Analytical Chemistry Research 12 (2017) 52-64

Contents lists available at ScienceDirect

Analytical Chemistry Research

journal homepage: www.elsevier.com/locate/ancr

Comparative sensing of aldehyde and ammonia vapours on synthetic polypyrrole-Sn(IV)arsenotungstate nanocomposite cation exchange material

Asif Ali Khan ^{a, *}, Rais Ahmad ^b, Mohd. Zeeshan ^{a, b, **}

^a Analytical and Polymer Research Laboratory, Department of Applied Chemistry, F/O Engineering and Technology, Aligarh Muslim University, Aligarh, 202002, India

^b Environmental Research Laboratory, Department of Applied Chemistry, F/O Engineering and Technology, Aligarh Muslim University, Aligarh, 202002, India

ARTICLE INFO

Article history: Received 22 December 2016 Received in revised form 18 February 2017 Accepted 21 February 2017 Available online 24 February 2017

Keywords: Polypyrrole nanocomposite Electrical conductivity Isothermal stability Vapour sensing

ABSTRACT

Polypyrrole-Sn(IV)arsenotungstate (PPy-SnAT) conductive nanocomposite cation exchange have been synthesized by in-situ chemical oxidative polymerization of polypyrrole with Sn(IV)arsenotungstate (SnAT). PPy-SnAT nanocomposite was characterized by Fourier transform infra-red spectroscopy (FTIR), X-Ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive x-ray (EDX) and thermogravimetric analysis (TGA). The ion exchange capacity (IEC) and DC electrical conductivity of nanocomposite was found to be 2.50 meq/g and 5.05 \times 10⁻¹ S/cm respectively. The nanocomposite showed appreciable isothermal stability in terms of DC electrical conductivity retention under ambient condition up to 130 °C. The nanocomposite cation exchange based sensor for detection of formaldehyde and ammonia vapours were fabricated at room temperature. It was revealed that the resistivity of the nanocomposite increases on exposure to higher percent concentration of ammonia and lower concentration of formaldehyde at room temperature (25 °C).

© 2017 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http:// creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Hazardous waste is discharged in the environment in many forms, like liquids, solids, gases, and sludge [1]. It can have an immediate as well as long-term devastating impact on ecosystem, comprising of plants and animals, making fish unfit for human consumption. Hazardous waste remains in the environment for a long time and in some cases for thousands of years. It may affect the environment in the form of hazardous gases like; ammonia, aldehyde and amines etc. [2-4].

Aldehydes are known to be highly toxic and corrosive, and even short-term exposure has major health risks. Consuming liquid aldehyde causes severe intestinal irritation and sometimes becomes fatal. Even at low levels, aldehyde gas causes eye, throat and skin irritation, nausea, wheezing and asthma attacks. Aldehydes are now classified as a known carcinogens, or cancer-causing agents, by the International Agency for Research on Cancer (IARC) [5]. The Environmental Protection Agency (EPA), for example, places a limit of 16 ppb (parts per billion) of aldehyde in the environment [6].

Poly(pyrrole) and its derivatives have received a great deal of attention due to their high electrical conductivity, good environmental stability, relatively easy synthesis and good redox reversibility. These properties are favourable for its applications in the area of secondary batteries [7], electro catalysis, electro chromic display devices, light-emitting devices, chemical sensors and biosensors [8–10]. However, the structure of poly(pyrrole) needs to be modified in order to be used in chemical sensor and biosensor fields since it has no functional group [11]. The conducting polymers also permit a charge transfer to produce electrochemical signals between the electrode and the immobilized biomolecules [12,13]. Thus for biosensor applications, the conducting polymers have been functionalized with carboxyl, amino, formyl or succinimidyl carbonate groups, and conjugated directly with various electronic mediators or bio-recognizable molecules to facilitate

2214-1812/© 2017 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).





CrossMark

^{*} Corresponding author.

^{**} Corresponding author. Analytical and Polymer Research Laboratory, Department of Applied Chemistry, F/O Engineering and Technology, Aligarh Muslim University, Aligarh, 202002, India; Environmental Research Laboratory, Department of Applied Chemistry, F/O Engineering and Technology, Aligarh Muslim University, Aligarh, 202002, India

E-mail addresses: asifkhan42003@yahoo.com (A.A. Khan), mohd.zee2010@ gmail.com (Mohd. Zeeshan).

immobilization.

