

Structure and optical properties of polyaniline-based hybrid nanocomposites by chemical oxidative method

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Titanium - polyaniline nanocomposites were prepared using polymerization of aniline. Structure (XRD), surface (SEM, AFM), chemical (FTIR) and optical (UV-Spectrophotometer) properties have been examined. The X-ray diffraction pattern observed the PANI/TiO₂ has a crystalline nature and the peak intensity increases with TiO₂ composition ratio, the results of SEM & AFM images show the surface of TiO₂-polyaniline have regular distribution and homogeneous structure. Furthermore, the grain size increases with increasing of TiO₂ compositions and was found to be 32.58nm, 36.21nm and 47.67 nm at x= 0.2, 0.5 and 0.8 respectively. Additionally, optical properties show that the absorption intensity increases with TiO₂ compositions compared to pure TiO₂. Hybrid of TiO₂/PANI has a vast attracted attention especially to improve photocatalytic activity. Simple design and high quality of nanocomposites play a crucial role in improving mechanical and physical properties.

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1. Introduction

Polyaniline (PANI) is conductive polymer and is polymerized from the monomer aniline[1]. Organic polymer is one of the most important discoveries that changed the conductive polymers' outlook. Shirakawa, Alan Heeger and Mac Diarmide discovered conductive polymers and were awarded the Nobel prize in physical chemistry in 2000 [2,3]. In fact, the development of polymeric materials began with the discovery of conductive polymers. Furthermore, progress in developing successive organic conductive polymers was widespread. Although conductive polymers are not metallic materials, successive polymeric chains have a higher regularity than other polymeric materials [4,5,6]. The organic polymer has an excellent optical, electrical, and mechanical properties, which open the door for broad applications. Polyaniline has been used in many applications especially in electronic devices as solar cells[7], sensor technology emitting diodes[8], photovoltaic [9] and batteries [10]. Polyaniline has non-toxicity and good stability[11]. Recently, extensive studies focused on the hybrid of titanium nanocomposites with conductive polymers [12]. Preparation conditions significantly affect the optical and structure properties[13]. New days, several works attracted attention to investigate TiO₂-PANI. Mohammad et al. in 2009 has prepared polyaniline/TiO₂ nanocomposites using chemical technique [14]. Moreover, Nur Aziera et al. in 2017 studied the photocatalytic properties of PANI-TiO₂ with different ratio [15]. Shepherd and Kriveshini in 2020 formed nan rods of titanium coated to polyaniline[16]. The objectives of this study are to describe the structure (XRD), chemical (FTIR), the morphological properties (AFM& SEM) and UV-Vis Spectrophotometer of the nanocomposites.

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2. Experimental part

Polyaniline has prepared by oxidation polymerization , pure aniline was dissolved in (15 ml) with (650 ml) from (2M) HF solution using the magnetic stirrer with cooling of a temperature at 5°C using an ice bath using simple distillation method. Ammonium persulfate solution (28.2 gm) was dissolved with (300 ml) of (1M) hydrochloric acid using the magnetic stirrer at 15 min. by separating funnel with continuous stirring within 2 hr. Additionally , the precipitate formed was filtered using a Buchner funnel, then the precipitate was dried to find blue crystals of pure polyaniline. Figure (1) shows the oxidation diagram of aniline during the polymerization process and the chemical formula of pure polyaniline. Before starting the doping process, the polymer grins using a special mortar and pestle. Doping process is done by mixing by taking different weight percentages $x=0.2,0.5$ and 0.8 from TiO_2 nanocomposites; the total weight is then mixed using the particular mill for a period of 5 min to obtain a powder of a high degree of fineness.

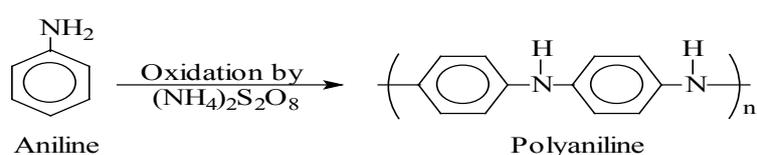


Fig. 1. Diagram of polymerization of aniline [17].

