Solid-state synthesis of PANI-TiO₂ nanocomposite: Investigation of reaction conditions, nature of oxidant and electrical properties

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Abstract. In the present work, polyaniline-titanium (IV) oxide (PANI-TiO₂) nanocomposites have been synthesized by solid-state (solvent-free) oxidative polymerization method of aniline as a monomer under green condition using both iron (III) chloride hexahydrate (FeCl₃·6H₂O) and ammonium peroxydisulfate (APS) as two different type of the oxidants as well as various modes and increasing of the ratios of monomer to oxidant. The structural and morphological of the nanocomposites have been characterized using kinetic and microscopic analysis. The electrical conductivities, cyclic voltammetry, bandgap energy (E_g), and morphology of the nanocomposites are mainly dependent on the type of oxidants and reaction conditions. Also, the nanocomposites were shown electro-active and functional properties. The I–V characteristics of PANI-TiO₂ in an Al/(PANI-TiO₂)/TiO₂/FTO solar cell are achieved by drawing the plot of the I–V curves. It is noted that nanocomposites with different conditions were shown similar FT-IR and UV-Vis spectra with different morphologies. The TEM images in different conditions showed a thin layer of TiO₂ nanoparticles in the outer wall of the nanotube when the APS was used as the oxidant, while when the FeCl₃ was used as the oxidant, the TiO₂ nanoparticles have been distributed on a plantain leaf of PANI matrix. The XRD results confirm completely results obtained from TEM. As a result, the nanocomposites with both methods showed a good P–N junction between TiO₂ and PANI.

Keywords: nanocomposites, solid-state synthesis, PANI-TiO₂, solar cell, nanotube and plantain leaf morphologies

1. Introduction

Organic material with a distinctive group of conjugated double bonds along the polymer backbone named a conductive polymer (CP) because it can be conduct electricity. In recent years, attraction toward to CPs is focused because upon partial oxidation–reduction it replace metals and act as conductors such as in lithium batteries and bioengineering [1, 2]. On the other hand, the appearance of nanoscience has rejuvenated the field of CPs with potential applications

ranging from flexible wearable electronic fields to transparent solar cells [3–7]. Moreover, CPs is inexpensive and easy to synthesize [8–10]. Specifically, polyaniline (PANI) has very attractive features among polymeric materials, such as a particular combination of highly stable conductivity and facile synthesis. Moreover, the optical and mechanical properties of PANI are available in a wide range of nanostructures [11–13]. One of the methods used to eliminate some of the disadvantages of polyaniline is the

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preparation of its nanocomposite [14, 15]. Recently, nanocomposites of organic polymer–inorganic nanoparticles have been considered due to their typical properties of the polymer and inorganic nanoparticles [16–25]. Encapsulating nanoparticles inside a layer of the conductive polymer is one of the essential aspects of nanocomposite preparation [26, 27]. Among the nanoparticles, titanium dioxide nanoparticles have been considered very much due to their unique chemical and physical properties [28–30]. Then, scientists have developed the synthesis of PANI–TiO₂ nanocomposites in a sol–gel method [31–34]. Many nanocomposites were prepared by chemical and electrochemical processes under challenging conditions. However, researchers are working to propose an easy way and mild condition for their preparation [21, 35–38]. Some researchers recently have reported the PANI–TiO₂ nanocomposites by an oxidative chemical polymerization method under solution condition and investigated optical and morphological properties and their applications as an efficient catalyst for the degradation organic pollutants under the visible light [19, 39], and for photoelectrochemical water splitting [37]. Furthermore, the various PANI–TiO₂ nanocomposites have been synthesized and investigated optical and morphological properties and their application as a counter electrode in dye–sensitized solar cells (DSSC) [40–45]. Moreover, the solution synthesis, the optical and morphological properties, and the application of different kinds of PANI–TiO₂ nanocomposites have been investigated in P–N heterojunction diodes [46–48]. This study presents a very simple but highly effective strategy for the synthesis of PANI–TiO₂ nanocomposites with different oxidants via a solid–state reaction method at room temperature. The method involves only mixing and rubbing of the TiO₂, oxidant, and aniline together in the solid–state. Since a significant role of oxidants in the morphology and the polymerization of PANIs cannot be underestimated, it is important to study the effects of the oxidants in preparation of PANI–TiO₂ nanocomposites. In this paper, nanocomposites PANI–TiO₂ were prepared through solid–state synthesis under green condition by using two various oxidants iron (III) chloride hexahydrate (FeCl₃·6H₂O), and ammonium peroxydisulfate (APS) and the effect of oxidant types on the properties of the obtained nanocomposites were investigated.

