Synthesis and Characteristics of Polyaniline (PANI) Filled by Graphene (PANI/GR) nano-Films

K I Ajeel1, Q S Kareem2
1Department of Physics, University of Basrah, College of Education for pure sciences, Iraq
2Department of Physics, University of Qadisiya, College of Education, Iraq
E-mail address: qstar691@gmail.com

Abstract. In this research polyaniline (PANI) was synthesized by using chemical oxidative polymerization method. The structural properties of polyaniline nano films pure and filled by graphene (GR) at different weight percentage of graphene like (1%, 3% and 5%) were investigated. The nano films prepared by using spin coating technique and deposited on glass substrate at room temperature. The structural and surface morphology of the nano films are evaluated by FT-IR, XRD and AFM. The results showed that FT-IR spectra of pure PANI is similar to the spectra of PANI/GR composites, While the results of XRD singular that the PANI has amorphous nature, As well as the results of AFM for all nano films of pure PANI and filled by graphene(PANI/GR) composites showed that Roughness average (Ra), Root mean square (Rms) value and average grain size (G.S) increase with increasing addition of GR ratio.

Keywords: Polyaniline, Graphene, Nanofilms.

1. Introduction

In the last decade modification and inventions of new polymers have acquired more focus, which is due to the spectacular properties of conducting polymers and their wide use in numerous applications [1]. Among these polymers, PANI especially offers interesting features according to its rich variety of oxidized states which can be controlled by appropriate oxidation and protonation processes [2,3]. During the last decade there has widespread interest in conducting polymer PANI is one of the most useful conducting polymers due to their high absorption coefficients in the visible light, interesting redox properties, lower density than metals, energy storage, easily synthesizable, relatively high conductivity, environmentally stable compound, low cost, good optical and electrical properties and can be reversibly transformed from conduction to insulation from using acid-base reactions or via either electrochemical or chemical doping [4-7]. It has therefore become a choice polymer for the present study of structure characterization correlation. PANI has a wide range of applications such as organic light-weight batteries [8], microelectronic devices [9], biosensors, chemical sensors [10] and solar cell, [11, 12]. However, PANI has relatively lower surface area, and it suffers from poor cycling stability due to the low mechanical strength during charging and discharging [13]. The structure of PANI is constituted by the repetition of aromatic ring and a nitrogen bridge. The chemical composition of PANI consists of vinyl ring with a (N-H Group). As shown in “figure 1” [14]. “Figure 2” is the general formula of (PANI) [15].

![Chemical structure of polyaniline (PANI)](image.png)
PANI can be found in one of three idealized oxidation states [16]: leucoemeraldine—white/clear and colorless, emeraldine—green for the emeraldine salt, blue for the emeraldine base and pernigraniline—blue/violet. The color change associated with polyaniline in different oxidation states can be used in Sensors and electrochromic devices [17]. Different structures depend on the value of \( \gamma \) (the degree of oxidative stress) in the general formula. Where, \( B \) and \( Q \) denote the \( \text{C}_6\text{H}_4 \) ring in benzenoid and quinoid as shown in Figure (2) [18-20]. It is composed of two benzenoid units and one quinoid unit that alternate and it is known to be a semiconductor [21,22]. On the other hand, graphene (GR) in the past few years, after its discovery in 2004, graphene has attracted more attentions and been widely studied by the researchers [23]. GR is a two-dimensional (2D) one atom thick planar sheet of sp2-bonded carbon atoms that are arranged in a honeycomb crystal lattice. It is the mother of other carbon allotropes like graphite, CNT and fullerenes [24]. Single-layer GR sheet was first isolated by Geim and Novoselov. GR can act as both n and p type conductors and due to the semiconducting nature this has raised some speculations of it replacing silicon in electronics in the future. Because of the electrical properties and transparency of Single-sheet graphene (SGR) layers combined with a good chemical resistance [25]. The discovery of graphene with its combination of extraordinary physical properties, The promising mechanical, electrical, optical, thermal and magnetic properties of graphene have led to the creation of a new subfield of nanoscience that studies graphene based polymer nanocomposites[26-30]. Polyaniiline can be synthesized using several methods is chemical oxidative polymerization [31] and electrochemical oxidative polymerization [32]. Both these methods consist of an oxidative polymerization of the monomer (aniline) in an aqueous acid hydrochloric acid. One previous studies in 2013 Jahed Nazeem et al studied the grapheneated polyaniline nanocomposite for the determination of polyaromatic hydrocarbons (PAHs) in water. They found that PANI/GR composite films clearly revealed the presence of the interaction of graphene and PANI in the composite with less intense in the characteristic bands of PANI and also almost similar in comparison with graphene. This is an indication that PANI is well adsorbed and intercalated on to the graphene surface. In this article reported the results of an experimental study on the PANI nano films prepared by spin coating technique, taking advantage of the expected filled by Graphene at different ratio to enhance the properties composite.

