

Optical and Structural Characterization of Polyaniline/Titanium Dioxide Nano Composites

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Abstract: Polyaniline/ titanium dioxide composite (PANI/TiO₂) was synthesized by in-situ chemical polymerization in an ice bath medium for polyaniline with different percentages of TiO₂ nanoparticles (3, 6, and 9) wt. %. UV-Vis spectrophotometer, Fourier Transforms Infrared (FTIR) spectrometer, X-ray diffraction (XRD), and Scanning Electron Microscopy (SEM) were used to characterize the materials. The XRD patterns showed polycrystalline structure for PURE PANI and PANI/TiO₂ composite of different TiO₂ ratios. The FT-IR investigated the presence of polyaniline. The analysis of UV-Vis spectra revealed that the energy gap for PANI/TiO₂ decreased with increasing the ratios of TiO₂ nanoparticles.

Keywords: Conducting polymer, Polyaniline (PANI), Titanium dioxide (TiO₂), Structure characterization, Optical properties, PANI composite.

1. Introduction

Conducting polymers and dielectric polymers are widely used in many applications such as gas sensors, rechargeable batteries, light-emitting diodes, etc. Many features of conducting polymers, such as their light weight and low cost compared with other materials, make them the most important materials for many applications [1]. Depending on the synthetic preparation of these polymers, the conducting polymer can be divided into two groups: conducting polymers chemically polymerized and conducting polymers electrochemically polymerized. Although electrochemical polymerization is attractive due to the direct production method, chemical polymerization has the advantage of low production costs [2]. Polymers can be conductive by one of two methods. In the first one, the polymer acts as a bonding matrix for particles of conductive materials such as metals or fibers. This method is attractive for industries due to various advantages such as the relatively simple forming to the required shape associated with the low cost and lightweight-to-strength

ratio. The second method is to make the backbone of the polymer conductive, which can be achieved by oxidation and reduction with an agent. The advantage of this method is to vary the conductivity by controlling oxidation or reduction. Although this method has the issue of environmental effect on stability, its potential advantages post the research in this field [3].

The field of researching conducting polymers emerged in 1974, with the polyacetylene discovery by Shirakawa [4]. Since then, numerous conducting polymers have been investigated and found useful in many application areas. Polyaniline (PANI) is one of the most unique and important conductive polymers due to its chemical and physical properties of being easily synthesized, environmentally stable, and low-cost compared with other conducting polymers [4-6]. The disadvantages of this polymer such as poor chemical stability, poor mechanical properties as well as low processing, these negative properties can be improved by adding metal or metal oxide

nanoparticles which change the characteristics of polyaniline and make it usable in many important applications [6]. PANI can be recognized from other polymers by the phenomena of π -* π transition which is described by the transition of an excited electron from the highest occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LOMO) [7, 8]. The non-conjugated carbon backbone is

one of the most important characteristics of polyaniline. Polyaniline can be found in three forms depending on the degree of oxidation and reduction: a fully reduced form is a leucoemeraldine base, a half-oxidized form is an emeraldine base, and the fully oxidized form is a pernigraniline base [9, 10]. These forms are illustrated in Fig. 1.

