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Phosphate ion sensor fabrication based on conductive polymer polypyrrole film coatings in doped phosphate using thick film technology

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Abstract

This study describes the development of chemical sensors to detect polypyrrole (PPy) based phosphate sensors in doped di-ammonium hydrogen phosphate (DAP) with thick film technology (TFT). Manufacturing screen-printed carbon electrode (SPCE) with thick film uses alumina substrate provided a more portable, miniature, inexpensive, and reduced use of samples and reagents. Polymer polypyrrole and di-ammonium hydrogen phosphate as sensitive membranes are electrodeposition on carbon electrodes. Characterization has been conducted to see the electrode morphology in scanning electron microscopy (SEM) test, which showed that sensitive material particles were distributed evenly on the surface of the sample and spherical. The energy dispersive spectroscopy (EDS) experiment results showed the atomic composition respectively carbon 86.95 %, nitrogen 6.94 %, oxygen 5.9 %, and phosphate 0.21 %, which were exposed to the electrode. The performance test of electrodes with a phosphate standard solution has proceeded at a concentration between 5 to 100 mg/l, which is measured using the galvanostatic method. The voltage range was from 0.252 to 0.957 V with R^2 at approximately 90.265 %. The results of sensor performance were concluded that the electrode was able to detect phosphate ions.

Keywords: carbon electrode; electropolimerization; phosphate; polymer polypyrrole; thick film.

I. Introduction

Excessive use of fertilizers on agricultural land causes the risk of environmental pollution, degradation of soil structure, and decreased groundwater levels. Monitoring and analysis of precision farming soil are needed to monitor the main nutrient contents such as nitrogen (N), phosphate (P), or potassium (K) on agricultural land before farming activities are carried out [1].

Therefore, instrumentation devices are needed to detect nutrient content on agricultural soil. In previous studies, sensor design and fabrication studies for precision farming. Sensor terminology is strongly influenced by the substrate, the conductivity of the electrode, and the sensitive material [2].

Microelectromechanical system (MEMS) technology is carried out to miniaturize the sensor, portable size, and reduce the consumption of the sample and reagent integrated into one piece of substrate. The substrate used for the phosphate sensor is a polyester film, polyvinyl chloride (PVC), filter paper, and carbon fiber [3][4][5]. The materials used for electrodes are gold paste, silver, cobalt, black carbon nanoparticles, graphite, and lead [6][7][8]. Sensitive polymer polypyrrole (PPy) membrane has been used for biosensors, electrochemical sensors, protein sensors, glucose biosensors, clofibric acid sensors, non-enzyme sensors, and nitrate selectivity sensors [9][10][11].

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According to the previous literature, this study will be carried out on the development of phosphate ion sensor fabrication of thick film technology. Sensitive membrane sensors based on polymer polypyrrole (PPy) film layer are doped with a solution of di-ammonium hydrogen phosphate (DAP) on a carbon electrode screened-printing onto the aluminum substrate. The study was conducted to improve the performance of electrodes to detect phosphate ions in precision farming.

This research focuses on the sensitive membrane used. It is printed on carbon electrodes using an alumina substrate with PPy membrane and DAP using thick-film technology. The phosphate ion sensor consists of three electrodes, the working electrode, the counter electrode, and the reference electrode. This study focuses on fabricating precision farming sensors that are specifically aimed to detect ion phosphate nutrients. The morphological characteristics testing and composition of electrode material were conducted using SEM and EDS [12]. The electrode performance testing is implemented to obtain a good sensor performance (sensitivity, limit detection, response time, and linearity).

II. Materials and Methods

A. Equipment and reagent

Supporting equipment are used in this study are screen printing, screen maker machine, printing machine, firing machine, oven, stative, beaker glass, micropipette, magnetic stirrer, nitrogen tube, power supply, Accumet solid-state half cell ISE (Fisherbrand), multimeters (SANWA PC-550), computers, SEM and EDS (SU3500).

Materials used in this study are alumina substrate (Al_2O_3), silver | silver chloride (Ag | AgCl) conductor paste (Ferro), platinized carbon paste (C2000511D1), protective film, ulana 133, ulano film, deionized water with 17 MΩ resistivities, 98 % grade pyrrole reagent (Aldrich), ammonium hydrogen phosphate (Merck), aluminum oxide (Merck), phosphate standard solution (Merck), and potassium chloride (KCL).