However, conducting polymer based ion exchangers with polyvalent sites have been poorly reported in the field of gas sensing although some researchers have explored the electrical conductivity and sensing activity on the polymer based cation exchanger. In the present work, we have reported polypyrrole-Sn(IV)arsenotungstate(Ppy-SnAT) nanocomposite cation exchanger with better ion exchange capacity (IEC) than other Sn(IV) based cation exchangers reported earlier [14]. Formalde-hyde, ammonia and mixed (formaldehyde + ammonia) solution vapour sensing behaviour on Ppy-SnAT nanocomposite cation exchanger is the sufficient part of our studies.

2. Experimental

2.1. Chemicals, reagents and instruments

Pyrrole monomer from Spectrochem, iron(III)chloride (Merck, 98%), HCl (35%) from E-Merck (India Ltd.) were used. Sodium arsenate (Finar reagent), sodium tungstate (CDH), stannic chloride (SnCl₄·5H₂O) (CDH), methanol from CDH (India Ltd. 98%), formal-dehyde from Fisher scientific, ammonia from Merck (India Ltd. 25%) and demineralised water (DMW) were used in the experimental work. All other reagents and chemicals were of analytical grade.

Fourier Transform Infra-Red (FTIR) spectrophotometry was performed using Perkin-Elmer, USA, model Spectrum-BX, range 4000–400 nm. Scanning Electron Microscopy (SEM), Energy Dispersive X-ray diffraction (EDX) and Transmission Electron Microscope (TEM) was done using LEO 435–VF Electron Microscope. Thermo-Gravimetric Analysis (TGA) was done using Thermal Analyzer-V2.2A DuPont 9900 with nitrogen atmosphere. X-Ray Diffraction (XRD) was performed using Rigaku X-Ray powder diffractometer with Cu anode (K $\alpha \lambda = 1.54186 \text{ A}^{\circ}$) using a PW, 1148/89 based diffractometer with Cu K α radiations. Four in-line probe conductivity meter (scientific equipment Roorkee) was used for conductivity and sensing measurements.

2.2. Preparation and ion exchange capacity (IEC) of polypyrrole-Sn(IV)arsenotungstate (Ppy-SnAT) composite ion-exchanger

2.2.1. Synthesis of Sn(IV)arsenotungstate inorganic precipitate

Sn(IV)arsenotungstate was prepared at room temperature $(25 \pm 2 \circ C)$ by mixing 0.1 M stannic chloride (prepared in 1 M HCl), 0.1 M sodium arsenate and 0.1 M sodium tungstate (in DMW) in 1:1:1 vol ratio respectively. The solution was constantly stirred and the pH was maintained at 1. As a result, white colored gel of Sn(IV) arsenotungstate was obtained as precipitate. Then, the precipitate was allowed to settle down for 24 h, filtered and washed under suction with DMW until the filtrate showed neutral pH. Finally it was dried in an oven at 80 °C. The different ratios of inorganic ion exchanger are given in Table 1. On the basis of high ion exchange capacity (IEC) sample **S-2** was selected for further studies.

Table 1

Synthesis and IEC of Sn(IV)arsenotungstate ion exchange material.

S. 0.1 M Stannic No. chloride (1 M HCl) (ml)	0.1 M Sodium tungstate (DMW)(ml)	0.1 M Sodium arsenate (DMW)(ml)	pH IEC Meqg ⁻¹
S-1 50	50	50	1 2.0
S-2 100	50	50	1 2.1
S-3 50	100	50	1 1.4
S-4 50	50	100	1 0.8

2.2.2. Preparation of polypyrrole-Sn(IV)arsenotungstate (Ppy-SnAT) composite ion-exchange material

Ppy-SnAT was synthesized by in-situ chemical oxidative polymerization of Polypyrrole in the presence of Sn(IV)arsenotungstate (S-2) particles. A certain amount of Sn(IV)arsenotungstate was dispersed in 200 ml DMW, taken in three necked round bottom flask, and stirred for 30 min with the help of magnetic stirrer. A definite amount of pyrrole monomer was then added and the mixture was stirred for 45 min for the adsorption of pyrrole on the surface of Sn(IV)arsenotungstate (S-2) particles. After that, a fixed amount of aqueous FeCl₃ solution (prepared by dissolving 2 g FeCl₃ in 50 ml DMW) was added to the mixture and constantly stirred for another 24 h. The resultant mixture slowly turned into black colored slurry indicating the formation of Ppy-SnAT. It was then filtered off, washed thoroughly with DMW followed by fixed amount of methanol to remove excess acid and any adhering trace of FeCl₃. The washed material was finally dried in oven at 50 °C to obtain Ppy-SnAT composite ion exchanger.

