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Wireless electromechanical readout of chemical information

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ABSTRACT: Collecting electrochemical information concerning the presence of molecules in a solution is usually achieved by measuring current, potential, resistance or impedance via connection to a power supply. Here, we suggest wireless electromechanical actuation as a straight-forward readout of chemical information. This can be achieved based on the concept of bipolar electrochemistry, which allows measuring the presence of different model species in a quantitative way. We validate the concept by using a free-standing polypyrrole film. Its positively polarized extremity participates in an oxidation of the analyte and delivers electrons to the opposite extremity for the reduction of the polymer. This reduction is accompanied by the insertion of counter ions and thus leads to partial swelling of the film, inducing its bending. The resulting actuation is found to be a linear function of the analyte concentration and also a Michaelis-Menten type correlation is obtained for biochemical analytes. This electromechanical transduction allows an easy optical readout and opens up very interesting perspectives not only in the field of sensing, but also far beyond, such as for the elaboration of self-regulating biomimetic systems.

INTRODUCTION

Conducting polymers are popular candidates to be used as smart materials for the transduction of chemical information, light emission, energy storage, photovoltaics and actuation due to their easy synthesis and interesting electrochemical properties.¹⁻⁵ Most importantly, their π -conjugated system allows charge transport as well as fast and reversible redox activity, and therefore makes them suitable as amperometric, potentiometric, conductometric and impedometric transducers.^{4,6-8} In all these cases the polymer needs to be connected to a power supply or an electric measuring device. Therefore, it is of great interest to explore alternative approaches using a wireless concept. As an example, conductometric wireless polyaniline sensors have been developed recently based on near field communication (NFC) technology.⁹ Typical features of conducting polymers such as color and volume change can equally be used as ingredients to develop sensors or biosensors.⁹⁻¹¹ In this context bipolar electrochemistry (BPE) is an interesting alternative to trigger in a wireless way a change of the above mentioned physical properties of the conducting polymer.^{12,13} BPE is a straight-forward way to break the symmetry of chemical systems and has been used in the past for many applications in various fields ranging from materials science to catalysis and analysis.¹⁴⁻¹⁶ It has been employed, among others, to modify conducting or semiconducting objects,¹⁶⁻²² allowing an easy access to Janus particles^{18,20}, to trigger electrochromism, photoluminescence and electroluminescence in conducting polymers^{12,13,23-25} and to generate directional motion or forced propulsion of particles.^{21,22}

We recently reported the use of BPE also for the wireless actuation of polypyrrole (PPy) based on an asymmetric volume change.²⁶ An electric field, generated in the electrolyte, breaks the symmetry of the PPy film due to its polarization with respect to the solution. This polarization results in spatially separated oxidation and reduction reactions, located at the two ends of the polymer object. Together with an additional intrinsic asymmetry, related to the different morphologies of

the two faces of the film, this allows a directional bending and motion of the PPy film.^{26,27}

We demonstrate here with several proof-of-principle experiments that this wireless mechanical deformation of a free-standing polymer layer can be directly correlated in a quantitative way with the concentration of different model molecules such as hydrogen peroxide, hydroquinone and glucose. BPE has been already proposed as an attractive approach to collect information about the chemical composition of a solution. Seminal work by the Crooks group demonstrated that the presence of an analyte can be coupled to either the dissolution of a metal²⁸⁻³⁰ or the generation of electrochemiluminescence (ECL).³¹ The latter concept could also be generalized to ECL emission in the bulk^{32,33} or from moving particles.³⁴ Various other interesting approaches have highlighted the outstanding features and advantages of BPE in the context of transduction of chemical information.³⁵⁻⁴³ However, the possibility of an electromechanical bipolar readout has not been explored so far. The principal of this concept relies again on the decoupling of the sensing chemistry from the reporting functions (Scheme 1). The bipolar object, a sheet of the conducting polymer, is placed between two graphite feeder electrodes.^{16,20} Upon application of a constant electric field, the PPy strip is polarized in an asymmetric way, the extremity with a polarization δ^+ acting as an anode, whereas the opposite extremity with a polarization δ^- behaving as a cathode. This break of symmetry triggers an oxidation and reduction reaction at the two terminal ends of the PPy, with the peculiarity that PPy can participate itself in the redox reactions.⁴⁴ Oxidized PPy does not undergo further oxidation, thus only the extremity involved in the reduction reaction shows actuation behavior. Reduction of the PPy is accompanied by an intake of cations in order to ensure electroneutrality. This movement of ions is responsible for the swelling of the PPy film. However, as the two faces of the PPy strip have a different morphology and surface roughness, their swelling behavior is not identical. The rough side (facing the electrolyte during preparation of the film by electropolymerization) allows a more efficient uptake

