

GLUCOSE SENSOR USING CYCLIC VOLTAMMETRIC METHOD BASED ON NiO/ITO ELECTRODE

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ARTICLE INFO		ABSTRACT
Received:	14/4/2021	Nickel oxide/Indium Tin Oxide (NiO/ITO) electrode was fabricated by electrodeposition method using the three-electrode system from 0.1 M NiSO ₄ and 0.1 M H ₂ SO ₄ electrolyte support solution to form Ni/ITO followed by oxidation in the air to convert Ni to NiO. The morphology and crystalline structure of NiO were characterized by SEM (Scanning Electron Microscope), XRD (X-Ray Diffraction), and Raman spectroscopy. The cyclic voltage method was used to investigate NiO/ITO electrode's electrochemical properties in the alkaline medium of NaOH solution and determine the glucose concentration. The conditions for Ni deposition onto ITO substrate were 0.1 M NiSO ₄ , electrolyte support of 0.1 M H ₂ SO ₄ under deposition potential -1.2 V (vs. Ag/AgCl reference electrode) for 360 seconds. The cyclic voltammetry (CV) technique method to determine the concentration of glucose showed the linear range detection of 0 to 500 µM, R = 0.9885 with high sensitivity of 2088 µAcm ⁻² mM ⁻¹ for positive scan and 0.5 to 13 mM, R = 0.9966 for negative scan, the detection limit of 5 µM.
Revised:	14/5/2021	
Published:	20/5/2021	
KEYWORDS		
Nickel oxide		
Chronoamperometry		
Cyclic voltammetry		
Glucose sensor		
Nonenzymatic		

CẢM BIẾN GLUCOSE SỬ DỤNG PHƯƠNG PHÁP QUÉT THỂ VÒNG DỰA TRÊN ĐIỆN CỰC NiO/ITO

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THÔNG TIN BÀI BÁO		TÓM TẮT
Ngày nhận bài:	14/4/2021	Điện cực NiO/ITO được chế tạo bằng phương pháp điện phân Ni từ dung dịch NiSO ₄ 0,1 M; với chất điện li hỗ trợ H ₂ SO ₄ 0,1 M sử dụng hệ ba điện cực để hình thành nên điện cực Ni/ITO sau đó oxi hóa trong không khí để chuyển Ni thành NiO. Hình thái học và cấu trúc của vật liệu được đo bằng phương pháp hiển vi điện tử quét (SEM), nhiễu xạ tia X (XRD) và phổ Raman. Phương pháp quét thể vòng được sử dụng để khảo sát tính chất của điện cực NiO/ITO trong dung dịch NaOH 0,1 M đối với glucose và đồng thời dùng để định lượng glucose trong dung dịch. Điều kiện để lắng đọng điện hóa Ni lên đế ITO trong dung dịch NiSO ₄ 0,1 M: với chất điện li hỗ trợ H ₂ SO ₄ 0,1 M ở thế -1,2 V (so với điện cực so sánh bạc/bạc clorua trong KCl bão hòa) với thời gian 360 giây. Phương pháp quét thể vòng xác định nồng độ glucose trong dung dịch cho thấy khoảng tuyến tính từ 0 đến 500 µM, R = 0,9885 độ nhạy 2088 µAcm ⁻² mM ⁻¹ cho chiều quét dương và từ 0,5 đến 13 mM, R = 0,9966 cho chiều quét âm, giới hạn phát hiện 5 µM.
Ngày hoàn thiện:	14/5/2021	
Ngày đăng:	20/5/2021	
TỪ KHÓA		
Niken oxit		
Chronoamperometry		
Quét thể vòng		
Cảm biến glucose		
Phi enzyme		

