Development of a Handmade Conductivity Measurement Device for a Thin-Film Semiconductor and Its Application to Polypyrrole

ARTICLE *in* JOURNAL OF CHEMICAL EDUCATION · NOVEMBER 2014

Impact Factor: 1.11 · DOI: 10.1021/ed500287q

4 AUTHORS, INCLUDING:

Seng Set
National Institute of Education, Cambodia

Masakazu Kita
Okayama University

JOURNAL OF CHEMICAL EDUCATION

Laboratory Experiment

pubs.acs.org/jchemeduc

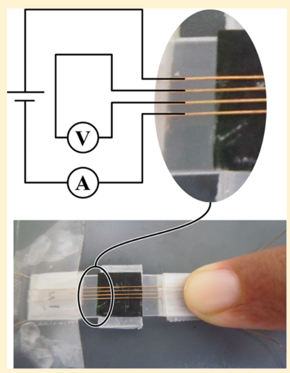
Development of a Handmade Conductivity Measurement Device for a Thin-Film Semiconductor and Its Application to Polypyrrole

Set Seng,* Tomita Shinpei, Inada Yoshihiko, and Kita Masakazu

Faculty of Education, Okayama University, Okayama 700-8530, Japan

Supporting Information

ABSTRACT: The precise measurement of conductivity of a semiconductor film such as polypyrrole (Ppy) should be carried out by the four-point probe method; however, this is difficult for classroom application. This article describes the development of a new, convenient, handmade conductivity device from inexpensive materials that can measure the conductivity of a thin-film semiconductor. Lessons on using the handmade device were conducted with high school students. The results show that the device was useful and trouble free for high school students to determine the electrical conductivity of Ppy.



KEYWORDS: *High School/Introductory Chemistry, Physical Chemistry, Polymer Chemistry, Hands-On Learning/Manipulatives, Conductivity*

■ INTRODUCTION

Electrical conductivity in polymers is not a common phenomenon, but such polymers have been made and are available. Three Nobel prizes were awarded jointly to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa in 2000 for their discovery and development of conductive polymers.[1] The conductivity of thin-film semiconductors such as polypyrrole (Ppy) has been a popular topic of discussion since well before the current research. In current technology, electrically conductive plastics are common materials in daily life and are used in electronic devices, chemical sensors, and biological applications due to their special properties besides conductivity such as oxidative polymer structure, stability, biocompatibility, etc.

In particular, Ppy is easily produced by polymerization of pyrrole through electrolysis and doped with various chemicals (dopants) in the laboratory.[2] Several researchers have suggested simple procedures for producing conductive Ppy electrochemically by using several kinds of dopant compounds, both organic and inorganic, and have studied their electrical properties.[3−12] Among the above methods, the conductive Ppy was synthesized simply through the electrolysis of aqueous pyrrole solution in the presence of surfactant such as sodium dodecyl sulfate (SDS) as dopant. However, the methods used to determine the conductivity of the Ppy in the above-mentioned research required complex techniques and expensive devices, and some used computer-controlled software. These methods are not suitable for introduction into high school lessons. Others have used simple methods to study Ppy conductivity by measuring the electrical resistance of the conductive film by direct ohmmeter measurements[9−11] or by observing the electric current passing through the conductive polymer by using a two-point probe technique.[12] Such techniques are thought to be suitable for application in classrooms due to their ease of use by students. However, the measurement of conductivity of a thin semiconductor such as Ppy by using the two-point probe method is not considered to provide accurate results, especially for thin semiconductor films with relatively high conductivity.[13] This is because the two-probe technique uses direct and strong current, which easily destroys or changes the properties of the thin film. Also, contact resistances between the metal probes and semiconductor material as well as wire resistances in the whole circuit contribute to errors that result from the low resistivity of the semiconductor material.

To obtain more accurate conductivity values for thin semiconductor films, researchers have suggested using a four-point probe technique,[13,14] sometimes also called four-wire sensing or four-terminal sensing. The four-probe technique could reduce the errors caused by contact resistances and the strong current passing through the semiconductor films. Even though several research studies have used the four-point probe technique to characterize the electrical properties of semiconductors such as Ppy,[4,11,13,15,16] they have used modern commercial instruments, which are expensive and not easy to introduce in high school classrooms.

