

Article

Proposal of a Facile Method to Fabricate a Multi-Dope Multiwall Carbon Nanotube as a Metal-Free Electrocatalyst for the Oxygen Reduction Reaction

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Abstract: In this study, a one-pot, low-temperature synthesis method is considered for the fabrication of heteroatom dope multiwall carbon nanotubes (MWCNT). Doped MWCNT is utilized as an effective electrocatalyst for oxygen reduction reaction (ORR). Single, double, and triple doping of boron, nitrogen and sulfur elements are utilized as the dopants. A reflux system with temperature of 180 °C is implemented in the doping procedure. Actually, unlike the previous studies in which doping on the carbon structures was performed using a furnace at temperatures above 700 °C, in this green and sustainable method, the triple doping on MWCNT is conducted at atmospheric pressure and low temperature. The morphology and structure of the fabricated catalysts were evaluated by Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and Raman spectroscopy. According to the results, the nanoparticles were encapsulated in the carbon nanotubes. Aggregated clusters of the sulfur in the case of S-MWCNT are considerable. Cyclic voltammetry (CV), rotating disk electrode, linear sweep voltammetry (LSV), and chronoamperometry electrochemical tests are employed for assessing the oxygen reduction activity of the catalysts. The results illustrate that by using this doping method, the onset potential shifts to positive values towards the oxidized MWCNT. It can be deduced that by doping the N, B, and S atoms on MWCNTs, the defects in the CNT structure, which serve as active sites for ORR application, increase. The N/S/B-doped graphitic layers have a more rapid electron transfer rate at the electrode/electrolyte interface. Thus, this can improve the electrochemistry performance and electron transfer of the MWCNTs. The best performance and electrochemical activity belonged to the NB-MWCNT catalyst (−0.122 V vs. Ag/AgCl). Also, based on the results gained from the Koutecky–Levich (KL) plot, it can be said that the ORR takes place through the 4 e[−] pathway.

Keywords: multiwall carbon nanotube; heteroatom doping; electrocatalyst; oxygen reduction reaction; fuel cell

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1. Introduction

Today, concerns regarding the immediate depletion of fossil fuel resources and, more significantly, environmental issues associated with their extensive utilization have pushed interests to seek clean energy conversion systems such as storage units and fuel cells [1,2]. The oxygen reduction reaction (ORR) has secured a unique place in various renewable energy systems mentioned above [3–5]. At present, the majority of the catalytic needs of the oxygen reduction reaction is met by platinum catalyst [3]. However, the widespread use of platinum catalyst in the ORR has led to a series of challenges such as exorbitant price, resource insufficiency, and simple poisoning [6,7]. These problems

severely limit the commercialization of platinum catalyst for use in renewable energy systems [6,7]. Such intrinsic shortcomings have spurred interest in completely replacing this catalyst with alternative electrocatalysts for ORR [8,9]. In light of this, metal-free carbon nanomaterials are considered as promising alternative catalysts due to their superb performance and low cost for ORR applications [10,11].

Therefore, in order to facilitate electrocatalysis of ORR by metal-free carbon nanomaterials, various nanocarbons such as graphene, carbon nanocapsules, carbon nanofibers (CNFs), and carbon nanotubes (MWCNTs) have been satisfactorily employed during recent years [12–14]. Among those, MWCNTs are considered extremely suitable materials for different electrochemical applications including supercapacitor [15,16], electrochemical redox [17,18], oxygen reduction reaction [19–21], and so on. Carbon nanotubes (MWCNTs) are suitable for energy-storage media, chemical sensors, molecular amplification in composites, and catalyst applications due to their substantial surface area and supreme electrical conductivity [22,23]. Furthermore, due to the structural and morphological features of MWCNTs, they are considered favorable support materials in catalysts [24]. However, the pristine utilization of these nanomaterials is confronted by the problems of electrochemical redox or ORR with restricted activity [25]. To prevail over the mentioned problems, doping heteroatoms [12,26] and adjusting carbon topological structures [27,28] could be employed to amend the electrochemical properties of MWCNTs [21].

According to the findings mentioned above, there is no doubt that doping different heteroatoms such as sulfur (S) [29,30], boron (B) [31], nitrogen (N) [32,33], and phosphorus [34] could be used to address the deficient electrocatalytic activity of pristine MWCNTs by creating active sites [35,36]. Nevertheless, despite the favorable results presented, exploring uncomplicated and prompt methods to synthesize the MWCNTs by doping different heteroatoms to further improve the electrochemical properties and to boost their potential application seems vital [24].

Recently, considerable amounts of investigations have been accomplished to improve the electrochemical properties of MWCNTs by doping different heteroatoms. For example, Ceragioli et al. [37] studied synthesis as well as characterization of multiwalled boron-doped MWCNTs. According to Raman measurements, increasing boron doping decreased the degree of C–C sp^2 order. Later, Chen et al. [38] applied ethylenediamine and pyridine as distinct precursors of nitrogen for producing N-doped MWCNTs to compare the performance of the resulting catalysts to improve the ORR in fuel cell applications. The results showed that EDA-NMWCNT had better ORR performance in terms of number of electrons transferred, limiting current density, and water selectivity compared with Py-NMWCNT. In another survey, Zhong et al. [39] analyzed the physical and chemical characterizations of N- and B- co-doped core-shell carbon nanoparticles as qualified catalyst for ORR in microbial fuel cells applications. The electrochemical results revealed that the dual doping of nitrogen and boron reduced the overpotential and increased the current density, respectively, resulting in increased oxygen reduction reaction kinetics. In line with that, a multiwalled MWCNTs-based catalyst doped with dual N & S components was synthesized by Patil et al. [40] for enhanced ORR. The ameliorated ORR was attributed to the existence of notable defect sited in the carbon structure. In another investigation, the Pd-Sn/Carbon nano-onion (CNO) was fabricated and evaluated for direct alcohol fuel cells [41]. This electrocatalyst illustrates improved durability and lower poisoning rate in the ethanol oxidation.

Furthermore, the single-, double-, and triple-doped MWCNTs by N, S, and B are fabricated by Liu et al. [42] for ORR. The considerable electrocatalytic activity as well as favorable stability for oxygen reduction reaction was observed in this study. Stacy et al. [43] reviewed recent and future developments of the catalysts used for the ORR. Recently, nanostructured carbons with nanowires, particles, and nanoribbons morphologies doped with nitrogen were investigated by Sui et al. [44]. They found that nanostructured carbon with nanoribbons morphology doped with nitrogen indicated favorable results in terms

of specific surface area, ORR activity, and onset potential compared with other N-doped porous carbons.

Although a remarkable number of studies have been devoted to investigating metal-free carbon nanomaterials doped with different heteroatoms as favorable catalysts for the cathode side, the method proposed for catalyst synthesis herein is not available in other studies. Accordingly, the target of current survey is to introduce and investigate a facile one-pot, low-temperature synthesis method for production of multi-dope, multiwall carbon nanotubes, which can be used as electrocatalysts. Its performance for ORR is examined here; however, this catalyst can be used in various applications reported in the literature. To do so, nitrogen, boron, and sulfur heteroatoms were doped separately and in combination on the multiwalled carbon nanotubes. Prepared catalysts were named N-MWCNT, S-MWCNT, B-MWCNT, NB-MWCNT, NS-MWCNT, and NSB-MWCNT, separately. It is worth noting that binary and ternary doping were carried out to investigate the synergetic effect between doping heteroatoms.

2. Synthesis Method

Materials: Multiwalled carbon nanotubes (MWCNTs), boric acid, urea, thiourea, and sodium sulfide were purchased from Sigma-Aldrich, St. Louis, MO, USA. Figure 1 illustrates the fabrication method by detail.

2.1. Oxidization of the Carbon Nanotubes

In this study, the presented procedure in a previous study [45] is used. A mixture of concentrated 8 M nitric acid and sulfuric acid was applied and then sonicated for 20 min, and after that refluxed at 110 °C for 6 h (magnet was used for mechanical stirring). It was then diluted with distilled water and rinsed by centrifugation several times with distilled water and ethanol until the pH of the wash water was the same as that of distilled water. Finally, it was dried in vacuum at a temperature of 80 °C for 8 h.

2.2. Nitrogen and Sulfur Co-Doping MWCNT

In a typical synthesis of NS-MWCNT, 50 mg of oxidized MWCNT was dispersed in 50 mL of ethylene glycol (EG) utilizing an ultrasonic device for 45 min. Then the dispersed oxidized MWCNT solution was added to 0.2 g thiourea in 50 mL of ethylene glycol. The solution was then sonicated again for 30 min and then transferred into a 250 mL volumetric flask and exposed to reflux for 3 h at 180 °C. Then, the product was washed with water and ethanol by centrifugation device. At the end, the gained N, S co-doped MWCNT was dried in vacuum for 4 h at 80 °C. For the synthesis of N-doped MWCNT and S-doped MWCNT, urea and Na₂S were used, respectively, instead of thiourea as the reference, using a similar method.

2.3. Nitrogen Sulfur and Boron Triple-Doping MWCNT

In the first step, 50 mg of oxidized MWCNT was sonicated in 50 mL of ethylene glycol for 1 h. In the second step, this dispersed solution was added to a 150 mg thiourea solution in 50 mL ethylene glycol and then the resulting solution was sonicated for 30 min. In the third step, this dispersed solution was added to 100 mg boric acid solution in 25 mL ethylene glycol and then sonicated for 30 min. In the fourth step, the resulting solution was transferred to a 250 mL volumetric flask and refluxed in a silicone oil bath for 3 h at 180–200 °C. Then, the product was washed with water and ethanol by centrifugation device. Finally, the achieved N, S, and B triple-doped RMWCNT was dried in vacuum for 4 h at 80 °C.

