

O 68. SYNTHESIS OF IN-SITU S DOPED FEW LAYER GRAPHENE BY CHEMICAL VAPOR DEPOSITION TECHNIQUE AND THEIR SUPERIOR GLUCOSE ELECTROOXIDATION ACTIVITY

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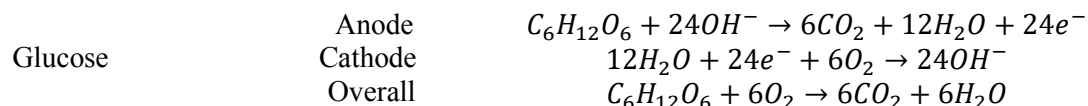
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ABSTRACT: In this study, sulfur (S)-doped graphene and insitu S-doped graphene are deposited on copper (Cu) foil by chemical vapor deposition (CVD) method. Then, S-doped graphene and insitu S-doped few-layer graphene on the Cu foils were coated onto few-layer the indium tin oxide (ITO) electrode for glucose electrooxidation. These electrodes are characterized by Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis (SEM-EDX) and Raman Spectroscopy. In addition, glucose electrooxidation was investigated with cyclic voltammetry (CV) and chronoamperometry (CA).

Keywords: Chemical Vapor Deposition, Few-Layer Graphene, Glucose Electrooxidation.

1. INTRODUCTION

Fuel cells have gained a great deal of importance due to increasing energy needs related population and growing industry (Ulas, Caglar et al. 2018). Besides, fuel cells are clean, efficient, and promising for the future (Çağlar, Aldemir et al. 2018). Direct glucose fuel cell (DGFC) is an energy device converting chemical energy into electrical energy. Glucose is alluring due to its strong demand in research subject as fuel for DGFCs (Chai, Zhang et al. 2018). The glucose is the richest carbohydrate in nature and could be readily extracted from biomass. When glucose is fed directly to the anode of a DGFC, it could produce 24 electrons by full electrooxidation to CO₂ given as follows (Brouzgou, Song et al. 2014):



Glucose can be employed as a fuel in fuel cells when it can be directly oxidized to produce electricity such as ethanol and methanol fuel cells (Brouzgou, Yan et al. 2014). Chai et al. (Chai, Zhang et al. 2018) reported that Pd₃Cu-B/C catalyst synthesized by a simple aqueous phase approach and examined glucose electrooxidation. Yan et al. (Yan, Brouzgou et al. 2014)] studied the activities of Pd_xAu_y/C binary electrocatalysts for glucose electrooxidation.

Herein, the S-doped graphene and insitu S-doped graphene were coated on Cu foil by the CVD method. The S-doped graphene and insitu S-doped graphene on the Cu foil were then coated onto few-layer the ITO electrode. ITO electrodes were employed as working electrode for electrochemical measurements in three electrode system. The S-doped G/ITO and insitu S-doped G/ITO electrodes were 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 S-doped graphene and insitu S-doped graphene Synthesis

The reactor medium was fixed to 5 sccm hexane and 50 sccm hydrogen gas for 20 min. The reactor temperature was increased to 950 °C. Then, quartz boat containing 1 mg of sulfur powder was brought closer to the reactor. After 10 min, the oven was shut down and allowed to cool. Cu foil was first pre-cleaned for insitu S doped graphene. The quartz bot containing 1 mg sulfur with Cu foil were placed

into CVD. The reactor medium was fixed to 5 sccm hexane and 50 sccm hydrogen gas for 20 min. The reactor temperature was increased to 950 °C. After 20 min, the oven was turned off and allowed to cool.

2.2. Transfer of S-doped graphene and insitu S-doped graphene on 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

The S-doped G/ITO and insitu S-doped G/ITO electrodes were characterized by SEM-EDX and Raman Spectroscopy. SEM-EDX measurement was obtained utilizing the zeiss sigma 300 to scan the surface of S-doped G/ITO and insitu S-doped G/ITO. Raman spectroscopy of S-doped G/ITO and insitu S-doped G/ITO was analyzed by using Raman Scope II to determine intermolecular vibration energy.