This paper describes the development of a simple, handmade conductivity measurement device based on the principle of the four-point probe technique, from inexpensive and available

Published: August 12, 2014

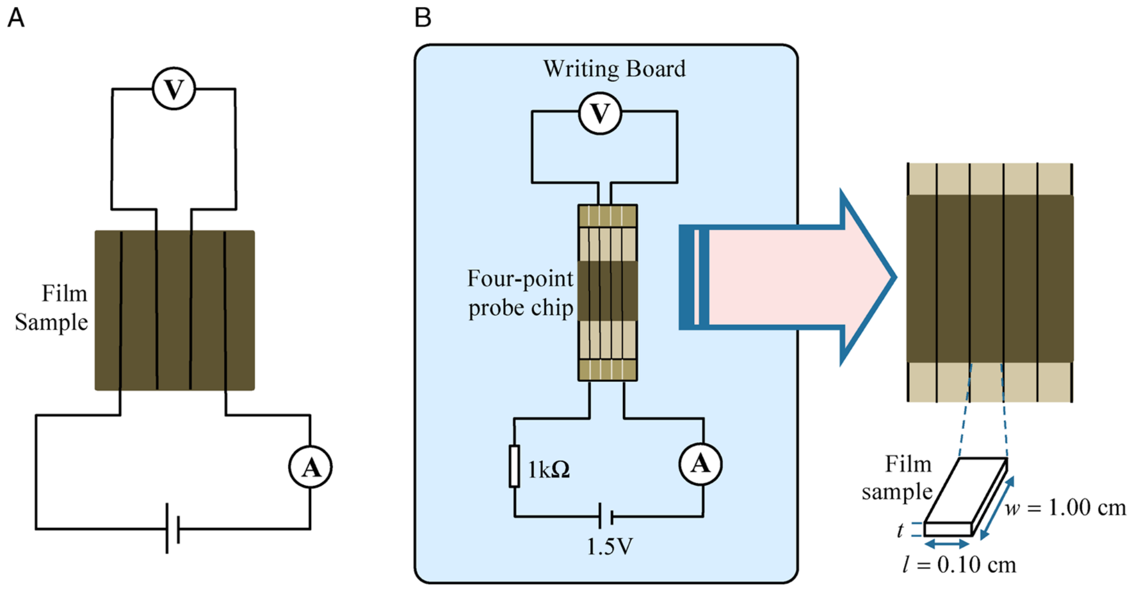


Figure 1. (A) Diagram of four-point probe principle. (B) Diagram of handmade device.

materials, and its application to measuring the conductivity of Ppy films.The accuracy of this device and its effectiveness as a teaching material in high school lessons were determined.

■ CONDUCTIVITY DEVICE

Handmade Device Setup

The four-point probe technique is conventionally set up in microscale using silver paste to attach each platinum wire probe onto a small sample of semiconductor film.[13,14] We tried to develop a simpler and easier device using the same technique. The device was simply assembled from inexpensive materials based on the principle of the four-point probe technique, where current sensing and voltage sensing are separated (Figure 1a,b). In this case, a piece of plastic from daily life (such as a food container) was cut to size 4.50 × 1.00 cm. Four Be−Cu wires (d = 0.20 mm) were laid along the plastic strip separated by a distance of 0.10 cm between each wire and held firmly in place by tape and glue at each end to prevent them from touching each other (see Figures 1b and 2b). After the four-point probe chip was prepared, it was connected into the circuit on a writing plastic board as shown in Figures 1b and 2a. The chip was attached to a plastic block (ca. 1.00 × 1.20 × 0.50 cm) on the writing board, so that one end of the chip was in contact with the board and the other end was raised (Figure 2b). In order to prevent a strong current from passing through the thin-film sample, a fixed 1 kΩ (1000 ohms) resistor was used in the current sensing circuit. Two digital multimeters were used, one for detecting current and the other for detecting voltage. The device was powered by a 1.5 V dc power source. Though use of a dry cell is possible, a dc electric transformer is recommended since it can provide more stable current and does not contribute contact resistance to the circuit. A much more detailed description of the handmade device setup is included in the Supporting Information.