2.4. Single Doping of Nitrogen, Boron and Sulfur

For single doping the same procedure is considered. Urea, boric acid and sodium sulfide were used for single doping of nitrogen, boron and sulfur respectively.

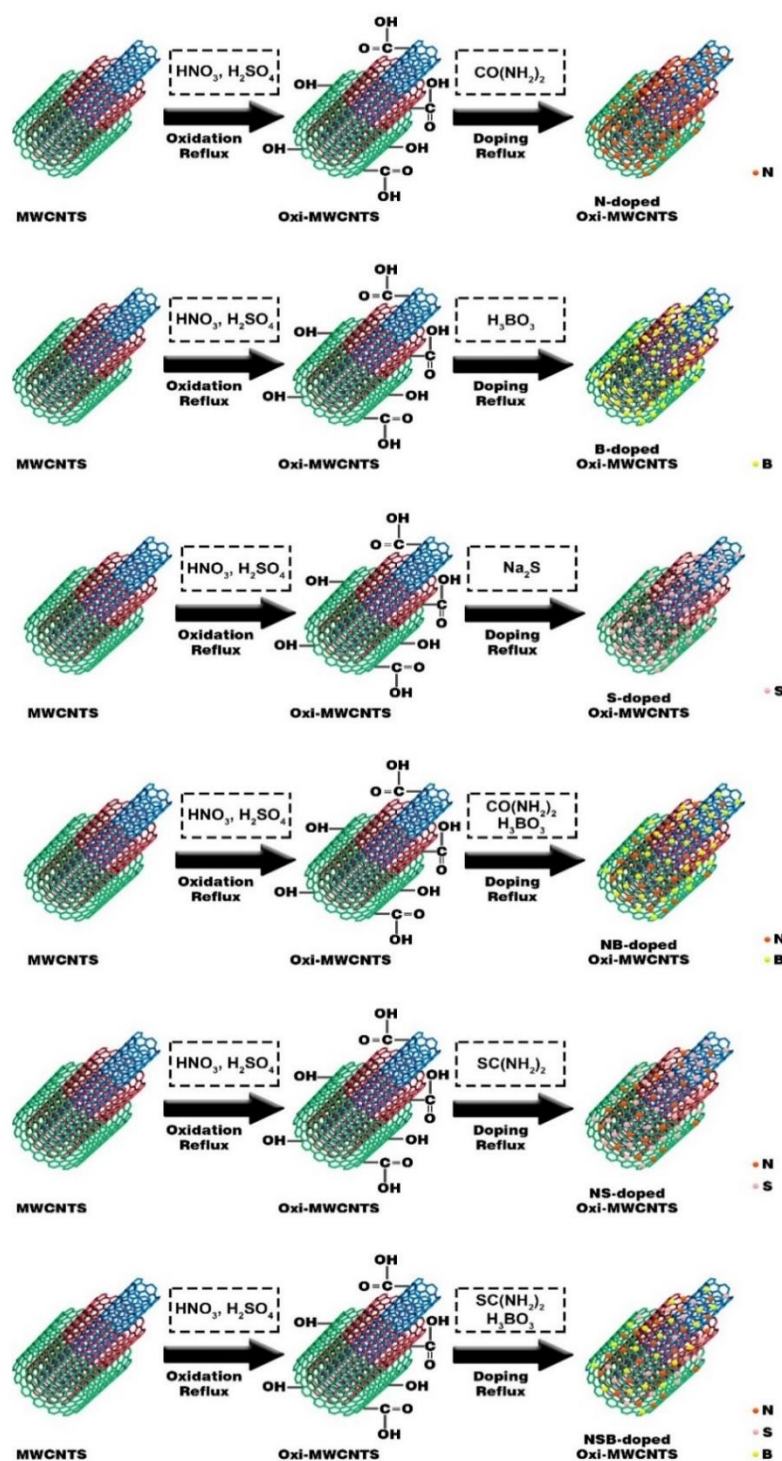


Figure 1. Schematic illustration of fabrication procedure for single and multi-doping of nitrogen, sulfur, and boron elements on MWCNT.

3. Physicochemical Methods Tests

The performed physical tests in this work include, Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), and Fourier-transform infrared spectroscopy (FTIR) spectra. The Raman measurement is done to show the ordered and disordered structures in each electrocatalyst. FTIR spectra is employed to specify the chemical bonds and functional groups. Figure 2 demonstrates the results of FTIR ($4000\text{--}40\text{ cm}^{-1}$) for single and multiple doping of nitrogen, sulfur and boron elements. Dominant peaks at 1250, 1372, 1445, 1736,

2362, 2851, 2925 cm^{-1} are related to the C–N, N–CH₃, MWCNT, C–O, and C–Hx, respectively. The strong peaks at 1252 and 1370 cm^{-1} reflect the C–N and N–CH₃ stretching vibrations [46]. These peaks can confirm the presence of intercalated N₂ atoms between the graphite layers. It has been found in previous studies [47–50] that substituting a nitrogen atom in place of a carbon atom in an sp²-bonded carbon network will enforce the strong IR activity because of a net dipole moment. As a result, the absorption in the 1200–1600 cm^{-1} region occurred if the nitrogen atoms are bonded into the C network. The multiple bonds between 500 and 1000 cm^{-1} illustrate the BO₂ (or BO) groups. B–O stretching is appeared at 1330 cm^{-1} . The bond is not outstanding but it indicates the presence of B in the MWCNT lattice [51]. The stretching vibrations of C–O and C–N appear in the weak absorption peaks at 920 cm^{-1} and 1100 cm^{-1} , respectively [52].

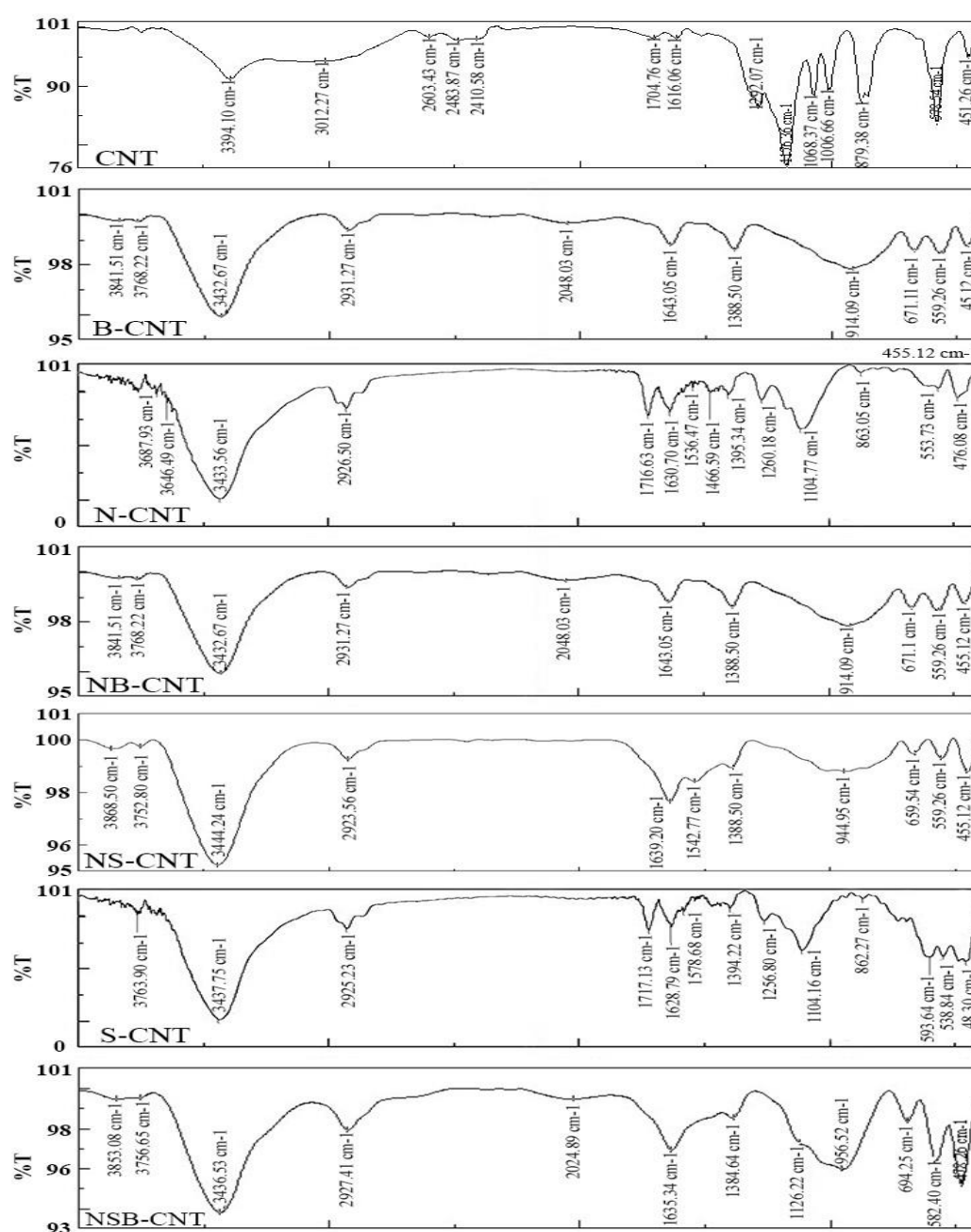


Figure 2. FTIR spectra of multiwall MWCNT for single and multiple doping of nitrogen, sulfur and boron elements as the dopants.