2.4. Electrochemical Measurements

The glucose electrooxidation activity of ITO, G/ITO, S-doped G/ITO, and insitu S-doped G/ITO electrodes was investigated by CV and CA in 1.0 M KOH + 0.5 M glucose solution. These measurements were investigated employing the CHI 660E potentiostat with three electrode systems. CV measurements were taken at a scan rate of 50 mV/s at -0.6–0.4 potential range in 1.0 M KOH + 0.5 M glucose solution. In order to measure the stability of the ITO, G/ITO, S-doped G/ITO, and insitu S-doped G/ITO electrodes, 1000 s and -0.5 V were examined in the CA.

3. RESEARCH FINDINGS

3.1. Characterization

The S-doped graphene and in situ S-doped graphene were characterized by SEM-EDX and mapping images. SEM and mapping images are shown in Figures 1 and 2. Carbon and sulfur are homogeneously dispersed on Cu foil. The S-doped graphene and in situ S-doped graphene, the atomic element compounds were obtained as 8.1 % C, 0.39 % S, 82.79 % Cu and 9.4 % C, 17.95 % S, 82.51% Cu, respectively.

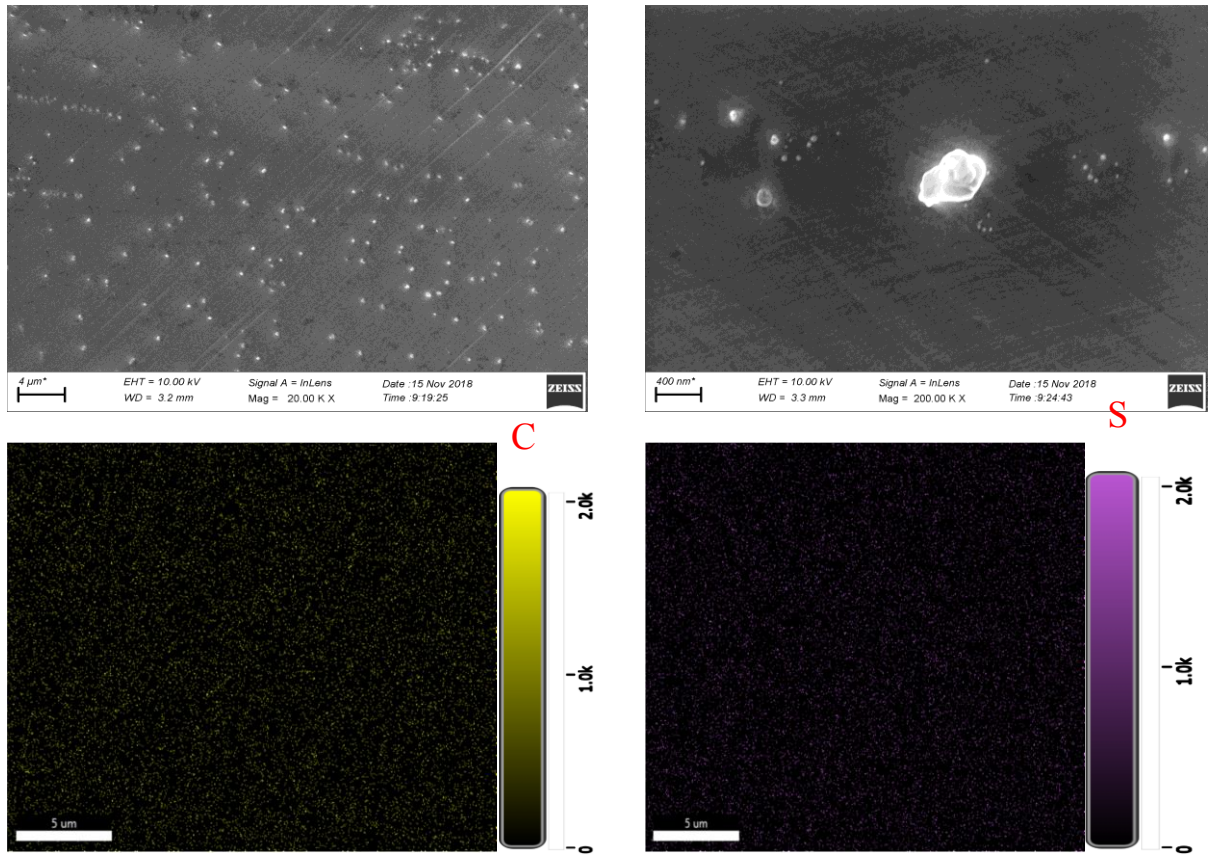


Figure 1. SEM and mapping images of S-doped G/ITO

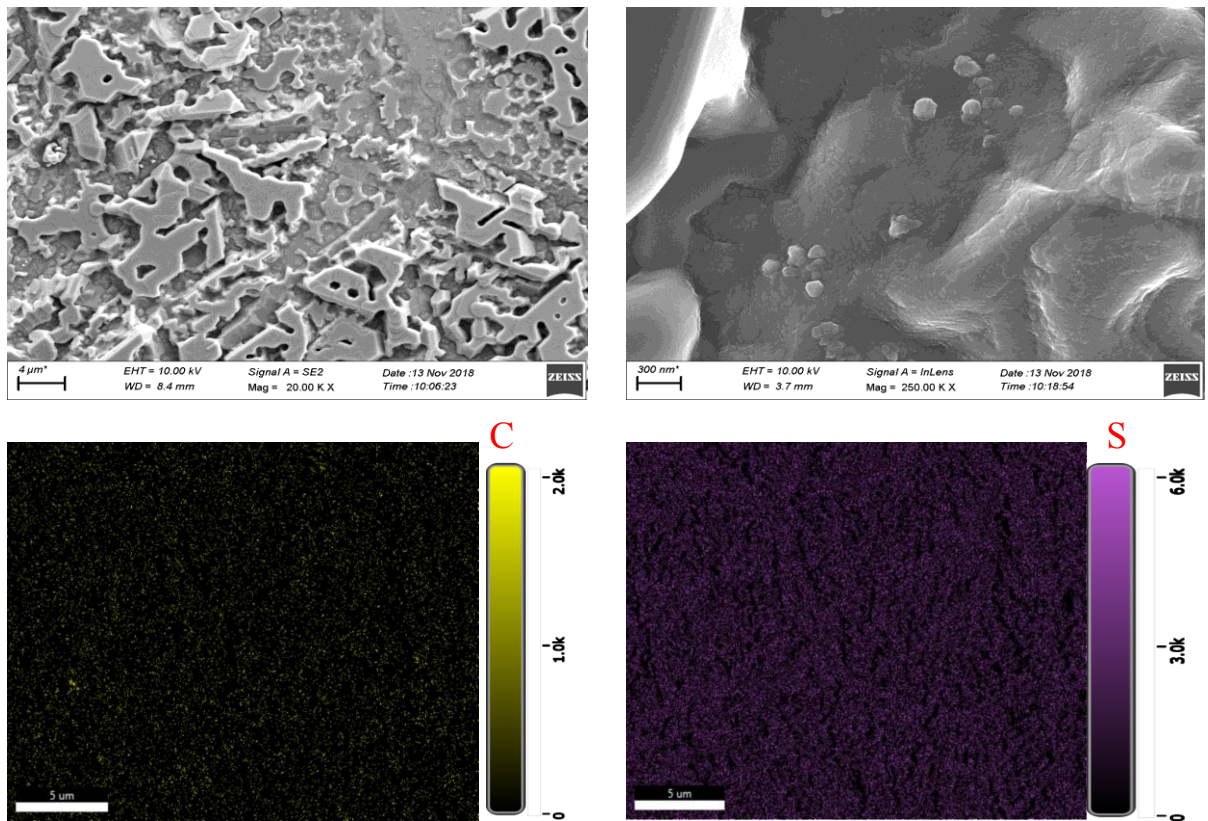


Figure 2. SEM and mapping images of insitu S-doped G/ITO

Figure 3(a,b) displays the Raman spectra of S-doped G/ITO and insitu S-doped G/ITO electrodes. The insitu S-doped G/ITO possessed higher D/G ratio than ITO/graphene ($0.190 > 0.138$) showing that doping the S on ITO/graphene increased the number defective sites. The crystallinity of graphene was significantly degraded by S doping on G/ITO surface. For raman spectroscopy of S-doped G/ITO electrode, the peak at 283, 330 and 615 cm^{-1} belongs to the characteristic peaks of copper and copper oxide.

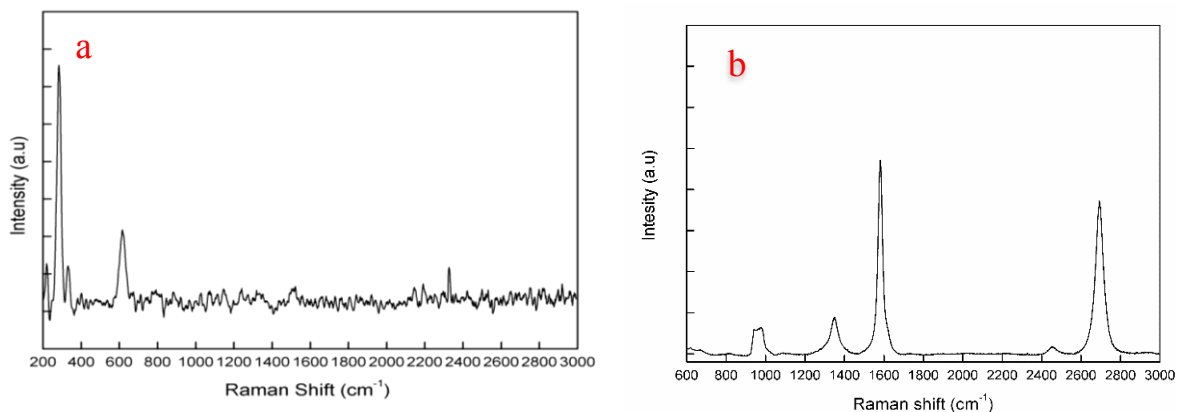


Figure 3. Raman spectra of a) S-doped G/ITO b) insitu S-doped G/ITO.

3.2. Electrochemical Measurements of ITO, Graphene/ITO, S-doped graphene/ITO, and insitu S-doped graphene/ITO Electrodes

Electrochemical measurements of obtained ITO, graphene/ITO, S-doped graphene/ITO, and insitu S-doped graphene/ITO were investigated via CV in 1.0 M KOH + 0.5 M glucose solution. CVs were taken at -0.6 V–0.4 V potential range at 50 mV/s scan rate. Figure 4 indicates CV behavior of ITO, graphene/ITO, S-doped graphene/ITO, and insitu S-doped graphene/ITO electrodes in 1.0 M KOH + 0.5 M glucose solution. The specific activity value of the insitu S-doped graphene/ITO electrode was obtained as 7.86 mA cm^{-2} . The insitu S-doped graphene/ITO electrode exhibited about 1.27, 1.2, and 4.2 times higher activity than S-doped graphene/ITO, graphene/ITO, and ITO electrodes, respectively.