of cations compared to the smooth side (facing the substrate during electropolymerization). Therefore, the bending occurs preferentially towards the smooth side and is perfectly reversible upon removal or inversion of the electric field. Since at the anodically polarized extremity the oxidation cannot involve PPy itself, the conversion of a redox active molecule from the electrolyte has to ensure charge equilibration. This enabled us to propose the development of a new analytical readout mechanism described in this contribution.

Scheme 1: Schematic illustration of the bipolar electrochemical cell used for electromechanical readout. The free-standing polypyrrole (PPy) film is placed between two feeder electrodes. δ^+ and δ^- indicate the polarization potential at the two extremities. Scanning electron microscopic images of the two faces of the PPy film are shown below. Scale bars: 30 μm .

RESULTS AND DISCUSSION

If the experiment depicted in Scheme 1 is carried out in an aqueous medium, water is the most abundant molecule which can be oxidized in order to provide the electrons needed for PPy reduction at the opposite end. The simultaneous, spatially separated, PPy reduction and water oxidation requires a threshold electric field which needs to be applied by the feeder electrodes. For the present set-up the critical experimental value is 1.8 V/cm. This is higher than the value calculated from the cyclic voltammogram in Figure S1 A (0.7 V/cm), among others due to overpotentials at the feeder electrodes and the bipolar electrode. If the electrolyte contains redox species which can be oxidized more easily than water, actuation will occur already at a lower electric field. Moreover, for an electric field with a given amplitude, actuation increases with increasing concentration of analyte. Therefore, an electric field which is slightly below the threshold value necessary for water oxidation is imposed on the bipolar electrode (<1.8 V/cm). In this case no bending is observed. Only after addition of the more reactive chemical species bending starts to occur and varies as a function of time. In a first set of proof-of-principle experiments we tested hydrogen peroxide and hydroquinone as target molecules to validate the general concept.

Hydrogen peroxide is known for its catalytic and electrocatalytic oxidation on metal surfaces which is easier to achieve than water oxidation.^{45,46} However, since H_2O_2 can also be reduced at relatively low overpotentials, it is necessary

to evaluate the possible competition between the reduction of PPy and H_2O_2 , which might interfere with the bending mechanism. Cyclic voltammograms of PPy with and without H_2O_2 have been recorded (Figure S1 A). In the presence of 75 mM H_2O_2 , higher currents are observed for potentials more positive than +0.4 V compared to the experiment in the absence of H_2O_2 . This is due to the electrooxidation of H_2O_2 which occurs before water oxidation. On the other hand, the reduction current is also increased, however without a significant potential shift with respect to the reduction of PPy. Thus, the charge generated during H_2O_2 oxidation at the positively polarized extremity can be at least partially used for PPy reduction. The favored H_2O_2 oxidation will help in decreasing the threshold electric field value for bipolar actuation and the bending will depend on H_2O_2 concentration. To prove this assumption, we performed BPE with different H_2O_2 concentrations (Figure 1). The minimum concentration required to achieve a significant bending at 1.6 V/cm is 10 mM. In the absence of H_2O_2 the same amplitude of bending can only be obtained when we apply a field of 1.8 V/cm between the two feeder electrodes. In this case a current of 30 μA is passing through the PPy film, which is enough to deliver a sufficient amount of charge at the time scale of minutes to obtain visible bending. When further increasing the H_2O_2 concentration, the degree of bending at a readout time of 60 s increases linearly up to 75 mM (Figure 1C).

