

**O 70. FEW-LAYER GRAPHENE COATED ON INDIUM TIN OXIDE ELECTRODE
PREPARED BY CHEMICAL VAPOR DEPOSITION AND THEIR ENHANCED
GLUCOSE ELECTROOXIDATION ACTIVITY**

Aykut Caglar¹, Berdan Ulas¹, Sibel Uygun^{2*}, Hilal Kivrak¹ and Ozlem Sahin²

¹*Van Yuzuncu Yil University, Faculty of Engineering, Department of Chemical Engineering, Van
65000, Turkey*

²*Konya Technical University, Faculty of Engineering, Chemical Engineering Department, 42031
Konya, Turkey*

E-mail: ozlem@selcuk.edu.tr

ABSTRACT: At present, few-layer graphene is deposited on copper (Cu) foil by chemical vapor deposition (CVD) method. The methane flow rate, hydrogen flow rate, and deposition time parameters with CVD method are transferred on Cu foil. Then, the graphene on the Cu foil is coated onto few-layer the indium tin oxide (ITO) electrode for glucose electrooxidation. These electrode is characterized by Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis (SEM-EDX) and Raman Spectroscopy. Furthermore, glucose electrooxidation is examined with cyclic voltammetry (CV) and chronoamperometry (CA).

Keywords: Fuel cells, Glucose Electrooxidation, Chemical Vapor Deposition.

1. INTRODUCTION

Energy needs have increased due to raising population and growing industry in the world. Hence, alternative energy sources are examined to satisfy the energy needs (Çağlar, Aldemir et al. 2018, Ulas, Caglar et al. 2018). Fuel cells are renewable energy sources that is clean, efficient, and promising for the future (Caglar, Sahan et al. 2018). Different types of fuel cells are presented such as direct formic acid fuel cells (DFAFCs) (Ulas, Caglar et al. 2018), direct ethanol fuel cells (DEFCs) (Sahin, Duzenli et al. 2016), direct methanol fuel cells (DMFCs) (Kivrak, Can et al. 2014), and direct glucose fuel cells (DGFCs) (Zhiani, Abedini et al. 2018). Glucose (C₆H₁₂O₆) is the most abundant monosaccharide in nature (Basu and Basu 2011). When the glucose is fed with an alkali membrane, it could produce 24 electrons for the complete oxidation of CO₂ (Li, Scott et al. 2013). In addition, literature studies with PdSn (Brouzgou, Song et al. 2014), PdRh (Brouzgou, Yan et al. 2014), PdAu (Yan, Brouzgou et al. 2014), NiCo (Gao, Liu et al. 2018), and PtPdAu (Basu and Basu 2012) catalysts were developed for the glucose electrooxidation.

Graphene has a hexagonal, single-atom, and two-dimensional (2D) sp²-hybrid carbon atom layer separated from 3D structured graphite (Bollella, Fusco et al. 2017). Graphene production techniques have been known such as Hummers method, sublimation of 4H-SiC, electrochemical reduction, and chemical vapor deposition (CVD). Among these methods, CVD layer system formed on the surface of a solid material is a short-time and simple method (Tan, Jayawardena et al. 2012). Vapor carrier gas exposes to the surface of a material via heating in a closed container, mostly used in graphene synthesis. At present, the few-layer graphene was coated on Cu foil by the CVD method. The few-layer graphene were transferred on Cu foil with 5 sccm hexan flow rate, 20 sccm hydrogen flow rate, and 20 min deposition time parameters via CVD method. The few-layer graphene on the Cu foil was then coated onto few-layer the ITO electrode. ITO electrode was used as working electrode for electrochemical measurements in three electrode system. The few-layer graphene/ITO electrode was characterized by SEM-EDX and Raman Spectroscopy measurements. To investigate their glucose electrooxidation activities, CV and CA electrochemical measurements were used.

