

Nanocomposite Graphene-Based Material for Fuel Cell Applications

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Cobalt and nickel oxides-graphene nanocomposites have been prepared by a simple chemical route. The structure, morphology and properties were characterized using X-ray diffraction (XRD) and Transmission Electron Microscope (TEM). The electrocatalytic activity for the methanol oxidation reaction in acidic medium of these nanocomposites compared to platinum has been confirmed using cyclic voltammetry technique.

Keywords: Graphene, Graphene oxide, Nanocomposite, Methanol Oxidation, Fuel Cells Electrocatalysis

1. INTRODUCTION

Graphene, one of the important research and application topics in recent years, has attracted the attention of many scientists, which found to have many important applications. Graphene is produced by reduction process of graphene oxide, which contains reactive oxygen function groups such as carboxylic, epoxides and alcohols with a carbon to oxygen ratio to be approximately three to one [1,2]. Graphene oxide is different from graphite oxide by the fact that, it can be exfoliated into monolayers.

Different techniques have been used to transfer graphite oxide to graphene oxide including thermal, mechanical and different chemical methods [3-8]. The chemical reactions targeted graphene oxide for different applications such as sensors [2,1, 10], batteries [1], capacitors [12], conducting [13,15] and biological applications [15-17]. On the other hand, finding new applications for graphene and graphene oxide is still under investigation. The high cost of using platinum (Pt), the best known active and stable metal for methanol oxidation as fuel in direct alcohol fuel cells encourages the researcher to develop new alternatives to reduce the usage of this expensive Pt, yet has high activity for alcohol oxidation kinetics. In the present work, we report the use of nickel and cobalt salts in addition to graphene oxide to form nanocomposite based graphene for Fuel cell applications. The prepared cobalt oxide/graphene nanocomposite has been used successfully for methanol oxidation as a fuel cell application.

2. EXPERIMENTAL

2.1 Preparation of Graphene Oxide (GO)

Graphene Oxide (GO) was synthesized by the modified Hummer's method [18]. Briefly, 1 g of graphite powder was mixed with 25 mL of 98% H_2SO_4 , and 1 g sodium nitrate in an ice bath for 3 hours followed by addition of 5 g potassium permanganate, the reaction was kept at 30 °C under vigorous stirring for 3 hours followed by slow addition of 100 ml of water; the resulting solution was placed at 80-90 °C for 2 hours, then the reaction treated with H_2O_2 (35%, 10 mL), the yellowish formed cake was finally filtered and washed thoroughly with several times with hot water.

2.2 Preparation of nano composite

The preparation of Ni oxide/Graphene nanocomposite was accomplished in two steps, first, an appropriate amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt and graphene oxide were mixed together with double distilled water in order to have a nickel oxide loading of 10 wt%. The solution pH was adjusted at 10 using 1 M NaOH solution and the mixture was stirred constantly for 4 hours, and then a 50 mL of 0.1M sodium borohydride or hydrazine hydrate solution was added. The reaction was completed by stirring the mixture for 3 hours in air then the resulting material was filtered and washed several times with double distilled water and dried in an oven at 80 °C. The dried mixture was then calcined at 400 °C for 3 h in air.

For the Co oxide/graphene nanocomposites, an appropriate amount of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and graphene oxide were mixed together with double distilled water in order to achieve a 10 wt% loading of cobalt oxide. The Co loading was fixed at 10 wt%. The solution pH was adjusted at 8 using 1M NaOH solution and the mixture was stirred constantly for 4 hours. An amount of 50 mL of 0.05M sodium borohydride or hydrazine hydrate solution was added and then the reaction was completed by stirring the mixture for 3 hours in air. Then the resulting material was filtered and washed at least for 3 times with double distilled water and then dried in an oven at 80 °C.

2.3 TEM / XRD characterizations

TEM analysis was done using a Philips EM 400 at an acceleration voltage of 200 kV. All images were taken at a magnification of 110,000.

For the TEM measurement, samples were firstly sonicated for 5 h in ethanol, and prepared by dropping highly diluted mixture on the carbon coated copper grid and left to dry overnight.

Powder XRD data were collected on PANalytical: X'Pert PRO diffractometer using Cu K α radiation source for the investigation of crystalline structure and phase. with a scanning rate of 0.07° s⁻¹ in a 2 θ range from 2° C to 80° C.

2.4 Electrochemical measurements of the electrocatalysts

All the electrochemical characterizations were done using a Volta Lab (PGZ 301) potentiostat connected to a PC. All the measurements have been done in a conventional 25 ml Pyrex glass cell. The reference electrode used in this work is 4 M KCl Ag/AgCl reference electrode. The counter electrode was a Pt wire or 1 mm diameter and 10 cm long. The work is mainly focusing on the graphene loaded with Co (CCG/Co) but for the sake of comparison, Ni catalyst will be shown too. During the measurements the electrolytic cell was open to air, i.e. no inert gas was purged before or during the measurements.