3. Results and discussion

Figure 2 illustrates XRD patterns of TiO_2 and $TiO_2/PANI$, polymer has crystalline properties in nature due to the presence of huge quinonoid and benzenoid chains in the polyaniline. The strong peaks were observed at $2\theta = 26.73^\circ, 38.33^\circ, 41.81^\circ$ and 43.52° corresponding to (101), (103), (020) and (200) respectively[18]. There are two crystal phases of TiO_2 anatase and rutile, Crystallinity intensity and increases with extent TiO_2 nano compositions. This can be seen to more doping extent of TiO_2 in PANI chains and can be referred to an increase in the size of the crystals [19].The doping of titanium nanocomposite in the polyaniline did not shift the position diffraction peaks of PANI chain. The grain size was calculated by the Scherer equation[20].

$$L = \frac{k\lambda}{B\cos\theta} \quad (1)$$

where B is the half maximum of the full width, $k= 0.9$ constant of Bragg

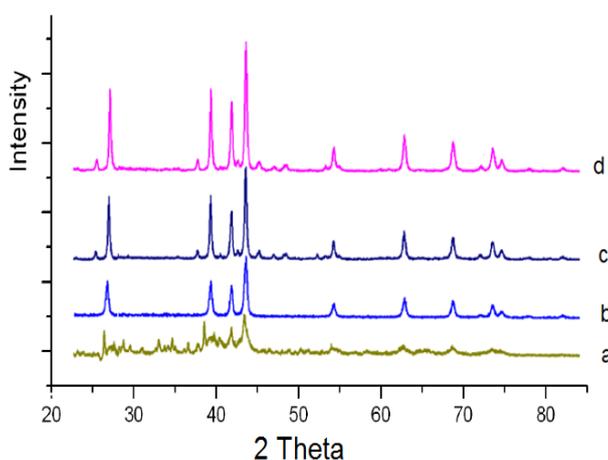


Fig. 2. XRD pattern (a) PANI, (b) $x=0.3$, (c) $x=0.3$, (d) $x= 0.7$ of TiO_2 nano composites.

Table 1. Grain size, compositions, FWHM, distance (d) of pure PANI and TiO₂/PANI.

Sample	Compositions (x)	L (nm)	FWHM (deg)	d (Å°)
PANI	0	14.66	0.754	1.723
TiO ₂ /PANI	0.2	31.78	0.563	1.611
TiO ₂ /PANI	0.5	34.65	0.531	1.526
TiO ₂ /PANI	0.8	45.78	0.411	0.188

3.1. Surface properties

Scanning Electron Microscopy images were subjected to understand the surface make up. Figure 3a shows that Polyaniline was good shape due to presence of aniline moiety and interaction π - π^* of molecule for benzenoid group [21]. Polyaniline and TiO₂ nanocomposite were performed, TiO₂ nano composition revealed uniform thin nanosheets shape. Titanium oxide was mixed on Polyaniline edged. Polyaniline becomes more crystalline with increasing doping for all the nano compositions of TiO₂. The presence of TiO₂ embedded inside the surface of polyaniline have regular geometry and have sharp edges with nucleation, which can be credited to an increase in the length of the polymer chain, these results are in agreement with the previous works [22]. The larger particle size was observed a spherical shape and a gradual increase with increasing of compositions TiO₂ in the range of 32.58nm - 47.67 nm due to the surface rebuilding as Figure 3 (b,c and d).