Figure 3 shows that the Raman spectra changes through single and multiple doping of N, S and B, elements that confirm the proper doping of different cases. Two bands at 1339 cm^{-1} (D band) and 1588 cm^{-1} (G band) reflect the presence of defects in the layer of graphite and original graphite, respectively. The intensity ratio (I_D/I_G) in the catalysts mean that there were remarkable edge plane defect sites existing on the surface of the electrocatalysts, which were predicted to indicate attractive electrochemistry activity. The amount of defects and desorbed structures is determined using the intensity ratio (I_D/I_G). After heteroatom doping I_D/I_G reaches to about 0.8 for different dopants. The presence of S, N and B elements as dopants causes the dissociation of graphitic structure and generates the higher defects and disordered moieties on carbon nanotube.

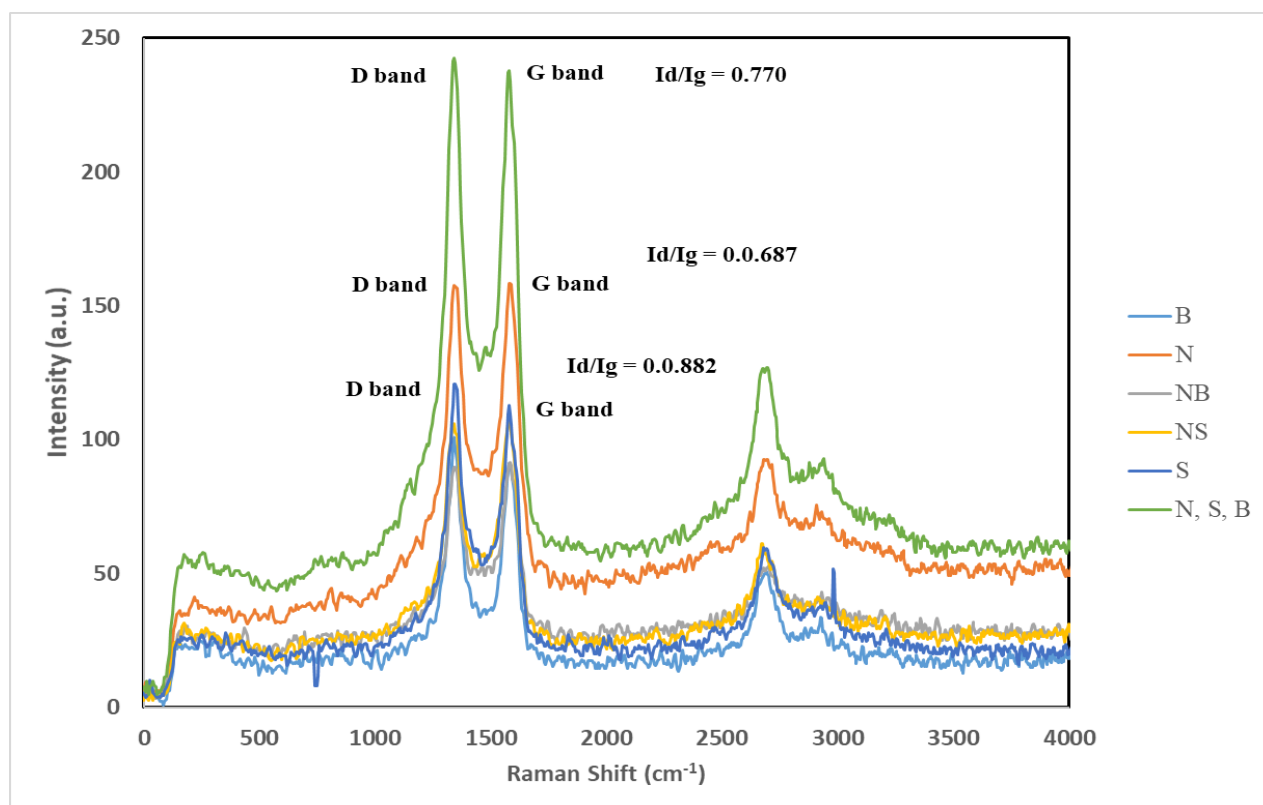
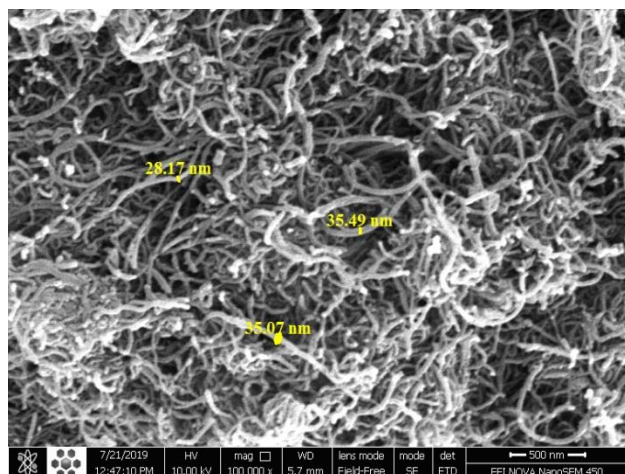
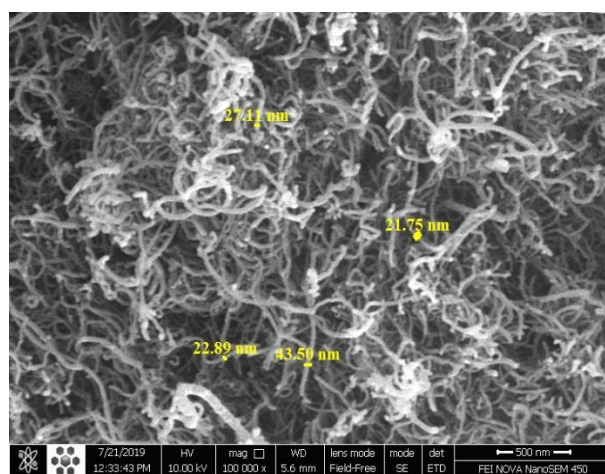
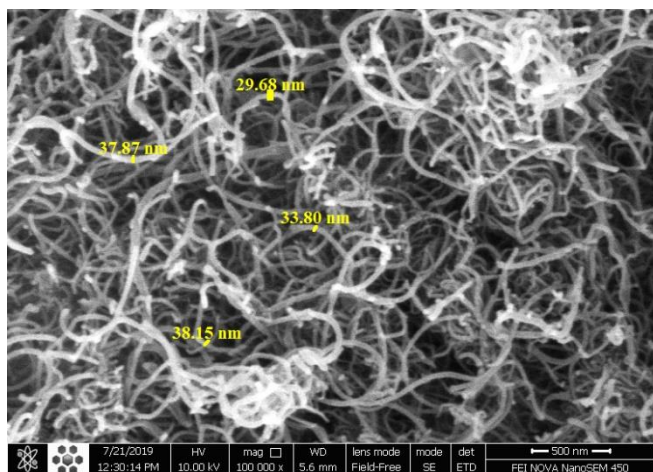
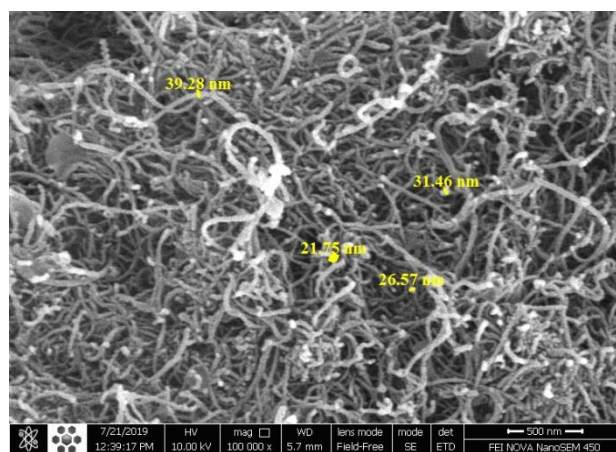
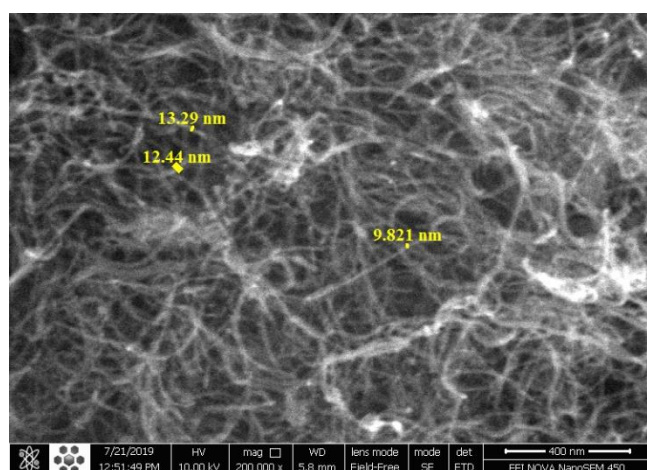
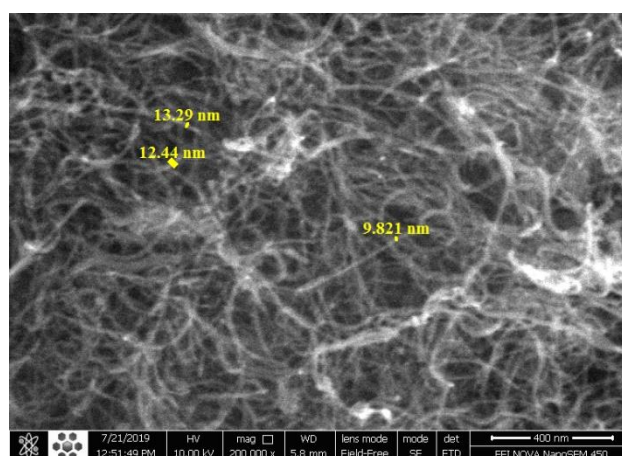


Figure 3. Raman spectra of the heteroatom doping of nitrogen, sulfur, and boron elements on MWCNT.