2.4.1. Electrochemical Technique

The electrochemical characterization for the prepared catalyst was done using the cyclic voltammetry technique. In this case the potential excitation that is applied across the electrode – solution interface in order to obtain a cyclic voltammogram has the following characteristics: (i) positive potential scan from -300 mV to +1200 mV vs. Ag/AgCl and (ii) a negative scan from +1200 mV to -300 mV vs Ag/AgCl. In some case this scanned potential window is a little narrower where the potential was scanned from -200 mV to + 800 mV vs. Ag/AgCl reference electrode and in some other cases the potential window is wider reaching + 1500 mV. Although the potential scan was terminated after the 5th cycle, it was continued for some number of cycles. The typical scan rate was 50 mV s⁻¹ in all experiments. The effect of scan rate on the peak current was checked by varying the scan rate from 100 mV s⁻¹ to 10 mV s⁻¹.

2.4.2 Electrode Preparation

The electrochemical composite catalyst was prepared as mentioned before, then 1.5 mg of it was sonicated for 1 h either (i) in 2 % Nafion solution (diluted with aliphatic alcohol) or (ii) dimethyl formamide solvent (DMF). After sonication, a 10 μ l of the resulted ink was casted over a glassy carbon electrode of an area of 0.071 cm² and dried at 70 °C in oven for about 20 minutes. Before inserting the electrode in the electrolytic cell, its surface was flushed with some electrolyte in which measurements will be carried out in order to confirm the surface wet ability.

3. RESULTS AND DISCUSSION

To identify the successful steps of the synthesis of nanocomposite, x-ray diffraction measurements have been done during different preparation steps. Figure 1 shows the XRD pattern corresponding to graphene oxide materials, which comes as successful oxidation process of graphite. The characteristic peak at 2θ of 11.5° indicates the effective oxidation of graphite and the formation of graphene oxide. On another hand, figure 2 shows the diffraction patterns after reduction of graphene oxide by sodium borohydride (or hydrazine hydrate) solution at pH 10. The disappearance of the graphene oxide XRD peaks in the XRD pattern of as-prepared graphene sample supports the formation of graphene sheets.

Figure 3 shows the XRD pattern of the prepared nickel oxide nanocomposite. It is clear that the diffraction bands centered at 2θ of 37.4, 43.2 and 63.1 correspond to (111), (200) and (220) reflection of Nickel oxide nanocrystals, which is confirmed by standard data for Nickel oxide monoclinic. The sharpness and the intensity of the peaks indicate the well crystalline nature of the prepared sample. On the other hand, the XRD pattern of prepared Cobalt oxide nanocomposite shows reflection bands that correspond to (111), (200) and (220) reflection of cobalt oxide at 2θ of 36.4, 42.4 and 61.6, which is confirmed by standard data for Cobalt oxide (data not shown).