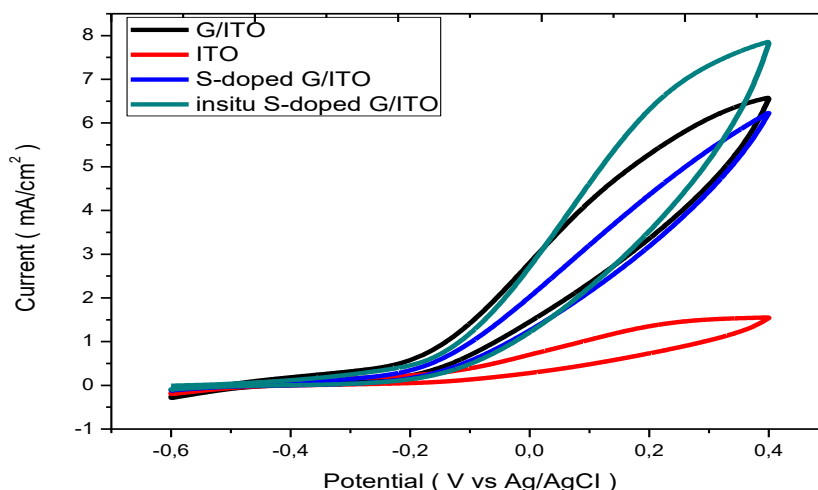


Figure 4. Cyclic voltammety obtained in ITO, G/ITO, S-doped G/ITO, and insitu S-doped G/ITO electrodes in 1.0 M KOH + 0.5 M glucose solution; scan rate: 50 mV s^{-1} .

The stability of ITO, graphene/ITO, S-doped graphene/ITO, and insitu S-doped graphene/ITO electrodes were obtained with CA at -0.15 V and 1000 s in 1.0 M KOH + 0.5 M glucose solution. The CA curves of these electrodes are illustrated in Figure 5. The insitu S-doped graphene/ITO electrode was realized higher activity and stability than ITO, graphene/ITO, and S-doped graphene/ITO electrodes.

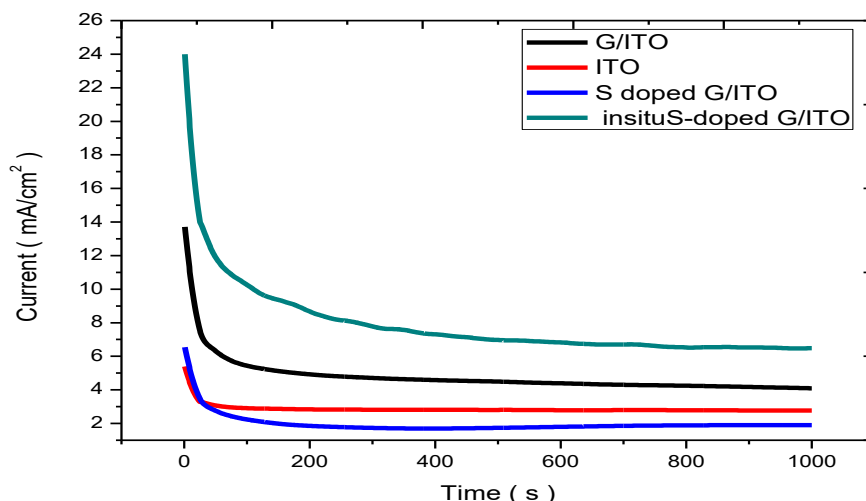


Figure 5. Chronoamperometry curves of ITO, G/ITO, S-doped G/ITO, and insitu S-doped G/ITO electrodes obtained at -0.15 V and 1000 s.

4. CONCLUSIONS AND DISCUSSION

At present, S-doped graphene and insitu S-doped graphene were coated on Cu foil by CVD method. Then, the S-doped graphene and insitu S-doped graphene on the Cu foil was coated few-layer on the ITO electrode. The graphene and sulfur structures were clearly visible from SEM images. The S-doped graphene and insitu S-doped graphene structures were confirmed by Raman analysis. The insitu S-doped graphene electrode has exhibited the highest electrochemical activity and stability toward the oxidation of glucose compared ITO, graphene/ITO, and S-doped graphene/ITO electrodes.

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REFERENCES

- 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.
- Chai, D., X. Zhang, S. H. Chan and G. Li., 2018, Facile aqueous phase synthesis of Pd₃Cu-B/C catalyst for enhanced glucose electrooxidation, *Journal of the Taiwan Institute of Chemical Engineers*.
- 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.
- 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.