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Enhancement of TiO_2 nanostructure for super capacitors Application

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A B S T R A C T

In this paper, TiO_2 nanoparticles were prepared, in addition to chemically synthesized PAni compounds by oxidation method, added 15% of PAni to 10%of TiO_2 to investigate super capacitance properties of TiO_2 after PAni addition. The structural properties of XRD and FE-SEM for the two materials were studied separately and then for composite. In order to understand the optical properties, UV-Vis spectrometer was used, where the energy gap of titanium oxide was calculated and was 4eV, as well as the polymer material was 4.6eV. The capacity characteristics were also studied and good results were shown for the super capacitors.

Keywords: *Enhancement, oxidation, TiO_2 Nanostructure*

1. Introduction

Among many metal oxides, titanium oxide has distinct properties such as a wide energy gap, which made it attractive to researchers as it has many applications in various fields in areas of design photodectors [1], gas and biosensors [2], supercapacitors [3], hydrogen production [4] photocatalysts [5] energy storage devices [6], and electro chromic switching [7]. Particularly, one-dimensionalTiO_2 nanotube displays invented by anodization of titanium (Ti) have been expansively examined as a auspicious electrode material for super capacitors because of their high surface area, respectable chemical steadiness and wide potential space. In addition, this precipitously focused on TiO_2 nanostructure displays deliver a straight path way for electron transportation laterally the long axis of nanotubes to the Ti foil substrate and can be active right as a supercapacitor electrode. However, the original (without intentional doping or modification) TiO_2 nanostructure displays usually suffer from poor capacitive performance, since TiO_2 is a wide bandgap semiconductor 4.6eVfor anatase and 4eV for rutile) [8] with a restricted conductivity. Therefore, large enhancement in conductivity of TiO_2 is desirable for super capacitor electrode materials. It is recognized that intensification

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in electrical conductivity of TiO_2 can be achieved through presenting metal [9] or nonmetal impurities [10] into the oxide, which can produce giver or acceptor conditions in the bandgap and thereby increase the absorption of charge movers. Consequently, numerous exploration efforts relating to the fixing or adjustment of TiO_2 material have been made. For illustration, Nakamura et al. [11] set plasma-treated TiO_2 precipitates by radio-incidence discharge under pressure about 2 Tor of H_2 gas at 673 K. The photocatalytic movement for NO elimination seemed in the observable light area up to 600 nm after giving the TiO_2 powders in the hydrogen plasma. They recognized the better photocatalytic movement of the plasma-treated TiO_2 powders to the anew formed oxygen vacancy situations among the valence and the transmission bands in the TiO_2 band structure. Schmuki et al. [12] indicated that TiO2 nanotube displays could be rehabilitated to a highly conductive phase by a high-temperature handling in acetylene. The as-prepared C-doped TiO_2 nanotube displays showed semi metallic conductivity, which could be used as a highly effective support for electro catalytic responses. Recently, Lu et al. [13] have revealed that hydrogenation can advance significantly the electrochemical performance of TiO_2 as electrode.

Polymer chains play an important part in the realm of optoelectronics. [14, 15] Between the conjugated polymers, Polyaniline (C6H7N) has been recognized for extra than a period in its "aniline black" form. Between the showing polymers, polyaniline is the greatest promising polymer due to its low cost, chemical stability [16], manageable electrical conductivity, outstanding ecological stability, Polyaniline has received great attention because it shows controlled susceptibility to electrical conductivity.

2. Experimental Work

2.1 Synthesis of TiO_2 Nanostructure

In archetypal way for groundwork of TiO_2 nanoparticles, 0.5 g TiO_2 balls were melted in to 30 ml NaOH explanation underneath robust moving at chamber temperature for 2 h. Then the yellowish explanation was treated in an ultrasonic bath (Power Sonic 405, 40 KHz and 350 W) for 2 h in ambient temperature. The resultant precipitates were then centrifuged, wash away and pour out with deionized water numerous times and dehydrated out at 60 ^{0}C for 24 h.

