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An experimental investigation on the sulfur and nitrogen co-doping and oxidation of prepared graphene by electrochemical exfoliation of pencil graphite rods

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Abstract

In this research, the electrochemical exfoliation of pencil rods was carried out for the synthesis of graphene sheets in different mixtures of H_2SO_4 and HNO_3 solution. Influence of different volume ratios of H_2SO_4: HNO_3 at a low concentration (0.6 M) on the morphology and structure of prepared graphene sheets was investigated by field emission electron microscopy (FESEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), Raman spectroscopy and atomic force microscopy (AFM) analyses. Results indicated that the mixtures of few-layered graphene, multi-layered graphene, and graphene oxide were achieved by applying an anodic voltage of + 10 V. However, the number of layers, degree of oxidation and defect density of the synthesized powders were different. By increasing the volume ratio of HNO_3 in electrolytes, the degree of exfoliation of graphite decreased. On the other hand, the highest degree of oxidation was achieved for the prepared graphene by electrochemical method in the mixture of H_2SO_4: HNO_3 with 1:1

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ratio. EDS results of the prepared powders demonstrated the occurrence of nitrogen and sulfur co-doping of graphene sheets.

Keywords: Co-doped graphene; Oxidation; Electrochemical exfoliation; Mixed electrolytes.

1- Introduction

Graphene oxide (GO) owing to the presence of oxygen functional groups on its surface has some advantages such as higher processability and dispersibility in solutions, in comparison to the pristine graphene. To date, various approaches have been introduced for the production of GO, but these methods mainly suffer from some disadvantageous such as the risk of explosions and consuming high energy (or time) [1-5]. The electrochemical method is a fast and eco-friendly method for the large-scale production of high-quality graphene [6-13]. However, there is little information about the synthesis of GO using the electrochemical method. Recent studies have focused on the ability of this route for the synthesis of few-layered GO. In literature, there are two groups of one-step [14-18] and two-step [19, 20] electrochemical methods for the synthesis of GO. As an example of a two-step method, Cao et al. [20] successfully synthesized GO using a two-stage electrochemical method. At first, they charged the graphite foils in a highly concentrated H_2SO_4 solution (≥95%) and then performed electrochemical exfoliation in 0.1 M $(NH_4)_2SO_4$ solution. Their results revealed that the higher degree of oxidation and exfoliation phenomena occurred by applying the higher anodic voltages.

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Although the two-step electro-oxidation of graphene has been reported as an effective way for the production of GO, it takes generally high time. Therefore, the preparation of the GO using a one-step electrochemical method is preferable. In literature, some efforts for the synthesis of GO using the one-step electrochemical method can be found [14-18, 21, 22]. For example, Sahoo et al. [14] investigated the effect of different electrolytes on the preparation of the graphene sheets by the electrochemical method. They used 1 M H_2SO_4, 1 M $HClO_4$, and 1 M HNO_3 solution as electrolytes. Their results indicated that the GO was synthesized using the 1 M $HClO_4$, and 1 M HNO_3 electrolytes. However, the related peaks of GO were not observed in the XRD patterns of powders prepared by the electrochemical method in a 1 M H_2SO_4 solution. The high rate of exfoliation process using the H_2SO_4 solution was introduced as the possible reason for the absence of GO in related XRD patterns.

A recent study by Lowe et al. [23] has indicated that the GO can be synthesized using the high concentration of the H_2SO_4 solution. Their results showed that the degree of oxidation was increased by raising the concentration of H_2SO_4 from 2 to 16 M. However, our previous research [24] has demonstrated that increasing the concentration of H_2SO_4 leads to an increase in the kinetic of reaction and only the expanded graphite was obtained. As another way for the production of GO by electrochemical method, Coros et al. [15] investigated the effect of different anodic voltages (2.5, 3.0, 5.5 and 6.0 V) on the morphology and structure of prepared graphene sheets by electrochemical exfoliation of graphite rods in a mixture of H_2SO_4: HNO_3 (3:1 ratio, and concentration of 0.5 M). Their

results proved that the mixtures of GO, few-layered graphene (FLG), and multi-layered graphene (MLG) were obtained via the electrochemical method in the mentioned electrolyte. By decreasing the applied voltage, the percentage of GO was decreased in their study. Therefore, they concluded that the application of the higher voltages leads to the production of higher contents of GO.

In another investigation, Gurzeda and Krawczyk [25] conducted an experimental study on the effect of different volume fractions of the 95% H_2SO_4: 65% HNO_3 solution (1:3, 2:3, 1:1, 3:2 and 3:1 ratio) on the electrochemical exfoliation of graphite flakes. Their results indicated that the partial exfoliation occurred using the mentioned electrolytes. However, by increasing the volume fractions of the H_2SO_4 solution, the exfoliation degree increased. However, their results strongly confirmed the oxidation of graphite. Thereby, the preparation of GO using the mixtures of high-concentrated H_2SO_4 and HNO_3 cannot be achieved. Therefore, this study aims to investigate the effect of different volume ratios of sulfuric acid: nitric acid at a low concentration of 0.6 M on the structure and morphology of the prepared powders by electrochemical exfoliation of pencil rods.

2- Experimental procedure

The pencil graphite rods (Baile, China), with a diameter of 2 mm were used as both anode and cathode electrodes, in this research. The used chemicals as electrolytes were H_2SO_4 (> 98%) and HNO_3 (65%). Different mixtures of H_2SO_4: HNO_3 solution (3:1, 1:1, and 1:3 ratio) with a constant concentration of 0.6 M were prepared as the electrolytes for

the electrochemical method. Table 1 shows the sample codes. The electrodes were placed at a constant distance of 2 cm and then, the electrochemical process was carried out using a constant anodic voltage of +10 V. After the electrochemical exfoliation process, the solutions were ultrasonically sonicated for 45 min (ultrasonic homogenizer 400 W, 24 kHz, FAPAN Co, Iran), to increase the efficiency of exfoliation. Then, the suspensions were washed with distilled water and filtered three times to remove impurities.