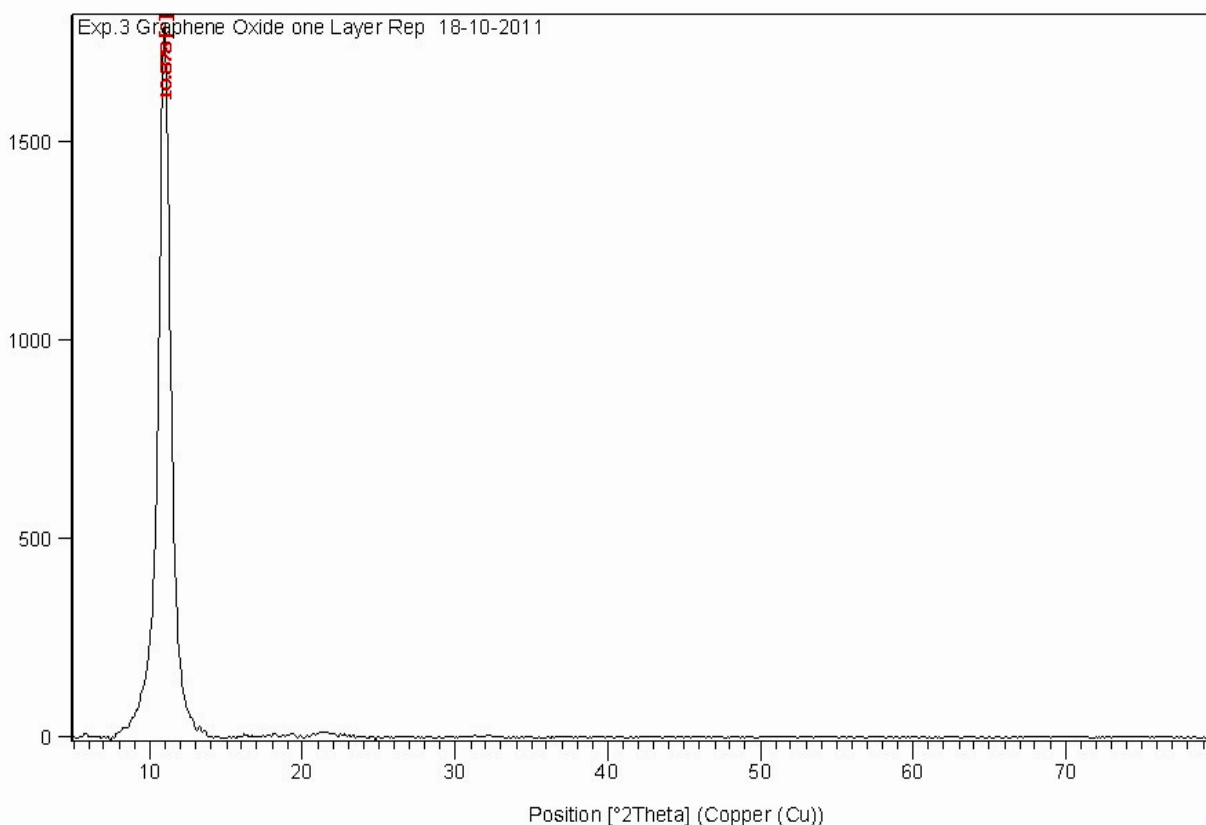


Figure 1. XRD pattern of Graphene Oxide.

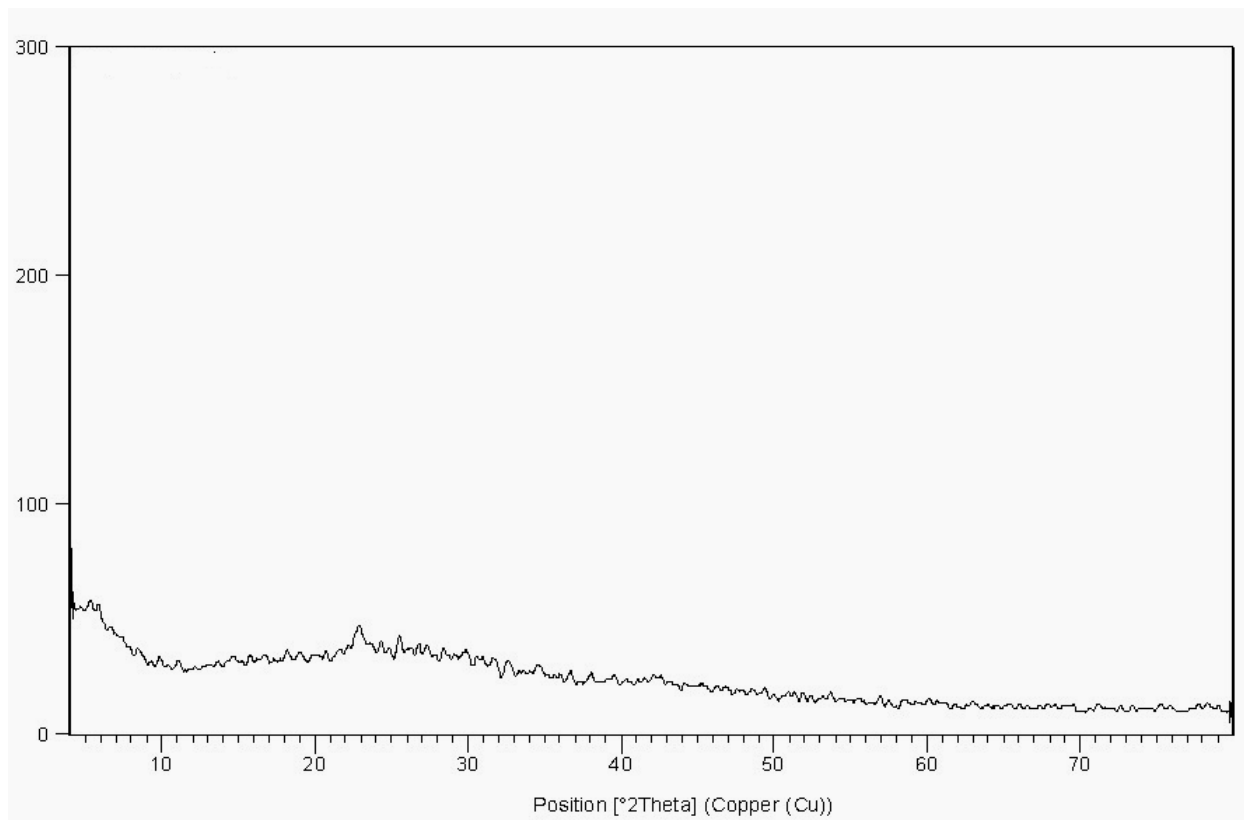


Figure 2. XRD pattern of Graphene.

