Bull. Chem. Soc. Ethiop. **2024**, 38(4), 1177-1188.
DOI: https://dx.doi.org/10.4314/bcse.v38i4.28

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

POLYANILINE/TiO_2 NANOCOMPOSITE FOR HIGH PERFORMANCE SUPERCAPACITOR

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(Received January 30, 2024; Revised March 27, 2024; Accepted March 28, 2024)

ABSTRACT. A binary polyaniline/TiO_2 and varied weight ratio TiO_2/PANI nanocomposite was successfully fabricated as an electrode for energy storage application. The TiO_2 nanoparticles were synthesized via manual irradiation system with wavelength 256 nm and power 125 W. Polyaniline/TiO_2 was then prepared by in situ polymerizing TiO_2 onto aniline monomer. Polyaniline nanofibers are loaded with TiO_2 to product core-shell system. The polyaniline/TiO_2 nanocomposite were characterized using XRD, XPS, TEM, TGA, CP and LCR measurements. The structure properties were examined by XRD and XPS, which confirmed preparing polyaniline/TiO_2 binary nanocomposite. The thermal stability was investigated using TGA and obtained high stability of polyaniline/TiO_2 compared with polyaniline, while the electrochemical properties were examined by LCR measurements. The LCR measurements were appeared dielectric constant and dielectric loss for incorporating TiO_2 through PANI. Varied weights ratio TiO_2 was worked in increasing the stored energy ability of polyaniline. Notably, the electrochemical investigate results appear that the PANI/TiO_2 has a high specific capacitance (250 F/g) compared with pure PANI (200 F/g).

KEY WORDS: Supercapacitor, UV irradiation, XPS, LCR, nanofibers

INTRODUCTION

Binary nanocomposites have been widely studied because of their potential uses. They include the excellent features, leading the materials with enhanced features [1]. Furthermore, conductive polymer such as polyaniline and their composite have important notice because of their electrochemical properties [2]. Supercapacitors, a mediator energy source between batteries and dielectric capacitors, have protruded as a substantial technology of energy storage because of the fast charge/discharge time, high density power, green energy and good cycling life. It have found several different applications as in hybrid electric vehicles, military, public transport buses, memory backup, aerial lift, airport control, etc. Depending on the mechanism of storing energy, supercapacitors are divide two mainly categories: pseudocapacitor and electric double layer capacitor. In the first type, the active materials are exhibit redox reaction while, in other type, the charges are accumulate at the separation region between electrodes and electrolyte solution [3]. Because of easily of preparing, low cost and excellent stability, the PANI was attracted large attention for researching [4-7]. Polyaniline is classified as the second type, pseudocapacitor. In

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spite of, it having high specific capacitance, but their low density of power and poor stability become weakness. For developing the electrodes of supercapacitors, PANI incorporating metal oxides (MOs) have been investigated because of creating different physical and chemical properties by doping oxide inside the polymer matrix [8, 9]. There are two methods are used to prepare polyaniline-oxide binary system. The first is incorporating oxide NPs inside the matrix of polymer, and the second is dispersing of MOs during process of polymerization. On the other hand, in situ polymerization is excellent method to incorporate the MO inside the matrix of polymer [10-15]. TiO_2 is concerning oxide between others semiconductors oxides because the physical and chemical properties. In addition to, it applicants in different area like batteries, capacitor, solar cell and photocatalyst [16-19]. Ozan *et al.* got 692.87 F/g for PANI/PNR/TiO_2 nanocomposite that synthesized via chemical oxidation method [20]. Bian *et al.* obtained 330 F/g for PANI-TiO_2 nanocomposite prepared via in situ polymerization method [21].

In this study, we reported dispersion of TiO_2 into polymer matrix to improvement of PANI properties. Thus different properties of TiO_2 combination with PANI can show new properties that could not be observed from the individual compound. On the other hand, we have improved chemical method for the synthesis of TiO_2 and polymerized it with aniline. The synthesis photolysis method we employed is simple in comparison with other routes. PANI-TiO_2 nanocomposite was synthesized via in situ polymerization of aniline monomer in the existence of TiO_2 NPs. The structural and electrochemical properties was studied using XRD, XPS, TEM, TGA, CP and LCR measurements.

EXPERIMENTAL

Chemicals

Chemical materials were supplied from Sinopharm and Sigma Aldrich companies and utilized without and future purification.

