O 72. SYNTHESIS OF B DOPED AND IN-SITU B DOPED FEW LAYER GRAPHENE BY CHEMICAL VAPOR DEPOSITION TECHNIQUE FOR HYDROGEN PEROXIDE DETECTION

Aykut Caglar[1], Berdan Ulas[1], Abdullah Nadeesh[2*], Hilal Kivrak[1] and Ozlem Sahin[2]

[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: osahin@ktun.edu.tr

ABSTRACT: In this study, boron (B)-doped graphene and insitu B-doped few-layer graphene are deposited on copper (Cu) foil by chemical vapor deposition (CVD) method. Then, B-doped graphene and insitu B-doped few-layer graphene on the Cu foils were coated onto few-layer the indium tin oxide (ITO) electrode for hydrogen peroxide (H_2O_2) sensor. These electrodes are characterized by Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis (SEM-EDX) and Raman Spectroscopy. In addition, H_2O_2 sensor is investigated with cyclic voltammetry (CV) and chronoamperometry (CA).

Keywords: Chemical Vapor Deposition, Indium Tin Oxide, Hydrogen Peroxide.

1. INTRODUCTION

H_2O_2 has a significant role in many fields processes such as food, pharmaceutical, disinfection and cleaning due to its strong oxidizing and reducing ability (Alal, Caglar et al. , Kazici, Salman et al. 2018). Therefore, fast and right determination of H_2O_2 is very important. Different analytical techniques have been realized to detect H_2O_2, such as chemiluminescence (Xu and Dong 1999), spectrophotometry (Luo, Abbas et al. 2008), fluorescence (Cathcart, Schwiers et al. 1983), and electrochemical methods (Düzenli, Sahin et al. 2018). Among these methods, electrochemical sensors are especially important for high sensitivity, selectivity, and simplicity for real-time sensing (Miao, Yuan et al. 2008).
Graphene has attracted strong scientific and technological interest with a hexagonal, single-atom, and two-dimensional (2D) sp2-hybrid carbon atom layer separated from 3D structured graphite in recent years. Graphene synthesis methods have been known such as thermal decomposition, chemical vapour deposition (CVD), and Hummers method (Bollella, Fusco et al. 2017). Shao et al. reported the selective development of electrochemical sensors and biosensors of graphene-based electrodes (Shao, Wang et al. 2010).
At present, the B-doped graphene and insitu B-doped graphene were coated on Cu foil by the CVD method. The B-doped graphene and insitu B-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 B-doped G/ITO and insitu B-doped G/ITO electrodes were characterized by SEM-EDX and Raman Spectroscopy measurements. To investigate their H_2O_2 sensor activities, CV and CA electrochemical measurements were used.

2. MATERIAL AND METHOD

2.1. The B-doped graphene and insitu B-doped graphene Synthesis

Cu foil was first pre-cleaned for B doped graphene. 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 boric acid 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 institu B doped graphene. The quartz bot containing 1 mg boric acid 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 B-doped graphene and insitu B-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 B-doped G/ITO and insitu B-doped G/ITO electrodes were characterized by SEM-EDX and Raman Spectroscopy. SEM-EDX measurement was obtained utulizing the zeiss sigma 300 to scan the surface of B-doped G/ITO and insitu B-doped G/ITO. Raman spectroscopy of B-doped G/ITO and insitu B-doped G/ITO was analyzed by using Raman Scope II to determine intermolecular vibration energy.

