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Polyvinylpyrrolidone/Multi-walled Carbon Nanotubes/Graphene Nanocomposite as Gas Sensor

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Abstract

In this work, polyvinylpyrrolidone (PVP), multi-walled carbon nanotubes (MWCNTs) nanocomposite was prepared and hybridized with Graphene (Gr) by the solution casting method. The morphological and electrical properties were investigated by field effect scanning electron microscopy (FESEM) images, portraying a uniform dispersion of graphene within the PVP-MWCNT nanocomposite. The AC conductivity increased from (1.45552) to (2.34812) **$(\Omega\ cm)^{-1}$** with the use of nanocomposite. The increasing continues for the AC conductivity after hybridized with graphene up to (7.20641) **$(\Omega\ cm)^{-1}$**. In addition, the performances of the prepared samples for gas sensor application have been investigated. It was seen that the sensitivity analysis portrayed higher value for the nanocomposite hybridized with Gr (S=2.2 and 5.4%) as compared to the pure sample (MWCNTs). Finally, the recovery and response times were increased when the temperature increased due to the increment of the adsorption of the gas that resulted from the free electrons.

Keywords: polyvinylpyrrolidone, Multi-walled carbon nanotubes, Graphene, electrical properties, gas sensor

متحسس الغازي للمتراكب النانوي لبولي فاينيل بيروالدين /انابيب الكاربون النانوي المتعدده الجدران مع الكرافين

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الخلاصة

في هذا العمل ، تم تحضير مركب البولي فينيل بيروليدون (PVP) والأنابيب النانوية الكربونية متعددة الجدران (MWCNTs) وتهجينه باستخدام الجرافين (Gr) عبر طريقة صب المحلول. تم فحص الخواص المورفولوجية والكهربائية بواسطة صور المسح المجهري الإلكتروني (FESEM) للتأثير الميداني، والتي تصور

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تشتتًا موحدًا للجرافين داخل المركب النانوي PVP–MWCNT. زادت التوصلية الكهربائية للتيار المتناوب من (1.45552) إلى (2.34812) **$(\Omega\ cm)^{-1}$** باستخدام المركب النانوي. تستمر الزيادة في توصيل التيار المتردد بعد تهجينه مع الجرافين حتى (7.20641)**$(\Omega\ cm)^{-1}$** . بالإضافة إلى ذلك ، تم فحص أداء العينات المعدة لتطبيق مستشعر الغاز. لوحظ أن تحليل الحساسية أظهر قيمة أعلى للمركب النانوي المهجن مع Gr (S = 2.2٪ ، 5.4٪) مقارنة بالعينة النقية (MWCNTs). أخيرًا ، تمت زيادة أوقات الاسترداد والاستجابة عندما زادت درجة الحرارة بسبب زيادة امتصاص الغاز الناتج عن الإلكترونات الحرة.

1. Introduction

In recent year, the importance of gas detection has gained a huge attention in several different fields such as industry, fuel emission control, automobile exhaust emission control, household security, and environmental pollution monitoring [1,2]. Gas sensors have been utilized in factories, laboratories, hospitals, and almost all technical installations [3]. Gases of interest include carbon dioxide (CO_2), carbon monoxide (CO), Nitrogen dioxide (NO_2), Sulfur dioxide(SO_2), Oxygen(O_2), Ozone(O_3), Hydrogen(H_2), Argon(Ar), Nitrogen(N_2), Ammonia(NH_3), organic vapours such as methanol (CH_3OH), ethanol (C_2H_5OH), isopropanol (C_3H_8O), benzene (C_6H_6), and several amines (organic compounds and functional groups that contain a basic nitrogen atom with a lone pair [4,5]. A characteristic feature of gas nanosensors is a transducer system that consists of nanometric materials [6].

Since the discovery of carbon nanotubes (CNT), wide range of applications have been accomplished. It is noteworthy that the CNTs have a hexagonal structure, consisting of carbon atoms that form rolled-up graphite sheets into a cylinder shape[7]. Two types of nanotubes can be distinguished based on the arrangement of the graphite sheets: single-walled nanotubes (SWCNTs), which is a single layer of cylindrical graphene, and multiwall nanotubes (MWCNTs), which have many concentric layers [8,9]. It should be also noted that CNTs are a suitable material for gas sensing layer realization due to their hollow shape and porous structure, as well as their size, large surface area and surface to volume ratio, and the existence of defects [10–12]. In addition, graphene (Gr) is arranged in two-dimensional honeycomb lattice consists of a single atomic layer of sp2-bonded carbon atoms; thus, it has gained an interest owing to its ultrahigh odd physical properties [13].