B. Fabrication of electrode

The electrode design is needed to determine the pattern, dimensions, and electrode layout that use thick film technology with a screen-printing technique that aims to determine the effect of the path width on the sensor sensitivity. The Electrode design is made by using Corel draw software. The thick film technology process consists of screen making, electrode printing, drying, firing, pin installation, and packaging.

As the first stages, the reference electrode and conjunction pad are printed on the alumina substrate using paste (Ag | AgCl). Then it was dried in an oven to minimize the liquid that is bound to the electrode. The process is continued by gradually firing with a temperature of 0 to 800 °C for 30 minutes in a furnace firing sinters machine. The next stage is printing the working electrodes and counter electrodes using platinized carbon paste, then dried material with a temperature of 0 to 120 °C for 15 minutes to bind the exposed carbon to the alumina substrate. Then the packaging is carried out, so the electrodes are ready to use. The configuration of electrodes fabrication stages is shown in Figure 1.

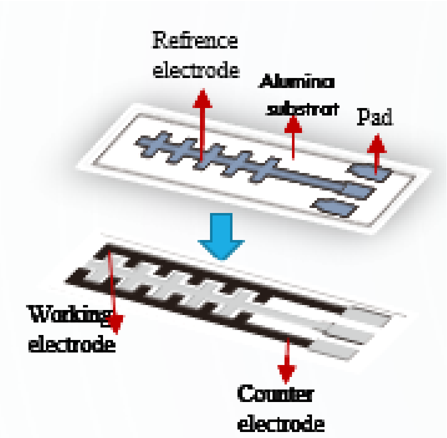

Figure 1. Screen printing electrode

C. Electrodeposition of polypyrrole doped DAP

Electrodeposition of pyrrole doped with DAP onto carbon was performed by an electrochemical process. In the first step, polypyrrole must be purified with powdered alumina oxide in a dark room to remove the substances that were oxidized with the air. Amperometric used as a constant voltage source for electrodeposition. The initial polymerization solution consisted of PPy (C_4H_4NH) [1M] doped with a solution of DAP ($(NH_4)_2HPO_4$) [0.1M] dissolved with deionized water. The electrodeposition with the amperometric method is implemented by adjusting the constant voltage source of 1 V connected to the carbon electrode and the platinum plate anode so that an oxidation reaction occurs to the sensitive membrane solution by flowing purging with nitrogen gas experiment. The deposition of the carbon electrode is executed for 30 minutes by measuring the changes in current during the electropolymerization process. Freshly prepare electrodeposition sample, the electrode then must be immersed in a solution ($(NH_4)_2HPO_4$) [0.01M] for 24 hours in a dark room.

D. Testing performance sensor

Sensor performance testing was conducted using a potentiostat to control the electrodes and measure the experiment electroanalytical (Figure 2). The previous research on measurement electrodes used the amperometric method [4]. The galvanostatic was used as a constant current source set at 0.7 V, with a resistance of 10 kΩ as input to get the response output voltage. The Electrodes are connected to the conditioning signal circuit, and then it is dipped into a phosphate standard solution (PO_4^{3-}) with a concentration of 5 mg/l, 25 mg/l, 50 mg/l, and 100 mg/l. The multimeter is connected to the sensor output to measure the output voltage, while the acquisition data is transferred to the computer. The testing is repeated five times in 10 minutes for each of test sample.

Figure 2. Testing performance sensor

III. Results and Discussions

A. Electrodes of sensor

The Phosphate sensor consists of three electrodes, the working electrode, the reference electrode, and the counter electrode. On 50 × 50 mm substrate alumina, the reference electrode was printed with a size of 21.21 × 3.5 mm and the conjunction pad sized on 3.95 × 1.5 mm. The Carbon electrodes in a comb shape were sized on 21.31 × 2.28 mm. The electrode Prototype to detect the phosphate fabricated ion by using thick-film technology is shown in Figure 3.

B. The morphological and composition material testing

The morphological characteristics testing was implemented by the scanning electron microscope (SEM) method. The 'before and after' of carbon electrode morphology is being coated with a polymer-sensitive polypyrrole membrane which is doped with ($(NH_4)_2$ HPO_4) solution is shown in Figure 4.

The differences of topographic surface in the before and after electrodes electropolymerization can be seen according to the morphological testing using SEM. The analyzed surface polypyrrole has using SEM to observe the morphology of ion-sensitive membrane [13]. The coated surface of the sensitive membrane is more evenly distributed than before. The particles have significantly shown dissimilar. The Polymerized electrodes were seen at a magnification of 20,000 secondary electrons with 10 kV. The morphology sample with a size of 2 µm showed that spherical particles were distributed evenly on the electrode surface.