2.3. Ion Exchange Capacity (IEC)

IEC expresses the amount of H^+ ions released by cation exchanger to the flow of neutral salt through it. To compute IEC, Ppy-SnAT composite was converted into H^+ form by keeping it in 1 M HNO₃ solution for 24 h with occasional shaking, and intermittently replacing the supernatant liquid. The excess acid was removed by washing it several times with DMW and dried it in the oven. The glass column (i.d.-1 cm) was packed with 1 g dry sample in H^+ form, 1.0 M sodium nitrate (NaNO₃) as eluent was used to elute the H^+ ions completely from the cation—exchange column keeping a flow rate of ~0.5 ml min⁻¹. The effluent was titrated against a standard 0.1 M NaOH solution using phenolphthalein as indicator [15].

On the basis of high IEC and better electrical conductivity sample Ppy-SnAT (**P-2**) was selected for further studies, results are shown in Table 2.

Table 2

Synthesis, IEC and conductivity of Ppy-Sn(IV)AT nanocomposite cation exchanger.

S	.No.	Sn(IV)arsenotungstate Inorganic ion exchanger (gm)	Pyrrole monomer in ml	FeCl ₃ (Water)(gm)	IEC Meqg ⁻¹	Electrical Conductivity (Scm ⁻¹)
P	-1	2	1	2	1.50	4.63×10^{-1}
Р	-2	2	3	2	2.50	5.05×10^{-1}
Р	-3	2	5	2	1.20	$3.99 imes 10^{-1}$
Р	-4	2	7	2	1.00	4.82×10^{-1}
Р	-5	2	9	2	0.80	4.92×10^{-1}
Р	-6	-	3	2	0.60	1.78

Table 3

Percent composition of Pure Polypyrrole, Sn(IV)arsenotungstate and Ppy-SnAT nanocomposite cation exchanger.

S. No.	Element	Percentage (%)			
		Pure Polypyrrole	Sn(IV)arsenotungstate	Ppy-SnAT composite	
1	С	32.36	-	53.05	
2	Ν	30.16	-	2.03	
3	Cl	7.45	-	4.90	
4	Fe	0.06	-	-	
5	0	_	34.51	17.55	
6	Sn	_	23.85	9.98	
7	W	_	22.97	8.08	
8	As	-	18.50	4.40	
9	Na	-	0.17	-	



Scheme 1. Schematic representation of preparation of Ppy-SnAT nanocomposite cation exchanger.

2.4. Characterizations of Ppy-SnAT composite cation exchanger

The properties, particle size, morphology, thermal stability and the functional groups present in the prepared pure Polypyrrole, Sn(IV)arsenotungstate and Ppy-SnAT composite ion exchanger materials were characterized by using SEM, EDX, TEM, FTIR, XRD and TGA. Energy-dispersive X-ray (EDX) studies were also used to obtain composition (Table 3) of Ppy-SnAT composite cation exchanger.

2.5. DC electrical conductivity of Ppy-SnAT composite cation exchanger

DC electrical conductivity of Ppy-SnAT composite cation exchanger was measured by using a four-in-line probe. The sample of Ppy-SnAT composite cation exchanger was dried at 40–50 °C in an oven up to 2 h 400 mg of the composite material was pelletized at room temperature with the help of a hydraulic press at 5 kN for 5 min. The conductivity (σ) was calculated using the following equations [16]:

$$\rho = \rho^{\circ}/G_7(W/S) \tag{1}$$

$$G_7(W/S) = (2S/W) \ln 2$$
 (2)

$$\rho^{\circ} = (V/I)2\pi S \tag{3}$$

$$\sigma = 1/\rho \tag{4}$$

Where $G_7(W/S)$ is a correction divisor, which is a function of thickness of the sample, as well as probe spacing, where I, V, W, and S are current (A), voltage (V), thickness of the film (cm), and probe spacing (cm) respectively.