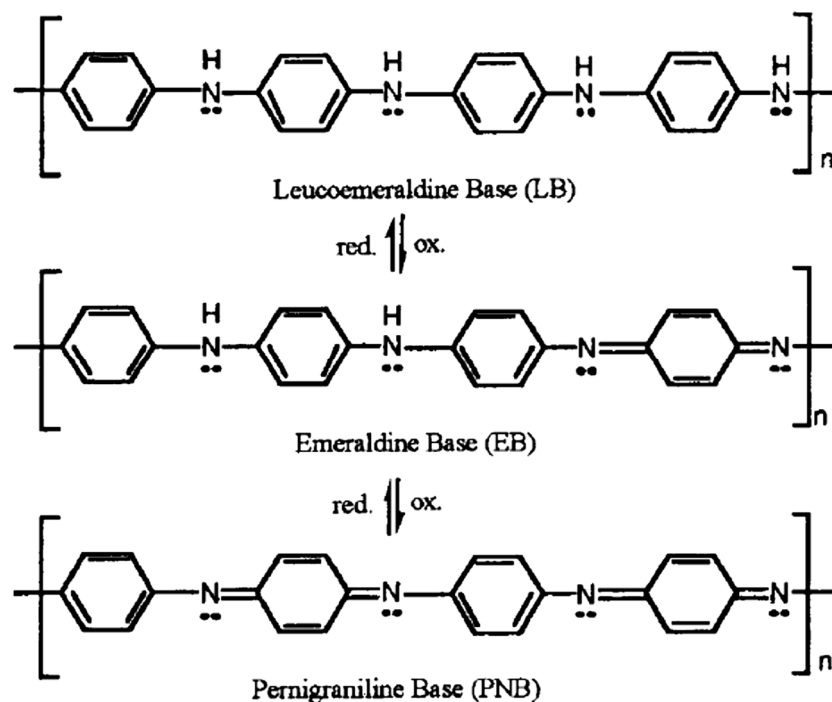


FIG. 1. Polyaniline of different forms [9].

Many studies investigated different properties of the PANI, such as the magnetic, electronic, and optical properties [11]. Many features of conducting polymers can be enhanced by adding metal or metal salts to the origin polymer [12]. The nanoparticles of TiO_2 can be added to the polyaniline because it is a nontoxic and chemically stable material with good physical and chemical features that can be applied in coating, manufacturing of sensors and solar cells, and photocatalytic reactions [13]. As a result, TiO_2 is used in many applications to increase their efficiency such as photoluminescence (PL) properties, energy efficient windows, photocatalysts, water and air purifications, UV protection creams, and dye-sensitized solar cells [8, 14]. The combination between organic polymer (polyaniline) and inorganic metal oxide (TiO_2) is important in many fields and many researchers have investigated the effect of this combination of the PANI properties [8, 14, 15]. Pawara et al. [15] found that the preparing a composite of

PANI/50% TiO_2 reduces the resistivity of TiO_2 almost by 50%. Nur Aziera Jumat et al. [8] studied the effect of different ratios of TiO_2 , (10, 20, 40) wt.% on the conductivity and energy gap of PANI. They found that maximum conductivity is achieved at 10% TiO_2 and the energy band gap decreases at the ratio of 10% TiO_2 without providing information about the energy gap at different TiO_2 percentages. Another study by Rahman et al. [16] showed that the band gap of PANI/ TiO_2 decreases as the molar ratio of TiO_2 increases. Thus, the band gap was 1.64 eV when the molar ratio was 0.3M and 1.75 eV when the molar ratio was 0.2 M.

However, to the best knowledge of the authors, the effect of adding a low percentage of TiO_2 to the PANI on the energy gap and the optical properties of PANI has not been investigated. Therefore, the goal of this investigation is to obtain a reduced energy gap for enhancement of the optical properties of polyaniline which can be used in many potential

applications such as detection sensors and photovoltaic solar cell panels.

2. Materials and Methodology

2.1 Materials

The utilized aniline, monomer (C_6H_5N), was purchased from Alpha Chemika, the ammonium persulphate ($(NH_4)_2S_2O_8$) was supplied by Thomas Baker, and the titanium dioxide (TiO_2) with an average particle size (50 nm) was supplied by US Research Nanomaterials, Inc. In this study, hydrochloric acid (HCl 37%) was used with deionized water to prepare the 1M of HCl. Also, deionized water, methanol (CH_3OH), and dimethyl sulphoxide DMSO (CH_3SOCH_3) were used in the current study.

