

An On-Chip Chemiresistive Polyaniline Nanowire-Based pH Sensor with Self-Calibration Capability

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Abstract— A pH sensor based on chemiresistive polyaniline nanowires, which makes use of the pH responsive conductivity of the polymer, requires an electrochemical system during measurements in order to maintain its oxidation state. In this work, we have developed an integrated electrochemical device where a reference, a counter, and a pair of working electrodes are all fabricated on a single chip. The polyaniline nanowires are grown between this pair of working electrodes that are separated by a microscale gap. This device can easily be connected to the external circuit for potential control and current measurements. Taking advantage of the fact that polyaniline becomes insulating when it is fully oxidized or fully reduced, the pH sensor can be electrically reset by controlling the electrochemical potential of the polymer. This paper presents the pH sensing results and the performance of the resetting function of the developed integrated device.

I. INTRODUCTION

Measuring an accurate pH level of a sample solution is crucial in many areas of biological science including immunoassay, enzymology, and various biosensors research. Conventional pH meters have their limitations of being bulky, fragile, expensive, and vulnerable to uncontrollable deviations in transducer parameters [1]. In order to overcome some of these drawbacks, solid-state devices such as ion selective field effect transistors (ISFETs) have emerged a few decades ago as alternatives to the traditional pH meter [2]. While an ISFET has the advantages such as fast response, microscale, and simple integration with the electrical circuit, they have the disadvantages of having a drift phenomenon, hysteresis effect, non-linear response, and requiring a calibration [3]. Hence, developing a simple and miniaturized pH sensor that gives accurate and reliable readings is an ongoing challenge. One possibility is the use of an electrically conducting polymer as a chemiresistive pH sensor. Unlike other conducting polymers, polyaniline possesses a unique electrical property, namely its tunable conductivity upon exposure to the varying pH level of the environment [4, 5].

Polyaniline exists in many different forms depending on the extent of its oxidation or reduction. Polyaniline can be generally categorized into the following three main oxidation states: a fully oxidized (pernigraniline) state, a fully reduced (leucoemeraldine) state, and a half-oxidized and half reduced (emeraldine) state. The emeraldine form of polyaniline is particularly interesting because, upon doping with acidic solutions, the polymer becomes electrically conducting. The level of oxidation of polyaniline depends on the

electrochemical potential of the polymer. The leucoemeraldine and pernigraniline form of polyaniline is rarely conducting even in a strong acidic environment. However, in emeraldine form, the conductivity can increase by several orders of magnitude if doped with strong acid. For a fixed potential of polyaniline in its emeraldine state, the conductivity depends on the acid concentration, i.e. the pH of the environment. This property makes polyaniline a unique candidate to be used in applications for pH sensors. However, the electrochemical potential of the polymer must be controlled in order to maintain its redox state which influences the resistance of the polymer [6-8]. An interesting observation is that this configuration demonstrates the transistor-like characteristics of polyaniline where the potential maintained at the conducting region represents the “on” state of the switch and, by shifting the potential to the fully oxidized or fully reduced region, the polymer essentially becomes insulating and can be represented as the “off” state of the switch [9, 10]. The electrochemical potential control of polyaniline can also be used as a self-calibrating function where the current measurement can be reset by making the polymer insulating as illustrated in Figure 1.

The described electrical self-calibrating step can eliminate the rinsing step of the device between