The isothermal stability of the pellet in terms of DC electrical conductivity retention was carried out on the selected sample at 50, 70, 90, 110, and 130 $^{\circ}$ C in an air oven. The electrical conductivity measurements were carried out at an interval of 10min.

2.6. Formaldehyde, ammonia and mixed solution

(ammonia + formaldehyde) sensing measurements of Ppy-SnAT composite cation exchanger

The formaldehyde and ammonia gas sensing measurements were done by recording the electrical responses of the nanocomposite cation exchanger when exposed to varying concentrations of formaldehyde and ammonia and alternately returning it to



Fig. 1. Temperature dependence electrical conductivity of Pure Polypyrrole and Ppy-SnAT nanocomposite cation exchanger.



Fig. 2. SEM images of (a) Pure Polypyrrole, (b) Sn(IV)arsenotungstate and (c) Ppy-SnAT nanocomposite cation exchanger.

air at room temperature. The sensing material was placed into the glass chamber and gently pressed by four-in-line probe to record the current–voltage characteristics using digital microvolt meter (DMV 001) and low current sources (LCS 02). The distance between sensing material and the solvent was kept 3–4 cm at the time of exposure to formaldehyde and ammonia on the sensing material at room temperature [17,18].

3. Result and discussion

3.1. Synthesis and characterizations of Ppy-SnAT composite cation exchanger

In this study a new organic—inorganic nano composite cation exchanger is introduced in the field of hybrid composites by the incorporation of organic polymer polypyrrole into the matrix of



Fig. 3. EDX images of (a) Pure Polypyrrole, (b) Sn(IV)arsenotungstate and (c) Ppy-SnAT nanocomposite cation exchanger.

inorganic precipitate Sn(IV)arsenotungstate (Table 1) by in-situ oxidative polymerization method. Ppy-SnAT composite cation exchanger shows good IEC for Na⁺ and was found to be (2.50 Meqg⁻¹) (Table 2) better than inorganic material Sn(IV)arsenotungstate (2.0 Meqg⁻¹). On addition of inorganic material in the formation of composite, the IEC increased due to more available exchangeable sites. On the basis of high IEC and electrical conductivity, PPy-SnAT (**P-2**) was selected for further study. The

schematic representation of the formation of Ppy-SnAT nanocomposite cation exchanger is shown in Scheme 1.

The electrical conductivity of the pure Polypyrrole and Ppy-SnAT nanocomposite was measured with increasing temperatures from 30 to 140 °C as shown in (Fig. 1). It was observed that the electrical conductivity increased with rise of temperature upto 130 °C for Ppy-SnAT, however no sufficient change in conductivity was observed in pure polypyrrole. This indicates the "thermal



2-zee_002 2Zee Print Mag: 399000x @ 7.0 in 3:04:00 p 01/14/15

100 nm HV=200.0kV Direct Mag: 50000x

Fig. 4. TEM image of Ppy-SnAT nanocomposite cation exchanger.



Fig. 5. XRD pattern of Pure Polypyrrole, Sn(IV)arsenotungstate and Ppy-SnAT nanocomposite cation exchanger.



Fig. 6. TGA images of Pure Polypyrrole, Sn(IV) arsenotungstate and Ppy-SnAT nanocomposite cation exchanger.



Fig. 7. FTIR spectra of Pure Polypyrrole, Sn(IV)arsenotungstate and Ppy-SnAT nanocomposite cation exchanger.

activated behaviour" of the nanocomposite [19]. To explain the conduction mechanism in the conducting polymers, the concept of polaron and bipolaron was introduced. Low level of oxidation of the polymer gives polaron and higher level of oxidation gives bipolaron. Both polarons and bipolarons are mobile and can move along the polymer chain by the rearrangement of double and single bonds in the conjugated system. The magnitude of the conductivity is dependent on the number of charge carriers available and their

mobility. With the increase in temperature, the mobility of charge carriers increases, hence a rise in conductivity was observed. Another factor which also affects the electrical conductivity is the molecular alignment of the chains within the entire system.