2. MATERIAL AND METHOD

2.1. The Few Layer Graphene Synthesis

The few layer graphene was coated on Cu foil with the CVD method. Firstly, Cu foil was cleaned with acetone and isopropyl alcohol. Then, Cu film was annealed at temperatures of 900-1000 °C to raise grain size under an atmosphere of Ar/H₂. After Cu foil was annealed, hydrogen gas was fed into the reactor medium for time. The reactor temperature was set to 950 °C. After the temperature reached the desired value, it was exposed to reactor medium 50 sccm hydrogen gas. Then, the reactor medium was fixed to 5 sccm hexane for 20 min. Finally, the reactor was brought to room temperature.

2.2. Transfer of Few-Layer Graphene/ITO Electrode

The protective polymer layer polymethylmethacrylate (PMMA) was utilized for transfer graphene to ITO surface. PMMA was covered on the graphene surface. Firstly, the amount of PMMA in powder structure was weighed and suffixed to glass bottle including chloroform. Then, the graphene-coated Cu foil was placed on the rotating table. PMMA solution was added onto the graphene and the coating was initiated. After this process, the sample was get onto a plate and it was completely dried graphene surface at 90 °C for 2 min.

2.3. Physical Characterization

Few-layer graphene/ITO electrode was characterized by SEM-EDX and Raman Spectroscopy. SEM-EDX measurement was obtained utilizing the zeiss sigma 300 to scan the surface of few-layer graphene. Raman spectroscopy of few-layer graphene/ITO electrode was analyzed by using Raman Scope II to determine intermolecular vibration energy.

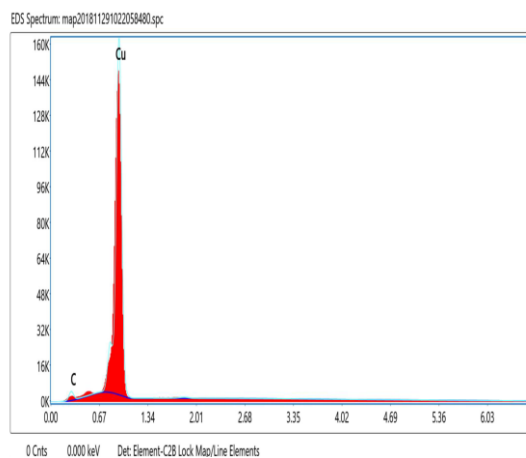
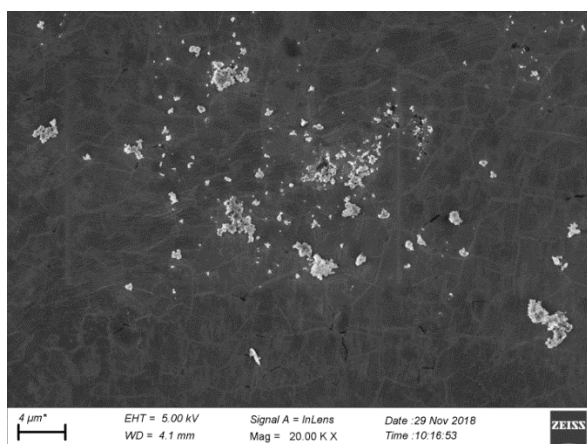
2.4. Electrochemical Measurements

The glucose electrooxidation activity of few-layer graphene/ITO electrode was examined by CV and CA in 1 M KOH + 0.5 M C₆H₁₂O₆ solution. These measurements were performed in a standard three-electrode cell using a CHI 660E Electrochemical Analyzer. CV measurements were recorded potential range in 1 M KOH + 0.5 M C₆H₁₂O₆ solution at a scan rate of 50 mV/s 0.6–0.4 V. In order to measure the stability of the few-layer graphene/ITO electrode, 1000 s and -0.5 V were examined in the CA.

