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Conducting Polymer Coated DNA

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Summary: Gold electrode was modified with a 4-aminothiophenol layer (4-ATPh) to immobilize DNA. The immobilized DNA served as a template for the alignment of positively charged anilinium ions. The electrochemical oxidation of the anilinium ions resulted in wrapping of the DNA with polyaniline. This polyaniline coated DNA was characterized by cyclic voltammetry (CV), impedance spectroscopy and UV-VIS absorption spectroscopy.

Keywords: DNA; electropolymerization; molecular wires; monolayers; Nanoelectronics; polyaniline

Introduction

The search for a new scientific insight that would allow the construction of structures on the nanometer scale drives the current interest in the field of molecular-nanoelectronics. The use of DNA and its derivatives as building blocks for molecular electronic devices will enable reducing the size of the current devices by around 1000 times and will improve the production process turning the complicated and defect-rich lithographic processes into processes that are based on self-assembly and self-organization.

Electrical properties of canonical double stranded DNA were characterized by several methods [1–2]. To improve the DNA conductivity long continuous DNA-based G4-wires composed of guanine tetrads were synthesized [3–4]. These structures are likely to serve best when applied in nanoelectronic [5]. Another way to improve conductivity of the double stranded DNA is to use the molecule as template for creating different types of molecular wires. Interaction of the negatively charged phosphate DNA backbone with various positively charged molecules and species results in formation of strong electrostatic complexes such as complexes of DNA with CdS semiconductor nanoparticles [6], with silver [7] and gold nanowires [8], and Pd clusters [9]. The above clusters and nanoparticles are usually wrapped by a charged organic layer, which acts as an electrical insulator preventing direct electrical contact between the clusters and the DNA template [7]. The utilization of positively charged conductive polymers wrapped around the template DNA, PC-DNA (Polymer Coated DNA) might provide a useful tool to make conductive wires. Polyaniline (PAN) is a good example of such a polymer; it is positively charged, highly conductive, mechanically flexible and stabile. These properties of PAN make it a perfect candidate for the coating of DNA [10–12]. DNA and PAN can be wrapped together to form conductive structures either in solution or on the surface. In the latter case the DNA is first complexed with the aniline monomer and the bound monomer is further on polymerized by oxidation yielding PAN-coated DNA. The oxidation of the anilinium ions, aligned by DNA, is performed either by chemical or enzymatic oxidation. The electrochemical oxidation, providing a most controllable way to produce the DNA-PAN complexes, has not been explored in detail so far. There is only one [13], to the best of our knowledge, of many researches to describe the direct electrochemical oxidation of

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anilinium on DNA which was carried out on gold surface. The gold surface was modified by 2-aminoethanethiol followed by absorption of the DNA aniline monomer complex and electrochemical polymerization of the aligned anilinium ions. Although the study showed the formation of PAN, no data were presented to indicate that PAN formation can be associated with DNA and not attributed to the defects or pinholes on the monolayer.

In this study we report on the electrochemical coating of double stranded poly(dG)-poly(dC) DNA with PAN layer. 4-ATPh (4-aminothiophenol) was used in the study as anchoring group for DNA immobilization. Being, an aniline derivative, 4-ATPh promote polymerization of aniline monomers complexed with DNA and as a result formation of PAN-DNA complex. Possible applications of the approach in nanoelectronics are being studied and discussed.

Experimental

Prior to modifying the surface, the gold electrode was cleaned by using the following procedure: the surface was rinsed with isopropanol, dried by nitrogen stream, cleaned with UV ozone cleaner and finally immersed into ethanol for 20 minutes.

The cleaned gold electrode was modified as follows: the electrode was immersed (for 15 min) into 1 mM of ATPh ethanol solution, rinsed by with ethanol, ethanol-water and water, then immersed in ~4 mM HCl solution for 5 minutes and finally it was three times washed with distillate water.

The modified surface was incubated with 20 nM of poly(dG)-poly(dC) in 20 mM tris-acetate buffer ($pH = 7$) for 30 minutes, rinsed with the same buffer, immersed into 10 mM aniline in 10 mM acetic acid-sodium acetate buffer ($pH = 3.8$) for 1 h and finally rinsed with 10 mM acetic acid-sodium acetate buffer ($pH = 3.8$). The electrode, prepared as described above, subjected to the electro-oxidative polymerization

