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تحضير الياف نانوية مميزة من البولي بيرول واستخدامها في خزن الطاقة بعد تطعيمها مع اكاسيد مختلفة

بحث مقدم من قبل

د. عمر عبد الكريم حميد الفهداوي

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Ministry of Planning
Central Organization for Standardization and quality Control
Metrology Department

Preparation of unique nanofibers of Polypyrol and their use in energy storage after doping them with different oxides

Dr. Omar Abdulkareem Hameed Alfahdawe

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المحتويات

Aim of the projects

The current work aims to prepare PPy nanofiber by chemical method then mix it with MW-CNT, TiO_2 and ZnO nanoparticles with different concentration to prepare nanocomposites and study its characterization. In addition, choose the optimum condition for prepared nanocomposites then using it in the electrochemical applications.

الخلاصة :

تم استخدام البلمرة الكهروكيميائية لإنتاج ألياف نانوية من بولي بيرول PPy . تم تطعيم الألياف النانوية لل PPy النقي بنسب مختلفة من مواد التطعيم المختلفة التي تم استخدامها (CNT و TiO_2 و ZnO) بنسب حجمية مختلفة (10٪ ، 20٪ ، 30٪ ، 40٪) حيث تم الحصول على الياف نانوية مغلفة بمواد نانوية. تم دراسة الاغشية والمركبات المحضرة باستخدام حيود الاشعة السينية ، والمجهر الالكتروني الماسح FE-SEM. تم استخدام FE-SEM لفحص مورفولوجيا البوليبيرول ، والتي كشفت عن شبكة ألياف نانوية للبوليبيرول. عند إضافة (CNT، TiO_2، ZnO) مع PPy ، لوحظ تغيير واضح في بنية المركبات النانوية. يتم توضيح الطابع غير المتبلور لـ PPy بواسطة قياسات XRD ، ولكن عندما يتم تطعيم ال PPy بـ CNT و TiO_2 و ZnO ، تصبح المركبات النانوية متبلورة. يُظهر من خلال قمم PPy / CNT مؤشراً على إنشاء هياكل كربون سداسية بسبب إضافة CNT داخل مصفوفة PPy ، وكذلك من خلال مركبات PPy / TiO_2 النانوية ينتج عن ذلك ظهور طورين اساسين نتيجة إضافة TiO_2 Anatase (Phase و Rutile Phase)، بينما في في حالة PPy / ZnO ، أثبتت الدراسة أن تكوين المركبات النانوية من PPy / ZnO نتيجة لتكوين ZnO سداسي المحضر بألياف PPy النانوية.

تم تحضير المكثفات الفائقة لكل من PPy وأقطاب الأداء الكهروكيميائية المكونة من PPy / CNT و PPy / TiO2 و PPy / ZnO من أجل الحصول على سعات عالية والاستقرار الدوري والتي تم تقييم ادائها باستخدام مقياس الجهد الدوري (CV). تشير القياسات الكهروكيميائية إلى أن المركبات النانوية تُظهر نشاطًا pseudocapacitive . في حين أن أكبر قدرة محددة للقطب الكهروكيميائي PPy النقي بمعدل مسح قدره 5 مللي فولت في الثانية كانت F / g (19.5). تم تحقيق السعة القصوى F / g (153) باستخدام 30٪ CNT للقطب المركب PPy / CNT بمعدل مسح قدره 5mV s^{-1}.

1-Introduction

Polypyrrole (PPy) is a highly essential conducting polymer with a heterocyclic structure that was first discovered in 1916 [1] . Polypyrrole (PPy) is an electrically conductive polymer that refers to an unique class of materials that combines metal and semiconductor properties [2]. Because of its high electrical conductivity, good environmental stability, and ease of synthesis and processing, (PPy) and its derivatives have attracted a lot of interest among the many conductive polymers. Furthermore, PPy is one of the few materials that can demonstrate the benefits of a gas sensor at room temperature, which provides an excellent chance for the development of practical applications [3]. When the monomer of pyrrole is oxidized, it forms a conjugated polymer chain with overlapping π-orbitals and a positive charge along the polymer backbone, similar to other organic molecules [4]. Polypyrrole has been the subject of numerous studies due to its wide surface area and fibrous nature, which makes it a high-capacity electrical material. PPy is a promising material because of its ease of preparation, intrinsic electrical conductivity, and high stability in both water and air systems [5]–[7]. Electrochemical capacitor has been a common energy storage system in recent years, consisting of electrode materials such as carbon materials, transition metal oxide and polymer conducting [13]–[8] . Due to its specific characteristics, such as high conductivity, fast charge-discharge mechanism, good thermal stability, low cost and high energy density, Polypyrrole (PPy) is one of the most promising p-type CPs for the Faradaic pseudocapacitor application. [14]–[18]. The PPy-based electrode's electrochemical activity also depends on the methods of electrode preparation and the effective surface area of the active electrode. A single-charge and multiple charge anion is usually doped with PPy

