LETTER

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Focus Article

Photomobility and photohealing of cellulose-based hybrids

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Abstract – In an effort to control the electronic and mechanical interaction between an inorganic surface and a defined polymeric coating, we present a new and easy method of a cellulose-based hybrid formation. We used Schweizer’s reagent, a specific copper ammonia hydroxide-based solvent for cotton dissolution and found the optimal concentration for the formation of photosensitive uniform cellulose coating on titania, TiO2-cellulose coating and free-standing hybrid. Photomobility, the material mobility induced by light, of a cellulose layer on a titania surface and of a TiO2-cellulose hybrid on a silicon wafer has been studied. This can be used for photohealing, and the most promising system is the one that can be healed with light due to in situ activation of titania nanoparticles assembled on cellulose fibers in a hydrogel. The interfacial contact between titania particles and fiber is important for local transport of electrons and ions, thus the most promising system was obtained by in situ synthesis of titania nanoparticles on cellulose dispersed in Schweizer’s reagent. We propose that cellulose coatings on titania surface and free-standing hybrids can be applicable for a wide range of photochemical devices: films for optics, drug delivery systems, and inks for printing of biologically relevant lab-on-chips.

Introduction. – Inorganic/organic composites are of special interest for functional and responsive materials development; while the inorganic part can lend the system high mechanical and functional stability, the organic part can provide responsive function and adaptability. Most prominent representatives for these materials are cellulose as most abundant biomaterial and TiO2 as a well-studied inorganic material with photoelectric, catalytic and optical functions. These hybrids are studied in this paper.

Cellulose systems with a broad range of uses—for example, in composites, cosmetics and medical devices—require simple methods of preparation for combination with active nanoparticles and molecules for a stimuli-response behaviour. Cellulose is one of the most important natural polymers, that has found a wide range of applications in industry and medicine because of its unique structural properties combined with hydrophilic nature, biocompatibility and non-toxicity [1,2]. Due to a high amount of hydroxyl groups on the fiber surface, cellulose can be easily functionalized or bio-conjugated, resulting in a rich source of new materials and platforms for diversified applications in biomedical fields such as tissue engineering and regenerative medicine or drug delivery devices [3–5]. Therefore, facile methods of cellulose processing are of high interest.

It is known [6,7] that local pH changes play an important role for drug delivery systems, dynamic regulation of adsorption/desorption of proteins [8], bacteria [9] and cells [10]. Light-pH coupling on TiO2 surfaces was shown to be efficient for high-amplitude non-destructive manipulation of polymers deposited on semiconductor
and red. In cellulose photomobility on the surface highlighted in green irradiation and change of titania surface bonds that may result (c) Hypothesis of possible formation of hydrogen bonds at the free standing hydrogel with titania nanoparticles (System III). Titania particles on the surface (System II), and cellulose-based assembly with hydrogen bonds between chains (shown in (b), (c) as a grey line). (b) Three types of hybrids are in focus: cellulose assembly on TiO$_2$ surface (System I), assembly of cellulose with titania particles on the surface (System II), and cellulose-based free standing hydrogel with titania nanoparticles (System III). (c) Hypothesis of possible formation of hydrogen bonds at the cellulose-titania interface and their reorganization because of irradiation and change of titania surface bonds that may result in cellulose photomobility on the surface highlighted in green and red.

surfaces [10–12]. Recently we have found that nanolayers of chitosan can be used in the development of high buffering coatings to control environmental pH changes [12]. However, much of the TiO$_2$ function depends on the different mobility of photogenerated electrons and holes, and, therefore, the preparation of TiO$_2$ is expected to be very important [13]. Above all there is a fundamental difference between a surface and a nanoparticle; while charge carriers can be separated in a particle only over a maximum distance of the particle dimensions, on a surface the separation can proceed over macroscopic dimensions. Hence the following cathodic and anodic reactions can be well separated.

In this article, we suggest formation of various hybrid cellulose (fig. 1) coatings from a suitable selected solvent (Schweizer’s reagent) and examine the photomobility, i.e., photo-induced material mobility, and photohealing of coatings and free-standing systems.

