

Decoration of TiO₂ with polyfuran to form a new nanocomposite via oxidative chemical polymerization

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ABSTRACT

TiO₂ was decorated with polyfuran to form a new nanocomposite (Polyfuran/TiO₂) by oxidative chemical polymerization of furan in ACN solvent using anhydrous FeCl₃ as oxidant at ambient temperature. These composites were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and conductivity measurements. The covering of PFu onto TiO₂ was endorsed by the FTIR studies. The main characteristic bands belonging to polyfuran and TiO₂ were observed in the spectrum of the PFu/TiO₂ composite. TGA results indicate that the PFu/TiO₂ composites had better thermal stability than PFu alone. In terms of initial decomposition temperatures and residual amount at 800°C, TiO₂ increased the stability of polyfuran significantly. The results of SEM analysis revealed distinct morphological features of PFu and its TiO₂ composites, which influenced their conductivity properties. The granular structure of composite disappeared and partially laminar structure appeared when the amount of TiO₂ decreased from 20% to 5% in the composite which may affect the conduction mechanism by electron jumps. TEM results shows formation of composite. The TEM images of composite revealed that the particle size of composite was in the range of 100-500 nm.

Key words: Polyfuran, TiO₂, composite, furan, conducting polymer

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INTRODUCTION

Combination of metal oxide nanoparticles with intrinsically conducting polymers (ICPs) to produce nanocomposites is an interesting implementation where the conducting polymer with the conjugated and delocalized π -electrons and metal oxide nanoparticles influence each other [1]. Recently, the research on electrically conductive polymers such as polythiophene, polyaniline and polypyrrole and their composites has increased due to the expansion of their application areas [2-4]. Among

conducting polymers, polyfuran has been the least investigated because of the difficulties in synthesizing it with a regular structure and high conductivity [5, 6] since furan rings are highly susceptible to oxidation. Having low level of conjugation in its polymeric chains, polyfuran has low electrical conductivity [7].

Polyfuran has prominent electrical properties although higher diene character rather than aromatic character in comparison to pyrrole and thiophene. However, it is difficult to synthesis the polyfuran without ring opening which can be detected with FTIR method. The use of polymer molecules containing furan ring has received significant interest both scientifically and technologically [8]. Recently, polyfuran (PFu) has been shown to have a great potential for the synthesis of its composites with inorganic particles to improve its processability, such as conducting electro-magnetic polyfuran/Fe₃O₄ nanocomposite [9], polyfuran-13X zeolite-polyaniline composite [10], conducting composite of polyfuran with acetylene black [11], polyfuran/Al₂O₃ and polyfuran/MMT clay composites [12]. Besides, furan comes from an agricultural and sideline product that is a reproducible resource. For this reason, furan can be obtained in a much cheaper way than pyrrole or thiophene [13]. Metal oxide semiconducting materials have stable chemical and thermal properties [14]. Titanium dioxide has extraordinary physical properties such as chemical stability, high dielectric constant and strong mechanical strength besides good insulating property. Moreover, TiO₂ thin films can be used in many applications such as optical coating and protective layers for very large-scale integrated circuits due to its high refractive index and optical transmittance in the visible range [15]. The conduction properties of TiO₂ can vary according to the physisorption and chemisorption of its oxygen atoms [16, 17]. TiO₂ is known as n-type semiconductor, while conducting polymers such as polyfuran, polyaniline and polythiophene are usually known as p-type semiconductor. The incorporation of these two materials can find many application areas in different fields.

The present study is intended to investigate the possibility of expanding the range of application areas of polyfuran and TiO₂ by bringing together preparing the composite material. To the best of our knowledge, the unique properties of PFu/TiO₂ nanocomposite were obtained by oxidative chemical polymerization method for the first time in this present work. To bring together these two material properties will be useful for technological applications. It was the purpose of this work to synthesize and characterize the PFu/TiO₂ nanocomposites. This study tries to provide a deeper insight in the properties of chemically PFu decorated TiO₂. Structural, morphological, thermal and conductivity properties of synthesized nanocomposites are highlighted in this article.