DOI: <https://doi.org/10.34238/tnu-jst.4337>

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1. Introduction

NiO is one of the materials that have many of these applications today, such as gas sensors [1], [2], supercapacity [3] - [5], magnetism [6], [7], etc., in which the electrochemical glucose sensor is one of the fields which have been interested and attracts many researchers. Glucose sensor plays an important role in the diagnosis of diabetes by signaling high levels of glucose in the blood [8], [9]. The glucose electrochemical sensor makes it portable, easy to fabricate, and usable at home, so it plays a big role in rapid diagnosis and continuous monitoring [8]. Although the enzymatic glucose biosensor has evolved to the third generation, the limitations of the enzyme electrode due to the nature of the enzyme are susceptible to denaturation by temperature, pH, and required stored at low temperature and complex enzyme immobilization process that prevented the application of it in the real sample. Therefore, the nonenzymatic glucose sensor was introduced as the fourth generation glucose sensor to overcome these limitations [10]. Materials with electrochemical catalytic activities have been focused on studying, such as novel metals Pt, Au, and Pd [11] - [13], transition metals Ni, Cu [14], [15] and compound of them CuO, NiO, CuS [8], [9], [16], [17]. However, although novel metals have high sensitivity, the electrode is poisoned by the environment and slow reaction kinetics. In contrast, the Cu and Ni metal-based electrodes show high sensitivity, but they are susceptible to toxicity by chloride ions [10]. NiO is one of the materials that has overcome these problems and is highly sensitive, inexpensive, and easy to fabricate. There is much research focusing on NiO materials because of various fabrication methods such as the sputtering method, hydrothermal [18], [19], etc. However, in order to form an electrode, it is necessary to have NiO fixed on the conductive substrate to ensure good adhesion and stability. Therefore, in this study, we directly create Ni film on ITO conductive substrate by electrolysis method using the three-electrode system from 0.1 M NiSO₄ solution in 0.1M H₂SO₄ support electrolyte followed by oxidation in the air to convert Ni to NiO and use the made NiO/ITO electrodes that are used in glucose electrochemical sensors without the use of enzymes.

2. Experimental method

2.1. Chemicals and apparatus

Chemicals of glucose, NiSO₄·6H₂O (the purity of 98%), concentrated H₂SO₄ were purchased from Sigma-Aldrich company. Other solvents such as ethanol and acetone were purchased from Xilong Chemical Company, China. Twice distilled water was distilled from STUART A4000D. The ITO substrates were cut into dimensions of 0.5 x 2 cm and then ultrasonic vibrating in turn in water, ethanol, and acetone solvents to clean the substrate surface. The potentiostat galvanostat machine the Autolab 302N was connected to the three-electrode system including the working electrode as the research electrode, platinum sheet as the counter electrode, and Ag/AgCl electrode (Ag, AgCl|saturated KCl) as the reference electrode. The above device was used to fabricate electrodes as well as investigate the electrochemical properties of glucose for research electrodes. The crystalline structure and the morphology of the NiO onto the ITO substrate were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) and scanning electron microscope (SEM, Hitachi S-4800), respectively.

2.2. Preparation of NiO/ITO electrode

Ni was deposited onto ITO substrate using electrodeposition at the potential of -1.2 V (vs. Ag/AgCl) from the solution of 0.1 M NiSO₄ and 0.1 M H₂SO₄ as supporting electrolyte using three-electrode systems in which ITO acted as the working electrode in Autolab 302N machine to form Ni/ITO electrode. After that, Ni/ITO electrode was cleaned with distilled water followed by oxidation at 400 °C in the air for 2 hours to form NiO/ITO electrode. An epoxy layer was covered partially to the electrode surface to fix the area of 0.5 x 0.5 cm (0.25 cm²) of the working area.

3. Results and discussion

3.1. The morphology and structure of the material

Figure 1 (a) presents the morphology of NiO onto ITO substrate that indicate the nano-size of NiO particle around 30 nm diameter. Figure 1 (b) shows XRD of NiO onto ITO substrate with atomic planes of (200) and (220) while the index of * belongs to ITO substrate.

