Applying Nanotechnology and Biology to Detect pH

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Nanobiosensors are highly sensitive and miniaturized and so can provide accurate on-site soil pH reading. The Red Team's project is to design a networked soil monitoring sensor, which will measure soil conditions and transmit these measurements wirelessly to a web server. This project involves analyzing two types of sensors (micro-cantilever and nanowire) for possible implementation.

Introduction

As the worldwide population grows, the agriculture industry has to increase crop production efficiency. To achieve the best crop yield, farmers have to ensure that crops are getting the necessary amounts of nutrients at the appropriate times. pH is a negative logarithmic scale of concentration of hydrogen ions; the lower the pH, the more hydrogen ions are present. Plants' nutrient uptakes are affected by the pH of the soil. Thus, knowledge of the soil pH is essential to growing crops as efficiently as possible.

Sensing chemicals in soil is difficult due to the complex mixture of chemicals present in soil and their minute concentrations. Traditionally, for farmers to learn the content of their soil, they must submit a soil sample to a lab for analysis. This is highly inefficient and costly. Possession of sensors that can analyze samples locally would improve this situation greatly, and nanosensors possess the required characteristics to do so: high sensitivity and high responsiveness.

The Red Team's work is to design networked soil monitoring sensors, where units will measure soil conditions and transmit them wirelessly to a web server. To keep this miniaturized, implementing a nanobiosensor to measure the soil pH is considered.

Theory/Background

Sensing Techniques

To sense hydrogen ions, properties of the sensing element change. This change can be detected by measuring the electrical properties of the element: its conductivity (conductometry), current (amporometric), and/or potential difference (potentiometry). Each of these methods have their advantages and disadvantages, as explained by Su et. al (2011). The electrical measurement used in one of the sensors used is amporometric, which is highly sensitive due to high sensitivities of current measuring tools.

Change can also be detected optically since the sensing element might change colors or shape in presence of the target chemical, in this case hydrogen ions. It's usually based on measurements of the luminescence, and fluorescence of sensors.

Types of Sensors

Biosensors are sensors that employ biological reaction to detect target chemicals. They achieve this by binding biomolecules (ex. enzyme) onto a sensing platform to react with the target. Upon reaction, the sensor will transform this event into a measurable signal (ex. current), as regular sensors do. Biosensors are highly selective as biomolecules will only react to certain chemicals or other biomolecules (Su et. al, 2011). The combination of nanotechnology with biosensors has led to an increase in amount of chemicals detectable by nanosensors.

Micro-cantilevers are micro-structures that translate an event into nano-mechanical motion and are a type of micro-electromechanical system (MEMS). Carrascosa et. al (2006) detail the combination of biosensor and micro-cantilever to increase biosensor sensitivity. By binding a biomolecule onto the surface of the cantilever, a biological reaction that occurs on its surface induces its bending (Figure 1a). This bending

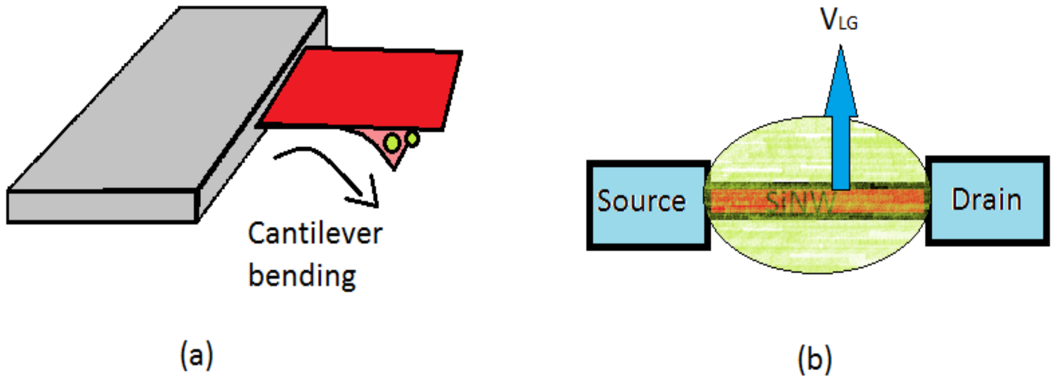

Figure 1 - Schematic of the two nanobiosensors. (a) Micro-cantilever bending in response to target chemical (green), red shows the biomolecule bonded to its surface. (b) Field-effect transistor with silicon nanowire channel coated with biomolecule (red). Conductivity of this channel changes with target chemical (green).

will be translated into either optical or electrical signals. The former is achieved through optical detection of displacement of the free end of the cantilever. The deflection in the micro-cantilever changes its resistivity, which is simply measured and does not require complicated materials unlike optical readings. However, an optical reading is less noisy than a piezoresistive reading, and does not require isolation of solution from cantilever's electrical connections. It is also found that an optical read-out achieved a better limit of detection (Carrascosa et. al, 2006).