Results

Impedance spectroscopy is an effective method to probe the electron transfer rates from the electrode to the redox active specie in solution. The impedance spectroscopy conducted with the help of modified electrodes also proved to be useful in DNA studies [14–15]. The immobilization of the DNA on the electrode surface resulted in the change of electron transfer resistance (R_{rt}) on the electrode surface. This can be seen in Figure 1, presenting impedance spectra before and after the DNA immobilization. The figure shows that the diameter of the semicircle in the spectrum, that represents the electron-transfer resistance (R_{et}) at the electrode surface, is changing upon binding of the DNA (compare curves a and b). The R_{et} values determined for the DNA modified and non-modified electrodes were correspondingly equal to 400 Ω and 100 Ω. This increase of the electron transfer resistance can be explained as follows: the electron transfer between the electrode not modified by DNA is promoted by the electrostatic attraction of the positively charged self-assembled ATPh layer on the surface of the electrode and the negatively charged redox probe $[Fe(CN)_6]^{-3/-4}$. Immobilization of negatively charged DNA neutralizes the positive charge of the electrode and thus eliminates the attraction between the electrode surface and the redox probe, leading to an increase of R_{et}. Another factor that influences the electron-transfer resistance is the thickness of the layer on the electrode surface; the increased value of R_{et} is partly due to the increased thickness of the layer as a result of the DNA binding to the electrode. The results presented in Figure 1, thus prove that incubation of the ATPh – functionalized electrode results in the DNA immobilization.

The DNA-modified electrode was incubated with anilinium ions to achieve spontaneous alignment of the aniline monomers along the DNA molecules. The electrochemical polymerization was carried out by cyclic voltammetry, by applying voltage

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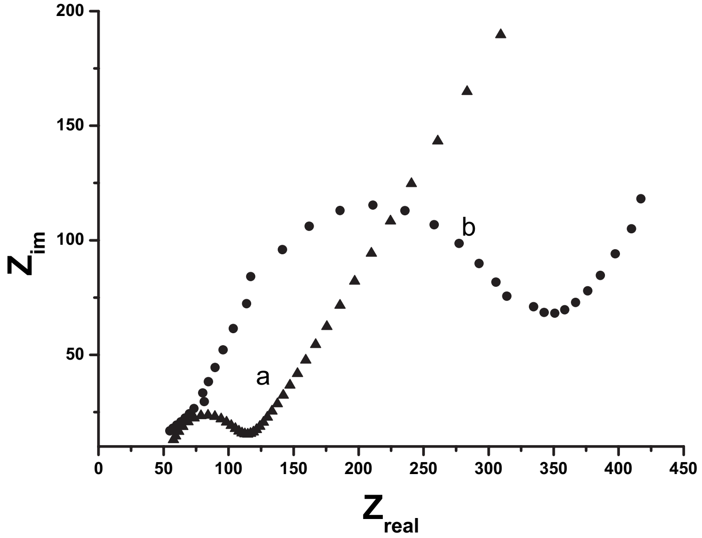

Figure 1.
Nyquist-diagram (Z_{im} vs. Z_{re}) for the AC impedance measurement of modified Au electrode in 5 mM $[Fe(CN)_6]^{-3/-4}$ and 0.05 M KCl with ATPh as anchoring group (a) before and (b) after DNA immobilization.

between 0–1.0 V at 50 mV/s. Figure 2 shows the electrochemical oxidation of the monomer and PAN formation on DNA. The oxidation reaction of the 4-ATPh layer on gold surface was investigated in several studies [16–17]. The two peaks around 0.6 V and around 0.8 V correspond to the first cycle of electrochemical oxidation (see

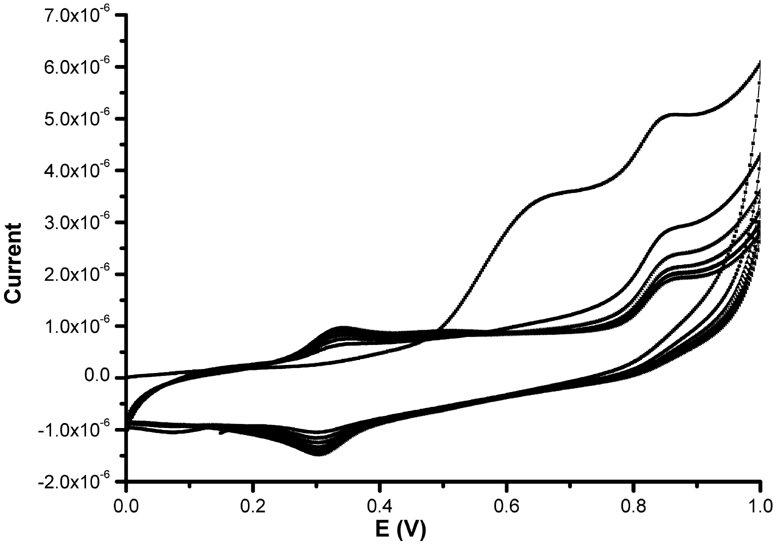

Figure 2.
CV of polyaniline formed electrochemically on poly(dG)-poly(dC) DNA modified Au electrodes (see Materials and Methods) between 0–1 V vs. Ag/AgCl at scan rate of 50 mV/s in 50 mM sodium acetate buffer (pH = 3.8).