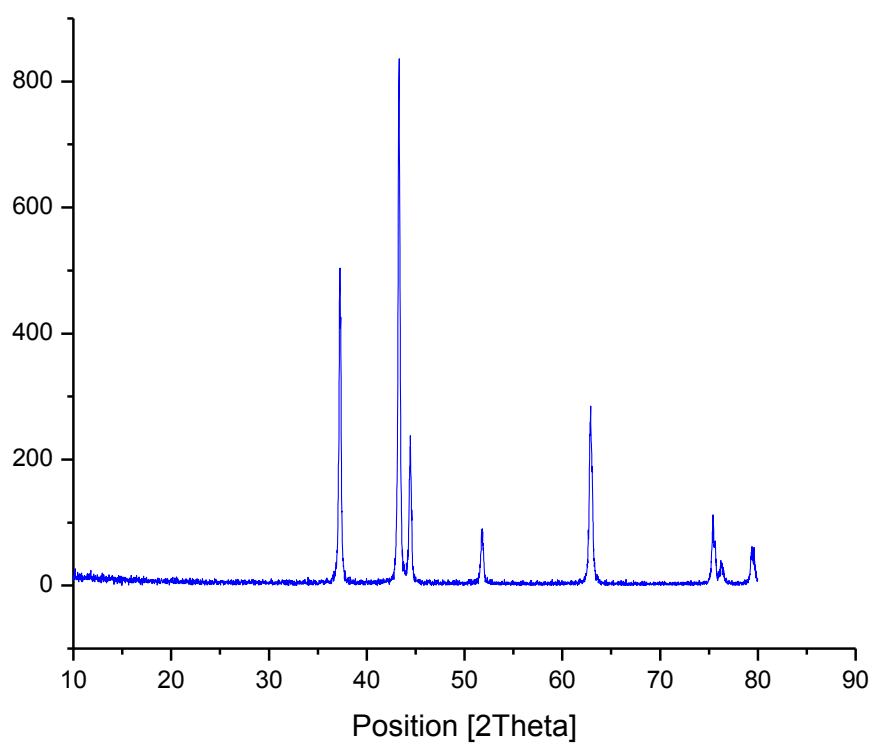


Figure 3. XRD pattern of Nickel Oxide nanoparticles.

3.1. Transmission electron microscope

Figure 4 shows the TEM images of prepared graphene, It was shown that a wrinkled paper like structure appeared in low magnification.

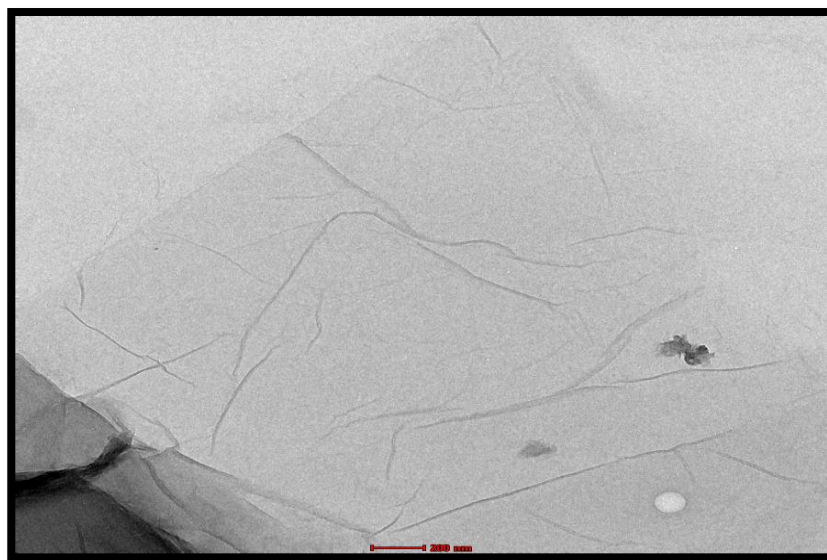


Figure 4. TEM images of graphene samples.