Figure 1: (A) Bipolar electromechanical set-up to measure H_2O_2 concentration in 0.1 M PBS buffer. Blue and red borders denote the negative and positive feeder electrodes, respectively. (B) Zoom at the negatively polarized PPy extremity in the presence of (a) 10, (b) 25, (c) 50 and (d) 75 mM H_2O_2 . The green colored PPy strip indicates its initial position and red the position after 60 sec. (C) Calibration curve for different H_2O_2 concentrations. The electric field between the feeder electrodes is 1.6 V/cm for all measurements.

From these results it is clear that a redox active analyte which is easier to oxidize than H_2O_2 should be able to decrease even more the threshold potential for actuation. To confirm this idea, hydroquinone has been selected. Similar to H_2O_2 , the oxidation of hydroquinone is first examined by cyclic voltammetry (Figure S1 B). In the presence of 20 mM hydroquinone, the current starts increasing for potentials more positive than 0.0 V. This indicates that the electrochemical oxidation of hydroquinone is much easier than water or H_2O_2 oxidation. On the other hand, the reduction of benzoquinone and PPy occur in a similar potential range. The expected threshold of electric field for triggering the actuation in the presence of hydroquinone can be again calculated by cyclic voltammetry (Figure S1 B) and a value of 0.2 V/cm is obtained. However, in the bipolar set-up a higher minimum field of 1.2 V/cm is neces-

sary for the same reasons as mentioned above. In order to be able to make a comparison between H_2O_2 and hydroquinone in terms bending efficiency, we've chosen also 1.6 V/cm for the bipolar actuation in the presence of hydroquinone. The fact that hydroquinone oxidation is much easier results in a more pronounced deformation of PPy. A linear dependence of the bending on concentration is obtained from 5 to 20 mM ($R^2=0.998$) (Figure S2).

Since H_2O_2 is the product of many enzymatic reactions and quinones are popular mediators in bioelectrochemical systems,⁴⁷ the presented approach might also be useful for biosensing. In such a case, the electromechanical readout would be based on a polymer strip modified with the corresponding enzyme. To validate this idea from a fundamental point of view, glucose has been chosen as a target molecule. As for H_2O_2 , the intention here is not to propose a new glucose sensor, but to provide a general demonstration that a coupling between an enzymatic reaction and a mechanical deformation is possible. This allows envisioning self-regulating biomimetic systems, based on electrochemical feed-back mechanisms, such as stimuli-responsive valves or intelligent drug-delivery systems. Classical electroenzymatic glucose sensing has been well developed in the past decades.⁴⁸⁻⁵⁰ For glucose oxidase (GOx), which can oxidize glucose to gluconolactone, a mediator is needed to shuttle electrons between the FAD/FADH₂ redox center of GOx and the electrode surface. In this work, we immobilized the organic charge transfer complex (CTC) tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) as a mediator along with glucose oxidase on the rough face of the PPy strip.^{48,51} TTF-TCNQ is well known for its redox activity around +0.1V.⁵² To avoid leaching of the enzymes from the PPy surface, a gelatin layer is casted on top. Following a strategy analogous to what has been reported in the literature,⁵³ it is possible to enhance the current originating from glucose oxidation by increasing the width of the positively polarized enzyme modified extremity (Figure 2A). The 8 times bigger surface area of this anodic extremity thus allows a higher loading with GOx and CTC, which therefore can provide comparatively more charges for the reduction of PPy and improve the actuation amplitude. The GOx-CTC modified side is fixed on a larger support in order to avoid bending purely due to the higher mass of conducting polymer, enzyme, mediator and protection layer.