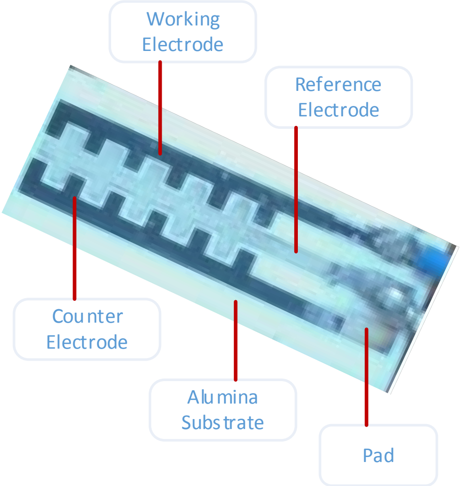

Figure 3. Prototype electrode

After that, energy dispersive spectroscopy (EDS) was tested (shown in Table 1) to determine the atom composition at the electropolymerized electrodes. The EDS results showed the composition of atoms, namely carbon at 86.95 %, Nitrogen at 6.94 %, oxygen at 5.9 %, and phosphate at 0.21 %. Based on the percentage, the phosphate atomic elements are greatly small because they are comparable with the concentration of the used solution ($(NH_4)_2HPO_4$) of 0.1 mol/l.

C. Electrodeposition testing

Measurement of current response by amperometric method on electrodeposition shows the occurrence of PPy and DAP as sensitive membrane coating on carbon electrodes. The Electrode electrodeposition experiment is shown in Figure 5. The Current measurement results for 30 minutes showed the output current response in the range of 0.03 to 0.2 mA with the presence of a stable current change during electropolymerization. In addition, there was an accretion of sensitive membranes on carbon electrodes.

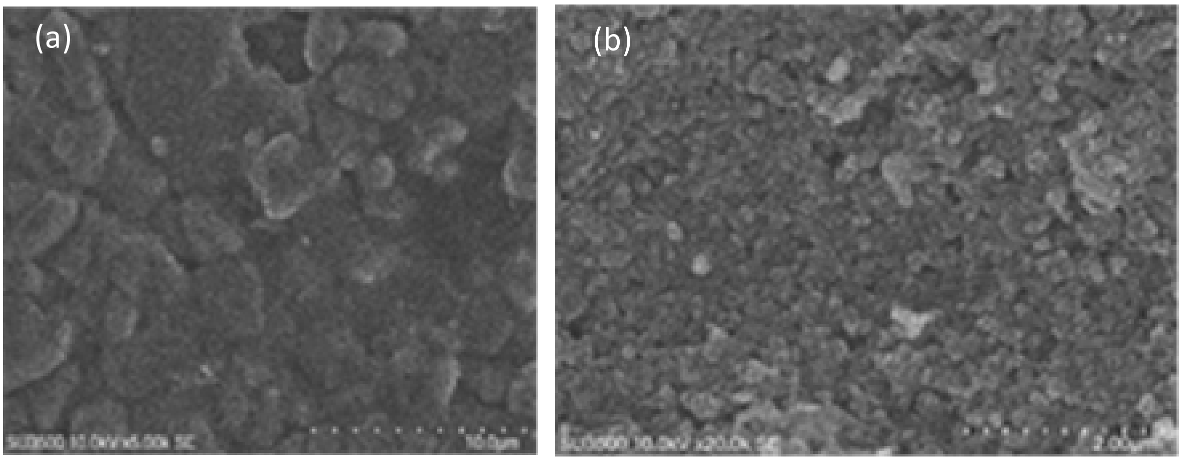

Figure 4. SEM photograph. (a) Electrode carbon before electropolimerization; (b) Electrode carbon and PPy after electropolimerization

Table 1.
Result of EDS electrodes experiment

Element	Element Composition							
	Weight percent (wt. %)	Atomic percent (at. %)	Data error (%)*	Net interpret element	The pure element standard (K-Ratio)	Atomic number corection (Z)	Atomic number corection (A)	Secondary fluorescence correctiion (F)
C K	84.10	86.9	3.5	24.95	0.680	1.01	0.80	1
N K	7.82	6.9	25.1	28.40	0.005	0.98	0.06	1
O K	7.59	5.9	17.8	68.90	0.007	0.96	0.09	1
P K	0.53	0.2	4.2	56.80	0.004	0.82	0.98	1