The morphology of prepared powders was analyzed by field emission scanning electron microscopy (FESEM, MIRA3 TESCAN, Czech). Also, atomic force microscopy (AFM, Bruker ICON, USA) was conducted with non-contact mode to evaluate the topology of the optimum sample. The structural analyses of samples were carried out using X-ray diffraction (XRD, Rigaku Ultima IV, Japan) patterns and Raman spectroscopy (TakRam N1-541, Teksan Co, Iran). The XRD analyses were performed by Cu Kα radiation and a step scan of 0.05˚. To characterize the defect density and structure of samples, Raman spectroscopy analysis with $\lambda = 532\ nm$ was used.

3- Results and discussion

3-1- XRD analysis

Fig. 1 shows the XRD patterns of the pencil rod and prepared samples by the electrochemical method. As can be seen in Fig. 1, there is only an intense diffraction peak at about 26º related to the (002) plane of graphite for pencil graphite rod sample, demonstrating the low impurity of the pencil graphite rods. For all prepared samples by electrochemical method, the (002) diffraction peak of graphite at about 26º is also visible. Besides, a broad peak in the range of 20-22º can be also found in the XRD pattern of the

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samples corresponding to the (002) peak of graphene. Using equation (1), the number of graphene layers can be obtained [26].

$$n = \frac{D}{d} \quad (1)$$

Where n is the number of graphene layers, D (Aº) is the mean crystalline size and d (Aº) is the interlayer distance between the graphene layers. The D and d values are calculated using the Scherer and Bragg equations. It has been reported that the diffraction peak near 26º is related to the MLG while the peak near the 22º is related to the FLG [15, 23, 27]. The results of the mentioned calculations for the prepared samples by the electrochemical method are given in Tables 2 and 3. According to Table 2, the number of graphene layers in MLG is the least for the S sample (about 14) and it can be seen that by increasing the concentration of HNO_3, the number of graphene layers in MLG has been generally increased. Table 3 presents the information on FLG. According to Table 3, it can be seen that the FLG in prepared S and S3N1 samples (about 4) have the lowest number of graphene layers, compared to the other samples. However, it can be seen that the N sample is composed of only MLG. In addition to the number of graphene layers, it can be deduced that by increasing the concentration of HNO_3 in solutions the d-spacing of graphene layers has been increased from 3.99 nm in S sample to 4.27 nm in N sample. The increased d-spacing layer of graphene can be related to the functionalization phenomenon.

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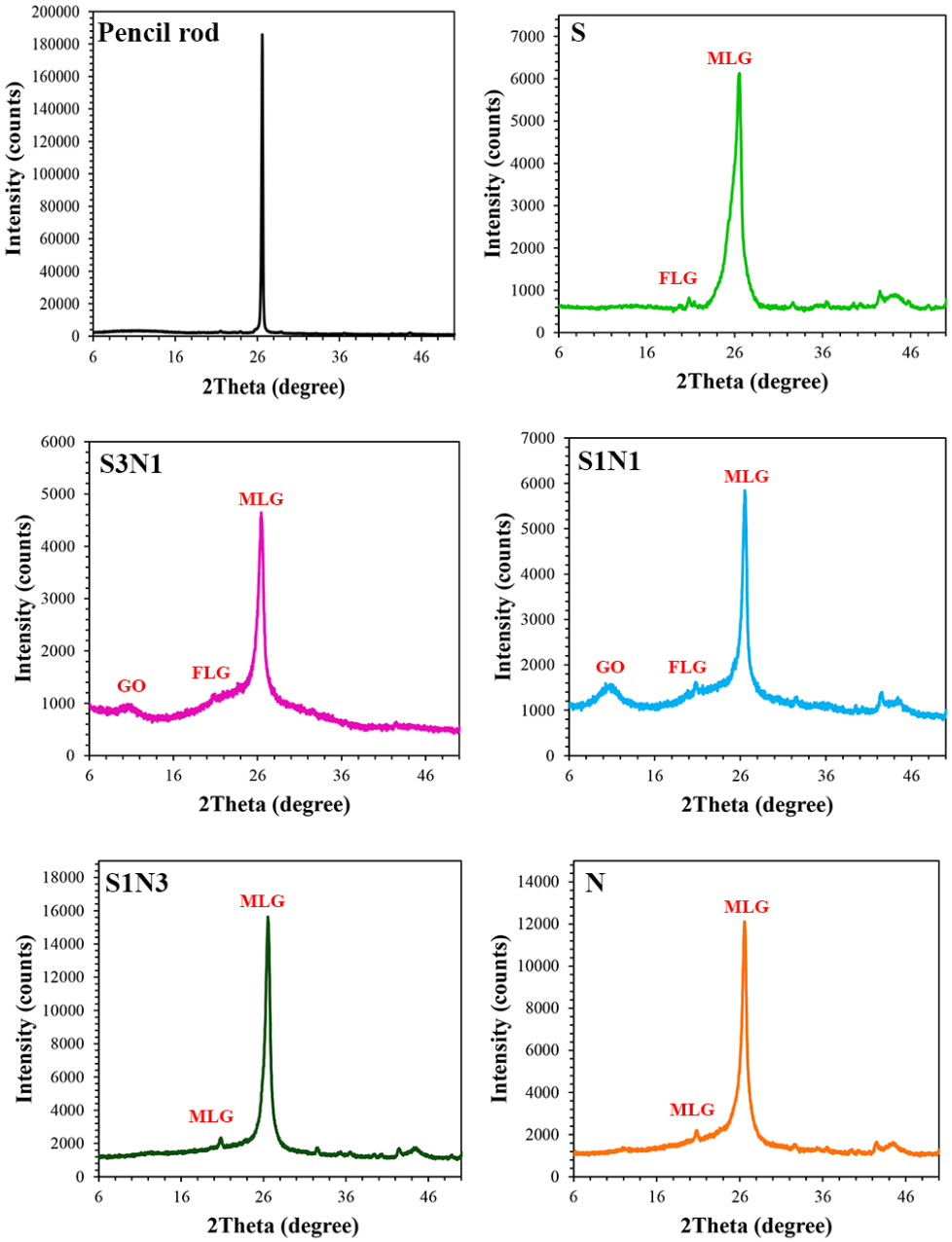

Fig. 1. The XRD patterns of samples.

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Table 1. The sample's codes.