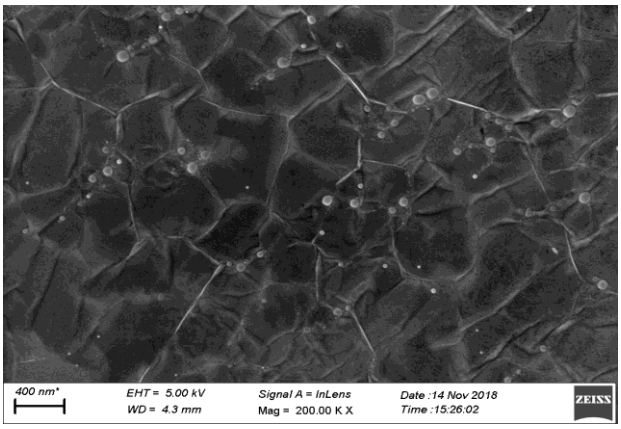
2.4. Electrochemical Measurements

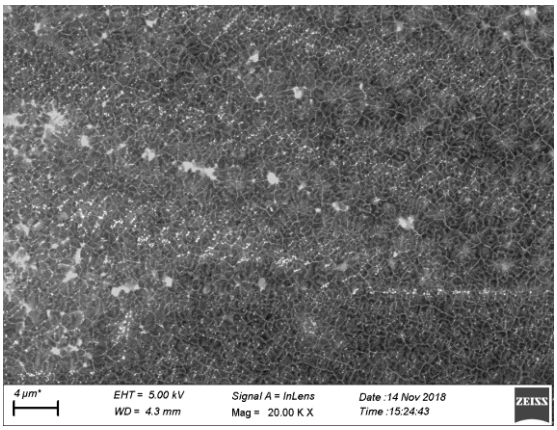
The H_2O_2 sensor activity of ITO, G/ITO, B-doped G/ITO, and insitu B-doped G/ITO electrodes was investigated by CV and CA in 0.1 M phosphate buffer solution (PBS). These measurements were carried out on a CHI 660E electrochemical workstation connected to a computer. CV measurements were taken at a scan rate of 50 mV/s at -0.6–1 V potential range. The CA measurements were executed in a 0.1 M PBS under stirred condition.

3. RESEARCH FINDINGS

3.1. Characterization

The B-doped graphene and insitu B-doped graphene were characterized by SEM-EDX and mapping images. SEM and mapping images are given in Figures 1 and 2. Carbon and Boron are homogeneously dispersed on Cu foil. The B-doped graphene and in situ B-doped graphene, the atomic element compounds were obtained as 7.6 % C, 5.13 % B, 83.75 % Cu and 9.57 % C, 5.61 % B, 81.58% Cu, respectively.





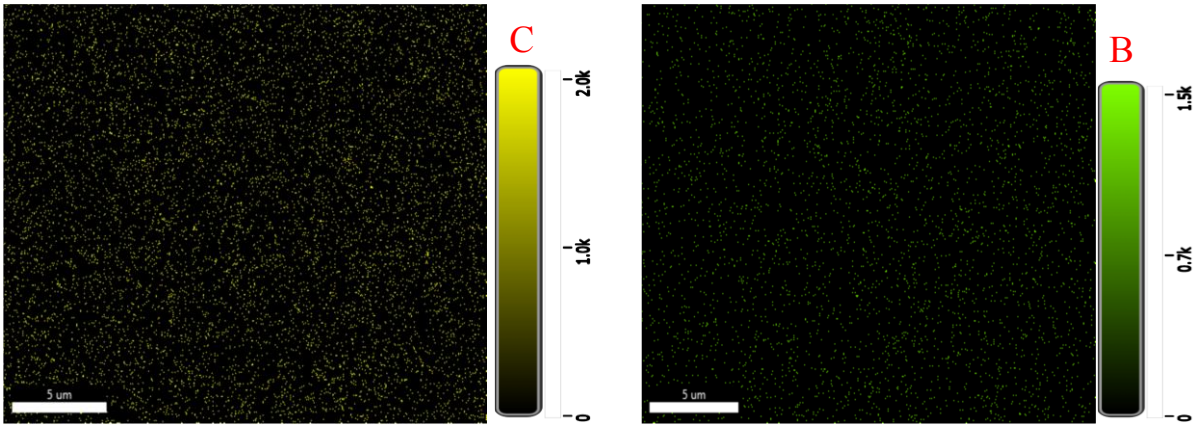


Figure 1. SEM and mapping images of B-doped graphene/ITO.