3. RESEARCH FINDINGS

3.1. Characterization

SEM analysis was performed to determine the surface properties of graphene. It is seen that few-layer graphene is distributed on Cu foil. The few-layer graphene contain 13.4% carbon and 86.59% Cu foil



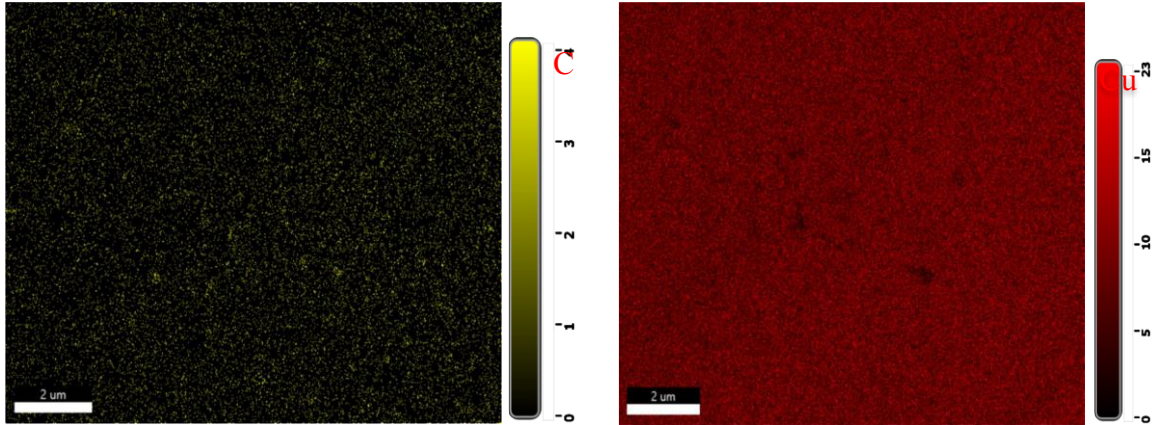


Figure 1. SEM-EDX and mapping images of few-layer graphene.

The chemical structure of few-layer graphene was revealed by Raman analysis technique. In the Raman spectroscopy characterization of few-layer graphene, the increase in 2D/G ratio shows that the number of layers decreases and the increase in D/G ratio increases the structural defects on the surface. The D/G and 2D/G ratio were found to be 0.135 and 1.35, respectively.

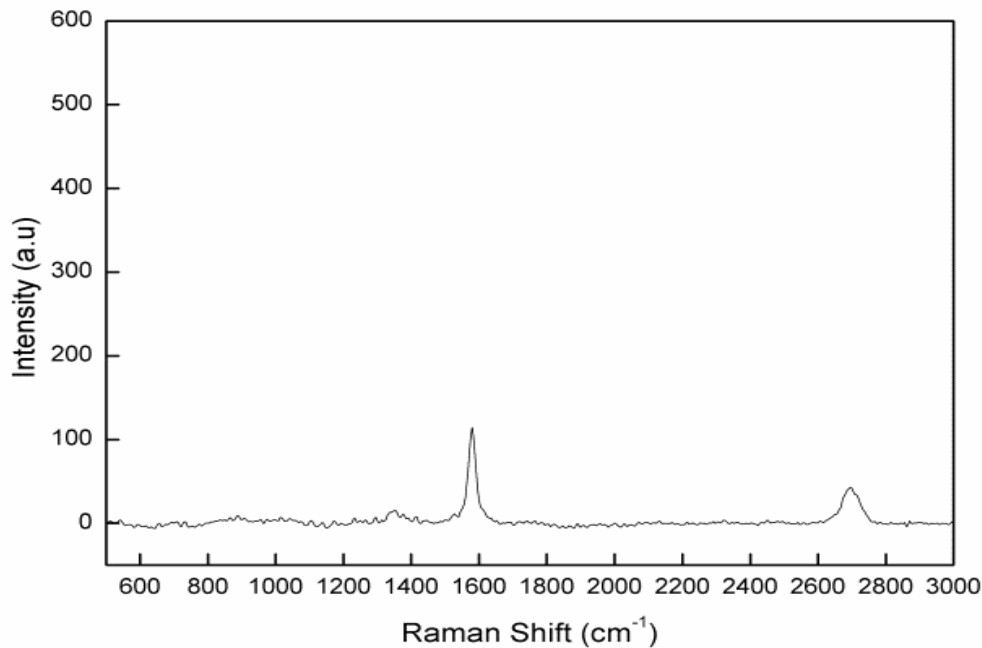


Figure 2. Raman spectra of the few-layer graphene.