Figure 4 represents the typical FESEM and TEM images for N-MWCNT, B-MWCNT, S-MWCNT, NS-MWCNT, NB-MWCNT and NSB-MWCNT and TEM images of MWCNT and NSB-MWCNT electrocatalysts. As can be noticed, the tangled MWCNTs and NMWCNTs with a length of more than one hundred nanometers grow on both sides of the Gr, forming a quasi-aligned MWCNT array. The catalyst's nanoparticles are detectable at the end point of the nanotubes. Also, as can be seen some of the catalyst's nanoparticles have been encapsulated in the carbon nanotubes.

Figure 5 illustrates results of the EDS analysis of the synthesized electrocatalysts. EDS is done for investigation of the changes of elemental percentage composition in the synthesized electrocatalysts. Table 1 shows the element content for the electrocatalysts. In oxidized MWCNT, the oxygen weight percentage is found to be 37.6%, which shows the presence of oxygen functional groups after oxidation of the MWCNT. Also, the weight percentage of C is 45.21%. After doping the N, S, and B dopants, the weight percentage of C increases to more than 86%. Also, the weight percentage of N, S, and B considerably increase. For instance, the weight percentages of N for N-MWCNT, NB-MWCNT, NS-MWCNT, S-MWCNT, and NSB-MWCNT are found to be 2.85%, 3.76%, 2.77%, 1.72%, and

1.65%, respectively. These values indicate that the doping of N, S, and B has been performed properly.

**B-MWCNT****N-MWCNT****S-MWCNT****NB-MWCNT****NS-MWCNT****NBS-MWCNT**



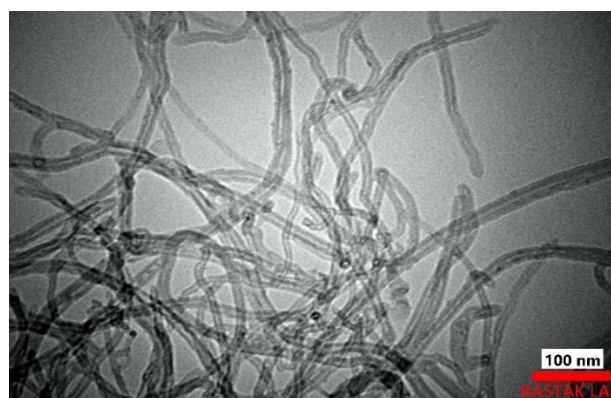
MWCNT (50 nm)



NSB-MWCNT (50 nm)

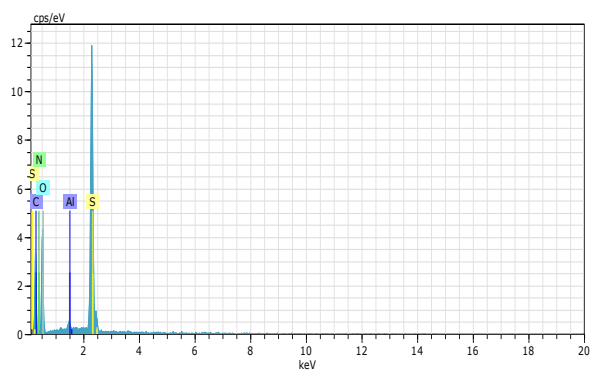


MWCNT (100 nm)

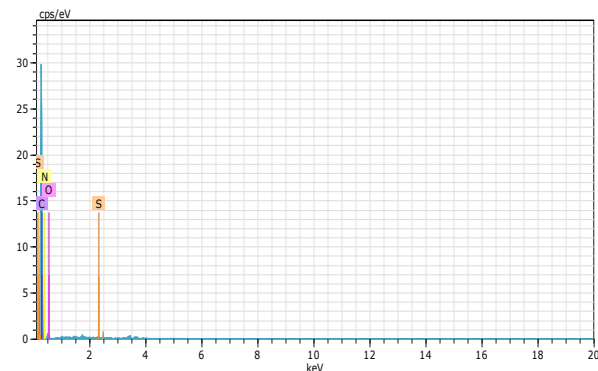


NSB-MWCNT (100 nm)

Figure 4. FESEM images of the N-MWCNT, B-MWCNT, S-MWCNT, NS-MWCNT, NB-MWCNT and TEM images of MWCNT and NSB-MWCNT.



Oxidized MWCNT



N-MWCNT

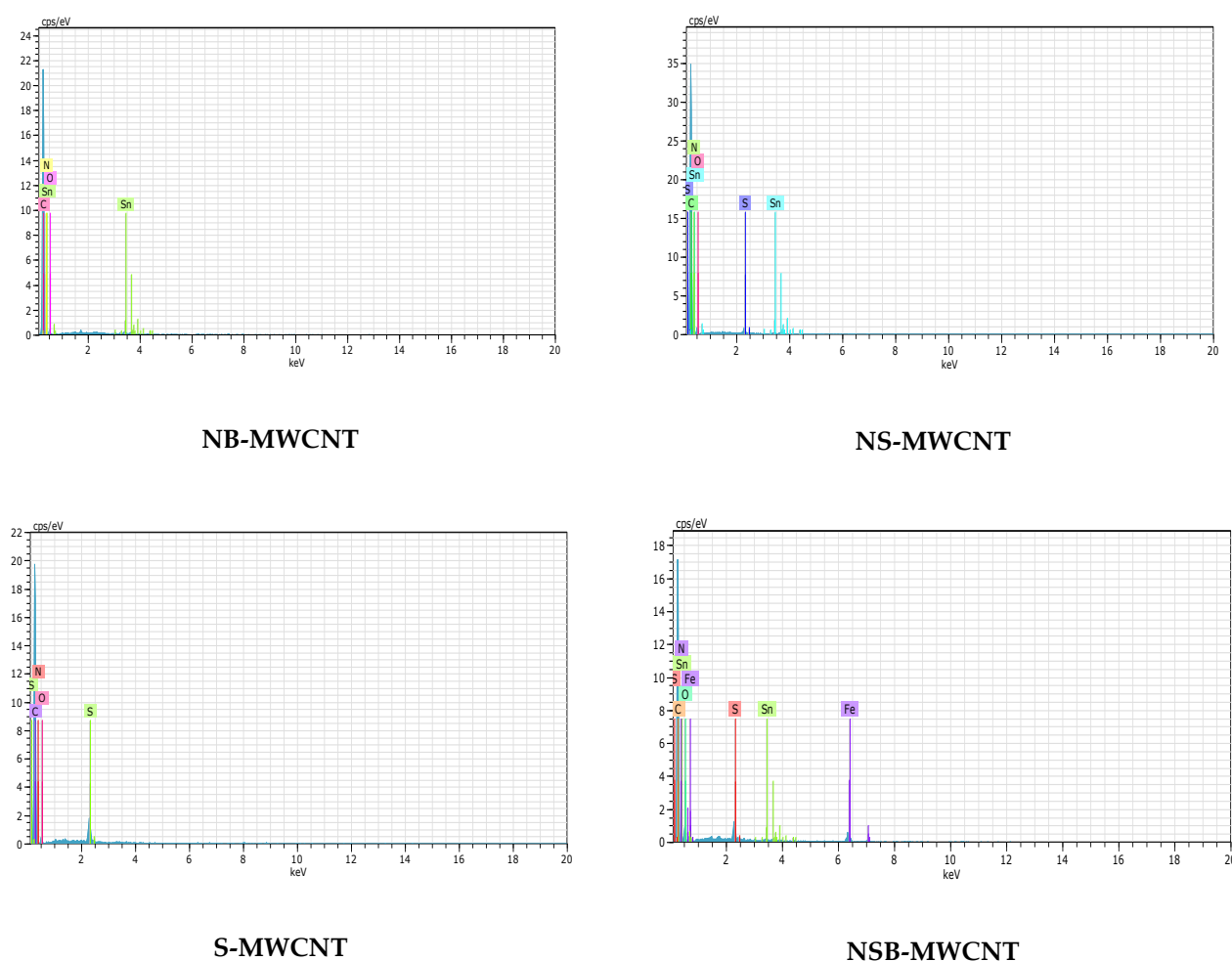


Figure 5. EDS test results for the synthesized electrocatalysts.

Table 1. The Element content for each electrocatalyst.

Catalyst	C wt. %	O wt. %	N wt. %	S wt. %	Other wt. % (Al, Sn)
Oxidized MWCNT	45.21	37.6	0.98	0	16.25
N-MWCNT	88.72	8.31	2.85	0.11	0
NB-MWCNT	87.19	8.41	3.76	0	0.64
NS-MWCNT	87.60	8.58	2.77	0.5	0
S-MWCNT	89.46	6.57	1.72	2.24	0
NSB-MWCNT	86.32	8.90	1.65	1.09	0.96

4. Electrochemical Test

Glassy carbon (GC) disk electrode (3 mm, HTW, Darmstadt, Germany) inserted in Teflon was considered as the catalysts support. A three-electrode system electrochemical cell was utilized including the catalyst modified working electrode, counter electrode made of platinum grid and reference electrode, Ag/AgCl/3 M KCl. Cyclic voltammetry (CV) and rotating disc electrode (RDE) tests were undertaken in the presence of oxygen purging and absence of oxygen at room temperature utilizing an Autolab, potentiostat/galvanostat. For all electrochemical measurements, 0.1 M KOH solution was employed as the electrolyte.

4.1. Method of Making Ink

Five mg of catalyst was mixed with 1000 μL of ethanol and 40 μL of 5 wt.% Nafion solution in an Eppendorf and the ink was then sonicated for 30 min in ultrasonic. Eight μL of this solution was then drawn by Hamilton syringe and deposited on electrode 3. After 30 min the ink was dried on the electrode and then the electrode was transferred to an alkaline medium for electrochemical tests.