MATERIALS AND METHODS

Experimental

Materials

Furan (Sigma Aldrich, St. Louis, MO, USA) was purified by distillation at reduced pressure before its use. Iron(III)chloride was purchased from (Sigma Aldrich, St Louis, MO, USA).

Nanodimensional TiO₂ (140 nm) was purchased from Sigma-Aldrich, United Kingdom.

Synthesis of nanocomposites

Iron(III)chloride (FeCl₃) was used for the chemical polymerization of furan. TiO₂ was selected as inorganic host material. Acetonitrile (ACN) was used as solvent for the experimental procedure. The molar ratio of monomer to oxidizing agent was selected as 1.5. The amount of TiO₂ was kept constant to optimize the amount of TiO₂ in the composite by increasing the amount of furan. Furan-TiO₂ mixture in 100 mL of ACN was treated in ultrasonic bath for 15 min. FeCl₃ was dissolved in

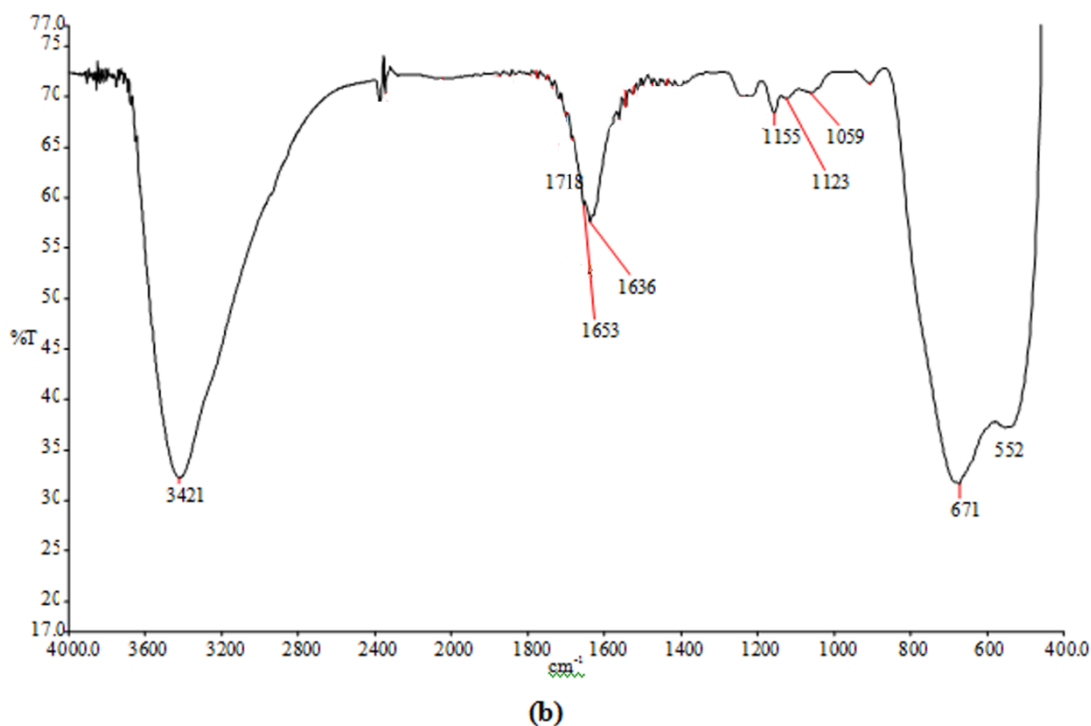
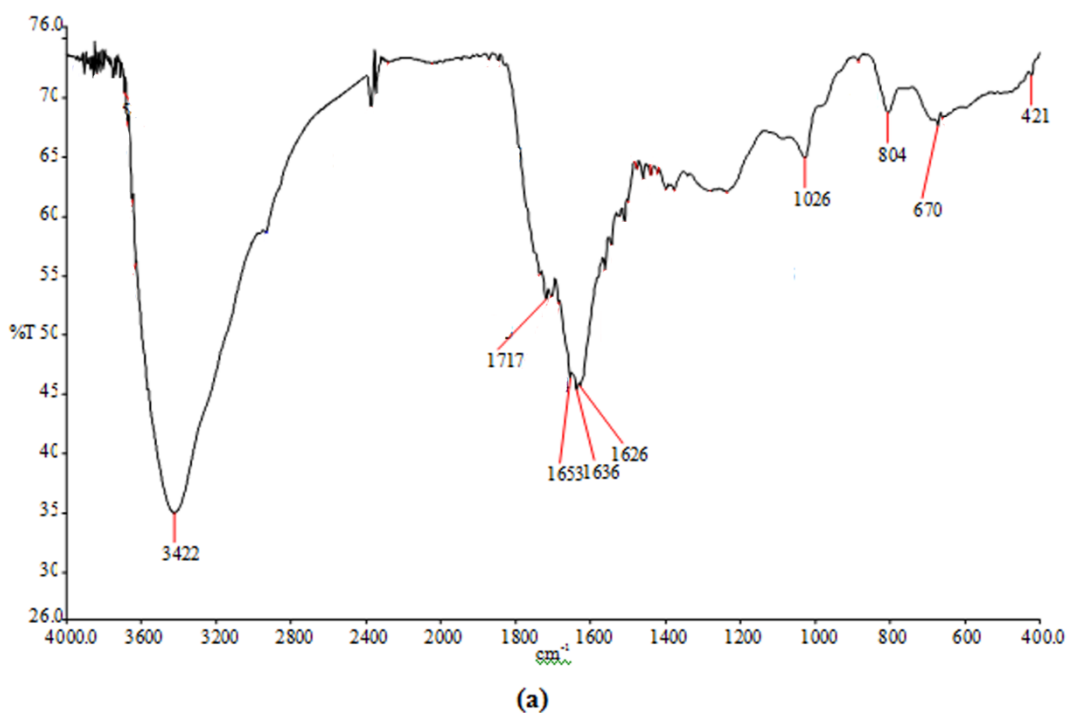
ACN and added to the reaction medium dropwise to initiate polymerization of the furan at room temperature. After adding FeCl_3 completely polymerization reaction continued for 24 hours. The polymer was filtrated and then it was washed with ACN and ethanol respectively, until the filtrate was colorless.