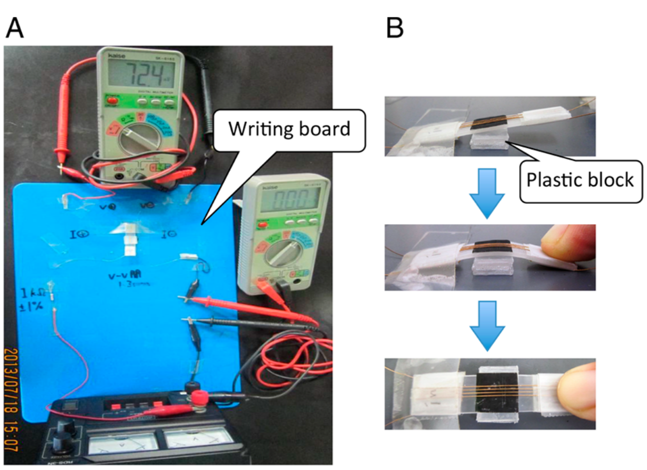


Figure 2. (A) Assembly of handmade device. (B) Four-point probe chip installation and its operation.

Theoretical Background

The conductivity value of a film sample can be simply examined through its resistivity. When a current passes through a sample with length l, width w, and thickness t, then the film resistance can be demonstrated as

$$R = \rho \frac{l}{wt} \quad (1)$$

where ρ is the resistivity of the sample. Therefore, the resistivity of the sample can determined as $\rho = Rwt/l$.

Conductivity, κ, is defined as the inverse value of resistivity. Therefore,

$$\kappa = \frac{1}{\rho} \quad \text{or} \quad \kappa = \frac{1}{Rwt} \quad (2)$$

With the handmade device, we could obtain voltage and current values by using multimeters. The film thickness could be simply measured with micro calipers, while l was set at a fixed value of 0.10 cm. If the film sample was cut to a width, w, of 1.00 cm, then the conductivity value of the sample could be calculated from the following relationship obtained from eq 2:

$$\kappa = \frac{0.10}{Rt} \quad (3)$$

where R is in Ω and can be calculated from Ohm's law ($R = V/I$, V is voltage in V and I is current in A), and t is film thickness

dx.doi.org/10.1021/ed500287q | J. Chem. Educ. 2014, 91, 1971−1975

in cm. Therefore, conductivity, κ, is determined in Ω^{-1} cm^{-1} or S/cm (S is siemens, where 1 S = 1 Ω^{-1}).

APPLICATION TO POLYPYRROLE

Ppy with Anionic Surfactants

Stainless steel plates of about 4.5 × 15 cm size and 0.5 mm thickness were used as electrodes for electrolysis. They were immersed in 100 mL of sample aqueous solution containing 0.05 M pyrrole and 1.0 g of a surfactant in a 200 mL beaker. Six types of surfactant dopants were used in the electrolysis to investigate six types of Ppy. The surfactants were sodium dodecyl sulfate (SDS), sodium dodecyl benzenesulfonate (SBS), sodium naphthalene-2-sulfonate (SNS), disodium naphthalene-1,5-disulfonate (SNDS), sodium laurate (SL), and daily soap. Each electrolysis was carried out with 4.5 V dc power supply for 10 min. After electrolysis, the electrodes with the deposited Ppy films were washed in distilled water and dried with tissue paper. Figure 3 shows assumption of Ppy structure interspersed with anions of surfactant.

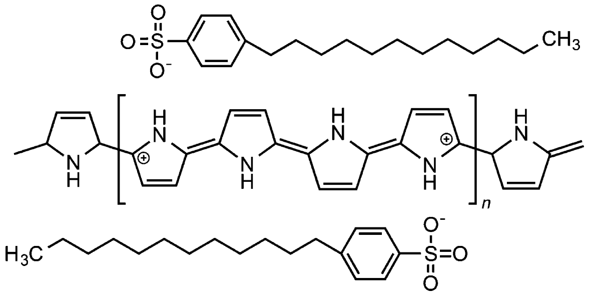


Figure 3. Conductive Ppy structure interspersed with anions of surfactant.