[19]. CPs-based research has focused extensively on PPy for the preparation of the pseudocapacitor electrode through chemical or electrochemical pathways in recent years. In the presence of excess surfactants, chemical oxidation-polymerization can synthesize a large variety of PPy nanostructure[20] .

In this research, the PPy/CNT, PPy/ZnO and PPy/TiO_2 nanocomposites composite was synthesized for supercapacitor use by chemical oxidation polymerization.

2- Experimental work

Materials used:

($FeCl_3$) Iron(III) chloride (Thomas Baker. India), Methyl Orange (MO) (sigma chemical Co) and Multi Walled Carbon nano tubes (Sky Spring Nanomaterials, Inc. USA) (Pyrole monomer (Sigma Aldrich. China) and Zinc Acetate, from HIMEDIA.

2-1 Synthesis of ppy nanofiber

During the procedure, 0.0818 g (2.5 mmol) of methyl orange (MO) was dissolved in (288 ml) cooled distilled water (5 °C) and combined with (1 ml, 14 mmol) pyrrole monomer, and the mixer was stirred (5min) until the mixture was fully melted and turned to red, at this point, the mixing phase is halted .In (33 ml) distilled water, (3.88 g) ($FeCl_3$) is dissolved and added drop by drop for two hours in a (MO-Pyrrole) cold solution. The reaction solution is placed in an ice bath and set on a stirrer and mixed for (24 hours). The precipitated PPy is then isolated by filtration and rinsing (water, acetonic alcohol) 2 times each stage, and then dried in an oven at 80 °C for 12 hours.

2-2 Preparation of PPy nanocomposite

0.02g of (CNT or ZnO) doped materials was dissolved in 20 ml (DMF), 0.04g of PPy was dispersed in 40 ml of distilled water, then different volume ratio of dopant where mixed with PPy (9:1, 8:2, 7:3 and 6:4) ml. The resulting solution was sonicated for two hours in order to get a homogeneous dispersion ready for use.

2-3 Preparation of capacitor device

(1×1) cm^2 Nickel Foam substance has been used for this reason. PPy and PPy nanocomposite were deposited on it by drop casting technique, and put in 1 ml of (H_2SO_4) as well as to test the cyclic voltammetry (CV) curves to determine its capacity.

3- Results and discussion

X-ray diffraction patterns of pure PPy and PPy doped with different ration value (10%–40%) of CNT, TiO_2 and ZnO were grown onto silicon substrates. Figure (1) (a–e) shows a contrast of the X-ray diffraction [XRD] spectra of pure PPy and different mixtures PPy/CNT (10%, 20%, 30% & 40% CNT) nanocomposites. The presence of a weak and broad diffraction peak for pure PPy at $2\Theta = 17 - 30$ means that the PPy is amorphous in nature. The pyrrole intermolecular spacing causes a broad diffraction peak at 25° for pure PPy. The XRD spectra for various mixtures of PPy/CNT show both the PPy wide peak (at 25°) and the strong CNTs peaks at (25.94° and 43º) for 20% CNT, (25.73° and 43º) for 30% & 40% CNT. The overlapping diffraction peaks of CNT with PPy demonstrate the formation of the PPy-CNT nanocomposite by the in situ polymerization synthesis process [21]. the average crystallite size increase with increasing CNT, were the minimum value of average crystallite size is 11.4 nm for PPy doped with 10% CNT and the highest value is 13 nm for PPy doped 40% CNT. Because the relationship between crystallite size and FWHM is inverse, increasing the CNT doping ratio causes a decrease in FWHM, according to Scherer's formula equation. Figure (2) illustrates an XRD pattern of the PPy/ ZnO (10%–40%) nanocomposites. It has clear and well-defined peaks with distinct orientation values. Furthermore, the expansive polypyrrole peak of strength is covered with molecules crystalline appearances of ZnO nano-particles seen that as the content of ZnO NPs in the polymer based composite expands, the polypyrrole diffraction peak becomes sharper and decreasing exceptional. From the XRD patterns high diffraction peaks can be seen at 31.8 °, 34.5°, 36.6 ° , 47.7 °, 56.8 °, 63°, 68 ° and 69.2 ° which correspond to (100) , (002), (101), (102), (110), (103), (112) and(201) planes respectively . This depicts the ZnO crystalline structure that has been preserved in nano-composite despite being dispersed in the PPy lattice.