Nanowires are another type of nanostructures that is often used in chemical and biological sensing. The basis of nanowire sensors is the field-effect transistor (FET), where conductivity of channel between two nodes (source and drain) are controlled by the voltage applied to gate node relative to the drain node. Silicon (Si) nanowire is the channel between the source and drain nodes. For biological and chemical sensing, the nanowire is coated with a biomolecule that reacts with the target (Figure 1b). This causes a surface charge of nanowire to change, and thus current through the silicon nanowire is dependent on concentration of target (Patolsky and Lieber, 2005).

Current Performance of pH Nano-biosensors

pH Detection using Micro-Cantilevers

Ji et al. (2001) created a pH sensor by chemically modifying silicon (SiO_2) and silicon nitride (SiN_4) micro-cantilevers. To create deflection, one side of the cantilever was coated with gold which does not react to hydrogen ions and the other side was the side that reacted with them, this imbalance caused a deflection that is proportional to the presence of hydrogen ions. The reacting side was either unmodified or modified with aluminum oxide, or aminosilane. Optical means were used to measure the degree of deflection. Testing was performed through flowing solutions with known pH through a micro-fluidic channel where the micro-cantilevers are held in place by a spring element.

Ji et al. (2001) found that responses depended on the chemicals bounded to the reacting surface of the micro-cantilever. Silicon nitride cantilever reacted to the widest range of pH and had a relatively high sensitivity. However, this cantilever had low sensitivity for the pH range 6 to 8. Aminosilane cantilever had the highest pH sensitivity and this sensitivity is mostly consistent for the 2-8 pH range. The unmodified micro-cantilever had a pH range of 6-12, thus combining the aminosilane cantilever with this one will yield a pH sensor with full pH range. However, it should be noted that none of

Table 1. Comparison of two Nansensor Technologies

Type of Nanosensor	Sensing reagent	Robust pH range	pH sensitivity	Advantages	Disadvantages
Silicon Micro-cantilever	SiO_2/Au	8-12	30nm/pH	Has larger pH range	Non-linear performance Optical measurement tools are harder to implement
	Aminosilane/ Au	2-8	49nm/pH		
Silicon FET-based Nanowire (SiNW)	Aminosilane	5-9	5.74 decade/pH ($\log(I/I_0)$)	Simple current output Highly sensitive Linear logarithmic response	Smaller pH range

these sensors yielded a linear relationship between the amounts of deflection and pH.

pH Detection using Silicon Nanowire

Lee et al. (2015) created a FET-based silicon nanowire (SiNW) biosensor that detect pH. An aminosilane molecule, is bonded to the SiO_2 surface of the SiNW. Testing was performed through exposing the SiNW to solutions with five different pH levels: 5, 6, 7, 8, 9 through a microfluidic channel. The current response of the sensor needed to be amplified to gain an appropriately large current range.

The current response had a logarithmic relationship with pH, where $\log(I/I_0)$ is 1/3 decade per pH (without amplification); I_0 is initial current and I is the measured current with pH. With amplification, current response is 5.74 decade/pH. While there's noise when pH levels changed, the MOSFET current quickly settles. Thus, with settling time, there's barely any noise in current readings.

Conclusion

As Table 1 shows, each sensor had its advantages and disadvantages. The micro-cantilever covers the pH range needed as normal soil pH range is 4-8, which is not covered by the SiNW. However, it's possible that another implementation of SiNW could be used in parallel to extend the pH range. In terms of manufacturing, both seem to be equal in difficulty and used mostly the same chemicals and materials. From these points, the Red Team will first choose the SiNW sensor as a potential base of design of their soil pH sensor. A linear response is the easiest to calibrate and use in the field. Furthermore, current is much easily measured than the optical readings needed for the micro-cantilever.

For both works discussed, pH was always tested in an aqueous solution. Further work would be needed to adjust sensors to be able to detect pH in soil. Another issue to investigate is hysteresis which is when past samplings affect current and future samplings. In this case, hydrogen ions remain at the detection site, preventing new hydrogen ions to be detected and causing reading of much lower pH than the reality. Lastly, a potential issue is if the biomolecule (Aminosilane) bonded onto surface of SiNW or micro-cantilever decreases over time. This could be caused if a hydrogen reaction with it causes it to be removed from nanosensors. These are the questions the Red Team will have to answer if they want to implement a nanobiosensor in their design of a soil monitoring device.

References

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