Ppy with Various Ratios of Anionic and Neutral Surfactants

The aqueous 0.05 M pyrrole solutions were prepared in the presence of anionic and neutral surfactant electrolyte. The anionic and neutral surfactant were dissolved as the electrolyte solutions in the ratios 4:0, 3:1, 2:2, and 1:3 by decreasing anionic surfactant concentration starting from 0.04 to 0.01 M respectively and increasing neutral surfactant concentration. Therefore, the amount of surfactant in the sample solutions was a constant 0.04 M. Four types of surfactant were used in the study, two of which were anionic and another two that were neutral, to study how surfactant concentration affected the electrical properties of Ppy. The two anionic surfactants were sodium dodecyl benzensulfonate (SBS) and sodium naphthalene-2-sulfonate (SNS), and the two neutral surfactants were polyoxyethylene (8) octyl phenyl ether (POE(8)OPE) and polyoxyethylene (30) docosyl ether (POE(30)DoE). Each solution was electrolyzed with 3.0 V dc power supply for 30 min. The electrodes with deposited Ppy were washed in distilled water and dried with tissue paper.

Measurement of Ppy Conductivity

The Ppy films were simply stripped off from the electrodes by applying and removing adhesive tape. The thickness of the tape was determined first, and then the thickness of the tape and the Ppy films was measured with micro calipers. The Ppy film thickness was calculated by subtraction, and then the films were cut into 1.00 × 1.00 cm squares. Finally, the conductivity of Ppy films was determined by inserting the square-cut sample below the four-wire probe of the four-point probe chip in the handmade device, which was then connected to the 1.5 V dc power supply, voltmeter, and ammeter (digital multimeters) as shown in Figure 2a,b. The chip at the raised end was pushed down with a finger to allow the four-wire probes to make good contact across the Ppy film. The current and voltage were recorded from the digital multimeters. The film resistances were calculated from Ohm's law, and the conductivity value of each Ppy film was calculated from eq 3.

HAZARDS

Pyrrole monomer 98% is harmful by inhalation, ingestion, and skin absorption.

RESULT AND DISCUSSION

Standardization of the Results

The data obtained by using our handmade device was compared to that obtained by conventional four-point probe techniques commonly used by researchers,[13,14] in order to determine its reliability (Table 1). The conventional techniques used the same Ppy film with Ag paste and platinum wires. In this case, the conductivity values obtained from the conventional four-point probe technique were plotted in a graph inverse to the values obtained from the handmade device as shown in Figure 4. The slope of the graph was 1.073, a 7.3% deviation from the ideal slope that could be attributed to a small determination error, and R^2 of 0.999 suggests that the conductive values from the handmade device were highly reliable.

Table 1. Standardized Data Table Comparing Handmade and Conventional Four-Point Probe Technique

Ppy with...	SNS 0.04 M	SBS 0.03 M:POE(8) OPE 0.01 M	SBS 0.02 M:POE(8) OPE 0.02 M	SNS 0.01 M:POE(30) DoE 0.03 M
Conventional (S/cm)	41.15	0.7746	0.2991	4.6230
Handmade (S/cm)	44.25	0.7974	0.3041	5.2938

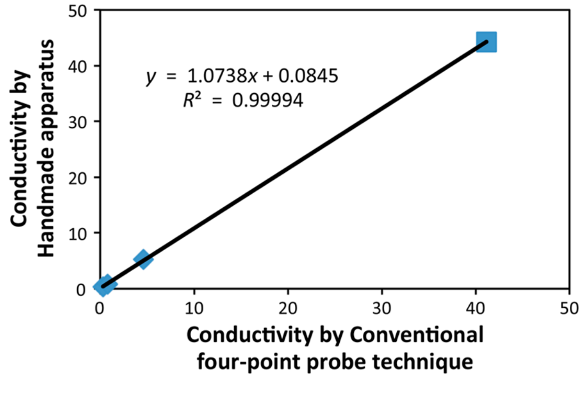


Figure 4. Standardized data graph between handmade and conventional four-point probe technique.

