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MWCNTs/SnZrMoP nano-composite as Ba (II)-selective electrode and heterogeneous catalyst for esterification of primary alcohols

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Abstract

The present investigation covers the synthesis, characterization and applications of a novel nano-composite of multiwalled carbon nanotubes–tin zirconium molybdophosphate (MWCNTs–SnZrMoP) ion exchanger. The synthesized material was characterized by various instrumental techniques viz. Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), and thermogravimetric/ differential thermal analysis (TGA/DTA). The nano-composite exhibited an ion exchange capacity of 2.56 meq g⁻¹, which is higher than its inorganic counterpart SnZrMoP (1.95 meq g⁻¹). The distribution studies confirmed that the as-synthesized nano-composite was selective for barium ions. The nano-composite was employed to fabricate an ion-selective electrode which showed a sub-Nernstian response for barium ions in the concentration range $1 \times 10^{-7} M$ — $1 \times 10^{-1} M$, with a response time of 11 s. The average slope of the calibration curve was observed to be 23.3 mV/ decade with $1.78 \times 10^{-8} M$ as limit of detection (LOD). The synthesized material was also used as a heterogeneous catalyst in esterification reactions of some primary alcohols due to its high mechanical, thermal and chemical stability. The esters produced were characterized by nuclear magnetic resonance (¹H-NMR) and FT-IR techniques.

 $\textbf{Keywords} \ \ Nano-composite \cdot MWCNTs/SnZrMoP \cdot Ion-selective \ electrode \cdot Esterification \cdot Potentiometric \ titrations$

Introduction

The toxic properties of heavy metal ions have been known for decades. The barium metal compounds, which are soluble in water, are harmful and can cause barium poisoning. Water-soluble barium salts are carbonates, nitrates, chlorides, and sulfides etc. Witherite (BaCO₃) salt is employed in rat poison, ceramic glazes, bricks and cement industry. Barium chloride is used as a reagent to test the presence

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Prit Pal Singh dhillonps2003@gmail.com of sulfate ions. It is also used in caustic chlorine plants for purification of brine solution, manufacturing of pigments, and in case hardening of steel. Barium nitrate is used in glass industry, whereas barite ($BaSO_4$) is used as a density filler in paper, plastics, paint, and rubber industry. The use of these salts is also reported as lubricant additives, in pharmaceutical and cosmetics industries. Barium in small amount is used as a muscle stimulant, but its higher amount harms the nervous system, and may cause cardiac irregularities, weakness, anxiety, shortness of breath, and paralysis. (Ware 1989; Jaccob et al. 2002; Stewart and Hummel 1984; Johnson and Tassel 1991; Ananda et al. 2013; Rhyee and Heard 2009). Thus, estimation of Ba^{2+} assumes significance due to its toxic effects. Several instrumental techniques are accessible for estimation of metal ions in solution (Tsalev 1995; Dehairs et al. 1987; Mauras and Allain 1979; Heitland and Koster 2006; Wen et al. 2009; Ullah and Haque 2010; Bonfil et al. 2000), but these techniques have their own limitations, particularly for estimation of Ba (II) ions at ppb level. Thus, there is a tenacious need for an inexpensive, simple and easily reproducible probe for quantitative estimation of Ba^{2+} .

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Earlier, sole inorganic ion exchangers and oxides of metals were utilized for the fabrication of purification membranes (Gohil et al. 2006; Mittal and Singh 1999). However, with the development in technology, the composite materials which display improved porosity and stability, have nearly supplanted these sole inorganic materials in separation and purification procedures (Hosseini et al. 2010; Kaur et al. 2020). Considering their enhanced properties, the composite materials have found many applications in the area of electrochemistry, photocatalysis, waste water treatment, removal of heavy metal ions and sensors (Gupta et al. 2013; Kaushal et al. 2020). Another important utility of nano-composite ion exchangers is their use as heterogeneous catalysts, in contrast to homogeneous liquid catalysts because of their higher catalytic activity and reactivity, ease of separation of solid catalyst from the reaction mixture and their easy regeneration again and again for repeated use (Sharma and Sharma 2014). Recently, the nanocomposites prepared by incorporating MWCNTs into organic or inorganic polymeric materials are getting much more importance, owing to their improved thermal, mechanical, catalytic and column operations (Sahoo et al. 2010; Wang et al. 2013; Moniruzzaman and Winey 2006; Kaushal et al. 2016a).

In the present work, MWCNTs/SnZrMoP nano-composite was prepared by incorporating multi-walled carbon nanotubes into an inorganic counterpart by sol-gel method. The nano-composite was utilized as an electroactive material for the fabrication of barium ion-selective electrode (ISE). The proposed sensor displayed remarkably high sensitivity, stability, and selectivity for Ba(II) ions over many other ions. Furthermore, the nano-composite was also used as a heterogeneous catalyst for esterification reaction of benzoic acid with n-butyl alcohol, and the reaction kinetics was also compared with that of conventional homogeneous liquid catalyst (concentrated H_2SO_4). The synthesized material possesses structural -OH functional groups with replaceable hydrogen ions (H⁺) which impart them, the inherent ability to act as a bronsted acid catalyst. To the best of our knowledge, no work has been reported in which MWCNTs are incorporated into any heteropoly acid salt having two cations as well anions, and simultaneously employed as an ion-selective electrode as well as heterogeneous catalyst.