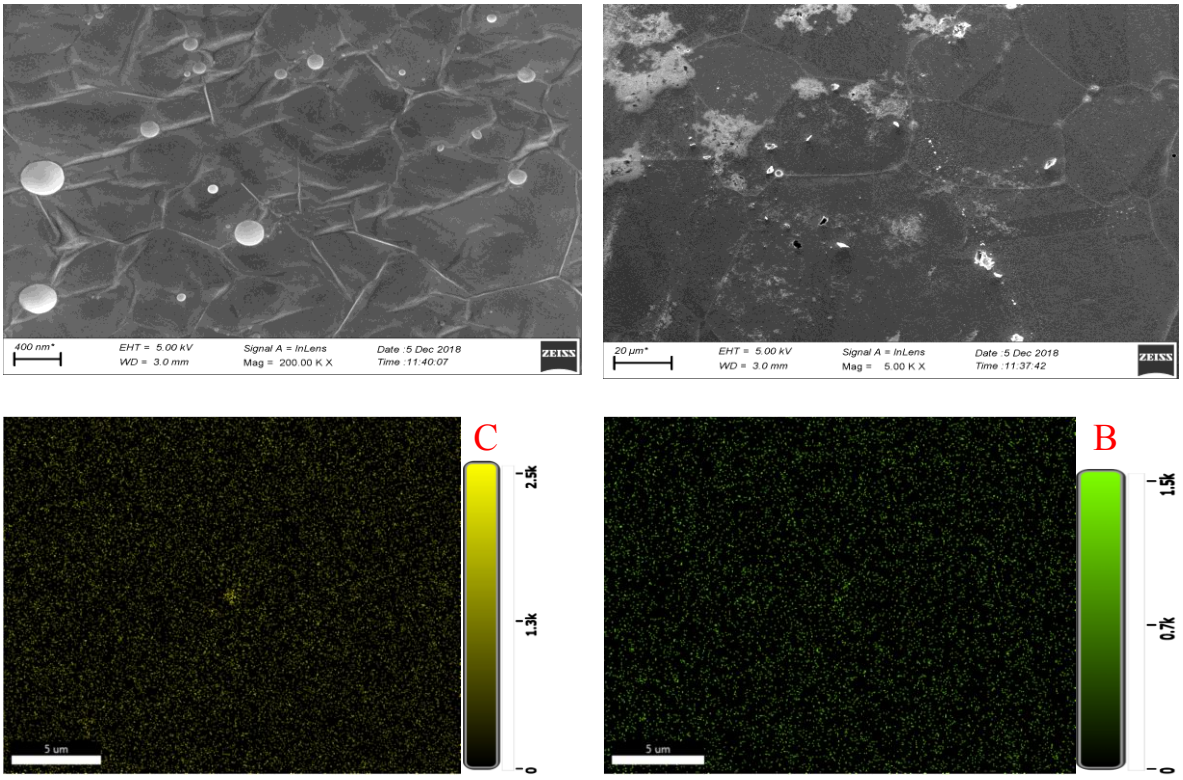


Figure 2. SEM and mapping images of insitu B-doped graphene/ITO.

Raman analysis of B doped and insitu B doped few layer graphene was performed to determine impact of defects and layers number of graphene. Figure 3 (a) shows the result of raman spectroscopy of the B-doped graphene/ITO. The D/G and 2D/G ratio were found to be 0.239 and 0.146, respectively. The raman analysis of insitu B-doped graphene/ITO is shown in Figure 3 (b). The D/G and 2D/G ratio were found to be 0.163 and 0.345, respectively. It was observed that the D/G ratio increased slightly while 2D/G ratio decreased compared to graphene/ITO (D/G=0.138 and 2D/G=1.387 for graphene/ITO).

