Tikrit Journal of Pure Science Vol. 28 (4) 2023

TJPS

https://doi.org/10.25130/tjps.v28i4.1307

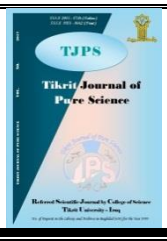
IASJ

المجلات الاكاديمية العراقية

Tikrit Journal of Pure Science

ISSN: 1813 – 1662 (Print) --- E-ISSN: 2415 – 1726 (Online)

Journal Homepage: http://tjps.tu.edu.iq/index.php/j



High Performance of ZnO/PANI Nanocomposites for Supercapacitors Applications

Sarwa A. Mohammed[1] , Adnan Raad Ahmed[2] , Isam M. Ibrahim [3]

[1]Mathematics Department, College of Education for Women, University of Tikrit, Iraq.

[2]Department of Physics, College of Education for Pure Sciences, University of Tikrit

[3]Department of Physics, College of Science, University of Baghdad

ARTICLE INFO.

Article history:

-Received: 23-3-2023

-Received in revised form: 29-4-2023

-Accepted: 22-5-2023

-Final Proofreading: 18-7-2023

-Available online: 25-8-2023

Keywords: Polyaniline (PANI), supercapacitor, nano fibers, aniline, electrochemical, XRD, SEM.

Corresponding Author:

Name: Sarwa A. Mohammed

E-mail: srwa.muhammad@tu.edu.iq

Tel:

ABSTRACT

One of the goals of current technology is to miniaturize electronic, operational, sensing and optical devices and their components. Thus, nanotechnology is an advanced technology favored by the scientific and industrial communities for its ability to exploit the unique properties of nanomaterials on a large scale. This study examined the polyaniline (PANI) solution with (ZnO) in different volume ratios through depositing (PANI: ZnO) on glass and silicon substrates. Alkalis were prepared and cleaned in a specific method and kept in tanks until they were used in a precipitation process using distillation casting techniques, which were carried out on silicon. The results showed that the as-prepared material has the characteristic of electrochemical performance. The synthesis test showed the consistency and compatibility among the materials used in the study with a maximum elapse time of (7.72 sec) and a maximum voltage of (0.203 V). The highest intensity for ZnO was at (36.3008°) with a Miller coefficient of (101) and for PANI was at (25°) with a Miller coefficient of (200). The X-ray diffraction results showed a successful matching procedure. When ZnO and PANI were mixed, the Miller coefficient (100) at (35o) angle provided the highest intensity. This proved that the materials used in the precipitation process were compatible. As for scanning electron microscopy, the results showed homogeneity and diffusion in the prepared material, where the grain volume decreased with the increase in ZnO. The best mixing ratio was (5:5) of (ZnO/PANI).

الأداء العالي للمتراكب ZnO / PANI النانوي لتطبيقات المكثفات الفائقة

سروة عبدالقادر محمد 1 عدنان رعد أحمد 2 عصام محمد ابراهيم 3

جامعة تكريت –كلية التربية للبنات–قسم الفيزياء 1

جامعة تكريت – كلية التربية للعلوم الصرفة – قسم الفيزياء 2

جامعة بغداد – كلية العلوم – قسم الفيزياء 3

الملخص

أحد أهداف التكنولوجيا الحالية هو تصغير الأجهزة الإلكترونية والتشغيلية وأجهزة الاستشعار والبصرية ومكوناتها ؛ وبالتالي ، فإن تقنية النانو هي تقنية متقدمة تفضلها المجتمعات العلمية والصناعية لقدرتها على استغلال الخصائص الفريدة للمواد النانوية على نطاق واسع. تم دراسة محلول