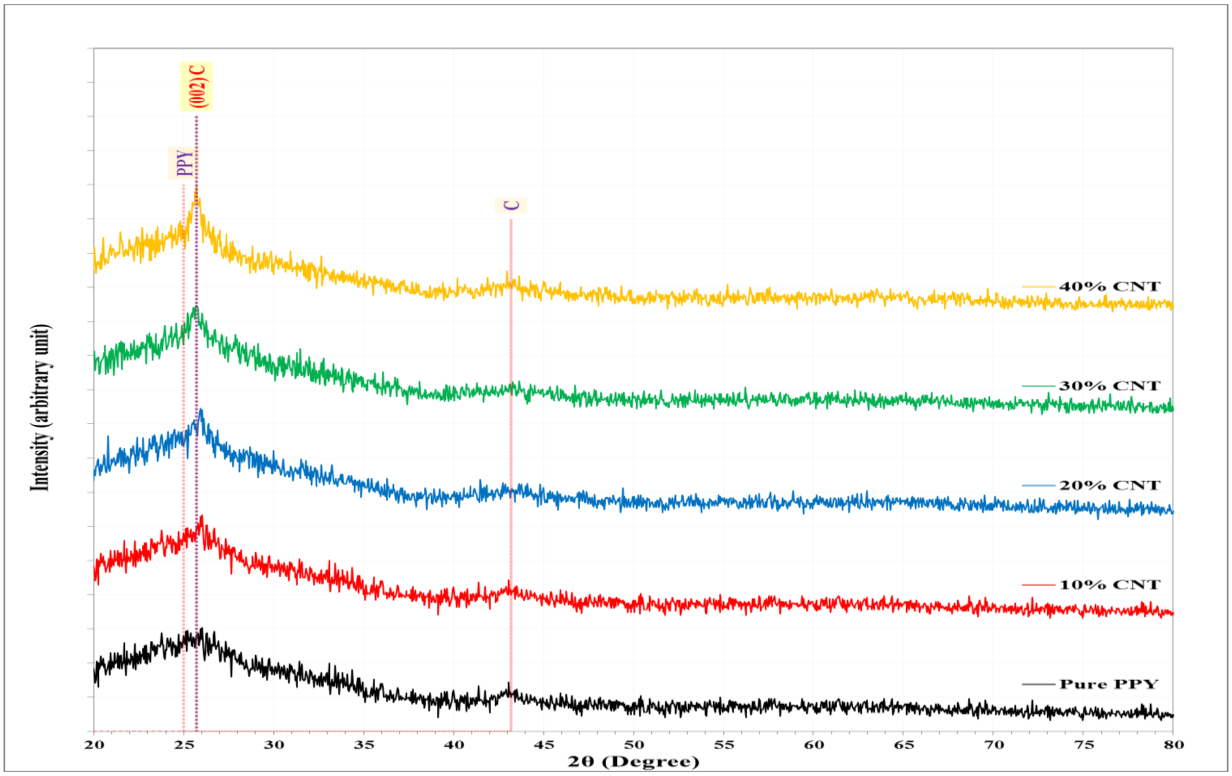

Figure 1: The pattern of the XRD of PPy/CNT (10–40%) nano-composites

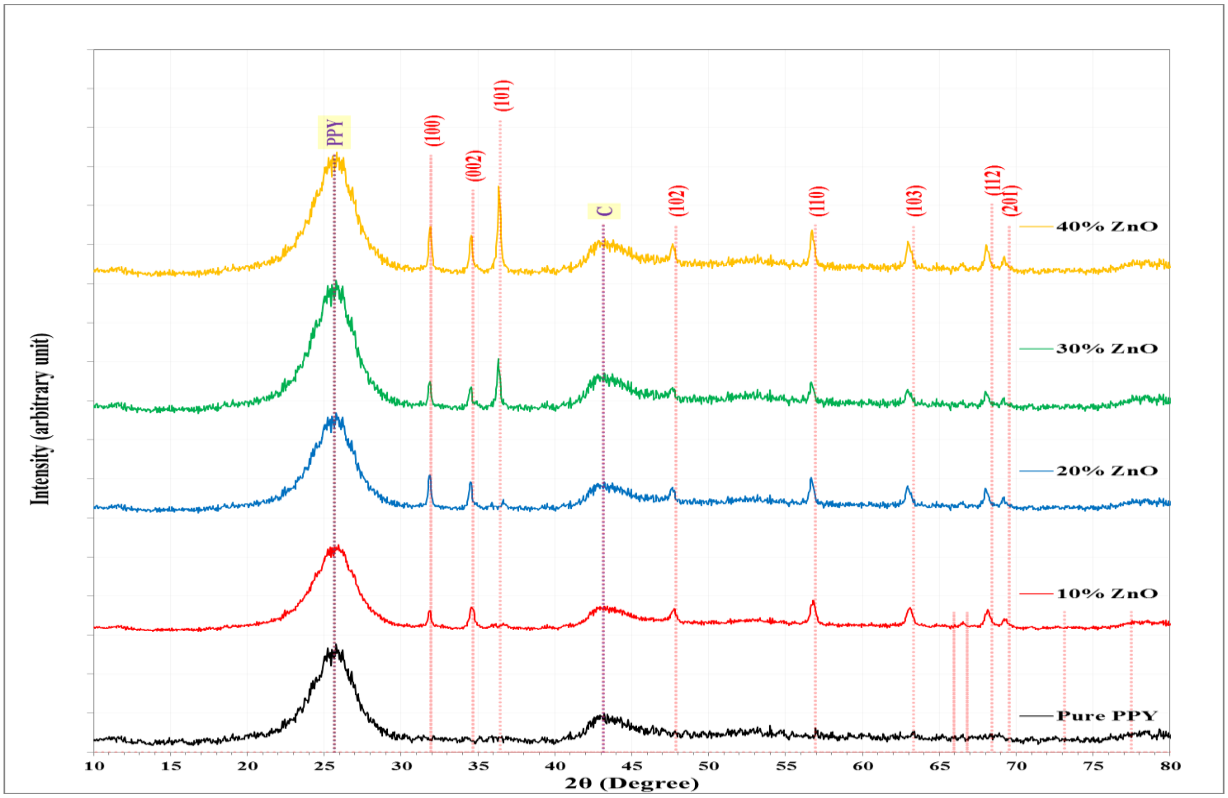

Figure 2: The pattern of the XRD of PPy/ ZnO (10–40%) nano-composites

The nanostructures of the materials prepared in this study are shown in FE-SEM pictures. The pure PPy, CNT & ZnO layer structure was shown in (Figure 3), where it clearly observe that the PPy layer is in the form of nanofibers structure, and CNT in the form of nano tubes while the ZnO layer in the form of nano flowers as can be seen in (Figure 3).