Ppy with Anionic Surfactants

The experimental results are shown in Table 2. They clearly reveal that each surfactant contributed a different conductive ability to polypyrrole. Among the surfactants used in doping during electropolymerization, carboxylate surfactants, sodium

dx.doi.org/10.1021/ed500287q | J. Chem. Educ. 2014, 91, 1971−1975

Table 2. Conductivity of Ppy by Different Dopants (Surfactants)

Ppy by Dopants	Voltage ($\times 10^{-3}$ V)	Current ($\times 10^{-3}$ A)	Resistance (Ω)	Thickness (cm)	Conductivity (S/cm)
SDS	14.7	3.186	4.61	0.001	21.67
SBS	11.3	2.865	3.94	0.001	25.35
SNS	9.2	2.268	4.06	0.0005	49.30
SNDS	13.3	2.382	5.58	0.0005	35.82
SL	N/A	N/A	N/A	N/A	N/A
Soap	N/A	N/A	N/A	N/A	N/A

laurate and soap, were not good dopants as they could not produce Ppy film within a reasonable time period, whereas the surfactants whose molecules contained sulfonate groups (detergents) contributed well to deposition of Ppy films on the cathodes. Different conductivity was observed from one film to another, though the one which produced the best conductivity was formed in the presence of sodium naphthalene-2-sulfonate. Among all surfactants investigated, sodium docecyl sulfate produced the most brittle polymer as the film was easily torn apart during the operation of the conductivity measurement.

The results suggest that the interactions between different surfactant molecules and the Ppy chains may contribute to successful Ppy film development and the differences in conductivity. The surfactant molecules formed monomer pyrrole micelles in the solution mixture of pyrrole and surfactant with their tails surrounding the pyrole molecules, before the polymerization.[17] The ions from the surfactants allowed the solution to be electrolyzed. This phenomenon could help contribute to electropolymerization and the formation of the Ppy film on the electrode. This observation leads to the assumption that the sulfonate surfactants could dissolve in the solution and form monomer pyrrole micelles better than carboxylate surfactants.

Ppy with Various Ratios of Anionic and Neutral Surfactants

The presence of the neutral surfactants caused a remarkable effect on the electrical properties of Ppy film. As shown in Figure 5, the conductivity of Ppy film decreased drastically with just a quarter of the neutral surfactant compared to the anionic surfactant present in the electrolyte solutions. However, the conductivity seemed to continue decreasing very slowly as the amount of the neutral surfactant increased. The two neutral surfactants used in the investigation had almost the same effect,

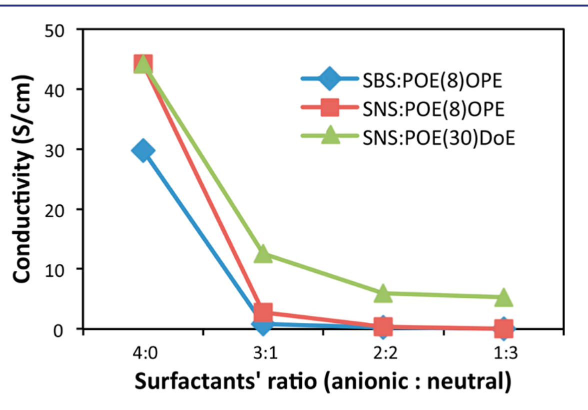


Figure 5. Conductivity of Ppy doped with different ratios of anionic and neutral surfactants.

though POE(8)OPE seemed to contribute a lesser conductivity than POE(30)DoE. Thus, we can assume that the molecules of neutral surfactants were also adsorbed or combined into the Ppy films together with anionic surfactants. In this case, the neutral surfactants could play the role of insulator that prevents the Ppy film from conducting electrical current.

APPLICATION TO CLASSROOM

We introduced the handmade device to high school students at 11th grade in Japan through lessons on Ppy and its conductivity, in July 2013. The concept taught to students was only the effect of anionic surfactants on the electrical property of Ppy. Three lab periods of 50 min were used. The students needed approximately 25 min to complete each experiment as a group, such as to synthesize the film samples and to examine the conductivity. In the first period, the instructor presented some basic knowledge about Ppy and its daily application. This included how Ppy is formed through electropolymerization, a brief chemical equation of polymerization, and a hint to examine and to calculate the conductivity value of a polymer film following the principle of the four-point probe method and deriving eq 3. During the second period, the students conducted electrolysis of pyrrole solutions in the presence of different types of anionic surfactant, such as SDS, SBS, SNS, SNDS, LS, and soap, in order to produce different conductive polymers. Each group of students made two types of the above anionic surfactants. During the last period, the students examined the conductivity of the Ppy film they produced by using the handmade conductivity device and made comparisons. The students shared with one another the films they produced among the groups. All groups of the students had opportunity to observe and to measure the conductivity of the six types of films. All the sample solutions and materials were prepared for the students before the class periods. The students got similar results to those shown in Table 2. The student handout, worksheets, and lesson plan for the teacher are available in the Supporting Information.