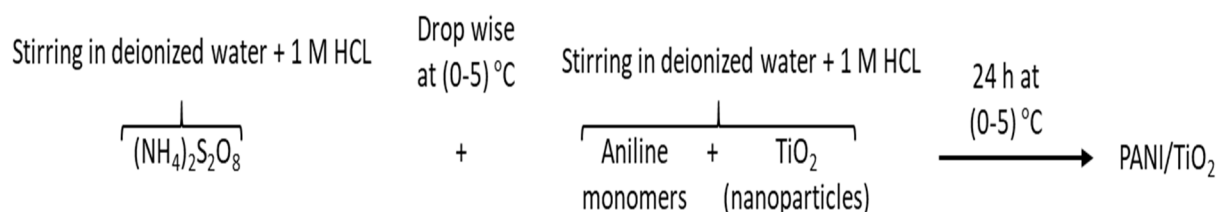
2.2 Preparation of PANI

The synthesizing of pure polyaniline was carried out by chemical oxidation where two solutions are prepared separately and then mixed. The first solution is prepared by mixing 2 g of aniline monomers with 100 ml of deionized water which contains 1 M of HCl under stirring, using a magnetic stirrer for 1 hour in ice medium to maintain a temperature at 0-5 °C. In another beaker, 4.56 g of ammonium persulphate was dissolved in 100 ml of deionized water which contains 1 M of HCl under constant stirring for half an hour in an ice bath medium at a temperature of 0-5 °C. Then the mixture of ammonium persulphate is added dropwise to the mixture of aniline and left in a constant stirring for 1 hour. After that, the solution was kept in a refrigerator in an ice bath medium for the next day. After 24 hours of polymerization at a temperature of 0-5 °C, the dark green color precipitate was collected on filtered paper No. (f2142) and then was washed three times with 100 ml of deionized water and then with 100 ml of methanol to remove the low molecular weight intermediates and oligomers. Subsequently, the mixture of dark green paste polyaniline was dried in an oven for 4 hours and finally obtained

as dried pieces of polyaniline. These small pieces were ground by a manual grinder to form a fine powder.

2.3 Preparation of PANI/TiO₂ composites

The preparation of PANI/TiO₂ follows almost the same steps as that of pure PANI, i.e. mixing the two previously prepared solutions. For PANI/TiO₂, The TiO₂ anatase is one of the TiO₂ forms that is metastable at all pressures and temperatures and its crystallization system. The TiO₂ nanoparticles were added to the first solution during the dissolving of the aniline monomers in the deionized water that contains 1M of HCl. In this study, three weight ratios of TiO₂ to aniline monomers were used which are 3%, 6%, and 9%. Accordingly, 0.06, 0.12, or 0.18 grams of TiO₂ was added with two grams of aniline monomers to 100 ml of deionized water that contains 1M of HCl. The following steps are similar to those used in preparing pure PANI where the first solution is mixed under a constant speed of magnetic stirrer for one hour. The second solution was prepared by dissolving an amount of 4.56 grams of ammonium persulphate in 100 ml of deionized water that contains 1M of HCl. The solution was mixed under the constant speed of a magnetic stirrer for one hour. Then, the second solution was added dropwise to the first solution which was placed in an ice bath to maintain a temperature of zero to five degree Celsius. The solutions were mixed together for one hour and kept in a desiccator for the next day at a temperature of zero to five degrees Celsius. The mixture was filtered using filter papers No. (f2142), and washed with 100 ml of deionized water followed by 100 ml of methanol. Finally, the product was dried at seventy degrees Celsius in an oven for four hours. The same procedure is repeated for each percentage of TiO₂ in order to produce PANI/TiO₂ 3%, PANI/TiO₂ 6%, and PANI/TiO₂ 9%. This preparation process can be illustrated as follows:



3. Result and Discussion

3.1 UV-Vis Spectra

The UV-Vis spectroscopy is considered to be one of the most important techniques to study the electronic absorption of the conducting polymers and to discover the backbone of the polymer in doping and oxidation state [9, 16].

The absorption spectroscopy was used to analyze the pure PANI and PANI/TiO₂ after being dissolved in the DMSO. The analysis covered the range of the wavelength from 200 to 1200 nm. Figure 2 shows the UV-Vis spectra for pure PANI and PANI/TiO₂ of different percentages.