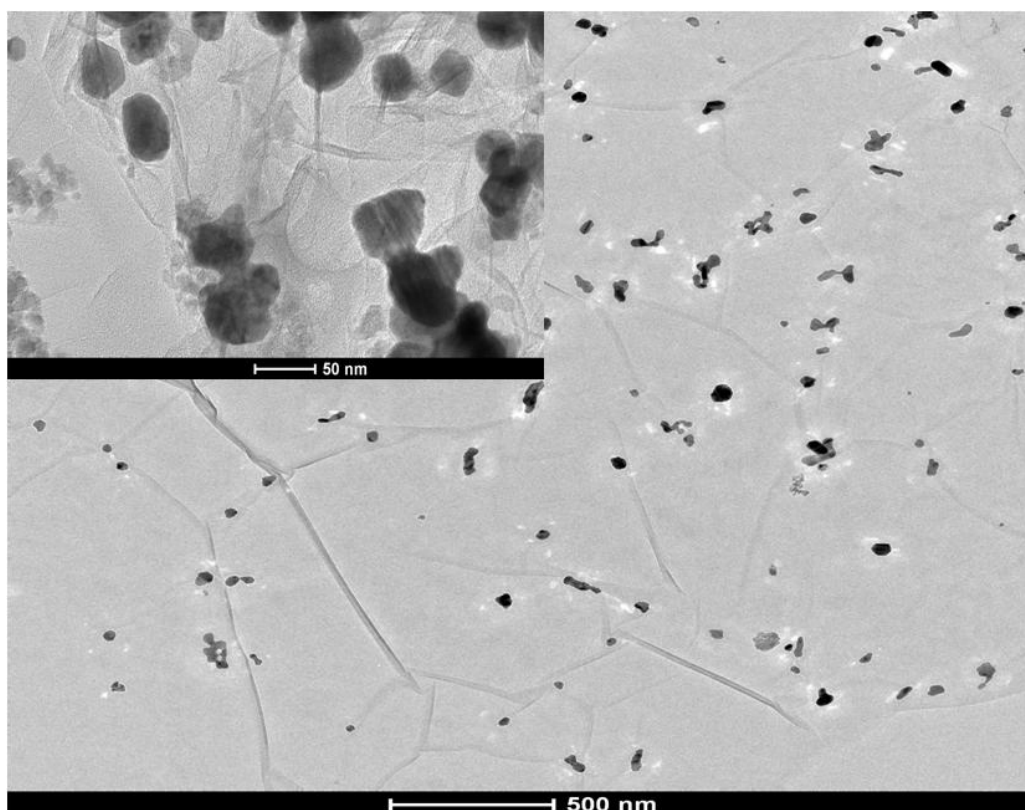


Figure 5. TEM images of Nickel oxide/graphene nanocomposite samples

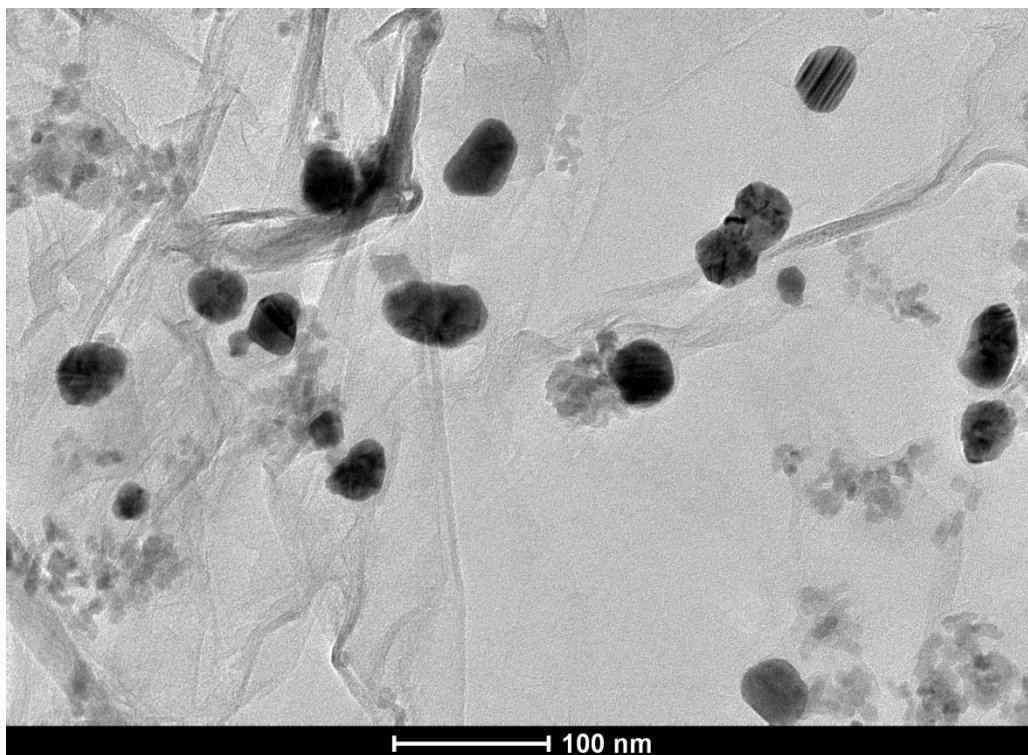


Figure 6. TEM images of Cobalt hydroxide/graphene nanocomposite samples

Morphology and size information of the cobalt oxide/graphene nanocomposite are depicted in figures 5 and 6. It shows the non-spherical shape of Ni oxide and Cobalt oxide nanoparticles supported by a graphene thin layer. Also it is noticed that a large number of particles are present with an average size around 45 nm which matches well with the particles size calculated from Scherrer's equation of the XRD data.

3.2. Electrocatalytic measurements

Figure 7 presents cyclic voltammograms (CVs) for (a) Glassy carbon (GC) , (b) Graphene (CCG) , (c) Graphene/Co oxide (CCG/Co) and (d) Graphene/Ni oxide (CCG/Ni) in a solution of 1 mM $K_3[Fe(CN)_6]$ / 1 M KCl at a scan rate of 50 mV s^{-1} . Figure 7 shows that graphene has the highest electrocatalytic activity than any other system shown in the same figure. Comparing CCG with the CCG/Co, Figure 7 shows that graphene (CCG) has a higher electrocatalytic activity (anodic peak current = $60 \mu\text{A}$) than that of the CCG loaded with Co since the oxidation/reduction peaks at potentials of 314 and 231 mV vs Ag/AgCl respectively are higher in case of the CCG ($60 \mu\text{A}$) than that in case of the CCG/Co ($44 \mu\text{A}$). To test the stability of the CCG/Co catalyst, the CV was repeated for higher number of cycles. Fig. 8 shows repeated CVs of Graphene/Co oxide in a solution of 1 mM $K_3[Fe(CN)_6]$ / 1 M KCl at a scan rate of 50 mV s^{-1} . It indicates that the CCG/Co catalyst is stable after repeating the scanning for 6 cycles. It is worthy to mention here that there are two extra peaks appeared in the 6th cycle that was not clear at the first cycle. The appearance for these peaks is

attributed to the activation of graphene/Co oxide catalyst for the oxygen reduction reaction since the solution during the measurements was opened to air [19].