Instrumental

Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm^{-1} at 4 cm^{-1} resolution with KBr pellets on a Perkin-Elmer Spectrum BX FTIR system (Beaconsfield, Buckinghamshire, HP91QA, England). The direct current electrical conductivity of PFu/ TiO_2 composites was measured by the standard four-probe method using PCI-DAS6014 (Measurement Computing Co Norton, MA, USA) with a current source, voltammeter and temperature controller. Dry powdered samples were made into pellets using a steel die having 13mm diameter in a hydraulic press under a pressure of 700MPa. Temperature dependent electrical conductivity of the polymer samples was measured by computerized four-probe system and, the temperature of pellets was recorded using a thermocouple. Conductivity of the samples was carried out between 25 and $50\text{ }^\circ\text{C}$. SEM was performed using Phillips scanning electron microscope (XL-30S FEG, USA). TEM images were observed using JEOL transmission electron microscope (TEM-1400-EDX, Germany). TGA thermograms were recorded by using a Perkin Elmer thermogravimetric analyzer in the presence of N_2 atmosphere from 50 to $900\text{ }^\circ\text{C}$ at heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

FTIR spectra of PFu/ TiO_2 nanocomposites

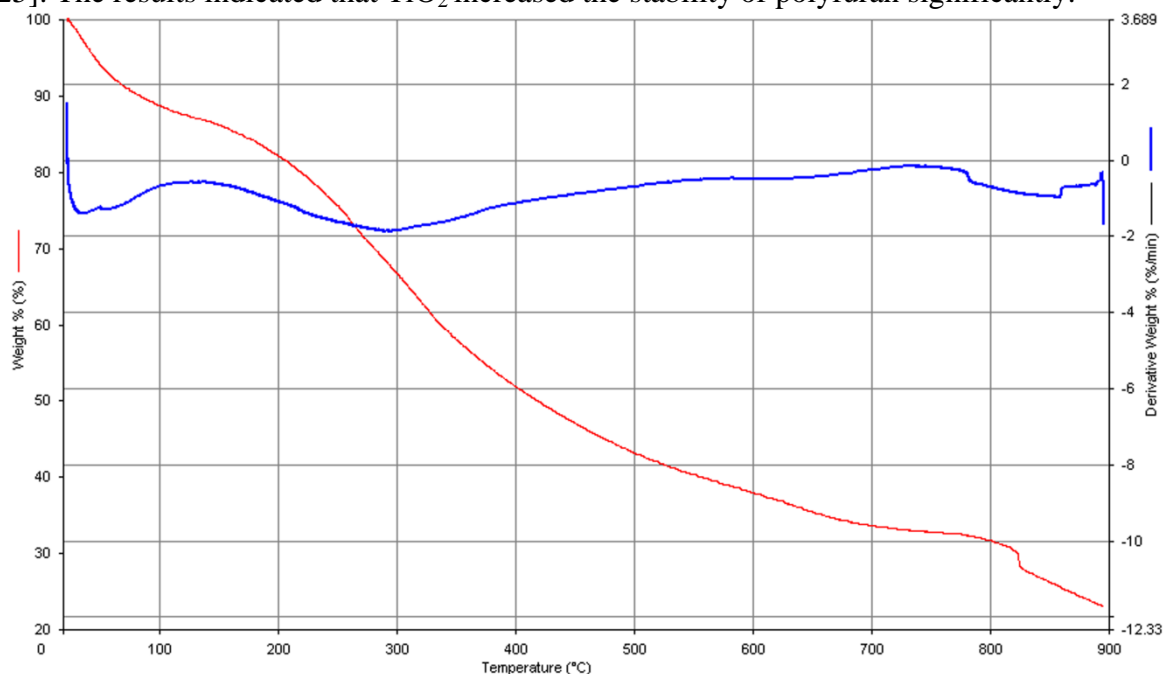
Fig 1a and b shows the spectra of polyfuran and the composite synthesized in the presence of TiO_2 used as a host material. Both spectra contained the characteristic peaks of polyfuran. Polyfuran has some characteristic bands of 2,5-disubstituted furan units, which are at about 700 cm^{-1} , 1026 cm^{-1} and $1626\text{--}1653\text{ cm}^{-1}$ attributed to C–H out-of-plane vibration, C–O–C stretching vibration and C=C stretching vibration in the furan ring, respectively [18]. The bands appeared significantly at about 1123 cm^{-1} concerning to symmetric C=C stretching vibration in aromatic ring. Asymmetric C=C vibration of aromatic ring can be seen at 1155 cm^{-1} [19]. These results supported the formation of polyfuran. Moreover, the other IR feature was that 804 cm^{-1} band suggested the α -position linkage between the furan rings [20]. In the spectra, the peaks at $1717\text{--}1718$, $2929\text{--}2930$ and $3421\text{--}3433\text{ cm}^{-1}$ attributed to the stretching of carbonyl, aliphatic C–H structures, and hydroxyl groups, respectively, were seen. The presence of these three bands suggested that some of the furan rings were opened. And this result supported the formation of the non-conjugated structure on the polymer chain. These peaks agree with the results of polyfuran prepared by electrochemical and plasma polymerization method [21–23]. Likewise, these main characteristic bands belonging to polyfuran were observed in the spectrum of the PFu/ TiO_2 composite (Fig 1b). The characteristic sharp peak at 671 cm^{-1} and the broad peak at 552 cm^{-1} indicate the Ti–O–Ti vibrations in composite structure [23].

