Photonic transduction of electrochemically-triggered redox-functions of polyaniline films using surface plasmon resonance spectroscopy

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Surface plasmon resonance (SPR) spectroscopy is used to follow the swelling and shrinking processes of a polyaniline redox-active polymer; SPR provides a reading signal for the electrochemical stimuli that activate the polymer.

Phase transitions of polymers and signal-triggered swelling processes of polymers are subjects of extensive research efforts.[1,2] Volume changes of polymers are triggered by temperature,[3] pH,[4] solvent composition[5] and light.[6] Electrochemical activation of redox-polymers provides a means to stimulate swelling.[7] Recently the stress induced on an AFM cantilever as a result of the redox-activation of polyaniline was used to develop an electrofueled microdevice[8] that may act as a micro-robot or micro-pump. Surface plasmon resonance (SPR) has been recently applied to study interfacial phenomena associated with electrochemical transformations of thin films at electrode surfaces.[9] Here we describe the SPR transduction of the redox-activation of polyaniline films, and the accompanying swelling and shrinking processes using *in situ* electrochemical/ SPR measurements.

Polyaniline was generated on a Au-covered glass-slide (*ca.* 0.64 cm²) used for SPR-measurements (Bio-Suplar 2, Analytical μ-Systems, Germany) by the electropolymerization of aniline, 0.1 M, in an electrolyte solution composed of H_2SO_4, 0.1 M, and Na_2SO_4, 0.5 M, (applied potential 0.8 V *vs.* Ag-wire quasi-reference electrode for 5 s).[10] The resulting film obtained upon passing charge of 9.7 mC, that corresponds to the formation of *ca.* 10 μg of the polymer, was washed with background solution composed of H_2SO_4, 0.1 M, and Na_2SO_4, 0.5 M, to exclude from the cell the residual monomer. The polyanilin film can be reversibly oxidized and reduced, eqn. (1), and the polymer exists in the oxidized positively charged state, $(An^{2+})_n$, and reduced neutral state, $(An)_n$, at the potential 0.4 and 0.0 V, respectively.[12]

$$[\text{structure}] \underset{+2ne^-}{\overset{-2ne^-}{\rightleftharpoons}} [\text{structure}] \quad (1)$$
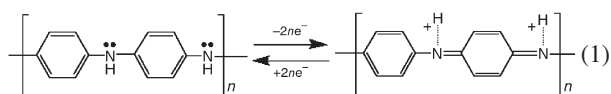
Fig. 1, inset (I), curve (x), shows the SPR spectrum of the bare Au-surface. The polyaniline film, $(An)_n$ was equilibrated at the potential 0.0 V in the electrolyte solution prior to the SPR-measurements. Fig. 1, inset (I), curve (y), shows the spectrum of the polyaniline film assembled on the Au-surface immediately after the application of the potential corresponding to 0.4 V on the electrode resulting in the oxidation of the polymer layer. While the dots correspond to the experimental points, the solid line corresponds to the theoretical fitting[11,12] of the data according to the Fresnel equation. The derived film thickness corresponds to *ca.* 150 nm. Fig. 1(A), curves (a–e), shows the SPR spectra at the potential of 0.4 V, conditions that retain the polymer in its oxidized state, $(An^{2+})_n$. These spectra are time-dependent and a decrease of the reflectance minimum is observed, because of the polymer swelling.[13] The spectrum