Synthesis of TiO_2

The synthesis of TiO_2 oxide was carried out by photolysis method [22-24] and use irradiation system with 15 watts (Figure 1), wherein 1 mole of $Ti[OCH(CH_3)_2]_2$ were used as source material. Then it transferred to reactor of irradiation system and irradiated under icing condition for 1 h and white precipitate formed, which was collected and washed with ethanol and deionized water for several times. Finally, it dried at 80 ºC and annealed at 400 ºC for 5 h in ambient.

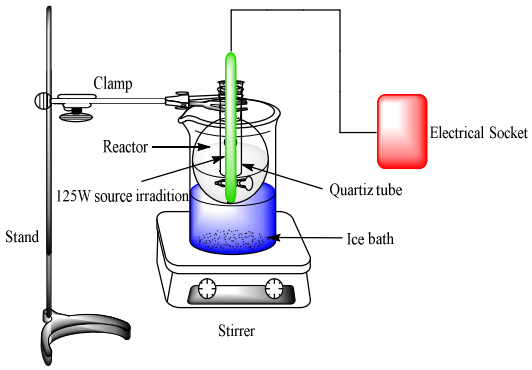


Figure 1. Manual irradiation system.

Preparation of PANI-TiO_2 nanocomposite

The PANI-TiO_2 binary nanocomposite was prepared by using oxidation polymerization method of aniline monomer in presence of TiO_2, HCl, APS as initiator, which the mole ratio TiO_2 to aniline monomer is (0.05:1; 0.1:1; 0.15:1, 0.2:1, 0.25:1) molar ratio. Firstly, 20 mL of (0.2 M) of APS was dropped into 0.1 M aniline hydrochloric acid solution containing TiO_2 nanoparticles in ice bath. After that, the mixture was transferred to fridge for 24 h. Then, it filtered and washed several times by distilled water until got clear solution. Finally, the product was dried at 80 ºC for 3 h. The polymerization process is shown in Figure 2.