Tikrit Journal of Pure Science Vol. 28 (4) 2023

TJPS

https://doi.org/10.25130/tjps.v28i4.1307

بوليانيلين (PANI) مع (ZnO) بنسب حجم مختلفة حيث تم ترسيب(PANI: ZnO) على الزجاج والقاعدة السيليكونية و تم تحضير القلويات وتنظيفها بطريقة معينة وحفظها في خزانات حتى يتم استخدامها في عملية الترسيب باستخدام تقنيات صب التقطير ، والتي تتم على السيليكون. أظهرت النتائج أن المادة المحضرة لها أداء كهروكيميائي مميز ، وأظهر اختبار التوليف عملية الاتساق والتوافق بين المواد المستخدمة في الدراسة بأقصى وقت انقضاء (7.72 ثانية) وجهد أقصى (0.203 فولت). إن أعلى شدة لـ ZnO عند (o36.3008) بعامل ميلر (101) ولـ PANI عند (o25)بعامل ميلر (200) ، أظهرت نتائج حيود الأشعة السينية إجراء مطابقة ناجحا. عندما تم خلط ZnO و PANI ، قدم معامل ميلر (100) بزاوية) 35(oأعلى كثافة ، مما يثبت أن المواد المستخدمة في عملية الترسيب كانت متوافقة. أظهرت نتائج الفحص المجهري الإلكتروني الماسح وجود تجانس وانتشار في المادة المحضرة ، حيث يقل حجم الحبيبات مع زيادة ZnO وكانت أفضل نسب خلط)5: 5).(ZnO / PANI).

الكلمات المفتاحية:- الباني انلين, المكثفات الفائقة ، الياف النانو ، البولي انلين ، انلين ، الكهروكيميائية ،اوكسيد الزنك ، حيود الاشعة السينية ، المجهر الالكتروني الماسح.

Introduction

Nowadays, the development of ternary nano fibers based on new materials can provide higher specific capacitance and supercapacitor. Nanostructure-retaining composites with larger surface areas and relatively shorter ion diffusion paths than the bulk exhibit higher energy storage properties [1,2]. According to the charge storage mechanism, supercapacitors can be divided into electric double layer capacitors (EDLCs) and pseudocapacitors [3]. Double-layer supercapacitors are realized by forming a double layer on the surface of electrode materials, while in pseudocapacitors, charges are stored both on the surface of the material through a double-layer mechanism and in the bulk of the material through Faradaic reactions. Therefore, it is clear that the charge stored in a pseudocapacitor is almost 10 to 100 times that of an electric double layer capacitance [4]. So far, the main material studied for supercapacitor electrodes is carbon material, which is unique to EDLCs and has excellent electrical and mechanical properties, but with low capacitance [5, 6]. Pseudocapacitors (i.e., transiting metal oxides and conducting polymers) have high specific capacitance, but are expensive due to their low conductivity.[8 ,7]

Thin films have attracted a lot of attention for making many components of thin electronic devices and detectors. Interference filters are used in various optical fields, such as studying the properties of material in the form of thin films. They have attracted the attention of physicists since the second half of the 17th century and have been electrochemical behavior of the resulting PANI/GO nanostructures.[11]

In 2020, Farah et al. synthesized zinc oxide (ZnO) nanoparticles in the form of nanoparticles. The electron and optical characterization of samples was performed via standard techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence, and visible the subject of numerous studies. As a significant field of research, films are known to produce matrix-based substances in the form of controlled deposition of one or more layers of molecules, atoms, or ions, and must not exceed 1 micron in thickness. Nano-zinc oxide is a non-toxic semiconductor material that can be used to make environmentally friendly coatings.[9]

There are a number of previous studies related to the topic of the current study. In this regard, Zhu et al. (2015) prepared polyaniline nanoparticles by utilizing hydrothermal method in the presence of CTAB oxidation. The results of (FTIR), (XRD), (FESEM) and (UV-Vis) showed that the composition of pure polyaniline consists of three different formulations depending on the variation of aniline and CTAB concentrations. In addition, the temperature and time of reaction have a significant effect on the form of a PANI polymer.[10]

