

Preparation and Characterization of Glassy Hafnium–Titanium Phosphate/Polythiophene and Polythiophene-co-Polyaniline Composites Using FeCl_3 and CuCl_2 as Oxidants

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Abstract

Glassy Mixed hafnium-titanium phosphates, $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ (where $x = 0.34$, and 0.50) were prepared and characterized by chemical, XRD, FT-IR, SEM, and TGA. The materials were found to be amorphous with a glassy appearance. The reaction of thiophene alone, and a 1:1 mixture of thiophene and aniline, with $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ led to the formation of $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2$ /polythiophene and $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2$ /polythiophene-co-polyaniline composites, respectively. These products were analyzed using elemental (CHNS) analysis and FT-IR spectroscopy. Electrical conductivity for resultant conducting polymers and copolymers represents a range of semiconductors

Keyword. Glassy Hafnium–Titanium Phosphate/Polythiophene, Polythiophene-co-Polyaniline Composites, Oxidants.

Introduction

Amorphous and layered crystalline hafnium and mixed hafnium-titanium phosphates of general formulae, $\text{Hf}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$, $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$, respectively (where $x = 0.1-0.9$ and $n = 1-3$) are insoluble compounds with good thermal stabilities, possess high ion exchange capacities[1, 2]. These materials resemble clay minerals[3] and exist as bi-dimensional (2-D) structures, of general formula $\alpha\text{-Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, $\gamma\text{-Hf} \cdot \text{PO}_4 \cdot \text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ [4, 5], show typical XRD, TGA, and FT-IR spectra trend of $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, $\gamma\text{-Zr} \cdot \text{PO}_4 \cdot \text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\alpha\text{-Zr}_x\text{Ti}_{1-x}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ [6–8]. Research on such types of materials and their conducting polymers and copolymers composites is still in its infancy. Preparation techniques are flexible, conducting polymers comprise polyaniline (PANI) and polythiophene (PThio)[9–12].

Many workers, scientists, researchers, and industrialists have predominantly paid attention to them due to their interesting electronic and optical properties. Other characteristic features include low cost and environmental stability, besides making them applicable to commercial applications, among others, in polymer solar cells, sensors, and batteries[13, 14]. Conducting copolymers of polythiophene and polyaniline composite by using thiophene and aniline monomers have been the subject of study more than any other conducting polymer because they can be produced at a relatively low cost, with easy processability, a promise of environmental stability, ability to carry exceptional electrical conductivity, unique redox properties, reversible doping/dedoping, and easily controllable various properties, especially electrical conductivity[13–17].

Based on tetravalent metal phosphates, polythiophene polyaniline copolymer composites are worth investigating. In the present work, the prepared mixed glassy hafnium-titanium phosphates/polythiophene and polythiophene polyaniline copolymers composites have been prepared and characterized using FeCl_3 and CuCl_2 as oxidants.

Materials and Methods

Chemicals

HfCl_4 , TiCl_4 , Thiophene, and H_2O_2 33% were purchased from Riedel-de Haën, and H_3PO_4 85% was from BDH. Aniline 99.5% was from Mendix, and Dimethyl sulfoxide (DMSO) was bought from Park. Anhydrous FeCl_3 was supplied by Merck, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ has been purchased without mentioning the supplier.

Instruments used for characterization

Spectra were registered in the region of $200\text{--}4000\text{ cm}^{-1}$ on FTIR-6100, Shimadzu spectrometers (Japan). The content of carbon, hydrogen, nitrogen, and sulfur was determined on a fully automated analyzer, Varian EL III (Germany). The pH values were observed by a WGW-521 pH meter. The identity as well as purity of the compound was also checked by standard analytical techniques.