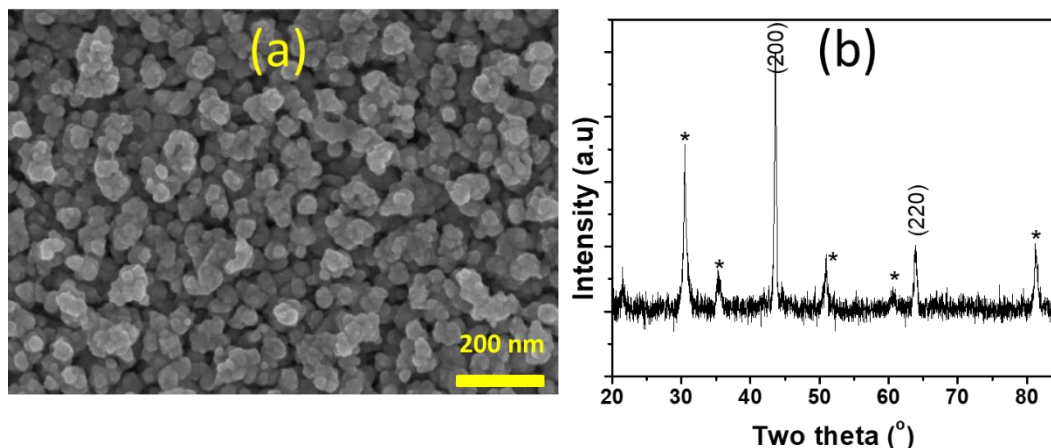


Figure 1. (a) SEM image and (b) XRD pattern of NiO onto ITO substrate

Using the Scherrer formula, the average crystallite size, L , is:

$$L = \frac{K\lambda}{\beta \cos \theta}$$

where λ is the X-ray wavelength in nanometer (nm), in this case $\lambda = 0.154$, β is the peak width of the diffraction peak profile at half maximum height from Figure 1 (b) of the plane (200), K is a constant related to crystallite shape, normally taken as 0.89. The angle value θ is 19.9° corresponding to the highest peak of the plane (200).

As a result, $L = 25.3$ nm was near the value observed in the SEM image. This result may suggest that each particle has a monocrystalline structure.

3.2. Effect of electrolyte solution on electrolysis at ITO electrode

The electrolysis process of Ni precipitation on ITO substrates was investigated through a CV scan from + 0.8 V to -2 V with a scan rate of 20 mV/s when immersing the ITO substrate in 0.1 M NiSO₄ solution with supporting electrolyte 0.1 M H₂SO₄. Results are shown in Figure 2.

Figure 2 shows that there was almost no current at a negative scan from + 0.8V until the cathode current (negative current) appeared at about -0.9 V, the cathode current rapidly increased and almost saturated at about 1.2 V. At inverse scan (positive scan), cathode current decreased and almost zero at about -0.6 V that much lower compared to positive scan. It can be explained that at the negative scan, the electrode was ITO, but at the positive scan, the electrode was Ni/ITO. At a potential of about -0.4 V, the anode current appeared and achieved a maximum at the potential of +0.1 V and +0.3 V with a smaller current. The peak at +0.1 V may be related to the dissolution of Ni ($\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$) that the value reported in [20] with nearly the same condition of pH of the electrolyte solution (CV of PANI in 0.5 M NiSO₄; 0.1 M H₂SO₄) was 0.2 V and in [21] with pH of 1.2 of it (CV of p-silicon in 5 M fluoride aqueous solution of pH 1.2; 50 mM NiSO₄) was about +0.0 V. The higher potential peak at +0.3 V may be related to water electrolysis ($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$) due to the easier oxidation of Ni than that of water. Based on the characters of electrodeposition of Ni on ITO using investigating CV above, the potential of -1.2 V was selected to deposit Ni on ITO in chronoamperometry technique.

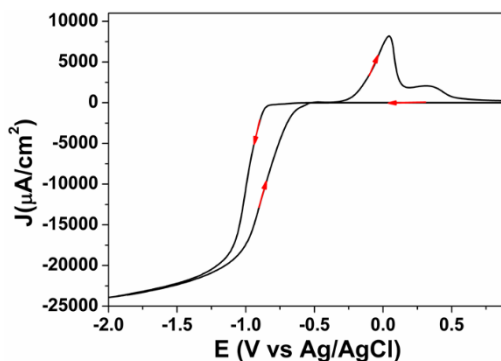


Figure 2. The CV of the ITO electrode in a solution of 0.1 M NiSO_4 ; 0.1 M H_2SO_4

3.3. Electrochemical properties of NiO/ITO electrode to glucose in 0.1 M NaOH

The CV of NiO/ITO electrode in 0.1 M NaOH with different scan rates and plot the anode current and cathode current vs. the square root of scan rate is shown in Figure 3. The linearity of peak current proved the diffusion-controlled kinetics of the CV reaction at the electrode.