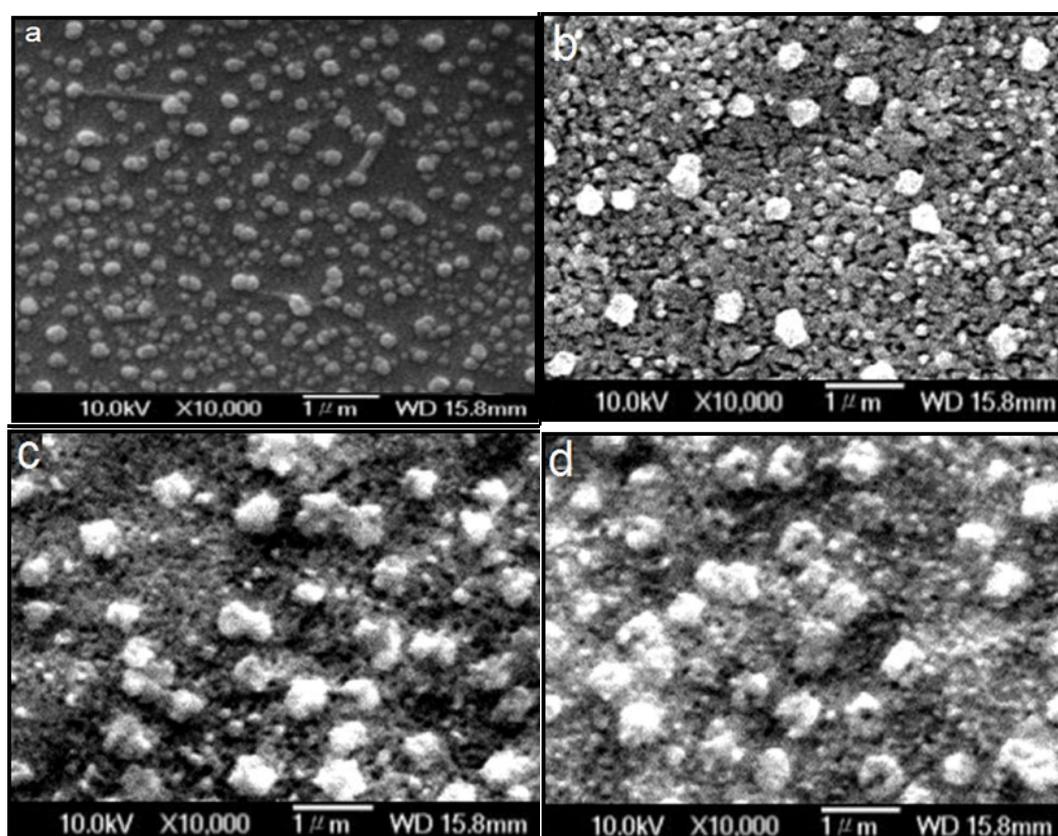


Fig. 3. SEM images (a) PANI, (b) $x=0.3$, (c) $x=0.4$, (d) $x=0.7$ of TiO₂ nano composites.

The atomic force microscope technique gives us information about sample surface features. Figure 4 shows AFM imaging of the sample surface. The surface roughness rate of Polyaniline and the mean square root were found (0.723 nm) and (0.837) respectively, as shown in Figure 4a. Figure 4 (b,c and d) shows nanocomposites of TiO₂ embedded into PANI. The surface roughness rate of TiO₂/polyaniline was found (0.676 nm), (0.632nm) and (0.585nm) for x= 0.2, 0.5 and 0.8, respectively, it can be seen granular interference, formed by grooves and part of which appears in large conglomerates and spherical -like structure [23]. The surface roughness rate decrease with increasing compositions of TiO₂.