2.2 Synthesis of PAni

Here are the following steps which have the same procedures of ref. [17]:

1- 12.5 mg Solution of Aniline (ANI), monomer was melted in 76 ml of concentrated water with continuous stirring at R.T. for 10 min.
2- 0.24 g of Ammonium Persulphate (APS) in 4 ml of purified water was melted with continuous stirring at R.T. for 10 min.
3- Solution of **step 2** was added drop wise to resultant solution of **step 1** with continuous stirring.

4- the precipitate explanation (black green precipitate) is put on cleaned silicon substrates by using drop cast.(In the dropper,5drops ware distilled on to glass or silicon until it dried on the heater under a temperature 80)

2.3 Preparation of TiO2-PAni nanocomposite

An appropriate amount of PAni was dispersed in distilled water and added to TiO2 with volume ratios of 10% :15% and subjected to ultrasonic waves for 1 hour to obtain a ready-to-use homogenous dispersion.

2.4 Preparation of the electrode

was used for this purposeTiO2-PAni and PAni nanocomposite was deposited on it by drop casting method to be ready for supercapacitor examination which is placed in 1.0 ml of sulphuric acid (H_2SO_4) and test the curves of the GCD examination, CV measurements in order to calculate its capacity.

Microstructure and structure of the synthesized materials have been characterized using field production skim through electron microscopy (FESEM) and X-ray diffusion (XRD)..The visual transmission and absorption spectra of the organic – Polyaniline solutions in the visible and NIR regions (190–1100) nm have been recorded using (UV–Visible1800 Double beam spectrophotometer). by using drop cast

3. Results and Discussion

The structural analysis and development orientation of the prepared nanostructured materials pure TiO_2, pure PANi, and TiO_2 -PANi were examined by HR-XRD diffraction, the XRD patterns are displayed in Figure (1,2,3). In Figure (1) the exact comparison of the documented XRD patterns with the typical JCPDS card No.TIO_2 Rutile JCPDS card No.-65-5714, and Anatase Tetragonal, JCPDS card No.- 21-1272, confirms the formation of pure TiO_2 phases with two phase Rutile, and Anatase. The peaks appear for the TiO_2-nanocomposites correspond to different planes of anatase, and rutile TiO_2 respectively. The diffraction patterns of pure TiO2 were indexed as (110), (101), (111), (200), in addition to the few detected weak peaks indexed as (004), for Rutile and Anatase phase respectively.In figure (2) shows XRD pattern of PANi proves a variety of the diffraction peaks at ranges $2\Theta = 10 - 45$, because of the amorphous presence of structured by the oxidative polymerization method [18]. The wide peak results from dissipating X-rays from the chain of the PAni [19-20]. Figure (3) illustrates an XRD peaks of the TiO2–PANi (%10:15%) nanocomposites. It shows diffraction peaks (101), (111),(210) and (101), (004), planes for Rutile and Anatase phase respectively planes, while the other weak peaks belongs to PAni