2. Experimental

2.1. Materials and equipment

Aniline hydrochloride (PhNH₃Cl), titanium (IV) oxide (TiO₂, anatase, and rutile) iron (III) chloride hexahydrate (FeCl₃·6H₂O), and ammonium peroxydisulfate (APS) were purchased from Sigma–Aldrich (USA) and Merck (Germany) companies and used as received. Fourier–transform infrared (FT–IR) spectra of the polymers were obtained by using a JASCO spectrum 2000 spectrophotometer using KBr pellets (frequency range 4000–400 cm^{–1}, USA). Absorption measurements of the samples in formic acid (FA) and *N*-methyl–2–pyrrolidinone (NMP) were done using UV–Vis spectrophotometer (PG Instrument Ltd. – Model T90+, Japan) in the range of 200–1200 nm. EDX spectra and SEM micrographs were obtained with a ‘Cambridge S–360 scanning electron microscopy’ (England). Electrochemical characterizations were carried out by an electrochemical workstation (SAMA, 500 electro analyzer, Iran). Transmission Electron Microscopy (TEM) images were acquired on a Philips CM–10 at 300 kV (Netherlands). X–ray diffraction (XRD) pattern was analyzed using XRD (GBC MMA instrument, Australia) with Cu–K α radiation (λ = 0.15418 nm) in the 2 θ range 10–80°. The conductivity of the nanocomposites was determined by using the four–probe technique at room temperature (Iran, Zahedan). The current–voltage characteristics were obtained by applying an external potential bias to the device and measuring the generated photocurrent with an I–V tracer (IV–25, Iran). Elemental analyses were determined by an Elemental Combustion System (ECS) 4010 (Costech Instruments, USA).

2.2. Methods

2.2.1. Synthesis of PANI–TiO₂ nanocomposites

Aniline hydrochloride was reacted in the solid–state gradually with oxidants: APS and FeCl₃·6H₂O. A typical solid–state synthesis of PANI–TiO₂ nanocomposites is explained as follows: In order to prepare the nanocomposite **4** as instant, TiO₂ (0.5 g) was ground to a fine powder using mortar. Then, the aniline hydrochloride monomer (1.667 mmol, 0.2160 g) was added slowly and ground. The oxidant (APS, 2.083 mmol, 0.4753 g) was then added in lower feed to the reaction mixture at room temperature and ground for 40 min until the color of powder changed

to green. The polymerization reaction was completed after 72 hr. After the polymerization reaction, the resultant residual was filtered and washed successively by double distilled water repeatedly until the filtrate turned colorless, and then the powder dried in an oven at 60 °C for 48 h and the green-black precipitation obtained. The polymerization process is shown in Figure 1. This general synthesis method was used to synthesize other nanocomposites 5–9 with the difference in the order of the addition of reactants (monomer, oxidant, and TiO₂). Table 1 shows the summary of conditions used for the one-step preparation of nanocomposites 4–9.

2.2.2. Simple preparation of solar cell

Al/(PANI–TiO₂)/TiO₂/FTO

The TiO₂ paste was deposited as a layer with light reflection capability on FTO (as the anode) by a modified Dr. Blade technique [21]. Then, the synthesized polymer dissolved in the NMP solvent and a thin

film of it was placed on the FTO–TiO₂ by Dr. Blade's method. Finally, Al plate (as the cathode) was placed on the active layer surface to form a sandwich-type structure. The dimension of the cells was 1 cm², and the made cell was characterized by a solar simulator with power intensity 60 mW·cm⁻² supplied by a Xenon lamp (200 W). The *I/V* curves have been obtained, and the solar efficiencies have been calculated for each design mentioned.