Fig 1. FTIR spectra of (a) PFu, (b) PFu/TiO₂

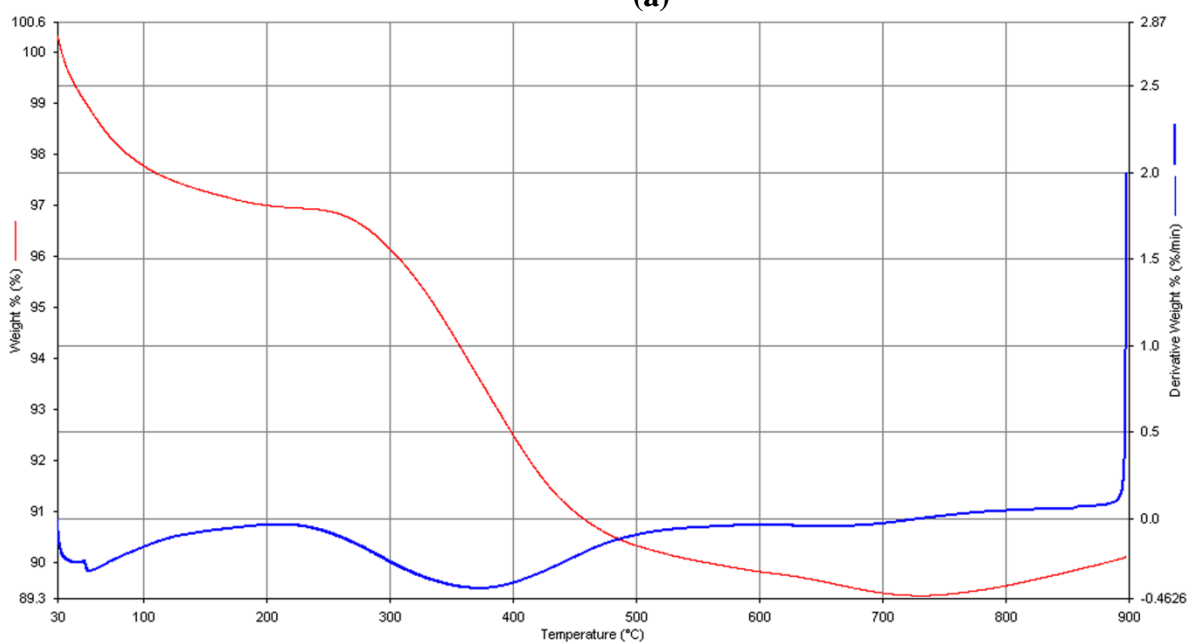
Thermal stability studies

Fig 2a and Fig 2b shows the thermograms of PFu and PFu/TiO₂. The release of acetonitrile and moisture occurred between 50-120 °C in both samples [24]. Table 1. shows the TGA results (decomposition temperatures and residues at 800 °C) of previous studies. PFu and PFu/TiO₂ show one-step decomposition without the step where the release of acetonitrile and moisture occurred. The initial decomposition temperature of PFu/TiO₂ was higher than that of PFu. The initial degradation

temperatures of polyfuran and its composite were 190 °C and 280 °C, respectively. The maximum degradation temperature of polyfuran (430 °C) was lower than that of composites (460 °C). The weight loss in the range of 190-670 °C and 280-640 °C for PFu and PFu/TiO₂ composite, respectively, occurred due to the removal of dopant anion and decomposition of the polymer backbone simultaneously. Additionally, TGA results indicated that the PFu/TiO₂ composite had better thermal stability than PFu according to their initial decomposition temperature and residues at 800 °C. The amount of (%wt.) TiO₂ in composite was calculated using the amounts of residue from the TGA. When the PFu/TiO₂ nanocomposite was prepared, only 10% of composite was decomposed and the rest remained in the medium at 800 °C. This behaviour was very similar to TiO₂ [25]. The results indicated that TiO₂ increased the stability of polyfuran significantly.