In 2018, Amin et al. conducted a traditional approach to the preparation of polyaniline/graphene oxide (PANI/GO) nanoparticles. They added aniline monomer and ammonium sulfate (APS) to an acidic solution of graphene oxide (GO) in a state where (GO) is first dispersed in acidic media containing (APS). Then, an aniline monomer was added for aniline polymerization at the site. They also investigated the effect of acid type including sulfuric acid (H2SO4), hydrogen chloride (HCl), perchloric acid (HClO4) and p-toluene sulfonic acid (PTSA) on the morphology and

ultraviolet (UV-Vis) spectroscopy. The point defect structures specific to each morphology were investigated in terms of their perception and location via the latest electron magnetic resonance spectroscopy (EPR).[12]

The current study aims to use the prepared Nano composites in electronic devices capacitors.

https://doi.org/10.25130/tjps.v28i4.1307

2.Experimental Details

2.1 Material

Table (1-3) Solid and liquid chemicals used in this study and their origins with their purity

Materials	Assay: Minimum	Origin	Chemical Formula
Zinc Acetate	97%	Germany	$(CH_2\ COO)_2\ Zn.2H_2O$
Aniline	99%	Germany	$C_6H_5.NH_2$
Ethanol	99.8%	Germany	Non
Ammonium	98%	Germany	$(NH_4)_2S_2O_8$
Stannous	97%	India	$SnCl_2.2H_2O$
Hydrochloric acid	99%	India	HCl

2.2 Preparation Method

- **Preparation of PANI**

Polyaniline (PANI) was prepared by taking (0.095g) of aniline with a concentration of (13.5mM) and then dissolving it in (76mL) of distilled water. The solution was mixed using a magnetic mixer for (10min). Then, another solution (0.237g) of ammonium sulfate was prepared with a concentration of (026M) and dissolved in (4mL) of distilled water. Then, it was placed in a magnetic mixer for (10min). After that, the two solutions were mixed (using gradual addition) to ensure that the reaction process was completed. Then, (1.4mL) of hydrochloric acid was added in the form of drops to the solution for a period of (10min). The solution was then covered and left for 24 hours at room temperature. After that, the solution was placed in a centrifuge to separate the precipitate. The polyaniline (PANI) precipitate formed was washed with distilled water and ethanol for several times, and then dried in the oven at a temperature of (70 °C) for a period of (4h). Then, it was melted in (40mL) of ethanol in order to be ready for the sedimentation process.

- **Preparation of ZnO**

In this part, (0.9269g) of zinc acetate $(CH_2\ COO)_2\ Zn.2H_2O$ was dissolved in (100mL) of ethanol. The solution was rotated on a magnetic starrier for half an hour. After that, drops of acetic acid were distilled until the solution became very clear, i.e. zinc acetate was completely dissolved. Then, the pH value was adjusted to (9) by distilling drops of ammonia. The resulting solution was filtered and then the resulting material was washed with ethanol and distilled water three times. After washing, it was placed inside the furnace at a temperature of (400 °C) for an hour.

- **Preparation of Blended PANI/ZnO**

Volumetric ratios (5/5) of (polyaniline (PANI: ZnO) were then placed in the ultrasonic device for a period of (2h) to ensure that the solution was mixed well and was ready for sedimentation on the glass and silicon substrates. These substrates were prepared and cleaned in a certain way to be used in the sedimentation process using the distillation casting technique.

2.3 X-Ray – Diffraction

An analysis of the prepared models was carried out to identify and follow up the structure of the materials and the phase transitions that can occur. The target used in the X-ray tube was copper with wavelength of (1.54060 Å).

2.4 Scanning Electron Microscope SEM

Scanning electron microscope (SEM) of the type (TESCAN) model (MIRA3) of French origin was used for observing the morphology of the samples surfaces, as well as following up the effect of the material when deposited on silicon substrate. SEM gave a three-dimensional, magnified and detailed image. This examination clarified the topography of the surface, defects and pores in the sample through the image given by the device.

