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Video Article

Manufacturing of a Nafion-coated, Reduced Graphene Oxide/Polyaniline Chemiresistive Sensor to Monitor pH in Real-time During Microbial Fermentation

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Abstract

Here, we report the engineering of a solid-state micro pH sensor based on polyaniline-functionalized, electrochemically reduced graphene oxide (ERGO-PA). Electrochemically reduced graphene oxide acts as the conducting layer and polyaniline acts as a pH-sensitive layer. The pH-dependent conductivity of polyaniline occurs by doping of holes during protonation and by the dedoping of holes during deprotonation. We found that an ERGO-PA solid-state electrode was not functional as such in fermentation processes. The electrochemically active species that the bacteria produce during the fermentation process interfere with the electrode response. We successfully applied Nafion as a proton-conducting layer over ERGO-PA. The Nafion-coated electrodes (ERGO-PA-NA) show a good sensitivity of 1.71 Ω /pH (pH 4 - 9) for chemiresistive sensor measurements. We tested the ERGO-PA-NA electrode in real-time in the fermentation of *Lactococcus lactis*. During the growth of *L. lactis*, the pH of the medium changed from pH 7.2 to pH 4.8 and the resistance of the ERGO-PA-NA solid-state electrode changed from 294.5 Ω to 288.6 Ω (5.9 Ω per 2.4 pH unit). The pH response of the ERGO-PA-NA electrode compared with the response of a conventional glass-based pH electrode shows that reference-less solid-state microsensor arrays operate successfully in a microbiological fermentation.

Video Link

The video component of this article can be found at <https://www.jove.com/video/58422/>

Introduction

pH plays a vital role in many chemical and biological processes. Even small changes in the pH value alter the process and adversely affect the outcome of the process. Hence, it is necessary to monitor and control the pH value during every stage of experiments. The glass-based pH electrode has been successfully used to monitor pH in many chemical and biological processes, although the use of a glass electrode poses several limitations to measuring pH. The glass-based pH electrode is relatively large, fragile, and small leakages of the electrolyte into the sample are possible. Furthermore, the electrode and electronics are relatively expensive for applications in 96-well screening fermentation systems. Moreover, the electrochemical sensors are invasive and consume the sample. Hence, it is more advantageous to use non-invasive, reference-less sensors.

Nowadays, miniaturized reaction systems are favored in many chemical engineering and biotechnology applications as these microsystems provide enhanced process control, along with many other advantages over their macro system analogs. To monitor and control the parameters in a miniaturized system is a challenging task as the sizes of the sensor to measure, for instance, pH and O₂, need to be minimized as well. The successful production of microreactors for biological systems require different kinds of analytical tools for process monitoring. Hence, the development of smart microsensors plays a significant role in carrying out biological processes in microreactors.

Recently, there have been several attempts to develop smart pH sensors using chemiresistive sensing materials like carbon nanotubes and conducting polymers¹. These chemiresistive sensors require no reference electrode and are easy to integrate with electronic circuits. Successful chemiresistive sensors make it possible to produce smart sensors that are cost-effective and easy to manufacture, require a small volume for testing, and are non-invasive.

Here, we report a method to develop an electrode with polyaniline-functionalized, electrochemically reduced graphene oxide. The chemiresistive electrode operates as a pH sensor during an *L. lactis* fermentation. *L. lactis* is a lactic-acid-producing bacterium used in food fermentation and food preservative processes. During fermentation, the production of lactic acid lowers the pH, and the bacterium stops growing at a low pH^{2,3,4}.

A fermentation medium is a complex chemical environment that contains peptides, salts, and redox molecules which tend to interfere with the sensor surface^{5,6,7,8,9}. This study shows that a pH sensor based on chemiresistive material with a proper surface protection layer could be used

to measure pH in this kind of complex fermentation media. In this study, we successfully use Nafion as the protection layer for polyaniline-coated, electrochemically reduced graphene oxide to measure the pH in real-time during an *L. lactis* fermentation.

Protocol

1. Preparation of Graphite Oxide

NOTE: Graphite oxide is prepared according to Hummers' method^{10,11}.

