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Nano Fibrous Cerium(IV) Hydrogen Phosphate Membrane Self Supported Indole Polymerization Agent

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Abstract: Nanosized fibrous cerium(IV) hydrogen phosphate membrane, $Ce(HPO_4)_2 \cdot 2.9H_2O$ ($nCeP_f$), was prepared and characterized by chemical, XRD (X-ray diffraction), TGA (thermogravimetric analysis), SEM (scanning electron microscopy) and TEM (transmission electron microscopy). Novel supported nanofibrous Ce(IV) phosphate/polyiondole nanocomposite membranes were prepared via in-situ chemical oxidation of the monomer that was promoted by the reduction of Ce(IV) ions present in the inorganic matrix. The presence of Ce(IV) ions allows redox reactions necessary to oxidative polymerization to occur. The resultant material was characterized by TGA, elemental (C, H, N) analysis and FT-IR (Fourier transform spectroscopy). SEM images of the resulting nanocomposite reveals a uniform distribution of the polymer on the inorganic matrix. Amount of polyindole polymer present in the composite is found to be ~ 7.0%.

Key words: Nanofibrous cerium(IV) hydrogen phosphate membrane, self support polymerization, indole.

1. Introduction

In recent years, heterocyclic conducting polymers containing nitrogen atoms like polyaniline and polypyrrole, and their substituted derivatives have received increasing attention in various fields, electronics, industry and others [1-3]. Their electrical and electrochemical properties show great promise for commercial applications. However, among various aromatic compounds-based conducting polymers, polyindole and its derivatives has been less investigated although there exists close structural similarities with the polymers mentioned above [4]. Polyindole can be obtained from chemical, electrochemical and interfacial polymerization of indole [2, 3, 5, 6]. Its electrical and electrochemical properties show great promise for commercial applications [5-10]. Polyindole is an electro active polymer, owns advantages especially fairly good thermal stability [5, 6]. Some studies shows polyindole has similar properties like polyaniline, based on their high conductance and good environmental stability [2, 4, 11-13]. Inorganic layered nanomaterials are receiving great attention because of their size, structure, and possible biochemical applications [14, 15], that have been proven to be good carriers for organic polar molecules. Examples of these are zirconium phosphates, $Zr(HPO_4)_2 \cdot H_2O$ (ZrP), which are inorganic cation exchange materials with high thermal stability, solid-state ion conductivity, resistance to ionizing radiation, and which are known as hosts capable of incorporating different types and sizes of guest molecules [15].

Researchers have been capable of encapsulating functional biomolecules into these inorganic matrices protecting them from interacting with environment, avoiding denaturation and enhancing their shelf life [14, 15]. Crystalline cerium phosphates have been studied for a long time as ion exchangers, their structures remains unknown until recently [16-18].

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The reason is that, the composition, the structure and the degree of crystallinity of their precipitates results from reaction of solutions containing a Ce(IV) salt which is mixed with a solution of phosphoric acid of [(PO_4)/Ce(IV) ratio], strongly depend on the experimental conditions such as rate and order of mixing of the solutions, stirring, temperature and digestion time, this also implemented on fibrous cerium phosphate [19]. To date, most of the work on fibrous cerium phosphate was carried out on its ion exchange [20], intercalation [21] and electrical conductance properties [22]. Studies on its polystyrene, polyacrylamide [23] and (polyvinyl chloride-based polyvinyl (alcohol) [24] composites have been reported. Nanoscaled tetravalent metal phosphates and their organic polymer composites comprise an important class of synthetic engineering. However, research in such area is still terra incognita [25-28]. Nanotechnologies are at the center of numerous investigations and huge investments. However, chemistry has anticipated for long the importance decreasing the size in the search of new properties of materials, and of materials structured at the nanosize in a number of applications relate to daily life. Organic-inorganic nanocomposite membranes have gained great attention recently [28, 29]. The composite material may combine the advantage of each material, for instance, flexibility, processability of polymers and the selectivity and thermal stability of the inorganic filler [26-30]. Conducting polymers are interesting materials owing to their electrical properties [25, 27]. Belonging to this class are polyaniline, polypyrrole, polybenzimidazole and others. Polyppyrole polymerization by fibrous ceium phosphate has been reported [31, 32].