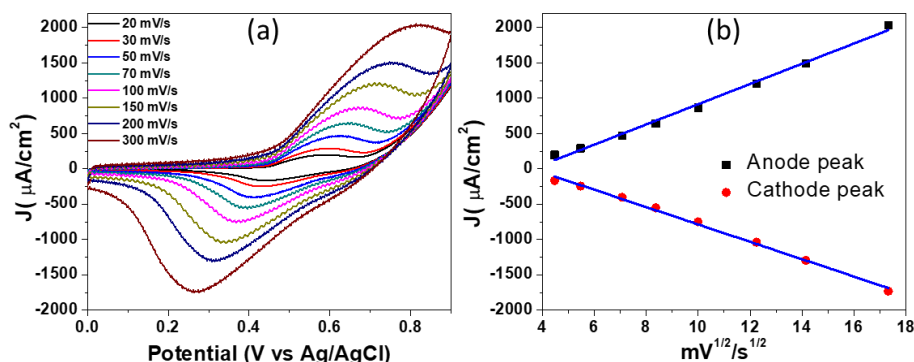


Figure 3. (a) CV of NiO/ITO electrode (for deposition time of 360 s) in 0.1 M NaOH and (b) cathode current vs. the square root of scan rate

Figure 4 (a) shows CV of NiO/ITO electrode in 0.1 M NaOH with different glucose concentrations (0; 0.5; 1; 2; 3; 4; 5 mM). Separating positive scan and negative scan is shown in Figure (b) and (c), respectively.

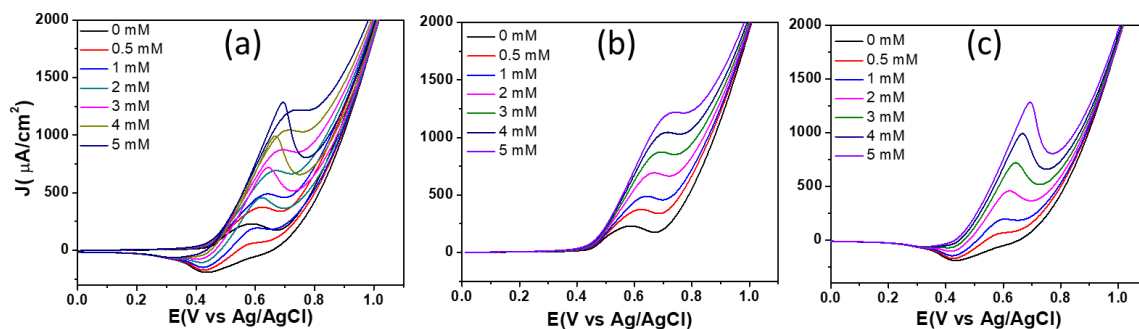


Figure 4. The CV of NiO/ITO electrode (with Ni electrodeposition time of 360 s) in 0.1 M NaOH with different glucose concentration

The current density increases vs. the increase of glucose concentration proved the oxidation of glucose at the electrode. As seen at the negative scan, the oxidation peak was sharper than the positive peak at higher glucose concentration (higher 0.5 mM) but less sharpness than that at lower concentration (0.5 mM). In order to optimize the Ni electrodeposition time, the NiO/ITO electrodes with different time of Ni electrodeposition times of 60; 120; 180; 360; 600 seconds were fabricated. Figure 5 performs the CV of these electrodes in 0.1 M NaOH with different glucose concentrations and shows the results in the negative scan.