The main question which we address here is whether cellulose layer photomobility or even cellulose hydrogel photohealing are possible due to a photoreaction on titania embedded in cellulose. Thus, on titania under supra-bandgap illumination, the illumination with energy high enough for the generation of photoholes and photoelectrons, higher than the energy of the forbidden zone ($E_g$), generates charges, that partly move, partly are trapped. The charge separation is converted into water splitting, and, thus, hydroxyl and proton generation are separated [13]. This causes local pH gradients [14]. If there is a polymeric coating, this in addition may bind selectively one of the produced ions, thus modulating the pH change [12]. Altogether the interplay between the photoreaction of titania and the different mobility and the different binding capacity and responsivity of the coating lead to a responsive system with many application perspectives.

**Experimental protocol.**

*Materials.* Sulphuric acid (1 M H$_2$SO$_4$), Cu (II) sulphate pentahydrate (purity grade ≥ 98%), ammonium hydroxide (28%, ≥ 98%), titanium(IV) butoxide (Ti(C$_8$H$_{14}$O)$_4$, ≥ 98%) were purchased from Sigma-Aldrich (Germany). Silicon (Si) wafers (100) were from CrysTech Kristalltechnologie. Pharmacy cotton wood was used as cellulose fiber precursor. TiO$_2$(Hombikat) nanoparticles were used as received. Millipore water (Milli-Q Plus 185) was used for preparation of aqueous solutions and sample washing.

**Titania photoactive layer preparation.** Si wafers with polished surface were used as substrate for titanium layers of 2 µm thickness deposited by physical vapour deposition using a BA 510 from Fa. Balzers, Liechtenstein. Ti-covered Si wafers were fixed in a homemade sample holder for high-intensity ultrasound (HIUS) modification. The samples were sonicated for 1 min in ethanol at a sonotrode to surface distance of 5 mm. Cavitation was produced by a UIP1000hd ultrasonic device from Hielser Ultrasonde Technology equipped with a B2-1.8 booster and a BS2d22 sonotrode (head area 3.8 cm$^2$). The operating frequency was 20 kHz with a maximum intensity of 140 W/cm$^2$ and an amplitude of 106 µm. The sonication medium was cooled using an ice bath to approximately 333 K [11,12]. The advantages of HIUS preparation of active materials to achieve photoactivity can be found in all details in our previous work [11–20].

**Cellulose coatings.** Schweizer’s reagent ([Cu(NH$_3$)$_4$]$_2$(H$_2$O)$_2$·(OH)$_2$) was prepared by precipitating copper(II) hydroxide from an aqueous solution of copper sulphate using sodium hydroxide, then dissolving the precipitate in a solution of ammonia hydroxide. Cellulose solution was prepared by dissolving 1–50 mg of cellulose in 10 ml Schweizer’s reagent. It is important for the formation of hybrid systems that additionally to cellulose other particles or molecules can be added to Schweizer’s reagent. Here, in the case of the formation of a TiO$_2$-cellulose coating deposited on silicon we added TiO$_2$ particles (Hombikat) into the solution of cellulose in Schweizer’s reagent. Cellulose-based coatings were obtained using spin-coating.

Spin coating was carried out under ambient conditions using a SCI spin coater (Novocontrol Technologies GmbH, Germany). A drop of the solution was placed onto the substrate rotating at 3000 rpm. One drop formed one cellulose layer. A thick cellulose layer was formed from a concentrated (up to 30 mg/ml) solution. Thin cellulose
films were obtained from a diluted solution (from 1.5 to 5 mg/ml). After deposition samples were rinsed in 0.1 M H$_2$SO$_4$ for 1 min, and then washed in Milli-Q water three times.

**Cellulose free standing hybrid.** For 10 ml of cellulose solution in Schweizer’s reagent, 100 μL of Ti(C$_4$H$_9$O)$_4$ were added under vigorous stirring. Then the mixture was squeezed out of a syringe into a solution of H$_2$SO$_4$. In the time of several washings of the hybrid, it changes colour from bright blue to white. The hybrid still containing copper ions and amino groups is blue opposite to the white one that is again just a cellulose-based hybrid.

A cellulose photomobility study was conducted using atomic force microscopy (AFM). A scratch was made on the cellulose coating by tweezers. The thickness of the cellulose layer was measured before and during UV illumination using AFM. The distance between the sample and a UV-light-emitting diode (UV 365 nm LED from Thor-Lab) was 2 cm. The intensity was 5 mW/cm$^2$.

