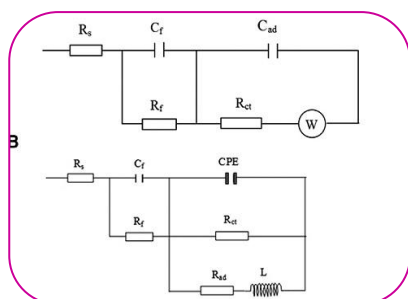




## PREPARATION AND CHARACTERIZATION OF POLYANILINE /TITANIUM DIOXIDE (PANI/TiO<sub>2</sub>) NANOCOMPOSITE VIA IN SITU POLYMERIZATION



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### ABSTRACT

Crystalline titanium dioxide nanoparticle has been successfully synthesized by sol-gel method. Polyaniline (PANI) as a promising conducting polymer has been used to prepare polyaniline/ nanoTiO<sub>2</sub> (PANI/TiO<sub>2</sub>) nanocomposite. Titanium dioxide (TiO<sub>2</sub>) nanoparticles with an average crystal size of 35 nm were encapsulated by PANI via the in situ polymerization of aniline on the surface of TiO<sub>2</sub> nanoparticles. Characterization of PANI, TiO<sub>2</sub> and PANI/TiO<sub>2</sub> nanomaterials are carried out using various techniques such as XRD, FTIR, UV-Visible, TEM and SEM. The SEM images indicate that the TiO<sub>2</sub> nanoparticles were embedded in the PANI matrix. The TEM of PANI/TiO<sub>2</sub> also shows the encapsulation of nanoTiO<sub>2</sub> with in the polymer matrix. The result of spectroanalysis illustrates that polyaniline and nano-TiO<sub>2</sub> composite particles are not simply blended or mixed up. There is a strong interaction between polyaniline molecules and nano-TiO<sub>2</sub> particles.

**KEYWORDS** : Crystalline titanium , nanoparticles , polyaniline molecules.

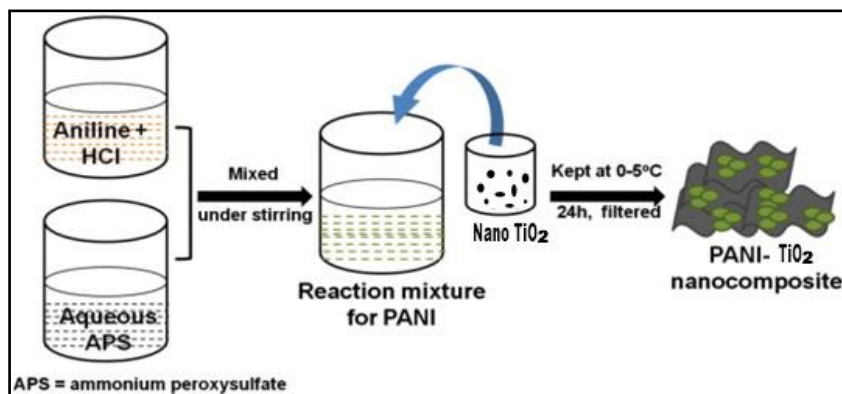
### 1. INTRODUCTION

Organic-inorganic nanocomposites for synergetic behavior and a wide range of potential users have triggered great interest and concern of the related academic organizations and researchers over the past decade [1-4]. Specifically, nanocomposites of organic conjugated polymers and inorganic nanocrystals have attracted great attention due to a large number of potential applications such as photonics, photo electronics, and catalysis [5]. Among the conducting polymer, conducting polyaniline (PANI) is often used as an organic part to prepare nanocomposite because of its low cost, easy preparation, controllable unique properties by oxidation and protonation state, excellent environmental stability, and potential applications in electronic devices [6].