1. Add 3 g of graphite into 69 mL of concentrated H₂SO₄ and stir the solution until the graphite has completely dispersed. Add 1.5 g of sodium nitrite and leave it for 1 h while stirring. Then, place the container in an ice bath.
2. Add 9 g of potassium permanganate into the dispersion and remove the container from the ice bath. Allow the solution to warm up to room temperature.
3. First, add 138 mL of distilled water dropwise. Then, continue to add 420 mL of distilled water. Maintain the temperature at 90 °C for 15 min using a hotplate. Add 7.5 mL of 30% hydrogen peroxide to the dispersion.
4. Collect the product by centrifugation at 10,000 x g for 20 min and discard the supernatant solution. Wash the pellet 4x with warm double-distilled water and 2x with a 10% HCl (v/v) solution. Finally, wash it 2x with ethanol and dry it at 50 °C in the oven.

2. GO-deposited Electrode Preparation

1. Disperse 10 mg of graphite oxide in 10 mL of water and then sonicate it in an ultrasonic bath for 6 h.
2. Remove the unexfoliated graphite oxide flakes by centrifugation for 30 min at 2,700 x g. Discard the solid particles after centrifugation and use the supernatant for further experiments.
NOTE: We used this exfoliated GO flakes dispersion as the stock solution.
3. Dilute the GO stock solution two-fold. Always prepare a fresh GO working solution from the stock solution.
4. Add 2 µL of the GO working solution on top of an exposed interdigitated gold electrode (**Figure 1A** and **Figure 2**). After drop casting, dry the electrode at room temperature for 12 h. This is the GO-deposited electrode.

3. Reduction of GO to Electrochemically Reduced Graphene Oxide

1. Insert the electrode in the polydimethylsiloxane (PDMS) electrode holder (bottom piece). Place the other part of the electrode holder, which serves as a solution reservoir, on top of the electrode as shown in **Figure 1A - 1C**. Assemble the holders by clipping the two parts together using two paper clips. Make sure that the PDMS holder does not cover the GO-deposited electrode part.
2. Pipet 300 µL of 0.2 M phosphate buffer (pH 7) in the reservoir. Then, place the reference and the counter electrode in the solution in such a way that the electrodes are placed close to the surface of the GO film, as shown in **Figure 1C**. This set-up serves as an electrochemical cell to perform electrochemical reduction of GO and for polyaniline deposition.
3. Connect the electrodes with the potentiostat connected to a computer for data acquisition. Use cyclic voltammetry for the electrochemical reduction: select 0 to -1.2 V as a potential range and 50 mV/s as the scan rate. Cycle the voltage over the electrode between 0 to -1.2 V 10x (**Figure 3**).
4. After the experiment, remove the electrode from the holder and repeatedly wash it with double-distilled water. Then, dry the electrode in an oven at 101 °C for 12 h.
5. When the electrode is dry, remove the electrode from the oven and allow it to cool down to room temperature. Then, measure the conductivity of the electrode with a multimeter. The electrode is now referred to as an electrochemically reduced graphene oxide (ERGO) electrode.

4. Polyaniline Functionalization of the ERGO Electrode

1. Prepare 10 mM aniline monomer for the polyaniline functionalization. Dissolve 5 µL of 10 mM aniline in 5 mL of 1 M H₂SO₄.
2. For the polyaniline functionalization, add 300 µL of aniline monomer to the solution reservoir. Place the ERGO-deposited electrode into the electrode holder as described in the procedure for GO reduction.
3. Use cyclic voltammetry for the electropolymerization of aniline to functionalize ERGO into ERGA-polyaniline (ERGO-PA): select 0 to 0.9 V as a potential range and 50 mV/s as the scan rate. Cycle the voltage over the electrode between 0 to 0.9 V for 50x (**Figure 4**).
4. After the polyaniline deposition, remove the electrode and repeatedly wash it with double-distilled water. Then, dry the electrode at 80 °C in the oven for 12 h.
5. Remove the electrode from the oven and allow it to cool down to room temperature before measuring the conductivity of the electrode with a multimeter.
6. Prepare a pH 5 buffer solution by adding 0.2 M NaOH to the Britton-Robinson buffer solution until pH 5 (see step 5.1). Keep the electrode in the buffer at pH 5 for 24 h.
 1. To prepare a Britton-Robinson universal buffer solution, mix 0.04 mol of phosphoric acid, 0.04 mol of acetic acid, and 0.04 mol of boric acid in 0.8 L of ultrapure water. Add 0.2 M sodium hydroxide dropwise to the buffer solution until the desired pH is reached⁴. Add ultrapure water until the final volume is 1 L.