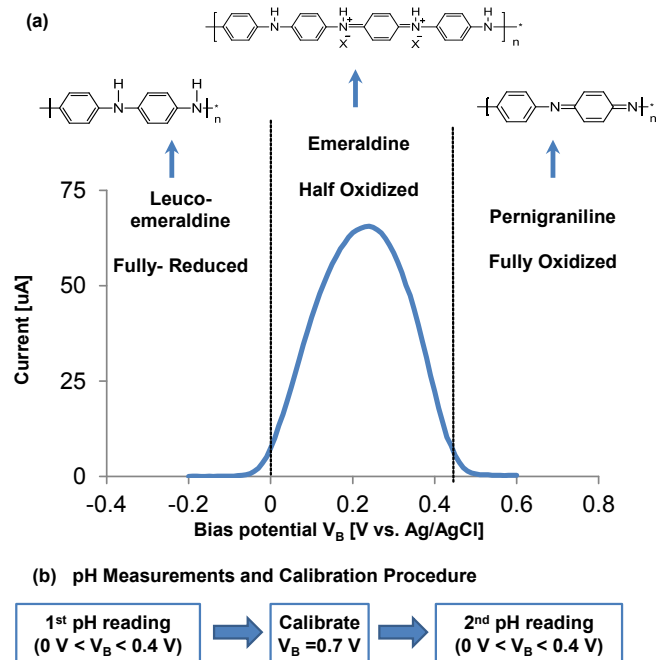


Figure 1. Redox states and pH dependence of polyaniline: (a) illustration of potential dependent oxidation levels and conductivity of polyaniline and (b) pH measurement and calibration procedure.

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measurements and can also provide continuous monitoring of pH level when the test solutions are frequently being changed. Other benefits of using polyaniline nanowires as a sensing material are its ease of synthesis, low cost, and high surface area-to-volume ratio due to its “spaghetti-like” morphology which is desirable for increasing sensitivity of the sensor.

In this paper, we present the development of an integrated on-chip pH sensor device which houses a reference, a counter, and a pair of closely spaced working electrodes whose gap is bridged by the electrochemical growth of polyaniline nanowires. We also present the pH sensing capability of the device by testing the sensor with various pH buffer solutions. Finally, we illustrate the electrical resetting of the device and demonstrate its feasibility.

II. DEVICE DESIGN AND EXPERIMENTS

A. Device Fabrication

The schematic representation of the device is shown in Figure 2 (a) which consists of four electrodes connected in an electrochemical setup controlled by a potentiostat. A bias voltage (V_B) is applied to the working electrode (WE_1), with respect to the reference electrode (RE), and a differential voltage (V_D) is applied between the two working electrodes, WE_1 and WE_2 . These voltages are controlled by a potentiostat circuit. The device was fabricated using the standard photolithography steps. First, Ti (5 nm) and Au (50 nm) layer was deposited on a glass slide and a positive photoresist (Shipley S1805) was spin coated on top at 3,000

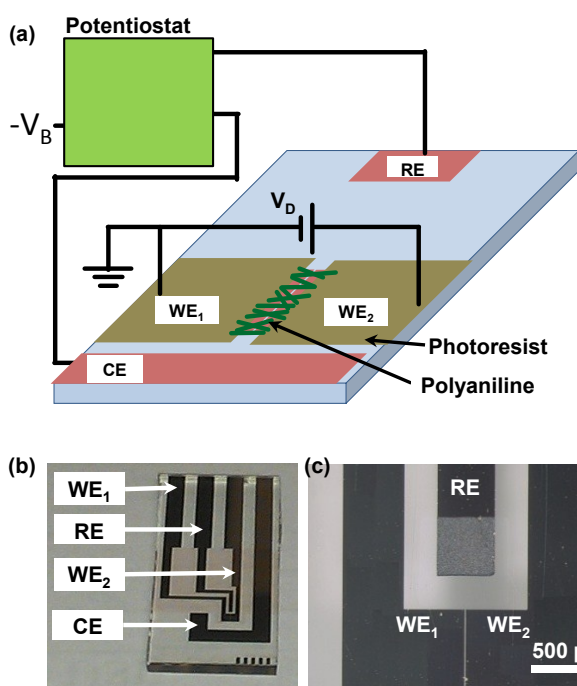


Figure 2. An on-chip chemiresistive pH sensor: (a) schematic illustration of the integrated pH sensor device with reference electrode (RE), counter electrode (CE), and two working electrodes (WE_1 and WE_2); (b) a photograph of the fabricated device, and (c) a magnified image of the electrode gap and the reference electrode. The potentiostat maintains the potential of WE_1 at the bias voltage V_B and the differential voltage between WE_1 and WE_2 at V_D .

rpm for 30 seconds followed by a soft bake at 115°C for 1 minute. Then the pattern was UV exposed (8.3 mJ/cm²) through a photomask. After dissolving the UV exposed photoresist area with a Microposit 351 developer, the gold and titanium layers were subsequently etched. After removing the remaining resist with acetone followed by methanol and DI water treatment, the device shown in Figure 2 (b) is obtained. During the electrochemical synthesis of polyaniline nanowires, the polymer needs to grow near the gap of the working electrodes. In order to control the growth only in the gap between the working electrodes, a photoresist was coated on the rest of the electrode area as a passivation layer so that the remaining area of the electrodes was physically separated from the electrolyte solution. The areas that are not covered by the resist layer are the electrode gap, the reference electrode area and the counter electrode. After patterning the passivation layer, it was hard baked at 180°C for 30 minutes to stabilize the coating.