2. The Experimental Work

2.1 Materials

Materials such as ammonium persulphate (APS) (purity 99.%) , hydrochloric acid (HCl) (purity 36.5%), graphene (GR) (purity 95%), acetone, dimethylformamide (DMF) (purity 99.8%), were all products of Sigma-Aldrich Chemicals.

2.2 Preparation of Polyaniline (PANI)

PANI was prepared by chemical oxidative polymerization method in accordance with the following steps: Pure PANI was prepared by dissolving of (2.59 g) of aniline hydrochloride (\( \text{C}_6\text{H}_5\text{NH}_2\text{HCl} \)) in (50 mL) of...
distilled water. Take (5.71 g) from ammonium peroxydisulfate \((\text{NH}_4)_2\text{S}_2\text{O}_8\) that dissolved in (50 mL) of distilled water, (2.59 g) and (5.71 g) values corresponding to (0.2M) and (0.25M) respectively. Both solutions were kept each separately for 1 hour at room temperature (~18–24 °C). Then the two solutions were then mixed in a beaker and stirred with a magnetic stirring bar, briefly stirred. The color change from colorless to dark green indicates the formation of PANI, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter paper, washed with three 100-mL portions of (0.2M) Hydrochloric Acid (HCl), and similarly with acetone. Polymer leaves for a full day (24 hours) to dry and then combines. "Figure 3" is schematic sketch showing the preparation process of PANI polymer.

2.3. Preparation of PANI and graphene (GR) solution and substrates cleaning.

The 0.16 g of PANI was dissolved in 10 ml of dimethyl forimade (DMF) solvent, the solution stirring for 2 hrs. to allow polymer to dissolve completely and yield clear solution. This process repeated three times. In the same way GR solution was prepared by weighted 0.007, 0.005 and 0.0085 g of GR and dissolved in 10ml of (DMF) and stirring for 3 hours separately. After allowing those to dissolve completely, the solution were mixed of PANI and GR and they were prepared separately. The final yield blend solution of each PANI and GR were kept into a clean glass beakers. On the other hand the cleaning of the substrate is very important because it has a great effect on the properties of the films. Glass slides of dimensions 2.5 cm \(\times\) 7.5 cm were used as substrate. which were cleaned by using detergent with deionized water to remove any oil or dust that might be attached to the surface of substrate. Then they were rinsed in distilled water using an ultrasonic bath unit for 15 minutes. After that, pure alcohol solution was used to remove any grease and some oxides. Finally, the glass slides eventually were dried by blowing air and wiped with soft paper. As well as we preparation of PANI and GR nano films by using spin coating technique after synthesized the solution concentrations of (PANI) and (PANI/GR). The films were deposited on the substrates with spinning speed is kept at 3000 rpm while the spinning time is 30 seconds. Then the prepared nano films were keeping at room temperature (R.T) about 24 hours to dry.
2.4 Structural Analysis

FTIR spectra were recorded by using solid KBr discs using Shimadzu FT-IR 8000 series Fourier Transform – Infrared spectrophotometer. XRD spectra of all samples were taken on Philips PW - 3050/60 (Theta/Theta), Automatic X-ray diffractometer using Cu-Kα radiation of wavelength 1.5406 Å, continuous scan of 2θ/ min., with an accuracy of 0.01 at 40 KV and 30 mA. For the observe of surface roughness and topography of thin films deposited, has take an atomic force microscope (AFM) with a digital microscope Intruments, Inc. BY3000. Typical data taken from images rise AFM include root mean square (RMS) roughness average (Ra) and grain size (G.S).