As can be seen, in Figure 5 (a-e), it was found that the current density of glucose oxidation increased with the increase of glucose concentration and the oxidation potential peak tended to shift to more positive potential. This trend can be explained that the reaction products accumulated on the electrode surface at high concentrations leading to higher glucose oxidation potential.

Figure 5 (f) shows that the slope of the dependent oxidation peak current density on glucose concentration was maximum for the sample fabricated at Ni electrodeposition time of 360 seconds. Therefore, the electrode position condition Ni with time 360 seconds was chosen as the optimal condition.

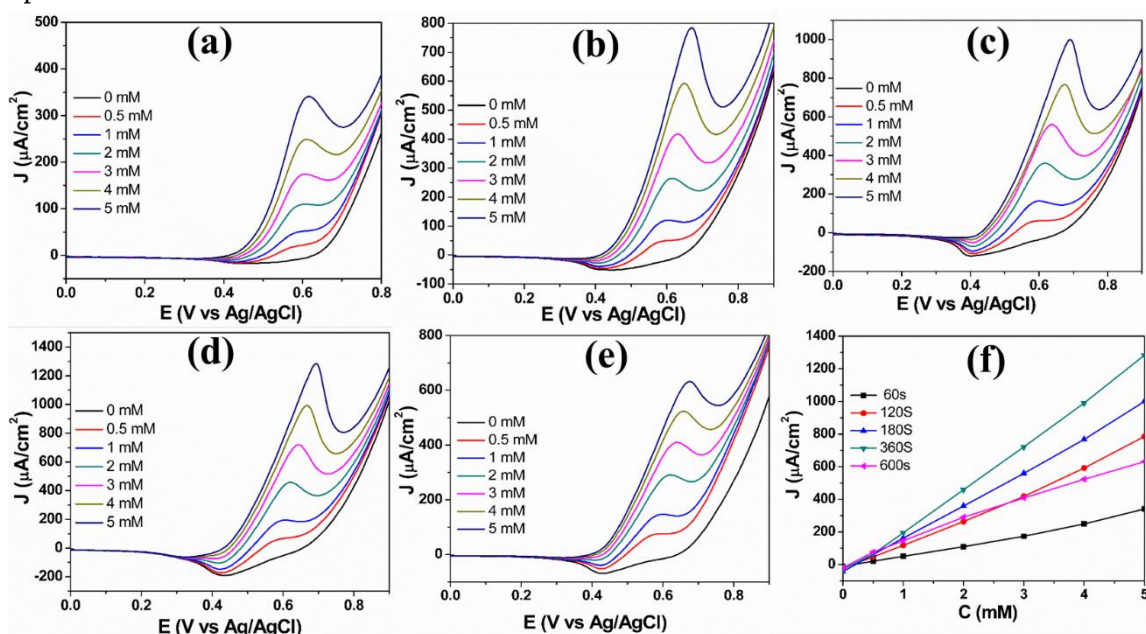


Figure 5. The CV of NiO/ITO electrodes in 0.1 M NaOH with different time of Ni electrodeposition (60; 120; 180; 360; and 600 s) in negative scan (a-e) and (f) the plot of peak current density on glucose concentration of them

3.4. CV technique to quantify glucose concentration in solution

The CV of NiO/ITO electrodes (potential and time for electrodeposition of -1.2 V and 360s, respectively) at different concentrations of glucose in 0.1M NaOH solution were presented in Figure 6. As the results, in the range of glucose concentrations below 0.5 mM, the glucose oxidation peak current in the positive scan increased linearly, but at higher concentrations, the linearity was poor (Figure 6a). Whereas for the negative scan at the glucose concentration below 0.5 mM, the current did not increase significantly, but at higher concentrations, the current increased steadily, and the linearity was very wide (Figure 6b). Therefore, we constructed two standard curves, one with a positive scan peak current at a glucose concentration of 0 to 0.5 mM and one for a peak current in the negative scan at a glucose concentration of 0.5 mM and higher. The sensitivity was calculated from the slope of the calibration curve results in the linear range of

0 μM to 500 μM , the sensitivity of $2088 \mu\text{Acm}^{-2}\text{mM}^{-1}$, $R = 0.9885$, and the wide linear range of 0.5 mM to 13 mM, the sensitivity of $165.5 \mu\text{Acm}^{-2}\text{mM}^{-1}$, $R = 0.9966$. The detection limit estimated via a signal to noise equal to 3 was 5 μM . Comparison with the results of previous studies of CuO and NiO in glucose sensor (Table 1) shows that this result is good for the synthesis of NiO nanoparticle by simple method but high effectiveness such as the sensitivity and wide linear range.