5. ERGO-PA Electrode Testing at Different pH (Pre-calibration Before Nafion Coating)

1. After conditioning the electrode in a pH 5 buffer solution, measure the resistance of the electrode in solutions of a different pH (from pH 4 to pH 9; see **Figure 5**).

1. For this measurement, dip the electrode directly into the buffer solution and connect the other part of the electrode to the computer-controlled potentiostat for data acquisition. Change the pH by titrating with 0.2 M NaOH.
2. Choose chronopotentiometry or amperometry i-t curve from the list of techniques and apply a 100 mV potential difference to the electrode.
NOTE: The potentiostat measures the current against time. The software controlling the potentiostat provides a graphical representation of the current against time.
3. Use Ohm's law (resistance equals voltage divided by current) to calculate the resistance value from the measured current and applied voltage.

2. After the measurements, dry the electrode at room temperature for 12 h.

6. Preparation of the Nafion-coated ERGO-PA Electrode

1. Add 5 μ L of 5 wt% Nafion on top of the ERGO-PA electrode and dry the electrode at room temperature for 12 h.
2. After the Nafion coating, keep the electrode in the buffer solution at pH 5 for 24 h before pH measurements.
3. After conditioning in pH 5, remove the Nafion-coated ERGO-PA electrode (ERGO-PA-NA) and measure the resistance of the electrode from pH 4 to pH 9 as mentioned in section 5.1 (**Figure 6**).

7. Preparation of *L. lactis* Culture Medium

1. Add 9.3 g of M17 powder into 250 mL of ultrapure water. Slowly agitate the solution until the powder dissolves completely. Autoclave the solution at 121 °C for 15 min.
2. Take a 250-mL sterilized flask with a magnetic stirrer bar and add 50 mL of the sterilized M17 medium to the flask. Then, add 8 mL of autoclaved 1 M glucose solution. Inoculate the solution with 10 μ L of an *L. lactis* culture, previously grown in the same culture medium.
NOTE: The bacterial strain was obtained from Jan Kok, Molecular Genetics, University of Groningen.
3. Place the flask with the inoculated culture medium for 18 h on a magnetic stirrer plate in an incubation oven at 30 °C while stirring and monitor the pH.

8. Testing of the ERGO-PA-NA pH Response in an *L. lactis* Fermentation Experiment

1. Place the ERGO-PA-NA electrode into the *L. lactis* culture and close it with a cotton plug. Then, place the set-up into the thermostat at 30 °C to grow *L. lactis*.
2. Apply 100 mV to the electrode and measure the current against time.
3. Take 0.5-mL samples at different time points (see, for instance, **Figure 7**) to measure off-line the optical density at 600 nm and the pH with a conventional glass electrode. Continue the measurements until the optical density of the culture becomes constant, indicating that the bacteria are not growing anymore.

Representative Results

The appearance of a strong reduction peak around -1.0 V (**Figure 3**) illustrated the reduction of GO to ERGO^{12,13,14,22}. The intensity of the peak depends on the number of GO layers on the electrode. A thick black film completely covered the gold wires on the electrode. At that point, the two insulated gold electrodes were conductive because the GO connected the two gold electrode wires. Electropolymerization of aniline deposited a green film on the ERGO^{15,16,17,18,19,20,21,22}. This green color is an indication of the formation of a conductive polyaniline layer on the ERGO. The conductivity of the ERGO electrode (resistance decrease) increased after the polyaniline functionalization.