It was interesting that, in response to questions in the lesson introduction, all students replied with strong confidence that no plastic or polymer could conduct electricity. This was the most important part of the lesson and was intended to "hook" the students' interest and motivate them toward a scientific and skilled investigation. During the investigation, the students were surprised that the Ppy polymer films were easily generated by electropolymerization and that they could conduct electricity. Beyond this, the students also observed that the Ppy films could be doped very well by some surfactants. The results showed that the surfactants containing the sulfonate group ($-SO_3^-$) in the molecule seemed to dope the Ppy films more easily than those containing the carboxylate group ($-COO^-$). During discussion the students understood that sulfonate surfactants might form micelles better than carboxylate surfactants by entrapping pyrrole molecules as monomers in the electrolyzed solution.

The students also found that, among the conductive polymers, there was a variety of electrical conductivity. Through group discussion, the students found out which factors caused Ppy films to have different conductivity, such as type of surfactant, duration of electrolysis, distance between electrolyte electrodes, electrolyte concentration, power supply, and so on. Therefore, the lessons provided students with an opportunity to study current science and technology about conductive plastics, which are being using commonly in daily life.

dx.doi.org/10.1021/ed500287q | J. Chem. Educ. 2014, 91, 1971−1975

■ CONCLUSION

The study revealed the effect of both anionic and neutral surfactants on the conductive properties of Ppy. The lessons on Ppy and its conductivity can help students understand the properties of conductive polymers, which rarely happens in real classrooms. Especially, by using the handmade device described here, students can measure and compare the conductivity of Ppy films they make themselves in the classroom. This handmade device was easily assembled from inexpensive and available materials. A fixed 1 kΩ resistor proved to be the best solution to sufficiently reduce current passing through the film samples. The four-point probe chip that we developed was very simple, did not use silver or lead paste, and provided a trouble-free measuring technique and reliable values consistent with those obtained by conventional devices. Therefore, as an addition to other student-made instruments published in this *Journal*,[18−24] this handmade device can be recommended for determining the electrical properties of semiconductors such as Ppy as well as being an effective teaching material for high school in both chemistry and physics classes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A detailed discussion of the development of this handmade device, handouts for students, and lesson plans. This material is available via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: setseng2004@yahoo.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the Ministry of Education, Science, Sports and Culture of Japan for financial support of this research through Japan Society for the Promotion of Science. We also wish to express our thanks to David Ford of The Royal University of Phnom Penh for helpful correction of our English and discussion of the present manuscript.

■ REFERENCES

(1) The Nobel Prize in Chemistry 2000. http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2000/ (accessed Jul 2014).

(2) Ramanaviciene, A.; Finkelsteinas, A.; Ramanavicius, A. Basic electrochemistry meets nanotechnology: Electrochemical preparation of artificial receptors based on a nanostructured conducting polymer, polypyrrole. *J. Chem. Educ.* **2006**, *83*, 1212−1214.

(3) Street, G. B.; Clarkke, R. H.; Geiss, V. Y.; Nazzal, P.; Scott, J. C. Characterization of Polypyrrole. *J. Phys.* **1983**, *C3*, 599−606.

(4) Kang, H. C.; Geckeler, K. E. Enhanced electrical conductivity of polypyrrole prepared by chemical oxidative polymerization: effect of the preparation technique and polymer additive. *Polymer* **2000**, *41* (18), 6931−6934.

(5) Rhee, H. W.; Jeon, E. J.; Kim, J. S.; Kim, C. Y. Doping characteristics of polypyrrole. *Synth. Met.* **1989**, *28* (1−2), C605−C610.

(6) Kupila, E. L.; Kankare, J. Electropolymerization of Pyrrole—Effects of pH and Anions on the conductivity and Growth-Kinetics of Polypyrrole. *Synth. Met.* **1993**, *55* (2−3), 1402−1405.