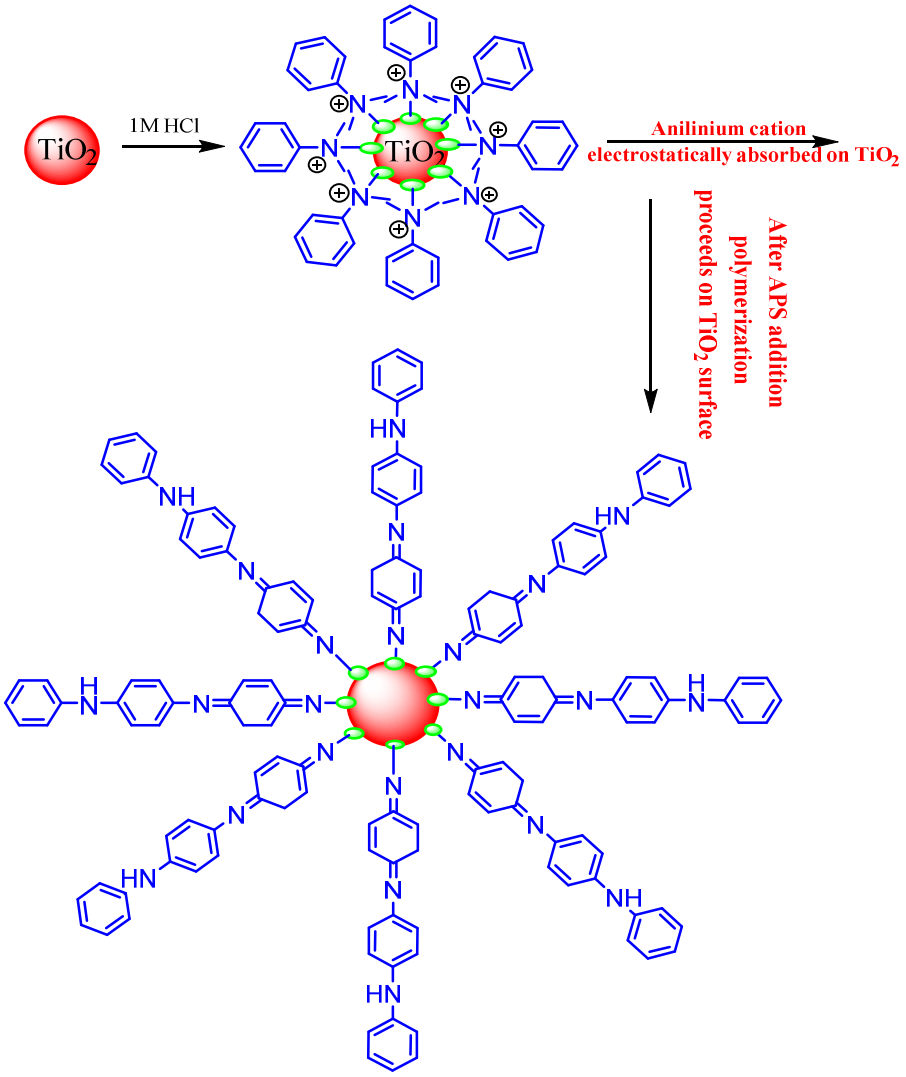


Figure 2. Polymerization process of TiO_2 incorporated PANI.

Characterization

X-Ray diffraction (XRD) and X-ray photoelectron microscopy (XPS) were carried out on Shimadzu X-ray diffraction with 30 kV acceleration, CuKα radiation λ = 1.5406 Å and Kratos Axis 165 with Al mono K_{α}X-ray. The morphology of prepared compounds were investigated by transmission electron microscopy (TEM) JEOL JEM 2100. The thermal stability was examined using thermogravimetric analyser of Perkin Elmer while, the electrochemical performance were measured in LCR-Q meter (Wayne, Kerr, 4300).

RESULTS AND DISCUSSION

The XRD of TiO_2, PANI and PANI/TiO_2 binary nanocomposite are illustrated in Figure 3a-c.

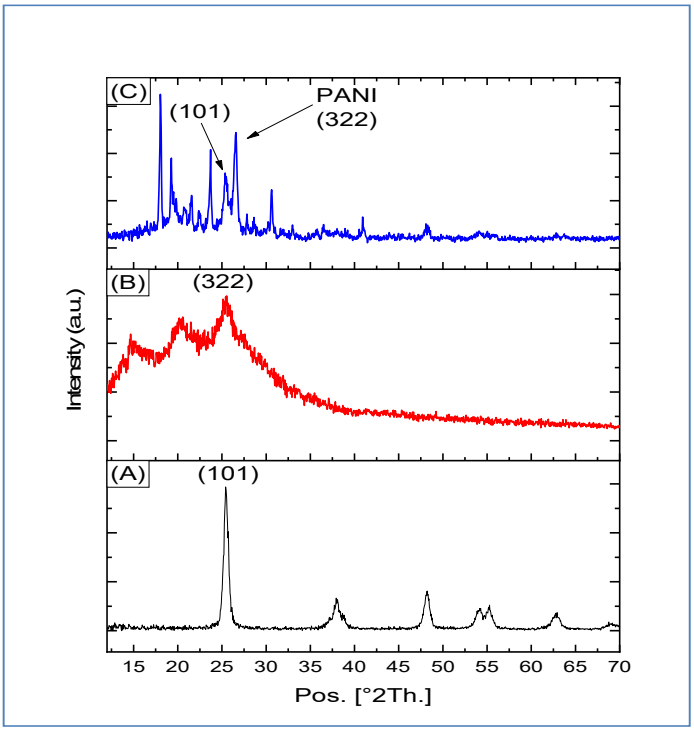


Figure 3. XRD of (A) TiO_2, (B) PANI and (C) PANI/TiO_2.

Figure 3a shows the XRD of TiO_2 with maximum peak centered at 25.46° which corresponding to (110) Bragg diffraction of tetragonal structure of anatase phase and the results are good agreement with JCPDS (no. 21-1272). In Figure 3b, three diffraction peaks centered at 14.67°, 20.51° and 25.47° corresponding to (121), (113) and (322), which assign to scattering polymer chains that the results are good agreement with JCPDS (no. 72-0634). The diffraction peaks are indicated that the prepared PANI in highly crystallite [37, 38]. The XRD pattern of PANI/TiO_2 is shown in Figure 3c. The results showed increasing in the sharping diffraction peaks of PANI after adding TiO_2, which indicating increasing in the crystallinity of PANI and the TiO_2

nanoparticles does not affect or disserve of growing the chain of PANI. On the other side, low shifting to high position in the diffraction peak (322) is noted, which indicating induce strain in the PANI matrix. The crystallite size of synthesized nanoparticles are estimated by Scherre equation [25] and it appeared that the crystallite size of nanocomposite are increased, which indicate boosting the crystalline of compound.