4.2. Electrochemical Tests

1. CV test in the presence of O_2 and N_2 gases, 2. LSV test in the presence of O_2 , 3. Chrono amperometry test in the presence of oxygen. Used ranges: For CV test: (−1.2 V–1 V), scan rate = 0.1, for LSV test: (−1.2 V–0.2 V), scan rate = 0.01, RDE = 500–2500 rpm, for chrono amperometry test: duration = 1000 s, interval time = 1 s, potential = −0.4 V

The activity of synthesized catalysts was evaluated by the electrochemical tests in alkaline solution. The 0.5 M KOH solution at 25 °C was used as the electrolyte. The implemented electrochemical tests consist of cyclic voltammetry (CV), linear sweep voltammetry (LSV), electron transferred number (n), and chronoamperometric. The occurrence of ORR is investigated by the CV measurement. This test is implemented in N_2 and O_2 saturated solution, and at the scan rate of 100 mV/s. For computing the onset potential of each electrocatalyst, LSV curves are used. This test is done in the O_2 saturated solution, and at the scan rate of 10 mV/s. For calculating the value of electron transferred number (n), the Koutecky–Levich (KL) equation is utilized as follows [53]:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{B\omega^{0.5}} \quad (1)$$

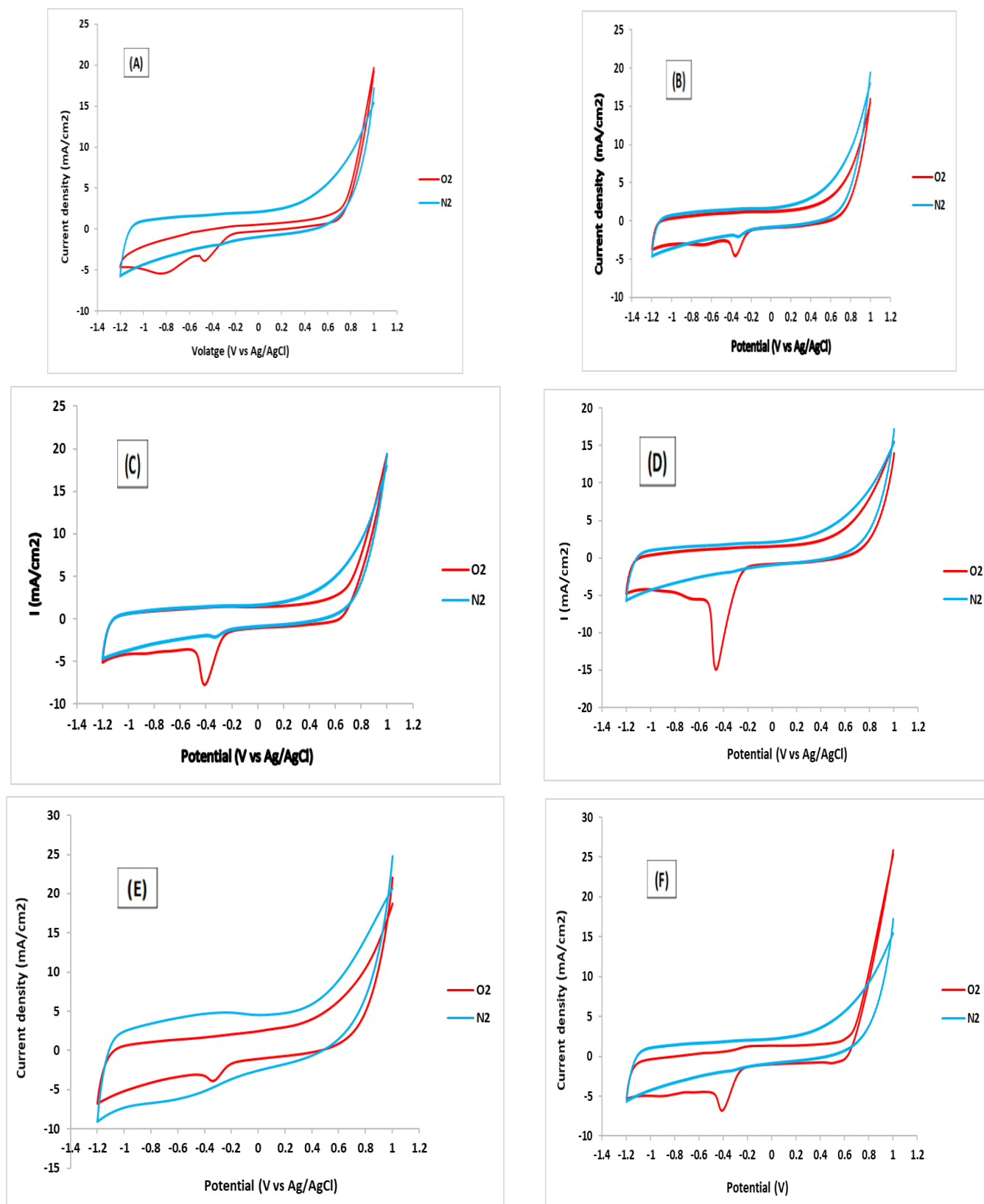
$$B = 0.62 n F C_{\text{O}_2} (D_{\text{O}_2})^{\frac{2}{3}} \nu^{-\frac{1}{6}} \quad (2)$$

In the above equations, J (mA/cm^2) and J_K (mA/cm^2) imply the limiting current density and kinetic current density, respectively. ω (rad/s) denotes the rotation speed of working electrode. n is related to the number of transferred electrons, and F is the Faraday constant. C_{O_2} and D_{O_2} represent the bulk concentration of oxygen ($1.2 \times 10^{-6} \text{ mole}/\text{cm}^3$) and diffusion coefficient of oxygen ($1.9 \times 10^{-5} \text{ cm}^2/\text{s}$), respectively. Also, the kinematic viscosity of the electrolyte is ν ($0.01 \text{ cm}^2/\text{s}$).

5. Results and Discussion

Figure 6 presents the CV curves of electrocatalysts synthesized in the solution of 0.1 M KOH. As can be seen, for all of the electrocatalysts, the peak related to the oxygen reduction reaction is not seen for the N_2 saturated solution. The peak corresponding to the ORR for oxidized MWCNT is obtained at −0.5 V. By doping the S functions, this peak shifts to positive values (−0.35 V). Moreover, the highest value of current density at the peak potential belongs to the N, S, B-MWCNT electro catalyst (−33.65 mA/cm^2). The electrochemical activity of the doped MWCNT are considerably increased by doping N, S, and B. Figure 7 illustrates the LSV curves of electrocatalysts synthesized in the solution of 0.1 M KOH and saturated O_2 . In this investigation, the rotating speed of the work electrode is considered to be variable from 500–2500 rpm (with the step of 500). According to the LSV results for all of the electrocatalysts, by increasing the rotating speed of the work electrode, the O_2 diffusion pathway is shortened. As a result, the current density (J) increases. The onset potential for oxidized MWCNT catalyst is −0.2 V vs. Ag/AgCl. By doping N, S, and B atoms on MWCNT, the onset potential shifts to the positive values. The onset potential of N-MWCNT and S-MWCNT are obtained to be −0.178 and −0.165 V vs. Ag/AgCl, respectively. The best performance and electrochemical activity belonged to the NB-MWCNT catalyst (−0.122 V vs. Ag/AgCl). As can be illustrated, the onset potential of 20 wt% Pt/C catalyst is near to zero. As a result, NB-MWCNT catalyst can be an inexpensive alternative for the ORR application. It can be deduced that by doping the N, B, and S atoms on MWCNTs, the defects in the CNT structure, which serve as active sites for ORR

application, increase. The N/S/B-doped graphitic layers have a more rapid electron transfer rate at the electrode/electrolyte interface. So, this can improve the electrochemistry performance and electron transfer of the MWCNTs.