Figure 2: (A) Bipolar electromechanical readout to estimate glucose concentration in 0.1 M PBS buffer using a CTC-GOx/gel modified PPy strip. Blue and red borders denote the negative and positive feeder electrodes, respectively. (B) Zoom of the negatively polarized PPy extremity in the presence of (a) 5, (b) 10, (c) 20, (d) 30 and (e) 50 mM glucose. Green color of the PPy strip represents its initial position and red the position after 60 sec. The electric field between the feeder electrodes is 1.3 V/cm.

An electric field of 1.3V/cm is used in this case to make sure that bending can only occur when the enzymatic reaction is involved. The deflection resulting from electroactuation of the negatively polarized side increases with increasing glucose concentration at a readout time of 1 min as shown in Figure 2 B. Relative errors have been calculated by measuring the deflection three times and are on average around 5% with an associated detection limit of 5mM. As the intention of this work is not to develop a new type of glucose sensor, the performance of the device has not been optimized, however the range of measurable concentrations is nevertheless compatible with classic values in blood (5-10mM). Electroenzymatic catalysis obviously continues after 1 min, but the direction of deflection starts to reverse. We monitored this peculiar long term evolution of the bending in the presence of 50 mM glucose (see detailed explanation in SI, Figure S3 and Video 1). The maximum deflection at 60 sec has been chosen to analyze quantitatively the actuation as a function of glucose concentration (Figure 3A). It needs to be mentioned that if the oxidation potential of the analyte is close to the one of PPy, a slow degradation of PPy might occur due to its partial overoxidation. In the present GOx-CTC system, since the oxidation potential of CTC (~0.05 V) is much lower than that of PPy (~0.4V), no obvious degradation of PPy was observed. At room temperature, the deflection experiment can be again carried out again with a comparable performance even after 6 h.

In parallel, the classic electrocatalytic response of a GOx-CTC modified PPy film was also evaluated by cyclic voltammetry (Figure 3B). For both calibration curves we observe a typical Michaelis-Menten type behavior. The apparent K_M for glucose was estimated to be 33 ± 2 mM with the classic electrochemical readout, compared to 53 ± 3 mM for the bipolar electromechanical readout. Taking into account the completely different measurement concepts, these values are quite comparable and in good agreement with the literature, indicating a K_M of 33-110 mM.^{54,55}

Figure 3: Calibration curves for (A) bipolar electromechanical readout at $t=1$ min and (B) conventional electrochemical measurement at +0.35 vs Ag/AgCl using a CTC-GOx/gel modified PPy strip as a biosensor. Inset: cyclic voltammograms of PPy/CTC-GOx/gel in the presence of different concentrations of glucose in PBS at a scan rate of 10 mV/s.

CONCLUSION

We demonstrate the possibility to achieve a quantitative wireless electromechanical readout of the presence of several chemical species in aqueous solution using free-standing PPy films in a bipolar electrochemical cell. In the case of an initially oxidized PPy strip, its anodically polarized side acts as a

center for chemical conversion and the cathodic side for the signal transduction in the form of actuation. Modulating the relative size of the anodic extremity with respect to the cathodic one allows controlling the amplitude of the readout. In a set of proof-of-principal experiments we were able to validate this concept of bipolar sensing for different molecules, including electroenzymatic conversion schemes. The main advantages of the approach are related to the intrinsic features of bipolar electrochemistry, namely a wireless transduction, the possibility of massive parallel screening and low cost. The readout concept might also be extended to the reductive detection of molecules under the condition to employ at least partially reduced PPy. In that case the optical detection should take place at the anodically polarized side due to the oxidation and subsequent bending of the polymer.