In our laboratory, we are carrying systematic investigations on novel tetravalent metal phosphates/organic heterocyclic conducting polymers nanocomposite membranes. Recently, we have reported [33] the preparation and characterization of fibrous cerium phosphate/polybenzimidazole nanocomposite membrane. The present study describes the preparation and characterization of novel supported fibrous cerium phosphate/polyindole nanocomposite membranes via in-situ chemical oxidation that was promoted by the reduction of Ce(IV) ions presenting in the inorganic matrix.

2. Experiments

Chemicals $Ce(SO_4)\cdot 2.4H_2O$, H_3PO_4 (85%) of British drug house, PVA (Polyvinylealcohol), MWt (molecular weight) = 25,125 g/mol of Aldrich., Indole of Reidel de-Haen, were used as such. Other reagents used were of analytical grade.

2.1 Instruments Used for Characterization

X-ray powder diffractometer Siemens D-500, using Ni-filtered CuKα (λ = 1.54056 Å); TG/DTA (thermogravimetric loss/differential thermal analysis), DTSIIExtra 6000 Thermogram and TG/DTA Perkin-Elmer SII; Fourier Transform IR spectrometer, model IFS 25 FT-IR, Bruker; SEM (scanning electron microscopy) Jeol SMJ Sm 5610 LV; TEM (transmission electron microscopy) Zeiss TEM 10CR and pH Meter WGW 521.

2.2 Preparation of Nanofibrous Cerium Phosphate Membrane: $Ce(HPO_4)_2\cdot 2.9H_2O$

Nanofibrous cerium phosphate membrane was prepared from adding 150 mL of 0.05 M $CeSO_4\cdot 4H_2O$ in 0.5 M H_2SO_4 solution, dropwise, to 150 mL of 6 M H_3PO_4 at 80 °C with stirring. After complete addition, the resultant material left to digest at that temperature for 5 h. To that, 1 L of hot distilled water, (~ 60 ^oC), was added with stirring for 1 h. The resulting fibrous cerium phosphate was subjected to washing by with distilled water up to pH 3, then filtered, washed with ethanol and dried in air.

2.3 Exchange Capacity

Exchange capacity of nanosized fibrous cerium phosphate membrane was determined by addition of 25 mL of 0.1 M NaCl solution to 100 mg of the

material, with stirring for 1 h, then titrated with 0.1 M NaOH solution.

2.4 Thermal Analysis

Thermal analyses were carried out at temperature range about 20-775 °C in nitrogen atmosphere, the rate was 10 °C/min.

2.5 Preparation of Nanofibrous Cerium Phosphate Polyindole Composite Membranes

Cerium phosphate/polyindole nanocompsite membranes were prepared as follows:

(1) By immersion of fibrous cerium phosphate self supported-sheet 160 mg in 10 mL ethanol solution containing 200 mg indole, at room temperature for 5 days. It was observed with time the color changes gradually (pale brown, brown and finally to dark brown). The impregnated sheet was removed, washed with ethanol and left to dry in air.

(2) By immersion of fibrous cerium phosphate self supported-sheet 160 mg in 10 mL ethanol solution containing 200 mg indole, at room temperature for 2 days. It was observed with time the color changes gradually (pale brown and finally to brown). The impregnated sheet was removed, washed with ethanol and left to dry in air.

3. Results and Discussion

Nanofibrous cerium phosphate membrane, Ce $(HPO_4)_2 \cdot 2.9H_2O$ (nCePf), was prepared and characterized by chemical, XRD, TGA, FT-IR, SEM and TEM.

XRD of nCePf is shown in Fig. 1, with d_{001} = 10.89 Å

Thermogram of nCePf is shown in Fig. 2. The thermal decomposition occurs in continuous process, the thermal analysis was carried out at temperatures between 10-775 °C, the final product was CeP_2O_7. Loss of water of hydration occurs between 60-200 °C, followed by POH groups condensation. The total weight loss found to be equal to 19.09%.