(a)



(b)

Fig 2. Thermographs of (a) PFu and (b) PFu/TiO₂

Table 1. TGA results for polyfurans and composites synthesized in variety of dopant anions

Reference	Polymer	Ti (°C)	Tm (°C)	Tf (°C)	Residue at 800 °C (wt %)
[26, 27, 20]	PFu(Oxidant:SbCl ₃)	114	181	273	0
		273	341	409	
		518	541	568	
[26]	P2IAn/PFu	172	278	359	35
[21]	P2ClAn/PFu	136	173	227	15
[27]	P2FAn/PFu	213	387	544	72
[20]	P2BrAn(FeCl ₃)/PFu(SbCl ₃)	196	216	240	
		310	345	383	
[20]	PFu(FeCl ₃)	164	207	249	65
		309	351	399	
[28]	PFu-BuNBF ₄	185	253	312	40
[22]	PFu-LiClO ₄	215	260	300	13
[23]	*PFu/TiO ₂	245	360	475	~55
[29]	PFu/3A	276	409	541	70
	PFu/4A	120	295	469	70
	PFu/5A	64	142	220	78
[25]	TiO ₂	120	310	500	92
In this study	PFu (FeCl ₃)	190	430	670	32
	PFu/TiO ₂ (FeCl ₃)	280	460	640	90

Ti: initial degradation temperature; Tm: maximum degradation temperature; Tf: final degradation temperature.

SEM and TEM results

Fig 3a-f show SEM images of PFu/TiO₂ composites were prepared using various amounts of TiO₂ to see the morphological differences. TiO₂ nanoparticles showed spherical and homogenous structure with diameters about nanometer levels [30]. Besides, TiO₂ nanoparticles acted as a core for the polymerization and homogenous shell formation of PFu. Fig 3a shows the cauliflower-like structure of polyfuran. However, it was noticeable that a partly layered structure was also formed. The SEM images of PFu/TiO₂ composites showed different morphological properties with the change of the amount of TiO₂. Polyfuran deposited on TiO₂ evenly (Fig 3b and Fig 3c), when the amount of TiO₂ is 20% in composite structure. The granular structure of composite disappeared and partially laminar structure appeared when the amount of TiO₂ decreased from 20% to 5% in the composite (Fig 3d, Fig 3e). The electron hopping conductivity mechanism can be supported by this laminar structure. The presence of TiO₂ in very small amounts in the composite structure increased the layered structure (Fig 3f). In this case, the composite structure became more rigid, difficult to handle and dissolve. In this respect, it is advisable to use 20% TiO₂ for this study.