A number of metal oxide particles have so far been encapsulated into the matrix of polyaniline giving rise to a host of the nanocomposite. The CeO<sub>2</sub>-Polyaniline (CeO<sub>2</sub>-PANI) nanocomposites prepared via chemical oxidation of aniline by CeO<sub>2</sub> were reported [7]. The carbon nanotube- polyaniline core-shell nanowires by in situ inverse microemulsion has been reported. Polyaniline - BaTiO<sub>3</sub> nanocomposite [8], polyaniline - molybdenum [9] and polyaniline - V<sub>2</sub>O<sub>5</sub> [10] were also reported. Titanium dioxide (TiO<sub>2</sub>) due to the advantages of high chemical stability, high photocatalytic activity, relatively low cost and nontoxicity, is one of the most important photoactive reagents which is widely used for degradation of air and water organic pollutant. TiO<sub>2</sub> is a typical n-type semi conductor polymer and PANI is usually considered as a p-type

conducting polymer [11]. Thus their combination brings a good capacitive material with good conductivity and stability [12]. There are several reports on the preparations, investigation of properties and applications of PANI/TiO<sub>2</sub> composite materials. Studies on the surface and interface of PANI/TiO<sub>2</sub> have indicated that a nanocomposite at the molecular level has been created.

Previous researchers have shown that properties of PANI/TiO<sub>2</sub> nanocomposite are quite different from pure PANI or TiO<sub>2</sub>, which is due to the existence of a strong interaction between two components [13]. Synthesis method has a great effect on the final properties of PANI/TiO<sub>2</sub> nanocomposite. A various method such as ultrasonic irradiations, in situ polymerization, self-assembly method, graft polymerization and UV curable polymerization method have been used to prepare PANI/TiO<sub>2</sub> nanocomposite system [14, 15]. In situ polymerization of aniline in the presence of TiO<sub>2</sub> has been used commonly for preparation of PANI/TiO<sub>2</sub> nanocomposite (Fig.1).



**Figure: 1 Schematic illustration of PANI/TiO<sub>2</sub> nanocomposite preparation.**

In this paper, we report the preparation of PANI/TiO<sub>2</sub> nanocomposite via in situ polymerization method. The TiO<sub>2</sub> powder of particle size  $\approx$  35 nm was synthesized by sol-gel technique and polyaniline was synthesized by the chemical oxidative polymerization of aniline. The nanocomposite was characterized by XRD, FTIR, UV-visible, SEM and TEM. The results were compared with corresponding data of pure PANI. The intensity of diffraction peak for PANI/TiO<sub>2</sub> nanocomposite is lower than that for TiO<sub>2</sub>. The characteristic FTIR peaks of pure PANI are observed to shift to a higher wave number in PANI/TiO<sub>2</sub> nanocomposite, which is attributed to the interaction of TiO<sub>2</sub> particles with molecular chains. The SEM image indicates the structure of PANI/TiO<sub>2</sub> nanocomposite.

## 2. EXPERIMENTAL

### 2.1 Materials

The aniline AR grade (MERCK) was distilled twice under reduced pressure. Ammonium persulphate (APS) [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] (Analytical reagent ,RANBAXY fine chemicals Limited India), hydrochloric acid AR grade( MERCK) , Titanium tetrachloride (TiCl<sub>4</sub>) AR grade (MERCK) and Ammonium hydroxide (NH<sub>4</sub>OH) AR grade (MERCK) were used to prepare the nanocomposite of this study. Water used in this investigation was de-ionized water.

### 2.2 Synthesis of TiO<sub>2</sub> nanoparticles

In the present study, nano TiO<sub>2</sub> has been prepared by sol-gel method. 100ml of high purity Titanium tetra chloride (TiCl<sub>4</sub>) was carefully diluted by adding drop-wise to 250ml of ice cold, well stirred double distilled water and the resulting solution was then diluted to 500 ml. 25 ml of the above diluted TiCl<sub>4</sub> was made acidic by adding around 1 ml of con.H<sub>2</sub>SO<sub>4</sub> in a beaker and diluted to 1 liter with double distilled water. Ammonium hydroxide was then added to the above solution until the p<sup>H</sup> of the solution reached 7 to 8. The obtained Titanium hydroxide gel was then filtered washed several times with water and dried. The oven dried TiO<sub>2</sub> was then ground in a mortar. The fine powder obtained was then annealed for 2 hours at 300 °C cooled to room temperature.