Fig. 3 shows FT-IR spectrum of fibrous $Ce(HPO_4)_2 \cdot 2.9H_2O$, with a trend similar to that of M(IV) phosphates. It consists of broad band centered at 3,350 cm^{-1} is due to OH groups symmetric stretching of H_2O, small sharp band at 1,628 cm^{-1} is related to H-O-H bending, and sharp broad band centered at 1,045 cm^{-1} is corresponds to phosphate groups vibration. The bands at the region 630-450 cm^{-1} are ascribe the presence of $\delta(PO_4)$.

SEM morphology image of the nanosized fibrous cerium phosphate (nCePf) is shown in Fig. 4. The photograph shows its average size is ~ 20.5 nm.

The ion exchange capacity of nanosized fibrous cerium(IV) phosphate, $Ce(HPO_4)_2 \cdot 2.9H_2O$, found to be equal to 5.21 meq/g.

TEM image of the nanosized fibrous cerium phosphate (nCePf) is shown in Fig. 5. The photograph shows its average size is ~ 15 nm.

New supported polyindole nanocomposite was

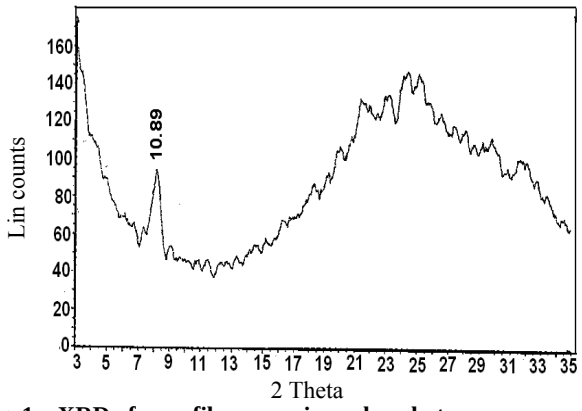

Fig. 1 XRD of nanofibrous cerium phosphate.

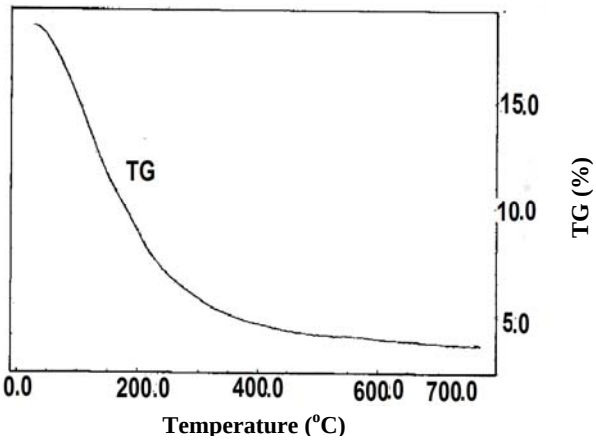

Fig. 2 TGA of nanofibrous cerium phosphate.

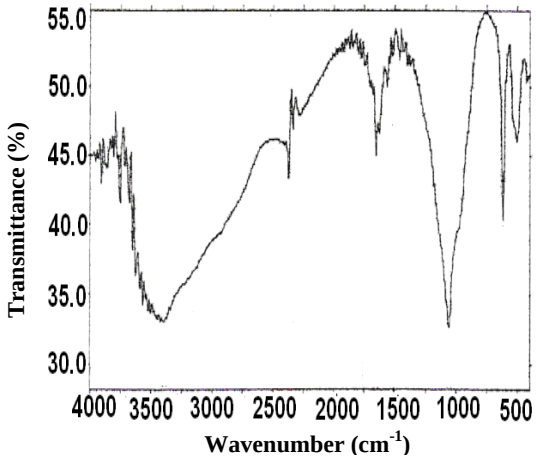

Fig. 3 FT-IR spectra of nanofibrous cerium phosphate.