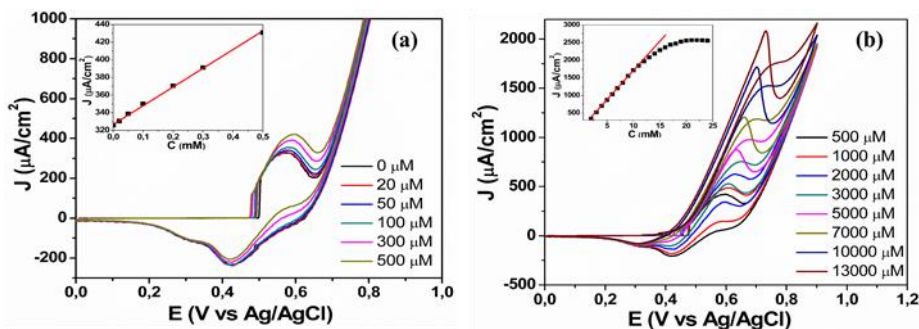


Figure 6. The CV of NiO/ITO in 0.1 M NaOH at different glucose concentration: (a) concentration of 0 to 0.5 mM, insert Figure (a) plot the peak current on glucose concentration; b) concentration of higher 0.5 mM to 1.3 mM; insert Figure (b) plot the peak current on glucose concentration

Table 1. Analytical parameters obtained for different glucose sensors

Electrode	Electrolyte	Applied potential (V)	Linear range (μM)	Limit of detection (μM)	Sensitivity ($\mu\text{Acm}^{-2}\text{mM}^{-1}$)	Ref.
CuO NPs	0.1 M NaOH	CV	10 - 4000	3	848.86	[8]
CuO/SWCNTs	0.1 M NaOH	+0.45	0.05 - 1800	0.05	1610	[10]
NiO/SWCNTs	0.1 M NaOH	+0.5	1 - 1000	1	907	[22]
NiO/CuO/PANI	0.1 M NaOH	+0.6	20 - 5000	2	-	[23]
NiO/GNS	0.1 M NaOH	+0.5	5-4200	5	667.71	[24]
Ni/NiO/CNTs	0.1 M NaOH	+0.53	8 - 1500	-	636.08	[25]
			2000 - 5000		284.58	
CuO/ITO film	0.1 M NaOH	+0.45	1 - 3600	0.61	283.6	[26]
CuO/ITO	0.1M NaOH	CV	0 - 3000	20	470.6	[27]
CuO/ITO	0.1 M NaOH	+0.5	10 - 4200	10	303.13	[28]
NiO/ITO	0.1 M NaOH	CV	0 - 500	5	2088	This
			500 - 13000		165.5	work

4. Conclusion

NiO/ITO electrode was fabricated by electrodeposition of Ni from the solution containing 0.1 M NiSO_4 and 0.1 M H_2SO_4 at a potential of -1.2V (V vs. Ag/AgCl) in 360 s. The CV was utilized to investigate the electrode's electrochemical properties and used to quantify glucose concentration in a solution by establishing the standard derivation curve. The NiO/ITO electrode exhibited high sensitivity of $2088 \mu\text{Acm}^{-2}\text{mM}^{-1}$ with a linear range of 0 to 500 μM (using positive scan), the detection limit of 5 μM ; the sensitivity of $165.5 \mu\text{Acm}^{-2}\text{mM}^{-1}$ (using negative scan) with a linear range of 0.5 mM to 13 mM.