Experimental

Reagents and instruments

All chemicals including zirconium oxychloride, stannic chloride, sodium molybdate, sodium dihydrogen phosphate, o-toluidine, potassium persulphate, disodium salt of ethylene diamine tetra acetic acid (Loba chemie, India), MWC-NTs (Sigma Aldrich) were of analytical garde, and used as received, without any further purification. A single electrode pH meter (Toshniwal, India) was used to perform pH studies. FTIR spectra were recorded on a Perkin Elmer RX1 FTIR spectrometer. X-ray diffraction patterns were obtained using PAN analytical system DY 3190 X-ray diffractometer. The topography and elemental composition of the synthesized particles were recorded using JEOL scanning electron microscope and JSM 6510LV energy dispersive X-ray detector. Transmission electron microscopy (TEM) studies were done using model MIC JEM 2100. Thermal analysis was performed by heating the nano-composite up to 900 °C, at a constant increment of 10 °C per minute in a nitrogen atmosphere, using Hitachi SGA7400 thermogravimetric analyzer. Cryo NMR spectrometer (Bruker) was used to record ¹H-NMR spectra.

Synthesis of MWCNTs/SnZrMoP nano-composite

Synthesis of SnZrMoP

Room temperature synthesis of inorganic gel of SnZrMoP was carried out by adding equimolar solutions of each of zirconium oxychloride, stannic chloride, sodium molybdate and sodium dihydrogen phosphate to EDTA (ethylene diamine tetraacetic acid) solution which acts as a capping

 Table 1
 Synthesis of MWCNTs/SnZrMoP nano-composite under varied reaction conditions

Sample code	Synthesis conditions Mixing volume ratio							Properties	
	ZC (0.1 M) (mL)	SC (0.1 M) (mL)	SM (0.1 M) (mL)	EDTA 0.01 M (mL)	SDP (0.1 M) (mL)	Wt. % of MWCNTs	pН	Yield (g)	IEC for Na ⁺ ions (meq g^{-1})
S-1	100	100	100	100	300	0.00	1	4.00	1.95
S-2	100	100	100	100	300	0.01	1	4.75	2.12
S-3	100	100	100	100	300	0.02	1	5.64	2.23
S-4	100	100	100	100	300	0.03	1	6.80	2.56
S-5	100	100	100	100	300	0.04	1	7.95	2.42

ZC-Zirconyl oxychloride; SC-Stannic chloride; SM-Sodium molybdate; SDP-Sodium dihydrogen phosphate

agent to control the nucleation of nanoparticles (Table 1). The white-colored gel obtained was used in the next steps of nano-composite synthesis (Kaur et al. 2019a,b; Valsaraj and Janardanan 2013).

Synthesis of MWCNTs/SnZrMoP nano-composite

Five samples of MWCNTs/SnZrMoP nano-composite were prepared by addition of different mass percentage of MWC-NTs to a fixed mass of inorganic gel, obtained in the above step (Table 1). The mixture of MWCNTs and SnZrMoP ion exchanger was refluxed at 50 °C for 2 h with continuous stirring. The obtained gel of MWCNTs/SnZrMoP nanocomposite was washed thoroughly with double distilled water (DDW) to remove the impurities, followed by filtration. The filtered gel was dried at a temperature of 40 °C in hot air oven. The granules of nano-composite were dipped in 1 M HCl solution, washed with DDW to remove excess acid, and dried at 50 ± 2 °C temperature, till the attainment of a constant weight (Kaushal et al. 2016a).

Characterization of MWCNTs/SnZrMoP nano-composite exchanger

The synthesized nano-composite was characterized for various parameters, to investigate its column stability, by the reported methods (Kaur et al. 2019b).

Na⁺ Ion-exchange capacity (IEC)

The Na⁺ ion exchange capacity denotes the tendency of an ion exchange material to undergo exchange of its H⁺ ions with Na⁺ ions present in the eluent. The IEC of nanocomposite was evaluated by the column method, in which a fixed amount of ion exchanger was filled in the glass-wool supported column. The replaceable H⁺ ions were eluted by 1 M NaNO₃ solution which were determined titrimetrically with 0.1 M NaOH. The following relation was employed to calculate Na⁺ IEC of the nano-composite:

$$IEC = \frac{N \times V}{W} meq/g$$
(1)

In the above equation, *N* stands for normality, *V* stands for volume (mL) of NaOH solution used, and *W* represents the mass (gram) of ion exchanger (Kaur et al. 2019b).

Column stability

The column stability of nano-composite ion exchanger MWCNTs/SnZrMoP was tested by investigating its elution behavior in a standard column process. The eluent volume required to elute H⁺ ions completely, from a given mass of exchanger was calculated by this method.

Eluent concentration effect on IEC

The column method was used to study this property which is helpful in optimization of eluent concentration that should cause maximum elution of H^+ ions from the ion exchanger (Kaur et al. 2019b).