The presented straight-forward approach can be generalized to a large variety of chemical or biological analytes, as long as they are easier to oxidize than water. Slightly adapting the device should also enable for example immunosensing, DNA analysis or enantioselective detection. This makes it a promising tool for various applications, not only in the field of sensing, but even for more sophisticated concepts, such as biomimetic electrochemical feed-back systems, allowing the design of stimuli responsive valves, intelligent drug delivery schemes or Boolean logic gates.

EXPERIMENTAL SECTION

Electrochemical synthesis of polypyrrole film. For the synthesis of the polypyrrole film, 25 mL of pyrrole (0.2 M) (Sigma Aldrich) are dissolved in Milli Q water along with 0.25 M dodecyl benzene sulfonate (Sigma Aldrich). After complete dissolution of both components, two gold coated glass plates (3 cm x 1.5 cm) are fixed in parallel in the beaker. Ag/AgCl was used as a reference electrode. A fixed current of 7.75 mA is applied for 5200 s for the polymerization of pyrrole. After completion of the polymerization, the polypyrrole coated gold surface is washed with distilled water. The polymer is then peeled off from the surface with the help of a sharp knife. The wet polymer film is kept between two glass slides overnight for further use. The polypyrrole surface is characterized using scanning electron microscopy (Hitachi, TM-1000) after Au sputtering the polymer surface to reduce electric charging.

Synthesis of tetrathiafulvalene-tetracyanoquinodimethane charge transfer crystals (TTF-TCNQ CTC). For the synthesis of TTF-TCNQ CTC, TTF (0.1 M) and TCNQ (0.1 M) is dissolved in 10 mL acetonitrile in two separate beakers. After complete dissolution, the TTF solution is added to the TCNQ solution under stirring. Black CTC are formed immediately. After 30 minutes of mixing, CTC are washed with acetonitrile followed by diethyl ether. Finally, the resulting CTC are dried in a hood at room temperature for 12 h. After drying the CTC are collected in a closed vial and used for immobilization.

Fabrication of glucose oxidase (GOx) modified polypyrrole. A polypyrrole strip with a size of 1.0 cm x 0.4 cm is cut. 6 mg TTF-TCNQ crystals are grinded in a pastel mortar, then mixed with 6 mg of GOx (from *Aspergillus niger*, Sigma Aldrich) predissolved in 100 μ L 0.1 M phosphate buffer (pH 7.0). 10 μ L of the mixture are drop casted onto the rough face of one half of the polypyrrole strip (roughly 0.5 cm x 0.4

cm). After complete drying, 2 μ L of a preheated gelatin solution (12.5 mg in 250 μ L) is casted on top of the enzyme layer. After drying, the width of the unmodified part of the polypyrrole strip is reduced to 0.05 cm. Such a GOx-CTC modified polypyrrole strip is used for glucose sensing in 0.1 M PBS (pH 7.0) by bipolar electrochemistry.

Bipolar electromechanical readout. For bipolar electro-mechanical readout of hydrogen peroxide and quinone, a pristine polypyrrole strip with a size of 10 mm x 1 mm is positioned at the center axis of the bipolar cell. For the electroenzymatic analysis of glucose, the GOx-CTC modified polypyrrole part is fixed at the top of a holder in the bipolar cell. Two graphite feeder electrodes are placed 5 cm apart on the right and left side of the polypyrrole strip. In all bipolar experiments, 0.1 M PBS (pH 7.0) is used as electrolyte to provide a sufficient amount of ions during the process of bipolar electrochemistry. Different concentrations of hydrogen peroxide, hydroquinone and glucose are added to the buffer solution in order to measure the degree of bending of the polypyrrole strip. Actuation was recorded using a macroscope (LEICA Z16 APO) in video mode.

ASSOCIATED CONTENT

Supporting Information

Cyclic voltammograms and deflection pictures of polypyrrole in the analyte medium. Video of polypyrrole actuation in the presence of analyte.

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# L.Z. and B.G. contributed equally.

Notes

The authors declare no competing financial interests.

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