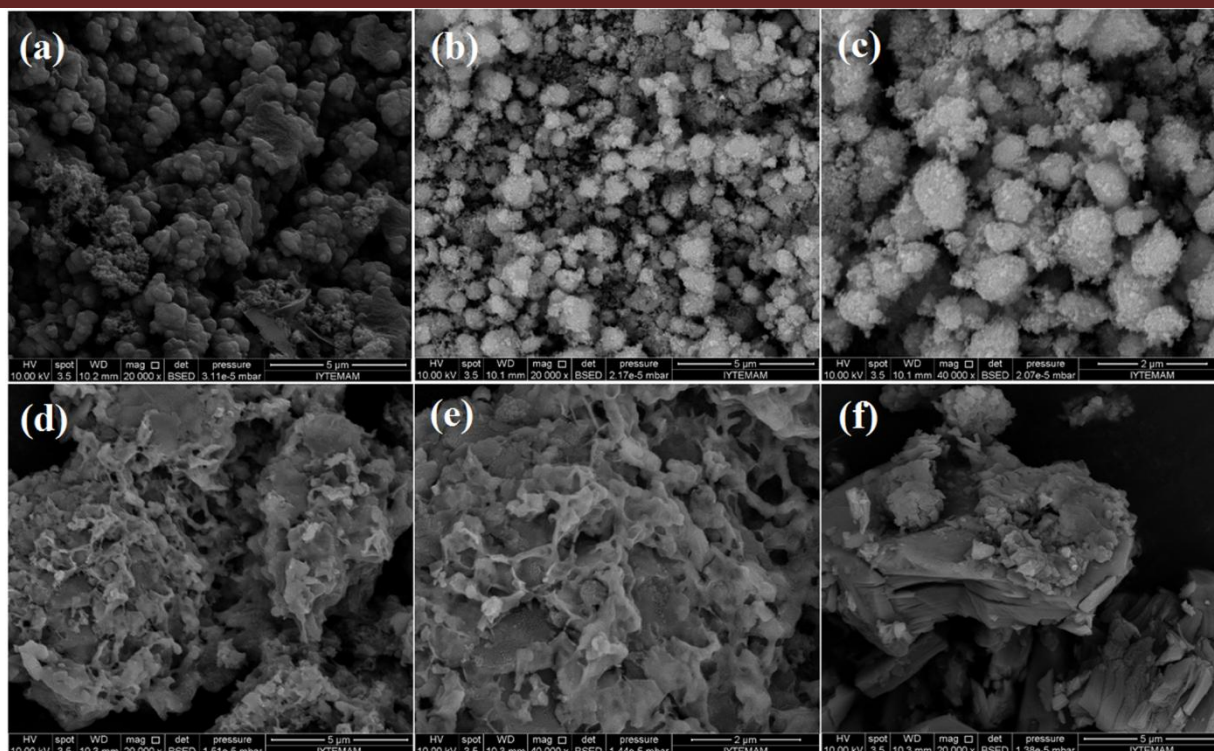


Fig 3. SEM images of (a) PFu, 5 μm , (b) PFu/TiO₂ (20%), 5 μm , (c) PFu/TiO₂ (20%), 2 μm , (d) PFu/TiO₂ (5%), 5 μm , (e) PFu/TiO₂ (5%), 2 μm , (f) PFu/TiO₂ (2.5%), 5 μm

In order to study the presense of polyfuran layer formed on the surface of TiO₂, TEM test was performed. As illustrated in Fig 4, it can be clearly found that the PFu coated on TiO₂ particles are uniformly distributed. The grey areas were the shells and the black areas were the cores. Thin layers of PFu on TiO₂ were clearly observed with shell thicknesses about 50-200 nanometers. The TEM images of composite revealed that the particle size of composite was in the range of 100-500 nm. These results proved the successful fabrication of nanocomposite structure.

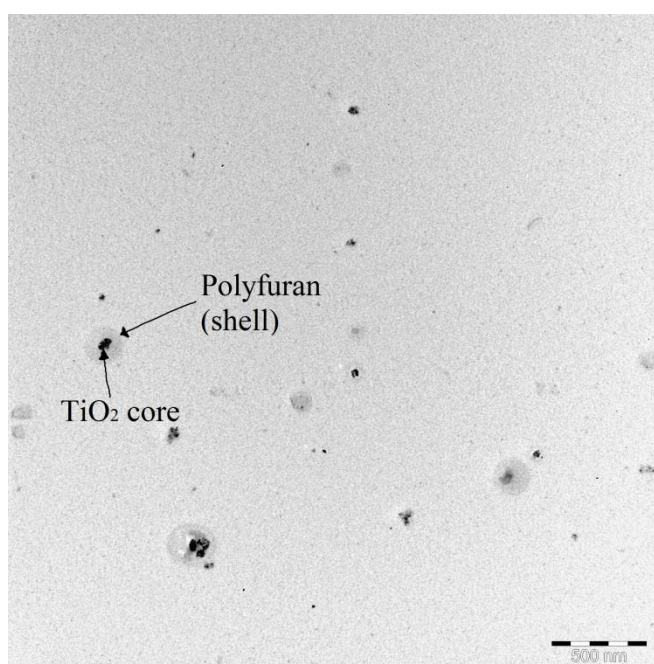


Fig 4. TEM image of PFu/TiO₂ (20%).