Electrolyte	Sample's code
0.6 M H_2SO_4	S
The mixture of H_2SO_4 and HNO_3 with volume ratio 3:1	S3N1
The mixture of H_2SO_4 and HNO_3 with volume ratio 1:1	S1N1
The mixture of H_2SO_4 and HNO_3 with volume ratio 1:3	S1N3
0.6 M HNO_3	N

Table 2. The detailed information of the graphitic peak of electrochemically-prepared powders.

Sample	FWHM (rads)	2θ (degree)	d_{002} (A°)	D (A°)	n (D/d)
S	0.0282	26.23	3.39	49.7739	14.67
S3N1	0.0151	26.37	3.37	92.70789	27.50
S1N1	0.0113	26.46	3.36	123.4719	36.74
S1N3	0.0122	26.5	3.36	115.2533	34.30
N	0.01745	26.5	3.36	80.67732	24.01

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Table 3. The detailed information of the graphene peak of electrochemically-prepared powders.

Sample	FWHM (rads)	2θ (degree)	d_{002} (A°)	D (A°)	n (D/d)
S	0.0872	22.23	3.99	16.9899	4.25
S3N1	0.0818	22.43	3.96	18.1268	4.57
S1N1	0.0413	21.72	4.08	35.722	8.75
S1N3	0.0349	21.00	4.28	42.06	9.82
H	0.0087	20.79	4.27	168.512	39.47

Besides, by careful viewing Fig. 1, it can be observed that a broad peak corresponding to the (100) plane of GO at about 10.55º is visible for all samples. However, the mentioned peak only for S3N1 and S1N1 samples is considerable while other samples have not any significant intensity. Therefore, it can be deduced that oxidation of the graphene has occurred significantly for S3N1 and S1N1 samples. The higher intensity of the (100) peak of GO in the S1N1 sample demonstrates the higher degree of oxidation in this condition, compared to the S3N1 sample. According to these results, it can be deduced that mixing the H_2SO_4 and HNO_3 with 1:1 volume ratio is the optimum electrolyte for achieving a higher degree of oxidation phenomenon. The increased degree of oxidation in the mentioned condition can be related to the delaying effect of HNO_3 on the exfoliation rate of graphite, promoting more times for electro-oxidation of graphene.

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This study is the first report on the appearance of the XRD peak of GO by electrochemical exfoliation penile graphite rods. There are few papers on the electrochemical exfoliation of pencil graphite rods. Liu al. [17] investigated the electrochemical exfoliation of pencil cores as both cathode and anode materials in the aqueous solution of H_2SO_4. Briefly, they applied an alternative voltage of -7 to +7 V for 5-8 min. Applying the alternative cathodic and anodic voltages led to the exfoliation of both cathode and anode materials during the process. Although their results indicated that the few-layered graphene was obtained, the XRD diffraction peak of GO was not reported in their work. Only the XRD diffraction peak of graphite was shifted from 26.5º to 26.4º, indicating the increased interlayer spacing of graphite due to the presented functional groups. Although they claimed that the GO was achieved, it seems that the degree of oxidation was low in their work. In another study, the electrochemical exfoliation of 5B pencil core as an anode electrode in 0.1 M $(NH_4)_2SO_4$ electrolyte was investigated by Chen et al. [28]. They applied anodic voltage of +10 V. Their results also indicated the few-layered graphene was obtained but the oxidation phenomenon was not reported in their study.

3-2- Morphological evaluations

The general morphologies of the prepared powders are given in Fig. 2. As visible, the large contents of graphite materials have been exfoliated in S and S3N1 samples and no thick graphitic materials can be found in these figures. However, as visible, by increased the HNO_3 volume content in the electrolytes the degree of exfoliation of graphite has been decreased. These results are in good agreement with the XRD results.

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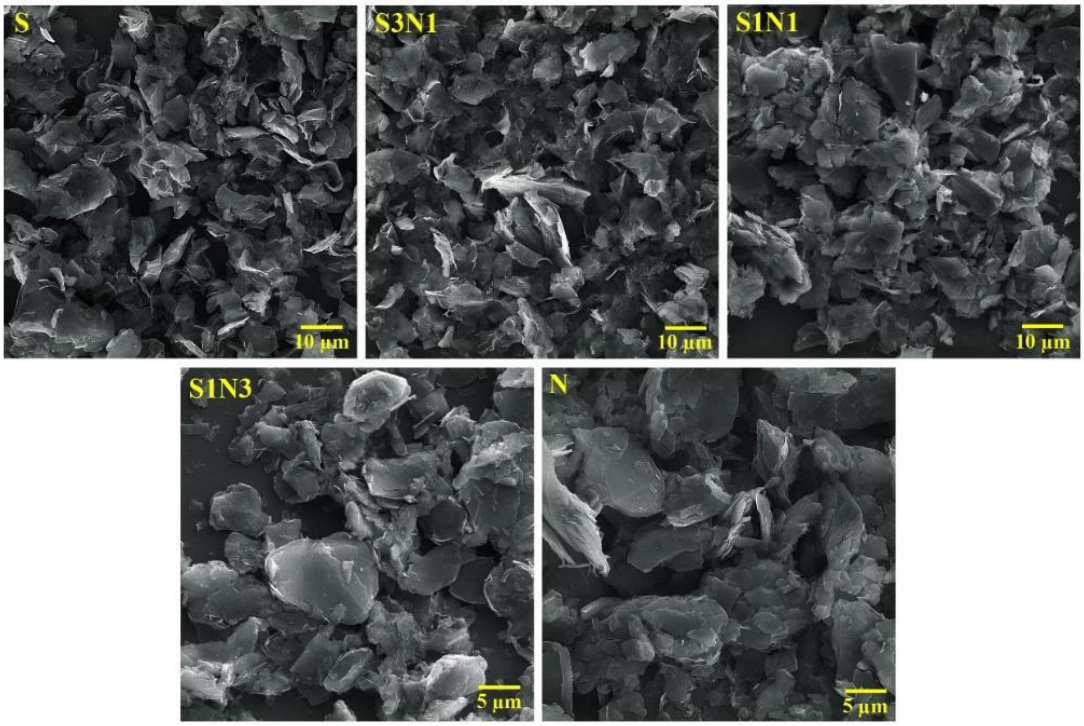

Fig. 2. The general morphologies of obtained powders in samples.

