-sized areas with fast on/off switching rates.[1] However, only a limited number of stimuli-responsive polymers are able to undergo light-initiated transitions. Well-known examples are polymers with azo-groups that undergo reversible isomerization upon irradiation.[2] Unfortunately, the response on the molecular level is relatively weak, because azobenzene molecules change their geometry from planar to non-planar with a decrease in the distance between the *para* carbon atoms only in the Ångström range.[2] Other examples are photo-crosslinkable polymers.[3] The photo-crosslinking technique is widely used in the casting industry and in photo-resist technology and can allow for the photo patterning of pixels.[4] However, such materials are difficult to use as stimuli-responsive systems, where changes should be totally reversible. It is of importance to find a strategy to actuate polymer systems: composites, hybrids. Light-actuating composite layer-by-layer (LbL) polyelectrolyte assemblies in most cases contain metal nanoparticles,[5–7] which couple light and temperature providing local heating and decomposition in LbL assemblies. Recently Tsukruk et al.[8] suggested using a light-initiated photochemical reaction, in which trivalent counterions, $[Co(CN)_6]^{3-}$, can be decomposed into monovalent and divalent ions, which dramatically affect the reversibly conformation and porosity of LbL films. The systems, however, are not comparable with the actuation amplitude of pH-sensitive LbL polymer films: change of thickness, stiffness. Our concept of is to couple light and pH and thereby actuate adjacent pH sensitive soft matter with light. We aimed to demonstrate the concept of nondestructive light–pH coupled switching of polymer films by activation of the pH change on titania and reversibly affecting polymer assembly (Figure 1).

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i) $TiO_2 + h\nu \rightarrow h_{vb}^+ + e_{cb}$

ii) $H_2O + h_{vb}^+ \rightarrow \ ... \ \rightarrow \ H^+ + O_2$ (inside irradiated spot)

iii) $O_2 + e_{cb} + H_2O \rightarrow \ ... \ \rightarrow \ OH^-$ (outside irradiated spot)

Figure 1. Surface decoration and photoinitiated light–pH reactions. Primary and secondary photocatalytic reactions on TiO₂ resulting in a local change of pH (ΔpH). The reactions are shown of i) light-stimulated charge separation, ii) primary reaction with photohole with final production of protons and local surface acidification of the irradiated area, iii) and photoelectron reaction. ΔpH will affect the dynamic layers assembled on the TiO₂ in terms of local changes in film thickness, stiffness, and permeability by regulating the time taken for the dynamic layer activation, the relaxation, and reversibility. vb = valence band, cb = conduction band.

Herein for the first time we focus on an efficient and controllable way of transforming the energy of electromagnetic irradiation into a local pH shift by using the well-established TiO₂ and, thus, into the mechanical reversible response of soft matter for high-amplitude actuation. pH-dependent polymers are a class of materials with tremendous structural variety. One example is the "weak" polyelectro-

lytes (PEs),[9] in which morphology and charge strongly depend on pH. Thus such weak polyelectrolytes as block copolymer micelles (BCM) can show a drastic response to pH.[10] The pH-responsive behavior of the block copolymer micelles can be controlled via the ionization degree of one of the constituting blocks.[11] Another class of pH dependent polymers are hydrogels.[12] They exhibit pronounced morphological changes in response to ΔpH and can also be used for multilayer formation.[13] It is important to assess, if the whole class of pH-sensitive polymers can be modulated/actuated with light, which is the focus of this study on actuating pH sensitive soft matter with light by using TiO_2 for proton pumping.

The concept is illustrated in Figure 1. We build up our system with the following blocks: the light sensitive part is a photocatalytically active nanostructured TiO_2 film. It is well established[14,15] that under supra-band gap illumination a photohole and a photoelectron are formed (Figure 1) on the surface of TiO_2. The active species formed can then take part in series of different photocatalytic reactions. Thus, the photoholes can convert the surface hydroxy groups, the photogenerated electrons can be scavenged by any scavenging agent, in most cases by oxygen. We suggest that during photocatalytic reactions both H^+ and OH^- can be generated on TiO_2. Focusing on nondestructive, temperature-independent modulation of polymers we used low power, short term irradiation and assembled LbL films on low photocatalytically active TiO_2 surfaces (Figure S1 in the Supporting Information).