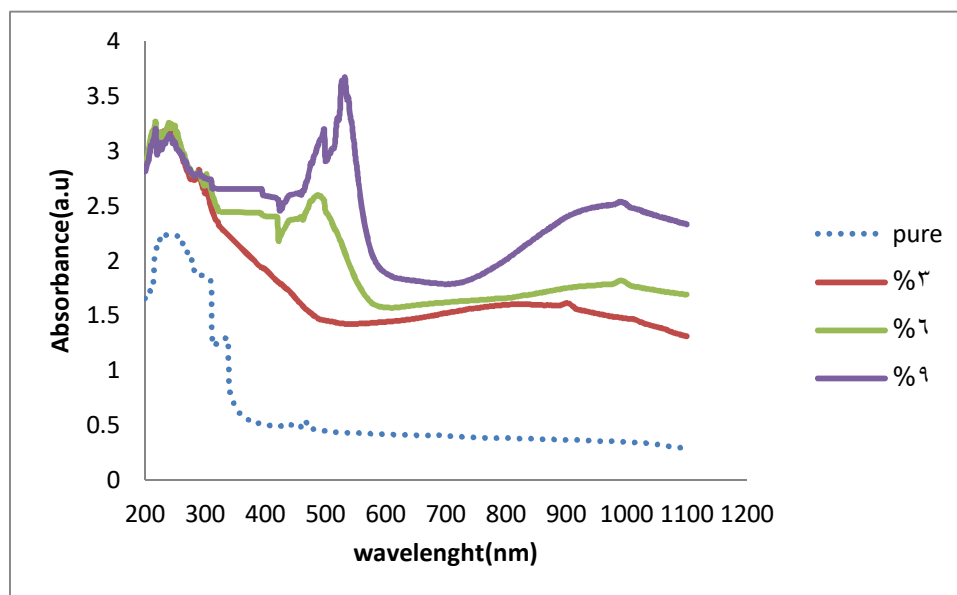


FIG. 2. UV-Vis spectra for PANI and PAN/TiO₂.

In general, the pure PANI shows peaks at a wavelength of 232 nm, 322 nm, and 454 nm. There are two peaks in the UV region and one peak in the visible region; these peaks represent the surface plasmon resonance (SPR) which indicates the more intense absorption reaction between the matter and radiation. The first and second absorption peaks at 232 nm and 322 nm indicate $\pi \rightarrow \pi^*$ transition with the benzenoid ring, which is the excitation state of the nitrogen atom in the benzenoid ring. The third peak, at the wavelength of 454 nm, indicates the quinoid rings [12]. Also, the peak at 454 nm shows the protonation state of PANI and the transition of polaron band- π^* . The phenomenon of polaron/bipolaron transition is found in PANI which is doped with other additives. These results agree with the previous studies [7]. As can be seen in Fig. 2, the sharpness of the peaks

of PAN/TiO₂ increases with the increase of TiO₂ percentage which indicates that there is an increase in the absorption band with the percentage growth of the TiO₂. The absorption peaks at the wavelengths of 472 nm, 488 nm, and 542 nm show the presence of TiO₂ nanoparticles. After calculating the energy of the incident photons ($h\nu$) and ($\alpha h\nu$), Fig. 3 was constructed. This figure can be used to determine the energy gap for each of the prepared polymers. It was found that for Pure PANI, the energy gap is 3.5 eV and it decreases with increasing the percentage of the TiO₂ until it reaches 2 eV at 9% TiO₂. The value of the energy gap is reduced due to the existence of doped TiO₂ cells in the original PANI gap which makes the composite more like a semiconductor media.