Conductivity results

Conductivity values of samples measured using four-probe technique were 3.99×10^{-5} , 2.18×10^{-5} and $4.81 \times 10^{-5} \text{ Scm}^{-1}$ for PFu, PFu/TiO₂ (5%) and PFu/TiO₂ (2.5%) respectively. Conductivity of the composite containing (20%) TiO₂ could not be measured due to non-uniform pellet structure. These values showed that the conductivity of samples was at a semiconductor level. Low electrical conductivities may be attributed to short conjugation lengths, as well as the ring-opening reaction as seen from FTIR results, the degree of cross-linking, and defects in morphologies [31]. Thereupon, we can conclude that the state of the polymer is partially oxidized.

Besides, when the amount of TiO₂ in the composite increased above a certain value, conductivity decreased. The conductivity of PFu/TiO₂ (5%) was halved when compared with PFu. The level of conductivity is based on macroscopic and microscopic morphologies and structures of polymers. At the macroscopic level, inhomogeneities in the composite (i.e., agglomeration of TiO₂ in composite, distance between polymer aggregates) affect conductivity, where as the microscopic level of conductivity depends on the conjugation length and doping level [23]. The SEM results of PFu/TiO₂ (5%) support the conductivity results due to distance between polymer aggregates, which prevents the charge transfer. The conductivity of PFu/TiO₂ (2.5%) was slightly higher than that of PFu. The lamellar and smooth morphology of PFu/TiO₂ (2.5%) might provide the electron hopping conductivity mechanism. Finally, the lower amount of TiO₂ in composites promoted the increase of conductivity for PFu/TiO₂ composites.

CONCLUSION

PFu/TiO₂ composites were prepared with different compositions. All composites had different thermal, electrical, morphological characteristics. FTIR, TGA, SEM, TEM and conductivity results showed that the composite structure was formed successfully. The main characteristic bands belonging to polyfuran were observed in the spectrum of the PFu/TiO₂ composite. The thermal stability of PFu increased in the presence of TiO₂. The SEM results of PFu/TiO₂ composites showed different morphological properties with the change of the amount of TiO₂. The TEM results supported the formation of nanocomposite. A low amount of TiO₂ in composites promoted conductivity. An increase in conductivity of composites was observed during thermal aging. PFu/TiO₂ composite prepared in this study seems to be a good candidate in different application areas of the polyfuran and TiO₂ such as humidity sensor and optical coating and protective layers for very large-scale integrated circuits, respectively.

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Table Captions

Table 1. TGA results for polyfurans and composites synthesized with various dopant anions

Figure Captions

Fig 1. FTIR spectra of (a) PFu, (b) PFu/ TiO_2

Fig 2. Thermographs of (a) PFu and (b) PFu/ TiO_2

Fig 3. SEM images of (a) PFu, 5 μm , (b) PFu/ TiO_2 (20%), 5 μm , (c) PFu/ TiO_2 (20%), 2 μm , (d) PFu/ TiO_2 (5%), 5 μm , (e) PFu/ TiO_2 (5%), 2 μm , (f) PFu/ TiO_2 (2.5%), 5 μm

Fig 4. TEM image of PFu/ TiO_2 (20%).

Fig 5. Temperature-dependent conductivity plots of composites includes two different amount of TiO_2 (a) PFu/ TiO_2 (5%), (b) PFu/ TiO_2 (2.5%)