3.2. Electrochemical measurements of ITO and Few-layer Graphene/ITO Electrodes

Electrochemical measurement of obtained few-layer graphene/ITO electrode was examined by CV in 1 M KOH and 1 M KOH + 0.5 M C₆H₁₂O₆ solution. CVs were recorded at -0.6–0.4 V potential range at 50 mV/s scan rate. Figure 3 shows CV behavior of ITO and few-layer graphene/ITO electrodes in 1 M KOH solution. Current values of H₂ adsorption-desorption peaks were obtained in the order of few-layer graphene/ITO>ITO electrodes. The glucose electrooxidation of ITO and few-layer graphene/ITO electrodes was illustrated in Figure 4. The few-layer graphene/ITO electrode exhibited about 4.2 times better activity than ITO electrode.

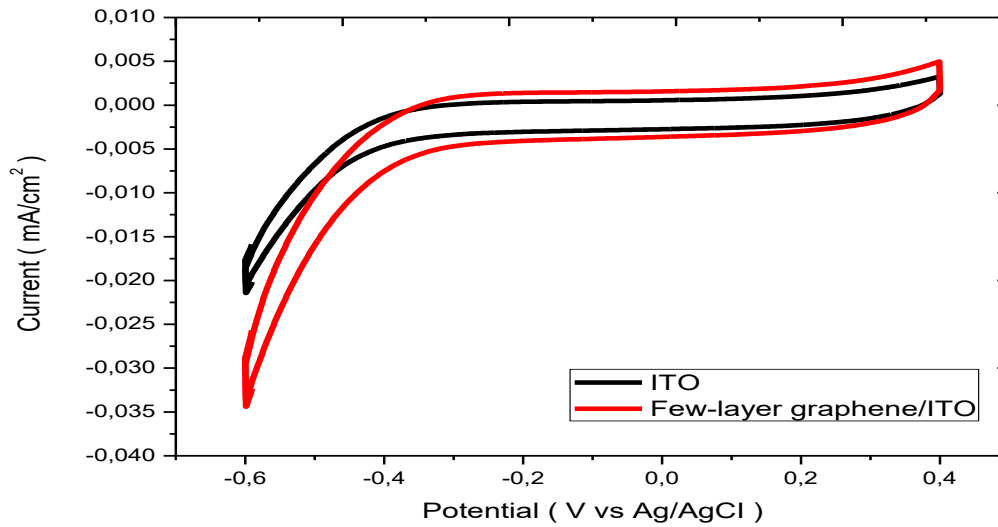


Figure 3. Cyclic voltammetry obtained in Few-layer garphene/ITO and ITO electrodes in 1 M KOH solution; scan rate: 50 mV s⁻¹.