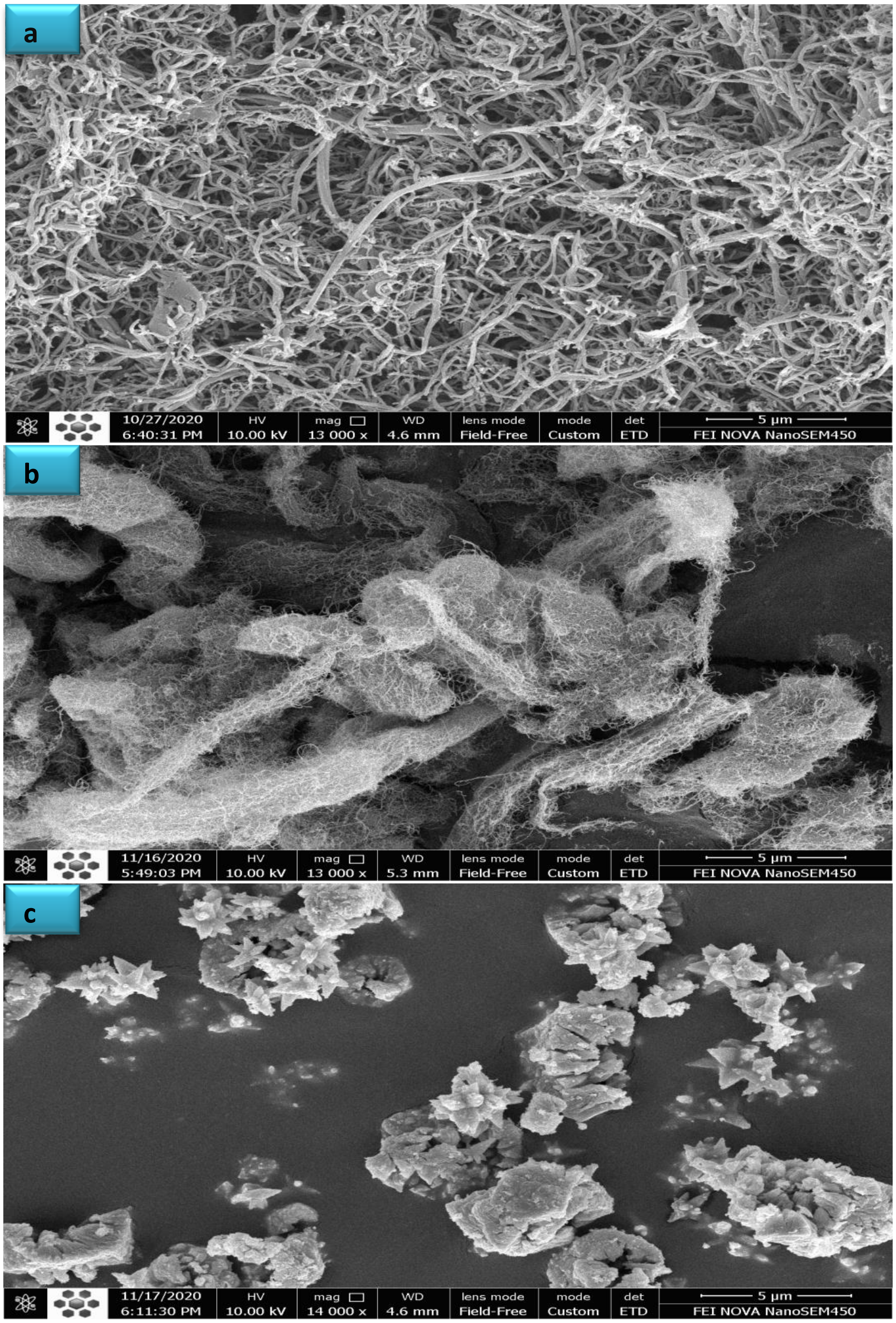

Figure 3: FE-SEM images of pure a- PPy , b- CNT , c- ZnO

The doping process of pure PPy with different volume ratio of (CNT and ZnO) significantly affects the surface properties and morphology of the PPy samples. It was found that CNT successfully grew on the surface of the PPy layer when PPy/CNT nanocomposites were prepared at varied rates of CNT. Figures (4) show the PPy/CNT morphology of composites. Due to the addition of CNT, tube-shaped particles are evenly distributed on the surface of the polymer, as seen in FE-SEM images. As a result, these images shows a gradual rise in CNT inside polymer chains.

Whereas, when we prepared the nanocomposite of PPy /ZnO at a different volume ratio of ZnO nanoparticles (10%, 20%, 30% and 40%), as shown in Figures (5). The FE-SEM images show that flower-shaped of ZnO nanoparticles are dispersed on the surface of PPy nanofibers.