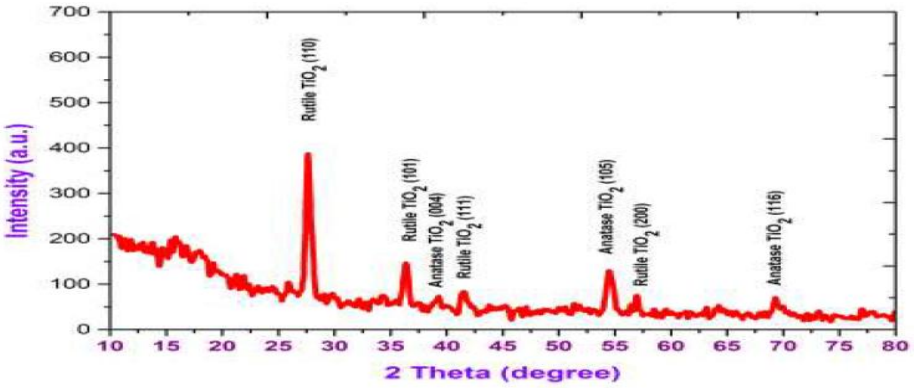

Figure 1. Pure TiO_2

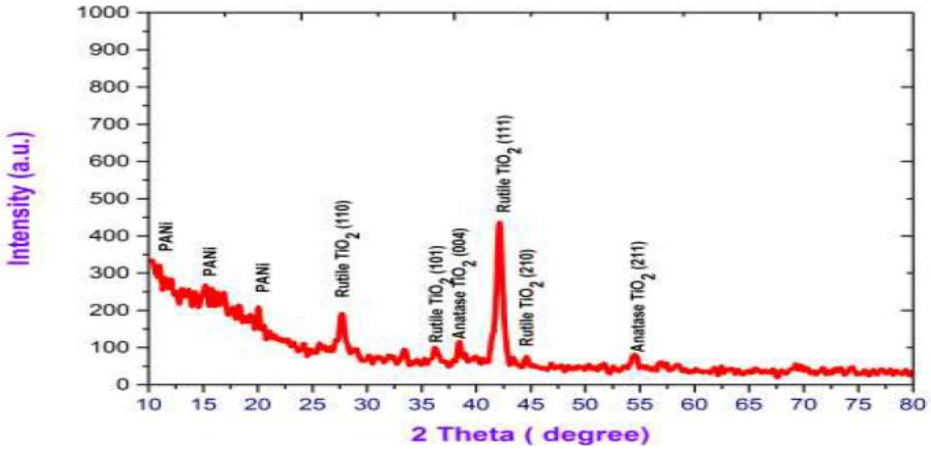

Figure 2. TiO_2 –PAni (10%-15%) nanocomposite grown on Si substrate.

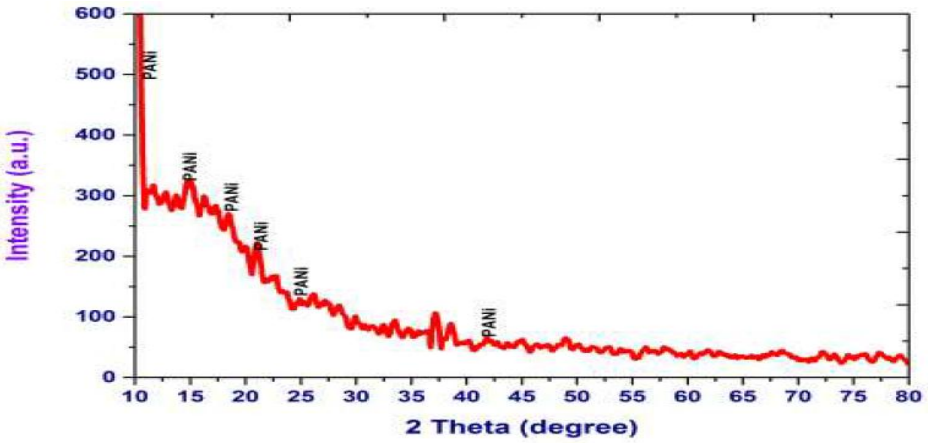

Figure 3. pure PAni

Figure(1,2,3) : High resolution X-ray diffraction (HRXRD) patterns of (1) pure TIO2 (2) TiO2-PAni (10%:15%) nanocomposite grown on Si substrate (3) pure PAni.