3. Results and discussion

3.1. FT–IR spectroscopy

Figure 2 shows the FT–IR spectra of pure TiO₂ and PANI–TiO₂ nanocomposites 4–9, and their main peaks are summarized in Table 2. The FT–IR spectrum of the TiO₂ exhibits broad bands at 688 and 3435 cm⁻¹ that is corresponding to Ti–O–Ti network and O–H stretching vibration. As observed in Figure 2 the FT–IR spectra of nanocomposites 4–9 are similar, and it proves that the chemical structures of the nanocomposites are the same. The main characteristic bands of nanocomposite 4 are assigned as follows: absorption peaks at 1568 cm⁻¹ (the aromatic C=C and C=N stretching of the quinonoid N=Q=N rings), 1488 cm⁻¹ (the aromatic C=C stretching of the benzenoid N–B–N rings), 1300 cm⁻¹ (the C–N stretching of the secondary aromatic amine), 1243 cm⁻¹ (the –C–N⁺H– stretching), 1125 cm⁻¹ (the =N⁺H– stretching), and 818 cm⁻¹ (the aromatic C–H out-of-plane deformation vibration) due to the existence of PANI in nanocomposites. Also, in PANI–TiO₂ nanocomposites, the bonds of TiO₂ are visible in 663 cm⁻¹. Clearly, the position of the peaks associated with PANI is impressed by the content of TiO₂. Specifically, the

Figure 1. Synthesis of nanocomposites 4–9.

Table 1. The summary of conditions used general method in synthesis of nanocomposites 4–9.

Nanocomposite	4	5	6	7	8	9
TiO ₂ (1)	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g	0.5 g
Aniline hydrochloride (monomer) (2)	1.667 mmol, 0.2160 g	1.667 mmol, 0.2160 g	1.667 mmol, 0.2160 g	1.667 mmol, 0.2160 g	1.667 mmol, 0.2160 g	1.667 mmol, 0.2160 g
APS (oxidant) (3a)	2.083 mmol, 0.4753 g	2.083 mmol, 0.4753 g	2.083 mmol, 0.4753 g	–	–	–
FeCl ₃ ·6H ₂ O (oxidant) (3b)	–	–	–	4.17 mmol, 1.1272 g	4.17 mmol, 1.1272 g	4.17 mmol, 1.1272 g
[Ox]/[M]	1.25	1.25	1.25	2.5	2.5	2.5
The overall testing process	(1+2)+3a	(1+3a)+2	(1+2+3a)	(1+2)+3b	(1+3b)+2	(1+2+3b)
The color of the reaction mixture after 5 minutes grinding	Clear green	Clear green	Clear green	Clear green	Clear green	Clear green
The color of polymer-bw	Dark green	Dark green	Dark green	Dark green	Dark green	Dark green
Total reaction time [hr]	72 hr	72 hr	72 hr	72 hr	72 hr	72 hr
The color of polymer-aw	Dark green	Dark green	Dark green	Dark green	Dark green	Dark green
Temperature	R.T.	R.T.	R.T.	R.T.	R.T.	R.T.

Figure 2. FT-IR spectra of TiO_2 (1) and nanocomposites (4–9).

peaks corresponding to the quinonoid (Q) and benzenoid (B) rings shifted to higher wavenumbers in the nanocomposite containing TiO_2 relative to PANI without TiO_2 , which indicated some interactions existed between PANI and TiO_2 particles in these hybrid nanocomposites, as it is shown in Figure 1. Furthermore, during the polymerization process, some of the nitrogen atoms in PANI are probable to form

coordinated nano-compounds with the exposed titanium atoms on the surface of TiO_2 . The ionic (or covalent) bonding between the titanium and the nitrogen as well as hydrogen bonds (shown in Figure 1) would limit the vibrational movements of the polymer chain structure. In addition, the nature of the electron emission of TiO_2 may transfer some of the electrons around the nitrogen in the PANI [35]. These phenomena probably cause observed chemical shifts of the quinonoid and benzenoid peaks to the side higher wavelengths in the FTIR spectra. Thus, the FT-IR result confirms the presence of TiO_2 and the formation of new hybrid organic-inorganic nanomaterials [35, 49–52].

Also, based on Figure 2, the main difference in the spectra of the nanocomposites 7–9 obtained with oxidant APS and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was found in the region of $1545\text{--}1450\text{ cm}^{-1}$ (Q and B rings). These bands were shown a blue-shift for nanocomposites 4–6 that obtained with APS oxidant when compared with nanocomposites 7–9 that obtained with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ oxidant. This behavior was because of the different degrees of doping in these two oxidants. On the other hand, the slight difference between nanocomposites with oxidant APS and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ spectra in the region of 1300 and 1100 cm^{-1} is attributed to the influence of the counter-ion group vibrations in the polymer backbone [53, 54].