When we put the ERGO-PA electrode in a solution with a pH between 4 and 9, the current value increased (**Figure 5**) due to the doping and dedoping of holes during the protonation/deprotonation process in ERGO-PA (**Figure 2**)²². The desired pH value for the measurement of the current value of the ERGO-PA electrode was obtained by titrating the Britton-Robinson buffer solution with 0.2 M NaOH. Hence, for every addition of 0.2 M NaOH, the current value of the electrode increased (**Figure 5** and **Figure 6**). The response of the electrode was immediately stable when the addition of 0.2 M NaOH stopped at a particular pH.

A thin film of proton-conductive Nafion formed after the solvent evaporated at room temperature. The conductivity of the electrode was not affected much, but a few ohms of difference in the resistance value occurred and changed the base current value of the ERGO-PA electrode. Similar to the ERGO-PA electrode, the resistance of the ERGO-PA-NA electrode changed when the pH of the buffer solution changed from 4 to 9, as shown in **Figure 6**¹⁸.

After placing the ERGO-PA-NA electrode inside the *L. lactis* culture, the current initially decreased and then took some time to reach a stable value. Once the growth of *L. lactis* started, the current of the ERGO-PA-NA decreased gradually. The decrease in current accelerated during the exponential growth-phase of *L. lactis* and reached a stable value at the end of the growth (**Figure 7**)¹⁸. The final value of the current (or resistance) is comparable to the current value of the ERGO-PA-NA electrode tested in buffer solution (pH 4 - 7), as shown in the inset of **Figure 7**.

Figure 1: Images of the bottom (left) and the top (right) part of the PDMS electrode holder. (A) The assembled cell with (B) reference and (C) counter electrode. (D) The interdigitated gold electrode with the scale bar in centimeters. [Please click here to view a larger version of this figure.](#)

Figure 2: Schematic of ERGO-PA-deposited interdigitated gold electrode with a graphical representation of ERGO and PA formation. The image also shows hole doping on ERGO-PA during protonation. [Please click here to view a larger version of this figure.](#)

Figure 3: Cyclic voltammetry of GO reduction with different GO concentrations at a scan rate of 50 mV/s. [Please click here to view a larger version of this figure.](#)

Figure 4: Cyclic voltammetry of polyaniline deposition at a scan rate of 50 mV/s. The first 10 scans from a total of 50 are shown. The vertical arrow marks the trend of the current increase during the scans, and the horizontal arrows mark the direction of the voltage scan. [Please click here to view a larger version of this figure.](#)

Figure 5: Resistance value of the ERGO-PA electrode against pH 4 to 9. [Please click here to view a larger version of this figure.](#)

Figure 6: Resistance value of the ERGO-PA-NA electrode against pH 4 to 9. [Please click here to view a larger version of this figure.](#)

Figure 7: Real-time continuous pH change of ERGO-PA-NA during *L. lactis* fermentation. The inset shows the expected resistance value of ERGO-PA-NA for pH 4 - 7 measured in Britton-Robinson buffer solution. [Please click here to view a larger version of this figure.](#)

Discussion

It is essential that the GO layers completely cover the gold electrode wires after the deposition of GO. If the gold electrodes are not covered with GO, polyaniline will not only deposit on ERGO but also on the visible gold electrode wires directly. Deposition of polyaniline on the gold electrode wires may have implications on the performance of the electrode. After the reduction of GO to ERGO, the electrode is dried at 100 °C to strengthen the bonding between the ERGO layer and the gold electrode wires. The resistance of each electrode varies based on the number of GO layers that are deposited on the gold electrodes. Therefore, it is important to have the same concentration of GO for each electrode, and it is difficult to manufacture the electrode with a resistance in a predetermined specified range that is compatible with the measuring circuit. This limits the easy mass production of the electrodes.

The preparation of reduced graphene oxide/polyaniline by an electrochemical method has some advantages over other reported preparation methods. The electrochemical method presented here does not require strong reducing and oxidizing agents (e.g., hydrazine and ammonium persulfate)^{23,26}. In addition, the material is directly deposited on the electrode and no further processing is required, making the fabrication process faster and easier. As GO is electrochemically reduced *in situ*, a good connection between the gold and the graphene is achieved, making the pH electrode more robust.