For pH sensitive modulation with light, it is important to understand how photoinitiated processes on TiO_2 result in the transformation of light to a pH change, including localization of the effect. We applied the in situ scanning ion-selective microelectrode technique (SIET) with a sensitivity better than ΔpH 0.2 units for mapping of the activity and migration of H^+ ions on a TiO_2 film in aqueous solution during UV irradiation. The SIET allows measurements of the concentration of specific ions (in particular in this case, H^+ ions) at a nearly constant microdistance over the surface (Figure S2).[16] The SIET map for a TiO_2 light irradiated surface is shown in Figure 2, confirming that it is possible for TiO_2 to release protons during its irradiation. Most of the photogenerated species are used for the reactions, and we could not detect any temperature change over the surface with a sensor with sensitivity below $\Delta T = 1°$. Thus pH changes are due to the photocatalytic reaction on the TiO_2 surface, and these changes are drastic.

Figure 2b demonstrates, how the pH in the center of the irradiated spot (Figure 2a) varies upon switching on and then switching off the local UV irradiation. The duration of irradiation correlates with the pH obtained: 5 s, 1 min, and 3 min of irradiation result in pH of 5.6, 4.5, and 4 peak values, respectively. After turning off the light, the pH relaxes to the initial value over approximately 40 min. To study possible localization (Figure 2a) of proton pumping from the TiO_2 surface the 3D SIET maps are monitored (Figure 2c,d).

The pH before irradiation is about 6 all over the TiO_2 surface (Figure 2c). After starting the local surface illumination, the pH decreases significantly over the light spot
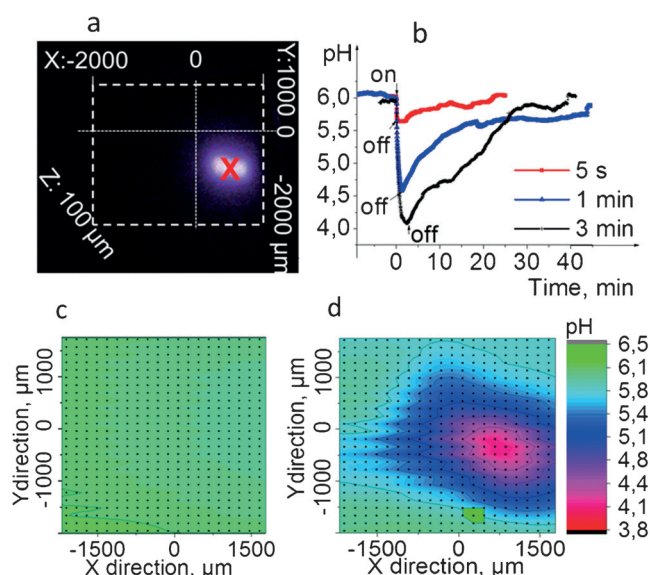
Figure 2. In situ local pH activity over a TiO_2 surface. a) Optical image of the surface during irradiation and measurements of SIET for mapping of the activity of H^+ ions over the TiO_2 film under local UV irradiation. b) Temporal evolution of the pH over the mesoporous TiO_2 film in the center of the irradiation zone (X in (a); on—illumination is switched on, off—illumination is switched off). c,d) SIET maps of proton activity c) before and d) during the exposure of certain localized areas.

(Figure 2d). In addition, there is a gradient of pH going from the center of the irradiated spot in horizontal and vertical (outside) directions. The action of different photoelectrochemical reactions (Figure 1) on the TiO_2 surface under UV illumination seems to be the only plausible explanation for the observed local acidification of the solution and confirms that TiO_2 is promising to demonstrate our concept.

The next step was the assembly of the pH-sensitive high-amplitude actuating polymer on low-photoactive TiO_2 (Figure S1). We worked with well-characterized pH-sensitive block copolymer micelles (positively charged layer, zeta-potential ca. 37 mV),[17] which had shown "smart" switching under pH change. We used a linear ABC triblock terpolymer consisting of polybutadiene (B), poly(methacrylic acid) (MAA), and quaternized poly(2-(dimethylamino)ethyl methacrylate) (Dq), BMAADq. In aqueous solution, BMAADq self-assembles into core–shell-corona micelles with a hydrophobic B core, a pH-sensitive MAA shell, and a strong cationic Dq corona. At low pH the pH sensitive MAA block is uncharged. At high pH, this block is negatively charged through the deprotonation of the carboxylic acid groups leading to intramicellar interpolyelectrolyte complex formation with the cationic corona of Dq. Hence, the composition of the micellar shell as well as the charge density of the corona can be controlled by the solution pH. A single block copolymer micelle layer is approximately 50 nm thick (Figure S3).