Fig. 2 shows the SEM images of the pure Polypyrrole, Sn(IV) arsenotungstate and Ppy-SnAT composite ion-exchange materials at same magnification indicating the binding of inorganic material with organic polymer. It has also been revealed that after binding of



Fig. 8. Conductivity of pure Ppy and different ratio of Polypyrrole Sn(IV) arsenotung statenano composite ion exchanger.

polypyrrole with Sn(IV)arsenotungstate the morphology has changed and the formation of new composite material can be established.

From EDX results the percentage composition of the elements present in the pure Polypyrrole, Sn(IV)arsenotungstate and Ppy-SnAT composite ion-exchange material can be analysed for C, N, O, Sn, As and W. These values are given in Table 3 and can be verified from Figs. 3 and 4.

On the basis of EDX result the tentative structure of Sn(IV) arsenotungstate is:

[(SnO₂)₂ (As₂O₅)₂ (WO₃)]_n

The XRD pattern shown of pure polypyrrole, Sn(IV)arsenotungstate and Ppy-SnAT composite material in Fig. 5. Pure pyrrole [20] and Ppy-SnAT composite showed similarity in amorphous region which indicates no peaks. However the peaks at $2\theta = 45^{\circ}$, 65° and 80° in case of Sn(IV)arsenotungstate showed in crystalline region.

The FTIR spectra of Polypyrrole, Sn(IV)arsenotungstate and Ppy-SnAT nanocomposite are shown in Fig. 6. The main characteristic peak of Polypyrrole at 3428 cm⁻¹ can be attributed to the free (nonhydrogen bonded) N-H stretching vibration [21]. The peak at 1542 cm⁻¹ is due to C=C stretching mode of the quinoid rings, the peaks at 1455 cm⁻¹ are due to C–C stretching mode of benzenoid rings. The peak at about 1302 cm⁻¹ can be attributed to the C–N stretching mode. At 909 cm⁻¹ the peak is usually assigned to an out-of-plane bending vibration of C-H of 1,4-disubstituted benzenoid rings which confirms the formation of Polypyrrole [22]. In the FTIR spectra of Sn(IV)arsenotungstate, peaks at 1626–1251 cm⁻¹ represent the free water molecule (water of crystallization). An assembly of peaks at 848-514 cm⁻¹ may represent the M-O groups [23] of the inorganic material. FTIR spectra of Ppy-SnAT nanocomposite cation exchanger shows similar peak at 3460 cm⁻¹ for N–H stretching vibration as in Polypyrrole. Another similar peak at 1542 cm^{-1} is due to C=C stretching mode of the quinoid rings which shows interaction of pyrrole with inorganic material. Peaks of M-O in composite material are slightly shifted and broader in comparison to the peaks of inorganic material.

Distinct weight losses due to temperature can be seen in TGA

curves of Fig. 7. In pure Polypyrrole polymer TGA curve shows ~20% weight loss from 50 to 80 °C which may be due to the removal of external water molecules. From 80 to 300 °C material starts to decompose and upto 840 °C about 70% of the weight is lost. The TGA curve of Sn(IV)arsenotungstate inorganic material shows weight loss upto 30% at 50-150 °C due to the removal of external water molecules, however this material retains ~15% of mass after heating upto 400 °C and further decomposition of the material, ~43% was also observed upto 850 °C. In the case of Ppy-SnAT nanocomposite cation exchanger, the degradation starts from 50 °C as in the same case of above two materials, first the water molecules were removed then ~85% degradation of this material at 820 °C is quite clear from the figure. Thus it is evident from the results of TGA that nanocomposite cation exchanger is as thermally stable as the inorganic material.

3.2. Electrical conductivity studies of Ppy-SnAT nanocomposite cation exchanger

It is quite evident from Fig. 8 that there is significant variation in conductivity on increasing the volume ratio of polypyrrole in the sample P-2. The electrical conductivity increases on addition of 3% polypyrrole, but further increases in the volume ratio of polypyrrole decrease the conductivity. The increase in conductivity of sample P-2 can be well understood from the percolative path in which the concentration of conducting particles increases, showing that the conductivity depends significantly on the carrier transport through the conducting fillers [17].