Preparation of glassy mixed hafnium titanium phosphates $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ ($x = 0.50, 0.34$)

glassy mixed inorganic hafnium titanium phosphates $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ was prepared according to the method reported [1,2]. Typically, glassy $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ preparation was carried out by mixing 20 ml 0.5M HfCl_4 and 5ml of 0.5M TiCl_4 in 4M HCl at room temperature. The resultant mixture was added dropwise slowly to 60 ml 12% H_3PO_4 with stirring at controlled room temperature for 2 hours. Then left to age in its mother liquor for 48 hours, the resultant gel was filtered, washed with distilled water carefully up to pH=3, dried in an oven at 60°C , then cracked with distilled water, and filtered to give a glassy (vitreous

look). $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$. Following the above-mentioned experimental parameters, glassy $\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ was prepared, taking into consideration stoichiometric mixing of molar ratios of HfCl_4 and TiCl_4 solutions.

Estimation of titanium contents

Titanium % contents of glassy mixed hafnium titanium phosphates were estimated according to the method already reported [1,2].

Preparation of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene composite

In the first synthesis, 0.25 g of glassy $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ was introduced into a solution containing 1 ml of thiophene dissolved in 40 ml of distilled water. The mixture was maintained under constant stirring at room temperature (30 °C). Subsequently, 15 ml of an aqueous solution of ferric chloride (10%) was added slowly, followed by the careful introduction of eight drops of hydrogen peroxide (33% w/w). Stirring was continued for a period of 48 hours to ensure complete reaction. The resulting product was isolated by filtration, thoroughly washed with distilled water and ethanol to remove residual reactants, and finally dried in air. In the second preparation, 1 ml of thiophene was dissolved in 40 ml of distilled water and poured over 0.25 g of glassy $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ with continuous stirring at room temperature (30 °C). To this suspension, 15 ml of an aqueous solution of copper (II) chloride dihydrate (0.20 M) was added gradually, after which eight drops of hydrogen peroxide (33% w/w) were introduced. The mixture was stirred for approximately 48 hours to allow the reaction to proceed. The product obtained was separated by filtration, washed sequentially with distilled water and ethanol, and subsequently dried in air.

Preparation of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composite

In the first experiment, 0.25 g of glassy $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ was combined with a mixture of 0.5 ml thiophene and 0.5 ml aniline dissolved in 40 ml of distilled water. The reaction was carried out at approximately 30 °C under continuous stirring. To this suspension, 15 ml of an aqueous solution of ferric chloride (10%) was added gradually, followed by the careful addition of eight drops of hydrogen peroxide (33% w/w). The mixture was stirred for a further 48 hours to ensure complete interaction of the reactants. The product obtained was separated by filtration, washed thoroughly with distilled water and ethanol to remove unreacted species, and subsequently dried in air. In the second synthesis, 0.25 g of glassy $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ was treated with a mixture of 0.5 ml thiophene and 0.5 ml aniline dissolved in 40 ml of distilled water, with stirring maintained at room temperature (30 °C). To this mixture, 15 ml of an aqueous solution of copper (II) chloride dihydrate (0.20 M) was added slowly, followed by the addition of eight drops of hydrogen peroxide (33% w/w). The reaction was allowed to proceed under continuous stirring for 48 hours. The resulting product was collected by filtration, washed sequentially with distilled water and ethanol, and finally dried in air.

Preparation of $\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composite

In the first synthesis, 0.25 g of glassy $\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ was combined with a mixture of 0.5 ml thiophene and 0.5 ml aniline dissolved in 40 ml of distilled water. The suspension was stirred continuously at room temperature (30 °C). To this mixture, 15 ml of an aqueous solution of ferric chloride (10%) was added gradually, followed by the careful addition of eight drops of hydrogen peroxide (33% w/w). Stirring was maintained for 48 hours to ensure complete reaction. The resultant product was separated by filtration, washed thoroughly with distilled water and ethanol, and subsequently dried in air. In the second preparation, 0.25 g of glassy $\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ was treated with a mixture of 0.5 ml thiophene and 0.5 ml aniline dissolved in 40 ml of distilled water, with stirring at room temperature (30 °C). To this suspension, 15 ml of an aqueous solution of copper (II) chloride dihydrate (0.20 M) was added slowly, followed by the addition of eight drops of hydrogen peroxide (33% w/w). The mixture was stirred continuously for 48 hours. The solid product obtained was isolated by filtration, washed sequentially with distilled water and ethanol, and finally dried in air.