### 2.3 Synthesis of polyaniline (PANI)

Polyaniline was synthesized by polymerization of aniline in the presence of hydrochloric acid as dopant and ammonium peroxodisulphate as an oxidant by the chemical oxidative polymerization method. For the synthesis, 50ml, 1M HCl, and 2ml of aniline were added together in a 250ml beaker with constant stirring at 0°C, 4.99g of ammonium persulphate in 50ml and 1 M HCl was suddenly added into the above solution. The temperature was maintained at 0°C for 5h to complete the polymerization reaction. The precipitate obtained after the polymerization reaction was washed repeatedly with water and acetone afterward dried at 60°C for 2 h under vacuum to obtain a fine dark green powder.

### 2.4 Synthesis of polyaniline/Titanium dioxide nanocomposite (PANI/TiO<sub>2</sub>)

TiO<sub>2</sub> nanoparticles (250mg) were dispersed in 100 ml of 1M HCl aqueous solution containing 2ml of aniline under ultrasonic vibration to reduce the aggregation of TiO<sub>2</sub> nanoparticles. The solution was mechanically stirred for 1h to obtain a uniform suspension containing TiO<sub>2</sub> particles, in an ice bath. 50 ml of a pre cooled 1M HCl containing 4.9g of ammonium persulphate was added dropwise into the solution containing aniline monomer under stirring. The mixture was allowed to polymerize under stirring for 2 h at 0°C. The precipitated dark green colored PANI-TiO<sub>2</sub> nanocomposite powder was filtered and washed with a large amount of deionized water, methanol and acetone. Finally, the product was dried at 80°C till the constant mass was reached.

### 2.5 Characterization techniques

The sample was characterized by scanning electron microscope (SEM) using Holland Philips XL30 microscope. XRD patterns of the sample were recorded in ambient air using a Holland Philips X-ray powder diffraction (Cu K  $\alpha$ ,  $\lambda = 1.5406 \text{ \AA}$ ), at scanning speed of 2°/min from 20° to 80°. UV- visible spectrum was prepared by Shimadzu analytical equipment (UV-2100). The Fourier transform infrared (FTIR) was studied by using a Bruker IR spectrometer of 4cm<sup>-1</sup> resolution in the 400-4000 cm<sup>-1</sup> range.

## 3. RESULT AND DISCUSSION

### 3.1 X-Ray Diffraction Analysis

The Figure-2 shows X-ray diffraction (XRD) pattern of HCl doped PANI, pure TiO<sub>2</sub> nanoparticles and PANI/TiO<sub>2</sub> nanocomposite. Figure-2(a) reveals that PANI also has some degree of crystallinity. A broad peak around  $2\theta = 25^\circ$  in XRD pattern of HCl doped PANI may be attributed to the scattering from PANI chains at interplanar spacing [16]. Figure-2(b) shows the appearance of a peak in XRD pattern of pure TiO<sub>2</sub> nanoparticles which can be indexed as the anatase polymorph of TiO<sub>2</sub> [17]. Also Figure-2(c) shows that there is no difference between XRD pattern of PANI/TiO<sub>2</sub> nanocomposite and XRD pattern of pure TiO<sub>2</sub> nanoparticles, which reveals deposition of PANI on the surface of TiO<sub>2</sub> nanoparticles which has no effect on the crystallinity of TiO<sub>2</sub> nanoparticles. Therefore, the polymorph of TiO<sub>2</sub> in the PANI/TiO<sub>2</sub> nanocomposite is still anatase. However, PANI peaks in the PANI/TiO<sub>2</sub> core-shell nanocomposite are not detected. This result suggested that the crystallization of PANI molecular chain has been hampered in the PANI/TiO<sub>2</sub> nanocomposite.[18]. This is because when PANI chains are adsorbed on the surface of TiO<sub>2</sub> nanoparticles, due to the restrictive effect of TiO<sub>2</sub> nanoparticles crystallinity of PANI is compromised. The crystallite size of pure TiO<sub>2</sub> nanoparticles and the PANI/TiO<sub>2</sub> nanocomposite was calculated 48 nm and 54.5 nm, respectively according to the Debye-Scherrer formula.