The surface morphology of TiO_2 and TiO_2/ PAni composites thin films deposited on a silicon substrate by spin coating technique at room temperature was examined by Field Emission Scanning Electron Microscope (FESEM). FESEM micrographs of nanocrystalline TiO_2 thin film are shown in (Figure4). From the figure, a randomly distribution of TiO_2

nanocrystallines over the scanned area can be observed and regular shapes can be clearly noticed. Due to high surface charge, agglomeration takes place according to Ostwald ripening process [21]. The FESEM micrographs of the TiO_2 thin film check that it comprises some pores or voids and vacancies caused by difference in experimental conditions, mainly the semiunform of solution during deposition, which is in agreement with other reports [21, 22]. The average grain size of TiO_2 nanoparticles was 45±2 nm. (The measurements were taken at the University of Tehran)

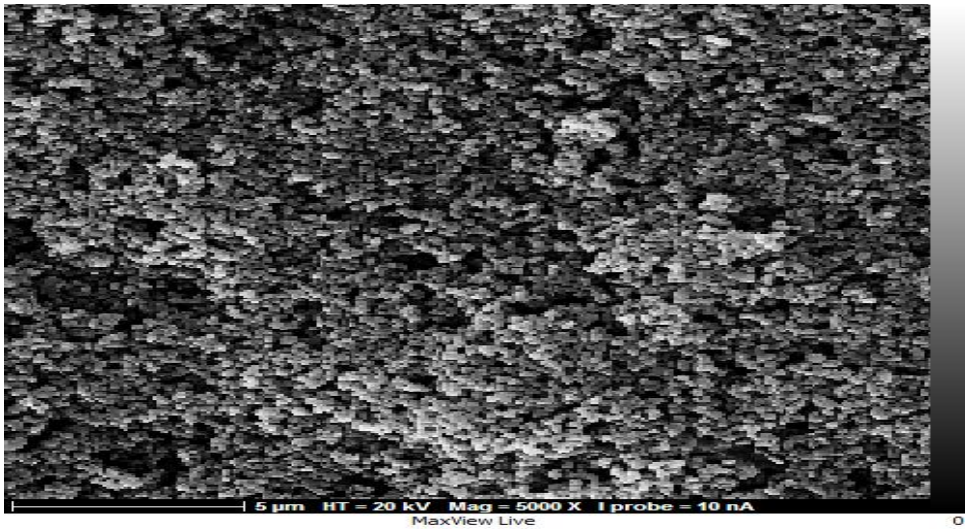

Figure 4. FESEM images of pure TiO_2 nanostructures grown on Si substrate

(Figure5) illustrates the images for PAni thin films at low and high magnifications. The FESEM spitting image of Polyaniline obviously point to that the polymer owns nanofiber resembling structure. This image similarly exposes that PAni holds certain apertures or emptiness [23]. The interlocked and entwined structure is also due to stable mixture which allows the easy forking with other fibers developing during polymerization process. This simplifies same nucleation in that way mean fine uniform and interrelated nanofibers of PAni, which is in agreement with other reports [24, 25]. The estimated average fiber diameter of PAni NFs from FESEM was 30±5 nm which also verifies the middling crystalline scope.