The different electrodes examined in the ferri-cyanide electrolyte were used for methanol oxidation reaction as depicted in Figure 9. Pt electrode has been mentioned in the literature as one of the best surfaces for electrocatalytic oxidation of methanol [20-23]. Thus, Figure 9 shows the cyclic voltammetry response of graphene oxide (GO), CCG/Ni, CCG/Co and CCG/Co (casted using DMF rather than Nafion) in 0.1 M H_2SO_4 containing methanol. The results revealed different electrocatalytic activities for the surfaces used for methanol oxidation. It has been reported that graphene has no catalytic activity for methanol oxidation [20, 24, 25]. For all electrodes examined and from the data of Figure 9, one oxidation peak (in the forward direction of the CV) can be identified around 0.7 V with distinctive current responses. Another peak can be distinguished in the reverse direction around 0.48 mV with similar variation in current response that is attributed to CO removal and other residual carbon species formed at the electrode surface during methanol oxidation. The effect of the scan rate on the peak current has been checked and is shown in Figure 11. Plotting the square root of the scan rate versus the peak current has shown a straight line which indicates the methanol oxidation process is diffusion controlled one.

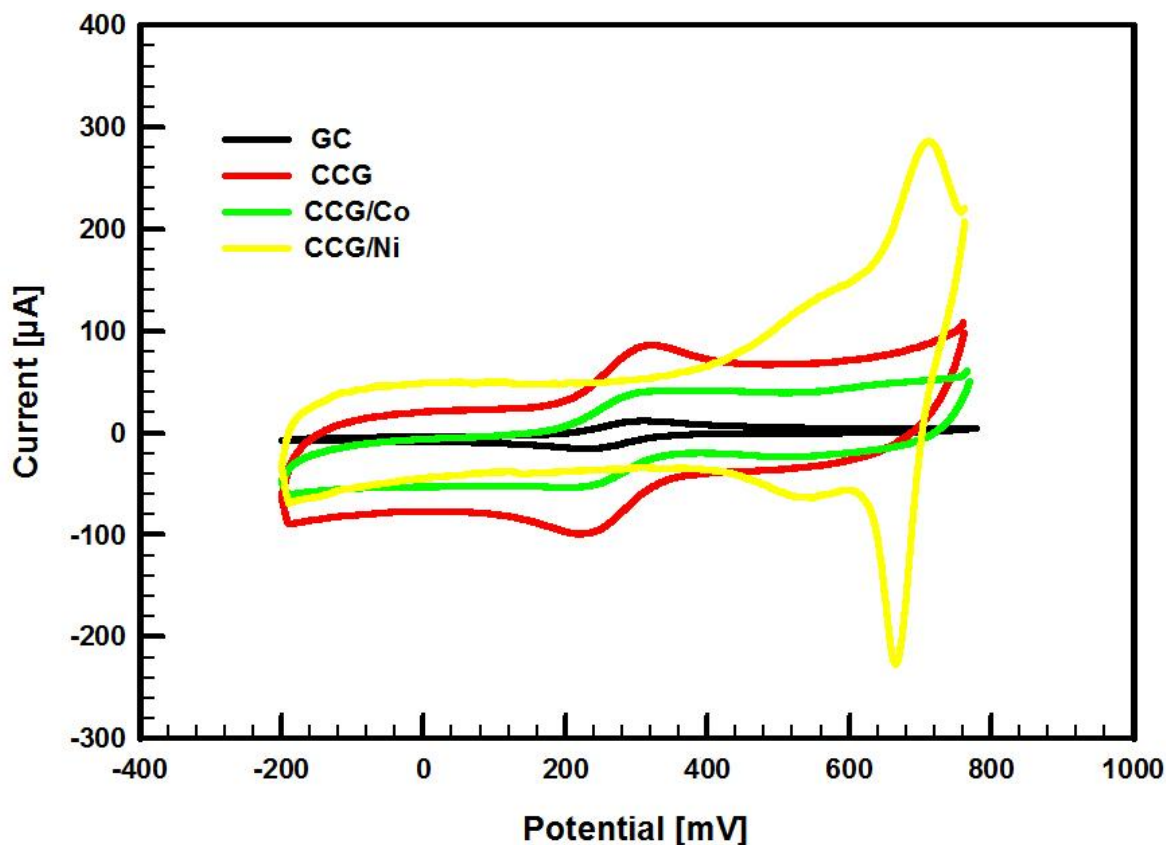


Figure 7. CV of (a) GC , (b) CCG , (c) CCG/Co and (d) CCG/Ni in a solution of 1 mM $K_3[Fe(CN)_6]$ / 1 M KCl at a scan rate of 50 mV s^{-1} .