Furthermore, in sample 8, the O–H broad band ($3200\text{--}3600\text{ cm}^{-1}$) intensity is much more than other samples. This result indicates that Fe ions may be linked with the surface; OH groups that hinder the loss of OH groups upon the formation of PANI and washing by water in workup. In fact, it can confirm the Fe^{3+} adsorption on the surface of TiO_2 nanoparticles in the nanocomposite 8. As reported elsewhere [55] under visible light irradiation Fe^{3+} ions can improve the photocatalytic activity of TiO_2 , Fe^{3+} ions

Table 2. Main bands [cm^{-1}] in FT-IR spectra of TiO_2 1 and PANI- TiO_2 nanocomposites 4–9.

Description	TiO_2	4	5	6	7	8	9
O–H and N–H	3435	3414	3396	3415	3384	3401	3429
C=N and C=C of quinonoid rings	—	1568	1567	1561	1554	1554	1557
C=C of benzenoid rings	—	1488	1483	1477	1452	1459	1460
C–N (the secondary aromatic amine)	—	1300	1301	1300	1281	1290	1294
–C–NH $^+$ –	—	1243	1250	1245	1241	1250	1243
=N $^+$ H–	—	1126	1125	1122	1118	1115	1120
C–H (out-of-plane)	—	818	820	820	812	813	813
Ti–O–Ti	688	663	667	662	675	672	672

can form complexation with hydroxyl groups bound to TiO_2 surface, upon illumination such complexation favors the formation of hydroxyl radicals ($\text{OH}^\bullet$).

3.2. UV–vis spectra and optical band gap energy (E_g^{Opt})

The UV–vis absorption spectra of PANI– TiO_2 nanocomposites 4–9 are given in Figure 3 and the data are given in Tables 3 and 4 in NMP and formic acid (FA) solutions, respectively. Two characteristic absorption peaks at ~ 305 – 340 and ~ 615 – 640 nm (Table 3 and Figure 3a) were observed in the NMP solvent. The absorption peaks at ~ 305 – 340 nm and ~ 615 – 640 nm are attributed to $\pi \rightarrow \pi^*$ electron transition of the benzenoid ring and $n \rightarrow \pi^*$ transition of benzenoid to quinoid, respectively. Indeed, all nanocomposites are blue colored in NMP solvent. The absorption at 640 nm is influenced by the oxidation state of the molecules. This result shows that PANI– TiO_2 is completely transformed from the emeraldine salt to the emeraldine base by the deprotonation of PANI– TiO_2 by NMP [21–25, 34, 56]. It is known that a strong hydrogen bond can be formed between the $-\text{NH}^+-$ and/or $=\text{NH}^+$ sites in the polymer backbone and the carbonyl group of NMP, which leads to deprotonation of the polymer backbone of polyaniline and conversion of emeraldine salt to emeraldine base. The color, changing from green to blue can also be evidence to these events. As a consequence, the interactions between polymer chains and solvent molecules have caused these differences. However, the small absorption peaks at ~ 455 – 465 nm can be assigned to the polaron $\rightarrow \pi^*$ transition from the charged cationic species, that is due to the solubility of some polymer chains protonated as a compact coiled (tightly coiled chains) conformation of PANI chains made by TiO_2 [21–25, 56, 57]. Moreover, when metal oxide (TiO_2) nanoparticles are dispersed in the PANI matrix, the absorption spectra were

changed clearly. The redshift of absorption transition to higher wavelength shows the successful interaction between metal oxide with the polymer chain [35].

On the other hand, due to the report of Khan and Swati [55], the small absorption band in around 450–470 nm in the nanocomposites attributed to the excitation of 3d electrons of Fe^{3+} to the TiO_2 CB (charge transfer transition) in NMP solvent, Figure 3. Unfortunately, its shifts in 6–9 nanocomposites are not regular and can be concluded. It can establish the existence of Fe in samples. However, this band has been shield by a broad band of polaron $\rightarrow \pi^*$ transition in the formic acid solvent. The UV–Vis absorption spectra of nanocomposites in formic acid (green) (Figure 3b) shows three absorption bands at ~ 251 – 265 ,

Table 3. Data of UV–Vis spectra of nanocomposites 4–9 in NMP solvent.

Nanocomposite	$\pi \rightarrow \pi^*$	Polaron $\rightarrow \pi^*$	$n \rightarrow \pi^*$	Color
4	335 nm	466 nm	625 nm	Blue
5	330 nm	455 nm	630 nm	Blue
6	335 nm	455 nm	630 nm	Blue
7	330 nm	460 nm	640 nm	Blue
8	340 nm	463 nm	630 nm	Blue
9	340 nm	465 nm	640 nm	Blue

Table 4. Data of UV–Vis spectra of nanocomposites 4–9 in FA solvent.