On the other hand, polymer composites have been regarded as a promising candidate to be utilized with CNT and Gr since it enhances the properties [14]. However, it is difficult to obtain homogeneous solution of polymer of CNTs and Gr due to the difficulty in the melting process. Polyvinylpyrrolidone (PVP) is an amorphous, nontoxic, versatile polymer in many applications fields; it has good binding properties with high stability [15,16]. PVP is soluble in water and many polar solvent such as ethanol, by which it is easy to prepare[17].

In this work, a the preparation of new composite of PVP/MWCNT hybrid with graphene using solution casting method is demonstrated as a new approach to fabricate gas sensor. The morphological properties and electrical properties were investigated using field emission scanning electron microscopic (FESEM) and A.C. conductivity analysis, respectively.

2. Materials and Methods

PVP (supplied by Sigma-Aldrich) is of average molecular weight of 64000g/mol. MWCNTs, outer diameter is 13-18nm with length of ~1-12 μm, and purity > 99 wt% was purchased from Neutrino. Gr platelet nanopowder with thickness of 608nm and average particle diameter 15μm was supplied by Skyspring nanomaterials Inc.

4mg/mL PVP was dissolved in distilled water and sonicated for 30 min. 0.005 g of MWCNT were dissolved in 50ml of ethanol and stirred for 2 hours at room temperature. Next, MWCNT was stirred with PVP for 90 min, followed by adding (0.5g) graphene powder to the nanocomposite during the stirring and sonicating processes (for 90 min). The resulted samples were dropped casting on top of the glass substrates with dimension of 2.5×2.5cm for characterization. The weight percentage wt% of the materials was calculated using the following formula:

$$wt\% = \frac{w_m}{w_m + w_p} \times 100\% \qquad (1)$$

Where: w_m and w_p are the weight of the mixture and the weight for the polymer, respectively.

The morphological analysis of the samples was examined by FESEM, while the A.C. conductivity for these samples was measured at room temperature in the frequency range (100Hz-5 MHz). The conductivity (σ) was calculated depending on the basic equation[18]:

$$\sigma = \frac{t}{RA} \qquad (2)$$

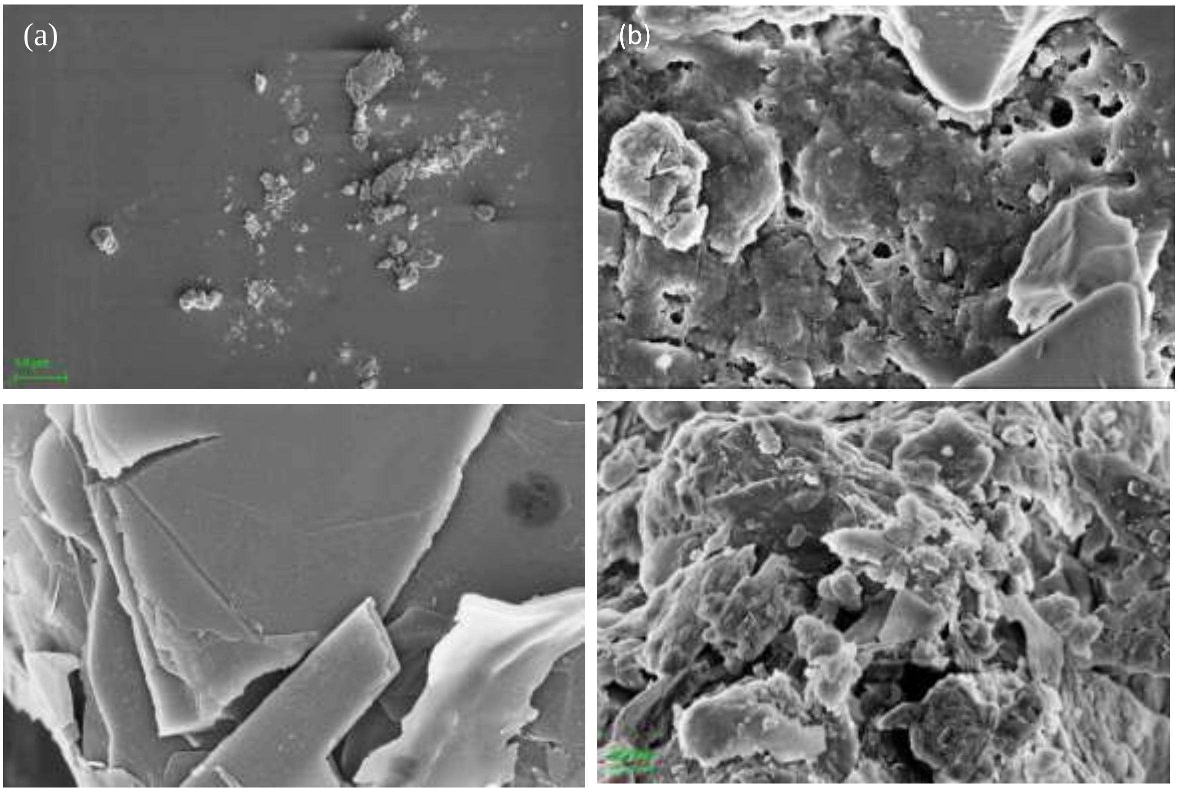
Where: t, R and A are thickness, resistance and surface area of the sample, respectively. Finally, the performances of prepared gas sensor were obtained by testing the A.C. conductivity. The applied bias was 6 volts. The sensitivity (S) was calculated depending on the following equation[19]:

$$S = \frac{R_g - R_a}{R_a} \times 100\% \qquad (3)$$

Where: R_g is the value of the resistance after exposure to the gas, R_a is the value of the resistance after exposure to the air.

3. Results and discussion

The morphological properties of the pure samples (PVP, MWCNT, Gr) and their nanocomposites were investigated by FESEM analysis as shown in Figure 1. As seen in Figure 1a, the PVP exhibited an amorphous distribution. The surface of PVP was smooth and uniform with no cracks. As it be unambiguously discerned in Figure 1b, MWCNT are of a prevailing smooth surface with a tendency to entangle due to the π-π* interaction between the nanotubes [20]. As shown in Figure 1c, the PVP/MWCNT nanocomposite demonstrated a proper compatibility, homogeneous although few voids were observed. The structure of Gr is crumpled and wrinkled as clearly observed in Figure 1d. It is noteworthy that when the Gr was added to the nanocomposite, it is presumed that the disparity of graphene in PVP/MWCNT nanocomposite was enhanced, which agrees with previous reports [15,16].



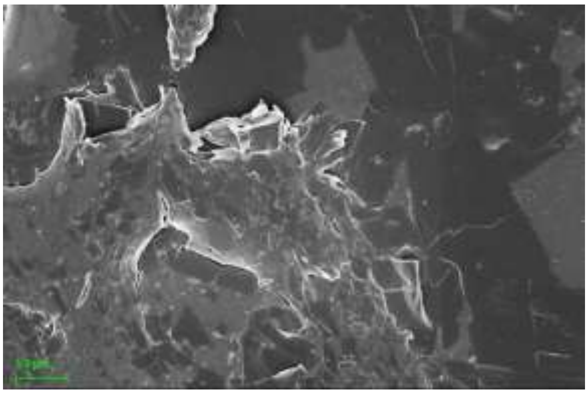


Figure 1-FESEM morphological analysis for (a) pure PVP, (b) pure MWCNT (c) pure Gr (d) PVP+MWCNTs nanocomposite (e) PVP+MWCNTs nanocomposite hybrid graphene.

The use of the Hall Effect on samples was studied and reported in our previous work [17], in which the conductivity and carrier mobility were observed to be high in the hybrid sample as compared with other samples. The Hall coefficient found to be positive for all samples which indicates that holes are the majority carriers and the samples acts as a p-type semiconductor as shown in Table 1.