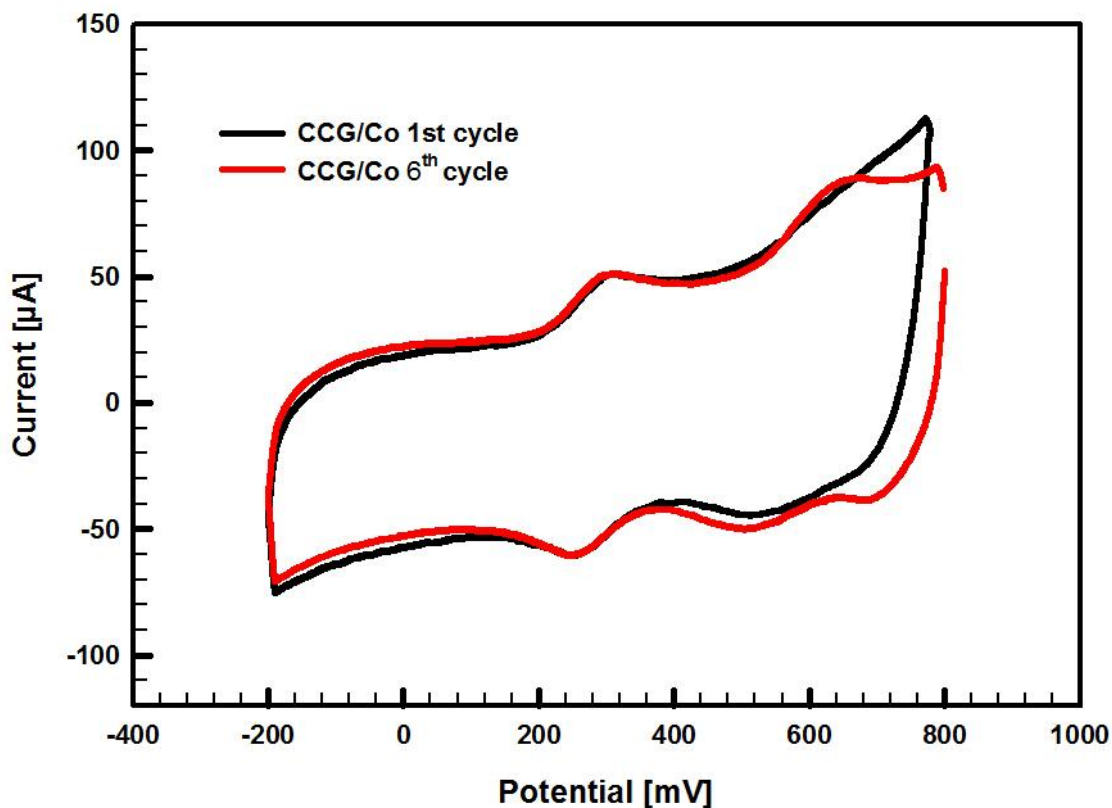


Figure 8. Repeated CVs of Graphene/Co in a solution of 1 mM $K_3[Fe(CN)_6]$ / 1 M KCl at a scan rate of 50 mV s^{-1} .

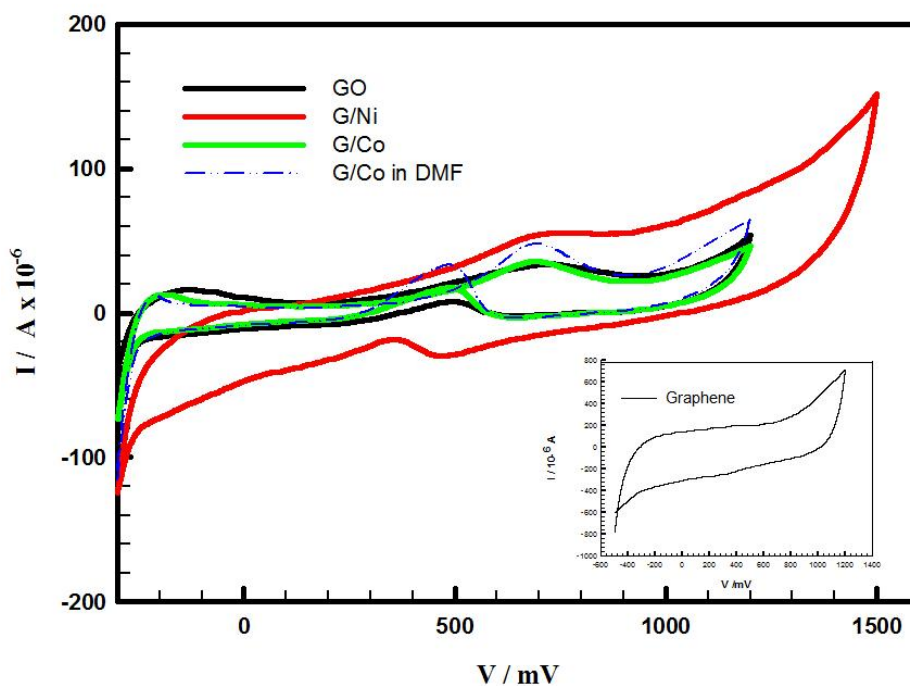


Figure 9. CV of (a) Graphene oxide , (b) CCG/Ni , (c) CCG/Co and (d)CCG/Co casted with DMF in 0.1M methanol/0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} .

