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Disassembly of redox responsive poly(ferrocenylsilane) multilayers: The effect of blocking layers, supporting electrolyte and polyion molar mass

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ABSTRACT

Layer by layer (LbL) organometallic multilayers, composed of poly(ferrocenylsilane) (PFS) polycations and polyanions, were fabricated and characterized. Disassembly of redox responsive PFS^-/PFS^+ films as well as multilayers consisting of PFS^-/PFS^+ combined with redox inert bilayers was studied. The influence of parameters on disassembly kinetics and mechanism, such as distance between redox PFS multilayers and the electrode, effect of the top inert layer, the choice of the supporting electrolyte, the ionic strength of the solution, and the molar mass of polymers, was investigated. The results elucidate the details of the disassembly mechanism and provide design criteria for preparing templates with highly controllable disassembly kinetics.

1. Introduction

Compared to other stimuli, such as pH, temperature, or light, the use of redox potential, to address "smart" polymers, offers distinct advantages. Redox potentials can be controlled in an easy and precise way and can also be employed to provide spatial control over domains with dimensions as thick as the thinnest conducting wires that can be obtained by nanofabrication (i.e., on the order of 10–20 nm) [1]. In addition to many applications as for example, mechanical actuators or sensors, redox responsive polymers can also act as a molecular release medium with tuneable release properties [2,3]. Such macromolecules can act as reservoirs for an active therapeutic cargo in form of thin films (polymer brushes, multilayer films, membranes) [4,5] or submicron particles (micelles, nanogels, capsules, mesoporous particles and vesicles) [6–8]. Among the listed structures, layer by layer (LbL) thin films are particularly versatile and suitable for incorporation of multiple functional or responsive components with controlled morphology, thickness, and film composition [9,10]. Fabrication of redox responsive LbL films combines the advantages of nanoscale electrochemical features with an easy processing, high control over the morphology, and tuneable functionality which is amenable to, e.g., medical delivery applications.

Poly(ferrocenylsilane) (PFS) is a unique organometallic polymer, exhibiting alternating ferrocene and silane units within the main chain [11–13]. Since reversible redox processes affect the ferrocene group within its backbone, PFS is undergoing dramatic and reversible changes in physicochemical properties upon oxidation. Protocols for preparation of PFS polymers, with additional positive and negative charges [14], make those macromolecules suitable for a LbL fabrication.

Only few polymers lend themselves for a construction of active LbL redox responsive release systems. Kwon et al. reported on an electroactive polymeric system, which rapidly changes from a solid state to solution in response to small electric currents, achieving modulated release of insulin [15]. The Hammond group presented remotely controlled release of precise quantities of chemical agents from Prussian Blue (PB) composite multilayers [16]. Recently, electrochemically tailored degradation of polyelectrolyte assemblies was described by Zambelli, and coworkers [17]. Degradation of engineered LbL capsules upon exposure to a cellular concentration of glutathione was also presented [18]. Despite the studies aiming at the assembly and disassembly, as well as controlled molecular release from LbL prepared PFS films [8,14,19–21], no systematic exploration was performed on various important aspects of electrochemically induced molecular behavior of PFS multilayers. Such a study would be indispensable for the design of smart platforms for molecular delivery applications.

In our recent communication, we reported on a redox responsive LbL system constructed with PFS polyelectrolytes, with

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particular focus on disassembly of films and release of guest molecules upon oxidation [22]. In the present contribution, we provide an enhanced mechanistic study of LbL PFS multilayer disassembly in the context of various external parameters like presence of blocking layers, ionic strength of electrolyte, counterion, and molar mass of the PFS influence. Oxidation potential shifts, electron transfer mechanisms and ion diffusion processes, phenomena related to the redox active film behavior, are also discussed. In-depth understanding of undergoing processes provides a set of tools to construct complex delivery systems and to host drug release profiles in a pre-programmed manner, in a real-time response to physiological changes.

2. Experiment

2.1. Materials

Poly(ethyleneimine) (PEI, $M_w \sim 2.5 \times 10^4$ g/mol), poly(styrene sulfonate) (PSS, $M_w \sim 7.0 \times 10^4$ g/mol), poly(acrylic acid) (PAA, $M_w \sim 4.5 \times 10^5$ g/mol), poly(allylamine hydrochloride) (PAH, $M_w \sim 5.6 \times 10^4$ g/mol), 3-aminopropyltrimethoxysilane, sodium chloride, sodium nitride, sodium perchlorate, and sodium sulfate were obtained from Aldrich and used as received.

2.2. PFS synthesis

Positively and negatively charged PFSs with $M_w = 1.67 \times 10^4$ g/mol, PDI = 1.3; $M_w = 5.3 \times 10^4$ g/mol, PDI = 1.3; and $M_w = 2.5 \times 10^5$ g/mol, PDI = 2.7 were synthesized by ROP of chlorinated cycloferrocenophane followed by the side group modification as described previously [23].