*Data error is comparison both eZAF (standardless- based correction factor nation) and P/B (peak to background ratio element) method

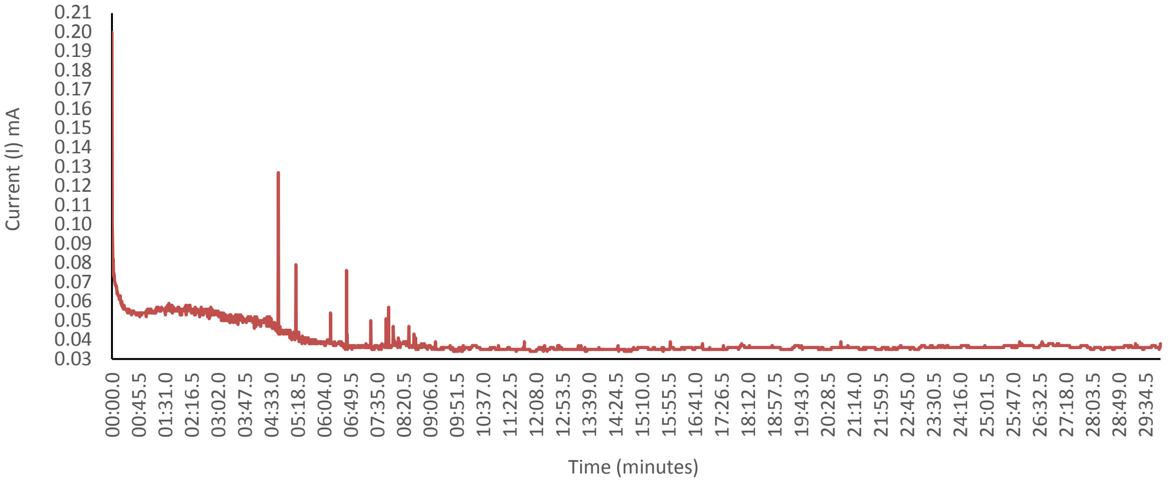

Figure 5. Output response of electrodeposition electrodes

D. Electrode stability

The reference electrode of the Ag | AgCl testing was implemented to see the stability of the electrode performance. As a result, the electrode has been the stability of the reference electrode [13]. The testing is executed by comparing the reference electrodes with commercial, which is tested in a KCl [3M] solution. The average voltage of the reference electrode test obtained the output at 6.8 to 7.4 mV. The reference electrode experiment is shown in Figure 6.

The test is executed for 30 minutes. The experiment shows that the reference electrode voltage is relatively stable.

E. Sensor performance testing

The output response of performance ion sensor using phosphate solution concentration is 0.252 V to 0.957 V, which indicates that the higher the phosphate concentration is detected, the output voltage is increased. The peak intensity was increased with the increasing phosphate concentration shows the sensor's better response with different concentrations of phosphate [6]. The discussed research has been shown the limit of detection ion phosphate based on different conductive electrodes [6][7][14]. This study's limit of detection ion phosphate is 5 mg/l with a linear range of 5 to 100 mg/l phosphate solution.

The result of the output voltage chart to the solution concentration obtained a sensitivity of 0.008 V for every addition concentration and regression value (R^2 = 90.265 %) which shows a linear response. Furthermore, measurement performance at the phosphate sensor resulted has shown that response linear [13][15].

Therefore, the output voltage at the electrode test can be used as a sensor to detect phosphate ions. The output response sensor performance of the average voltage from the electrode is shown in Figure 7. Improvement is achieved result compared to previous research, the analytic parameter sensor phosphate detection is shown Table 2.