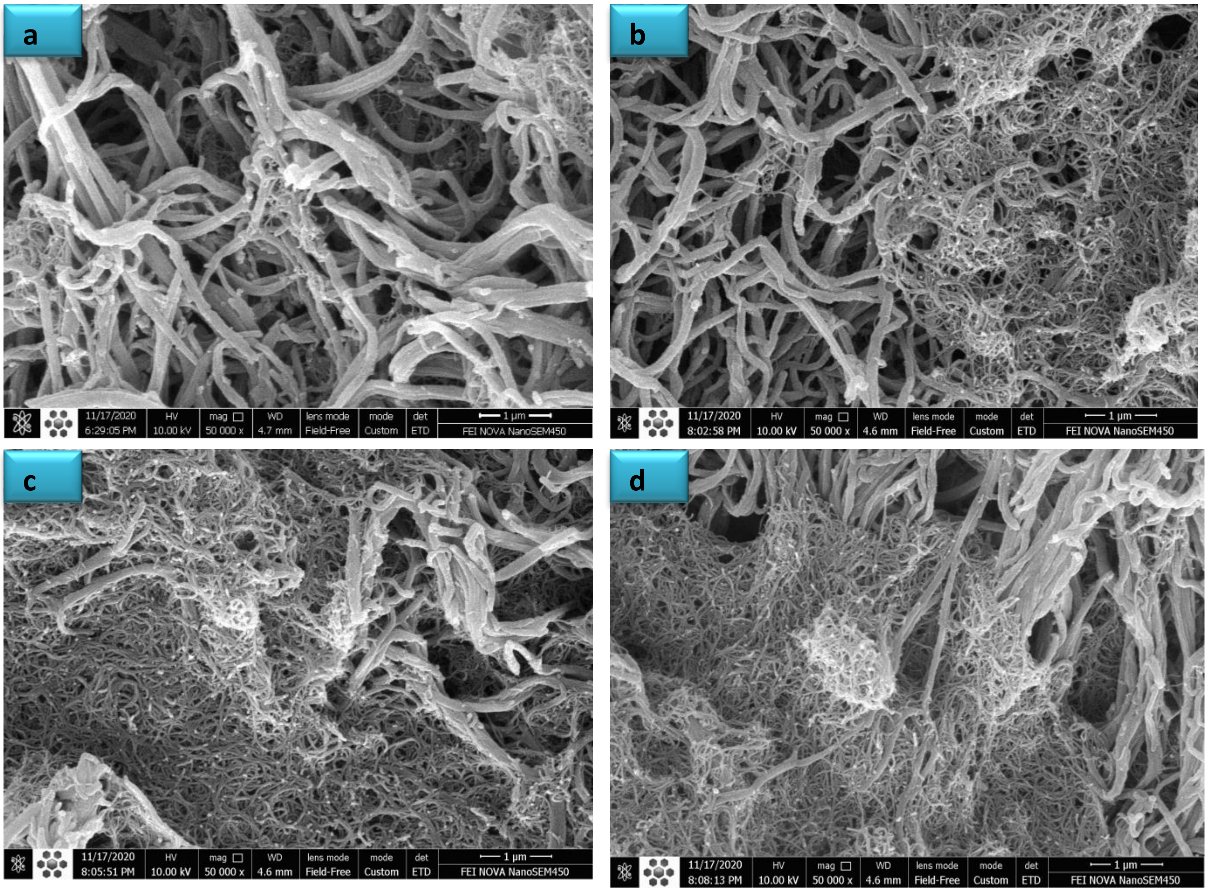

Figure 4: (a , b, c, d) FE-SEM pictures of PPy/CNT composites with various CNT doping rates (a- 10% , b-20% , c-30% and d-40%)