Electrical conductivity measurements

A JENWAY 4510 conductivity meter was used at 25 °C. Precisely 0.02 g of polythiophene and its aniline copolymers obtained from their composites were dissolved in 10 mL DMSO. After calibration, measurements were taken by placing the cell into these solutions and waiting for readout stabilization before recording the results. In order to avoid any contamination, the cell was washed with deionized water between each sample, shaken to remove possible droplets inside, wiped outside as well, and then immersed in the next sample solution. When measurements were completed, the cell was washed thoroughly with deionized water.

Results and Discussion

Glassy hafnium-titanium phosphates, $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$, were prepared and characterized according to the method already reported by Shakshooki *et al.* [2]. Found to be amorphous with a vitreous distinct visual look.

XRD of of glassy $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$

(Figure 1) shows a typical X-ray diffractogram of the resultant glassy $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$, which is identical to the X-ray diffractogram of amorphous M(IV)phosphates. The absence of peaks indicates the amorphous nature of the material [1,2].

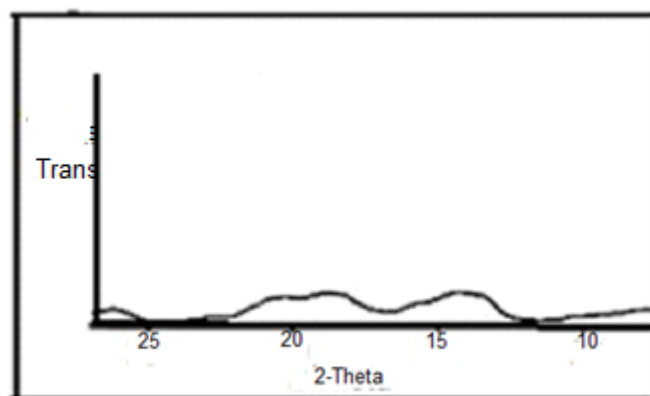


Fig. 1. Typical XRD of (g-HfTiP)

 $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2$ / polythiophene, polythiophene-co-polyaniline composites

This study planned to obtain polythiophene and polythiophene-co-polyaniline composites by the reaction of thiophene monomer and its co-monomer aniline over $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2$ formed on drying under in-situ conditions with FeCl_3 and an oxidizing agent of aqueous CuCl_2 as the polymerization agents. The results obtained have indicated successful synthesis for polythiophene- and polythiophene-co-polyaniline-based $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2$ composites. Elemental analysis, C, H, N, S data, FT-IR spectra, UV-visible spectral properties, as well as measurements of conductivity were used in its characterization. The weight % of polythiophene and its copolymer with polyaniline is given in this table.

Table 1. The % in wt. of (CHNS) of polythiophene and its polyaniline copolymers. (Values in blue for PTh and values in black are for PANi)

	compound	C%	H%	N%	S%	oxidant
1	$\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / PTh	14.94	0.62	===	9.96	FeCl_3
2	$\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / PTh	18.81	0.78	===	12.54	CuCl_2
3	$\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / PTh-co-PAni	11.25 19.95	0.47 1.38	=== 3.88	7.50 ===	FeCl_3
4	$\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / PTh-co-PAni	8.31 25.40	0.35 1.76	= 4.94	5.54 ===	CuCl_2
5	$\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2$ / PTh-co-PAni	0.97 13.88	0.04 0.93	=== 2.60	0.65 ===	FeCl_3
6	$\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2$ / PTh-co-PAni	2.65 15.37	0.11 1.06	=== 2.99	1.77 ===	CuCl_2

FT-IR spectra of $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2$ / polythiophene composites.