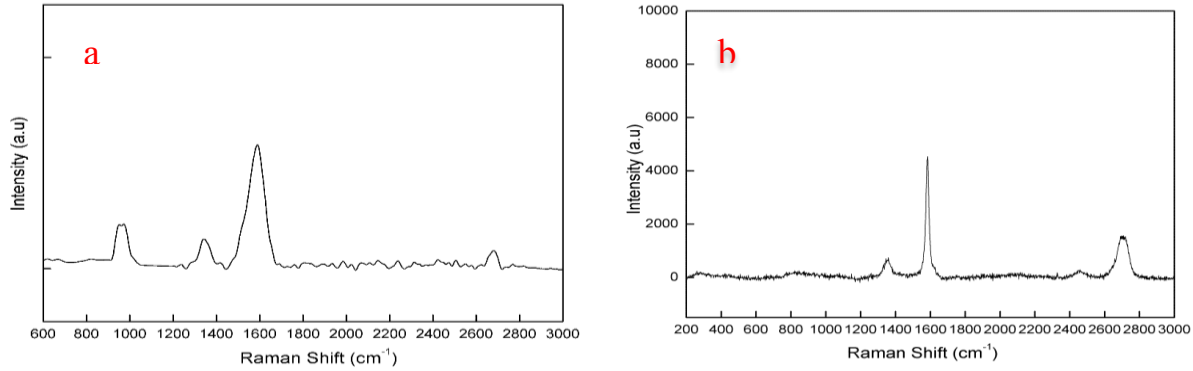


Figure 3. Raman spectra of a) B-doped graphene/ITO b) insitu B-doped graphene/ITO.

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

The ITO, graphene/ITO, B-doped graphene/ITO, and insitu B-doped graphene/ITO electrodes were prepared for detection of H_2O_2. The electroreduction of H_2O_2 measurements on these electrodes were realized by CV in 0.1 M pH 7.4 PBS. The H_2O_2 sensor activities of B-doped graphene/ITO and insitu B-doped graphene/ITO electrodes in the presence of different H_2O_2 concentration (0-20 mM) in N_2-saturated 0.1 M pH 7.4 PBS at scan rate of 50 mV/s were presented on Figure 4 (a,b). The current raises stepwise with successive additions of H_2O_2, ascribed to the sensitive and rapid response to the H_2O_2 reduction of the electrodes. The cyclic voltammograms of the ITO, graphene/ITO, B-doped graphene/ITO, and insitu B-doped graphene/ITO electrodes in the presence (Figure 5) of 5 mM H_2O_2 were recorded. As it could be seen in Figure 5, ITO, graphene/ITO, B-doped graphene/ITO, and insitu B-doped graphene/ITO electrodes exhibited for H_2O_2 at around ~0.0 V which corresponded to the reduction reactions of H_2O_2 on electrode surface. Maximum current density for these electrodes was obtained for insitu B-doped graphene/ITO electrode.

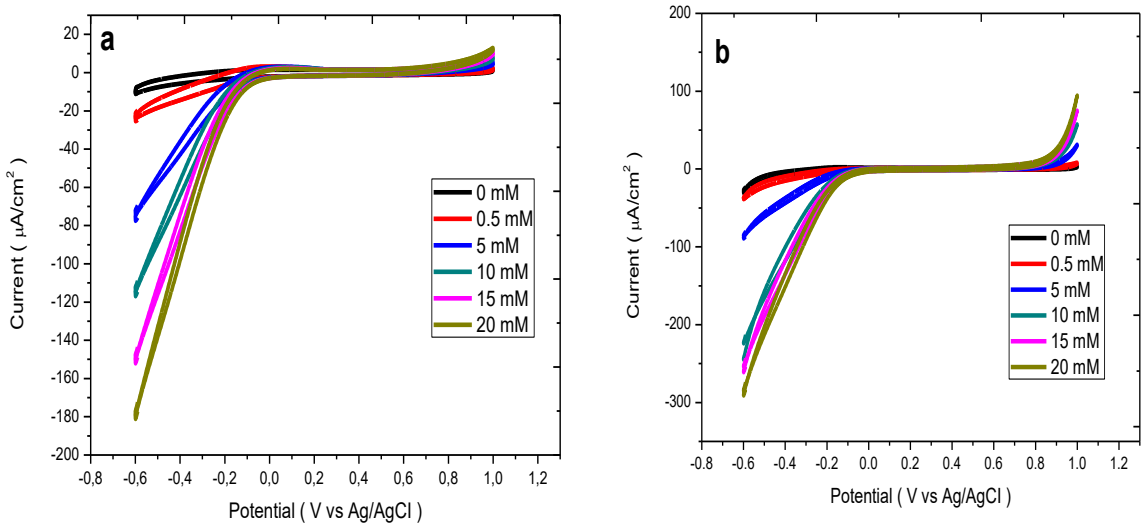


Figure 4: Cyclic voltammograms obtained in 0.1 M PBS (pH 7) solution for electrodes modified with B-doped graphene/ITO (a) and insitu B-doped graphene/ITO (b) (scan rate: 50 mV s^{-1}).