Effect of calcination on ion exchange properties of nano-composite

The effect of heating on the stability and exchange properties of nano-composite was investigated by thermal studies. The activated ion exchanger was heated from 50 °C to 800 °C temperature. The percentage loss of its mass and Na⁺ IEC at different temperatures was estimated (Kaur et al. 2019a).

pH-titration study

The functionality of nano-composite ion exchanger was studied by pH titrations, performed by Topp and Pepper method (Topp and Pepper 1949).

Chemical stability

This investigation is helpful to test the stability of ion exchanger in different chemical reagents. A fixed amount of exchanger was treated with varying concentrations of HCl, NaOH and 10% solutions of organic solvents. The percentage loss in its mass and IEC was calculated after each treatment.

Characterization techniques

The common analytical techniques viz. FT-IR, powder XRD, FE-SEM, HR-TEM, and EDX spectroscopy were employed to study the morphology, topography, chemical composition and particle size of inorganic and nano-composite ion exchangers. The thermal behavior of inorganic and composite ion exchangers was investigated by TGA/DTA studies.

Distribution studies

In these studies, the adsorption of metal ions on the nanocomposite, from their solutions in different solvents was investigated (Kaur et al. 2019a,b).

Applications of MWCNTs/SnZrMoP nano-composite

Fabrication and characterization of ion exchange membrane based on nano-composite MWCNTs/SnZrMoP

Preparation and conditioning of membranes The heterogeneous ion exchange membrane based on MWCNTs/SnZrMoP nano-composite was fabricated by mixing the powdered nano-composite exhaustively with Araldite (an epoxy resin) to make a slurry. The slurry was placed in the form of a thin layer between the folds of parchment paper that was placed for 24 h, between two glass plates under a pressure of 2.0 kg cm⁻². Being non-sticky, the parchment paper was easily removed from the membrane surface. The sheet of membrane thus obtained, was cut into circular discs (diameter ≈18 mm). Further studies were performed on membrane discs with better surface qualities (Kaushal et al. 2016b).

Physical and morphological characterization of synthesized

membrane The fabricated membrane, after conditioning, was tested for parameters like water content, thickness, swelling, porosity, IEC, etc. The effect of the ratio of ion exchanger: binder, on physical properties of the membrane was also investigated.

Water content

This property is used to check the imbibition of membrane in aqueous medium (Kaushal et al. 2017). The membrane was immersed in DDW for 24 h. The membrane water content (%) was estimated by the following relation:

Water content (%) =
$$\frac{m_w - m_d}{m_d} \times 100$$
 (2)

Where m_w and m_d represent mass of wet and dry membrane, respectively.

Thickness and swelling

The difference in the thickness of dry membrane and the membrane equilibrated with 1 M NaCl solution for 24 h, is called swelling.

Porosity

Porosity (ε) denotes the volume of water retained per unit volume, in the pores of membrane. It is determined by the equation given below:

$$\varepsilon = \frac{m_w - m_d}{A L \rho_w} \tag{3}$$

where m_w and m_d represent the mass of wet and dry membrane, respectively, A is surface area and L is thickness of membrane, and ρ_w is density of water (Kumari et al. 2020).

Ion Exchange capacity (IEC)

IEC of the fabricated membrane was assessed by batch process. The membrane was activated in 1 M HCl and dried at a temperature of 40 °C, after washing with DDW to remove excess HCl. Then, it was soaked in 1 M NaNO₃ solution for 24 h, with intermittent shaking. Afterwards, the membrane was removed from NaNO₃ solution, and the leftover solution was titrated with 0.1 M NaOH solution, to calculate the released H⁺ ions. The IEC of the membrane was determined by Eq. 1.

FE-SEM studies

FE-SEM studies of the membranes based on pristine EP (EP-stands for epoxy resin), and nano-composite MWCNTs/ SnZrMoP were carried out to reveal information about the distribution of exchanger in binder phase, and distribution of pores in membrane structure.

TGA-DTA Studies

The thermal behavior of membranes based on pristine EP and nano-composite MWCNTs/SnZrMoP was investigated through TG/DTA analysis using Hitachi SGA7400 thermogravimetric analyzer, by heating up to 900 °C in nitrogen atmosphere.

Fabrication and characterization of ion-selective electrode

Fabrication of ion-selective electrode (ISE) and cell assembly

In the optimization process, all the fabricated membranes were tested for ion exchange properties, and the membrane with best exchange properties and greater physical strength was used to fabricate the ISE. The selected membrane disc was fixed at the flattened end of a Pyrex glass tube (outer and inner diameter 1.6 cm and 0.8 cm, respectively) using Araldite. The electrode assembly was dried for 24 h, and then equilibrated with barium nitrate solution (0.1 M) for 7 days. The glass tube was filled to 3/4 with 0.1 M Ba(NO₃)₂ solution. Two saturated calomel electrodes (SCE) were used in cell assembly, one was inserted in Pyrex glass tube to make the electrical contact, whereas the other one was inserted in test solution. The following cell assembly was employed for potentiometric measurements:



The potentiometric measurements were carried out at pH 3.5, in an air thermostat maintained at 27 ± 0.1 °C temperature. When not in use, the electrode was preserved in 0.1 M Ba(NO₃)₂ solution (Kaushal et al. 2016b).