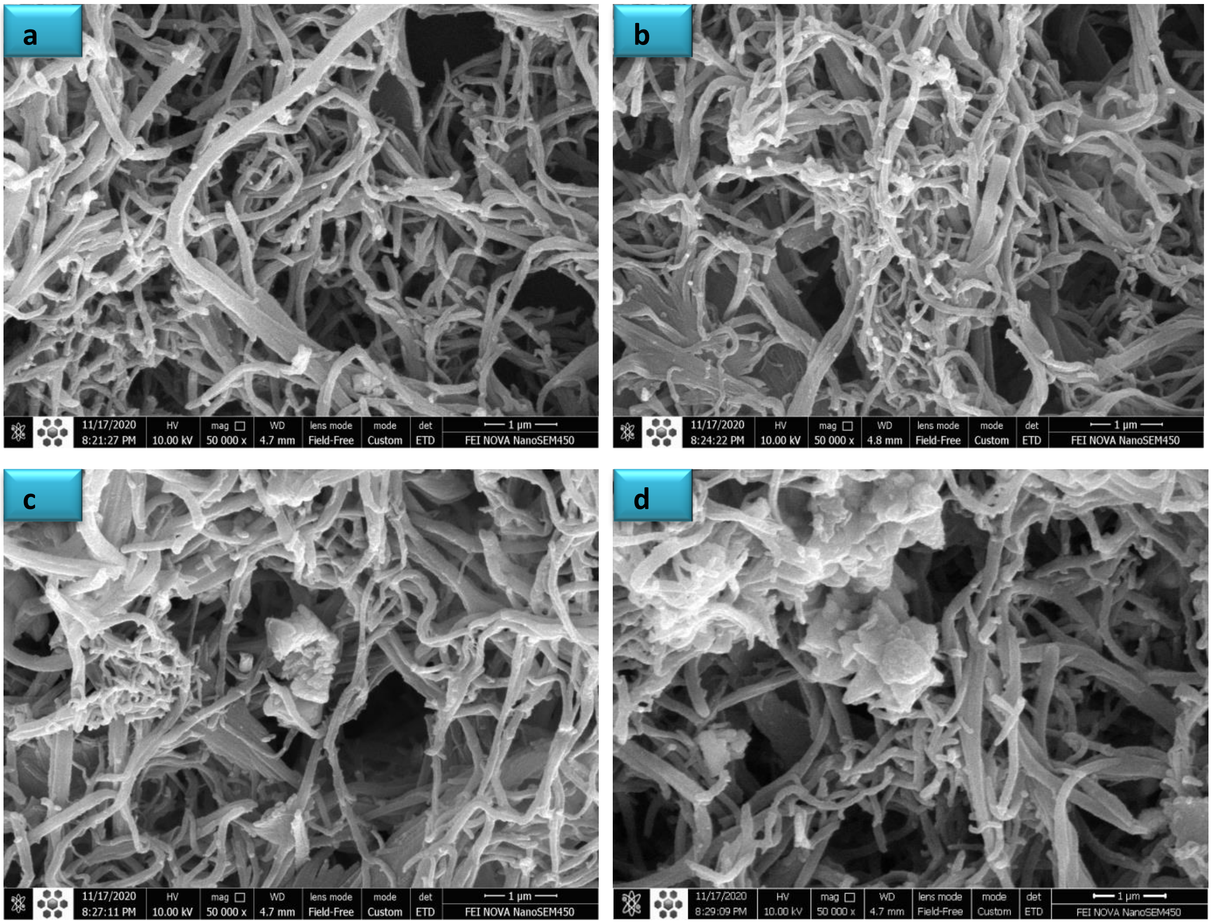

Figure 5: (a , b, c, d) FE-SEM pictures of PPy/ZnO composites with various ZnO doping rates (a- 10% , b-20% , c-30% and d-40%)

Cyclic voltammetry (CV) curves were used to initially characterize of the electrochemical performance. Cyclic voltammetry (CV) curves of the PPy and PPy nanocomposites supercapacitor in 1.0 ml H_2SO_4 acid at 5 mV/s scan rates, as shown in Figure (6). The impact of doping PPy with various fractions of CNT on cyclic voltammetry (CV) results was investigated in order to get the best electrochemical efficiency of the PPy nanofibre electrode. Due to, Carbon nanotubes are effective electron conductors, so they can supply the electron transfer path for the composite and contribute to fast charge/discharge characteristics in the composite film. Due to the reversible faradic redox reaction, the PPy/CNT CV curves displayed a pair of well-defined redox peaks at all doping levels. The pseudocapacitance activity was found in the (CV) curves of the PPy/CNT electrode due to the effects of oxidation and reduction processes. the effect of doping PPy with different proportions of CNT on the cyclic voltammetry (CV) results were studied in order to obtain the optimum electrochemical efficiency of PPy nanofibre electrode. Thus the PPy / CNT composite film combines the benefits of carbon nanotubes and polypyrol.

The average specific capacitance was determined according to equations (1) from the CV curves.

$$\boldsymbol{C} = \frac{\int \boldsymbol{I dV}}{\boldsymbol{2m\Delta V\, v}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where : v is scan rate (mv/s), ΔV is voltage window , m is the mass of the electrode $\approx$ 0.5 mg/ cm^2 , I is the applied current. In order to achieve the charge (Q), the capacitance was measured by integrating the area of the CV curve and then dividing the charge by the mass (m) of the electrode and the potential window 'V' . PPy/CNT electrode outcomes have variable capacitances of 9.8 F g^{-1}, 129.6 F g^{-1}, 153 F g^{-1} and 78.2 F g^{-1} respectively at doping concentrations of (10 % , 20 %, 30 % and 40% CNT).The basic capacitance of pristine PPy film, on the other hand, is only 19.5 F g^{-1} at 5 mV s^{-1}. This shows the capability of rapid charge/discharge and the composite film's good rate efficiency as a supercapacitor electrode.

Whereas the PPy conductive polymer is doping with various proportions (10%, 20%, 30% and 40%)vol ratio, of ZnO nanoparticles as shown in Figure (7), we notice that the super-activity capacitor's has decreased and that the capacitance is lower than that seen in the pure PPy. At doping concentrations of 10%, 20%, 30% and 40% ZnO, the PPy/ZnO electrode findings have variable capacitance of 2.01 F g^{-1}, 7.53 F g^{-1}, 11.58 F g^{-1} and 11.27 F g^{-1} ,respectively.