Table 1- Hall Effect measurements for all samples

Samples	**(n_H) [/ cm^3]**	**(μ) [cm^2/V_s]**	**(ρ) [Ω cm]**	**(RH) [cm^3/C]**	**(σ) $(\Omega\ cm)^{-1}$**	**type**
Pure PVP	7.381E+13	1.731E+01	4.886E+4	4.626E+5	2.047E-5	p
Pure MWCNT	1.972E+18	1.166E+2	2.715E-2	3.265E-1	3.683E+1	p
Pure graphene	3.314E+12	3.905E+1	4.822E+4	9.807E+5	2.074E-5	p
PVP/MWCNT nanocomposite	1.99E+02	5.86E+01	3.99E+02	2.34E-01	2.51E+02	p
Hybrid graphene	2.11E+02	5.41E+04	4.23E-02	2.29E+02	2.36E+02	p

Figure 2 shows the change in A.C conductivity in relation to frequency for the pure MWCNT, PVP/MWCNTs nanocomposite and PVP/MWCNTs hybrid nanocomposite. As shown in the figure, the increment in the A.C conductivity after adding MWCNT and graphene is mainly attributed to tunneling conduction processes (TCM); in which, this result might be due to the presence of the charge carriers of MWCNT as well as charge carriers of PVP, that causes an increase in the number of the hopping charge carriers on the polymer chain [16,21]. In addition, the low concentration of MWCNTs which is uniformly dispersed in the polymeric matrix, leads to interactions. In turn, this interaction would result in an effective conductive pathway in the polymer matrix. This result is comparable with results of previous studies [16,22]. It is also worth noting that when MWCNT is included, nanocomposites become frequency independent, indicating the electron type of charge transfer. As it can also be observed that the change in electrical conductivity is proportional to the quantity of MWCNT present in the nanocomposites[23]. At a modest scale, the conductivity of the nanocomposites increases with increasing frequency while at higher amount the conductivity shows a direct current and a non-dielectric behavior.

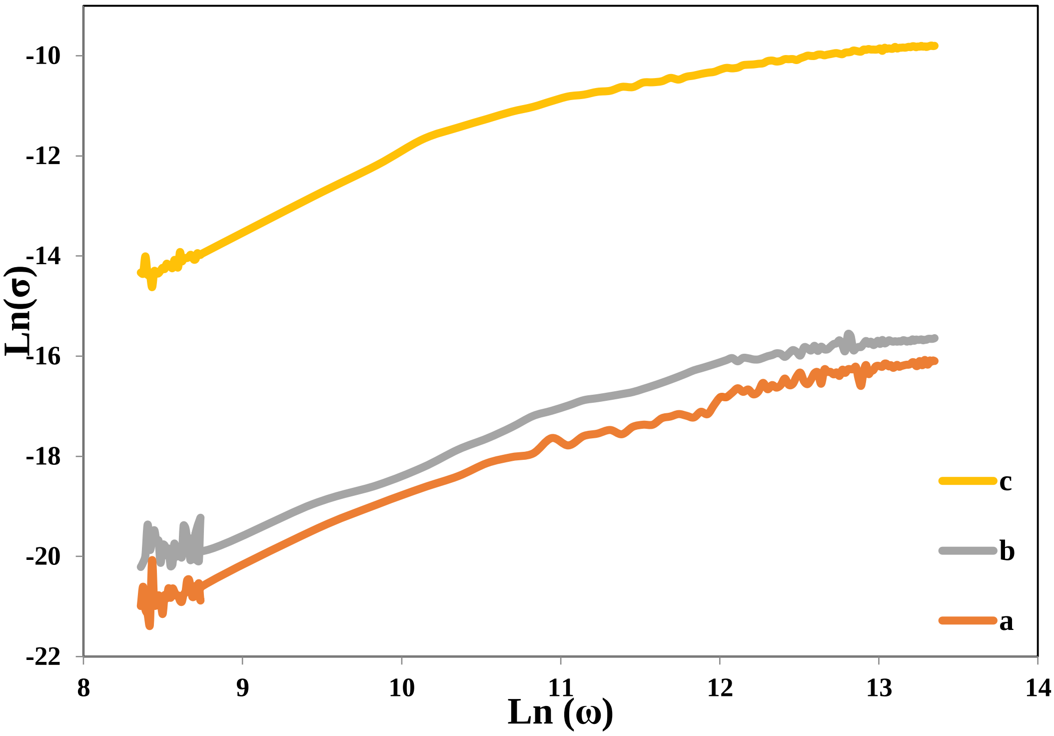


Figure 2-Variation of conductivity with angular frequency for (a) pure MWCNT, (b) MWCNT/PVP nanocomposite and (c) MWCNT/PVP nanocomposite hybrid with graphene samples.