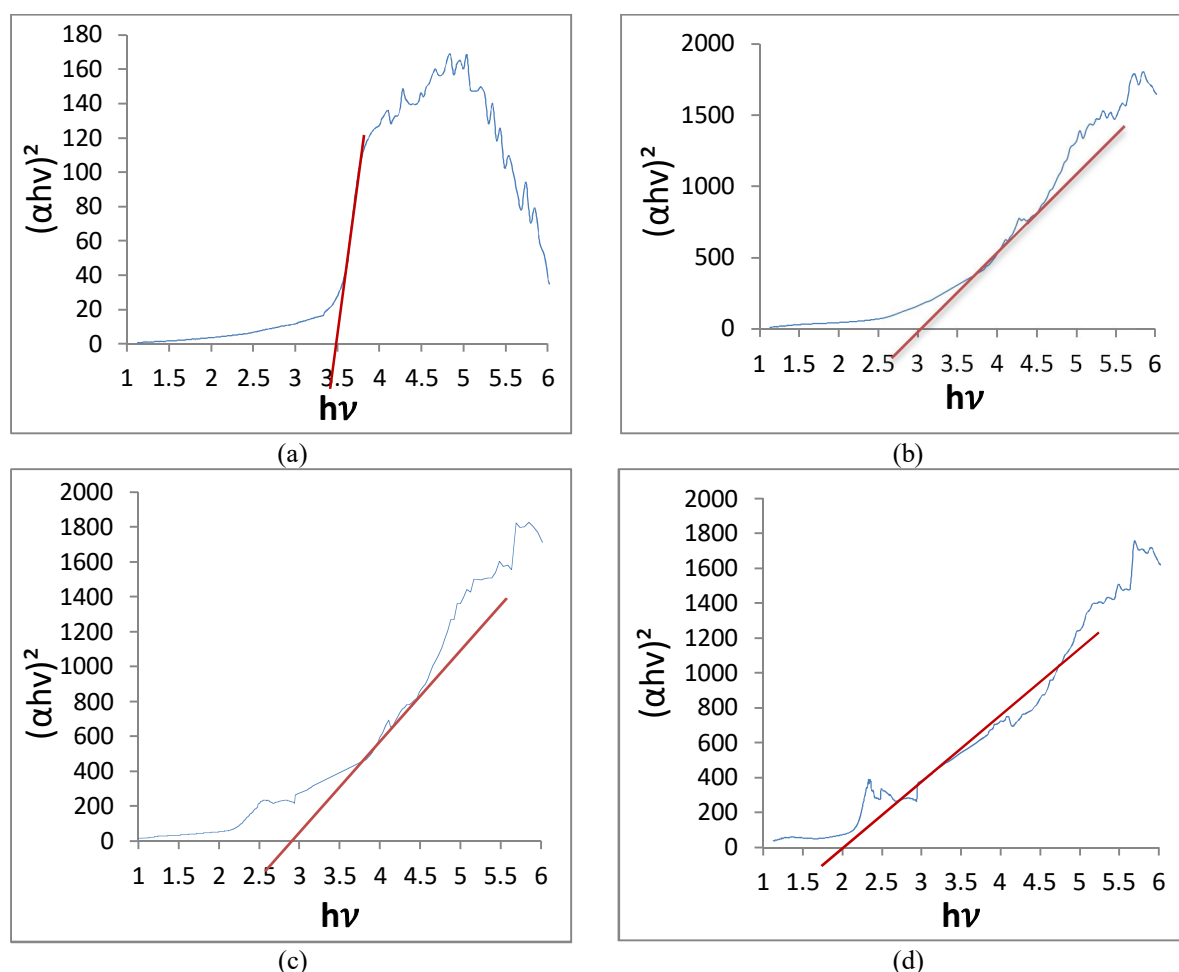


FIG. 3. Tauc plot for the energy of the incident photon ($h\nu$) vs. $(\alpha h\nu)^2$ (a) Pure PANI (b) PANI+3% TiO_2 (c) PANI+6% TiO_2 (d) PANI+9% TiO_2 .

3.2 X-ray diffraction patterns

X-ray diffraction is one of the most unique techniques that characterizes the nature and the structure (amorphous and crystalline) of the material and points to the generated stresses. The XRD for the prepared samples and the used TiO_2 was conducted using a PANalytical x-ray diffractometer with $\text{CuK}\alpha$ wavelength ($\lambda = 1.540598 \text{ \AA}$) and 2θ range from 20-80 degrees. For the TiO_2 , the crystallite size was 3.57 nm and calculated using the Scherrer formula at $2\theta = 25.29^\circ$.

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$

where D is the average crystallite size (\AA), λ the wavelength of X-ray radiation (Cu $\text{K}\alpha$), β the full width at half maximum (FWHM) intensity of the peak, and θ the Bragg diffraction angle.

Figure 4 shows the resulting XRD patterns of PURE PANI, TiO_2 , and PANI/ TiO_2 with different ratios of TiO_2 .

The sharp peaks in Fig. 4 correspond with the peaks of the planes (110), (111), (211), and (101) and these peaks have been identified before as indicators for the crystallinity of Pure PANI and PAN/ TiO_2 [6]. The high peaks at $2\theta = 25^\circ$ indicate the presence of pure PANI chain and the peaks at $2\theta = 25.55^\circ$, $2\theta = 37.65^\circ$ and $2\theta = 48.35^\circ$ refer to the presence of TiO_2 anatase according to standard JCPDS card No. 21-1272. The TiO_2 anatase is one of the TiO_2 forms that is metastable at all pressures and temperatures and its crystallization system is tetragonal [17]. When the PANI is doped with TiO_2 anatase nanoparticles, the peaks of pure PANI overlap with the peaks of TiO_2 at $2\theta = 25^\circ$. These results agree with the reference [18]. The growth of the peaks' intensity seen in the y-axis indicates the increase in the matter concentration.