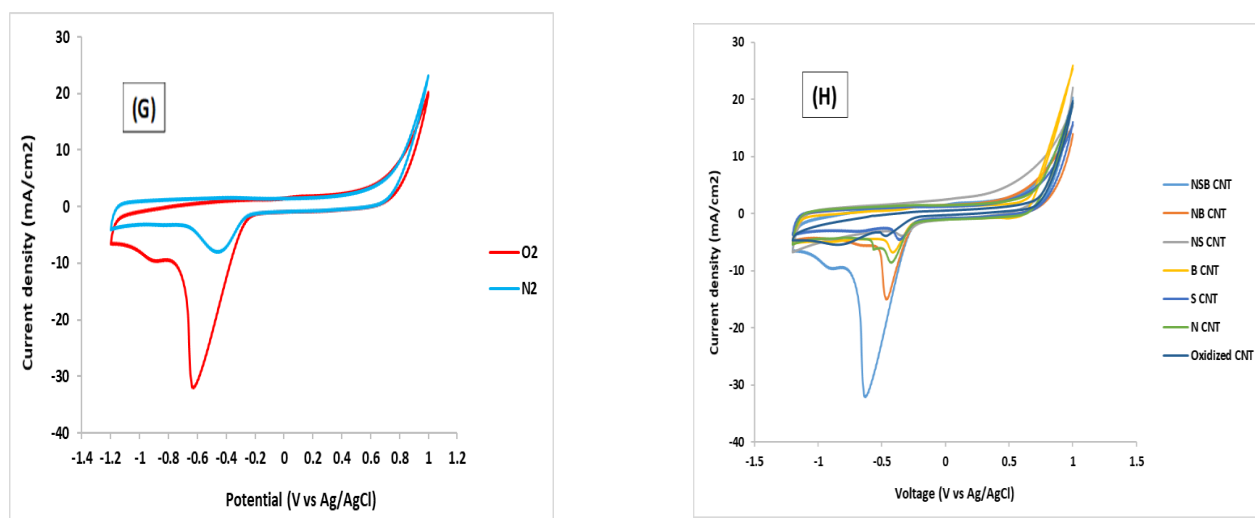
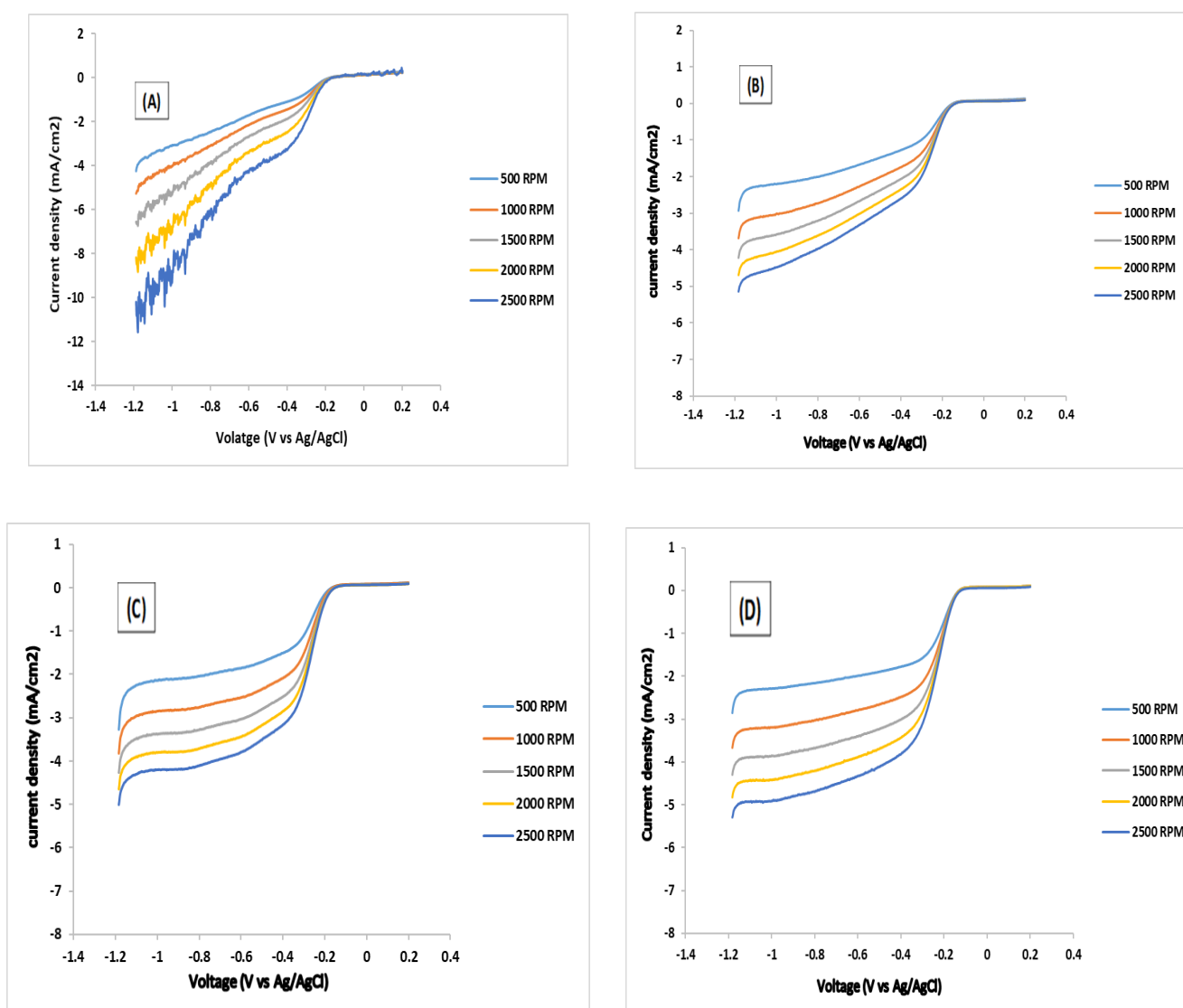


Figure 6. The results of CV test for synthesized electrocatalysts-(A): oxidized MWCNT; (B): SMWCNT; (C): N-MWCNT; (D): NB-MWCNT; (E): NS-MWCNT; (F): B-MWCNT; (G): NSB-MWCNT. (H): Comparison of electrocatalysts.



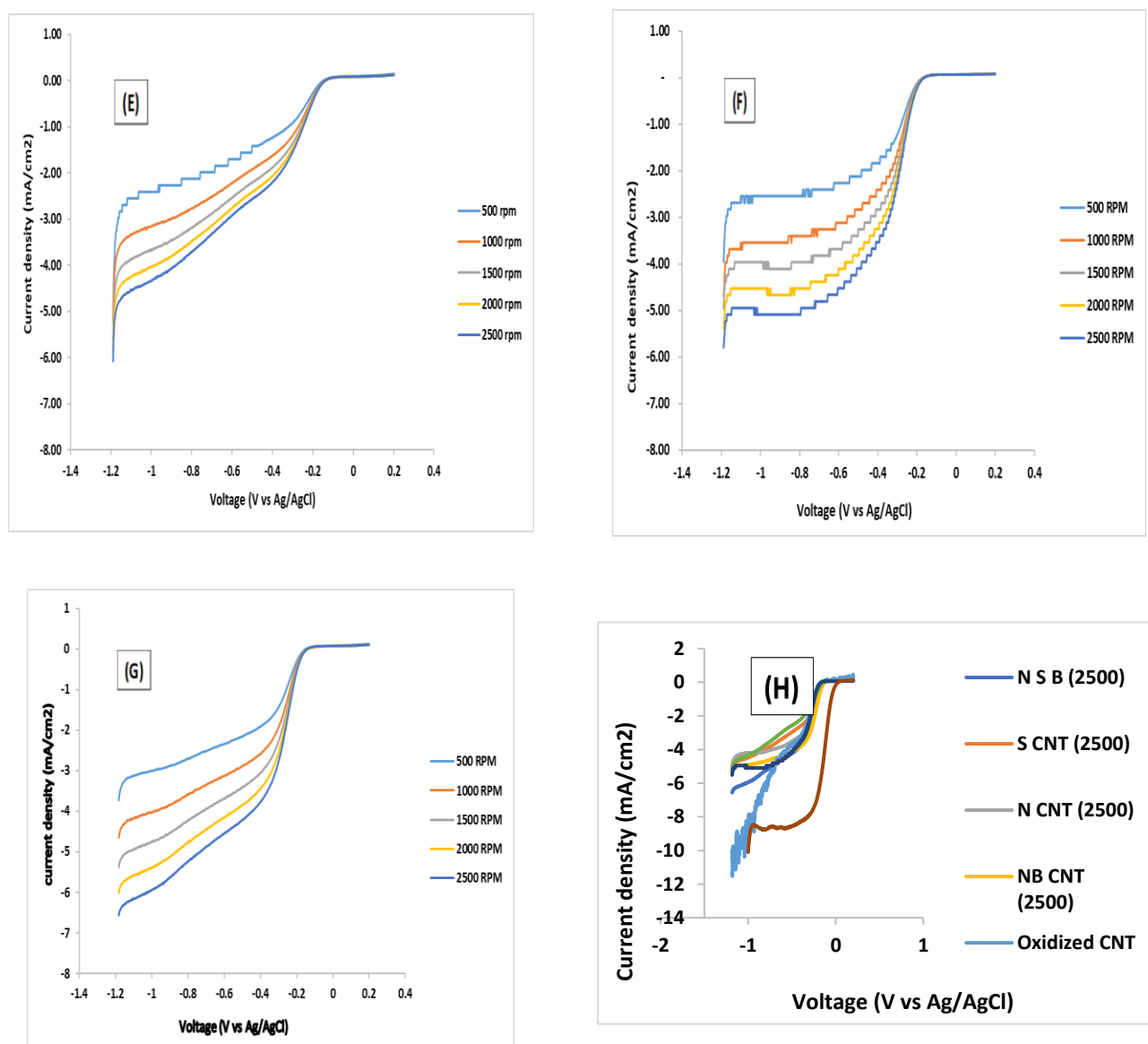
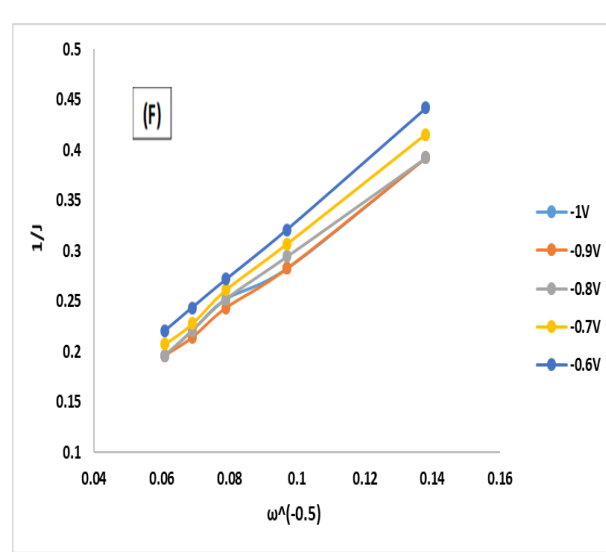
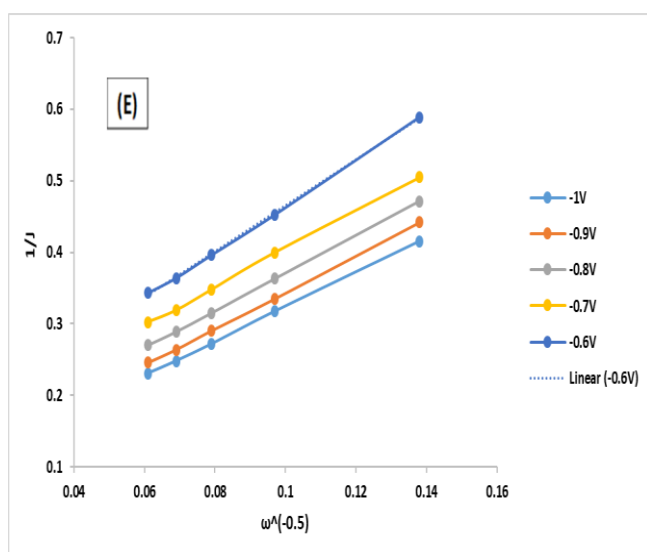
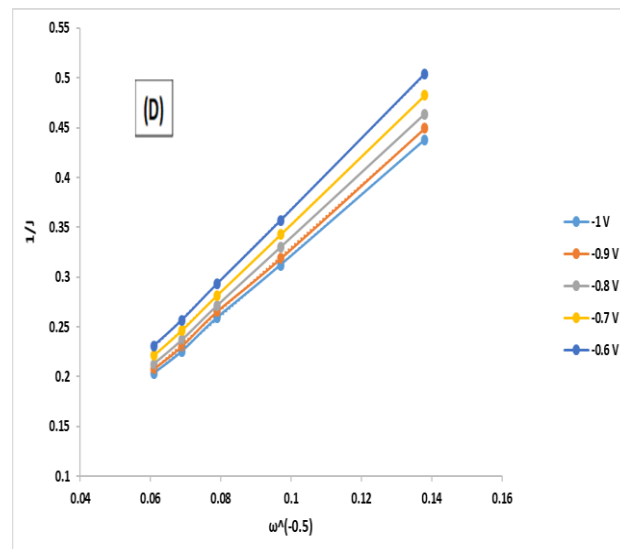
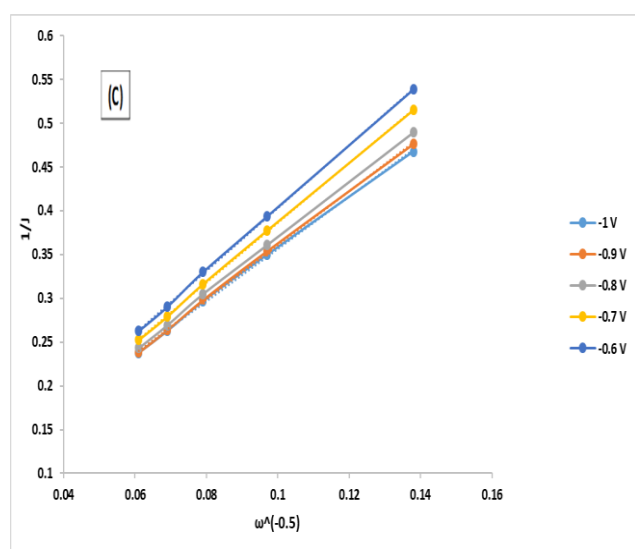
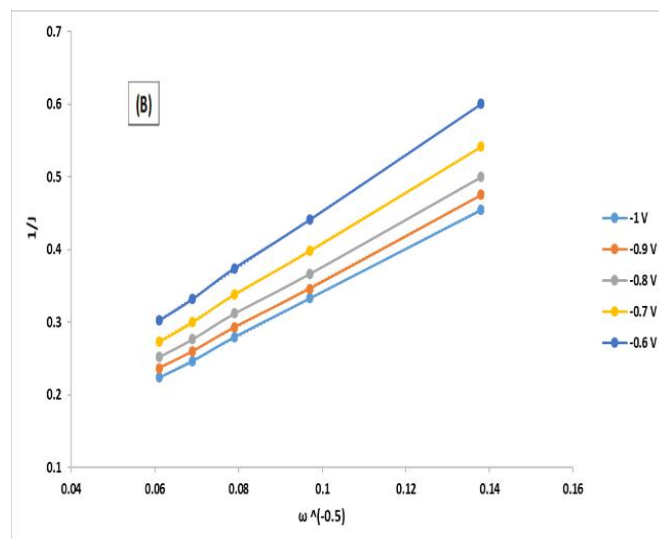
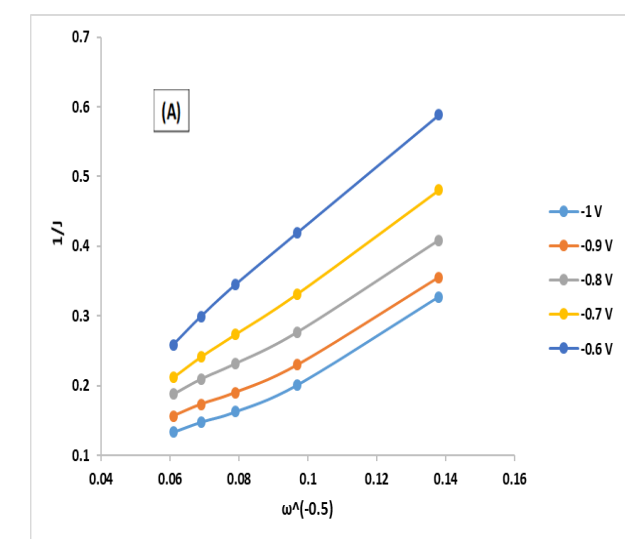