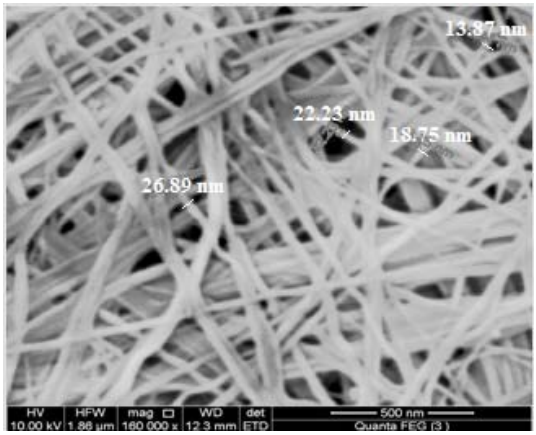

Fig. 4 SEM morphology image of (nCePf).

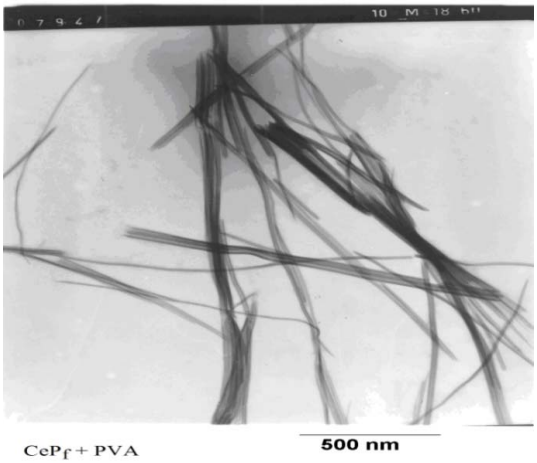

Fig. 5 Miograph image (TEM) of (nCePf) composite thin film in PVA matrix.

prepared and investigated in this work. Self-supported sheet of nanosized fibrous cerium(IV) hydrogenphosphate, $Ce(HPO_4)_2 \cdot 2.9H_2O$ (nCePf), was used as the inorganic matrix, since the fibrous morphology present by this material makes molding possible, giving desired shape to the final (nCePf)/polyindole naoncomposite membrane. It was found that when nanosized fibrous cerium(IV) hydrogen phosphate immersed in ethanolic solution of polyindole the color of self supported sheet gradually changes with time to (pale brown, brown and finally to dark brown) due to the formation of nanocomposite membrane. It is important to note that the self-suported sheet integrity is preserved. This result is interesting because the shape integrity makes the building of molded conducting device possible. The resultant material was characterized by elemental (C, H, N) analysis TGA and by FT-IR spectroscopy.

From elemental (C, H, N) analysis, the amount of organic material present in the (nCePf) polyindole naoncomposite was 6.81% in weight. The % of elemental (C, H, N) related to the organic polymer found to be C = 5.58%, H = 0.41% and N = 0.82%. From TGA analysis, the amount of the organic polymer found to be 7% in weight. However, on repeating the same experiment for a period 48h time immersion of fibrous cerium phosphate in indole solution, gave low yield of polyindole (3.97% in weight). It is elemental (C, H, N) analysis, were C = 3.26%, H = 0.327% and N = 0.475%. So, the degree of polymer loading can be controlled by varying aging time.

Fig. 6 shows SEM image for (nCePf)/polyindole naoncomposite membrane, reveal a uniform distribution of the polymer on the inorganic matrix, coating the nCePf and filling the empty spaces between the fibers. Amount of polyindole present in the composites was found to be 7% in weight.

Fig. 7 shows FT-IR spectrum of (nCePf)/polyindole nanocomposite membrane. It consists of broad band centered at 3,425 cm^{-1} is due to OH groups symmetric stretching of H_2O, small sharp band at 1,632 cm^{-1} is related to H-O-H bending, and sharp broad band centered at 1,055 cm^{-1} is corresponds to phosphate groups vibration. Small band at 2,921 cm^{-1} corresponds

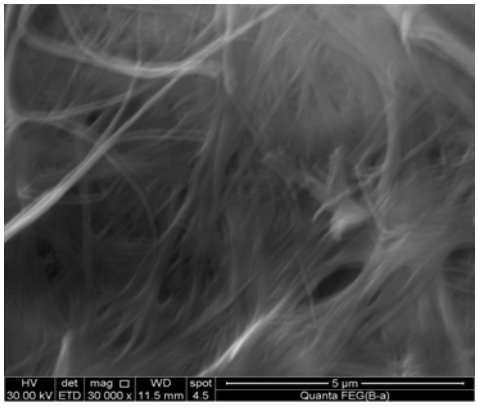

Fig. 6 SEM image of (nCePf)/polyindole nanocomposite.