For a better comparison of the morphologies of obtained graphene in samples, different morphologies of MLG, FLG, and edge sections of obtained graphene in different samples have been selected and presented in Fig. 3. Figs. 3a-3e indicate the obtained MLG in different samples. It can be seen that not only the degree of exfoliation phenomenon is different for samples, but also the degree of wrinkles of sheets is different. As visible, the obtained MLG in S, S3N1 and S1N1 samples have few layers, compared with the S1N3 and N samples. On the other hand, the degree of wrinkles of the MLG in S and S3N1 samples (Figs. 3a and 3b) are higher than that of other samples. The morphologies of FLG have been shown in Figs. 3f to 3j. As can be seen, the amount of FLG in the S, S3N1, and S1N1 samples are more than S1N3 and N samples. There is no significant difference

between the FLG and MLG in S1N3 and N samples. In other words, it can be said that only MLG has been formed in S1N3 and N samples. Besides, the degree of exfoliation of graphite in samples can be compared by viewing Figs. 3k to 3o, indicating more efficiency of electrolytes containing the higher volume fraction of H_2SO_4 in the exfoliation phenomenon.

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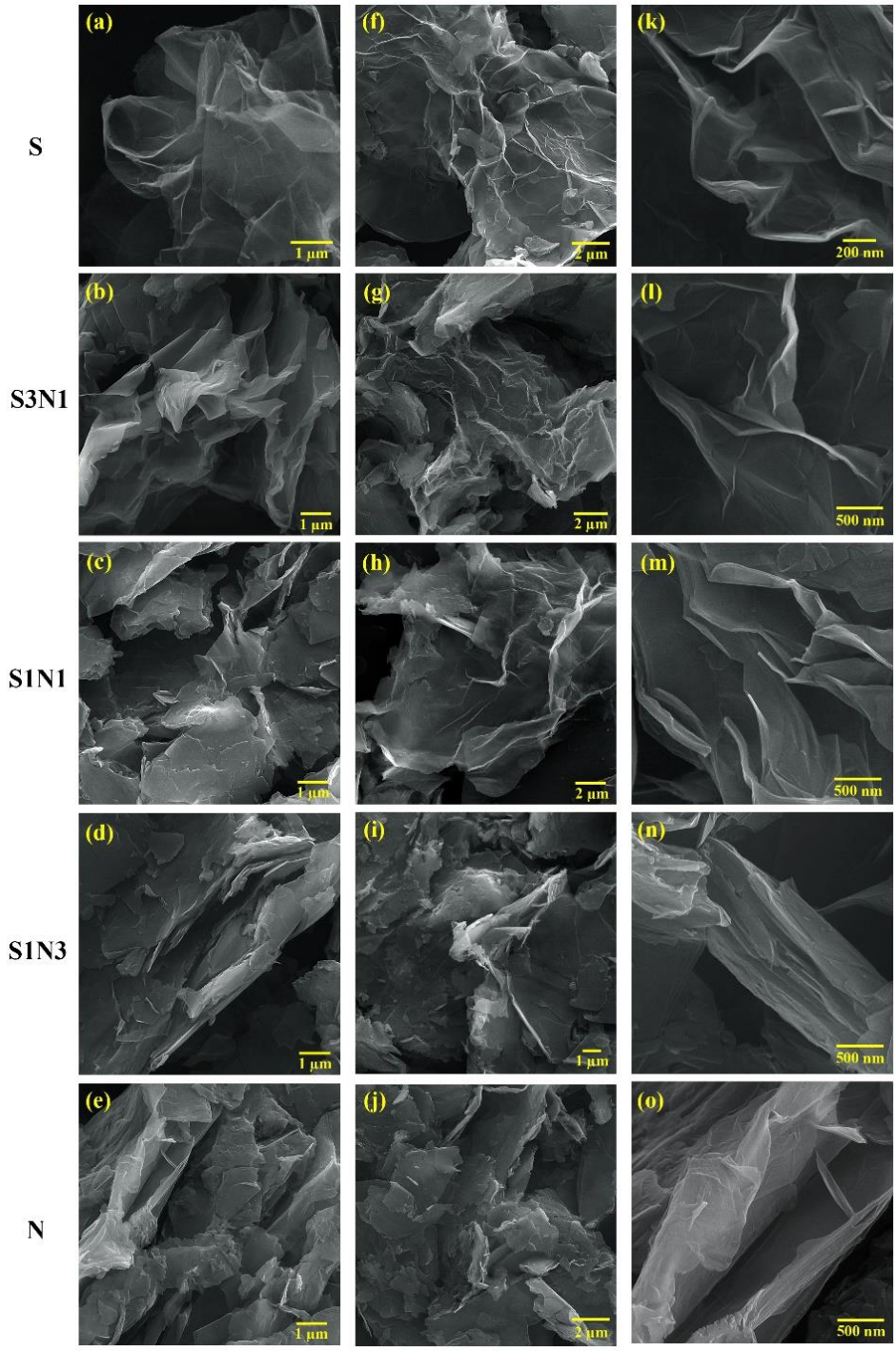

Fig. 3. The FESEM images of prepared graphene sheets by electrochemical method.

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As shown by FESEM images (Figs. 2 and 3), by the increase in the volume fraction of the HNO_3 in the electrolytes, the degree of exfoliation phenomenon has decreased. Therefore, the introduction of the mechanism of electrochemical exfoliation of graphite is necessary (Fig. 4). At the first step of the electrochemical method, by applying voltages, the electrolyze of water leads to the formation of the hydroxyl and oxygen free-radicals. These radicals can help in opening the edge of graphite. After that, the formed SO_4^{2-} and NO_3^- ions intercalate thorough the interlayer spacing of graphite and lead to increasing the distance between layers and exfoliation phenomenon. It is well-understood that the gas generation during the electrochemical exfoliation has a significant influence on the preparation of the FLG. The following reactions can occur by applying the anodic voltage of +10 V. According to the equations (2) to (5), the release of CO_2 and O_2 gaseous species during the electrochemical exfoliation of graphite causes the exfoliation of graphite layers.

$$C_x + H_2O \rightarrow C_{x-1}OH + H^+ + e^- \quad (2)$$

$$C_x + 2H_2O \rightarrow C_{x-1} + CO_2 + 4H^+ + 4e^- \quad (3)$$

$$C_x + 2H_2O \rightarrow C_{x-1}COOH + CO_2 + 3H^+ + 3e^- \quad (4)$$

$$H_2O \rightarrow 2H^+ + 2e^- + 1/2O_2 \quad (5)$$

As indicated in XRD patterns and FESEM images (Figs. 1 and 3), the degree of exfoliation has decreased by increasing the volume ratio of the HNO_3 in electrolytes. Similarly, in previous studies, it has been reported that the electrolytes containing sulfate ions are the best choices for the electrochemical exfoliation of graphite [14, 29].