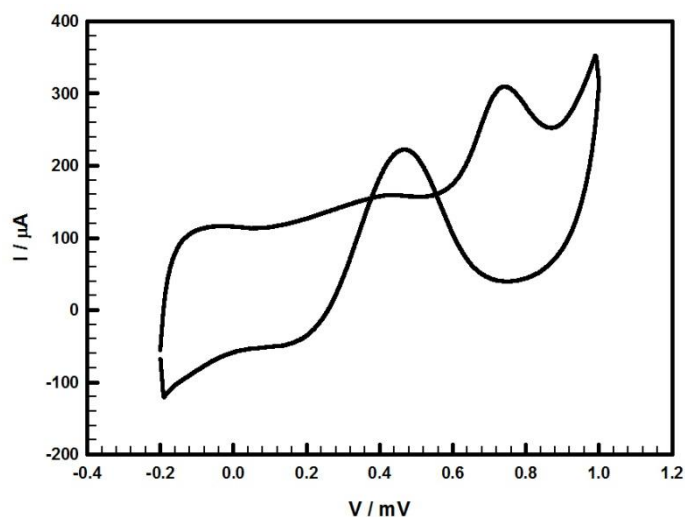


Figure 10. CV of Pt in 0.1M methanol/0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹.

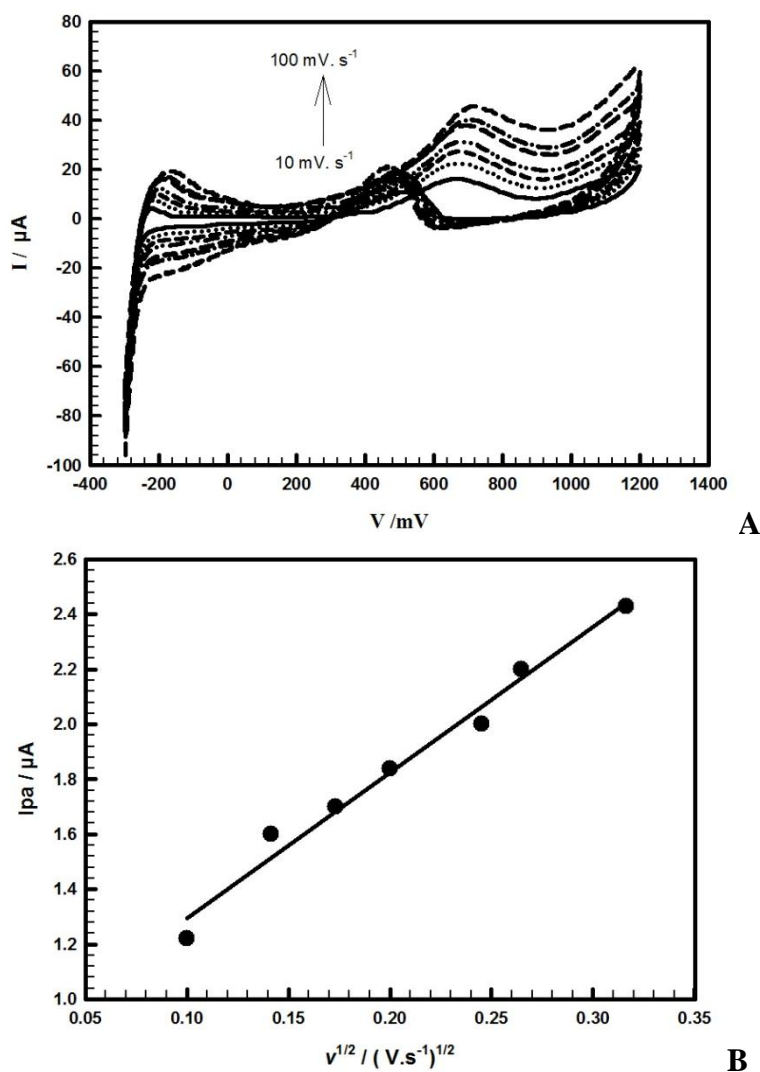


Figure 11. (a) CV of CCG/Co in 0.1M methanol/0.5 M H₂SO₄ at different scan rate and (b) relation between scan rate vs anodic peak current).

4. CONCLUSION

Nickel oxide / graphene and cobalt oxide / graphene nanocomposites have been prepared chemically using the co-reduction method of the metal salt and the graphene oxide that was previously prepared using the modified Hummer's method. The electrocatalytic behavior of these nanocomposites was tested as candidate catalysts for the methanol oxidation reaction in acidic medium. It has been shown that the electrocatalytic activity of the Co oxide/ graphene catalyst is higher than that of the Ni oxide one. In addition, the reaction in case of the Co oxide nanocomposite was found to be controlled by diffusion which is not the case of Ni oxide one. Comparing the electrocatalytic current for the oxidation of methanol, the cobalt oxide/graphene nanocomposite to that of Pt/graphene, it is almost one sixth which indicates that the Pt catalyst is still unbeatable as a catalyst for the methanol oxidation reduction. An interesting behavior has been noticed during the test for the stability of the catalyst which is the electrocatalytic activity of the cobalt oxide/graphene catalyst towards the oxygen reduction reaction which will need further investigation.

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