3. Results and discussion

3.1 Fourier Transformer-Infra Red spectroscopy (FT-IR) analysis

The new prepared PANI / GR nano films were identified by IR spectroscopy. The samples were run in the wavelength range between 4000 – 400 cm⁻¹. The FT-IR spectra of synthesized pure polyaniline (PANI), graphene (GR) and PANI / GR nano films at different concentrations of GR (1%, 3% and 5%) are presented in figures below 4, 5, 6, 7 and 8. Figure 4 represents FT-IR spectra of synthesized pure PANI. The characteristics peaks of PANI including broad peaks range 3016.67 - 3417.86 cm⁻¹ corresponding to (N–H stretching vibrations of secondary amine) and sharp peak at 1560.41 cm⁻¹ (C=C stretching of quinoid ring (N=Q=N)), 1413.82 and 1475.54 cm⁻¹ (C=C stretching vibration of benzenoid ring (N-B-N)), 1244.09, 1298.09 (C-N stretching of secondary aromatic ring), 1130.29 cm⁻¹ (Aromatic C–H in-plane bending vibrations), 611.43, 719.45 and 804.32 cm⁻¹ are attributed to (Aromatic C–H out-of-plane bending vibrations). These peak positions match well with those reported in the literature [34-37]. The FT-IR spectrum of GR (figure 5) showed broad stretching peak at 3396.64 cm⁻¹ corresponding to O-H water stretching (intercalated water), 1612.49 cm⁻¹ is attributed to (C=C stretching vibrations in the phenyl Stretch), while peaks at round 1230.58 and 1381.03 cm⁻¹ are due to C-OH stretching vibrations or C-0-C-OH group, 1120.64 and 1166.93 cm⁻¹ (C-O-C bonding of alkoxy group), 596.00, 680.87, 424.34 cm⁻¹ (Aromatic C–H out-of-plane bending vibrations). These results in agreement with reported in literature [38,39]. The FT-IR spectrum, after added PANI with GR (PANI/GR) nanocomposites at different ratio of filled (1%, 3% and 5%) are shown in figures 6, 7 and 8 figures that the intensity of emission is changed as it can be observed from the changed this is corresponding to each bond, while not noticed any change in the position of the bonds. The spectra information are presented in tables below 1 and 2. FTIR spectra of the PANI/GR composite is matched with that of pure (PANI) so there is a big similarity between Figures 6, 7 and 8.
Figure 4. FT-IR for synthesized pure PANI

Figure 5. FT-IR for (GR)

Figure 6. FT-IR for PANI/GR (1%)

Figure 7. FT-IR for PANI/GR (3%)

Figure 8. FT-IR for PANI/GR (5%)
Table 1. FT-IR Spectral data for synthesized pure polyaniline (PANI)

| Compound | Vibration Bond range (cm⁻¹) | Observed Position(cm⁻¹) | Expected vibrations |
|----------|-----------------------------|-------------------------|---------------------|
| PANI     | 600-900                     | 611.43, 719.45, 804.32  | Aromatic C–H out-of-plane bending vibrations |
|          | 1000 – 1180                 | 1130.29                 | Aromatic C–H in-plane bending vibrations |
|          | 1200 – 1300                 | 1244.09, 1298.09        | C – N stretching of secondary aromatic ring. |
|          | 1400 -1480                  | 1413.82, 1475.54        | C=C stretching vibration of benzenoid (B) ring (N-B-N) |
|          | 1500-1600                   | 1560.41                 | C=C stretching of quinoid (Q) ring(N=Q=N) |
|          | 3000-3500                   | 3016.67, 3024.38, 3099.61, 3417.86 | N–H stretching vibrations of secondary amine |

Table 2. FT-IR Spectral data for Graphene (GR)

| Compound | Vibration Bond range (cm⁻¹) | Observed Position(cm⁻¹) | Expected vibrations |
|----------|-----------------------------|-------------------------|---------------------|
| GR       | 600-900                     | 424.34, 596.00, 680.87  | Aromatic C–H out-of-plane bending |
|          | 1000 – 1180                 | 1120.64, 1166.93        | C-O-C bonding of alkoxy group |
|          | 1200 – 1300                 | 1230.58, 1381.03        | C-OH stretching vibrations |
|          | 1600-1700                   | 1612.49                 | C=C vibrations in the phenyl Stretch |
|          | 3300-3600                   | 3396.64                 | O-H water (intercalated water) |

3.2. X–Ray Diffraction Analysis (XRD) for PANI and GR

X-ray diffraction is one of the widely used experimental techniques for determining lattice parameters. Figure 9 shows the XRD pattern of the synthesized polyaniline (PANI). From the figure, it can be observed that, two broad bands are ascribed to the periodic parallel and perpendicular features of the polymer chains of PANI. They are centered at 2θ = 20.320° and 25.210° corresponding to (020) and (200) crystallographic planes reflections of PANI respectively. The interlayer spacing (d) for all samples was evaluated according to Bragg’s law

\[ n\lambda = 2d \sin\theta \]  