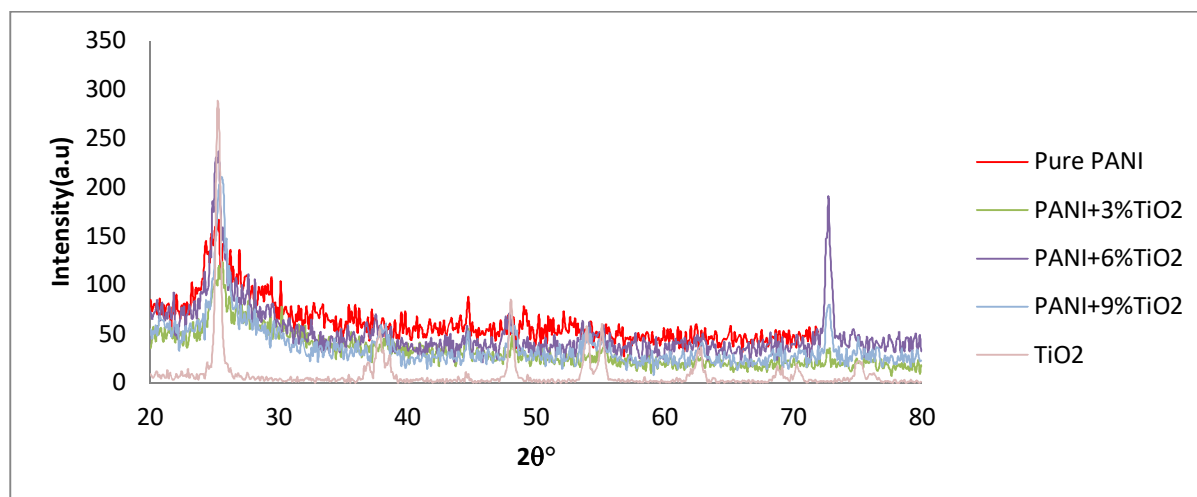


FIG. 4. XRD Patterns for PANI, TiO_2 and PANI/ TiO_2 with different ratios of TiO_2 .

3.3 FT-IR Spectra

The chemical structure and the chemical bond established were investigated by FT-IR Spectroscopy. Figure 5 illustrates the bands of PURE PANI, the $\text{C}=\text{C}$ at the bands 1477 and 1585 cm^{-1} indicates the quinoid and benzenoid rings at the vibration stretching mode of $\text{C}=\text{C}$. The quinoid ring was found at the wavenumber of 1301 cm^{-1} which indicates the presence of a $\text{C}-\text{N}$ bond. The bands at 1477 , 1301 , and 1141 cm^{-1} refer to the polyaniline salts. The band at 1301 cm^{-1} indicates the presence of delocalized

induced π -electrons in the polymer chain as well as the stretching vibration of $\text{C}-\text{N}$ secondary aromatic amine. The band at 1543 cm^{-1} indicates the stretching mode of $\text{C}=\text{N}$. The peaks around 1297 cm^{-1} and 1299 cm^{-1} represent the $\text{C}-\text{N}$ stretching mode as well as the protonation state of PANI. The $\text{O}-\text{H}$ of absorbed water molecules at the band from 1600 cm^{-1} and above represents the bending vibration of $\text{O}-\text{H}$. The vibrations of $\text{N}-\text{H}$ bonds occur in the range of $3000\text{ cm}^{-1} - 3500\text{ cm}^{-1}$.