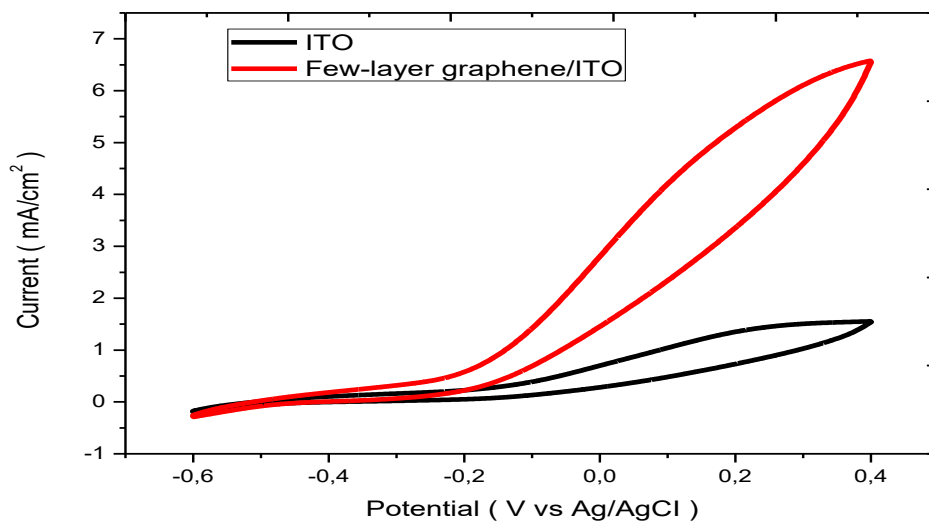


Figure 4. Cyclic voltammetry obtained in Few-layer grapheme/ITO, and ITO electrodes in 1 M KOH + 0.5 M C₆H₁₂O₆ solution; scan rate: 50 mV s⁻¹.

The stability and response of ITO and few-layer graphene/ITO electrodes were obtained with CA at -0.15 V and 1000 s in 1 M KOH and 0.5 M C₆H₁₂O₆ solution. Figure 5 indicates the CA curves of these electrodes. The few-layer graphene/ITO electrode was carried out better activity and stability than ITO electrode. Furthermore, the few-layer graphene/ITO electrode was realized high activity in CA results as with CV results.

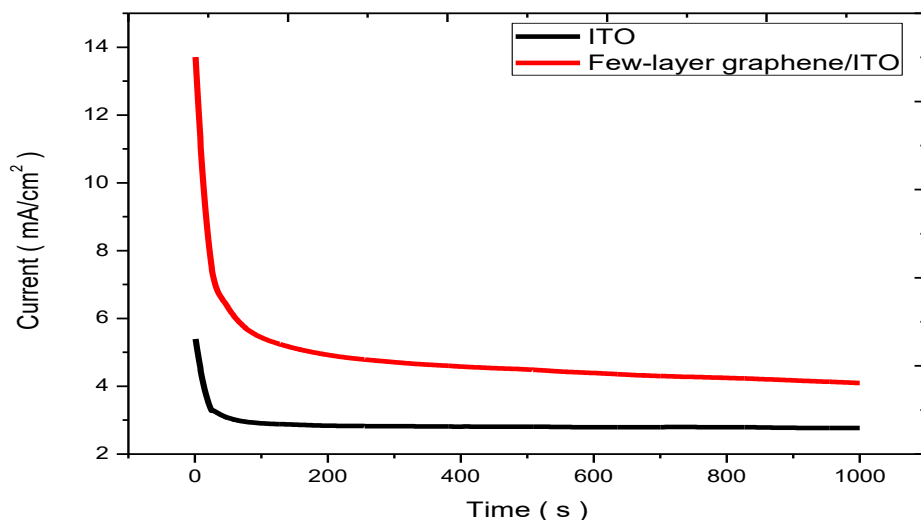


Figure 5. CA curves of ITO and Few-layer graphene/ITO electrodes obtained at -0.15 V and 1000 s.

4. CONCLUSIONS AND DISCUSSION

Herein, few-layer graphene was coated on Cu foil by CVD method. The few-layer graphene were transferred on Cu foil with 5 sccm hexan flow rate, 20 sccm hydrogen flow rate, and 20 min deposition time parameters via CVD method. Then, the graphene on the Cu foil was coated onto the few-layer ITO electrode. The graphene structure was clearly visible from SEM images. The few-layer graphene structure was confirmed by Raman analysis. The few-layer graphene/ITO electrode was exhibited higher electrochemical activity and stability than ITO electrode for the oxidation of glucose.

ACKNOWLEDGEMENTS

Hilal Kivrak would like to thank for the financial support for The Scientific and Technological Research Council of Turkey TUBITAK project (project no:116M004).