REFERENCES

- [1] U.T. Nakate, R. Ahmad, P. Patil, Y. Yu, and Y.B. Hahn, "Ultra thin NiO nanosheets for high performance hydrogen gas sensor device," *Applied Surface Science*, vol. 506, pp. 144971, 2020.

- [2] Q. Zhou, W. Zeng, W. Chen, L. Xu, R. Kumar, and A. Umar, "High sensitive and low-concentration sulfur dioxide (SO₂) gas sensor application of heterostructure NiO-ZnO nanodisks," *Sensors and Actuators B: Chemical*, vol. 298, pp. 126870, 2019.
- [3] T. Liu, L. Zhang, B. Cheng, W. You, and J. Yu, "Fabrication of a hierarchical NiO/C hollow sphere composite and its enhanced supercapacitor performance," *Chemical Communications*, vol. 54, pp. 3731 - 3734, 2018. .
- [4] W. Sun, L. Xiao, and X. Wu, "Facile synthesis of NiO nanocubes for photocatalysts and supercapacitor electrodes," *Journal of Alloys and Compounds*, vol. 772, pp. 465 - 471, 2019.
- [5] S. Xiong, S. Jiang, J. Wang, H. Lin, M. Lin, S. Weng, et al., "A high-performance hybrid supercapacitor with NiO derived NiO@ Ni-MOF composite electrodes," *Electrochimica Acta*, vol. 340, pp. 135956, 2020.
- [6] K. Amemiya and M. Sakamaki, "Effect of Electric Field on Magnetism of Ni Thin Films via Antiferromagnetic NiO," *e-Journal of Surface Science and Nanotechnology*, vol. 16, pp. 186 - 189, 2018.
- [7] M. Sakamaki and K. Amemiya, "Effect of interface NiO layer on magnetism in Fe/BaTiO₃ thin film," *Japanese Journal of Applied Physics*, vol. 57, pp. 0902B9, 2018.
- [8] N. Q. Dung, T. T. T. Duong, T. D. Lam, D. D. Dung, N. N. Huy, and D. V. Thanh, "A simple route for electrochemical glucose sensing using background current subtraction of cyclic voltammetry technique," *Journal of Electroanalytical Chemistry*, vol. 848, pp. 113323-8, 2019.
- [9] N. Q. Dung, T. T. T. Duong, T. D. Lam, D. D. Dung, N. N. Huy, and D. V. Thanh, "Communication—A Simple Empirical Method for Determination of CuOOH/CuO Redox Couple in Electrochemical Nonenzymatic Glucose Sensing," *Journal of The Electrochemical Society*, vol. 168, pp. 017506, 2021.
- [10] N. Q. Dung, D. Patil, H. Jung, and D. Kim, "A high-performance nonenzymatic glucose sensor made of CuO-SWCNT nanocomposites," *Biosensors and Bioelectronics*, vol. 42, pp. 280 - 286, 2013.
- [11] Y.H. Wei, C.K. Hsieh, and F.G. Tseng, "Highly-sensitive non-enzymatic glucose sensor via nano platinum crystals fabricated by phase-controlled electrochemical deposition," *Journal of The Electrochemical Society*, vol. 165, pp. B48, 2018.
- [12] G.X. Zhong, W.X. Zhang, Y.M. Sun, Y.-Q. Wei, Y. Lei, H.P. Peng, et al., "A nonenzymatic amperometric glucose sensor based on three dimensional nanostructure gold electrode," *Sensors and Actuators B: Chemical*, vol. 212, pp. 72 - 77, 2015.
- [13] J. S. Ye, C. W. Chen, and C. L. Lee, "Pd nanocube as non-enzymatic glucose sensor," *Sensors and Actuators, B: Chemical*, 208, pp. 569 - 574, 2015.
- [14] S. Marini, N. Ben Mansour, M. Hjiri, R. Dhahri, L. El Mir, C. Espro, et al., "Non-enzymatic Glucose Sensor Based on Nickel/Carbon Composite," *Electroanalysis*, vol. 30, pp. 727 - 733, 2018.
- [15] H. Chen, G. Fan, J. Zhao, M. Qiu, P. Sun, Y. Fu, et al., "A portable micro glucose sensor based on copper-based nanocomposite structure," *New Journal of Chemistry*, vol. 43, pp. 7806 - 7813, 2019.
- [16] R. Ahmad, M. Khan, N. Tripathy, M. I. R. Khan, and A. Khosla, "Hydrothermally Synthesized Nickel Oxide Nanosheets for Non-Enzymatic Electrochemical Glucose Detection," *Journal of The Electrochemical Society*, vol. 167, pp. 107504, 2020.
- [17] M. Cao, H. Wang, P. Kannan, S. Ji, X. Wang, Q. Zhao, et al., "Highly efficient non-enzymatic glucose sensor based on CuxS hollow nanospheres," *Applied Surface Science*, vol. 492, pp. 407 - 416, 2019.
- [18] P. Salunkhe, M. A. AV, and D. Kekuda, "Investigation on tailoring physical properties of Nickel Oxide thin films grown by dc magnetron sputtering," *Materials Research Express*, vol. 7, pp. 016427, 2020.
- [19] K. Nguyen, N. D. Hoa, C. M. Hung, D. T. T. Le, N. V. Duy, and N. V. Hieu, "A comparative study on the electrochemical properties of nanoporous nickel oxide nanowires and nanosheets prepared by a hydrothermal method," *RSC advances*, vol. 8, pp. 19449 - 19455, 2018.
- [20] T. Trung, T. H. Trung, and C. S. Ha, "Preparation and cyclic voltammetry studies on nickel-nanoclusters containing polyaniline composites having layer-by-layer structures," *Electrochimica Acta*, vol. 51, pp. 984-990, 2005.
- [21] P. Gorostiza, M. A. Kulandainathan, R. Díaz, F. Sanz, P. Allongue, and J. R. Morante, "Charge Exchange Processes during the Open-Circuit Deposition of Nickel on Silicon from Fluoride Solutions," *Journal of The Electrochemical Society*, vol. 147, pp. 1026-1030, 2000.