(1)

Where n is an integer, \( \lambda \) is the XRD wavelength (0.15406 nm) and \( \theta \) is the angle between the incident ray and the scattering planes. The 20 value for the most prominent peak was used in estimating the interlayer spacing value (d). From eq. (1) interlayer spacing (d) of 3.5297 Å (0.35297 nm) was obtained for synthesized PANI. It is shown that PANI is amorphous nature. The XRD pattern shows the highest intensity peak at 25.210°. Which represent the characteristic peak in the PANI and it is agreement with the reported data in literature[40-42]. The XRD Pattern for graphene exhibited a wide peak range between (10-25) degrees with plane (002) in XRD pattern as represented in figure 10. It shows a wide peak centered at 2θ = 24.6° corresponding to lattice planes (002) with d-spacing 3.6144Å (0.36144 nm.) which agreement with results reported before [43]. It can be seen that, the broad nature can be attributed to the loosely stacked sheets in graphene.

3.3 X – Ray (XRD) Pattern for PANI/GR nano films

Figures 11, 12 and 13 show the XRD spectra of the PANI/GR nano films synthesized at different addition ratio (1%, 3% and 5%). After added only one broad peak was shown for each filled ratio centered at 25.649°, 25.291° and 25.021°, with d-spacing to be 3.4703 Å (0.34703 nm), 3.5186 Å (0.35186 nm).
and 3.5560 Å (0.35560 nm) respectively. It can be shown from the d-spacing results that the PANI/GR (5% filled ratio) is greater than 1.3% addition ratio. The PANI/GR nanocomposite revealed broadened peaks that are similar in comparison to both graphene and PANI, showing the interaction and merged peaks of both PANI and graphene in the composite. The increasing in crystallinity of the polymer is caused by increasing graphene addition ratio. However, that the intensity of crystal planes of PANI decreases compared with PANI/GR at different ratio of filled (1%, 3% and 5%). The crystalline size (D) can be determined using Debye Scherrer formula:

\[ D = K \frac{\lambda}{\beta \cos \theta} \]  

(2)

Where: D is the crystallite size (nm), K, shape factor for an average crystallite (0.9) depending on the Miller index of the reflecting plane and the shape of the crystal, \( \lambda \) is the XRD wavelength (nm), \( \beta \) is the width at half maximum (FWHM) of crystallite peak (measured in radians) and \( \theta \) is Bragg’s angle (deg.) of the XRD peak. It was observed that, FWHM of pure polyaniline was decreasing with increase in graphene loading. While the crystal size of pure polyaniline was increased with increasing content graphene. This was a clear evidence of PANI coating formation on graphene. It can be seen from figures 11, 12 and 13 for PANI/GR nano films at different ratio of filled (1%, 3% and 5%) that the high intensity diffraction peaks at centers decrease with increasing ratio doping. And the XRD data for PANI, GR, and PANI/GR nano films are presented in table 3.

| Compound   | 2θ(deg.) | θ(deg.) | d (nm.) | FWHM (β) | D(nm.) |
|------------|----------|---------|---------|-----------|--------|
| PANI       | 25.21°   | 12.60°  | 0.35297 | 0.753     | 0.1886 |
| GR         | 24.61°   | 12.61°  | 0.36144 | 0.094     | 1.5097 |
| PANI/GR1%  | 25.64°   | 12.82°  | 0.34703 | 0.272     | 0.5227 |
| PANI/GR3%  | 25.29°   | 12.64°  | 0.35186 | 0.560     | 0.2537 |
| PANI/GR5%  | 25.02°   | 12.51°  | 0.35560 | 0.386     | 0.3679 |

Table 3. XRD data used for calculation interlayer spacing, crystalline size (D) of different samples.