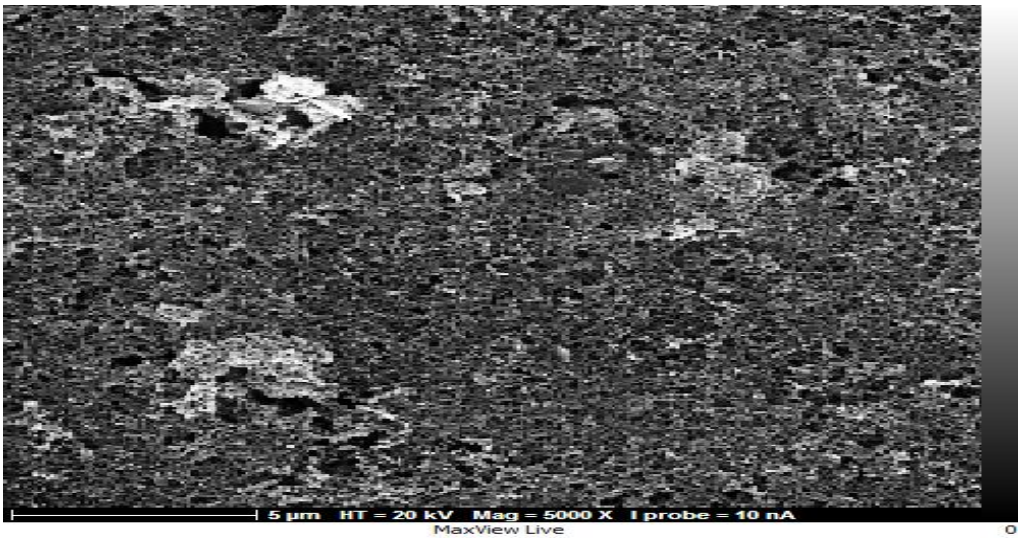

Figure 5, FESEM images of pure PANi nanostructures grown on Si substrate

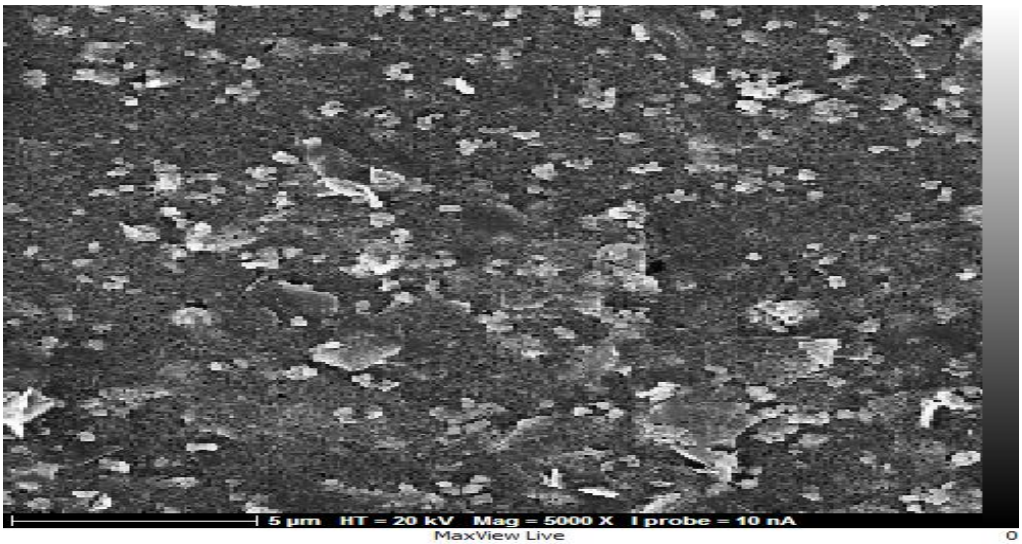

Figure 6. shows the resulting mixture of nano fibers for TiO_2 and nanofibers for PAni in ratio of 10%:15%

For TiO_2- PAni thin films which have been deposited on a glass substrate, the values of the optical energy gap (Eg) were specified with the use of the Tauc formula as in. It is found that ($\alpha>10^4$)which means that there is a direct transition of the ocular band gap (Eg) which is specified through extrapolation of the straight-line helping of the scheme $(\alpha h\upsilon)^2$ vs. (hυ) for 0 worth of the coefficient of the absorption. $(\alpha h\upsilon)^2$ vs. (hυ) variation has been depicted in the optical energy gap for TiO_2 is about 3.3 eV. The obtained band gap is smallest than that of TiO_2 – PAni that may be ascribed to quantum confinement impacts as a result of the small size of PAni nanostructures, where after adding PAni at different volume ratios (15) volume percent to TiO_2, the optical energy gap increased from 4eV to 4.6 eV due to the chemical bonding of TiO_2 nanoparticles and PAni nano fibers and such variation means that the TiO2 nanoparticle electronic characteristics have

been modified strongly by the existence of PAni nanofibers and provide a higher level of the electrical conductivity in composite [26].