Recently the groups of Fery[18] and Sukhishvili[19] suggested that block copolymer micelle stability and reversibility of switching can be improved combining micelles with

polyelectrolytes via LbL assembly. Moreover the LbL assembly of block copolymer micelles (BCM) and polyelectrolytes allows coatings to have different thicknesses.[8] We LbL assembled block copolymer micelles, as the positively charged layer, and poly(acrylic acid) (PAA), as the negatively charged layer. Initially the thickness of the two bi-layers coating on $TiO_2/(BCM/PAA)_2$ was 150 nm (Figure 3a,c; Supporting Information, Figure S4). The question remains, if we could reversibly switch the LbL assemblies that are deposited on the TiO_2 surface, with light. The low power (ca. $5\,mW\,cm^{-2}$) and low duration (less than 10 min) of irradiation did not lead to degradation of the LbL assembled coating, which is verified in control experiments using Fourier transform infrared spectroscopy (FTIR; Figure S5). There are no differences in spectra detected besides a change in water content, which can be explained by a change of LbL thickness and water trapping in the LbL matrix, confirmed also with a quartz-crystal microbalance (QCM; Figure 3d).

To demonstrate the light-induced change of LbL assembly thickness and stiffness, the relaxation kinetics and process reversibility we investigated the LbL film on the surface of TiO_2 using atomic force microscopy (AFM; Figure 3). Then the illumination was switched on and changes in thickness were monitored with AFM. The thickness increased within 10 min, reaching a maximum and remaining the same the next several minutes, then starting to relax slowly, full relaxation took approximately 20 hours. Colloidal probe atomic force microscopy (CP AFM, Figure 3c(inset)) measurements confirmed that the LbL polymer assembly on the photoactive TiO_2 film became softer (ca. Young modulus 28 kPa) during irradiation compared to the initial stiffness (ca. 1.67 MPa), and the process was reversible (Figure 3c(inset)).

Interestingly our recent study proved that even short (seconds) irradiation suffices to activate the LbL assembly. QCM measurements (Figure 3d) confirmed the LbL deposition of two bilayers of (BCM/PAA) on a TiO_2 covered chip. Then we switch on the light for several seconds. It is seen that the frequency started to decrease reflecting the increase of the mass corresponding to water uptake and the LbL film thickness increased by activation as a result of H^+ production (shown in schematic Figure 3d).

After irradiation is switched off the relaxation of the LbL assembled coating occurs. However, owing to the complex character of the LbL assembly building blocks, for example, block copolymer micelles as one pH sensitive layer, the coating relaxation is relatively slow. The relaxation to 150 nm requires more than 20 h, which characterizes the system as fast activated and slowly relaxing. Such systems are of great interest for biological applications (see an example in the Supporting Information, Figure S6).