Figure 7. The results of LSV test for synthesized electrocatalysts-(A): oxidized MWCNT; (B): S-MWCNT; (C): N-MWCNT; (D): NB-MWCNT; (E): NS-MWCNT; (F): B-MWCNT; (G): NSB-MWCNT; (H): Comparison of electrocatalysts.

The Figure 8 displays the KL plots of electrocatalysts synthesized at the different potentials. As can be shown, the KL curves are plotted in the range of -0.6 – (-1) V. The n for oxidized MWCNT at -0.6 V is obtained to be 2.3. By doping the heteroatoms, the kinetic performance of catalyst is improved considerably. The largest value of electron transferred number (n) at -0.6 V is related to the NB-MWCNT (3.5). As a result, by employing this catalyst at the cathode side, the ORR occurs through the $4 e^-$ pathway. Figure 9 exhibits the normalized chronoamperometric responses of electrocatalysts synthesized in the solution of 0.1 M KOH and saturated O_2 . The durability of electrocatalysts is investigated by applying the chronoamperometric test. In this study, the chronoamperometric test is performed at the saturated O_2 , with a constant voltage of -0.4 V vs. Ag/AgCl for 1000 s. Based on Figure 9, it can be concluded that all of the electrocatalysts have an acceptable stability under the operating conditions. The fastest time to reach durability belonged to the NSB-MWCNT. It can be shown that after less than 80 s, the current density reaches a steady amount and this is continued for up to 1000 s.



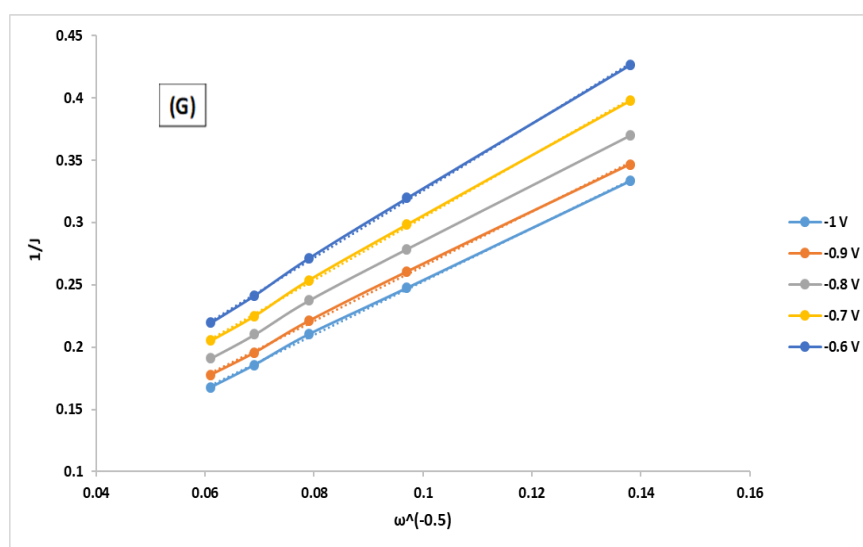
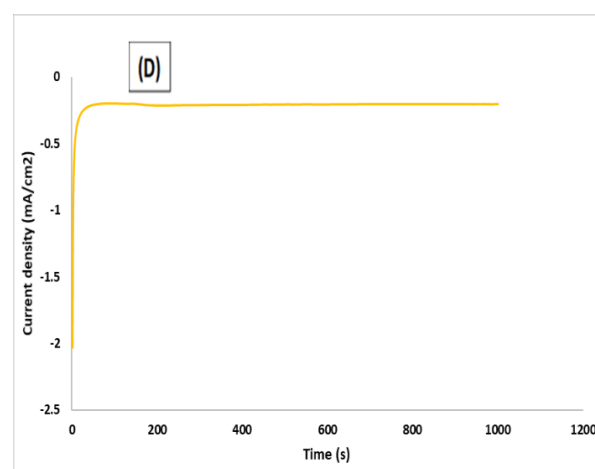
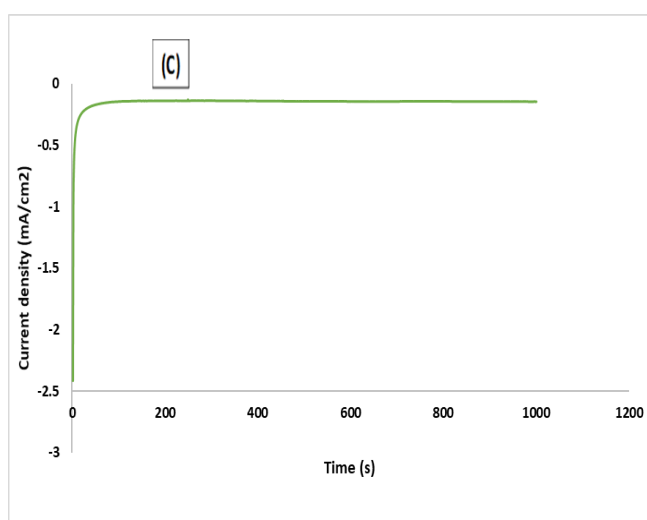
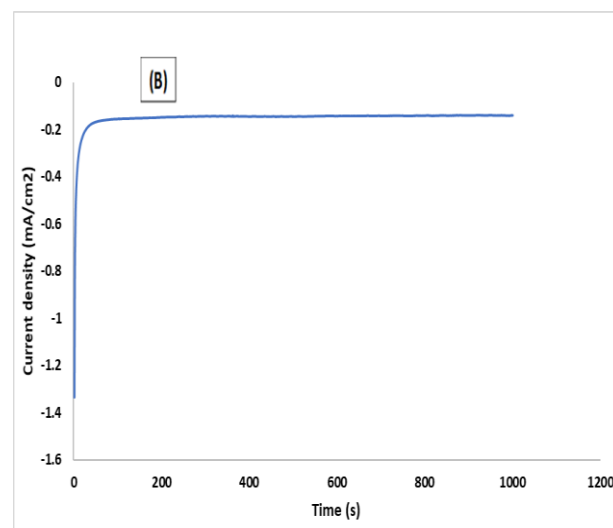
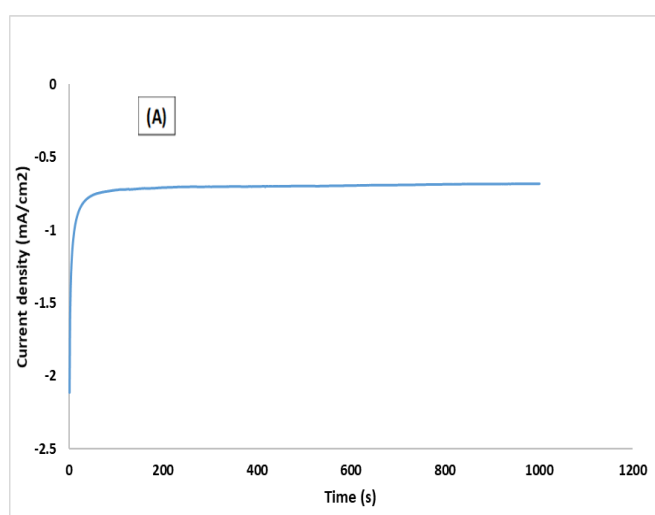