Figures 3 (a, b) shows the resistivity of pure MWCNTs as a function of operation temperature of 25°C and 120°C, respectively. As shown in the figure, the MWCNTs are partially of non-stoichiometric shape that has a huge number of localized centres of restricted electrons, demonstrating the noticeable sensors response sensitivity at room temperature. Furthermore, when NH_3 gas was introduced, the resistance of the sensor element tremendously increased. This phenomenon might be attributed to the adsorption of NH_3 onto the surface of the semiconductor and the role of NH_3 as an oxidizing gas [24]. Besides, the accepter in NH_3 was oxygen that extracted electrons from the conduction band.

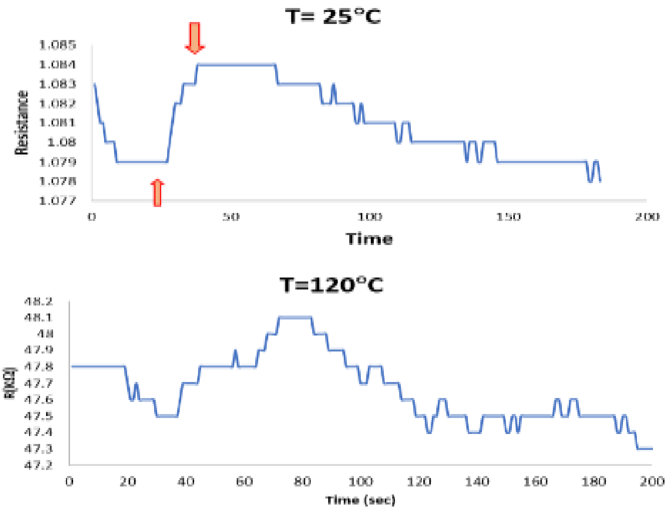


Figure 3-Resistivity at two operating temperature of (a) 25°C and (b) 120 °C for pure MWCNTs.

Figure 4 shows resistivity of for PVP /MWCNT nanocomposite hybrid with Gr as function of time at 25°C and 120 °C, respectively. Table 1 lists the values of sensitivity, response and recovery time of pure MWCNTs and PVP/MWCNT nanocomposites. It is noteworthy that the nanocomposites gas sensing exhibited higher resistivity by adding graphene, this indicates that Gr played an important role in enhancing the gas sensor performance properties [24].