recorded 10 min after the application of the oxidizing potential of 0.4 V, Fig. 1(A), curve (e), corresponds to a polymer thickness of *ca.* 180 nm. Thus, the swelling process occurring at 0.4 V results in the increase of the polymer thickness by *ca.* 30 nm. It should be noted that the similar thickness change was observed by AFM upon the electrochemically-induced shrinking–swelling process of a polyaniline layer.[14] Fig. 1(A), curve (f), was recorded under conditions where the applied potential
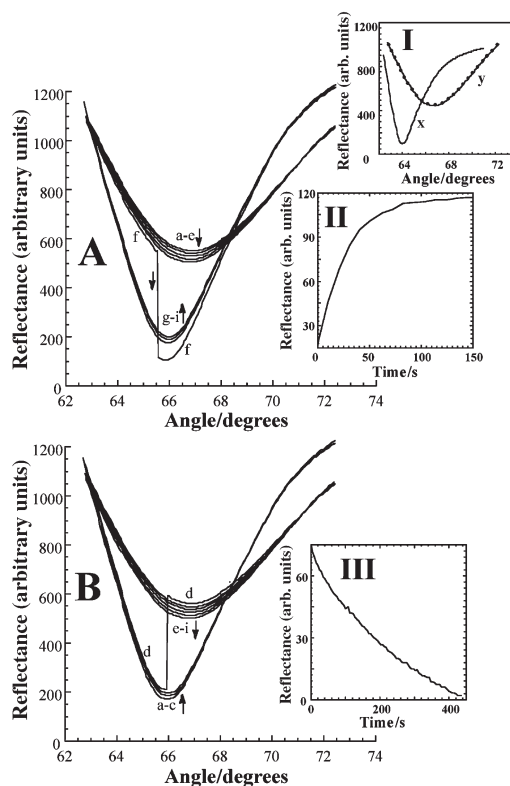

Fig. 1 SPR spectra measured for the polyaniline-modified Au-surface upon electrochemically-induced shrinking and swelling processes. (A) The polymer was equilibrated at 0.0 V for 5 min prior to the measurements. (a–e) The spectra measured after the potential was changed to 0.4 V. (f) The spectrum measured during the potential change to 0.0 V. (g–i) The spectra measured after the potential was changed to 0.0 V. (B) The polymer was equilibrated at 0.4 V prior to the measurements. (a–c) The spectra measured after the potential was altered to 0.0 V. (d) The spectra measured during the potential change to 0.4 V. (e–i) The spectra measured after the potential was changed to 0.4 V. Inset I: (x) The SPR spectrum for the bare Au-surface and (y) the SPR spectrum for the oxidized polymer film measured at 0.4 V (the dots show selected experimental points and the solid line is the best theoretical fit). Inset II: Time-dependent reflectance changes measured at a fixed angle of incidence ($\theta = 65°$) immediately after the applied potential was changed from 0.4 to 0.0 V. Inset III: Time-dependent reflectance changes measured with the fixed angle of incidence ($\theta = 65°$) immediately after the applied potential was changed from 0.0 to 0.4 V. All SPR measurements were performed in the background solution: H_2SO_4, 0.1 M, and Na_2SO_4, 0.5 M.

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on the polymer-modified electrode was suddenly altered from 0.4 to 0.0 V. This spectrum shows the transition from the oxidized state of the polymer, $(An^{2+})_n$ to the reduced state, $(An)_n$. The instantaneous change in the spectrum mainly originates from the change of the refractive-index of the polymer as a result of its reduction. The subsequent SPR spectrum recorded at the potential of 0.0 V, Fig. 1(A), curve (g), shows a noticeable increase of the reflectance minimum after which only minor changes of the spectra were observed, Fig. 1(A), curves (h) and (i). These spectra changes can be attributed to the shrinking process of the reduced polymer and they reach a constant value after *ca.* 4 min. The main decrease in the polymer thickness as a result of the shrinking process occurs in the first minute after the potential change to 0.0 V, faster than the time-interval required to record the complete SPR spectrum. Thus, measurements with a fixed angle of incidence ($\theta = 65°$) were applied to evaluate the kinetics of the shrinking process upon the potential change from 0.4 to 0.0 V, Fig. 1, inset II. The experimental results reveal a biexponential kinetics with rate constants corresponding to 9×10^{-3} and 5×10^{-4} s^{-1}. The fast and slow components exhibit the same population. The fast shrinking component may be attributed to the collapse of the hydrophobic polymer chains, formed upon reduction to a metastable configuration. The slow component is then attributed to the formation of an organized, densely-packed structure that expels the residual water. Similar biexponential dynamic changes were observed upon the compression of proteins.[15]