Nanocomposite	$\pi \rightarrow \pi^*$ ^a	Polaron $\rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ ^b	$\pi \rightarrow \text{Polaron}$	Color
4	251 nm	392 nm	$> \sim 750$ nm	Green
5	250 nm	380 nm	$> \sim 750$ nm	Green
6	251 nm	390 nm	$> \sim 750$ nm	Green
7	265 nm	393 nm	$> \sim 750$ nm	Green
8	252 nm	390 nm	$> \sim 750$ nm	Green
9	265 nm	394 nm	$> \sim 750$ nm	Green

^a $\pi \rightarrow \pi^*$ electron transition of the quinoid rings and/or TiO_2 .

^bThe blue shift of polaron $\rightarrow \pi^*$ transition and/or a red shift of $\pi \rightarrow \pi^*$ electron transition of the benzenoid rings in the emeraldine salt (ES).

Figure 3. UV–Vis spectra of nanocomposites 4–9; a) in NMP and b) in FA.

~380–394, and >~750 nm (Table 4). An absorption band at ~251–265 nm is related to $\pi \rightarrow \pi^*$ electron transition of the quinoid rings and/or TiO_2 [58]. The band at ~380–394 nm is attributed to the blue shift of polaron $\rightarrow \pi^*$ transition and/or a redshift of $\pi \rightarrow \pi^*$ electron transition of the benzenoid rings in the emeraldine salt (ES). The delocalized polaron band >~750 nm indicates an expanded-coiled conformation of PANI (relatively linear and planar chains) and reveals the presence of PANI in its secondary doping and conducting form (ES) [21–25, 56, 57]. Nanocomposites have different absorption bands in NMP and FA because of the basic and acidic nature of the solvents (aprotic and protic that causes different conformations due to secondary doping) and their limited solubility [21–25, 56, 57, 59–63].

Figure 4 shows optical band gaps (E_g^{Opt}) of nanocomposites **6** and **7**. The $E_g^{\text{Opt}}(s)$ were calculated by absorption edges using the Equation (1):

$$E_g^{\text{Opt}} = \frac{1242}{\lambda_{\text{onset}}} \quad (1)$$

where λ_{onset} is the longest absorption wavelength [64, 65]. The absorption edge for each nanocomposite was determined and shown in Table 5. The optical bandgap of the nanocomposite **6** is lower than that

Table 5. Absorption edge and band gap energies of nanocomposites **6** and **7**.

Sample	Assignments	Absorption [nm]	E_g^{Opt} [eV]
Nanocomposite 6	$\pi \rightarrow \pi^*$	421	2.95
	$n \rightarrow \pi^*$	806	1.54
Nanocomposite 7	$\pi \rightarrow \pi^*$	407	3.05
	$n \rightarrow \pi^*$	791	1.57

of the nanocomposite **7** that it is compatible with their better electrical conductivities [65]. Also, this indicates that the optical bandgap of the polyaniline is varied by the polymerization method and doping [66, 67].

3.3. Conductivity of nanocomposites

Conductivity is a key parameter for this type of polymers; for typical $\text{PANI} \cdot \text{HCl}$ it attains the values of some $[\text{S} \cdot \text{cm}^{-1}]$ [68]. The electrical conductivity of nanocomposites was observed, and the results of these measurements are summarized in Table 6. As observed, the conductivity of the nanocomposites **7–9** obtained with oxidant $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is lower than APS; similar results have been reported in the literature [69]. This can be based on the reduction of oxidizing power in the case of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, which makes the growth rate of PANI in nanocomposites relatively low. Then, it is probably due to the difference in the reaction rate and, subsequently, a gradual increase in acid concentration (a gradual decrease of pH, ‘falling pH’ effect).

Furthermore, the low conductivity of the nanocomposites **7–9** with oxidant $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ can be due to the lesser content of the oxidized form of PANI chains (quinoid structures) in them, that is, the lower conjugation extent of chains of PANI of the nanocomposites **7–9** than the conjugation extent of PANI chains in case of APS, the nanocomposites **4–6**.

Also, when the monomer is added to the polymerization reaction mixture at the last step, the electrical conductivity is observed to decrease (compare samples **8** with **7** and **9** in Table 6). This may be because of the increase of iron chloride before the addition of monomer results in the formation of a complex of

Table 6. The conductivities of nanocomposites (**4–9**).