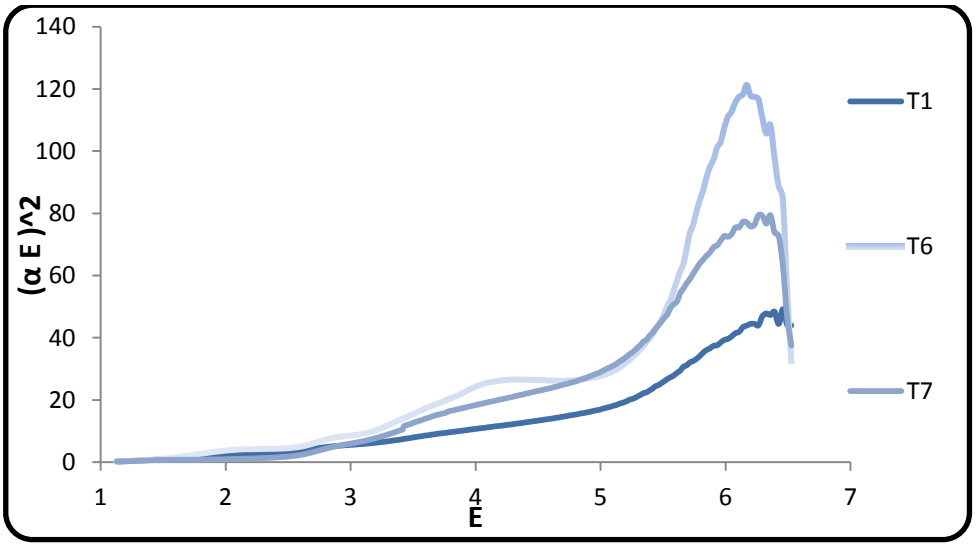

Figure 7. Tauc plot of TiO_2 with different volume ratios of PAni.