Characterization of the ISE

Response time Two concentrations of barium nitrate solution, i.e., 5×10^{-2} M and 5×10^{-3} M were used to determine this property of ISE. The proposed sensor was introduced in 5×10^{-3} M solution of barium nitrate, and then transferred immediately to 5×10^{-2} M solution of the same ion, and the electrode potential was determined as a function of time. The electrode potential was first recorded just after the insertion of electrode in the test solution and, then recorded as a function of time (s). The time period during which the electrode attains a constant potential, is called response time of electrode.

Slope and detection limit Potential measurements were carried out using standard solutions of barium nitrate in the concentration range 1×10^{-10} to 1×10^{-1} M, prepared by ten fold dilution of a stock solution (Toth et al. 1980). The graphs of observed electrode potentials versus log of the activities of barium ions were plotted. The reproducibility of the system was confirmed by repeating the same process thrice. During all these measurements, concentration of barium nitrate solution in the Pyrex glass tube was fixed at 5×10^{-2} M. The electrode was stored in 0.1 M barium nitrate solution after each measurement.

Effect of change in internal solution concentration The potential of the electrode was also observed after altering the concentration of barium nitrate solution taken in the Pyrex glass tube of ISE. The concentrations of internal solutions were set as 1×10^{-2} , 5×10^{-1} and 1×10^{-3} M. The observed electrode potentials were plotted against the log of activities of analyte.

Effect of partially non-aqueous medium This parameter was used to study the response of proposed electrode in the presence of traces of some organic solvents in water. The electrode potentials observed in the presence of non-aque-

ous solvents were plotted as a function of the log of activities of barium nitrate solution.

Effect of pH The effect of variation in pH of $Ba(NO_3)_2$ solution on the electrode potential was studied in the pH range 1 to 13 (Kaushal et al. 2016b).

Potentiometric titrations The potentiometric determination of barium ions in a test sample was carried out by titration with a standard EDTA solution $(1 \times 10^{-2} \text{ M})$, using the proposed sensor. The end point of the titration was determined from the plot of observed values of electrode potential versus the volume of EDTA solution consumed.

Selectivity coefficients The response of proposed sensor towards primary ions (Ba²⁺) in the presence of other ions is evaluated on the basis of selectivity coefficients ($K_{A,B}^{Pot}$), which were determined by fixed interference method (Pungor 1997; Guilbault 1980; Bakker 1997). In this process, concentration of interfering ions was fixed as 1×10^{-4} M. The selectivity coefficients were calculated by the following relation:

$$K_{A,B}^{Pot} = (a_A) / (a_B)^{Z_A/Z_B}$$
(4)

where a_A , a_B represent the activities of primary and secondary (interfering) ions, respectively, and z_A , z_B denote charges on primary and secondary ions, respectively (Kaushal et al. 2016b).

Lifetime of electrode This property was investigated to test any appreciable change in response time and slope of the electrode with time. The electrode potentials were determined with different concentrations of barium nitrate solution after 15, 30, 60, 90 and 120 days.

Esterification of benzoic acid with n-butyl alcohol using MWCNTs/SnZrMoP nano-composite ion exchanger as heterogeneous catalyst

The esterification reaction of benzoic acid with n-butyl alcohol was carried out by the Fischer's esterification process. In the process, 5 g of benzoic acid and 50 mL of n-butyl alcohol were added to a 100 mL flask, followed by the addition of 2 g of MWCNTs/SnZrMoP nano-composite ion exchanger. After refluxing for 30 min, the mixture was cooled to room temperature. The product obtained was washed with DDW and extracted with dichloromethane. The excess alcohol was removed by evaporation, whereas the leftover benzoic acid was washed off, using a 10% NaHCO₃ solution. Freshly prepared silica plates were used for TLC studies. TLC was run in ethyl alcohol: hexane (4: 1) solvent system. The spot

of the product was compared to the spot of benzoic acid. Detailed kinetic studies of esterification of benzoic acid with n-butyl alcohol in the presence of MWCNTs/SnZr-MoP nano-composite ion exchanger were carried out and compared with those employing conventional homogeneous liquid catalyst (conc. H_2SO_4). The formation of esters was confirmed by FTIR and ¹H-NMR spectroscopy (Sharma and Sharma 2014; McMurry 2004; Hart and Craine 1991).

Results and discussion

Physiochemical properties

The sol-gel method was employed to synthesize MWCNTs/ SnZrMoP nano-composite ion exchanger. The Na⁺ IEC of inorganic ion exchanger increases from 1.95 to 2.56 meq g⁻¹ on incorporation of MWCNTs (Sample S-4, Table 1) which may be due to the interactions between MWCNTs and SnZrMoP. This interaction is also responsible for a better mechanical, thermal and chemical stability of the nanocomposite. It was further observed that increase in wt% of MWCNTs in nano-composite to a certain limit, leads to increase in IEC of the nano-composite. EDTA used in the synthesis process acts as the capping agent and is also responsible for enhancing the IEC of the nano-composite (Nabi et al. 2008,2009; Sadjadi and Khalilzadegan 2015). Further studies were carried out on sample S-4, on the basis of optimization studies of reaction conditions.