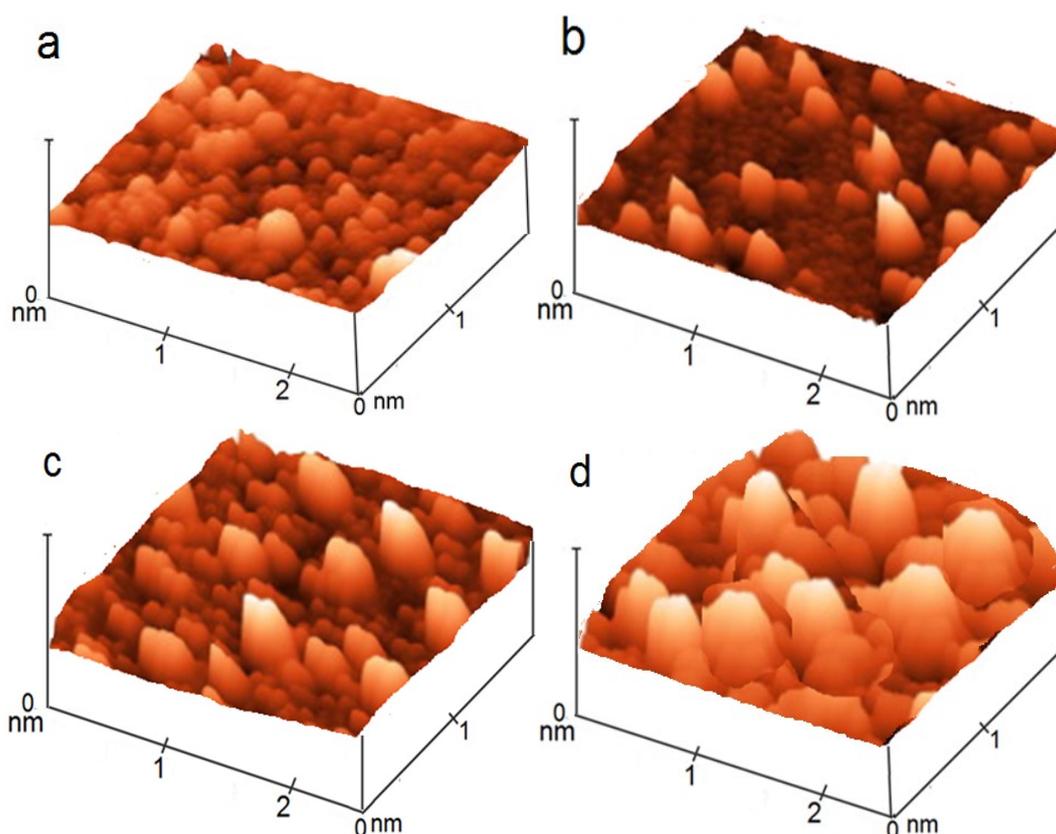


Fig. 4. AFM images (a) PANI, (b) x=0.3, (c) x=0.4, (d) x= 0.7 of TiO₂ nano composites.

3.2. Chemical properties

FTIR spectroscopy is used to determine the chemical bonds, transmission FTIR spectra of pure polyaniline and PANI with titanium nano composition are shown in Figure 5. The main peaks of polyaniline appeared at 1577, 2256 and 3412 cm⁻¹. The band 3412 cm⁻¹ corresponded to the stretching of N-H sp³ band. the peaks 2256 cm⁻¹ and 1577cm⁻¹ are attributed to benzenoid group and C-H, respectively [24]. The FTIR spectra of the titanium nanocomposites have superior intense, the band 645 cm⁻¹ corresponded to the Ti-O stretching vibration for a tetrahedral surrounding of the titanium atoms. We see the spectral consist many other bands, this bands come from non-purity O=H hydroxyl groups due to indicate the existence water adsorbed on the surface as the peak 1577 cm⁻¹. Furthermore, aromatic C=C stretching mode correspond to the peaks at 2256 cm⁻¹ and 3412 cm⁻¹ adsorbed on the photo catalyst surface [25].

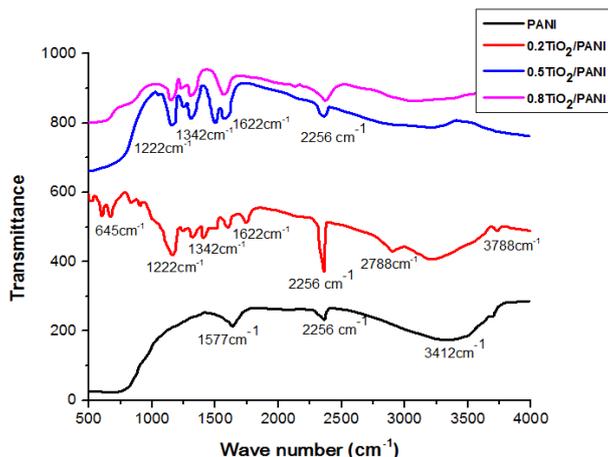


Fig. 5. Transmittance against wave number of the PANI and the TiO₂ nano composites.