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

For diffraction peak (322), the results demonstrated increasing the intensity and decreasing in FWHM of it with TiO_2 incorporating, which indicate increasing in the crystalline of PANI [26].

To confirm incorporating of TiO_2 nanoparticles in the structure of PANI, TEM was carried out. The results appeared uniformly distribution of TiO_2 particles inside the fibers of PANI, which indicate successfully incorporating as shown in Figure 4, and the particle size are in agreement with XRD results.

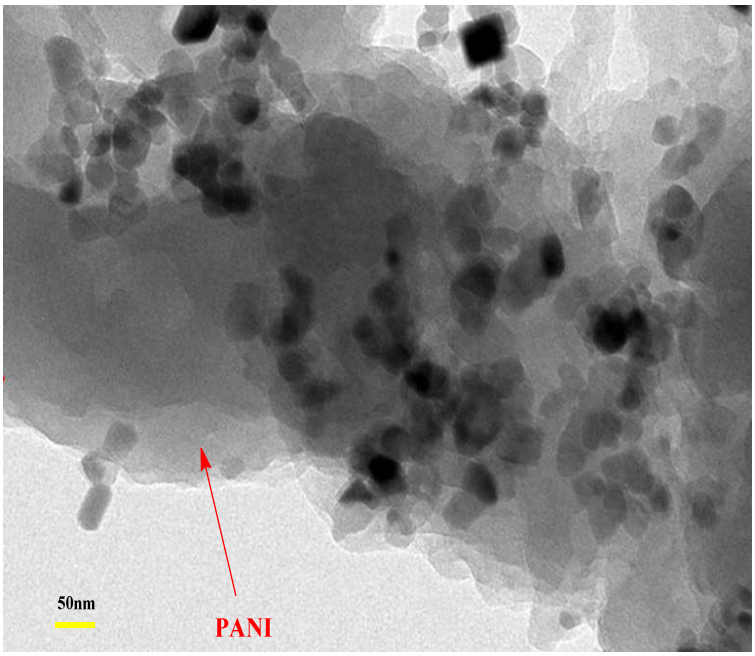


Figure 4. TEM image of PANI/TiO_2 binary nanocomposite.

The thermal stability of PANI and PANI/TiO_2 binary nanocompsoite are displayed at Figure 5. The results obtained three sequential weigh losing steps, which are loss of adsorbed water at 180 °C, unreacted monomers at 200 °C to 320 °C and backbone of polymer at 430 °C, respectively. On the other side, the results appeared that the thermal decomposition of PANI/TiO_2 is less than PANI, which indicate that the TiO_2 nanoparticles are adding thermal resistance to PANI chains and the improvement related to the interfacial reaction between PANI and TiO_2 nanoparticles [27].