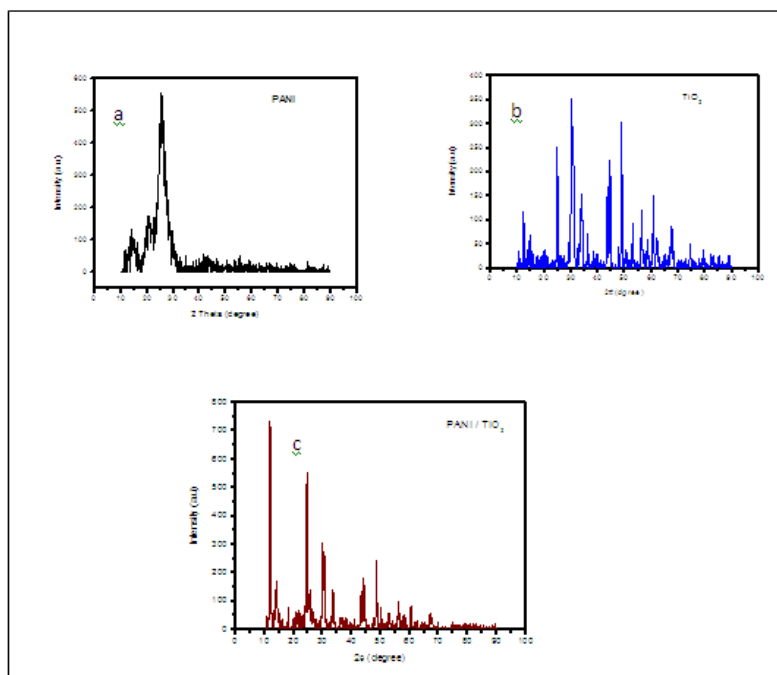


Figure 2. X-ray diffractogram of (a) HCl doped PANI, (b) nano TiO<sub>2</sub>, (c) PANI/TiO<sub>2</sub> nanocomposite

### 3.2 Furrier Transform Infrared (FTIR) analysis

Figure-3 shows the FTIR spectra of doped polyaniline, nano TiO<sub>2</sub> particles, and polyaniline/TiO<sub>2</sub> nanocomposite. The Figure-3(a) shows band at 3450 cm<sup>-1</sup> is attributable to N-H stretching mode, C=N and C=C stretching mode for the quinoid and benzenoid rings occur at 1576 and 1483 cm<sup>-1</sup>. The band at about 1304 and 1242 cm<sup>-1</sup> have been attributed to C-N stretching mode for benzenoid ring, while the peak at 1127cm<sup>-1</sup> is assigned to a plane bending vibration of C-H (mode of N=Q=N, QN<sup>+</sup> H-B, and B-N<sup>+</sup> H-B), which is formed during protonation[19]. In Figure-3(b) indicate that the main characteristic bands of doped polyaniline and nano-TiO<sub>2</sub> all appear in FTIR spectra of polyaniline/TiO<sub>2</sub> nanocomposite. However, the incorporation of nano- TiO<sub>2</sub> particles leads to the shift of some bands of polyaniline. The bands at 1576,1483 and 1242 cm<sup>-1</sup>, corresponding to the stretching mode of C=N, C=C, and C-N, all shifted to lower wavenumbers. Meanwhile, the band at 1127cm<sup>-1</sup> which is formed during protonation obviously splits. These obvious changes reveal that the bond strengths of C=N, C=C, and C-N become weaker in polyaniline/TiO<sub>2</sub> nanocomposite and incorporation of nano TiO<sub>2</sub> particles have an effect on the doping of conducting polyaniline. This means that there is a strong interaction between polyaniline macromolecules and nano-TiO<sub>2</sub> particles. The strong interaction may be associated with the interaction of titanic and nitrogen atom in polyaniline macromolecules. Because titanium is a transition metal, titanic has intense tendency to form coordination compounds with the nitrogen atom in polyaniline macromolecules. This interaction may weaken the bond strength of C=N, C=C, and C-N in polyaniline macromolecules. Moreover, the action of hydrogen bonding between nano-TiO<sub>2</sub> particles and polyaniline molecule is also contributory to the shift of bands [15, 20]. Figure-3(c) represents the pure nano TiO<sub>2</sub>, the band centered at 660 cm<sup>-1</sup> is assigned to the Ti-O stretching vibrations. The very weak adsorption bands at 1620-1630 cm<sup>-1</sup> is attributed to CO<sub>2</sub> adsorbed on the surface of the nanoparticles. The band at 3450 cm<sup>-1</sup> is due to OH stretching vibrations.