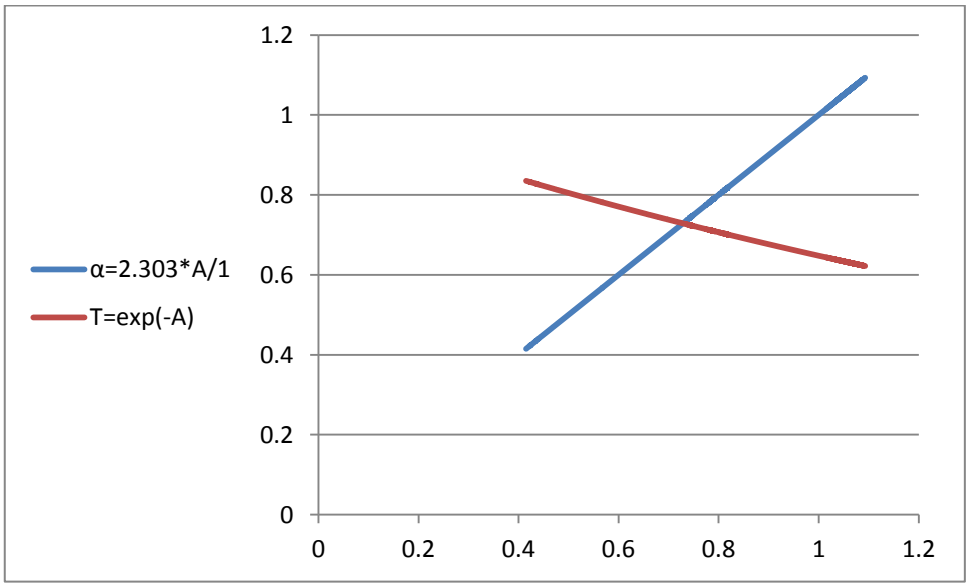

Figure 8. TiO_2 pure

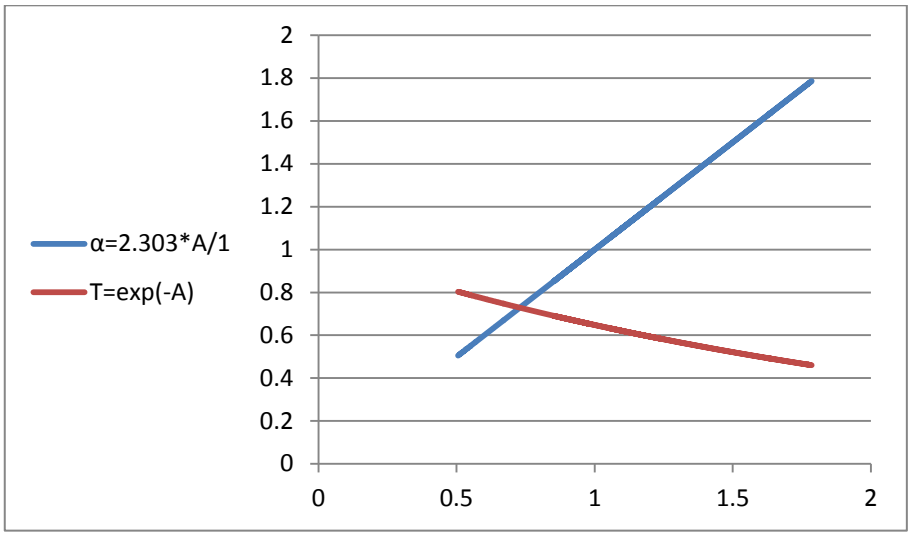

Figure 9. TiO_2 – PAni (10%-15%)

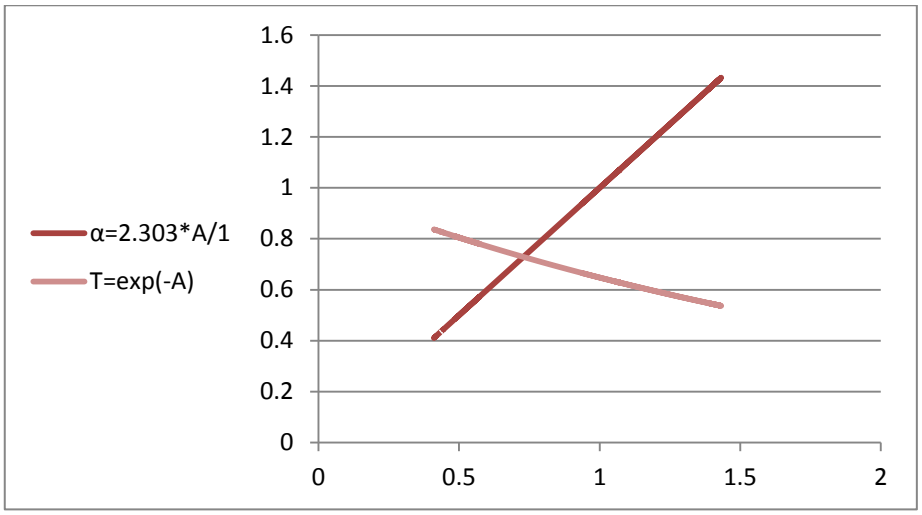

Figure 10. PAni pure

For using TiO_2, PAni and TiO_2/ PAni as superconductors, cyclic voltammetry (CV) bends were portrayed in Figure 5. by repeating the scan rate, clear peaks of the anode and cathode can be noticed respectively [27]. The results of the Cyclic Voltammetry showed that all of the materials are electro-chemically dynamic in potential territory contemplated. TiO_2 -PAni mixture film incorporates electro-chemical practices of the TiO2 as well as the PAni. As observed from Figure (6), the nano-organized PAni film terminal experiences an observable electrochemical response underneath a negative potential of - 0.50V. The cathodic procedures may be credited to H+ addition to the PAni, and anodic procedures compare to H+ extraction from structure. Such addition procedure can happen in PAni and might be portrayed. During the CVs forms, PAni film is shaded alongside the cathodic procedures and blanched at anodic procedures. Notwithstanding the bend shape, it was seen that the force of the electrochemical

sign is to a great extent expanded in TiO2-PAni composites contrasted with TiO_2 or PAni that shows that TiO_2 –Pani materials have higher electro-chemical movement compared to the TiO_2 or PAni. It may be clarified by 2 different means. The first is the synergistic impact of the polyaniline and PAni, and the second is the impact of p–n hetero junctions. PAni acted like an n-type semiconductor, and TiO_2 carried on as a n-type semiconductor. Hence, the p-type TiO_2 formed a p–n intersection with the polyanline. Consequently, the p–n heterojunctions are liable intended for the way by which the TiO_2-PAni nanocomposite film had greater charge density compared to the polyaniline film [28].