Figure 9. X-Ray diffraction for (PANI)  
Figure 10. X-Ray diffraction for (GR)
3.4 Atomic Force Microscope (AFM) Analysis

The properties of the surface was studied using the topography AFM. The results of the tests AFM of the nano films for synthesized pure polyaniline (PANI) and filled with different ratio of GR films which prepared by spin coating which showed a uniform granular surface morphology, as in figure 14. It can be noticed that, the Roughness average (Ra) increased with increasing the ratio of filled. The roughness average (Ra) increased due to high surface area. As well as the root mean square (Rms) increased with increasing of ratio of doped. The grain size (G.S) also it exhibits the same behavior.
Figure 14. AFM images of synthesized pure PANI nano films for (a) 2-D and (b) 3-D, AFM images of the prepared nano films of PANI/GR with ratio 1% for (c) 2-D and (d) 3-D, AFM images of the prepared nano films of PANI/GR with ratio 3% for (e) 2-D and (f) 3-D and AFM images of the prepared nano films of PANI/GR with ratio 5% for (g) 2-D and (h) 3-D.
Table 4. Morphological characteristics of PANI/GR nano films

| Sample | PANI / GR (wt%) | Roughness average (nm) | Root mean square (nm) | Grain Size (nm) |
|--------|----------------|------------------------|-----------------------|-----------------|
| 1      | 0              | 1.93                   | 2.47                  | 40.41           |
| 2      | 1%             | 3.92                   | 4.66                  | 49.05           |
| 3      | 3%             | 4.52                   | 5.29                  | 52.37           |
| 4      | 5%             | 8.66                   | 10.3                  | 70.61           |

4. Conclusions

From the present work, it can be written the following Conclusions.

The method synthesis of polymer PANI by chemical oxidative polymerization was successful because using aniline hydrochloride as a monomer, spin coating technique is good method in preparation nano films of pure PANI and filled with GR at different addition ratios (1%, 3% and 5%). The structural and surface morphology of the prepared nano films are estimated by FT-IR, XRD and AFM. FTIR spectra of the PANI / GR composites is similar to that of pure PANI but some the bands are shift in wave numbers due to interaction between PANI and GR. It is observed from (XRD) results that, the high intensity diffraction peaks at centers decrease with increasing ratio filled of (PANI/GR) nano films this refer to the presence of the GR reduces the percentage of PANI in the composite and hence weakens diffraction peaks of PANI. The Grain size (G.S) and Roughness (Ra) were evaluated by using (AFM). It can be observed that (RMS) and (G.S) increased with increasing filled ratio for (PANI/GR) nano films.

The most effective property influenced by the addition of graphene is surface topography characteristics, this no mean that others properties no effect by addition of GR, also we observed the best addition of GR is 5% compare with 1% and 3% for all characteristics.