3.3. Stability in terms of DC electrical conductivity retention of Ppy-SnAT nanocomposite cation exchanger

The isothermal stability of the pure Polypyrrole and Ppy-SnAT composite material in terms of DC electrical conductivity retention was carried out at 50, 70, 90, 110 and 130 °C in an air oven. The electrical conductivity measurements were done five times after intervals of 10 min at a particular temperature. The electrical conductivity measured with respect to time is presented in Fig. 9(a–b). It was observed that the nanocomposite materials followed the Arrhenius equation [24] for the temperature dependence of the electrical conductivity from 50 to 70 °C and after that a deviation in



Fig. 9. Isothermal stability of (a) Pure Polypyrrole and (b) Ppy-SnAT cation exchange nanocomposite in terms of D.C. electrical conductivity retention at 50°, 70°, 90°, 110°, and 130°.

electrical conductivity was observed, it may be due to the loss of dopant and degradation of materials. The stability of pure Polypyrrole and Ppy-SnAT, nonocomposite ion exchanger in terms of DC electrical conductivity retention was found to be fairly good as studied by isothermal technique. The pure Polypyrrole and Ppy-SnAT nanocomposite ion exchanger can be used in electrical and electronic applications below 90 °C under ambient conditions.

3.4. Vapour sensing studies of formaldehyde, ammonia and mix solution (ammonia + formaldehyde) on Ppy-SnAT nanocomposite cation exchanger

In this study, the sensing capabilities of Ppy-SnAT nanocomposite cation exchanger towards the formaldehyde (0.2, 0.4, 0.6, 0.8, and 1.0 M) and ammonia (0.2, 0.4, 0.6, 0.8, and 1.0 M) vapours has been explored in Fig. 10(a–b). The electrical resistivity response is measured in the presence of formaldehyde and ammonia vapours and air, respectively. The resistivity of Ppy-SnAT nanocomposite cation exchanger increases on exposer at low concentration (0.2 M) of formaldehyde and high concentration of ammonia (1.0 M). The response time and recovery time due to change of resistivity was observed for 5 s on exposure to ammonia and formaldehyde vapour and air on surface of Ppy-SnAT Fig. 11(a–b). Since ammonia and formaldehyde are the electron donating species, therefore conductivity decreases. In case of formaldehyde a rapid response in low concentration of formaldehyde vapour was observed but in the case of ammonia quick response was observed in high concentration. The reproducibility in the response can be attributed to the adsorption and desorption of the analyte vapours during exposure and removal of vapours. It was observed that formaldehyde vapour sensing response was better and reproducible than ammonia vapour. The response of this polymeric sensor with fixed molarity of formaldehyde (0.2 M) and ammonia (1.0 M) mixture were also investigated as shown in Fig. 11(c). Formaldehyde is more polar and larger in size than ammonia. Hence it would interact more efficiently than ammonia.



Fig. 10. Effect on the resistivity of Ppy-SnAT cation exchange nanocomposite on exposure to different concentrations of (a) formaldehyde and (b) ammonia with respect to time.

3.5. Sensing mechanism

When small amount of ammonia comes in contact with conducting form of Polypyrrole, lone pair of NH₃ interact with the positive charge of polaron and bipolaron of Ppy in Ppy-SnAT, which decreases the intensity of charge and hence the mobility of charge carrier decreases resulting in the increase in resistivity. If high concentration of ammonia is exposed to conducting polymer, it is reduced to nonconducting form. Since Cl⁻ present in polymeric form of Polypyrrole reacts with ammonia to form NH₄Cl⁻, an increase in the resistivity of the material is observed. However the composite regains its conductivity on exposure to air [25].

On exposure of formaldehyde the lone pair of oxygen also interact with the positive charge of polaron and bipolaron of Ppy in Ppy-SnAT, which decrease the intensity of positive charge of polaron and bipolaron, hence the mobility of charge carrier decreases. High concentration of formaldehyde reduces the conductivity of the composite, $H_2COH^+CI^-$ is formed due to presence of $CI^$ in the material. But the material regains its conductivity. The mechanistic representation of the electrical compensation of polypyrrole with formaldehyde and ammonia is given in Scheme 2. But in case of mixed solution of formaldehyde and ammonia an unstable compound methamine is formed which gives the resistivity [26]. The compound shows less sensing behaviour than ammonia and formaldehyde.