The studies (Figure S1a) revealed that 1.0 M solution of NaNO₃ as eluent is appropriate for maximum elution of H⁺ ions from the ion exchanger. The elution studies revealed that initially, the rate of exchange was fast, and all the replaceable H⁺ ions in 500 mg of sample can be eluted with 300 mL of NaNO₃ (1 M) solution.

The stability of nano-composite at high temperature was investigated by its thermal studies. On heating the ion exchanger to 300 °C, ~ 73.44% of its initial mass and ~ 78.20% of its IEC was retained. This thermally stable behavior of the nano-composite might be due to the binding of MWCNTs with SnZrMoP. After 300 °C, decomposition of MWCNTs and transformation of nano-composite into oxide form, results in sharp decline in its IEC (Figure S2). The weight loss due to decomposition of carbon nanotubes occurs in temperature range of 400 to 600 °C. The MWCNTs get completely burnt up to a temperature of 900 °C, resulting in change in color of sample.

The pH-titration curves were drawn under equilibrium for NaCl/NaOH, KCl/KOH and LiCl/LiOH systems, to determine the functionality of MWCNTs/SnZrMoP nanocomposite (Fig. 1). It was observed from pH titration curves that the exchanger is tri-functional in nature. The low pH value (\sim 2.3) of the solution, before the addition of OH⁻ ions, indicated its strongly acidic nature. It was also observed that the rate of exchange of H^+/Na^+ and H^+/Li^+ is slower than that of H^+/K^+ . This may be attributed to the smaller size of hydrated K^+ ions compared to that of Na^+ and Li^+ ions.

The nano-composite exhibited excellent chemical stability. The leaching of nano-composite in different solvents is almost negligible, which might be due to strong interactions between MWCNTs and inorganic matrix. The nanocomposite was resistant to dissolution even in a strongly acidic medium, and a negligible weathering was observed in organic solvents. Despite its strongly acidic nature, its dissolution in alkaline medium was insignificant (Table S2).

Characterization of nano-composite

The nano-composite MWCNTs/SnZrMoP was characterized by FT-IR, XRD, EDX, FE-SEM and HR-TEM techniques. FT-IR spectrum of inorganic counterpart, SnZrMoP (Figure S3 a) shows the characteristic peaks at 3431.77 and 1630.04 cm⁻¹, which may be ascribed to O-H stretching and H-O-H bending vibrations, respectively, of water molecules in the exchanger (Inamuddin et al. 2007; Rao 1963). A peak at 1050.45 cm⁻¹ indicated the presence of ionic PO_4^{-3} groups in SnZrMoP (Gupta et al. 2000). The peaks at 601.40 and 576.70 cm^{-1} are due to the vibrations of M–O bonds. In the FT-IR spectrum of MWCNTs/SnZrMoP (Figure S3 b), two new peaks appeared at 2964 and 1752.50 cm⁻¹ which may be ascribed to— CH_2 , C=O, groups present on the surface of carbon nanotubes (Lampman et al. 2010; Fathy et al. 2014). A band at 1381 cm^{-1} is attributed to the P–OH group. The incorporation of multiwalled carbon nanotubes was confirmed by a slight shift in the frequencies and intensities of



Fig. 1 pH-titration curves of MWCNTs/SnZrMoP nano-composite

characteristic absorption bands of the inorganic counterpart, and the appearance of some new absorption bands in the FT-IR spectrum of the nano-composite.

The globular particles with regions of aggregations and agglomerations can be clearly seen in the FE-SEM image of SnZrMoP ion exchanger (Fig. 2a, b). The FE-SEM images of nano-composite ion exchanger (Fig. 2c, d) revealed the presence of spherical particles of nano-dimensions with a high degree of agglomeration (Fig. 2c). In Fig. 2d, a cluster of some tube-like material is visible, which is aggregate of MWCNTs which were added to the exchanger to improve its properties. The EDX spectrum of MWCNTs/SnZrMoP indicated the presence of Zr, Sn, Mo, P, C, N and O (Fig. 2e).

Figure 3a–c depicts high-resolution transmission electron microscopic (HR-TEM) images of the dry samples of SnZrMoP. It can be seen that spherical particles having size $\approx 2-3$ nm of the inorganic counterpart form a network. Diffuse rings are seen in the selected area diffraction (SAED) pattern of SnZrMoP (Fig. 3d) which indicate semi-crystalline nature of the inorganic ion exchanger. This observation is in agreement with the XRD studies. The globular particles of size range $\approx 10-20$ nm are clearly visible in the HR-TEM images (Fig. 3e–g) of the nano-composite. The carbon nanotubes and their interaction with the inorganic polymer matrix can be seen in Fig. 3f, g. The selected area diffraction (SAED) pattern

of nano-composite (Fig. 3h) shows diffraction rings with bright spots which may be due to the interlayer spacing between different graphite layers.

The XRD spectrum of inorganic ion exchanger SnZrMoP shows some broad and less intense peaks at lower 2 θ values (Fig. 4a) which confirm its semi-crystalline nature. It has been observed that the characteristic peaks of MWCNTs appear at 25.03°, which correspond to (002) reflection planes or interlayer spacing between contiguous graphite layers (Kaushal et al. 2015). The diffraction pattern of synthesized nano-composite MWCNTs/SnZrMoP shows a significant band near 2 θ value of 26° which may be due to the presence of a small proportion of MWCNTs in the designed nano-composite (Fig. 4b). Nearly flat, lowintensity peaks in the XRD pattern of nano-composite ion exchanger depict its amorphous profile.