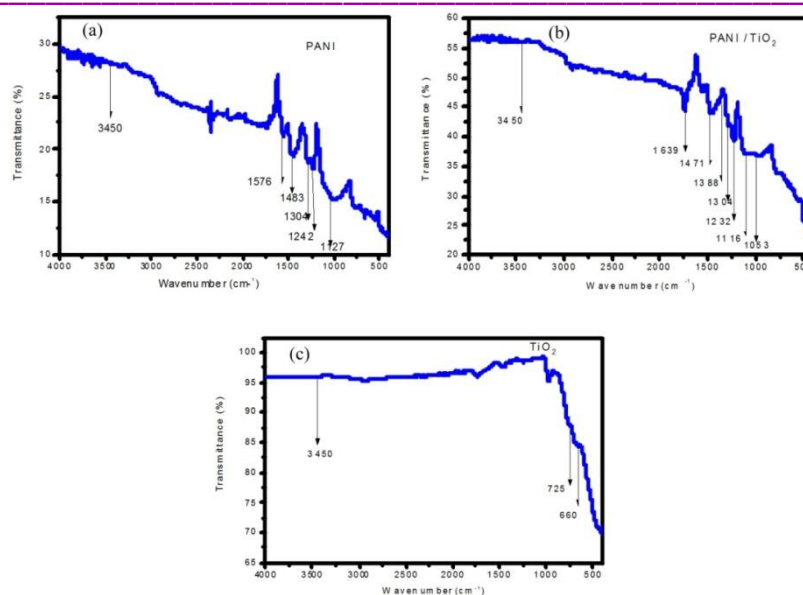


Figure: 3 FTIR spectra of (a) HCl doped PANI, (b) PANI/TiO<sub>2</sub> nanocomposite, (c) nano TiO<sub>2</sub>

### 3.3 UV-visible analysis

UV-visible spectra of HCl doped polyaniline, polyaniline/TiO<sub>2</sub> nanocomposite, and nano-TiO<sub>2</sub> are given in Figure-4. Among this Figure-4(a) shows that three distinctive peaks of doped polyaniline appear at about 365, 456 and 900 nm, which are attributed to the  $\pi-\pi^*$ , polaron- $\pi^*$  and  $\pi$ -polaron transition [21, 22], respectively. From Figure-4(b), it can be noted that the characteristics peaks of nano-TiO<sub>2</sub> and doped polyaniline all appear in PANI/TiO<sub>2</sub> nanocomposite, and a new peak is observed, which is at 290 nm. Moreover, the peaks at 900 nm are obviously shifted from 900 to 878 nm. It indicates that encapsulation of nano-TiO<sub>2</sub> particles has the effect on the doping of conducting polyaniline, while this effect should owe to an interaction at the interface of polyaniline and nano-TiO<sub>2</sub> particles. The low wavenumber region exhibits a strong vibration around 725 nm which corresponds to the antisymmetric Ti-O-Ti mode of titanium oxide, Figure-4(c).