The second experiment was started by equilibration of the polymer-modified electrode at 0.4 V when the polymer is oxidized. The first SPR spectrum was recorded after the potential was shifted to 0.0 V, Fig. 1(B), curve (a). It should be noted that the time-scale of the measurements did not allow us to register the SPR spectrum characteristic of the metastable shrunken polymer film. The secondary slow kinetics of the shrinking process at the potential of 0.0 V is clearly visible in the SPR spectra, Fig. 1(B), curves (a–c). These changes reach a constant value after *ca.* 3 min. During the registration of the next spectrum, Fig. 1(B), curve (d), the applied potential was changed from 0.0 to 0.4 V. The immediate change of the SPR spectrum originates mainly from the change of the refractive-index of the polymer as a result of its oxidation. Continuous SPR measurements at the potential 0.4 V show the decrease of the polymer layer reflectance corresponding to the slow swelling process, Fig. 1(B), curves (d–i). The kinetics of the swelling process was recorded at a fixed angle of incidence ($\theta = 65°$), Fig. 1, inset III. The kinetics of the swelling process corresponds to a first-order monoexponential process with a rate constant of 3×10^{-4} s^{-1}. It should be noted that upon redox-induced swelling and shrinking of the polymer film the uptake and release of counter-anions may change the conductivity of the film and thus may alter the reflectance. For redox-active films that lack swelling, *e.g.* Prussian blue, the reflectance changes due to ion transport are, however, minute.

The sequence of potential steps applied in the two experiments results in similar changes in the thickness values of the reduced or oxidized polymer films independently on the sequence of the reduction or oxidation steps that lead to a shrunken or swollen polymer film, respectively. Thus, the reversible transformation of the polymer layer between shrunken and swollen states with different thicknesses is possible. However, the complete shrinking–swelling cycle proceeds on the time scale of minutes. Realizing that the refractive index of the polymer undergoes very fast changes upon the reduction–oxidation process, one may use the polyaniline film as an interface for the reversible SPR transduction of electronic signals that actuate the polymer. Fig. 2(A) shows the chronoamperometric transients upon oxidation (0.4 V) and reduction (0.0 V) of the polyaniline layer. In this experiment, a potential-step that oxidizes $(An)_n$ to $(An^{2+})_n$ is applied. The polymer is not allowed to swell, and the opposite reductive potential-step is applied to generate the metastable $(An)_n$ that is oxidized again before it undergoes shrinking. By the cyclic application of the oxidative and reductive potential
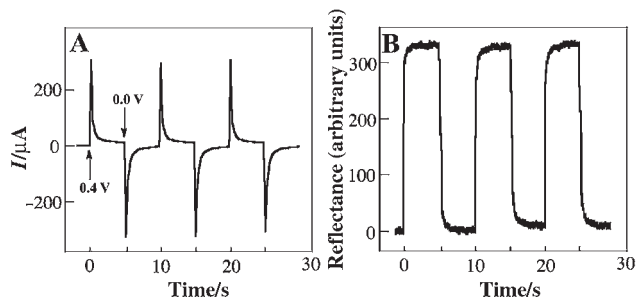

Fig. 2 (A) Multi-potential step chronoamperometric measurements corresponding to the oxidative and reductive transformations of the polyaniline layer. (B) Time-dependent reflectance changes measured at a fixed angle of incidence ($\theta = 65°$) upon the multi-potential step experiment. The arrows show the time of the application of the oxidative (0.4 V) and reductive (0.0 V) potentials. The chronoamperometric and *in situ* SPR measurements were performed in a background electrolyte solution composed of H_2SO_4, 0.1 M, and Na_2SO_4, 0.5 M.

steps, the reversible SPR transduction of the polymer state is accomplished, Fig. 2(B).

In conclusion, we have applied surface plasmon resonance spectroscopy for following the swelling and shrinking processes of a polyaniline redox-active film. SPR provides a reading signal for the electrochemical stimuli that activate the polymer.

Notes and references

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