2.3. Multilayer fabrication

Multilayers were deposited on Indium Tin Oxide (ITO)-glass or ITO-Quartz substrates (Ssens, the Netherlands), which were cleaned in advance by immersing them into a mixture of H_2O, H_2O_2, and NH_4OH with a volume ratio of 5:1:1 for 20 min., followed by extensive rinsing with MilliQ water and drying under nitrogen stream. The cleaned ITO substrates were first immersed in a toluene solution of 3-aminopropyltrimethoxysilane (0.1 mM) to impart positive charges onto the surface. The modified substrates were alternatively immersed in the polycation and polyanion aqueous solutions (1 mg/ml, 0.5 M NaCl) for 10 min with rinsing, dipping into pure MiliQ water and drying with a stream of nitrogen gas. Different types of composite multilayers were fabricated.

2.4. Characterization

UV/Vis spectra were recorded on a Varian Cary 300 Bio instrument in double beam mode using an uncovered quartz slide as a reference. Cyclic voltammetry measurements were carried out on an Autolab PGSTAT 10 (Ecochemie, Utrecht, the Netherlands) potentiostat in a three-electrode configuration. The ITO substrates acted as the working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode. Different electrolyte solutions including ($NaClO_4$, NaCl, $NaNO_3$, and Na_2SO_4) were used. Prior to the measurements, the electrochemical cell was degassed by passing nitrogen through the electrolyte solution for 5 min. A series of cyclic voltammograms were recorded after holding the oxidation potentials at different values for different time intervals. The amount of transferred charge Q was calculated based on the integration of the area under each cyclic voltammogram. The film disassembly was monitored by CV or in situ electrochemical UV/Vis as described in [22]. For in situ electrochemical UV/Vis cell configuration, see supplementary data.

3. Results and discussion

LbL assemblies composed of positively charged PFS^+ and negatively charged PFS^- polyelectrolytes were fabricated using materials and methods previously reported by our group [21,22] (Scheme 1a and b). The thickness development during fabrication of the multilayer on ITO and Au coated glass substrates was monitored by cyclic voltammetry (CV), ellipsometry, quartz microbalance (QCM), and UV/Vis spectroscopy [14,20–22]. PFS multilayers exhibit linear growth with an average thickness increase of 3 nm/bilayer on ITO substrate in dry state. The linear increase in CV's peak current versus scan rate suggested that all electroactive material within the multilayers is addressed during the electrochemical cycle. Upon oxidation of the PFS multilayers, the oxidation and the reduction currents decrease owing to a dissolution of the film deposited on the electrode [22].

3.1. Blocking effect

For composite multilayers, with a short separation distance between redox active species and the electrode, e.g., mixed poly(styrene sulfonate) and poly(ferrocenylsilane) $(PSS^-/PFS^+)_5$, the electroactivity of the PFS layer is clearly observable [22]. Charge transport mechanism within LbL for such cases was discussed by the group of Schlenoff and Laurent [24]. In the present study, the tailored designed PFS composite multilayers provided the opportunity to evaluate the distance dependence of electron transfer from the electrode to the redox active materials.

In order to assess the role of blocking films at the electrode surface, electroactive $(PFS^-/PFS^+)_3$ bilayers were fabricated on top of the redox inactive spacer. Poly(acrylic acid) (PAA^-) and poly(allylamine hydrochloride) (PAH^+), were deposited in form of $(PAA^-/PAH^+)_n$ multilayers, as a bottom inert blocking film (n = 1–5), (Scheme 1c). Samples with increasing numbers of $(PAA^-/PAH^+)_n$ layers were subjected to the cyclic voltammetry in 0.1 M $NaClO_4$ as shown in Fig. 1a. The shape of the cyclic voltammogram is effected by the single bilayer, $(PAA^-/PAH^+)_1$ showing an increase in the separation of the cathodic and anodic peaks, respectively. This refers to a decrease in the rate constants for electron transfer due to build up of an insulating barrier separating the redox pair from the electrode. Fig. 1b shows the charge passed for oxidation/reduction of ferrocene as a function of the number of electrochemically inactive double layer number, as determined by the integration of the areas under the redox peaks. Deposition of two blocking layers decreases the current by nearly 97% and four blocking layers terminate detectable redox activity. The approximate threshold distance to prevent redox events in our system is 9 nm corresponding to 3 bilayers. This behavior also confirms earlier conclusions that there are no salt counterions in the multilayers. Our observations are in agreement with Schlenoff et al., who considered the blocking effect of PSS^-/PAH^+ layers on electrochemically active viologen containing polyions [24]. They found that in LbL films, the redox active material interpenetrated into the blocking inert parts of the film for a distance of approximately 2.5 bilayers. We note that such interpenetration of polyelectrolytes has also been confirmed by neutron reflectivity [25].

Moser et al. in earlier work considered electron transfer in proteins assuming tunneling [26]. The maximum distance the electron can tunnel is a few angstroms, and the rate of electron transfer k follows the relationship [27,28] $k = k_0\exp[-\beta R]$, where β is the decay constant, on the order of 1 $Å^{-1}$ and R is the distance between donor and acceptor sites or between electrode and electroactive species. In this cited study, the value of electron rate constant falls from ca. 10^{13} s^{-1} to 10^0 s^{-1} from contact to 2.5 nm separation, respectively. This value is smaller but still within the bulk part of