(Fig. 2) shows FT-IR spectra of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene composite. The oxidant was FeCl_3 . The spectrum shows a band at 1672 cm^{-1} assignable to the C=C stretching vibration of thiophene overlapping with the bending vibration of H-O-H. An absorption band at 1146 cm^{-1} may be due to PO_4 groups. A broad doublet centered at 890 and 811 cm^{-1} can be taken as tensile vibration out-of-plane of the thiophene ring C-H bonds. The band observed at 534 cm^{-1} could be attributed to the C-S bond; in other words, this is evidence for thiophene monomer inside the polymer backbone. The very broad band in the region of 3600 - 2900 cm^{-1} with a maximum at 3193 cm^{-1} is due to moisture. Bands in the region of 2192 - 1989 cm^{-1} could be due to C-H bonds. (Fig. 3) shows FT-IR spectra of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene composite. The oxidant was CuCl_2 . Broad bands observed within the range of 3600 - 2900 cm^{-1} are ascribed to moisture, while those falling at 2374 - 2032 cm^{-1} may most probably be due to CH bonds. The band at 1670 cm^{-1} can be assigned to the C=C bond of thiophene, and it lies in the region of fingerprint absorption and also overlaps with bending vibrations of H-O-H. Absorption centered at about 1050 cm^{-1} is characteristic of PO_4 groups. A band at 793 cm^{-1} may be attributable to tensile vibrations of the C-H bond outside the thiophene ring structure. The band observed at about 536 cm^{-1} can be assigned to a C-S bond; this is an indicator for thiophene monomer content in the polymer backbone.

FT-IR spectra of $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composites

(Figs. 4 and 5) show typical FT-IR spectra of $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composites. FTIR spectroscopy also confirmed the presence of aniline and thiophene units in the copolymer regardless of the type of oxidant used, hence proving that the monomers are chemically attached to each other in the copolymer. The FT-IR spectra of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composite are shown in Figure 4 with FeCl_3 as an oxidizing agent. A band at 1600 cm^{-1} relates to $\text{C}=\text{C}$ thiophene (being in the fingerprint region) that superimposes with $\text{H}-\text{O}-\text{H}$ bending. Absorption bands within the region $1501\text{--}1100\text{ cm}^{-1}$ may be assigned to the vibration of the $\text{C}-\text{C}$ bond, $\text{C}-\text{H}$ aromatic, $\text{C}=\text{C}$, and $\text{C}-\text{N}$ stretching of polyaniline. The broad band centered at 832 cm^{-1} is assigned to the vibrational shift of PO_4 groups. A band observed at 534 cm^{-1} can be attributed to the $\text{C}-\text{S}$ bond, which proves the existence of thiophene monomer in the polymer backbone. In addition, a peak appearing at about 1100 cm^{-1} proves the existence of $\text{N}-\text{S}$ bonding that was created due to the reaction between aniline and thiophene copolymer. This shows that nanoparticles are uniformly distributed within the copolymer. (Fig. 5) shows FT-IR spectra of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composite. The oxidant is CuCl_2 . Almost identical to the FT-IR of Figure 6. This goes on to show that both aniline and thiophene units are joined within the copolymer structure and that the monomers have been joined by chemical bonding in the derived copolymer product. The peak found at 1600 cm^{-1} can be assigned to the $\text{C}=\text{C}$ vibration of thiophene, falling within the fingerprint region where it overlaps $\text{H}-\text{O}-\text{H}$ bending. Absorption bands found between $1501\text{--}1100\text{ cm}^{-1}$ can be correlated as belonging to $\text{C}-\text{C}$ bond vibration, aromatic $\text{C}-\text{H}$, $\text{C}=\text{C}$, and $\text{C}-\text{N}$ stretching modes of polyaniline. A broad band located at 832 cm^{-1} is due to PO_4 groups' stretching vibration. The band observed at 534 cm^{-1} belongs to the $\text{C}-\text{S}$ bond, hence proving the existence of thiophene monomer units in the polymer backbone. Also, a peak near 1100 cm^{-1} gives proof of $\text{N}-\text{S}$ bonding formation.