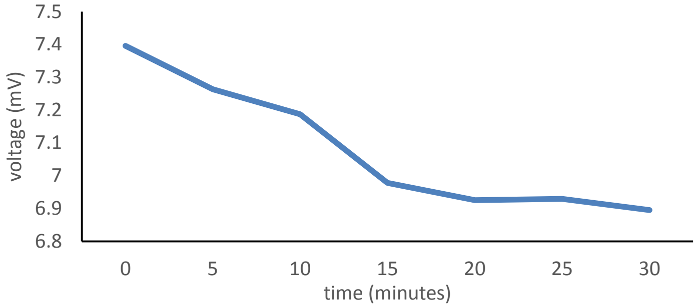

Figure 6. Output response stability reference electrode

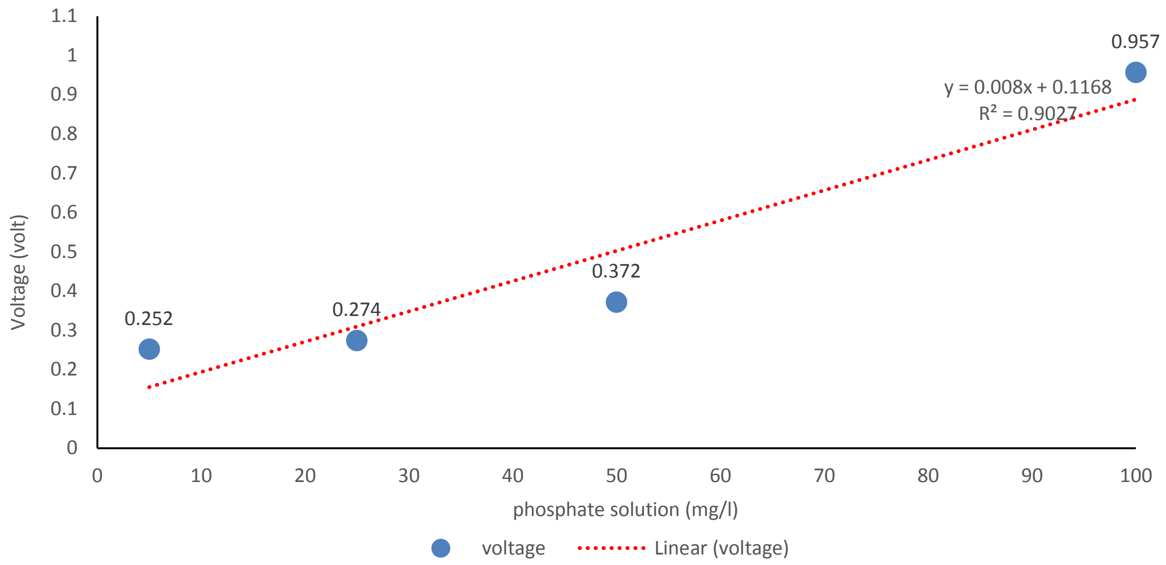

Figure 7. Output response performance sensorparticles

Table 2.
Comparison of analytic parameter phosphate detection with a different electrochemical sensor

No	Electrodes	Composition	Method	Linear range	Limit of detection	Ref
1	CBNPs	Phosphate and molybdate	Amperometric	6 to 20 µM	6 µM	[4]
2	CBNPs-SPEs	Molyb date phosphate	Cyclic voltametry	0.5 to 100 µM	0.1 µM	[6]
3	Paper CB-SPE	Molyb date, H_2SO_4, and KCl	Cyclic voltametry	1 to 300 µM	4 µM	[5]
4	SPCE	AMT/AgNWs	Cyclic voltametry	5 µM to 1mM	3 µM	[14]
5	SPCE	PPy, DAP and water de-ionized	Galvanostatic	5 to 100 mg/l	5 mg/l	This work

IV. Conclusion

Sensitive membrane coating that uses polymer polypyrrole doped with di-ammonium phosphate was successfully implemented using the electropolymerization method. The occurrence of electropolymerization is shown by the output current flowing in the electrode ranging from 0.2 to 0.03 mA. The sensitive membrane layer in the SEM test shows that it is evenly distributed on the surface of the electrode and spherical. According to the EDS test, it showed the percentage of each atom those are carbon (C) 86.95 %, nitrogen (N) 6.94 %, oxygen (O) 5.9 %, and phosphate (P) 0.21 %. The stability test of reference versus commercial electrodes shows a stable voltage output in the range of 6.8 to 7.4 mV. The performance testing at a concentration of 5 to 100 mg/l phosphate standard solution - shows the output voltage ranges from 0.252 V to 0.957 V, with a sensitivity of 0.008 V for every addition concentration and linear regression performance of sensor ion phosphate (R^2 = 90.267 %). According to the testing, as the results, the electrode is capable of detecting the phosphate ion.

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Declarations

Author contribution

Norfriyani contributed as the main contributor of this paper. All authors read and approved the final paper.

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Conflict of interest

The authors declare no known conflict of financial interest or personal relationships that could have appeared to influence the work reported in this paper.

Additional information

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References

[1] V. I. Adamchuk, J. W. Hummel, M. T. Morgan, and S. K. Upadhyaya, "On-the-go soil sensors for precision agriculture," *Comput. Electron. Agric.*, vol. 44, no. 1, pp. 71–91, Jul. 2004.