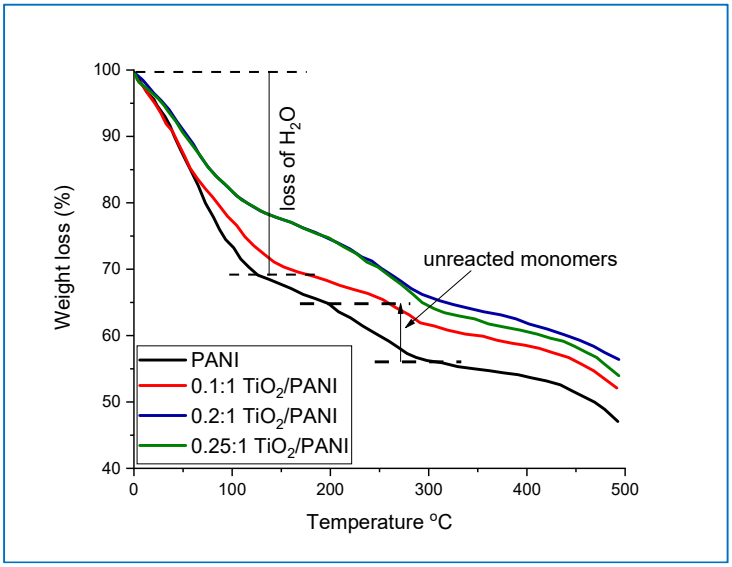
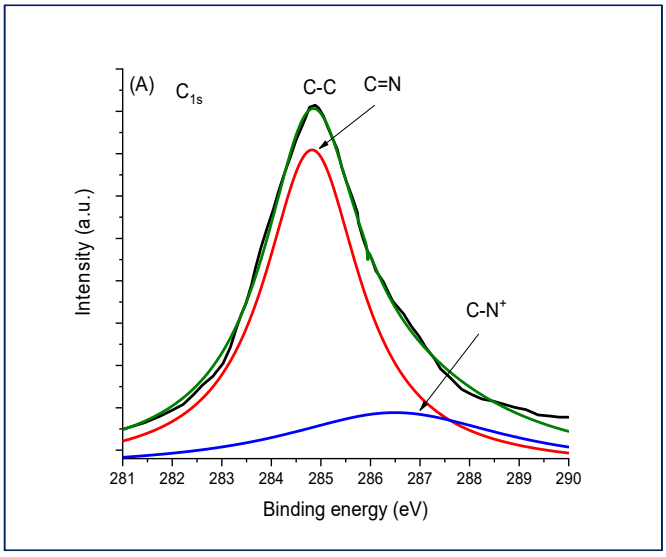
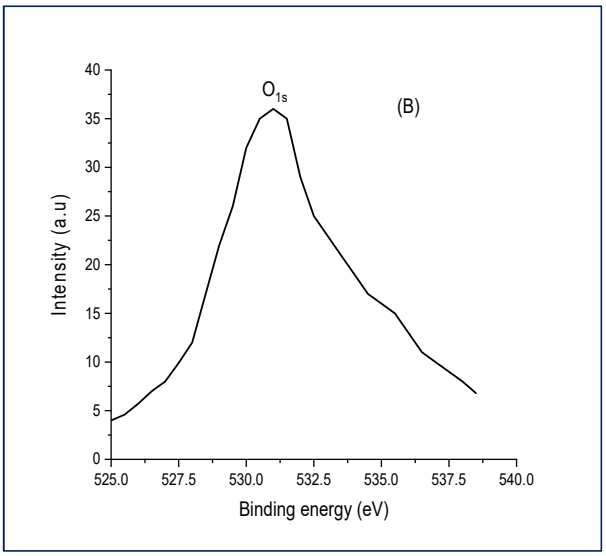
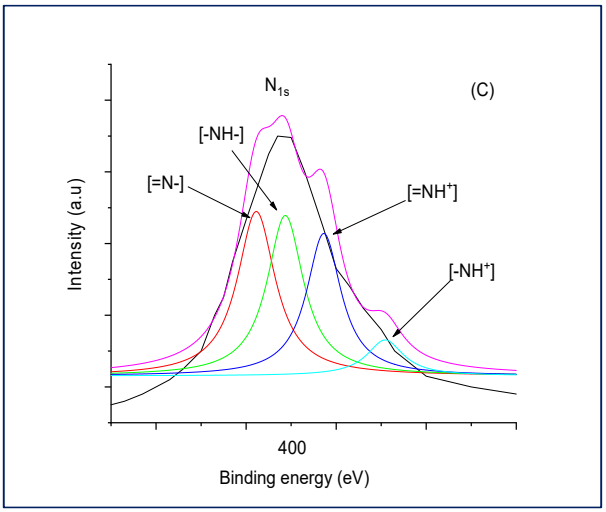


Figure 5. TGA of PANI and TiO_2 incoparated PANI.

The XPS spectrum of PANI/TiO_2 binary nanocomposite and the information of C_{1s}, O_{1s}, N_{1s} and Ti_{2p} level energies are shown in Figure 6a-d. Firstly, Three binding energies centred at 284.6, 285.5 and 287.1 eV corresponding to sp^2 C-C, C=N and C-N^+ bonds as appeared in Figure 6a. The binding energy located at 531.2 eV (Figure 6b) assign to O^{-2} ions of O_{1s}. In Figure 6c, four binding energies find at 399.5, 400.3, 400.5 and 402.3 eV back to [=N-], [-NH-], [=NH^+] and [-NH^+] quinoid, benzoid imine and cationic nitrogen [28].