Nanocomposite	4	5	6	7	8	9
Conductivity $[\text{S} \cdot \text{cm}^{-1}]$	$1.15 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$1.02 \cdot 10^{-3}$	$0.05 \cdot 10^{-3}$	$0.92 \cdot 10^{-3}$

Figure 4. UV–Vis absorption spectra of PANI– TiO_2 nanocomposites a) **6** and b) **7** in NMP for obtaining energy levels difference of HOMO and LUMO and the band gap energy.

Fe (III) with the surface oxygen's of TiO_2 that it subsequently reduces the oxidation potential of Fe (III).

3.4. CHN and EDX analysis of nanocomposites

The CHN results of nanocomposites **6** and **7** are mentioned in Table 7. The C:N atomic ratios achieved from the elemental analysis in all the samples are very close to 6, this C:N ratio is very close to the atom ratio (6:1) of C and N in the PANI, indicating these nanocomposites are mainly composed of polyaniline [70].

Figure 5 shows EDX of nanocomposites **6** and **7**. It is observed that oxygen, nitrogen, and carbon elements are present in nanocomposites **6** and **7**. An intense peak of Ti element and O atom is clearly observed in the nanocomposites structure. Therefore, the TiO_2 nanoparticles can be incorporated in the PANI during the polymerization of aniline. Furthermore, the EDX spectra clearly indicated the presence of Fe (Fe^{3+} and Fe^{2+} ions) in the samples. Then, the main constituents of Ti and O for TiO_2 , CHN for PANI, and Fe for doping and oxidant confirm to produce nanocomposites, and further no impurities were observed in the sample.

3.5. Morphology of nanocomposites by TEM

Figure 6 shows the TEM images of the nanocomposites **6** and **7**. In Figure 6a, a thin layer of TiO_2 is clearly observed on the outer wall of the nanotube

Figure 6. TEM images of nanocomposites; a) **6** and b) **7**.

that the thickness of the conformal TiO_2 layer is around 3–5 nm. Consecutive P–N junctions of TiO_2 nanoparticles and PANI are formed in the nanocomposite **6**. It can be seen from the TEM image in Figure 6b, TiO_2 nanoparticles as black or dark spots with sizes around 7 nm are randomly distributed in the PANI matrix in nanocomposite **7** that is similar as a plantain leaf, and they have created a kind of shallow levels (both donor and acceptor) in the nanocomposite. This result is completely in parallel with our results of XRD spectra.

Because the presence of P–N junction between TiO_2 nanoparticles and PANI nanocomposite matrix will give rise to the lower activation energy for easier adsorption of the electron. Also, the P–N junction can also control the electric current flow in TiO_2 semiconductor that electrons would be available for conduction [71].

An important result of this work is that only by changing the polymerization conditions can their

Table 7. The results of the elemental analysis (CHN).

Elements	C	H	N	Ti+O+Cl	Σ	C/H	C/N
	[wt%]					[mol]	
Nanocomposite 6	14.38	1.18	2.74	81.70	100	1.01	6.12
Nanocomposite 7	11.09	0.89	2.06	85.96	100	1.04	6.28

Figure 5. EDX spectra of the nanocomposites a) **6** and b) **7**.

morphology be changed from nanotube to plantain's leaf when APS and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ are oxidants, respectively.

3.6. X-ray diffraction (XRD) spectroscopy

Figure 7 displays the XRD patterns of nanocomposites **6** and **7**. The main peak of XRD pattern emerged at $2\theta = 25.4^\circ$ corresponding to the plane (101), and other small peaks centered at $2\theta = 38.1, 48.6, 54.2, 55.2, 63.4, 69.1, 70.9$, and 75.5° correspond to (004), (200), (105), (211), (204), (116), (220) and (215), respectively, belonging of anatase phase of TiO_2 . It was observed that even after dispersion in the polymer matrix, the TiO_2 nanoparticles still retained their anatase nature.

However, due to report of Khan and Swati [55] for the study of nanosized Fe^{3+} -doped TiO_2 photocatalyst, comparison of XRD of our samples with those PANI/ TiO_2 composites reported in the literature [71–73] shows that peaks intensity increased and peaks width (FWHM, full width at half maximum) decreased as two the peaks [211] and [220] at (54.96°) and (69.74°) on 2θ axis in the powders have well been appeared. In fact, these fragmented into two peaks (54.20° [105], 55.20° [211]), and (68.89° [116], 70.30° [220]), such changes are attributed to the enhancement in crystallinity without calcination [55]! Since there is no diffraction peak for PANI that might be due to its amorphous phase and it's too low intensity in the nanocomposites, as similar results reported in the literature [71–73], everyone has to draw conclusion coating of PANI by the crystal TiO_2 nanoparticles. In other words, PANI has been coated by the crystal TiO_2 nanoparticles that it is completely compatible with TEM images. Then, these two results can be caused by Fe available in nanocomposite.