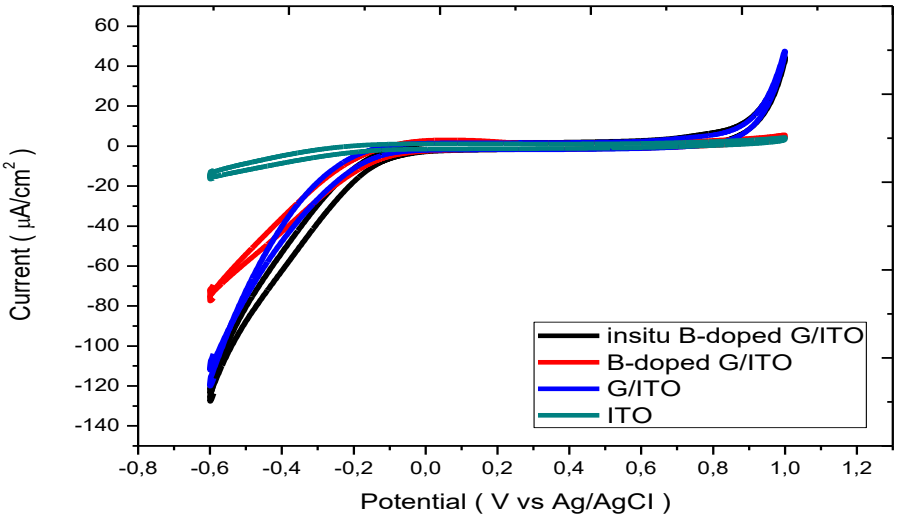


Figure 5: Cyclic voltammograms obtained by the addition of 5 mM H_2O_2 in pH 7 0.1 M PBS for electrodes modified with insitu B-doped G/ITO, B-doped G/ITO, G/ITO, and ITO (scan rate: 50 mV s^{-1})

Moreover, the amperometric curves were taken via CA technique by successive additions of H_2O_2 with different concentrations into the stirring 0.1 M N_2-saturated PBS at an applied potential of -0.5 V. Typical amperometric responses of the ITO, graphene/ITO, B-doped graphene/ITO, and insitu B-doped graphene/ITO electrodes were illustrated in Figure 6.

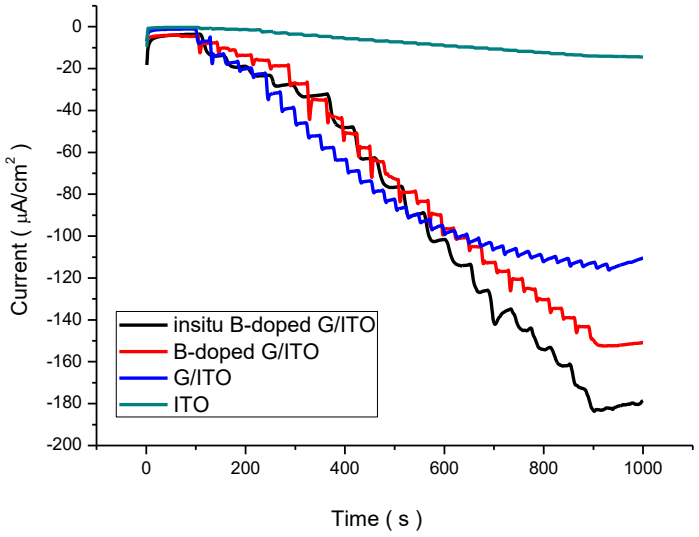


Figure 6: Amperometric response of H_2O_2 successive additions at -0.5 V for electrodes modified with insitu B-doped G/ITO, B-doped G/ITO, G/ITO, and ITO (pH=7 0.1 M PBS).

4. CONCLUSIONS AND DISCUSSION

Herein, the B-doped graphene and insitu B-doped graphene were coated on Cu foil by CVD method. Then, the B-doped graphene and insitu B-doped graphene on the Cu foil were coated onto few-layer the ITO electrode. The B-doped graphene and insitu B-doped graphene structures were clearly visible from SEM images. The insitu B-doped graphene/ITO electrode was exhibited an enhanced catalytic current, ascribed to the structure sensitivity compared other electrodes.

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