B. Ag/AgCl Reference Electrode Fabrication

An on-chip silver/silver chloride (Ag/AgCl) reference electrode (RE) was fabricated using electroplating method similar to the ones described in the literature [11-13]. Briefly, the tip of the RE of the device near the electrode gap, 400 μm × 400 μm in area, was electroplated with Cyless II RTU silver solution (Technic Inc.). A constant cathodic current of 0.5 mA/cm² was applied for 30 minutes using a galvanostat. Then, the electroplated silver was chloridized to produce AgCl by supplying an anodic current of 0.5 mA/cm² in 1 M KCl solution for 30 minutes. Figure 2 (c) shows the result of the miniaturized on-chip reference electrode.

C. Polyaniline Nanowire Synthesis

Polyaniline nanowires were grown electrochemically between the two working electrodes separated by a 10 μm gap. A miniaturized on-chip Ag/AgCl as described in the previous section is used as a reference electrode, and patterned gold layers are used for both counter and working electrodes. The integrated device was partially immersed in 15 ml of a mixture of 0.05 M aniline monomer and 1 M H₂SO₄ solution so that the electrode gap was in contact with the electrolyte. The voltage of the two working electrodes were both maintained at 0.78 V vs. Ag/AgCl using the potentiostat circuit, i.e. the bias voltage of $V_B = 0.78$ V vs. RE and the differential voltage of $V_D = 0$ V in Figure 2 (a). The redox current generated at the working electrodes was measured with a Keithley 6485 picoammeter. The synthesis continued until this current reached approximately 1 μA and the device was thoroughly rinsed with DI water.

D. pH Measurements and Device Self-Calibration Procedures

For pH sensing experiments the polyaniline deposited area of the device was immersed in a pH buffer solution and the current passing through the polymer nanowires was measured. The potentiostat control and the analog signal measurements were performed with LabView FieldPoint module (National Instruments). All the pH buffer solutions were prepared with equal ionic strengths to offset the influence of the solution conductance. The bias voltage V_B of the working electrode was maintained at 0.1 V or 0.3 V

vs. RE and the differential voltage V_D was set to 20 mV. The resetting of the device was performed by changing the bias voltage to +0.7 V vs. RE where polyaniline is expected to be fully oxidized and therefore insulating. Each measurement lasted between 30 and 50 seconds followed by a resetting period of 30 seconds. The measurements were also repeated multiple times in order to observe repeatability.

III. RESULTS AND DISCUSSIONS

A. Characterization of Polyaniline Nanowires and Its Electrochemical Behavior

Figure 3 shows the microscope image and the scanning electron microscope (SEM) image of the synthesized polyaniline nanowires. The dimensions of the nanowires are approximately 100–150 nm in diameters and several micrometers in length. The SEM image shows a highly porous and interconnected “spaghetti-like” framework whose large surface area is beneficial for sensor applications providing higher sensitivity.

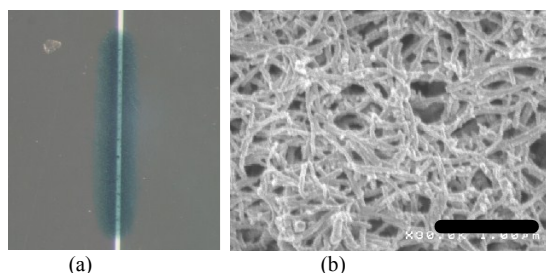


Figure 3. Electrochemically synthesized polyaniline nanowire network: (a) microscope image of polyaniline nanowire network grown between the 10 μm gap electrodes and (b) SEM image of polyaniline nanowires (scale bar: 5 μm).