**Characterization methods.** AFM measurements were performed in air at room temperature using a Nanoscope multimode AFM (Digital Instruments Inc., USA) operating in tapping mode. Typical cantilever values: resonance frequency: 300 kHz; spring constant: 42 N/m.

Infrared reflection absorption (IRRA) spectra were acquired with an IFS 66 FT-IR spectrometer (Bruker, Germany). For all measurements at 40 mN/m, p-polarized radiation was used at an angle of incidence of 70°. A total of 200 scans were acquired with a scanner velocity of 20 kHz at a resolution of 8 cm$^{-1}$. The spectra were obtained in a range of 400–4000 cm$^{-1}$.

Scanning electron microscopy (SEM) was conducted with a Gemini Leo 1550 instrument (Leo Elektronen-mikroskopie GmbH, Germany) at an operating voltage of 3 keV. Prior to microscopy the samples were sputtered with gold.

Transmission electron microscopy (TEM) measurements were performed on a Zeiss EM 912 Omega (Carl Zeiss AG, Germany) transmission electron microscope operated at 300 kV.

**Results and discussion.** – Cellulose fibers have a number of hydrogen bonds between individual chains [21] enabling facile functionalization, fig. 1(a).

Cellulose is known to be derived from D-glucose units, which condense through β(1 → 4)-glycosidic bonds [22]. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen atoms on the same or on a neighboring chain, holding the chains firmly together side by side and forming fibrils with high tensile strength. This makes a cellulose straight chain polymer. Due to the structural rigidity cellulose is insoluble in water and in most organic solvents [23]. Carbohydrates in aqueous alkaline solution are multiply deprotonated in the presence of tetraamine-diaquacopper dihydroxide and form chelate complexes (fig. 2). This breaks the hydrogen bonds and makes cellulose soluble.

In order to test various cellulose hybrids with induced photosensitivity, we prepared three systems: cellulose coating on TiO$_2$, coating of cellulose and TiO$_2$ nanoparticles, and free-standing cellulose-titania hybrid (fig. 1(b)).

The coatings were prepared by spin coating (fig. 3(a)). Optimization of the solution concentration is a critical issue for the formation of a uniform film [24]. Thus, a relatively high concentration of cellulose results in a viscous solution, and a spin-coated film forms from 30 mg/ml solution with different thickness over the surface (fig. 3(b)). Variation in thickness of the coating results in different light reflection. Nevertheless, high concentrations are not appropriate for spin coating, a viscous solution may be interesting, for example, for an inkjet technology to create coloured interference layers with high accuracy without the need for high-temperature fixing. This could be useful in combination with titania nanoparticles yielding coatings with a high refractive index (ca. 2.00 over the entire visible range) when naturally dried [25]. The lack of dyes in the proposed method has good environmental prospects, because the applied systems based on a TiO$_2$/cellulose composite are non-toxic and biologically inert. Moreover, our work below explores in detail the principle of photosensitivity of cellulose-based hybrids and in situ changes of film thickness.

At lower concentration (3 mg/ml) a uniform film was formed (fig. 3(c)). After the deposition, the coating was rinsed in sulfuric solution for the removal of the copper complex and the recovery of cellulose fibers. The nodule-like morphology of the cellulose coating formed on titania is shown in fig. 4(a),(b).

To study the photomobility of the cellulose layer we scratched the polymer layer (fig. 4(c)). Figure 4(d) shows changes of the scratch after illumination. It is seen that...
part of cellulose layer moved to the scratched side to reduce the surface energy probably due to light-induced fluidization of functional groups on the titania surface: charge separation in titania leads to a reorganization of the surface groups and water splitting, leading to a reorganization of the cellulose coating.

We see that photomobility is not due to cellulose degradation. The IRRA spectra before and after irradiation (fig. 4(e)) are identical. The IRRA spectra show the characteristic bands for cellulose and the presence of Ti-O bonds. A peak at 3650–3585 cm$^{-1}$ can be attributed to the hydroxyl stretching vibration caused by intermolecular hydrogen bonds [26]. The broad bands at 3010–3060 cm$^{-1}$, 1760–1700 cm$^{-1}$, 1380 cm$^{-1}$, 1220 cm$^{-1}$ and 970 cm$^{-1}$ can be assigned to vibrations of carbonyl groups and composite bending vibrations of (CHO), (C–C–O), (C–O) and (C–C) of substituted glucopyranose cycles of cellulose [27–29]. The peaks at 3010–3060 cm$^{-1}$, 1460 cm$^{-1}$ and 780 cm$^{-1}$ are attributed to the C–H stretching vibration. The strong band in the region of 400–700 cm$^{-1}$ can be assigned to the formation of Ti–O and Ti–O–Ti bonds [30].