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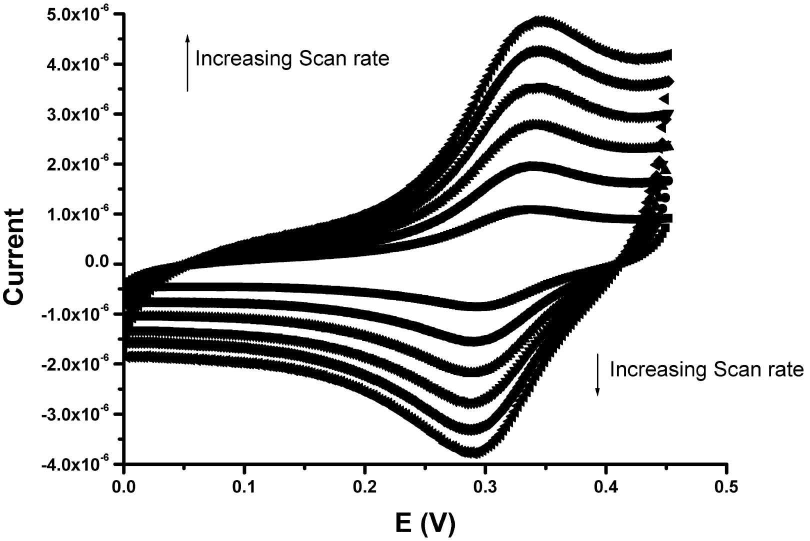

Figure 3.
CVs of polyaniline formed electrochemically on the DNA modified Au electrodes (see Experimental Section) measured at different scan rates between 50–300 mV/s in 50 mM sodium acetate buffer pH = 3.8.

Figure 2, first trace). The former peak is attributed to the oxidation of 4-ATPh while the second one to the oxidation of the anilinium ions. The peak at 0.8 V is gradually decreased with the increasing number of oxidative cycles and a new peak around 0.30 V is being formed. We suggest that the latter peak is corresponding to the redox transition of the PAN formed as a result of aniline monomer oxidation. In order to prove that indeed the first cycle of electrochemical oxidation resulted in polymerization of aniline monomers and formation of PAN we performed the following experiment. The electrode was withdrawn from the solution, rinsed with water and repetitively immersed into a fresh assay solution containing the buffer and

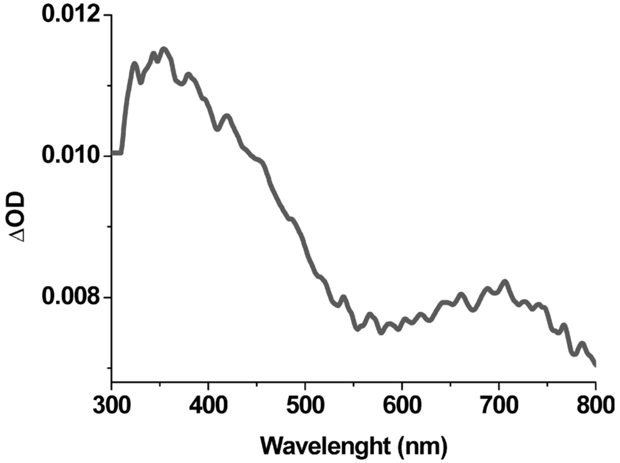

Figure 4.
UV-Vis. spectrum of PAN coated DNA formed on semitransparent Au electrode.

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ferricyanide (see Experimental section) and CVs were recorded with variable scan rate, between 50–300 mV/s (see Figure 3).

It is seen in Figure 3 that even the first cycle of electrochemical oxidation characterized by the peak centered around 0.30 V which corresponds to the oxidation potential of the PAN layer, thus confirming that the PAN is being formed on the electrode surface. The data presented in figure also demonstrate that the anodic and cathodic peaks are stable, reversible and characterized by higher currents at faster scan rates.

We suggest that 4-ATPh interacts with the oxidative product of anilinium ions, and is introduced in the polyaniline backbone, thus becoming an integral part of PAN

The formation of PAN was also investigated by means of absorption spectroscopy. The differential UV-Vis spectrum of the PAN coated DNA prepared as described in the Experimental section is shown in Figure 4. The spectrum shows two peaks; the peak centered on 700 nm corresponds to polaron state of PAN, the peak at 350 nm corresponds to π-π^* transition in polyaniline. The optical density of the sample is similar to that of a single PAN monolayer [18]. Thus we can conclude that electrochemical oxidation of aniline ions bound to DNA results in the formation of a single PAN-DNA monolayer on the electrode surface.

Conclusion

We demonstrated the formation of the conductive PAN-DNA monolayer on the surface of Au-electrode modified with ATPh. We showed that using ATPh as an anchoring group for DNA provides a more efficient way of wrapping DNA with the polymer compared to those used earlier. The PAN coated DNA obtained here is characterized by better-defined redox peaks and lower potentials compared to those obtained earlier. We suggest that 4-ATPh is introduced in the polyaniline backbone, thus becoming an integral part of PAN-DNA complex. This allows a complete (from the top and the bottom) covering of DNA with the conductive polymer. As a result of complete covering of DNA with the conductive polymer there appears an efficient electric contact of the polymer with the electrode. The results presented herein could prove useful for creating single nanowires based on complexes of conducting polymers with DNA.

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