Figure 8. The KL plots for synthesized electrocatalysts-(A): oxidized MWCNT; (B): S-MWCNT; (C): N-MWCNT; (D): NB-MWCNT; (E): NS-MWCNT; (F): B-MWCNT; (G): NSB-MWCNT.



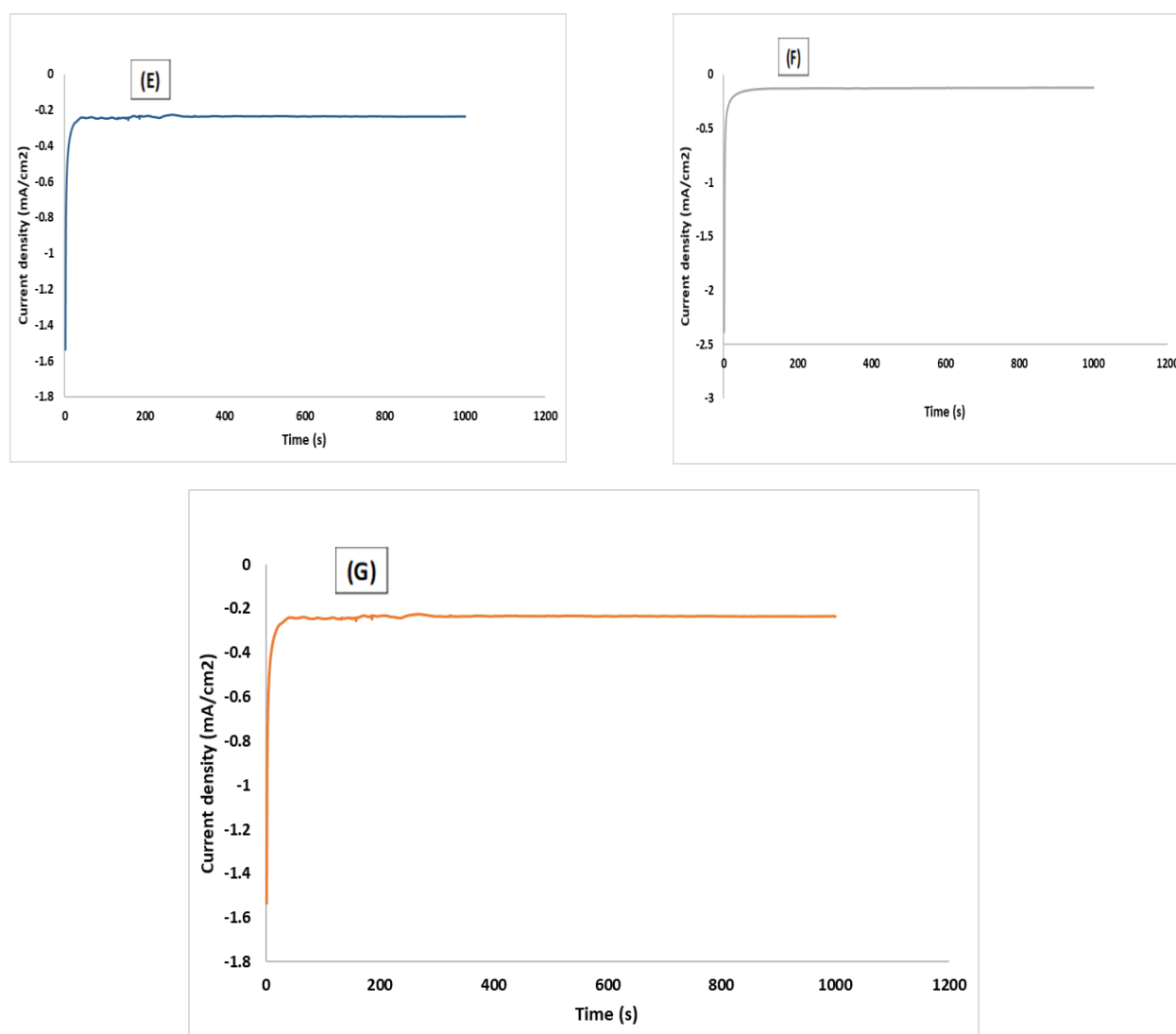


Figure 9. The results of chronoamperometric responses for synthesized electrocatalysts-(A): oxidized MWCNT; (B): S-MWCNT; (C): N-MWCNT; (D): NB-MWCNT; (E): NS-MWCNT; (F): B-MWCNT; (G): NSB-MWCNT.

Table 2 states the comparison between the onset potential of synthesized catalyst in this investigation and previous studies. It can be shown that the electrochemistry activity of NB-MWCNT composite is better than the synthesized electrocatalysts in last investigations.

Table 2. The achieved onset potentials for this study and previous investigations at 0.1 M KOH.

<i>Electrocatalyst</i>	<i>V_{Onset} (V vs. Ag/AgCl)</i>	<i>Reference</i>
NB-MWCNT	−0.122	Current project
Co-Oxybis	−0.197	[54]
Cu ₂ (TMBDI) (H ₂ O) ₂	−0.131	[55]
CoFe-LDHs/PDAS	−0.0182	[56]
(Fe/Co)-BTC	−0.132	[57]

6. Conclusions

In the current project, a facile and low temperature fabrication method for heteroatom doping of the sulfur, nitrogen and boron elements on oxidized multiwall carbon

nanotubes is investigated and discussed. MWCNT doped with the abovesaid elements can be employed as the electrocatalyst of ORR. The physical analysis tests results show that single and multiple doping have been undertaken successfully with the proposed method. Electrochemical analysis was completed on the synthesized electrocatalysts. Results also indicate 4e-electron transfer number for the MWCNT dope catalysts. Multi-doping with N and other dopants has better performance against single doping by N. The synergy between different dopants can increase the catalytic activity of the MWCNT. Between dual-dope synthesized electrocatalyst catalysts NB-MWCNT showed the best performance. The addition of boron can remove the c-o bonds and improve the electrochemistry activity of MWCNT. Also, the stability of the fabricated catalysts was evaluated by the chronoamperometric response.

The effects of the different atomic ratios of N, S, and B on the catalytic performance can be investigated for future works.

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Nomenclature and Abbreviations

abbreviations

CNT	Carbon Nanotube
GO	Graphene Oxide
RGO	Reduced Graphene Oxide
ORR	Oxygen Reduction Reaction
CV	Cyclic Voltammetry
MWMWCNT	Multiwall Carbon Nanotube
LSV	Linear Sweep Voltammetry
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
FTIR	Fourier Transformed Infrared
EDS	Energy-Dispersive X-ray Spectroscopy
TEM	Transmission Electron Microscopy
GCE	Glassy Carbon Electrode

Elements

C	Carbon
N	Nitrogen
S	Sulfur
B	Boron
Pt	Platinum
Na	Sodium
Mn	Manganese
K	Potassium

H	Hydrogen
Ag	Silver
<i>Parameters utilized in KL equation</i>	
J	Current density (mA/cm ²)
ω	Rotation speed (rad/s)
n	Electron transferred number
F	Faraday constant (96,485 C/mole)
ν	Kinematic viscosity of the electrolyte (0.01 cm ² /s)
C_{O_2}	Bulk concentration of oxygen (1.2×10^{-6} mole/cm ³)
D_{O_2}	Diffusion coefficient of oxygen (1.9×10^{-5} cm ² /s)

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