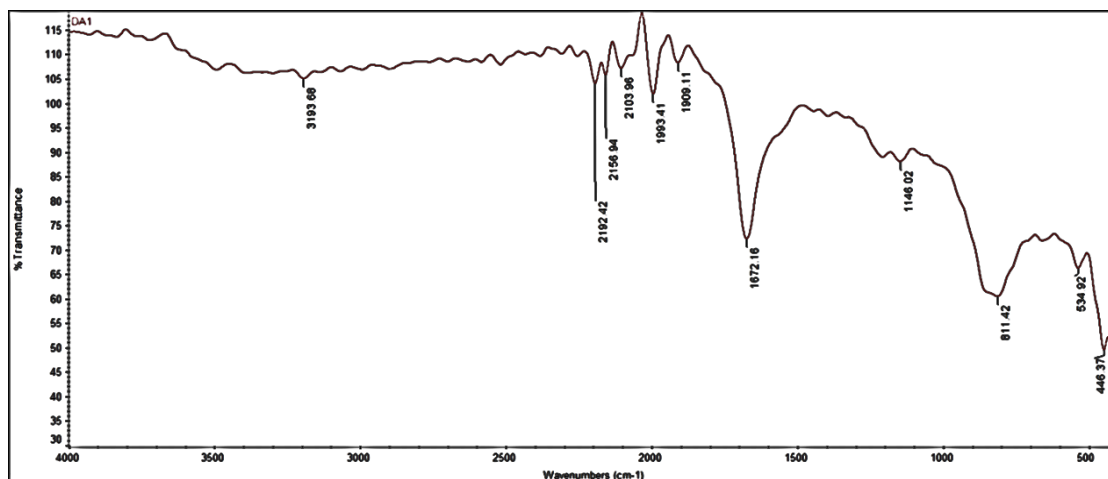


Fig. 2. FT-IR spectra of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene composite., the oxidant is FeCl_3

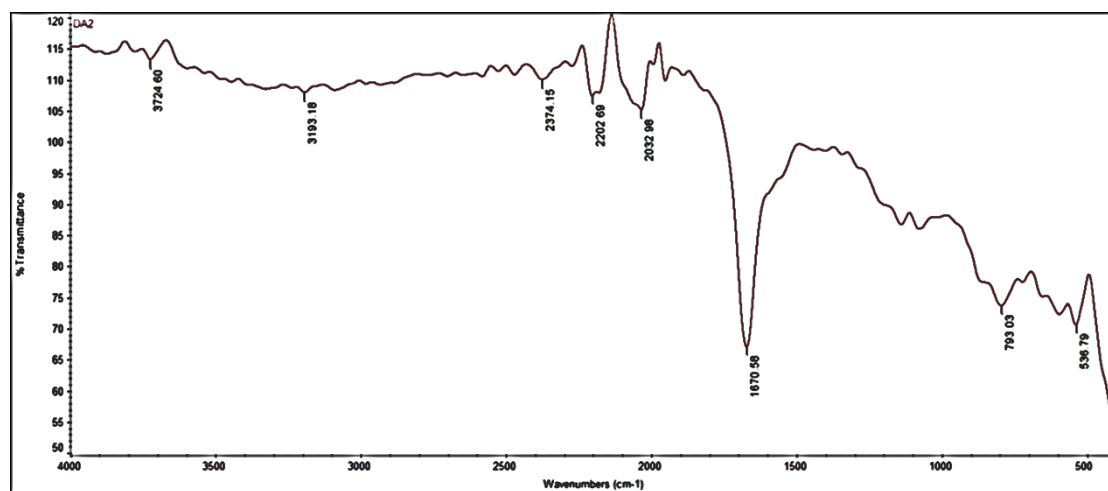


Fig. 3. FT-IR spectra of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene composite. The oxidant is CuCl_2