to C-H bonds, bands in the region of 1,557-1,500 cm^{-1} are related to stretching C-C bonds characteristic of indole unites, bands in the region 1,500-1,400 cm^{-1} corresponds to C-N bonds. The band at 742 cm^{-1} is correspond to out of plane deformation of C-H bond in the benzene ring [34].

Thermogram of (nCePf)/polyindole nanocomposite membrane is shown in Fig. 8, the weight loss up to 180 °C is 7.35% due to the removal of external water molecules. The weight loss occurs between 180-700 °C corresponds to the decomposition of polyindole and condensation of P-OH groups of the inorganic material to pyrophosphate, CeP_2O_7. The POH groups condensation found to cuoerimose with that of polyindole. The total weight loss found to equal to 18.562%. From thermal and elemental (carbon, hydrogen, nitrogen) C, H, N analysis, the resultant

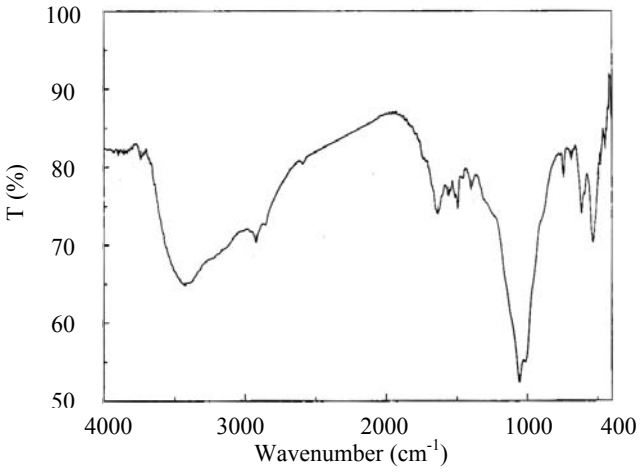

Fig. 7 FT-IR spectrum of (nCePf)/polyindole nanocomposite.

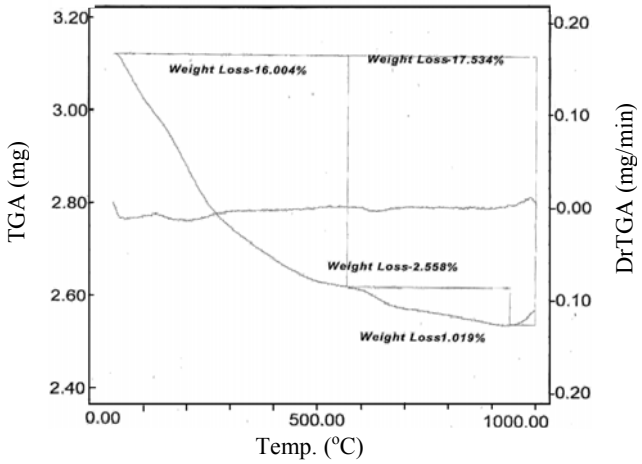

Fig. 8 TG/DTA of (nCePf)/polyiondole nanocomposite.

product was formulated as: $Ce(HPO_4)_2 \cdot (PInd)_x \cdot 2.1\ H_2O$., where, x = ~ 7.0%.

4. Conclusions

Novel supported nanofibrous cerium phosphate/polyindole nanocomposite membrane was prepared via in-situ chemical oxidation of the monomer that was promoted by the reduction of Ce(IV) ions present in the inorganic matrix. The presence of Ce(IV) ions allows redox reactions necessary to oxidati.ve polymerization to occur. The self-supported sheet integrity is preserved. This result is interesting because the shape integrity makes the building of molded conducting device possible. The formulation of the fibrous cerium phosphate nanocomposite was supported by thermal, elemental (C, H, N) analysis, FT-IR spectrum and SEM. The degree of polymer loading can be controlled by varying aging time.

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