Equilibrating the ERGO-PA electrode in a buffer with a pH between 3 and 9 before applying the Nafion improved the sensitivity of the electrode (data not shown). Omitting this step requires a soaking of the ERGO-PA-NA electrode in a buffer pH 5 for more than 24 h before use.

Furthermore, the ERGO-PA electrode must be dry before applying Nafion. A wet ERGO-PA electrode resulted in an aqueous layer between the ERGO-PA and Nafion and increased the response time of the pH sensor. The resistance or measured current of ERGO-PA-NA in solutions with a different pH varied between electrodes. This variation in resistance or current for each electrode is, most likely, caused by the difference in the number of GO layers deposited on the gold electrode wires. Just like with other pH electrodes, proper calibration of the ERGO-PA-NA electrode is necessary to obtain reliable pH values.

After placing the electrode inside the *L. lactis* culture, an initial stabilization time is necessary to obtain a constant current. In the *L. lactis* fermentation, the initial pH is 7.2. During the growth of *L. lactis*, glucose is converted into biomass and into lactic acid that acidifies the fermentation liquid. The growth stops when the pH of the fermentation medium becomes too low to support proper growth or when there is no glucose left. The current (or resistance) value of ERGO-PA-NA before and after growth are equal to the current (or resistance) value of ERGO-PA-NA previously calibrated in different buffer solutions. The initial pH and end pH of the *L. lactis* fermentation medium was confirmed using a conventional glass pH electrode.

The pH sensor can be easily manufactured in-house using cheap chemicals. The low manufacturing costs allow researchers to use this electrode in applications where a large number of pH electrodes are necessary (e.g., in a bacterial fermentation screening platform). Another application of the pH electrode is envisioned in situations where the diffusion of KCl from a conventional glass pH electrode into the measuring solution is not wanted. The pH electrode of this protocol has no internal liquids that can diffuse into the sample.

Compatibility of the chemiresistive sensor with currently available wireless electronic circuits^{1,27} makes it possible to easily develop applications using wireless pH sensors.

Disclosures

The authors have nothing to disclose.