[2] L. Tymecki, S. Glab, and R. Koncki, "Miniaturized, Planar Ion-selective Electrodes Fabricated by Means of Thick-film Technology," *Sensors*, vol. 6, no. 4, pp. 390–396, Apr. 2006.

[3] D. Pathania, M. Thakur, G. Sharma, and A. K. Mishra, "Tin (IV) phosphate/poly(gelatin-cl-alginate) nanocomposite: Photocatalysis and fabrication of potentiometric sensor forPb (II),"

Mater. Today Commun., vol. 14, no. November 2017, pp. 282–293, Mar. 2018.

[4] D. Talarico, S. Cinti, F. Arduini, A. Amine, D. Moscone, and G. Palleschi, "Phosphate Detection through a Cost-Effective Carbon Black Nanoparticle-Modified Screen-Printed Electrode Embedded in a Continuous Flow System," *Environ. Sci. Technol.*, vol. 49, no. 13, pp. 7934–7939, Jul. 2015.

[5] S. Cinti, D. Talarico, G. Palleschi, D. Moscone, and F. Arduini, "Analytica Chimica Acta Novel reagentless paper-based screen-printed electrochemical sensor to detect phosphate," *Anal. Chim. Acta*, vol. 919, pp. 78–84, 2016.

[6] D. Talarico, F. Arduini, A. Amine, D. Moscone, and G. Palleschi, "Screen-printed electrode modified with carbon black nanoparticles for phosphate detection by measuring the electroactive phosphomolybdate complex," *Talanta*, vol. 141, pp. 267–272, Aug. 2015.

[7] S. Shahrokhian and E. Asadian, "Electrochemical determination of l-dopa in the presence of ascorbic acid on the surface of the glassy carbon electrode modified by a bilayer of multi-walled carbon nanotube and poly-pyrrole doped with tiron," *J. Electroanal. Chem.*, vol. 636, no. 1–2, pp. 40–46, Nov. 2009.

[8] K. Xu, Y. Kitazumi, K. Kano, and O. Shirai, "Phosphate ion sensor using a cobalt phosphate coated cobalt electrode," *Electrochim. Acta*, vol. 282, pp. 242–246, Aug. 2018.

[9] M. Boota, B. Anasori, C. Voigt, M. Zhao, M. W. Barsoum, and Y. Gogotsi, "Pseudocapacitive Electrodes Produced by Oxidant-Free Polymerization of Pyrrole between the Layers of 2D Titanium Carbide (MXene)," *Adv. Mater.*, vol. 28, no. 7, pp. 1517–1522, Feb. 2016.

[10] U. Baig, R. A. K. Rao, A. A. Khan, M. M. Sanagi, and M. A. Gondal, "Removal of carcinogenic hexavalent chromium from aqueous solutions using newly synthesized and characterized polypyrrole–titanium(IV)phosphate nanocomposite," *Chem. Eng. J.*, vol. 280, no. Iv, pp. 494–504, Nov. 2015.

[11] Xiaochen Wang, J. Church, Woo Hyoung Lee, and H. J. Cho, "Phosphate sensors based on Co-Cu electrodes fabricated with a sacrificial glass fiber paper template," in *2015 IEEE SENSORS*, Nov. 2015, pp. 1–4.

[12] W. Zhou, R. Apkarian, Z. L. Wang, and D. Joy, "Fundamentals of Scanning Electron Microscopy (SEM)," in *Scanning Microscopy for Nanotechnology*, New York, NY: Springer New York, 2006, pp. 1–40.

[13] R. V. Manurung, T. M. S. Soegandhi, and Hiskia, "Electropolymerization of Pyrrole in Aqueous Solution on Carbon Electrodes for Ion Sensor," in *Proc. of International Conference on Materials Engineering (ICME)*, 2010, no. November 2010, pp. 0–3.

[14] M. F. Kabir, M. T. Rahman, A. Gurung, and Q. Qiao, "Electrochemical Phosphate Sensors Using Silver Nanowires Treated Screen Printed Electrodes," *IEEE Sens. J.*, vol. 18, no. 9, pp. 3480–3485, May 2018.

[15] S. Berchmans, R. Karthikeyan, S. Gupta, G. E. J. Poinern, T. B. Issa, and P. Singh, "Glassy carbon electrode modified with hybrid films containing inorganic molybdate anions trapped in organic matrices of chitosan and ionic liquid for the amperometric sensing of phosphate at neutral pH," *Sensors Actuators B Chem.*, vol. 160, no. 1, pp. 1224–1231, Dec. 2011.