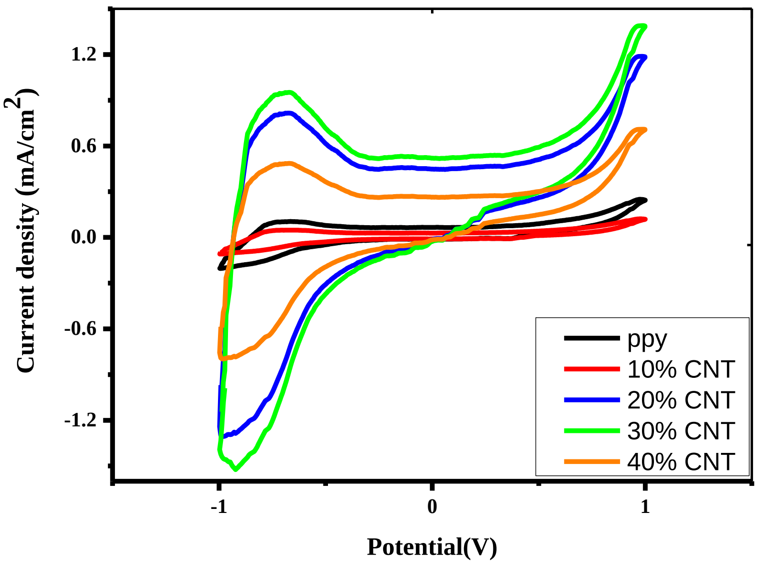

Figure 6: CV curves of the PPy/CNT composite film under different doping rate (10%-40%), at the scanning rate 5 mV s^{-1}

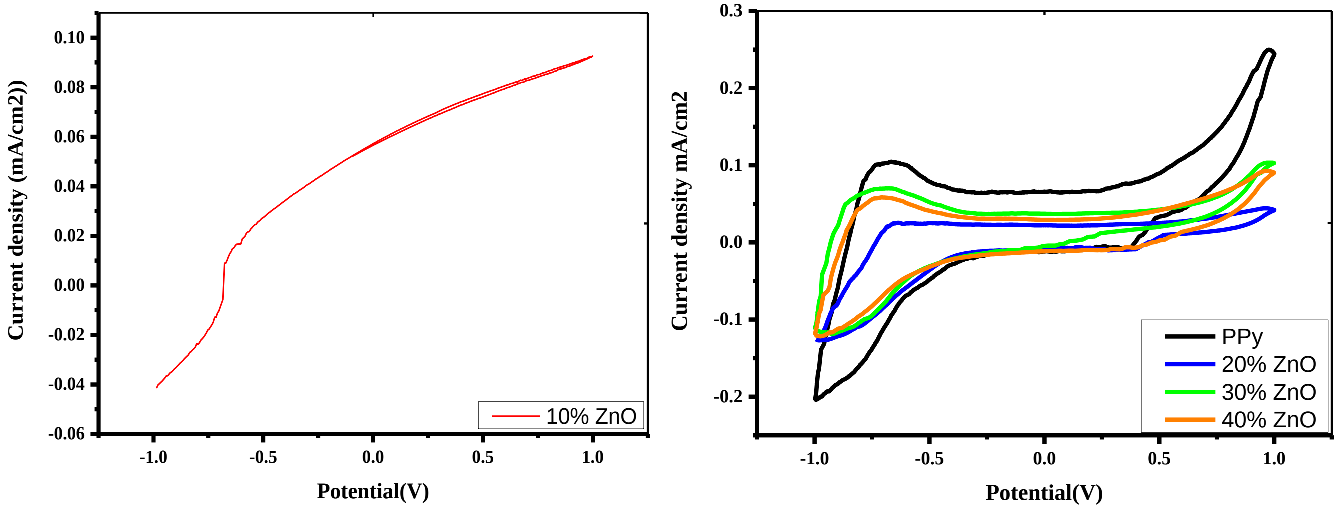

Figure 7: CV curves of the PPy/ZnO composite film under different doping rate (10%, 20%, 30% and 40%), at the scanning rate 5 mV s^{-1}

4- Conclusions

In summary, PPy nanofiber and nanocomposites of (PPy / CNT & PPy / ZnO) have been prepared by simple method. The composite film of PPy and CNT is a good electrode material for electrochemical supercapacitor. The maximum capacitance values (152 Fg-1) that determined by CV curves were obtained from PPy nanofibers doped with 30% CNT, but for pure PPy the capacitance is very small compared to PPy doping with CNT . On the other hand, when PPy is doped with ZnO nanoparticles, the capacitance decreases less than that of pure PPy. Therefore, doping plays a very important role in improving the capacitance of supercapacitor.

5- Suggestions for future work

1- Use some metal oxide such as (MgO_2 and Fe_3O_4) for using as dopant materials with pure PPy for Electrochemical Capacitor.
2- Using PPy and PPy nanocomposites for manufacture of chemical sensor against some toxic materials (H_2S , NO_2).
3- Such these composites are deposited on FTO and ITO to evaluate the solar cell system.

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