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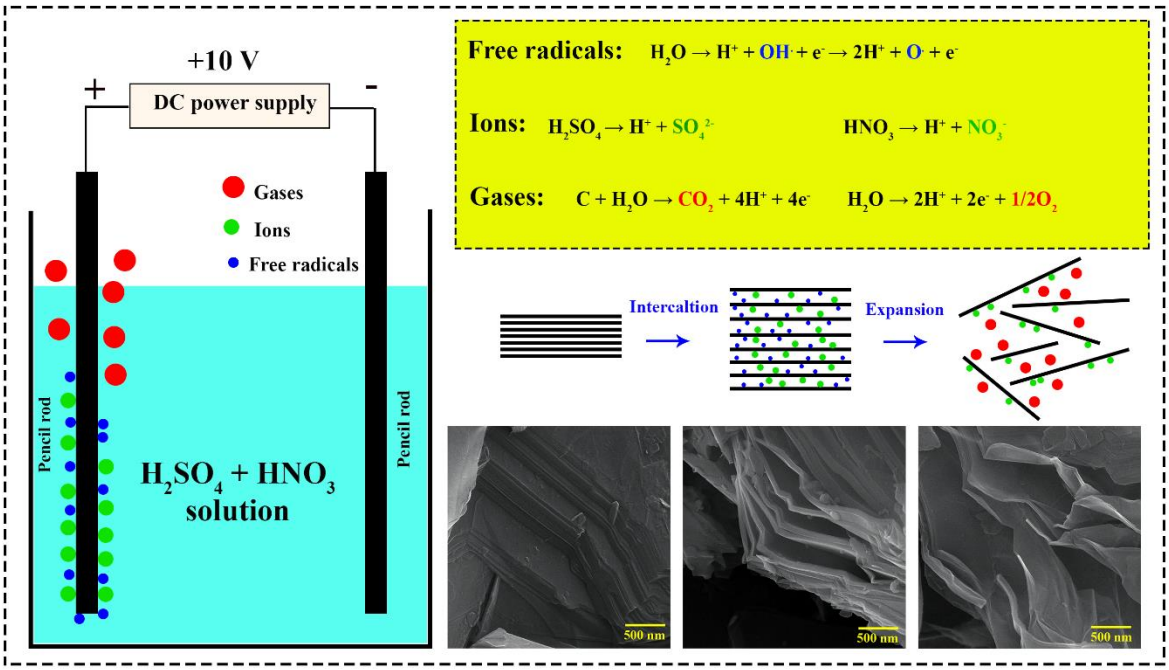

Fig. 4. Schematic illustration of the electrochemical exfoliation of graphite in a mixture of H_2SO_4 and HNO_3 solution.

Fig. 5 shows the FESEM image along with the energy dispersive X-ray (EDX) spectrum of the S1N1 sample. As can be seen in the EDS-mapping of this sample, the elements of C, O, N, and S are present. According to this analysis, it can be concluded that the electrochemical exfoliation of graphite in a mixture of H_2SO_4 and HNO_3 solutions has led to both oxidation and co-doping of S and N elements. As indicated in the XRD pattern, the diffraction peak of GO was only significant for the S1N1 sample, and from the EDS-point analysis of this sample, the C:O ratio is about 2.29 that shows the high degree of oxidation phenomenon. Also, it is clear that the atomic weight percentage of N in this sample is about 3.13% and for S is about 0.29%. Also, the FESEM image along with EDS analysis of the S1N3 sample are shown in Fig. 6. As can be seen, the oxidation and co-

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doping of N and S elements have also occurred in this sample. From EDS-point analysis, it can be seen that the C:O ratio is about 2.62. Furthermore, the atomic weight percentage of N in this sample is about 4.96% and for S is about 0.26%. The considerable increase in the atomic weight percentage of N elements in the S1N3 sample can be attributed to the higher volume ratio of HNO_3 in this electrolyte.