A related question on the feasibility of the process is: how many protons and photons are needed from the surface to locally change the pH from 7 to, for example, 4, on the surface and activate the block copolymer micelles? To calculate the concentration of protons needed for activation we assume for $1\,cm^2$ of TiO_2 to achieve a pH 4 or $[H^+] = 10^{-4}\,M$ or $6 \times 10^{19}\,L^{-1}$ a coating with thickness of, for example, 150 nm in our case, that is $V = 1.5 \times 10^{-8}\,L$. The concentration of protons in the system is then $[H^+] = 9 \times 10^{11}$ protons cm^{-2}, which is about
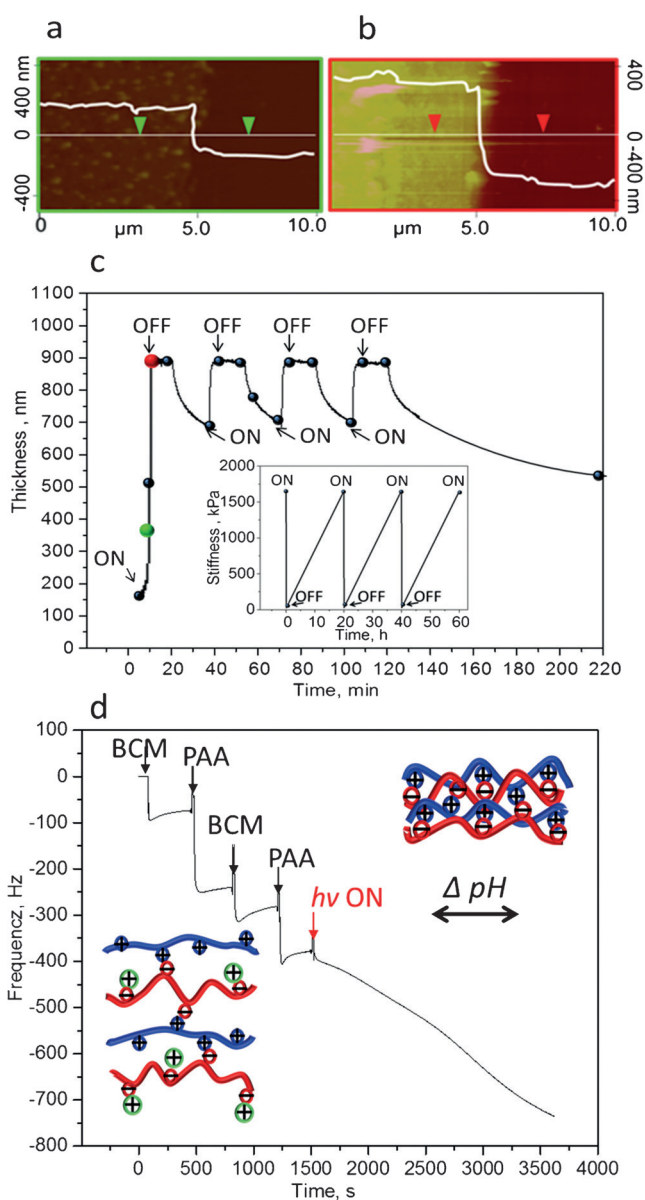
Figure 3. Light activation and relaxation of a high-amplitude switchable pH-sensitive LbL assembly on a low-photoactivity TiO_2 layer. a),b) AFM images of changes in LbL thickness during irradiation for a) 3 min; b) for 10 min; color equates to $z = 0$–1200 nm. c) Change of thickness and (inset) stiffness: LbL activation is significantly faster than its relaxation, cycles of light switching are marked as "ON" and "OFF", correspondingly. d) Quartz crystal microbalance measurements of LbL assembly and photoactivation by seconds-long pulse irradiation. Inset: schematic representation of the protonation of the LbL assembly and increase of its thickness.

0.1% of the lattice sites of a typical solid (10^{15} lattice sites cm^{-2}). This means that only 0.1% of the surface atoms have to be charged to achieve pH 4, if no losses exist. Even if we consider a low radiation intensity of $1\,mW\,cm^{-2} = 10^{16}$ photons $cm^{-2}\,sec^{-1}$ for a quantum yield proton/photon conversion of 0.1% the photons from 100 ms irradiation would create enough protons on the TiO_2 surface to achieve LbL switching on the surface of TiO_2. This also means that also less-photoactive solids could create the same effect.

We still need to answer a lot of questions, and more quantitative studies are needed. How can the photogeneration of charges in a solid be used to change the properties of adjacent soft matter with high selectivity? The question contains topics, such as photon absorption, migration, storage, carrier generation, chemical conversion into a pH gradient, lifetimes, and polymer stability. Sub-questions then are: a) the dependence on LbL architecture, b) the specificity for TiO_2 as a semiconductor, effectiveness of doping, duration, and intensity of irradiation.

However it is already clear that there is great potential for the conversion of energy from electromagnetic irradiation into pH gradients, thus enabling spatial regulation by localization of the irradiation spot on the semiconductor TiO_2 surface. Using localized in situ SIET measurements we show for the first time the possibility of efficient transformation of electromagnetic energy in the form of irradiation into a local pH shift. The LbL assembly provides an efficient structure for the fast trapping of photogenerated H^+ ions. The kinetics of light–pH coupled actuation and modulation show that such LbL surfaces are fast switchable and slowly relaxing. We thus demonstrate that the photogenerated charges in a solid can be used to change the properties of adjacent soft matter. Quantitative analysis for the promising pH sensitive assembly of architecture TiO_2/BCM/PAA/BCM/PAA reveals a modulation of the thickness by a factor of 4 and a change of elastic modulus by more than an order of magnitude. The light–pH coupled actuation of soft matter is efficient for the formation of drug delivery capsules,[7,20] self-repairing coatings, and to guide cells via local elasticity changes (Figure S6),[21] microfluidics, lab-on-chip, sensors, nano-lithography.[22]

In conclusion, we demonstrate here a simple process: irradiation of a semiconductor surface causes a charge separation, leading to water splitting and to a pH change. Unexpectedly the pH value could be reduced to pH 4, it could be localized by focusing of light, maintained over hours and effected repeatedly and reversibly.

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