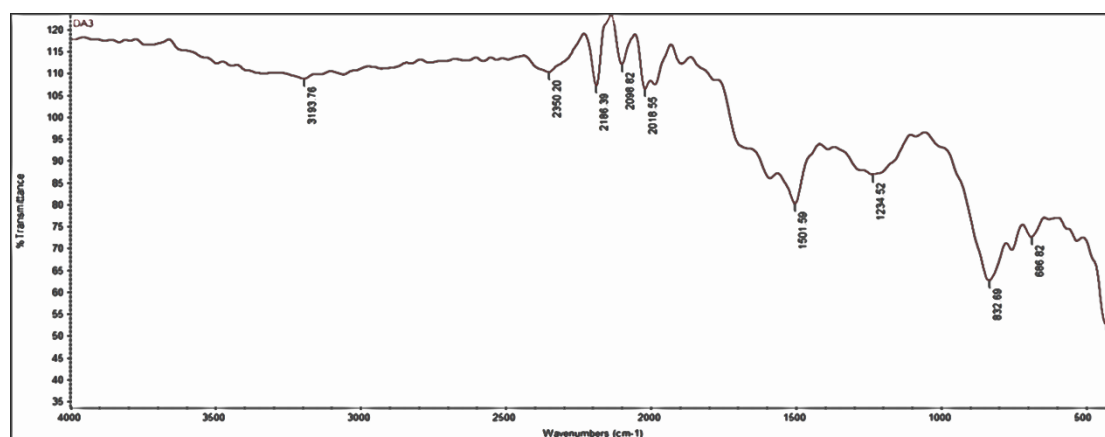


Fig. 4. FT-IR spectra of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composite the oxidant is FeCl_3

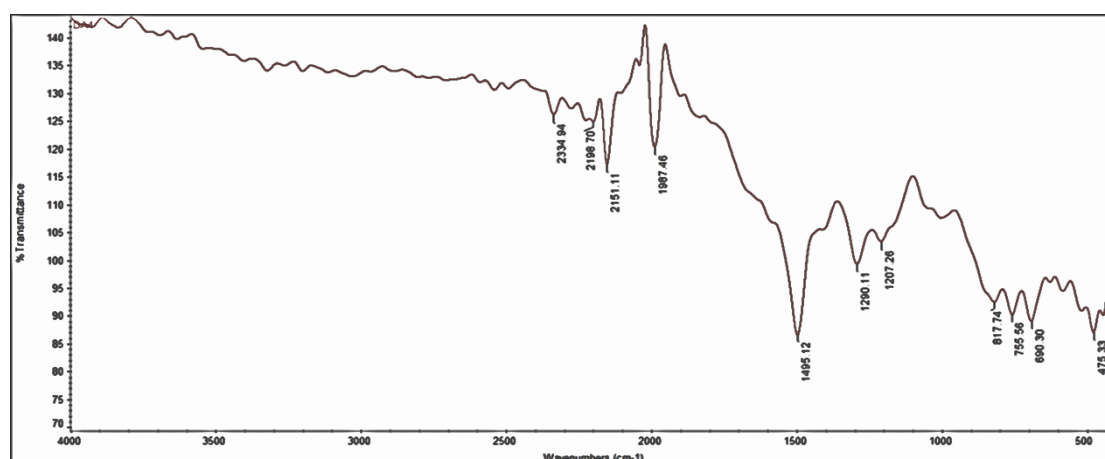


Fig. 5. FT-IR spectra of $\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composite, the oxidant is CuCl_2

FT-IR spectra (Figures 6,7) of $\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composite. The oxidants are (FeCl_3 or CuCl_2) found to follow the same trends, confirming This denotes that both aniline and thiophene units are put into the structure of copolymers, no matter which oxidant is used. The monomers are chemically joined within the copolymer. (Fig. 6) A small band at 1600 cm^{-1} , which relates to $\text{C}=\text{C}$ thiophene, which is in the fingerprint region and superimposes with H-O-H bending. Absorption bands found between $1505\text{--}1200\text{ cm}^{-1}$ can be assigned to the vibration of the C-C bond stretching in benzoid rings, C-H aromatic, C=C, and C-N stretching of polyaniline. A broad band centered at 998 cm^{-1} can be assigned to the PO_4 groups vibration. The band at 744 cm^{-1} corresponds to the tensile vibration of the C-H bond located outside the plane of the thiophene ring. The band seen at 583 cm^{-1} can be related to a C-S bond, hence the presence of thiophene monomer in the polymer backbone. A broad band in region $3600\text{--}2900$ centered at 3043 cm^{-1} can be assigned to moisture. Bands in region $2332\text{--}1906\text{ cm}^{-1}$ can be related to C-H bonds.