On exposure to the ammonia and formaldehyde vapour, adsorption of vapours take place by which plaron and bipolaron neutralises by the lone pair of ammonia and formaldehyde which results in increase in resistivity. When the material exposed to the air the desorption of vapour take place by which resistivity of the Ppy-SnAT decreases.

4. Conclusion

In the present work, Ppy-SnAT nanocomposite cation exchanger was synthesized by in-situ polymerization and characterized by using different instrumental techniques such as TEM, SEM, EDX, XRD, TGA and FTIR. The results of the studies reveal that the



Fig. 11. Variation in resistivity of Ppy-SnAT nanocomposites cation exchanger on exposure to 0.2 M formaldehyde, 1 M ammonia and mixed solution of (0.2 M formaldehyde + 1 M ammonia).

polymerization of Pure pyrrole has been successfully achieved on the surface of the Sn(IV)arsenotungstate. This indicates the formation of a new composite ion exchange material having good IEC as well as electrical conductivity properties. The results showed that the electrical conductivity of 3% Ppy-SnAT nanocomposite is higher than that other volume ratio Ppy-SnAT. The sensing behaviours of Ppy-SnAT nanocomposite are better in 0.2 M formaldehyde and 1 M aqueous NH₃ vapour.

Acknowledgments

Authors are thankful to the Department of Applied Chemistry for providing the research facilities and also to University Grant Commission and DST Purse programme phase II, Government of India for financial support.



Scheme 2. The mechanistic representation of the electrical compensation of polypyrrole with formaldehyde and ammonia.

References

- [1] T.J. Paul Scheepersa, Nelly E. van Brederodeb, Peter M.J. Bosb, Nicole J. Nijhuisc, H.J. van de Weerdtd, Irene van der Woudee, Martin L. Eggensf, Human biological monitoring for exposure assessment in response to an incident involving hazardous materials, Toxicol. Lett. 231 (2014) 295–305.
- [2] J.N. Sahu, K.K. Mahalik, A.V. Patwardhan, B.C. Meikap, Equilibrium studies on hydrolysis of urea in a semi-batch reactor for production of ammonia to reduce hazardous pollutants from flue gases, J. Hazard. Mater. 164 (2009) 659–664.
- [3] M.M. Rahman, Ki-Hyun Kim, Exposure to hazardous volatile pollutants back diffusing from automobile exhaust systems, J. Hazard. Mater. 241–242 (2012) 267–278.
- [4] M. Karla, R.F. Wrightb, T.F. Berglena, B. Denbya, Worst case scenario study to assess the environmental impact of amine emissions from a CO2 capture plant, Int. J. Greenh. Gas Control 5 (2011) 439–447.
- [5] IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, WHO Press, 88, (2006).
- [6] R. Dales, L. Liu, A.J. Wheeler, N.L. Gilbert, Quality of indoor residential air and health, Can. Med. Assoc. J. Can. Med. Assoc. J. 179 (2008) 147–152.
- [7] N. Mermilliod, J. Tanguy, F. Petiot, A study of chemically synthesized polypyrrole as electrode material for battery applications, J. Electrochem. Soc. (1986) 1073–1079.
- [8] K.M. Mangold, F. Meik, K. Jüttner, Polypyrrole/palladium composites for the electrocatalyzed Heck reaction, Synth. Met. 144 (2004) 221–227.
- [9] W.J. Kuo, Y.H. Chen, R.J. Jeng, L.H. Chan, W.P. Lina, Z.M. Yang, Peripheral arylsubstituted pyrrole fluorophores for glassy blue-light-emitting diodes, Tetrahedron 63 (2007) 7086–7096.
- [10] S.A. Waghuley, S.M. Yenorkar, S.S. Yawale, S.P. Yawale, Application of

chemically synthesized conducting polymer-polypyrrole as a carbon dioxide gas sensor, Sens. Actuators B Chem. 128 (2008) 366-373.