5. References

[1] Topart, P., Hourquebie, P 1999 Thin Solid Films P. 352
[2] Mac D and Epsten 1989 polyaniline a novel class of Conducting polymers, Faraday Discuss. Chem.Soc.88, P.317
[3] Cao, Andreatta, Heeger and Smith 1989 influence of chemical polymerization condition on the properties of polyaniline, polymer, Vol. 30 , P. 2305
[4] Chen and Wen2003 Power Sources vol. 117 p 273
[5] Taleghain, Aleahmad and Eisazadea 2009. World Applied Sciences Journal, Vol.6, 12,PP. 1607-1611
[6] Ali, M, Saion, E, Yahya, N.; Kassim, A.; Dahlan, K., Hashim, 2007 Synthesis of conducting polyaniline nanocomposites by radiation doping. J. Eng. Sci. Technol.,2, PP.111–118
[7] Reda, S, Al-Ghannam 2012Synthesis and electrical properties of polyaniline composite with silver nanoparticles. Adv. Mater. Phys. Chem.,2, PP.75–81
[8] Kaneko and Nakamura 1985Photoresponse of a liquid junction polyaniline film, Journal of the Chemical Society, Chemical Communications ,No.6,pp.346–347
[9] Chen and Fang 1993 Polyanline schottky barrier:effect of doping on rectification and photovoltaic characteristics Synthetic Metals ,vol 60,No.3,PP 215–222
[10] Geng, Zhao, Huang, Wang and Zhang, 2007Characterization and gas sensitivity study of polyaniline/SnO2 hybrid material prepared by hydrothermal route Sensors and Actuators B,Vol 120,No.2,PP.568–572
[11] Hee L 2009, prog.polymer. Sci., vol. 34, P.783-810
[12] Schoch J1994 IEEE electric Insutat Mag,vol.10 P. 29-32
[13] Kötz., Carlen 2000 , Electrochim vol 45 , P.2483
[14] Diarmind and Huang1987 Synth. Met-18,P. 285
[15] Ndangili, et 2012 Electronics of Conjugated Polymers (I): Polyaniline
[16] Virji S, Huang J, Kaner RB, Weiller BH 2004. Nano Lett; 4: P.491 – 496
[17] Rivers TJ, Hudson TW, Schmidt CE. 2002 Adv Funct Mater; 12: P.33–37
[18] Shimano and A.G. MacDiarmid, Synth. Met. 2001 vol123 P.251-262
[19] Green and Woodhead, J. Chem. 1912 Soc., Trans,101 , P.1117-1123
[20] Wudi, Nowak and Heeger J. Amer1986. Chem. Soc.,108, P. 8311-8313
[21] Masdarolomoor 2006 in Novel nanostructured conducting polymer systems based on sulfonated polyaniline, Doctral dissertation (Department of Chemistry, University of Wollongong, Australia)
[22] Rajapakse, R., Perera, and Premasiri 2000. Polyaniline retained glass templates as sensors for acidic/basic and/or redox gases. Journal of the National Science Foundation of Sri Lanka28(4): P. 277-285
[23] Novoselov, Geim, Morozov, et al 2004 Science vol 306, P.666–669
[24] Matthew, J., et al. Honeycomb carbon2010: a review of graphene, Chem. Rev. 110, P.132-145
[25] Compton, O. and Nguyen, S., Small 2010, vol 6, P.711 – 723
[26] Lee, C., Kysar and J. Hone 2008 Measurement of the elastic properties and intrinsic strength of monolayer grapheneScience 321(5887): P.385-388
[27] Balandin, A., Ghosh, W, Calizo, D. Teweldebhran, F.Miao and. Lau. Superior 2008 thermal conductivity of single-layer graphene. Nano Letters 8 (3):P. 902-907
[28] Bolotin, Sikes, Z. Jiang, Klima, Fudenberg, Hone, Kim and Stormer 2008 Ultrahigh electron mobility in suspended graphene. Solid State Communications 146(9–10): P.351-355
[29] Stoller, Park, Zhu and Ruoff 2008 Graphene-based ultracapacitors. Nano Letters8(10): P.3498-3502
[30] KausarA 2016. Thermal conductivity measurement of polyvinyl-pyrrolidone/polyethylene/graphene nanocomposite Nanoscience and Nanotechnology.
[31] Sapurina, I., Riede, and Stejskal 2001 In-situ polymerized polyaniline films: 3. Film formation. Synthetic Metals., 123(3): P. 503-507
[32] John, R. Electrochemical 1992 Studies of heterocyclic conducting Polymers, in Department of Chemistry., (University of Wollongong) P. 294
[33] Yilmaz, F. 2007 Polyaniline: Synthesis, Characterization, solution properties and composites, in Natural and Applied Sciences (Middle East Technical University) p. 148
[34] EBOGODI, K OTLHAO and KLINK. 2017 studies of Synthesis and Characterization of Graphene/Polyaniline Nanocomposite Using Green Solvents, Asian Journal of Chemistry; vol. 29, No. 6, p.1206-1214
[35] Zhang, Zhang, Zhao and J. Wu, Chem. Mater 2010. vol 22, P.1392
[36] Goswami, Maiti, Maiti, Nandy, Mitra and Chattopadhyay, Carbon 2011, vol.49. P.2245
[37] Theme, Moloto, Dikio, Nyangwe, Kotsedi, Maaza and Khenfouch J. Chem2012 Article ID 150536
[38] KUMAR M., BHANDARI, M. RAHAMAN,DIP AK KHASTGIR 2013 studies Morphology and cyclic voltammetry analysis of in situ polymerized polyaniline/graphene composites, p. 157-166
[39] Wang., Jiang, X. Wang, Electrochim. Acta 2011 vol 56 , p. 3338-3344
[40] Lijuan Z, Hui P, Paul A. Kilmartin, Christian Soeller, and Jadranka T 2008 studies Poly(3,4-ethylenedioxythiophene) and Polyaniline Bilayer Nanostructures with High Conductivity and Electrocatalytic Activity, vol 41,P. 7671-7678
[41] Sharma, Saini and Sharma 2013 Structural, optical, morphological and electrical characteristics of polyaniline for device applications, vol 20, pp. 145-149
[42] Grammatiki G. Papagianni, Dimitrios V. Stergiou 2012 studies Synthesis, characterization and Performance of polyaniline–polyoxometalates, pp.346-353
[43] Hameed H 2018 study Synthesis of Graphene as Support for the Catalysts in the Hydrodesulfurization of Heavy Naphtha