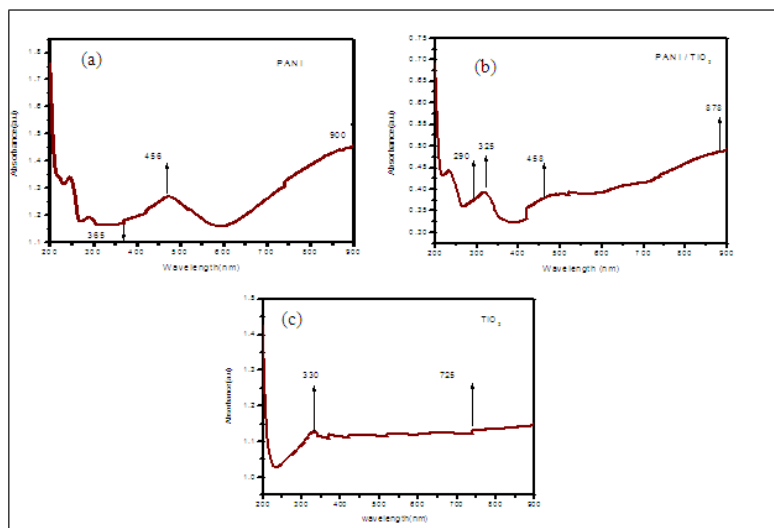
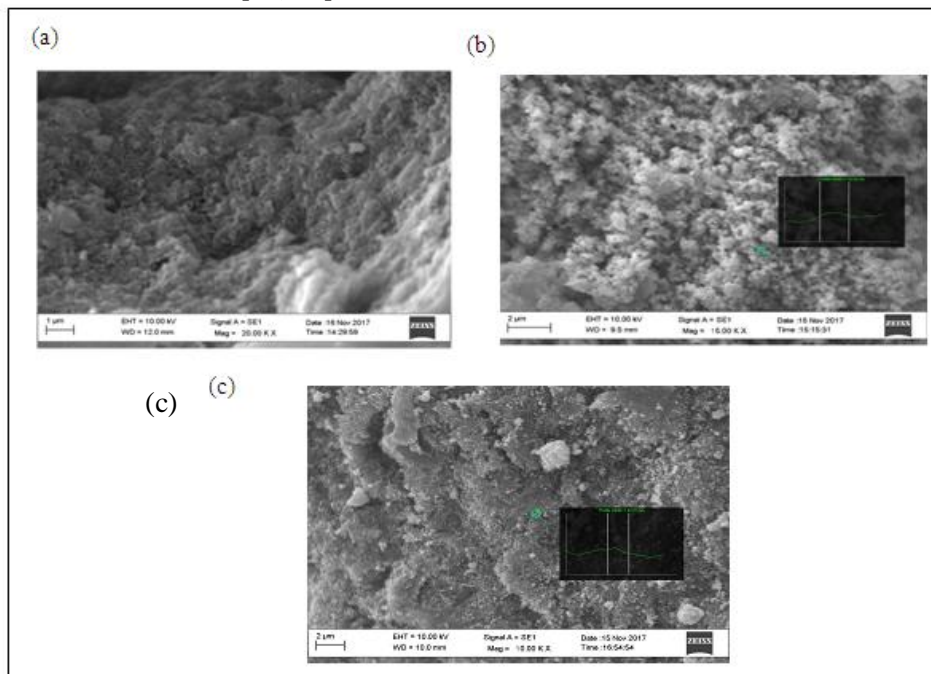


Figure: 4. U.V-Visible spectra of (a) HCl doped PANI, (b) PANI/TiO<sub>2</sub> nanocomposite, (c) nanoTiO<sub>2</sub>