To establish the System II we added TiO$_2$ nanoparticles into the solution of cellulose in Schweizer’s reagent and spin-coated the solution with nanoparticles. The initial morphology is different for the coating with particles (fig. 5(a), (b)); however, again the analysis of the profiles of AFM images before and after irradiation (fig. 5(c), (d)) proves that the TiO$_2$ particles activate cellulose, although, in this case, to a smaller degree.
Fig. 5: (Colour online) System II: (a), (b): AFM images showing cellulose-based coating formed from a 3 mg/ml solution of cellulose that has 1 mg/ml TiO$_2$ (Hombikat) in solution. (c), (d): study of the change of the hybrid orientation of the surface: (c) before illumination and (d) after 10 min illumination at 5 mW/cm$^2$, 365 nm. (e) Zoom in (from (c) and (d)) on AFM profiles from the same line pointing more clearly to the photomobility of cellulose chains.

Fig. 6: (Colour online) Photographs of cellulose-titania hydrogels after squeezing out of a syringe Schweizer’s reagent with a dissolved cellulose solution forming titania nanoparticles in the solution of H$_2$SO$_4$. The blue hybrid still contains copper ions and amino groups. After several washings of the hybrid, it changes colour from bright blue to white, which is typical for a solely cellulose-based hybrid.

Fig. 7: (Colour online) System III: (a) SEM image of hydrogel fibers, (b) TEM image of the fiber showing the contact of polymer fibers with TiO$_2$ nanoparticles covering the fiber, with (c) schematic of the fiber/titania interface. (d)–(f) Light curing of cellulose/titania-based hybrid (hydrogel). Optical images of (d) composite hydrogel cut; (e), (f) light healing of the material (e) at the initial moment of irradiation, (f) after 15 min of irradiation. The red box in (a), (b) indicates higher resolution from fiber network to individual fiber. The blue box in (b), (c) shows the schematic of TiO$_2$ assembly along the fiber.

We analysed the cellulose hydrogel after washing out of Schweizer’s reagent. Electron microscopy images (fig. 7(a),(b)) provide clear evidence of the formation of a fibre assembly in the hydrogel matrix. Moreover, it is seen that individual fibers are covered by nanoparticles of TiO$_2$ maximising, as shown in the schematic (fig. 7(c)), the interface between TiO$_2$ and cellulose.

We tested the behaviour of hydrogel —fiber assemblies— under irradiation. We cut one piece of hydrogel (fig. 7(d)), irradiated it and observed photohealing of the hydrogel (fig. 7(f)) due to the reorganization of alkoxy and hydroxyl groups at the TiO$_2$ interface that affects the mobility of polymer segments leading to the healing of the coatings.

Since there are several aspects, including light-pH coupling on TiO$_2$, cellulose can be followed in the presence of protons and/or electrons and the crosslinking mechanism of cotton through proton attraction is more likely. The TiO$_2$ under irradiation forms the pair of electron (e$^-$) and hole (h$^+$). Oxygen as a nucleophile portion of cellulose is attached to carbon with positive charge, may be activated and crosslink [40]. The mechanism through electron attack can be suggested by the oxygen radical attack to hydroxyl groups of cellulose [41].

Conclusions. – Processes at the interface of an inorganic material and an organic coating can sensitively be controlled by light, and this may contribute to their understanding. Here we concentrated on 2 widely studied systems, titania and cellulose, and show that photoinduced charge separation of titania can affect the organic
coating. It leads to material movement over microscopic dimensions and can finally be used for annealing of defects or scratches.

More specifically a facile method for the formation of optically active cellulose-based coatings is presented. Both types of hybrid coatings—cellulose on titania surface and TiO$_2$/cellulose on a silicon wafer—are photomobile. Here photosensitivity is due to TiO$_2$ photoactivation that changes its surface groups and produces charges in the coating. Free-standing hybrids of TiO$_2$/cellulose may recover its structure under illumination—we are able to cure the hydrogel under irradiation.

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