Figure 7. XRD pattern of nanocomposites; a) **6** and b) **7**.

Moreover, no presence of the crystalline phase containing Fe showed that the Fe dopant ions were successfully incorporated into the framework of anatase TiO_2 because XRD is sensitive enough to record such minor changes to TiO_2 . This result also revealed that Fe^{3+} ions do not react with TiO_2 to form new crystalline phases such as $\alpha\text{-Fe}_2\text{O}_3$ or Fe_2TiO_5 . The average size of crystals D [nm] for both nanocomposites **6** and **7** was calculated according to the Debye–Scherrer formula $D = K\lambda/(\beta\cos\theta)$, where K is a shape factor (0.95), λ is the X-ray wavelength, β is the full width at half maximum of the peak, and θ is the Bragg angle [71]. Moreover, the calculated size for nanocomposites **6** and **7** (4.94 and 6.06 nm) was in parallel with our results of TEM images.

3.7. Cyclic voltammograms, energy levels of HOMO and LUMO, and bandgap energies (E_g^{CV})

Cyclic voltammetry studies on nanocomposites **6** and **7** were measured in 1.0 M HCl electrolyte. The analysis was performed on three-electrode mode with Ag/AgCl as a reference electrode, glassy carbon electrode as the working electrode, and platinum wire as counter-electrode, respectively. The working electrode was prepared by dropping a concentrated nanocomposite onto a glassy carbon electrode. The potential was cycled between -0.2 and $+1.2$ V at a scan rate of 0.05 V/s. As mentioned in Figure 8, the CV results taken from nanocomposites **6** and **7** show two redox pairs. These peaks indicate the redox transitions between a leucoemeraldine form (semiconducting state) and a polaronic emeraldine (conducting state) designated as peaks C1/A1, and the Faradaic transformation of emeraldine to pernigraniline initiates the redox peaks C2/A2 [74]. However, the current – potential responses of nanocomposite **6** display a better shape with respect to the zero-current line. Moreover, a more rapid current response on voltage reversal found at end potential with larger electrochemical response current. It suggests that it is the better electrochemical capacitance in contrast to nanocomposites **7**. As a result, these nanocomposites are electro-active and functional.

Figure 9 shows the electrochemical properties of nanocomposites **6** and **7** and the assessment of the levels of energy of HOMO and LUMO. Cyclic voltammetry (CV) was done using a standard three-electrode system, which consists of a platinum wire as the counter electrode, a glassy carbon disk as the

Figure 8. Cyclic voltammograms of PANI–TiO₂ nanocomposites; a) **6** and b) **7**.

working electrode that the polymer electrode was prepared by drop-casting of a polymer solution onto the glassy carbon electrode, and a silver wire as the reference electrode. *CV* was recorded in CH₃CN solution of Bu₄NClO₄ (0.1 M) electrolyte under N₂ atmosphere as the supporting electrolyte. The electrochemical bandgap energy (E_g in [eV]), as well as HOMO and LUMO energy levels in [eV] the nanocomposites, were calculated with the equations mentioned below (Equations (2–4)) [75, 76]:

$$E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{Ox}} + 4.4) \text{ [eV]} \quad (2)$$

$$E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{Red}} + 4.4) \text{ [eV]} \quad (3)$$

$$E_g^{\text{CV}} = -(E_{\text{HOMO}} - E_{\text{LUMO}}) \text{ [eV]} \quad (4)$$

where $E_{\text{onset}}^{\text{Ox}}$ and $E_{\text{onset}}^{\text{Red}}$ are the onset oxidation and reduction potentials, respectively. Using cyclic voltammetry, E_{Ox} and E_{Red} of the nanocomposites, **6** and **7** films were found, and the calculated data are summarized in Table 8. It is noteworthy that there is a small difference between the E_g^{CV} and E_g^{Opt} . It seems that the oxidation and reduction of these nanocomposites go forward in isolated electron and hole transporting segments.

Table 8. The frontline molecular orbital and energy gap of nanocomposites **6** and **7**.