The TGA/DTA curves for nano-composite (Fig. 5) reveal that the weight loss up to 150 °C is 14.35%, resulting from the loss of interstitial water molecules in the sample. An endothermic peak is present in the same region of DTA curve. The weight loss in 130–291 °C temperature range is $\approx 6.33\%$, which may be attributed to loss of water of crystallization. The transformation of inorganic phosphate into pyrophosphate takes place in the temperature range 291 – 502 °C that corresponds to a weight loss of $\approx 2\%$ in this region (Khan and Sheen 2014). The



Fig. 2 FE-SEM images of: a-b SnZrMoP; c-d MWCNTs/SnZrMoP nano-composite ion exchanger; e) EDX spectrum of MWCNTs/SnZrMoP nano-composite



Fig. 3 HRTEM images and SAED pattern of: a-d SnZrMoP; e-g MWCNT/SnZrMoP nano-composite



Fig.4 X-ray diffraction patterns of: **a** inorganic SnZrMoP; **b** MWC-NTs/SnZrMoP nano-composite

decomposition of MWCNTs accounts for weight loss of $\approx 0.25\%$ in 502–594 °C temperature range (Guan et al. 2017; Hsieh et al. 2010; Mahajan et al. 2013; Buzarovska et al. 2015). The weight loss after 500 °C is ascribed to

conversion of metal compounds to their oxide form (Malik and Shrivastava 1983).

Distribution studies

The distribution studies, to explore the separation potential of the nano-composite, were performed in aqueous medium for about 15 different metal ions. The observed order of selectivity coefficients for different metal ions is: Ba^{2+} (495) > Hg^{2+} (233.33) > Pb^{2+} (178.57) > Sr^{2+} (100) > Co^{2+} (89.19) > Fe^{3+} (61.77) > Ca^{2+} (54.88) > Zn^{2+} (54.46) > Cu^{2+} (32.26) > Cr^{3+} (26.53) > Ni^{2+} (23.91) > Mg^{2+} (21.54) > Cd^{2+} (15.94) > Al^{3+} (5.73). Thus, the nano-composite exhibited high selectivity for Ba^{2+} , and can be utilized for separation of these ions from contaminated effluents. In the present work, the exchanger MWCNTs/SnZrMoP was also utilized for designing a Ba^{2+} ISE.

Fabrication of membrane

Preparation and conditioning of membranes

The exchanger was tested to evaluate its Na⁺ ion exchange capacity, and the sample S-4 (Table 1) was utilized for the





fabrication of IEM. The membrane was synthesized by making use of an epoxy resin (Araldite) as a binder and MWC-NTs/SnZrMoP as a functional group reagent. Araldite and MWCNTs/SnZrMoP were mixed in the ratios (w/w) 1: 9 (10 mg:90 mg), 2: 8 (20 mg:80 mg), 3: 7(30 mg:70 mg), and 4: 6 (40 mg:60 mg), for the fabrication of four different sets of ion-exchange membranes (Table 2).

Physical characterization of membrane

All these fabricated membranes were tested for properties like thickness, water content, porosity, IEC, swelling etc. It was observed from physical characteristics (Table 2) that the membrane MW-2 has moderate thickness, porosity, and water content, and highest IEC among all sets of fabricated membranes. Hence, it was selected for fabrication of ionselective electrode. The higher value of IEC of MW-2 might be due to proper and uniform distribution of nano-composite particles in the binder phase.

Morphological and thermal characterization of the synthesized membrane

Figure 6a represents the surface view of the membrane based on pristine EP (EP- stands for epoxy resin) which demonstrates the presence of air pockets and pores on the membrane surface. In the cross-sectional view (Fig. 6b) of this membrane, number of air pockets and pores are almost negligible. On the other hand, surface view of the membrane based on MWCNTs/SnZrMoP nano-composite (Fig. 6c) clearly reveals the uniform distribution of MWCNTs. The surface of this IEM seems to be more smooth and uniform in comparison to that of pristine EP membrane. The crosssectional view of the IEM based on MWCNT/SnZrMoP shows the distribution of pores and air pockets in its interior structure.

Figure S4a, b shows the comparison between thermal studies of membrane based on pristine EP, membrane based on MWCNTs/SnZrMoP, and pure MWCNTs/SnZrMoP, respectively. It is clearly observed that the nano-composite imparted thermal stability to the fabricated membrane. The thermogravimetric and differential thermal analysis of the membrane based on pristine EP is shown in Figure S4a. It is evident that the weight loss below 150 °C is 1.46%,

Table 2Physiochemicalcharacteristics of MWCNTs/SnZrMoP based ion exchangemembranes

Sample code	Epoxy resin (binder): ion exchanger (W/W)	Thickness (mm)	Water content (%)	Porosity	Na ⁺ IEC (meq/g)	Swelling (mm)
MW-1	1:9	0.266	10.53	0.68×10^{-2}	0.90	0.018
MW-2	2:8	0.300	9.09	0.70×10^{-2}	1.26	0.028
MW-3	3:7	0.354	11.48	0.59×10^{-2}	1.08	0.023
MW-4	4:6	0.392	7.32	0.45×10^{-2}	0.96	0.012