### 3.4. Scanning Electron Microscopy (SEM) Analysis

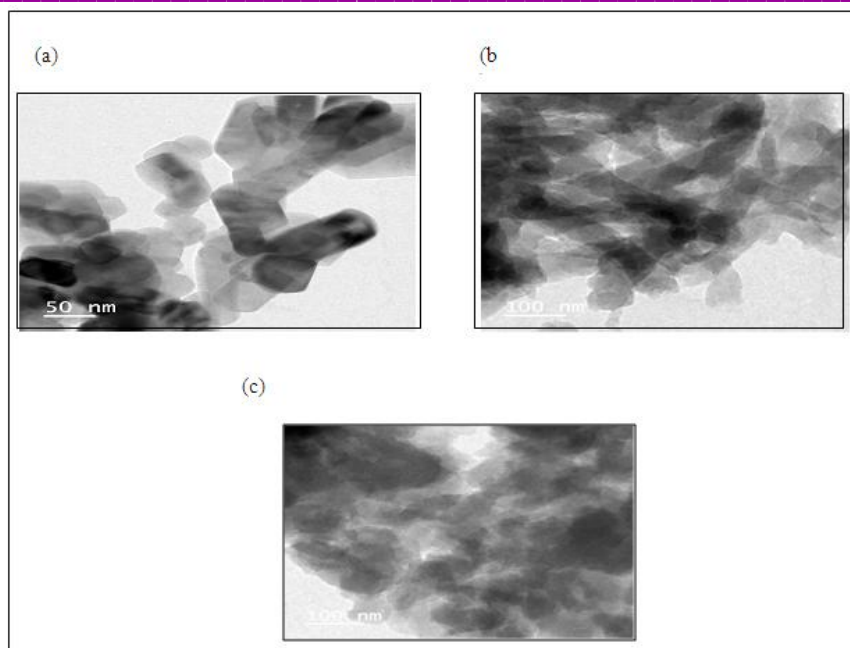
Figure-5(a) shows the SEM image of Polyaniline (PANI), which show pseudo fiber morphology with an average diameter of 80 nm. The SEM image also confirms the porous structure of polyaniline nanofibers. Figure-5(b) shows the images of TiO<sub>2</sub> consist of homogeneous rod shaped nanostructures with agglomeration of nano particles are observed. Figure-5(c) shows the SEM images of PANI/TiO<sub>2</sub> nanocomposites. It reveals that TiO<sub>2</sub> nanoparticles are distributed in the polyaniline nanofiber. The size of nanocomposites from the SEM images was calculated as 94.51 nm [15, 23].



**Figure: 5. The SEM images of (a) HCl doped PANI, (b) nanoTiO<sub>2</sub>, (c) PANI/TiO<sub>2</sub> nanocomposite**

### 3.5 Transmission Electron Microscopy (TEM) Analysis

Detailed information about the microstructure and morphology has been provided by TEM examination of the sample. Figure-6(a) shows the TEM image of TiO<sub>2</sub> it indicates the formation of nanorods and prism like structure. The crystallite size calculated from XRD results closely matches with the average particle size obtained from TEM. The fiber like PANI nanostructures are confirmed by TEM image. Figure-6(b). It is found that more than 95% of of the sample in nano fibers with diameter approximately from 20 to 80 nm. The length of the fiber range from 150 up to 500 nm. The nanofibers tend to agglomerate into interconnected nanofibers networks, rather than bundles. Figure 6(c) shows PANI/TiO<sub>2</sub> nanocomposite here nano TiO<sub>2</sub> is clearly visible in the PANI matrix [24, 25].



**Figure 6 TEM images of (a) nano TiO<sub>2</sub>, (b) polyaniline (c) polyaniline/TiO<sub>2</sub>**

#### 4. CONCLUSION

TiO<sub>2</sub> nanoparticles were successfully encapsulated by PANI via in situ chemical oxidative polymerization method. Encapsulation of TiO<sub>2</sub> in the matrix of PANI to form nanocomposite at the molecular level was confirmed. The result of X-ray diffraction shows that the polyaniline has no effect on the crystallization performance of nano-titanium dioxide particles. Fourier transforms infrared spectra and UV-Visible spectra indicate that polyaniline and nano-titanium dioxide particles are not simply blended or mixed up. A strong interaction exists at the interface of polyaniline macromolecules and TiO<sub>2</sub> nanoparticles. The strong interactive force may be attributed to the tendency to form coordination compound between titanate and nitrogen in polyaniline molecule and the action of hydrogen bonding between nano-TiO<sub>2</sub> particles and polyaniline molecule. SEM and TEM images of PANI/ TiO<sub>2</sub> nanocomposite clearly show that polyaniline deposited on the surface of the nano-TiO<sub>2</sub> particles.

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