REFERENCES

- Basu, D. and Basu, S., 2011, Synthesis and characterization of Pt–Au/C catalyst for glucose electro-oxidation for the application in direct glucose fuel cell, *International Journal of Hydrogen Energy*, 36 (22), 14923-14929.
- Basu, D. and Basu, S., 2012, Performance studies of Pd–Pt and Pt–Pd–Au catalyst for electro-oxidation of glucose in direct glucose fuel cell, *International Journal of Hydrogen Energy*, 37 (5), 4678-4684.
- Bollella, P., G. Fusco, C. Tortolini, G. Sanzò, G. Favero, L. Gorton and R. Antiochia., 2017, Beyond graphene: Electrochemical sensors and biosensors for biomarkers detection, *Biosensors and Bioelectronics*, 89, Part 1, 152-166.
- Brouzgou, A., S. Song and P. Tsiakaras., 2014, Carbon-supported PdSn and Pd₃Sn₂ anodes for glucose electrooxidation in alkaline media, *Applied Catalysis B: Environmental*, 158-159, 209-216.
- Brouzgou, A., L. L. Yan, S. Q. Song and P. Tsiakaras., 2014, Glucose electrooxidation over Pd_xRh/C electrocatalysts in alkaline medium, *Applied Catalysis B: Environmental*, 147, 481-489.
- Caglar, A., T. Sahan, M. S. Cogenli, A. B. Yurtcan, N. Aktas and H. Kivrak., 2018, A novel Central Composite Design based response surface methodology optimization study for the synthesis of Pd/CNT direct formic acid fuel cell anode catalyst, *International Journal of Hydrogen Energy*, 43 (24), 11002-11011.
- Çağlar, A., A. Aldemir and H. Kivrak., 2018, Alcohol electrooxidation study on carbon nanotube supported monometallic, Pt, Bi, and Ru catalysts, *Fullerenes, Nanotubes and Carbon Nanostructures*, 1-8.

Proceeding Book of ISESER 2019

- Gao, M., X. Liu, M. Irfan, J. Shi, X. Wang and P. Zhang., 2018, Nickle-cobalt composite catalyst-modified activated carbon anode for direct glucose alkaline fuel cell, *International Journal of Hydrogen Energy*, 43 (3), 1805-1815.
- Kivrak, H., M. Can, H. Duru and O. Sahin., 2014, Methanol Electrooxidation Study on Mesoporous Silica Supported Pt–Co Direct Methanol Fuel Cell Anode, *International Journal of Chemical Reactor Engineering*, 12, 369.
- Li, L., K. Scott and E. H. Yu., 2013, A direct glucose alkaline fuel cell using MnO₂–carbon nanocomposite supported gold catalyst for anode glucose oxidation, *Journal of Power Sources*, 221, 1-5.
- Sahin, O., D. Duzenli and H. Kivrak., 2016, An ethanol electrooxidation study on carbon-supported Pt–Ru nanoparticles for direct ethanol fuel cells, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 38 (5), 628-634.
- Tan, Y. Y., K. D. G. I. Jayawardena, A. A. D. T. Adikaari, L. W. Tan, J. V. Anguita, S. J. Henley, V. Stolojan, J. D. Carey and S. R. P. Silva., 2012, Photo-thermal chemical vapor deposition growth of graphene, *Carbon* 50 (2), 668-673.
- Ulas, B., A. Caglar, A. Kivrak and H. Kivrak., 2018, Atomic molar ratio optimization of carbon nanotube supported PdAuCo catalysts for ethylene glycol and methanol electrooxidation in alkaline media, *Chemical Papers*.
- Ulas, B., A. Caglar, O. Sahin and H. Kivrak., 2018, Composition Dependent Activity of PdAgNi Alloy Catalysts for Formic Acid Electrooxidation, *Journal of Colloid and Interface Science*.
- Yan, L., A. Brouzgou, Y. Meng, M. Xiao, P. Tsiakaras and S. Song., 2014, Efficient and poison-tolerant Pd_xAu_y/C binary electrocatalysts for glucose electrooxidation in alkaline medium, *Applied Catalysis B: Environmental*, 150-151, 268-274.
- Zhiani, M., A. Abedini and S. Majidi., 2018, Comparison of Electro-Catalytic Activity of Fe-Ni-Co/C and Pd/C Nanoparticles for Glucose Electro-Oxidation in Alkaline Half-Cell and Direct Glucose Fuel Cell, *Electrocatalysis* 9 (6), 735-743.