3. Results and Discussion

3.1 Structural Analysis

https://doi.org/10.25130/tjps.v28i4.1307

- **XRD**

Figure (1) shows the results of X-ray diffraction of the prepared materials for both ZnO and PANI after depositing them on silicon. Distance data (d) and (2θ) were obtained by ray intensities. The Miller indices of the materials used in the prepared model were determined using the international map. While the phases formed were obtained by comparing the distance values between the individual planes (d) and diffracted ray intensities using the American Standard Table (A.S.T.M). Calculated values appeared specifically for phases of (PANI, ZnO). Since the highest intensity of ZnO was at an angle of 36.3008 degrees, the Miller coefficient was (101). In PANI, the highest intensity was at an angle of 25 degrees, and the Miller coefficient was (200). Then, ZnO and PANI were mixed. As for silicon, the highest intensity was at an angle of 35 degrees and the Miller coefficient was (100). This indicates that there is a match between the materials used in the settling process [13].

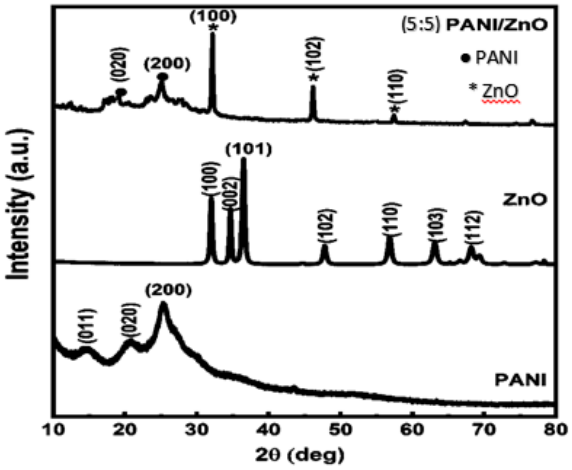
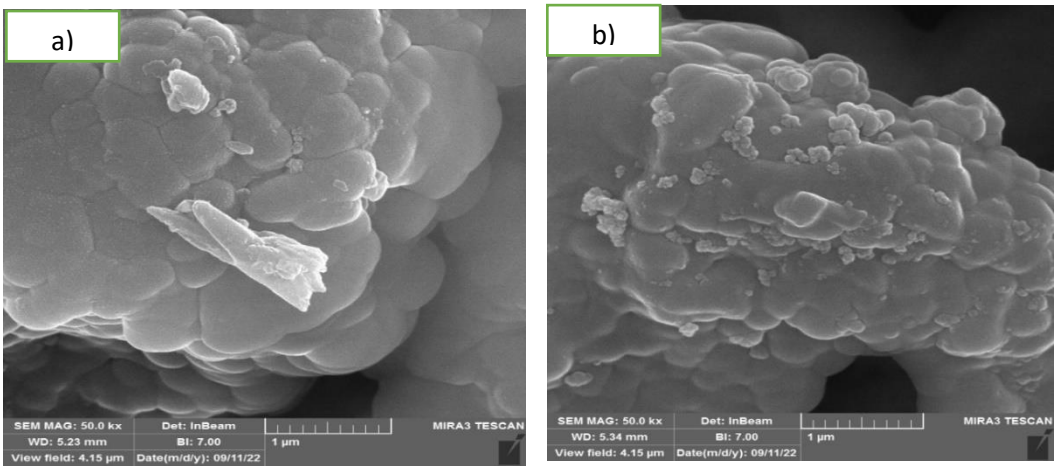


Fig. 1: XRD of PANI/ZnO

Scanning electron microscope (SEM)

Figure (2) shows the microscopic topographic images of the surfaces of the harmful models and the examination of electron microscopy at magnification. Here, (1µm) was observed, indicating a distribution and diffusion of molecules of the materials forming the conglomerates and clusters at some possible parts of mixing with PANI and depositing on silicon. This led to porosity distances between the molecules of the material bonding and homogeneity of the molecules with each other. The grain size was (123.43nm). Hence, increasing the ratio leads to a decrease in the granular size.



https://doi.org/10.25130/tjps.v28i4.1307

Fig. 2: SEM micrograph of a) (1:9) PANI/ZnO b) (5:5) PANI/ZnO

3.2

Electrochemical Characterization

The electrochemical properties of PANI/ZnO and multi-layer structures were investigated using galvanic discharge and cyclic voltametric measurement. PANI and ZnO were mixed and deposited on silicon. Annular voltammogram diagrams of these layers showed three peaks in the anode region and three peaks in the cathode region as shown in Fig. 3. These peaks were associated with proton and anion doping, as well as changes in polyaniline (PANI) shapes during possible surveys. The transformation of colorless emeralds into emerald-shaped polyaniline (PANI) was responsible for the first oxidation peak, which appeared at about (+0.2 V). The second wide peak at approximately (0.5 V) might be the result of head-to-tail dimerization and polyaniline (PANI) sealing. The conversion of emeralds to pernigranelin led to a third peak at (0.8 V) [14,15].