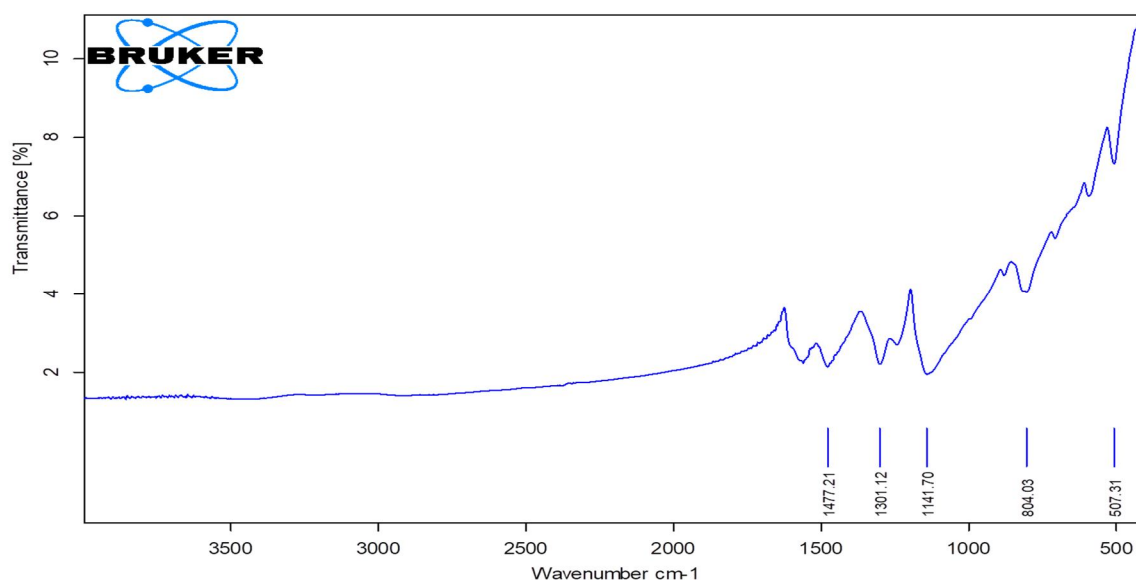


FIG. 5. FT-IR spectra for PURE PANI.

3.4 SEM

The particles size and the morphology of PANI and PANI/ TiO_2 with different ratios of TiO_2 nanoparticles were observed using SEM as shown in Fig. 6. The first observation from this

figure is the different particle sizes at different TiO_2 percentages with the biggest particle size of the PURE PANI and the smallest particle size of the compound with the highest TiO_2 percentage. This difference may result in different mechanical properties, however, this was not

investigated as it is out of the scope of this study. The Energy Dispersive X-Ray Spectroscopy EDS for different regions on the PANI/TiO₂ of different percentages shows the existence of Ti which reveals the homogenous distribution of TiO₂. Through the polymerization reaction, most of the TiO₂ nanoparticles were capsuled with PANI and this led to that granular particles. The PURE PANI has a spherical grain-shaped morphology with an inhomogeneous distribution and some pores or cavities according to SEM image examinations of the PURE PANI and PANI/TiO₂. The PANI/TiO₂, on the other hand, has a granular morphology with uniform dispersion and negligible cavity or porosity. The spherical shape of TiO₂ particles can be seen all around the PURE PANI surface. During the synthesis process, the spherical shape of TiO₂ appears to be fused with a surface of PURE

PANI via an adsorption mechanism. This method will cause agglomeration in the PANI/TiO₂ structure. TiO₂ nanoparticles are generally aggregated because of the high surface energy. An increase in TiO₂ content may have induced a relative decrease in PANI content, resulting in a decrease in composite particle diameter. The SEM images supported the finding that TiO₂ doping had a significant impact on PANI morphology and that as the TiO₂ level increased, the composite morphology changed from normal fibrous PANI to particles. The results demonstrate that TiO₂ nanoparticles are more agglomerated, whereas TiO₂ nanoparticles modified by PANI (PANI/TiO₂ nanocomposites) are more separated. The PANI on the surface of TiO₂ nanoparticles might be developed, resulting in repulsion between nanoparticles and preventing agglomeration.