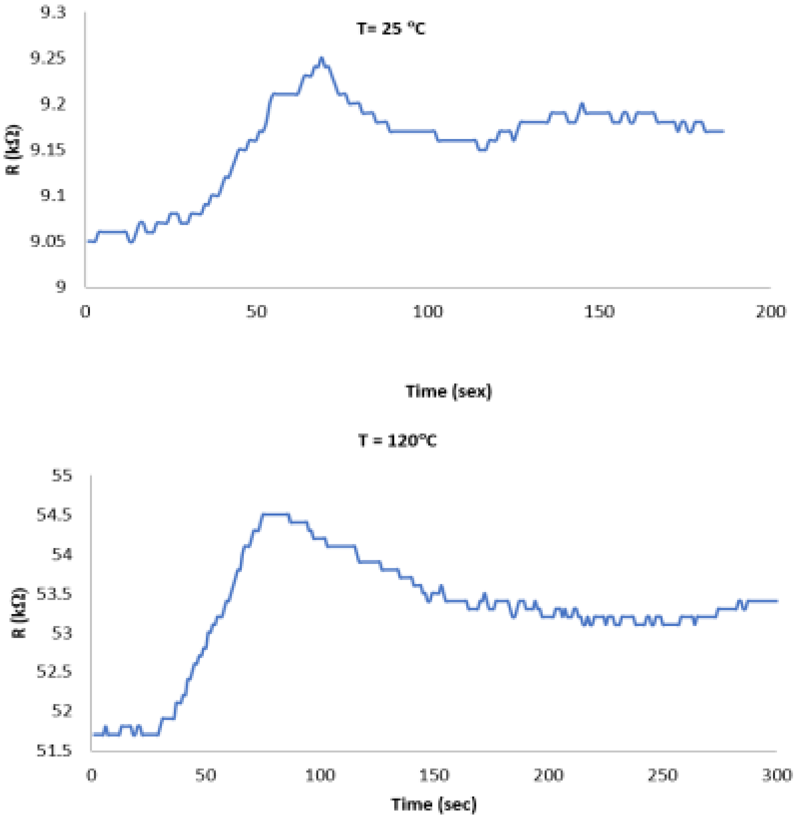


Figure 4- resistivity with the two operating temperature (25 and 120)° C for nanocomposites hybrid with graphene.

Table 2-The sensitivity, Response and Recovery time of pure MWCNTs and PVP/MWCNT nanocomposites

Sample	T (°C)	S%	ts (s)	tc (s)
Pure MWCNTs	25	0.4%	19	23
	120	0.6%	23	29
PVP/MWCNT nanocomposite hybrid with graphene	25	2.20%	22	24
	120	5.4%	29	64

Conclusion

A solution casting technique method was employed to prepare PVP /MWCNT nanocomposite hybrid with Gr at room temperature. The electrical conductivity revealed that even a little quantity of MWCNT, could improve the electrical performance. In addition, further enhancement was achieved by adding Gr. It was seen that the MWCNTs portrayed a prevailing smooth surface with a tendency to entangle due to the π-π* interaction between the nanotubes. Furthermore, it was found that the PVP/MWCNT nanocomposite exhibited a proper compatibility and homogeneous structure despite of the existence of few voids. The result of gas sensor measurement showed that PVP/MWCNT nanocomposite hybrid with Gr has higher sensitivity, response and high recovery time because the free electrons increase the adsorption of the gas and better results were obtained at 120°C.

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References

[1] E. T. Abdullah and O. A. Ibrahim, "Capacitance and Resistivity Measurements of Polythiophene /Metallic Nanoparticles-based Humidity Sensors," *Iraqi Journal of Scienc.*, vol. 62, no. 4, pp. 1158–1163, 2021.

[2] M. H. zaheydarali and V. Ghafarinia, "A smart gas sensor insensitive to humidity and temperature variations," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 17, no. 1, pp. 1–8, 2011.

[3] V. Kruefu, A. Wisitsoraat, A. Tuantranont, and S. Phanichphant, "Gas sensing properties of conducting polymer/Au-loaded ZnO nanoparticle composite materials at room temperature," *Nanoscale Res. Lett.*, vol. 9, no. 1, pp. 1–12, 2014.

[4] L. Zhu and W. Zeng, "Room-temperature gas sensing of ZnO-based gas sensor: A review," *Sensors Actuators, A Phys.*, vol. 267, no.1, pp. 242–261, 2017.

[5] A. Dey, A. Singh, D. Das, and P. K. Iyer, "Organic semiconductors: A new future of nanodevices and applications," *Thin Film Structures in Energy Applications, Switzerland: Springer International Publishing,Switzerland*, 2015, pp. 97–128.

[6] Y-F Sun, S-B Liu, F-L Meng, J-Y Liu, Z. Jin, L-T Kong, and J-H Liu, "Metal oxide nanostructures and their gas sensing properties: A review," *Sensors*, vol.12, no.3, pp. 2610–2631, 2012.

[7] I. I.Nassif, , & B. M. Al-Shabander, "Effects of MWCNTs on the Tensile Properties and Thermal Conductivity of BaTiO3 /Epoxy Nanocomposites". *Iraqi Journal of Science*, vol.61, no. 9,pp. 2226-2231, 2020.

[8] S. A. Kamal, , M. A., Jaleel, & A. A Mohsin,. "Study the Effect Some of Electrodeposition Parameters on Wear Resistance for Cu-MWCNT Composite Coating", *Iraqi Journal of Science*, vol.60, no.3, pp509-515, 2019.

[9] B. Fiedler and K. Schulte, "Carbon nanotube-based composites," *Compr. Compos. Mater*. II, vol. 4, no. 1, pp. 201–229, 2017.

[10] S.S.Kumar, B. Thomasa, V. R. Kar, "A Comprehensive Review on CNTs and CNT-Reinforced Composites: Syntheses, and Applications," *Mater. Today Commun.*, vol. 25, no. 101546, pp. 1–37, 2020.