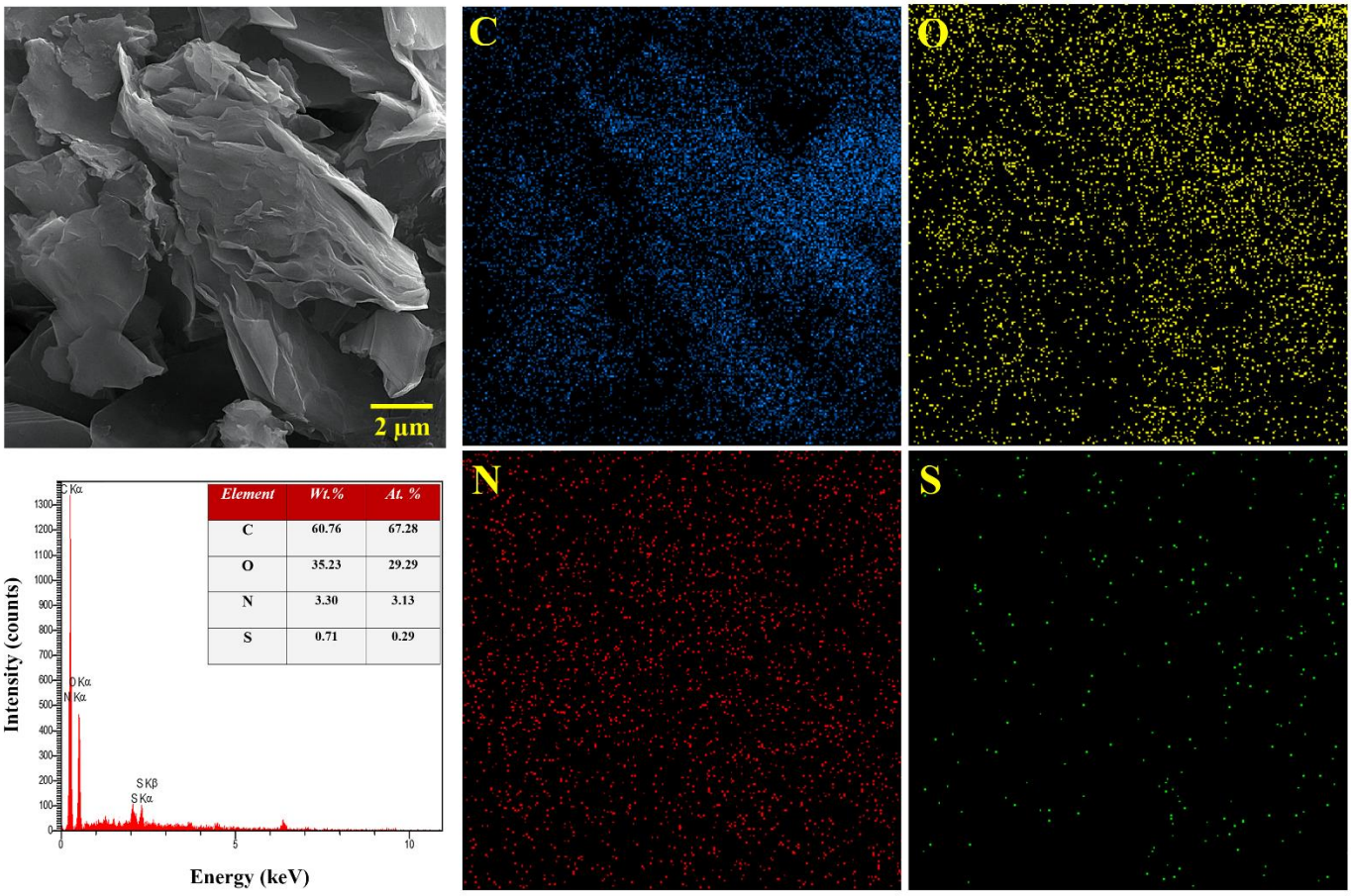

Fig. 5. FESEM image along with EDS-pint and EDS-mapping of S1N1 sample.

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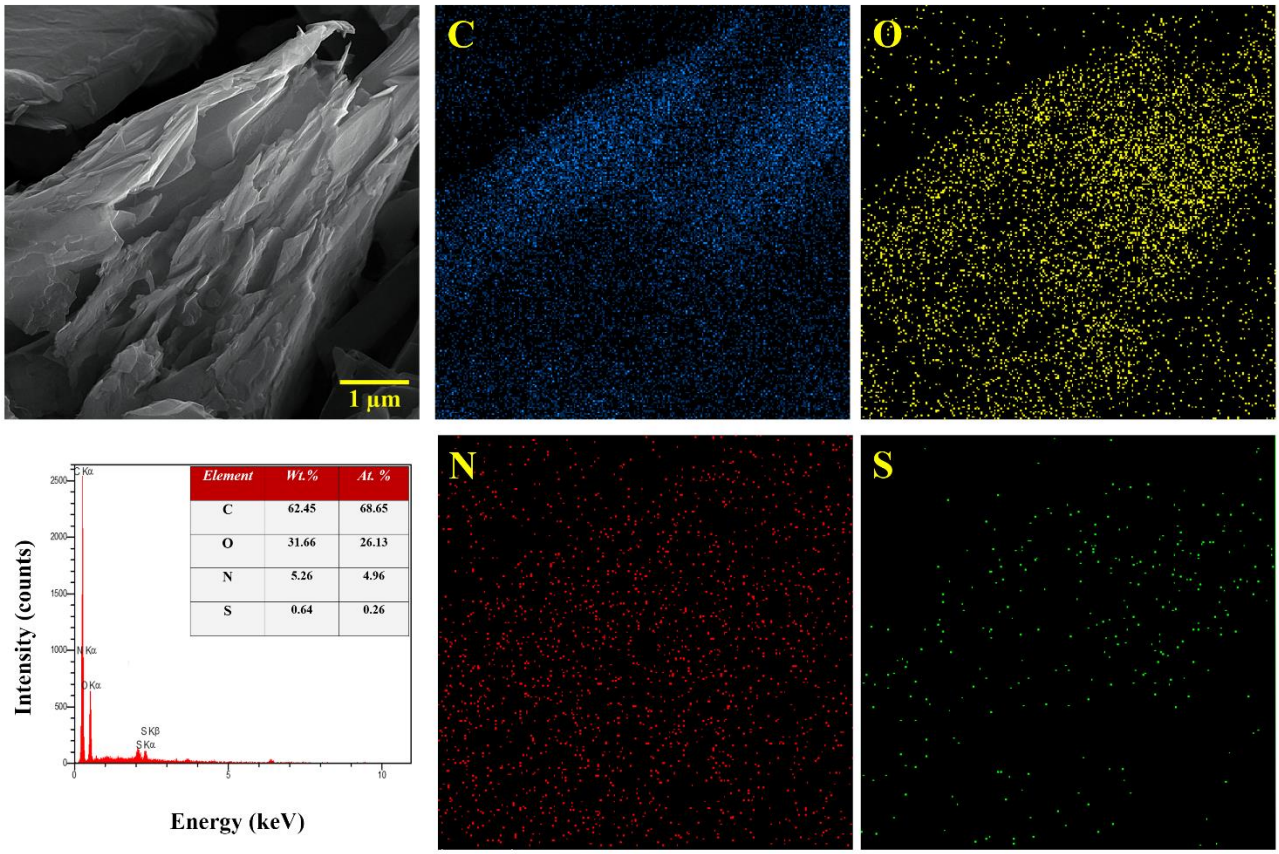

Fig. 6. FESEM image along with EDS-pint and EDS-mapping of S1N3 sample.