(7) Crayston, J. A.; Kakouris, C.; Walton, J. C. Poly(N-hydroxypyrrole) and poly(3-phenyl-N-hydroxy-pyrrole): Synthesis, Conductivity, Spectral Properties and Oxidation. *Synth. Met.* **1992**, *48*, 65−77.

(8) Saville, P. Polypyrrole: Formation and Use. *Defence R&D Canada—Atlantic* **2005**, 1−33.

(9) Steven, W. K.; Thomas, E. M. Experiments illustrating metal-insulator transitions in solid. *J. Chem. Educ.* **1993**, *70*, 855−860.

(10) Bunting, R. K.; Swarat, K.; Yan, D.; Finello, D. Synthesis and Characterization of a Conducting Polymer: An Electrochemical Experiment for General Chemistry. *J. Chem. Educ.* **1997**, *74* (4), 421−423.

(11) Morales, J.; Olayo, M. G.; Cruz, G. J.; Castillo-Ortega, M. M.; Olyao, R. Electronic conductivity of pyrrole and aniline thin films polymerized by plasma. *J. Polym. Sci.* **2000**, *38*, 3247−3255.

(12) Puanglek, N.; Sittattrakul, A.; Lerdwijitjarud, W. Enhancement of Electrical Conductivity of Polypyrrole and Its Derivative. *Sci. J. UBU* **2010**, *1* (1), 35−42.

(13) Li, J. C.; Wang, Y.; Ba, D. C. Characterization of Semiconductor Surface Conductivity by using Microscopic Four-Point Probe Technique. *Phys. Procedia.* **2012**, *32*, 347−355.

(14) Konkov, V. L.; Rubtsova, R. A. A theory for probe measurements of electrical conductivity of semiconductor films. *NASA Tech. Transl.* **1965**, 135−141.

(15) Joo, W. L.; Francisco, S.; Jonatha, N.; Christine, E. S. Carboxylic Acid-Functionalized Conductive Polypyrrole as a Bioactive Platform for Cell Adhesion. *Biomacromolecules* **2006**, *7*, 1692−1695.

(16) Hasiah, S.; Ibrahim, K.; Seni, H. B.; Halim, K. B. K. Electrical conductivity of chlorophyll with polythiophene thin film on indium tin oxide as P-N Heterojunction solar cell. *J. Phys. Sci.* **2008**, *19* (2), 77−92.

(17) Leonavicius, K.; Ramanavicience, A.; Ramanavicius, A. Polymerization Model for Hydrogen Peroxide Initiated Synthesis of Polypyrrole Nanoparticles. *Langmuir* **2011**, *17*, 10970−10976.

(18) Seng, S.; Kita, M.; Sugihara, R. New Analytical Method for the Determination of Detergent Concentration in Water in Fabric Dyeing. *J. Chem. Educ.* **2007**, *84* (11), 1803−1805.

(19) Agbeko, J. K.; Kita, M. A Qualitative Experiment to Analyze Microbial Activity in Topsoil Using Paper and a handmade reflection Photometer. *J. Chem. Educ.* **2007**, *84* (10), 1689−1690.

(20) Teerasong, S.; Maclain, R. L. A Student-Made Microfluidic Device for Electrophoretic Separation of Food Dyes. *J. Chem. Educ.* **2011**, *88* (4), 465−467.

(21) Peterson, K. I. Measuring the Density of a Sugar Solution: A General Chemistry Experiment Using a Student-Prepared Unknown. *J. Chem. Educ.* **2008**, *85* (8), 1089.

(22) Hoffman, A. R.; Britton, S. L.; Cadwell, K. D.; Walz, K. A. An Integrated Approach To Introducing Biofuels, Flash Point, and Vapor Pressure Concepts into an Introductory College Chemistry Lab. *J. Chem. Educ.* **2011**, *88* (2), 197−200.

(23) Janusa, M. A.; Andremann, L. J.; Kliebert, N. M.; Nannie, M. H. Determination of Chloride Concentration Using Capillary Zone Electrophoresis: An Instrumental Analysis Chemistry Laboratory Experiment. *J. Chem. Educ.* **1998**, *75* (11), 1463.

(24) Hiemenz, P. C.; Pfeiffer, E. A general chemistry experiment for the blind. *J. Chem. Educ.* **1972**, *49* (4), 263.