Fig. 6 FE-SEM images of: **a**, **b** membrane based on pristine EP; **c**, **d** membrane based on MWC-NTs/SnZrMoP nano-composite



which may be attributed to the loss of interstitial water, other volatile solvents and desorption of gaseous materials entrapped in the membrane. The thermogram of epoxy resin in a nitrogen atmosphere can be recognized by a steep degradation peak. The thermogram depicts that degradation of epoxy resin starts at 350 °C and completed at \approx 500 °C. The weight loss in this temperature range is 77.44%, which may be ascribed to carbonization of hydrocarbon compounds present in polymer membrane. In contrast to pristine EP membrane, the loss of interstitial water from the binder and exchanger phase, below 150 °C results in weight loss of only 4.09% in case of membrane based on MWCNTs/SnZrMoP. The weight loss, owing to the loss of water of crystallization, between 150 to 350 °C is 14.95%, the energy requirement for which is confirmed by the presence of endothermic peak in the same region of DTA curve. The decomposition of epoxy resin and transformation of inorganic phosphate into pyrophosphate are responsible for weight loss in temperature range of 350 to 500 °C (Khan and Sheen 2014). Complete degradation of epoxy resin and MWCNTs accounts for the weight loss in temperature range 500 to 900 °C (Buzarovska et al. 2015).

Electrode characteristics

The response time of the electrode was 11 s, as observed from the plot of electrode potential versus time (Figure S5). The recorded values of electrode potentials were plotted against the log of activities of analyte ions. The reproducibility of the system was verified by repeating the experiment thrice. The proposed electrode displayed 1.78×10^{-8} M as the lowest detection limit, with sub-Nernstian slope of calibration curve (23.3 mV/decade) for Ba (II) ions (Fig. 6). The sub-Nernstian response of the electrode may be due to the variation in activities of ions in solution and the phase boundary. Similar behavior was also been reported earlier (Kaushal et al. 2016c). The proposed electrode exhibits a linear response in concentration range 1×10^{-7} M to 1×10^{-1} M. All these parameters were calculated according to IUPAC recommendations (Toth et al. 1980; Pungor 1997; Guilbault 1980). It was observed that a ten fold change in concentration of internal solution has no major effect on the response of proposed electrode, and only a small variation was noticed in the intercepts of calibration curves (Figure S6) (Fig. 7).

The studies on electrode response in non-aqueous media containing acetone or ethanol revealed that there is almost negligible effect on the slope of calibration curve. Thus, the proposed ISE can be safely employed for studies in aqueous solutions contaminated with low concentrations of non aqueos solvents (Table S2).

The effective pH range for proper functioning of electrode was observed to be 3 to 9.5 (Figure S7). The sharp rise in electrode potential at pH lower than 3 may be attributed to the response of electrode towards both Ba (II) and H_3O^+ (hydronium) ions, while precipitation of Ba (II) ions as Ba(OH)₂ is responsible for sharp decline in electrode potential above pH 9.5 (Kaushal et al. 2016c).

The potentiometric estimation of Ba (II) ions in aqueous medium was carried out using fabricated electrode as an



Fig. 7 Calibration curve of proposed Ba (II)-selective electrode based on MWCNTs/SnZrMoP nano-composite

Table 3 Selectivity coefficients $K_{A,B}^{POT}$ for different interfering ions

Interfering ion (B)	$K^{POT}_{A,B}$	Interfering ion (B)	$K_{A,B}^{POT}$
Li ⁺	1.00×10^{-2}	Co ²⁺	3.55×10^{-6}
Na ⁺	3.98×10^{-3}	Mn ²⁺	1.00×10^{-5}
K^+	1.26×10^{-2}	Ni ²⁺	3.16×10^{-6}
Al ³⁺	1.79×10^{-4}	Pb ²⁺	2.23×10^{-6}
Ca ²⁺	5.62×10^{-6}	Cr ³⁺	2.82×10^{-4}
Mg ²⁺	1.79×10^{-5}	Fe ³⁺	4.47×10^{-4}
Cu ²⁺	7.94×10^{-6}	Ba ²⁺	2.24×10^{-6}
Sr ²⁺	5.62×10^{-5}	Zn ²⁺	3.55×10^{-6}

indicator electrode and 0.01 M EDTA solution as titrant. The end point of the titration was detected from plots of electrode potential versus volume of EDTA solution used (Figure S8 a, b).

The preferential response of ISE towards primary ions in the presence of interfering ions is predicted on the basis of selectivity coefficients ($K_{A,B}^{POT}$) which were calculated (Table 3) using low concentration of interfering ions (1×10⁻⁴ M), by fixed interference method (FIM) (Umezawa et al. 1995). It was observed that the value of $K_{A,B}^{POT} < 1$ for all the interfering ions, indicating high selectivity of proposed electrode for Ba (II) ions in the presence of other interfering ions.

The lifetime of the proposed electrode was tested to be 4 months (Figure S9), and no appreciable variation in response time and slope of the electrode was observed during this period. The leaching of membrane material with test solution might be responsible for the possible change in response time and slope of the electrode.