O1s
(B)
Intensity (a.u)
Binding energy (eV)
0
5
10
15
20
25
30
35
40
525.0
527.5
530.0
532.5
535.0
537.5
540.0


N1s
(C)
[-NH-]
[=N-]
[=NH+]
[-NH+]
Intensity (a.u)
400
Binding energy (eV)

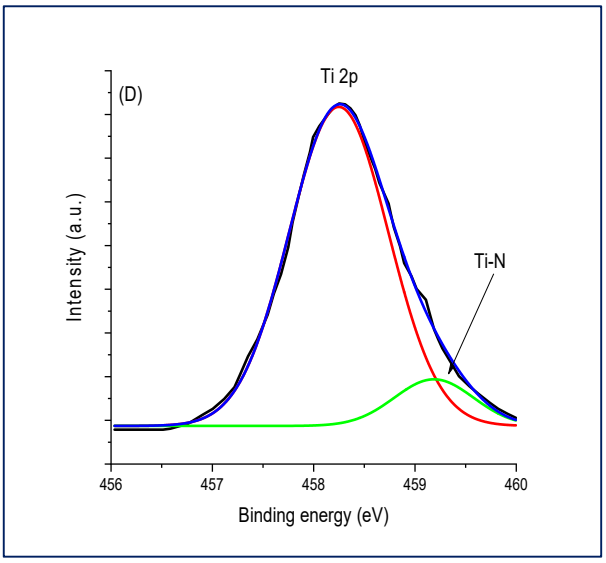


Figure 6. XPS spectrum of PANI/TiO_2 binary nanocomposite.

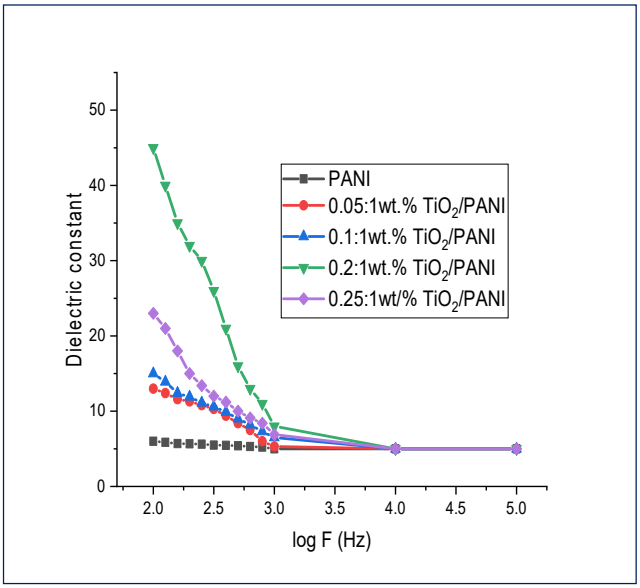


Figure 7. Dielectric constant of PANI and wt.% TiO_2/PANI.

The electrochemical performance of prepared materials were characterized using LCR meter and cyclic voltammetry. The real dielectric and dielectric loss constants are shown in Figure 7 and 8. In Figure 7, the real dielectric is decreased with increasing frequency because of the

segments doesn't have enough time to orient with electric field on themselves. With adding different ratio of TiO_2, the response to electric field was improved and the better results appear with 20 wt.% TiO_2 incorporating because of increasing the interaction between nanoparticles and polyaniline polar part, as well as, increasing the interfacial polarization [29]. On the other hand, the results showed that with increasing the incorporated ratio to 25% wt. TiO_2, the real dielectric constant is decreased because of the inhomogeneity which cause decreasing the interaction between nanoparticles inside the polyaniline chains.

To investigate the losing of electric, the dissipation factor (tanδ) of prepared compounds was studied and the results are shown in Figure 8. The results obtained that the dissipation factor is decreased steeply with increasing frequency. Commonly, the values of factor depended on the improving of space charge polarization and the carrier movements are high at low frequency. On the other hands, the results appeared that the loss factor of %wt. TiO_2 incorporated is more than pure polyaniline and the maximum losing shown in incorporated 20 wt.% because the strong space charge polarization at this ratio and this cause relaxation process [29].

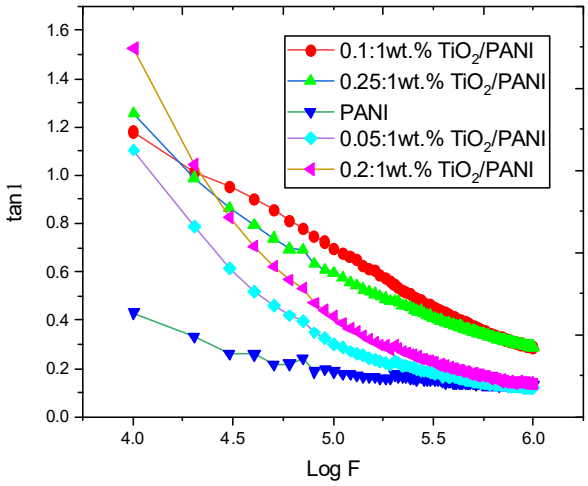


Figure 8. Dielectric loss tangent of PANI and wt.% of TiO_2/PANI.