According to Table 2, it can be seen that the XRD diffraction peak of MLG of samples is located at lower angles compared to the pencil graphite rod (26.59º). The peak shifting to the lower angles reveals the increaser interlayer spacing of the graphite due to the formation of functional groups. Besides, as given in Table 3, by increasing the volume ratio of the HNO_3 in the mixtures, the d_{002} spacing values of FLG has been decreased from 0.399 nm in the S sample to 0.427 nm in N sample. The increased d-spacing of the graphene by increasing the HNO_3 volume ratio can be related to the presence of oxygen functional groups, sulfur, and nitrogen groups. The diameter of sulfur (0.204 nm) is higher than that of

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carbon atoms (0.154 nm). This observation is in good agreement with the literature [30, 31].

The occurrence of the S and N doping phenomenon of graphene by one-step electrochemical exfoliation of graphite rods has been also very little reported in the literature. Parveen et al. [30] reported the one-step S-doping and exfoliation of graphite rods by the electrochemical process in the mixture of $Na_2S_2O_3$ and H_2SO_4 solution. The addition of $Na_2S_2O_3$ in electrolytes was for the S-doping while the H_2SO_4 was used for the exfoliation of graphite. The N-doping and exfoliation of graphite rods using a one-step cathodic plasma electrochemical method were reported by Yen et al. [32]. In their work, the electrochemical exfoliation process was conducted in a 2 M mixture of NaOH and NH4OH solutions by applying a voltage of 100 V. The produced radical from NH_4OH led to the N-doping and exfoliation of graphite rods. In another investigation, Thirumal et al. [33] synthesized N-doped graphene by electrochemical exfoliation of high-purity graphite rods in a mixture of H_2SO_4 and CH_4N_2O. They used a solar panel to obtain DC. In their study, the CH_4N_2O was added to the electrolyte as the source for N-doping. In another work, the one-step electrochemical exfoliation of graphite rods by applying the -5 V and +5 V mixed voltage in the mixture of 0.006 M of $C_3H_6N_6$ and 0.1 M of $(NH_4)_2SO_4$ was investigated by Liu et al. [31]. Their results indicated the occurrence of S and N co-doping of graphene.

The AFM image of the S1N1 sample has been shown in Fig. 7. As can be seen, the thickness of the shown graphene particle is lower than 50 nm, indicating the presence of

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MLG in this sample. Also, the lateral size of the shown graphene is about 5 µm. This result is in line with XRD and FESEM images.

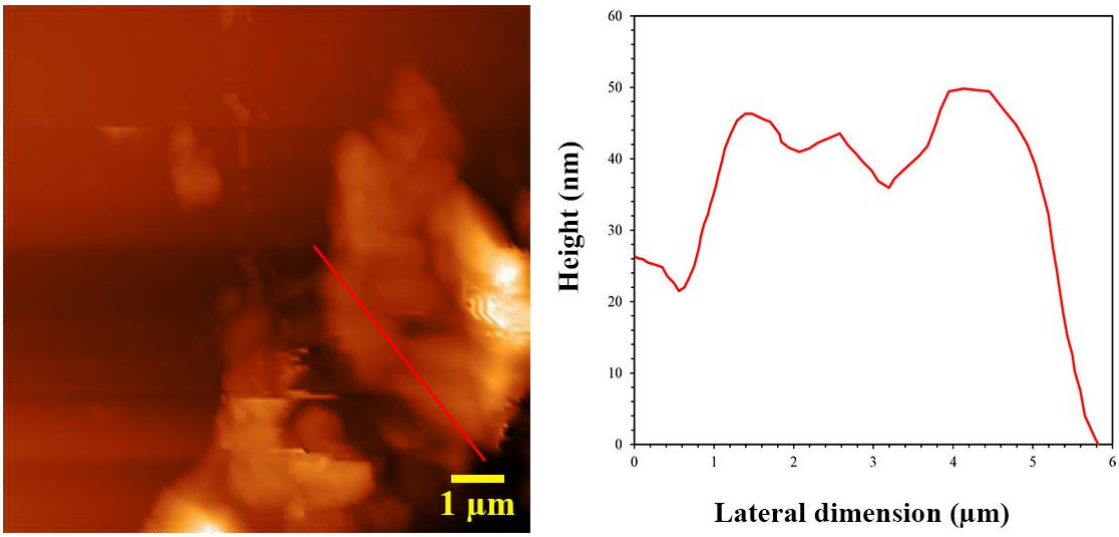

Fig. 7. AFM image of the S1N1 sample.

3-4- Raman spectroscopy

Raman spectroscopy is a non-destructive and powerful tool for the structural characterization of the carbon materials. Fig. 8 shows the Raman spectra of samples. As can be seen, four peaks of D, G, 2D, and D + G can be distinguished for all samples; the D peak at 1343-1353 cm^{-1}, the G peak at 1574-1589 cm^{-1}, 2D peak at 2714-2731 cm^{-1} and D + G peak at 2923-2938 cm^{-1}. The D peak arises from the defects and disordered nature of graphene. The G peak is related to the sp^2 hybridized carbon atoms. Moreover, the appearance of an additional peak at 2900 cm^{-1} (D + G) is an indication of the high defect

density of graphene [34-36]. The presence of functional groups on the surface of graphene oxide is the reason for the appearance of the D + G peak. It has been reported that, in addition to the I_D/ I_G ratio, the calculation of the I_{D+G}/ I_{2D} can be also used for determining the defect level of graphene materials. As given in Fig. 8, the I_D/ I_G ratio values of 0.93, 0.77, 0.90, 0.63, and 0.72 have been obtained respectively for S, S3N1, S1N1, S1N3, and N samples. The highest I_D/ I_G values are for the S and S1N1 samples. Also, the I_{D+G}/ I_{2D} values of 0.93, 0.91, 1.0, 0.72, and 0.83 were achieved for the S, S3N1, S1N1, S1N3, and N samples, respectively. According to the mentioned results, it can be deduced that S and S1N1 samples have the highest defect densities while S1N3 and N samples have the lowest ones.