Nanocomposite	UV–Vis		CV				
	λ_{onset}	E_g^{Opt} [eV]	$E_{\text{onset}}^{\text{Ox}}$ [V]	$E_{\text{onset}}^{\text{Red}}$ [V]	E_{HOMO} [eV]	E_{LUMO} [eV]	E_g^{CV} [eV]
6	421 806	1.54	0.85	–0.93	–5.25	–3.47	1.78
7	407 791	1.57	1.17	–0.81	–5.57	–3.59	1.98

Figure 9. Cyclic voltammograms of nanocomposites; a) **6** and b) **7** in CH₃CN solution of Bu₄NClO₄ (0.1 M) electrolyte at a scan rate of 100 mV/s.

3.8. Photovoltaic performance

(*J*–*V*) characteristics of Al/(PANI–TiO₂)/TiO₂/FTO solar cells are presented in Figure 10. The overall power conversion efficiency (PCE) which calculate using short-circuit current density (*J*_{sc}) and the open-circuit photovoltage (*V*_{oc}) (Equation (5)); The values of (*V*_{oc}) and (*J*_{sc}) are extracted at *J* = 0 and *V* = 0, respectively. The maximum voltage and current (*V*_{max} and *J*_{max}) are obtained at the maximum output power point (*P*_{max}). The fill factor (*FF*) is the ratio between the maximum power from the hetero-junction solar cell to the product of *J*_{sc} and *V*_{oc} (Equation (6)).

The overall solar energy conversion efficiency is the maximum power extracted compared to the incident solar power [77, 78] (Equations (5) and (6)):

$$\eta = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{in}} \quad (5)$$

$$FF = \frac{J_{max} \cdot V_{max}}{J_{sc} \cdot V_{oc}} = \frac{P_{max}}{J_{sc} \cdot V_{oc}} \quad (6)$$

FF, *V*_{oc}, *J*_{sc}, and efficiency was calculated at 0.35 mA/cm², 0.43 V, 2.86, and 0.71%, respectively of Al/(PANI–TiO₂)/TiO₂/FTO for nanocomposite 7. For the nanocomposite 6, all these values were enhanced, and the power conversion efficiency (PCE) increased from 0.71 to 0.84%. The results clearly show that the oxidant nature can play an important role in improving the electrical properties.

Figure 11 shows energy levels diagrams of the solar cells of Al/(PANI–TiO₂)/TiO₂/FTO for nanocomposites

Figure 10. a) P–N heterostructure solar cell as Al/(PANI–TiO₂)/TiO₂/FTO. b) Current–voltage plots (*I*–*V*) for nanocomposites 6 and 7.

6 and 7. It is a well-observed motion of electrons and holes is forward to anode and cathode, respectively. This can justify relatively high efficiency (PCE). Furthermore, it can easily establish P–N junction between TiO₂ nanoparticles and PANI in nanocomposites matrix that is from staggered gap type (type II), and it is confirmed by literature [46–48].

4. Conclusions

In this paper, new nanocomposites from PANI and TiO₂ with different two oxidants (APS and FeCl₃·6H₂O) with the different orders were directly synthesized by using solid-state polymerization method under green condition. The results of FT–IR, EDX, and UV–Vis measurements indicate that the nanocomposites containing both PANI and TiO₂ are successfully prepared. TEM results clearly show the different morphology by different oxidants. Indeed, TEM images show a thin layer of TiO₂ nanoparticles on the outer wall of the nanotube when APS is the oxidant. However, it is clearly observed that TiO₂ nanoparticles have been distributed on a planar leaf of PANI matrix when FeCl₃ is applied as an oxidant. In fact, PANI is coated by TiO₂ nanoparticles that confirmed by TEM and XRD. As a result, those appear representation of a good P–N junction [staggered gap type (type II)] between TiO₂ nanoparticles and PANI matrix that it is established by TEM and energy levels diagrams. Furthermore, XRD shows the anatase phase and the enhancement in the crystallinity of TiO₂ nanoparticles without calcination! Electrical properties and conductivity of the nanocomposites were studied, and it became clear that the nanocomposites are electro-active and functional. The current–voltage (*I*–*V*) characteristic of PANI–TiO₂ heterostructure showed a nonlinear behavior. As a result, we observed that the nature of oxidant and reaction conditions plays a significant role in the formation of the nanocomposites and their optical and electrical properties.

Figure 11. Energy levels diagrams of the solar cell of Al/(PANI–TiO₂)/TiO₂/FTO for nanocomposites: a) 6 and b) 7.

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