To calculate the specific capacitance at different applied voltages, 1 M H_2SO_4 electrolyte solution and -1.0-0.1 V scan rate, the CV of prepared compounds were evaluated. The specific capacitance at different applied voltage is estimated by following equation [30]:

$$C_{sp} = \frac{A}{2\gamma m(\Delta V)} \tag{2}$$

where ΔV: potential window, m: mass of active electrode and γ: applied scan rate. The results (Figure 9) depict rectangular box and low contact resistance for pure and 0.2 wt.% TiO_2 incorporated TiO_2 which indicate good supercapacitor behavior and pseudocapacitive nature of nanocomposite. On the other hand, the results appear enhancement after incorporating of TiO_2 in PANI framework, which confirms increasing of specific capacitance [31].

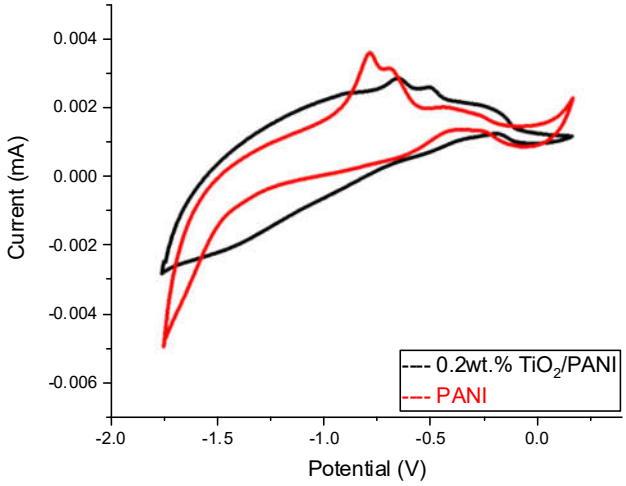


Figure 9. CV of pure and 0.2 wt.% TiO_2/PANI at 10 scan rate.

The specific capacitance of pure and 0.2 wt.% TiO_2 incorporated PANI were evaluated at different scan rate (5-100) mV/s and the results are presented at Figure 10. At high scan rate, the results appear reducing in capacitance because of the incompleteness of redox process and this causes outstrip of transition inside the electrodes [32].

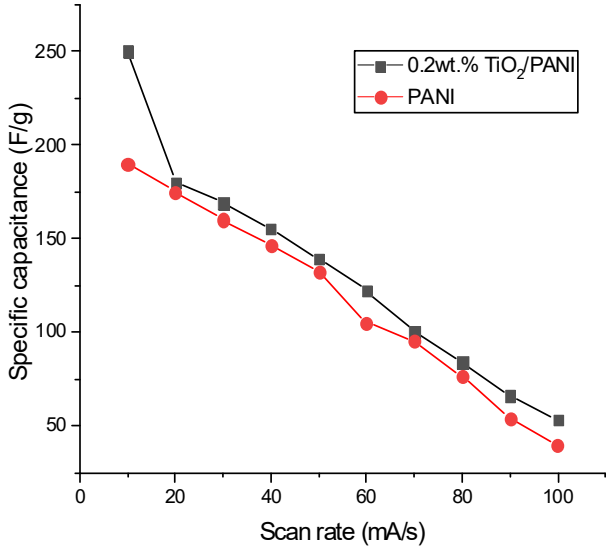


Figure 10. Specific capacitance at different scan rates.

CONCLUSION

The binary PANI/TiO_2 nanocomposite successfully prepared by in situ polymerization method and supercapacitor performance was investigated. The XRD, XPS and TEM results were shown success incorporating TiO_2 in the matrix of PANI. The TGA measurement was appeared increasing in thermal resistance of PANI after incorporating with varied ratio of TiO_2. The dielectric measurements were appeared excellent storing behavior for PANI/TiO_2 compared with PANI.

ACKNOWLEDGMENT

Special thanks to University of Diyala to support us the chemical materials for preparing the nanocomposite

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