Static charging of galvans under different applied currents was explored in order to better study the charge discharge behaviors of the electrochemical functions of PANI - ZnO electrodes. The electrostatic charge discharge of PANI-ZnO films was carried out in a potential window from (0 V) to (0.8 V). Figure (4) shows the typical charge discharge characteristics of multiple layers in different applied currents (0.190, 0.185, 0.180). The internal resistance of the electrodes might be reflected in the rapid decline of the first discharge [16]. The following formula was used to obtain the specific capacity of the electrode material [16]:

$$C_{s.p} = I \times \frac{\Delta t}{(\Delta V . m)}$$

Where I represents the discharge current (A), t represents the discharge time (s), V represents the potential window (V), and m is the mass of the active component.

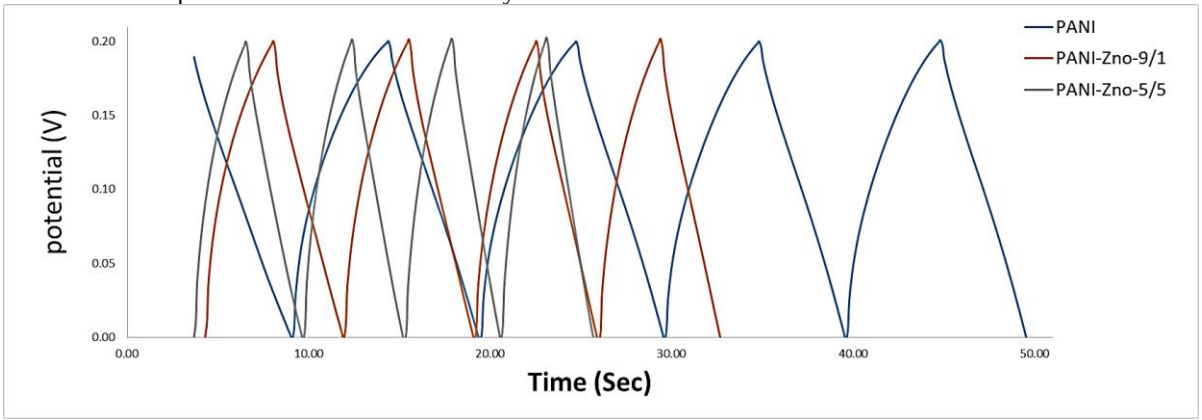


Fig. 3: Charge-discharge properties of multilayer films made of PANI/ZnO at various applied currents (0.190, 0.185, 0.180).

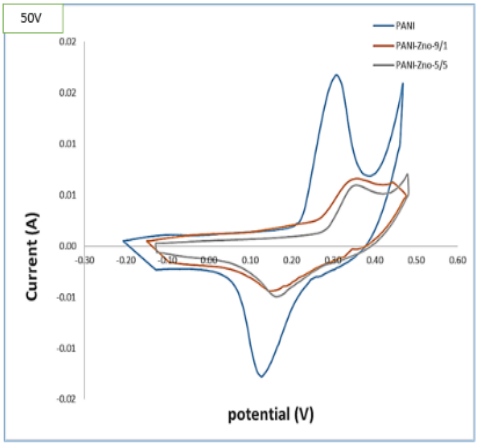
As shown in Fig. 4, the voltages were (50, 100, 150)V multilayer. The charge-discharge properties of the multilayer films PANI-ZnO revealed that the discharge time lengthens with falling current. The inner electrode received a complete electrolyte ion diffusion at low currents, improving the accessible surface area and specific capacitance. At greater current densities and finite diffusion times, this lowered the capacitance to the inner surface [17]. The highest and lowest values were obtained for both time and potential, as shown in table (2).