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- [22] N. Q. Dung, D. Patil, H. Jung, J. Kim, and D. Kim, "NiO-decorated single-walled carbon nanotubes for high-performance nonenzymatic glucose sensing," *Sensors and Actuators, B: Chemical*, vol. 183, pp. 381 - 387, 2013.
- [23] K. Ghanbari and Z. Babaei, "Fabrication and characterization of non-enzymatic glucose sensor based on ternary NiO/CuO/polyaniline nanocomposite," *Analytical biochemistry*, vol. 498, pp. 37 - 46, 2016.
- [24] G. Zeng, W. Li, S. Ci, J. Jia, and Z. Wen, "Highly dispersed NiO nanoparticles decorating graphene nanosheets for non-enzymatic glucose sensor and biofuel cell," *Scientific reports*, vol. 6, pp. 1-8, 2016.
- [25] H. Yin, J. Zhu, J. Chen, J. Gong, and Q. Nie, "MOF-derived in situ growth of carbon nanotubes entangled Ni/NiO porous polyhedrons for high performance glucose sensor," *Materials Letters*, vol. 221, pp. 267 - 270, 2018.
- [26] T. T. T. Duong, N. Q. Dung, T. D. Lam, P. H. Chuyen, and N. T. Dai, "Facile synthesis of CuO/ITO film via the chronoamperometric electrodeposition for nonenzymatic glucose sensing," *Communications in Physics*, vol. 30, pp. 161-170, 2020.
- [27] N. Q. Dung, D. T. Huong, N. V. Tien, and N. H. Nhung, "A cyclic voltage method for glucose electrochemical sensor based on CuO/ITO electrode," *Journal of Physical, Chemical and Biological analysis*, (in Vietnamese), vol. 22, pp. 98-105, 2017.
- [28] T. T. T. Duong, N. Q. Dung, and T. D. Lam, "Chronoamperometry technique in glucose sensor based on CuO/ITO electrode," *Journal of Chemistry*, (in Vietnamese), vol. 56 (3E12), pp. 15-20, 2018.