[11] W. S. Khan, R. Asmatulu, and M. M. Eltabey, "Electrical and thermal characterization of electrospun PVP nanocomposite fibers," *J. Nanomater.*, vol. 2013, no. 1, pp. 1–9, 2013.

[12] K.K.Gangue, S. Maddila, S.B.Mukkamala, S. B. Jonnalagadda, "Characteristics of MOF, MWCNT and graphene containing materials for hydrogen storage: A review" *J. Energy Chemistry*, vol.30, Pages 132-144,2019.

[13] B. G. Nassef, G. A. Nassef, M. A. Daha,"Graphene and Its Industrial Applications – A Review", *International Journal of Materials Engineering*, vol.10, no.1, pp.1-12, 2020.

[14] A. G. Enad, E. T. Abdullah, and M. G. Hamed, "Study the Electrical Properties of Carbon Nanotubes/Polyaniline Nanocomposites," in *Journal of Physics: Conference Series*, vol. 1178, no. 1, pp. 1–7, 2019.

[15] P. Boonsuk, K. Kaewtatip, S. Chantarak, A. Kelarakis, and C. Chaibundit, "Super-tough biodegradable poly(vinyl alcohol)/poly(vinyl pyrrolidone) blends plasticized by glycerol and sorbitol," *J. Appl. Polym. Sci.*, vol. 135, no. 26, pp. 1–22, 2018.

[16] I. M. Alibe, K. A. Matori, H A. Sidek, Y. Yaakob, U. Rashid, A. M. Alibe, M. H. Moh Zaid, S. Nasir & M. M. Nasir, "Effects of polyvinylpyrrolidone on structural and optical properties of willemite semiconductor nanoparticles by polymer thermal treatment method," *J. Therm. Anal. Calorim.*, vol. 136, no. 6, pp. 2249–2268, 2019.

[17] S. M. Omran, E. T. Abdullah, "Preparation and Characterization of Polyvinylpyrrolidone/Multi-walled Carbon Nanotubes Nanocomposite hybrid with Graphene", *Basrah Journal of Science*, Vol. 39,no.2, pp. 264-532, 2021.

[18] H.M.Zidan, E.M. Abdelrazek, A. M. Abdelghany, A. E. Tarabiah, “Characterization and some physical studies of PVA/PVP filled with MWCNTs,” *J. Mater. Res. Technol.*, vol. 8, no. 1, pp. 1–10, 2018.

[19] E. T. Abdullah, S. M. Hassan, and R. S. Ahmed, “Electrical Properties of Polyaniline/Functionalized Multi Walled Carbon Nanotubes Nanocomposite,” *Int. J. Curr. Eng. Technol.*, vol. 6, no. 2, pp. 617–621, 2016.

[20] B. M. Alhreb, K. Almasri, and S. Alhariri, “Fabrication and characterization of poly(3-hexylthiophene) (P3HT)sensor in two techniques (Dip-coating and Spin-coating) and Sensitivity compared for various vapors,” Inter. J. Chem. Tech. Research, vol.6, no.1, pp. 3690-3696, 2014.

[21] E.M. Abdelrazek, A. M. Abdelghany, A. E. Tarabian and H. M. Zidan, “AC conductivity and dielectric characteristics of PVA/PVP nanocomposite filled with MWCNTs,” J. Mater. Sci. Mater. Electron., vol. 30, no. 16, pp. 15521–15533, 2019.

[22] S. H. Yetgin, “Poly(vinyl pyrrolidone) wrapped multi-walled carbon nanotube/poly(vinyl alcohol) composite hydrogels” journal of materials research and technology, vol.8, no.5, pp.4725–4735, 2019.

[23] S. I. Abdullah, S F. Al Naim, H. AlFannakh, S. Arafat, “Characterization of PVC/MWCNTs Nanocomposite,” Sci Eng Compos Mater, vol. 27, pp. 55–64, 2020.

[24] S. Sharma, S. Hussain, S. Singh, and S. S. Islam, “MWCNT-conducting polymer composite based ammonia gas sensors: A new approach for complete recovery process,” *Sensors Actuators, B Chem.*, vol. 194, pp. 213–219, 2014.