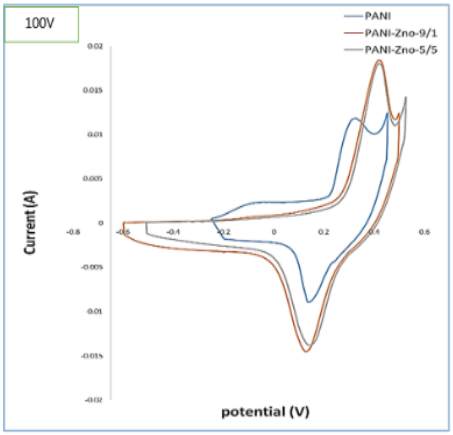
Table (2): The highest and lowest values for elapsed time and potential

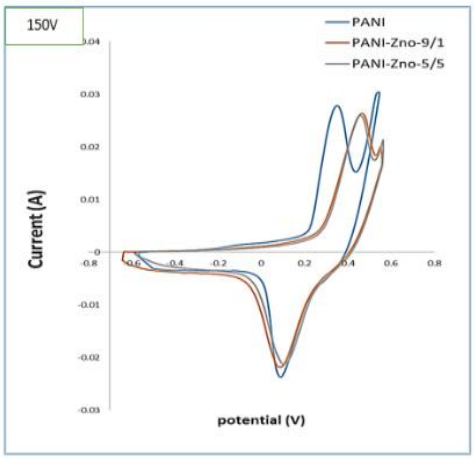
Content	Max Time (sec)	Min Time (sec)	Max Potential (v)	Min Potential (v)
PANI	49.60	3.68	0.209	-0.00326

https://doi.org/10.25130/tjps.v28i4.1307

9%PANI -1%ZnO	32.7	4.3	0.202	-0.00045
5%PANI -5%ZnO	7.72	3.6	0.203	-0.000407







00,150) V multilayer film (10 cycles)

4. Conclusion

PANI was prepared by chemical method and mixed with prepared zinc oxide nanoparticles. The properties of nanocomposites prepared to be used in electronic devices applications, such as electrochemical applications and photovoltaic applications, were examined. The results showed that the prepared materials were homogeneous with each other when mixed. This was evidenced by results of X-ray diffraction, which showed a good matching process. In addition, SEM test showed good results in terms of the diffusion process of materials and homogeneity with each other. The polynilene and maoxide materials were mixed and deposited on the glass substrate. The best mixing ratio was (5:5) (PANI/ZnO) with a maximum elapse time of (7.72 sec) and a maximum voltage of (0.203 V).

References:

1. Wen-Dong Wang, Xiao-Qiang Lin, Hai-Bo Zhao, Qiu-Feng Lü,Nitrogen-doped graphene prepared by pyrolysis of grapheneoxide/polyaniline composites as supercapacitor electrodesJournal of Analytical and Applied Pyrolysis (2016)JAAP-3705; No. of Pages 10.

2. S. Najib , F. Bakan,N. Abdullayeva, R. Bahariqushchi, S. Kasap, G. Franzò, M. SANKIR, N. Demirci Sankir, S. Mirabella and E. Erdem, NanoscaleTailoring morphology to control defect structures in ZnO electrodes for highperformancesuper capacitor devices,Article in Nanoscale,June (2020),DOI: 10.1039/D0NR03921G.

3. E. Mitchell a, J. Candler , Felipe De Souza , R.K. Gupta , Bipin Kumar Gupta b,L.F. Dong,High performance supercapacitor based on multilayer of polyaniline and graphene oxide,Synthetic Metals 199 (2015) 214–218.