3.3. Optical properties

Figure 6 optical absorbance spectra were carried out for PANI, TiO₂-PANI of compositions $x=0.2, 0.5$ and 0.8 . Titanium nanocomposite samples have stronger absorption compared to pure polyaniline in the UV region. Furthermore, the intensity increases with the composition of titanium. Absorption edges were about 420 nm for pre-polyaniline and TiO₂-PANI samples due to the polaron- π^* interaction of the quinoid chain[23]. The UV-Vis spectra suggested that PANI could be an effective photosensitizer for TiO₂ [26].

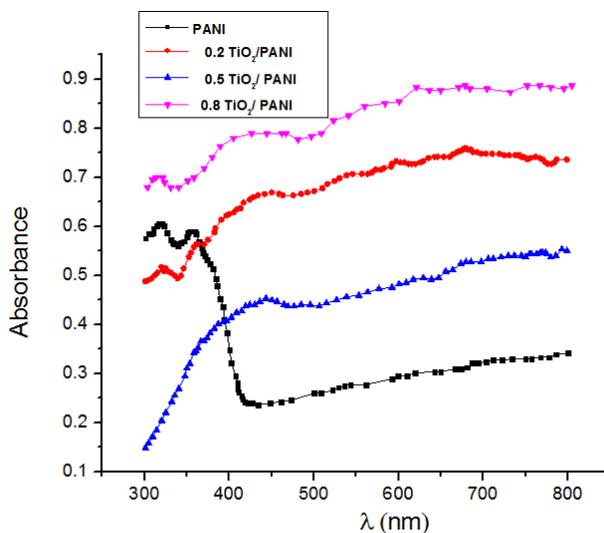


Fig. 6. Absorbance against wavelength (a) PANI, (b) $x=0.2$, (c) $x=0.5$, (d) $x=0.8$ of TiO₂ nano composites.

The energy gap can be determined using the relation[27]

$$\alpha = (h\nu - E_g)^{1/2} \quad (1)$$

where α is the absorption coefficient and $h\nu$ is photon energy. The plots of α^2 vs $h\nu$ for PANI and TiO₂-PANI nanocomposite are given in Figure 7 the band gap of the pure TiO₂ was greater than that of the TiO₂-PANI for all the compositions. The band gap continuously decreased from 1.95

eV for pure TiO₂, 1.53eV for x=0.2, x=0.5 for 1.73 eV and x= 1.43eV for x=0.8 .Band gaps of all the compositions of -TiO₂-PANI lie in the semiconductor range which makes them suitable for light sensor applications [28,29,30,31,32].

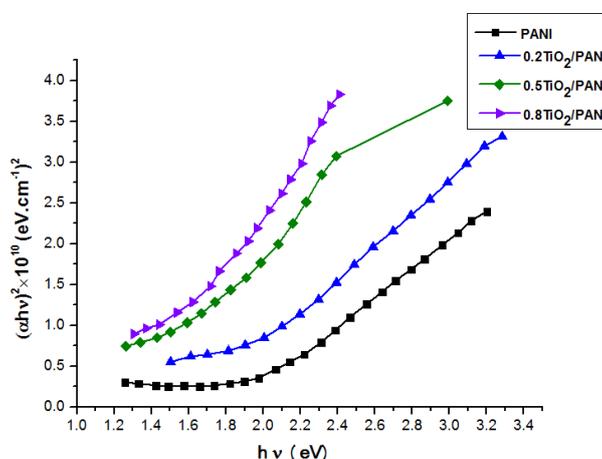


Fig. 7. $(\alpha hv)^2$ against $h\nu$ (a) PANI, (b) $x=0.2$, (c) $x=0.5$, (d) $x=0.8$ of TiO₂ nano composites.

4. Conclusion

As a general summary of this work, hybrid TiO₂/ PANI nanocomposite was prepared by polymerization. Surface of PANI depends on the preparation conditions. The surface of the hybrid TiO₂/ PANI has homogeneous structure with increasing of TiO₂ nanocomposite. Values of band gap for various nano compositions of TiO₂ were determined for both PANI and TiO₂/PANI. The band gap values decreased with increasing of TiO₂ nano compositions from 1.95 eV to 1.43eV. TiO₂/PANI nano compositions have strong absorption compared to pure TiO₂. This makes them suitable for light sensor applications and as photodiodes. This can open the possibility of improving the properties of the samples.

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