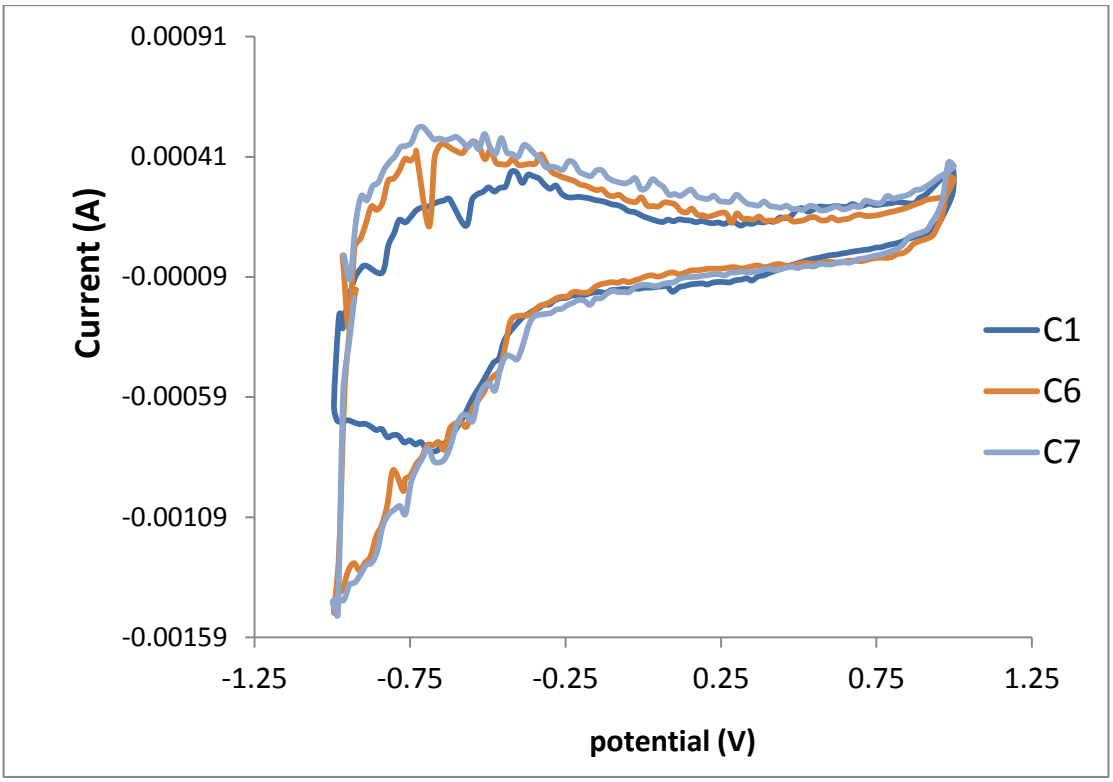

Figure 11. Cyclic voltammetry for the pure TiO2 and TiO2 -PAni at 50 mV.

4. Conclusions

The TiO_2-PAni nanocomposites were study successfully by a simple oxidative method. The TiO_2-PAni nanocomposite has a higher electrochemical movement than that of the pure TiO_2 or PAni. The highest cyclic voltammetry stability of TiO_2-PAni was at 10% of PAni, The UV-Vis was estimated to calculate the energy gap and was for TiO_2 4 eV, and the PAni was for 4.6 eV. And it was in a good range.

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