The cyclic voltammetry (CV) curve shown in Figure 4 indicates two sets of distinct redox activity, where the first set of redox peaks between 0 V and 0.2 V is associated with the conversion of fully reduced leucoemeraldine base to partially oxidized emeraldine, and the second set of redox peaks occurring between 0.6 V and 0.7 V pertains to the conversion of emeraldine to fully oxidized pernigraniline form. In the CV experiment, V_B was scanned at 50 mV/s from -0.2 V to 0.9 V vs. Ag/AgCl, and V_D was set to zero in order to measure only the Faradaic current generated by the redox process. The dependence of polyaniline conductivity

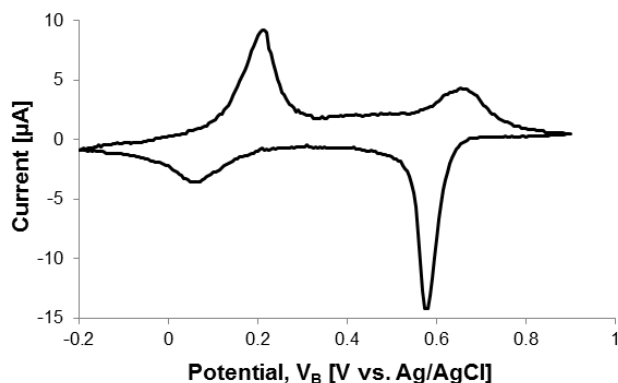


Figure 4. Typical cyclic voltammogram of polyaniline-bridged gold electrode gap in pH 1 HCl solution. The scan rate was 50 mV/s.

on the electrochemical potential is illustrated in Figure 5. In this experimental setup, V_B was varied from -0.2 V to 0.6 V while keeping V_D constant at 20 mV in pH 3 buffer. The graph shows that the conductivity of polyaniline changes in an upside down U-shape, with maximum conductivity occurring at 0.2 V however, the polymer becomes almost insulating when V_B is less than -0.2 V or greater than 0.5 V. This illustrates that, for pH sensor applications, controlling the electrochemical potential of polyaniline nanowires is crucial in optimizing the pH sensing capability. Therefore, in order to optimize stability of the sensor, a bias potential must be maintained to a constant value during the pH measurements.

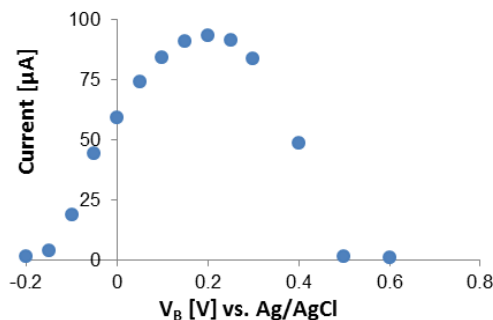


Figure 5. Conductivity variation of polyaniline as a function of potential. V_B was varied from -0.2 V to 0.6 V and V_D was set to 20 mV.

B. Response of a Polyaniline based pH sensor and Its Electrical Self-Calibrating Capability

As previously reported [7], the conductivity of polyaniline in high pH environment is maximized when the electrochemical potential of the polymer is near 0.1 V vs. saturated calomel electrode (SCE). On the other hand, in a low pH environment, e.g. between pH 1 and 3, the conductivity of polyaniline reaches a maximum when the potential of the polymer is approximately 0.3 V vs. SCE. During our experimental study, we observed no current flow through polyaniline in pH 5 and 6 unless the potential is kept between 0 V and 0.1 V. For strong acids such as pH 1 and 2, the current was maximized when the potential was between 0.3 V and 0.4 V. For our device testing, we chose a value of $V_B = 0.1$ V vs. RE for high pH detection and 0.3 V vs. RE for low pH detection. At these potentials, a wide range of pH detection would be possible where each pH level would give a distinct current level, and stronger acid would lead to higher current flow. The differential voltage V_D was set to 20 mV for all measurements for the sake of consistency. With this potential setting, the integrated pH sensor was tested with various pH buffer solutions to evaluate its performance, and the results are shown in Figures 6 and 7. With these two bias potentials, the implemented device was able to detect the pH of a test solution between the range pH 1 and 6. The steady state current value for pH 1 solution when $V_B = 0.1$ V was lower than that of the pH 2 (see Figure 6) and hence pH 1 is considered not detectable at this potential. However, when V_B is raised to 0.3 V, the current level of pH 1 is the highest as shown in Figure 7, and therefore it is deemed measurable at this potential. At $V_B = 0.3$ V vs. RE, buffer solutions of pH 5 and 6 did not produce significant current levels. With regards to the response time of the device, the

steady state current levels were obtained within 30 seconds, and for low pH buffers, steady state was achieved much faster within a few seconds.