4. Peng C, Zhang SW, Jewell D, Chen GZ Ultrathin porous NiMnO3 nanosheets on carbon cloth for use as supercapacitor electrode (2008) ,Prog Nat Sci 18:777

5. Zhu.y, Murali.S, . Stoller.D, Velamakanni.A , Piner and R. S. Ruoff, "Microwave Assisted Exfoliation and Reduction of Graphite Oxide for Ultracapacitors," Carbon, Vol. 48, No. 7,(2010), pp. 2118-2122. http://dx.doi.org/10.1016/j.polymdegradstab.2005.01.004 RS (2010) Carbon 48:2118

6. Kaempgen M, Chan CK, Ma J, Cui Y, Gruner G. Printable thin film supercapacitors using single-walled carbon nanotubes. Nano Lett.(2009) May;9(5):1872-6. doi: 10.1021/nl8038579. PMID: 19348455.

7. Hu C.C., Chang K.H., Lin M.C., Wu Y.T. Design and tailoring of the nanotubular arrayed architecture of hydrous RuO2 for next generation supercapacitors. Nano Lett. (2006);6:2690–2695.

8. Liu R, Lee SB. MnO2/poly(3,4-ethylenedioxythiophene) coaxial nanowires by one-step coelectrodeposition for electrochemical energy storage. J Am Chem Soc. 2008 Mar 12;130(10):2942-3. doi: 10.1021/ja7112382. Epub (2008) Feb 15. PMID: 18275200.

9. Ismail Salih Mohammed, Jasim Mohammed Mansoor, & Hind W Abdullah. . Micro and Nano of ZnO Particles Effect on Some Mechanical and Thermal Properties of Epoxy Resin Composites. Tikrit Journal of Pure Science,(2021),26(5), 48–55. https://doi.org/10.25130/tjps.v26i5.176

10. X. Zhu, K. Hou, C. Chen, W. Zhang, H. Sun, G. Zhang and Z. Gao, "Structural-controlled synthesis of polyaniline nanoarchitectures using hydrothermal method", High Performance Polymers,(2015), Vol. 27, No. 2, pp. 207-216, .

11. Amin Goljanian Tabrizi , Nasser Arsalani , Abdolkhaled Mohammadi ,Laleh Saleh Ghadimi , Iraj Ahadzadeh , Hassan Namazi A new route for the synthesis of polyanilinenanoarrays on grapheneoxide for high-performance supercapacitors, Electrochimica Acta 265 (2018) 379e390

12. Farah Naeem, Sumayyah Naeem , Zhe Zhao b, Gang-qiang Shu , Jing Zhang , Yongfeng Mei , Gaoshan Atomic layer deposition synthesized ZnO nanomembranes: A facile route towards stable supercapacitor electrode for high capacitance,Huang Journal of Power Sources 451 (2020) 227740. Available journal homepage: www.elsevier.com/locate/jpowsour

13. B. K. Sharma, A. K. Guptha, N. Kharea, S. K. Dhawan, H. C. Guptha. Synthesis and characterization of polyaniline-ZnO composite and its dialectical behavior, Synthetic Metals,(2009) 159: 391-395.J.-G. Wang, Y. 14.Yang, Z.-H. Huang, F. Kang, Interfacial synthesis of mesoporous MnO2/polyaniline hollow spheres and their application in electrochemical capacitors, J. Power Sources 204 (2012) ,236–243.

15.Chen.W.-C. Wen., T.C,. Gopalan. A, ,Negative capacitance for polyaniline (PANI): an analysis via electrochemical impedance spectroscopy, Synth. Met(2002),128 ,179–189.DOI:10.1016/S0379-6779(01)00667-1

16. Qiong Wu, Yuxi Xu, Zhiyi Yao, Anran Liu, and Gaoquan ShiSupercapacitors based on flexible graphene/ polyaniline (PANI) nanofiber composite films, ,(2010) ,ACS Nano 4 ,1963–1970.DOI: 10.1021/nn1000035 Wang.J.. Yang.G, Y, . Huang.Z.-H, Kang .F, Interfacial synthesis of mesoporous MnO2/polyaniline (PANI) hollow spheres and their application in electrochemical capacitors,(2012), J. Power Sources 204 , 236–243.DOI 10.1016/j.jpowsour.(2011).12.057