- [11] K. Ghanbari, S.Z. Bathaie, M.F. Mousavi, Electrochemically fabricated polypyrrole nanofiber-modified electrode as a new electrochemical DNA, biosensor, Biosens. Bioelectron. 23 (2008) 1825–1831.
- [12] M.Q. Liu, J.H. Jiang, Y.L. Feng, G.L. Shen, R.Q. Yu, Glucose biosensor based on immobilization of glucose oxidase in electrochemically polymerized polytyramine film and overoxidised polypyrrole film on platinized carbon paste electrode, Chin. J. Anal. Chem. 35 (2007) 1435–1438.
- [13] J. Njagi, S. Andreescu, Stable enzyme biosensors based on chemically synthesized Au-polypyrrole nanocomposite, Biosens. Bioelectron. 23 (2007) 168–175.
- [14] R. Niwas, A.A. Khan, K.G. Varshney, Synthesis and ion exchange behaviour of polyaniline Sn(IV)arsenophosphate: a polymeric inorganic ion exchanger, Colloids Surf. A Physicochem. Eng. Aspects 150 (1999) 7–14.
- [15] A.A. Khan, S. Shaheen, U. Habiba, Synthesis and characterization of poly-oanisidine Sn(IV)tungstate: a new and novel 'organic-inorganic'nano-composite material and its electro-analytical applications as Hg (II) ion-selective membrane electrode, J. Adv. Res. 3 (2012) 269–278.
- [16] A.A. Khan, S. Shaheen, Electrical conductivity, isothermal stability and amine sensing studies of a synthetic poly-otoluidine/multiwalled carbon nanotube/ Sn(IV) tungstate composite ion exchanger doped with p-toluene sulfonic acid, Anal. Methods 7 (2015) 2077.
- [17] A.A. Khan, U. Baig, Electrical conductivity and ammonia sensing studies on in situ polymerized poly(3-methythiophene)-titanium(IV)molybdophosphatecation exchange nanocomposite, Sens. Actuators B Chem. 177 (2013) 1089–1097.
- [18] A.A. Khan, R.A. Khan Rao, N. Alam, S. Shaheen, Formaldehyde sensing properties and electrical conductivity of newly synthesized Polypyrrole-

zirconium(IV)selenoiodate cation exchange nanocomposite, Sens. Actuators B 211 (2015) 419–427.

- [19] N. Parvatikar, S. Jain, S.V. Bhoraskar, M.V.N.A. Prasad, Spectroscopic and electri-cal properties of polyaniline/CeO2 composites and their application as humidity sensor, J. Appl. Polym. Sci. 102 (2006) 5533–5537.
- [20] A. Manik, G.S. Chougulea, S.G. Pawara, R. Prasad, N.R. Godsea, S.S. Mulika, P.B. Vikas, Synthesis and characterization of polypyrrole (PPy) thin films, Soft Nanosci. Lett, 1 (2011) 6–10.
- [21] G. Ruhi, S.K. Dhawan, Conducting Polymer Nano Composite Epoxy Coatings for Anticorrosive Applications Chapter 5, 1–40, http://dx.doi.org/10.5772/ 58388.
- [22] C. Xu, J. Sun, L. Gao, Synthesis of novel hierarchical graphene/polypyrrole nanosheet composites and their superior electrochemical performance,

J. Mater. Chem. 21 (2011) 11253.

- [23] D.K. Singh, S. Singh, Synthesis, characterization and analytical applications of zirconium(IV) sulphosalicylophosphate, Ind. J. Chem. Technol. 11 (2004) 23–28.
- [24] N. Parvatikar, S. Jain, S.V. Bhoraskar, M.V.N.A. Prasad, Spectroscopic and electri-cal properties of polyaniline/CeO2 composites and their application as humidity sensor, J. Appl. Polym. Sci. 102 (2006) 5533–5537.
 [25] M.O. Ansari, S.P. Ansari, S.K. Yadav, T. Anwer, M.H. Cho, F. Mohammad,
- [25] M.O. Ansari, S.P. Ansari, S.K. Yadav, T. Anwer, M.H. Cho, F. Mohammad, Ammonia vapour sensing and electrical properties of fibrous multi-walled carbon nanotube/polyaniline nanocomposites prepared in presence of cetyltrimethylammonium bromide, J. Ind. Eng. Chem. 20 (2014) 2010–2017.
- [26] H.S. Luftman, Neutralization of formaldehyde gas by ammonium bicarbonate and ammonium carbonate, Appl. Biosaf. 10 (2005) 101–106.