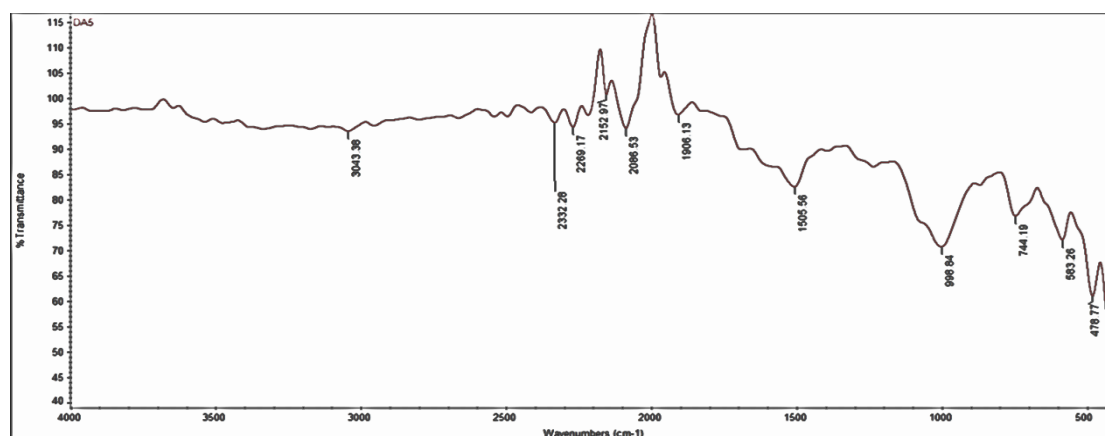


Fig. 6. FT-IR spectra of $\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composite, the oxidant is FeCl_3

(Fig.7) represents the FT-IR spectra of $\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2$ /polythiophene-co-polyaniline composite, where polythiophene-co-polyaniline, by oxidation with CuCl_2 , shows a broad region between 3600 and 3000 cm^{-1} centered at 3382 cm^{-1} , assignable to moisture. Bands in the region from 2219 to 1880 cm^{-1} could be due to C-H bonds. A weak band seen at 1600 cm^{-1} could be assigned to the C=C vibration of thiophene, lying within the fingerprint region where it merges with bending vibrations of H-O-H. Absorption bands noted between 1149 and 1291 cm^{-1} relate to benzoid rings from C-C bond stretching vibrations and aromatic C-H, C=C, and C-N stretching modes of polyaniline. A broad band centered at 992 cm^{-1} relates to the vibrational modes of PO_4 groups. The band at 753 cm^{-1} may be due to the tensile vibration of the C-H bond out of plane from the thiophene ring. Also, a band observed at 583 cm^{-1} is for the C-S bond and hence proves that thiophene monomer units are present in the polymer backbone.