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References

- Gou, P. *et al.* Carbon Nanotube Chemiresistor for Wireless pH Sensing. *Scientific Reports*. **4**, 4468 (2014).
- Hols, P. *et al.* Conversion of *Lactococcus lactis* from homolactic to homoalanine fermentation through metabolic engineering. *Nature Biotechnology*. **17**, 588-592 (1999).
- Luedeking, R., Piret, E. L. A kinetic study of the lactic acid fermentation. Batch process at controlled pH. *Journal of Biochemical and Microbiological Technology and Engineering*. **1**, 393-412 (1959).
- Britton, H. T. S., Robinson, R. A. Universal buffer solutions and the dissociation constant of veronal. *Journal of the Chemical Society*. **0**, 1456-1462 (1931).
- Ambrosi, A., Chua, C. K., Bonanni, A., Pumera, M. Electrochemistry of Graphene and Related Materials. *Chemical Reviews*. **114**, 7150-7188 (2014).
- Xie, F., Cao, X., Qu, F., Asiri, A. M., Sun, X. Cobalt nitride nanowire array as an efficient electrochemical sensor. *Sensors and Actuators B*. **255**, 1254-1261 (2018).
- Xie, F., Liu, T., Xie, L., Sun, X., Luo, Y. Metallic nickel nitride nanosheet: An efficient catalyst electrode for sensitive and selective non-enzymatic glucose sensing. *Sensors and Actuators B*. **255**, 2794-2799 (2018).
- Xie, L., Asiri, A. M., Sun, X. Monolithically integrated copper phosphide nanowire: An efficient electrocatalyst for sensitive and selective nonenzymatic glucose detection. *Sensors and Actuators B*. **244**, 11-16 (2017).
- Wang, Z. *et al.* Ternary NiCoP nanosheet array on a Ti mesh: A high-performance electrochemical sensor for glucose detection. *Chemical Communications*. **52**, 14438-14441 (2016).
- Hummers, W. S., Offeman, R. E. Preparation of Graphitic oxide. *Journal of the American Chemical Society*. **80**, 1339 (1958).
- Kumar, S., Chinnathambi, S., Munichandraiah, N., Scanlon, L. G. Gold nanoparticles anchored reduced graphene oxide as catalyst for oxygen electrode of rechargeable Li-O₂ cells. *RSC Advances*. **3**, 21706-21714 (2013).
- Guo, H. L., Wang, X. F., Qian, Q. Y., Wang, F. B., Xia, X. H. A green approach to the synthesis of graphene nanosheets. *ACS Nano*. **3**, 2653-2659 (2009).
- Ramesha, G. K., Sampath, S. Electrochemical Reduction of Oriented Graphene Oxide Films: An *in Situ* Raman Spectroelectrochemical Study. *The Journal of Physical Chemistry C*. **113**, 7985-7989 (2009).
- Amal Raj, A., Abraham John, S. Fabrication of Electrochemically Reduced Graphene Oxide Films on Glassy Carbon Electrode by Self-Assembly Method and Their Electrocatalytic Application. *The Journal of Physical Chemistry C*. **177**, 4326-4335 (2013).
- Bhadani, S. N., Gupta, M. K., Sen Gupta, S. K. Cyclic voltammetry and conductivity investigations of polyaniline. *Journal of Applied Polymer Science*. **49**, 397-403 (1993).
- Genies, E. M., Tsintavis, C. Redox mechanism and electrochemical behaviour of polyaniline deposits. *Journal of Electroanalytical Chemistry*. **195**, 109-128 (1985).
- Jannakoudakis, P. D., Pagalos, N. Electrochemical characteristics of anodically prepared conducting polyaniline films on carbon fibre supports. *Synthetic Metals*. **68**, 17-31 (1994).
- Deshmukh, M. A., Celiesiute, R., Ramanaviciene, A., Shirsat, M. D., Ramanavicius, A. EDTA/PANI/SWCNTs Nanocomposite Modified Electrode for Electrochemical Determination of Copper (II), Lead (II) and Mercury (II) Ions. *Electrochimica Acta*. **259**, 930-938 (2018).
- Deshmukh, M. A. *et al.* EDTA-Modified PANI/SWCNTs Nanocomposite for Differential Pulse Voltammetry Based Determination of Cu(II) Ions. *Sensors and Actuators B Chemical*. **260**, 331-338 (2018).
- Deshmukh, M. A., Shirsat, M. D., Ramanaviciene, A., Ramanavicius, A. Composites Based on Conducting Polymers and Carbon Nanomaterials for Heavy Metal Ion Sensing (Review). *Critical Reviews in Analytical Chemistry*. **48**, 293-304 (2018).
- Deshmukh, M. A. *et al.* A Hybrid Electrochemical/Electrochromic Cu(II) Ion Sensor Prototype Based on PANI/ITO-Electrode. *Sensors and Actuators B Chemical*. **248**, 527-535 (2017).
- Chinnathambi, S., Euverink, G. J. W. Polyaniline functionalized electrochemically reduced graphene oxide chemiresistive sensor to monitor the pH in real time during microbial fermentations. *Sensors and Actuators B Chemical*. **264**, 38-44 (2018).
- Sha, R., Komori, K., Badhulika, S. Amperometric pH Sensor Based on Graphene-Polyaniline Composite. *IEEE Sensors Journal*. **17** (16), 5038-5043 (2017).
- Huai-Ping, C., Xiao-Chen, R., Ping, W., Shu-Hong, Y. Flexible graphene-polyaniline composite paper for high-performance supercapacitor. *Energy & Environmental Science*. **6**, 1185-1191 (2013).
- Xiang, J., Drzal, L. T. Templated growth of polyaniline on exfoliated graphene nanoplatelets (GNP) and its thermoelectric properties. *Polymer*. **53**, 4202-4210 (2012).
- Xiangnan, C. *et al.* One-step synthesis of graphene/polyaniline hybrids by *in situ* intercalation polymerization and their electromagnetic properties. *Nanoscale*. **6**, 8140-8148 (2014).
- Azzarelli, J. M., Mirica, K. A., Ravnsbæk, J. B., Swager, T. M. Wireless gas detection with a smartphone via rf communication. *Proceedings of the National Academy of Sciences of the United States of America*. **111** (51), 18162-18166 (2014).