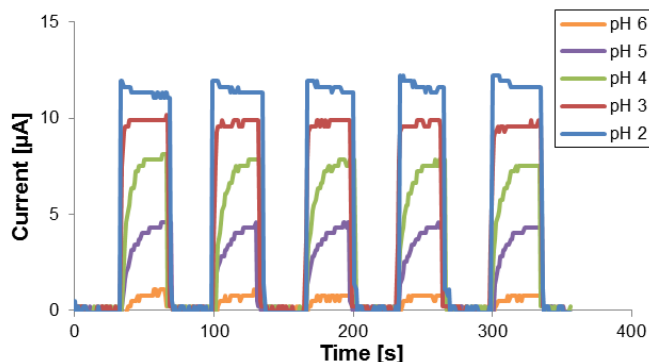


Figure 6. pH response of a polyaniline nanowire-based pH sensor with $V_B = 0.1$ V vs. RE and $V_D = 20$ mV. The calibration voltage was 0.7 V vs. RE.

In Figure 5 we illustrated a transistor-like behavior of polyaniline where the polymer is insulating when fully oxidized (+0.6 V vs. RE or higher) or fully reduced (-0.2 V vs. RE or lower) and is highly conducting when the polymer is partially oxidized with the electrochemical potential set in the intermediate region of the voltage range. Here, we utilize this “on” and “off” state of the polyaniline nanowires as a method to calibrate our chemiresistive sensor device. The device calibrating with the bias potential of 0.7 V vs. RE is demonstrated in Figures 6 and 7, and it shows that the measurements were highly repeatable. An alternative method to electrically reset the device is to fully reduce the polyaniline material, i.e. by applying -0.2 V vs. RE. However, this method was relatively slower in response time, and upon resetting and switching the device back to the “on” state, the current levels gradually diminished after each subsequent measurement.

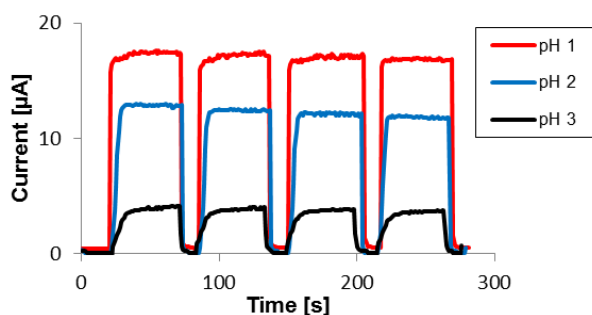


Figure 7. pH response of the device with $V_B = 0.3$ V vs. RE and $V_D = 20$ mV. The resetting voltage was 0.7 V vs. RE.

IV. CONCLUSIONS

We have developed a fully integrated electrochemical device with a reference, a counter and two working electrodes on a single chip with polyaniline nanowires grown between the microscale electrode gap to be used as a chemiresistive pH sensor. A large change in the electrical conductivity of polyaniline produced by a change in electrochemical potential can be utilized to reset and

calibrate the device. A complete oxidation of polyaniline by applying a +0.7 V vs. RE is a preferred calibration method over a complete reduction by applying a relatively negative potential, because the former yields faster response and more repeatable current measurements than the latter. The proposed resetting method of the polyaniline-based sensor was shown to be highly reliable. pH measurements in the range of pH 1 – pH 6 was successfully obtained with each pH level producing a distinct current value. The repeatability of the sensor was also demonstrated by calibrating the device multiple times and obtaining a repeatable current level after each reset. Since polyaniline is insulating in neutral or basic environment, detection of pH 7 or higher is not possible with polyaniline. However, synthesis of a modified polyaniline or combining polyaniline with other types of pH sensitive material that is conductive in base and neutral solution could lead to the development of a full range pH sensor.

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