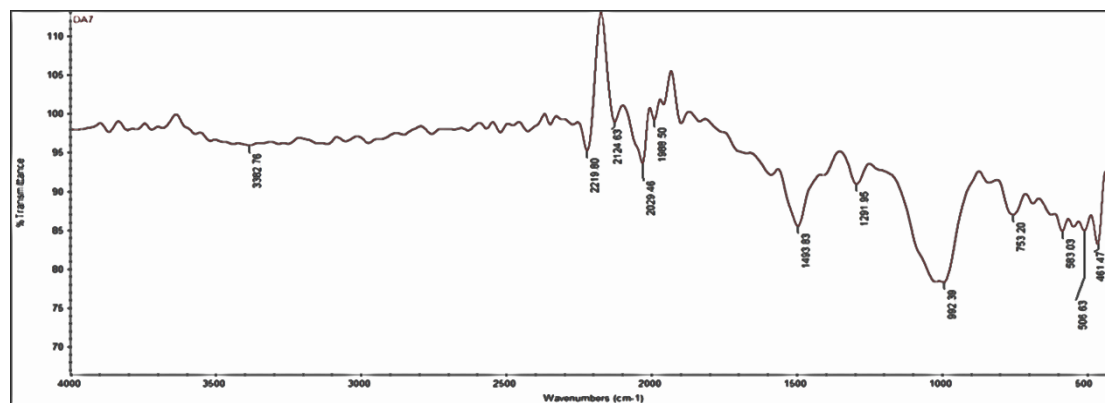


Fig. 7. FT-IR spectra of $\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2$ / polythiophene-co-polyaniline composite. The oxidant is CuCl_2

Electrical conductivity of DMSO extract of polythiophene and polythiophene-co-polyaniline composites

Conductivity is a basic property of matter showing a broad span from very conducting materials like metals to insulators, which include plastics and glass. Solution conductivity speaks to the ability of a solution to carry electric current from one electrode to another. This is possible only due to ion movement; hence, the higher the concentration of ions in the solution, the greater will be its conductivity. In practical applications, it is the measured cell constant that is fed into the meter, either by direct means or as a user calibration factor, enabling conversion from conductance to conductivity, which then can be worked out and displayed. This paper reports on the electrical conductivity of DMSO-extracted polythiophene and polythiophene-co-polyaniline composites synthesized from their composite materials $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ ($x = 0.80, 0.50, 0.34$). Some results lead to a conclusion about these resulting composite materials having properties typical of semiconductors. (Table 2) shows the electrical conductivity of polythiophene and polythiophene-co-polyaniline extracted by DMSO from their composites.

Table 2. Electrical conductivity of the polythiophene and polythiophene-co-polyaniline

Extracted CPs	Conductivity (Scm^{-1})	oxidant
$\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / PTh	1.606×10^{-4}	FeCl_3
$\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / PTh	9.698×10^{-5}	CuCl_2
$\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / PTh-co-PAni	1.04×10^{-4}	FeCl_3
$\text{Hf}_{0.50}\text{Ti}_{0.50}(\text{HPO}_4)_2$ / PTh-co-PAn	4.69×10^{-5}	CuCl_2
$\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2$ / PTh-co-PAn	1.64×10^{-4}	FeCl_3
$\text{Hf}_{0.34}\text{Ti}_{0.66}(\text{HPO}_4)_2$ / PTh-co-PAn	3.80×10^{-5}	CuCl_2

The electrical conductivity of the synthesized polymers significantly depends on the type of oxidizing agent used during the doping process. Based on the calculated values, ferric chloride outperformed cupric chloride, yielding higher conductivity. This disparity can be attributed to the higher standard redox potential of FeCl_3 . The Ions act as more effective dopants by efficiently removing electrons from the polymer backbone, thereby generating a higher density of charge carriers (polarons or bipolarons). This increased carrier concentration enhances electronic hopping along the polymer chains.

Conclusion

Glassy Mixed hafnium-titanium phosphates, $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ (where $x = 0.34$, and 0.50) were prepared and characterized, found to be amorphous with a vitreous visual look. Novel $\text{Hf}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2$ /

polythiophene, and polythiophene-co-polyaniline composites were prepared via chemical oxidation of their parent monomers by using FeCl_3 and CuCl_2 as oxidant agents, and characterized by elemental (CHNS) analysis and FT-IR spectroscopy. Electrical conductivity for resultant conducting polymers and copolymers represents a range of semiconductors. The beneficial properties of the resultant composite can be regarded as novel conducting polymer composites, with the ability to carry exceptional electrical conductivity, unique redox properties, reversible doping/dedoping, and easily controllable various properties, especially electrical conductivity.

Conflict of Interest

There are no conflicts to declare.

Funding Information

The article contains all the analysis and experimental data.

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