This is the accepted manuscript (postprint) of the following article:
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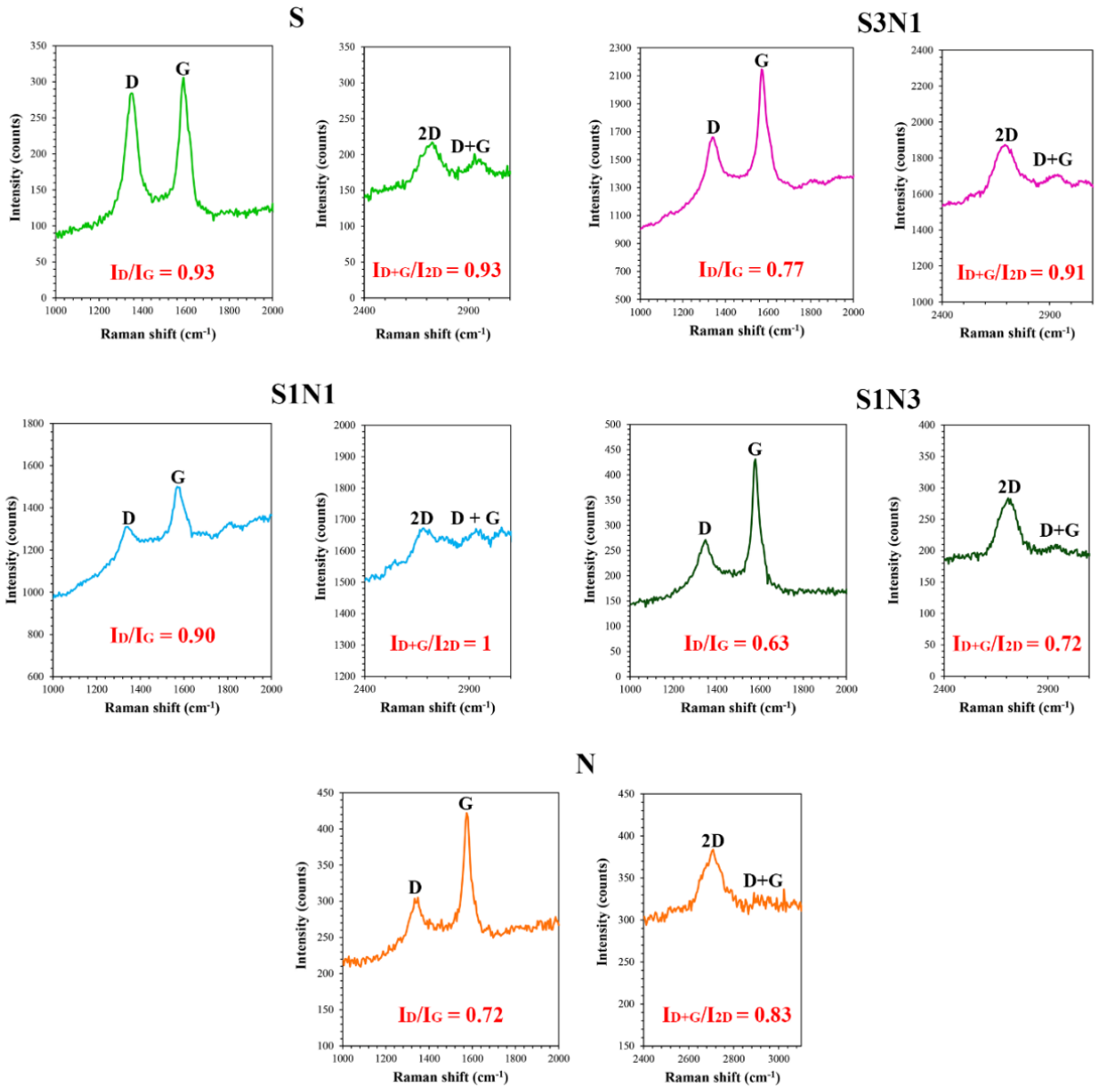

Fig. 8. The Raman spectra of samples.

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According to the previous reports, one of the affecting factors on the I_D/ I_G ratio of graphene materials is their wrinkles degree [36]. As shown by FESEM images, the S and S3N1 samples had a higher wrinkles degree in comparison to other samples. Therefore, the higher I_D/I_G ratio of S sample in comparison to the other samples can be due to the higher wrinkles of the prepared graphene sheets in this sample. As mentioned earlier, the probability of the gas generation during the electrochemical process using the solutions containing more SO_4^{2-} ions is higher than that of other solutions. Besides, the higher I_{D+G}/ I_{2D} value of the S1N1 sample can be attributed to the higher electrochemical oxygenation phenomenon. It has been reported that the appearance of a broad peak of 2D and also D+G peak in the Raman spectrum of samples can be used as a demonstration for the graphene oxide. Interestingly, it can be seen that the 2D peak in the S1N1 sample is broader than those of other samples. This feature of the 2D peak is typical for graphene oxide [36-40]. The sharp decrease in the intensity and also broadening of the 2D peak are mainly attributed to the steric effects of oxygen moieties on the stacked layers as well as to the partial amorphization and reduction in sp^2 domains. On the other hand, the lower defect density of the S1N3 and N samples can be related to their relatively flat morphology of graphene sheets and the lower occurrence of the oxidation phenomenon.

4- Conclusion

An electrochemical exfoliation of pencil rods as a fast, simple, and the economical route was conducted in the mixtures of low concentration of H_2SO_4 and HNO_3 solutions for the large-scale production of graphene. The effects of different volume ratios of mixtures of

H_2SO_4 and HNO_3 solutions on the morphology and structure of prepared graphene sheets were evaluated. XRD and FESEM images indicated that the mixtures of few-layered graphene, multi-layered graphene, and graphene oxide were achieved. The lowest number of layers for both few-layered graphene (about 4) and multi-layered graphene (about 14), was obtained for electrochemically exfoliated pencil rods in electrolytes with higher H_2SO_4: HNO_3 volume ratios. Besides, the H_2SO_4: HNO_3 with a 1:1 ratio was the optimized electrolyte for the preparation of graphene oxide. The XRD patterns of samples indicated the increasing the interlayer spacing of few-layered graphene by increasing the volume ratio of HNO_3 in the electrolytes, that this phenomenon was related to the sulfur and nitrogen co-doping and oxidation phenomena. The mentioned phenomena were also demonstrated by EDS results. Raman studies revealed that the prepared samples by electrochemical exfoliation in the electrolyte with higher volume ratios of H_2SO_4 had a higher defect density, compared to the electrolytes with higher volume ratios of HNO_3.

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