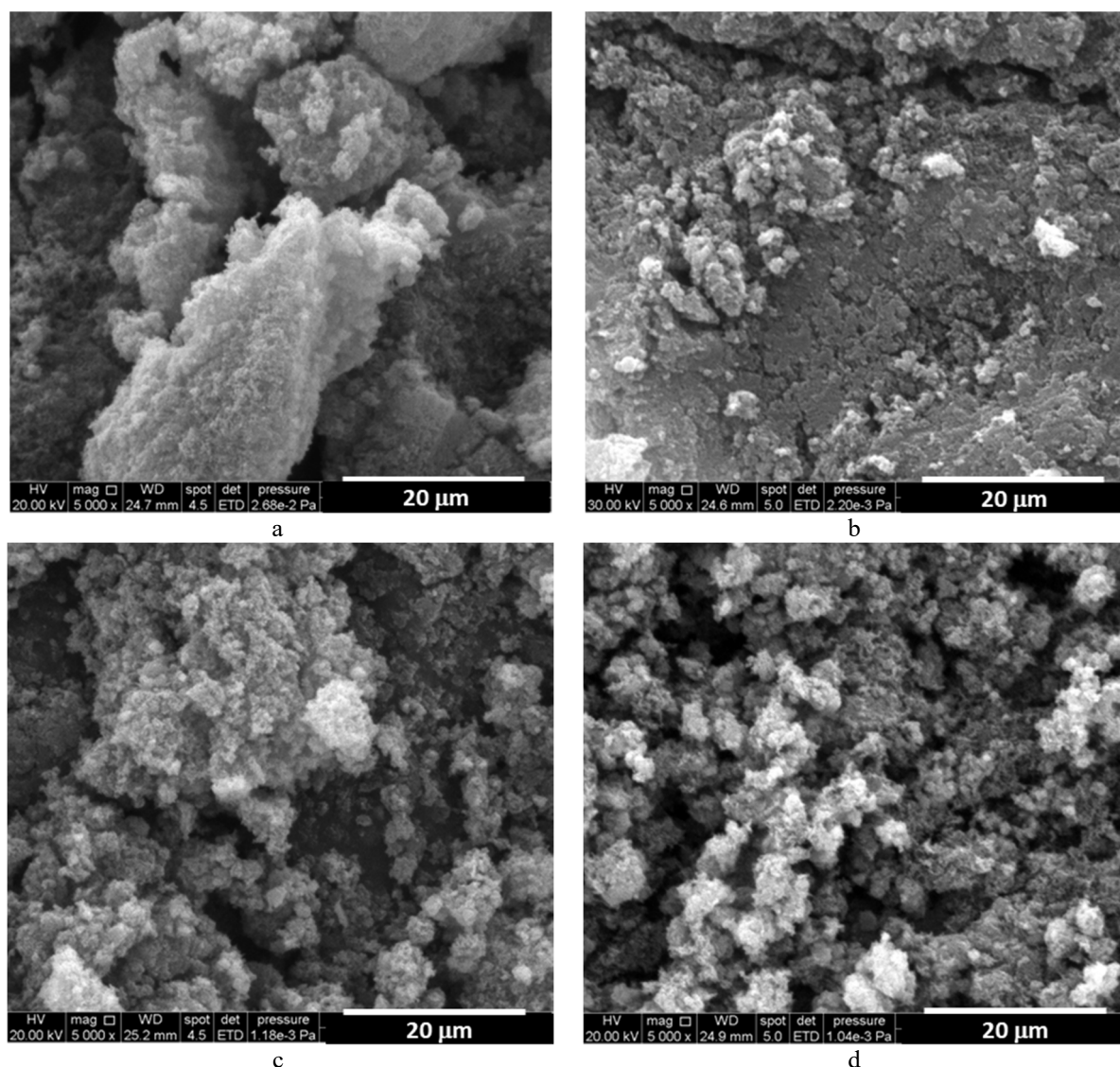


FIG. 6. SEM images for the prepared PANI (a) Pure PANI (b) PANI+3%TiO₂ (c) PANI+6% TiO₂ (d) PANI+9% TiO₂.

4. Conclusions

The main conclusions based on the findings of the current study can be summarized in the following points.

- 1- The energy gap decreases with increasing the percentage of the TiO₂ in the PANI+%TiO₂ composite until it reaches 2 eV at 9% TiO₂. The PANI composite may transport to an effective semiconductor which can be used as a gas sensor where adding ratios of TiO₂ to the PURE PANI makes it more structurally stable as the orientation peaks take higher values.
- 2- The UV-Visible spectrum of PURE PANI and PANI with different concentrations of TiO₂ displayed many peaks in different locations. These peaks illustrated the benzenoid and quinoid rings as well as interference between the TiO₂ nanoparticles and the polymer chain peaks. These peaks were changed to higher wavelengths as TiO₂ was added to the PANI chain.
- 3- XRD results showed that PURE PANI is crystalline and it shows sharp peaks. The XRD results exhibited higher crystalline peaks for PANI+TiO₂ due to the influence of TiO₂ nanoparticles. Also, it is observed that the intensity of the XRD peaks increases by increasing the percentages of TiO₂.
- 4- The SEM illustrated the morphology of the PURE PANI with different percentages of TiO₂. It is observed that there is interconnecting between TiO₂ and PANI. The spherical shape of TiO₂ particles can be seen all around the PURE PANI surface. During the synthesis process, the spherical shape of TiO₂ appears to be fused with a surface of PURE PANI via an adsorption mechanism. This method will cause agglomeration in the PANI/TiO₂ structure. TiO₂ nanoparticles are generally aggregated because of the high surface energy.

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