Moreover, the performance of the proposed sensor was compared with those of previously reported barium-selective membrane electrodes, and the results are listed in Table 4.

The proposed ISE exhibits fast response time (11 s), bettter linear range $(1 \times 10^{-7} \text{ M to } 1 \times 10^{-1} \text{ M})$ and lower detection limit $(1.78 \times 10^{-8} \text{ M})$ as compared to the earlier reported sensors for Ba²⁺.

Esterification of primary alcohol using nano-composite MWCNTs/SnZrMP as catalyst

The nano-composite MWCNTs/SnZrMoP was used as a heterogeneous catalyst for the esterification reaction of benzoic acid with n-butyl alcohol as shown in Figure S10. The results and reaction kinetics were also compared with those of traditional homogeneous acid catalyst. It is a well-known fact that the heterogeneous catalyst offers following benefits

Reference	Response time (second)	Slope (mV/decade)	Linear range (M)	LOD (M)	pH range
53	15	20.70	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	6.31×10^{-7}	3.5-9.0
55	_	30.00	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	2.0×10^{-6}	1.6-8.1
56	10	29.7 ± 0.4	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	7.6×10^{-7}	3.0-11.0
57	18	30.00	$1.41 \times 10^{-6} - 1.0 \times 10^{-1}$	1.0×10^{-6}	2.5 - 7.0
58	20	28.7 ± 0.4	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$	2.5×10^{-6}	4.5-10.0
59	10	29.7 ± 0.2	$3.6 \times 10^{-6} - 1.0 \times 10^{-1}$	1.9×10^{-6}	2.5-7.5
60	20	29.10	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	0.6×10^{-5}	2.0-6.0
61	20	58.90	$1.0 \times 10^{-5} - 2.0 \times 10^{-2}$	_	-
62	_	30.00	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	5.0×10^{-6}	4.0-9.0
63	_	29.70	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	5.2×10^{-7}	3.4-10.6
64	_	29.60	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	5.6×10^{-7}	2.6-11.0
Present studies	11	23.30	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$	1.78×10^{-8}	3.0-9.5

Table 4Comparison of theperformance of proposedbarium ISE based on MWCNTs/SnZrMP nano-composite withreported electrodes

over a traditional homogeneous liquid catalyst: (1) easy isolation from the reaction mixture after the completion of reaction; (2) economical as well as eco-friendly as the exchanger can be regenerated again and again after exhaustion; and (3) it helps to shift the equilibrium in forward direction using water, a byproduct of the reaction. It was observed experimentally that the decrease in ion exchange capacity was only about 10% of its initial value, after four regeneration cycles. No weathering, color loss or weight loss was observed which confirmed its long-range chemical and thermal stability. The proposed mechanism for the esterification reaction of alcohols is illustrated in Figure S11.

The reaction kinetics were observed by analyzing the concentration of benzoic acid in the reaction mixture after fixed intervals of time. In this process, a fixed amount of reaction mixture was taken out and benzoic acid in this lot was neutralized with a standard solution of NaOH. A standard solution of HCl was used to estimate the un-reacted NaOH. It is clear from Fig. 8 that the reaction rate is fast during initial 20 min, and a fast decline in concentration of benzoic acid was observed during this period. A steady decline in reaction rate was observed afterwards, and after 140 min, the rate became almost constant. Thus, it can be concluded that the esterification reaction is initially fast in the presence of MWCNts/SnZrMoP, and has low activation energy than that in the presence of a conventional liquid acid catalyst (conc. H_2SO_4).

It has also been observed that the conversion of benzoic acid to n-butyl benzoate increased from 40 to 60%, on increasing the amount of catalyst from 0.5 g to 2 g. The increment in reaction time also increased the percentage yield of the reaction product. The potential efficacy of the



Fig.8 Reaction kinetics of esterification reaction with conventional homogenous catalyst (conc. H_2SO_4) and the heterogeneous nano-composite catalyst (MWCNTs/SnZrMoP)

MWCNTs/SnZrMoP as a heterogeneous catalyst can be assessed from the fact that there was only a 10–15% decline in the yield of ester, even after four regeneration cycles. It is evident from the reported literature that this decrease in the activity of heterogeneous catalyst results from the obstruction of its active sites by bulky molecules of reaction mixture (Sharma and Sharma 2014).

Characterization of synthesized esters

The product of esterification reaction was extracted with dichloromethane, and characterized by FT-IR and ¹H-NMR studies. FT-IR spectrum of n-butyl benzoate (Figure S12) revealed that the C-H stretching peak for the sp² carbon of aromatic compounds appears at ~ 3090-3064 cm⁻¹. Two peaks at 1781 and 1719 cm⁻¹ are ascribed to the carbonyl (C=O) group (Kaushal et al. 2020). The slight variation in these frequencies is due to α , β -aryl conjugation in case of aromatic esters. Two bands at ~2960.9 and 2874 cm^{-1} are attributed to asymmetric and symmetric -CH₃ stretchings, respectively. The band at ~ 2935 cm^{-1} is due to asymmetric $-CH_2$ stretching. The bands in the region 1300–1000 cm⁻¹ are attributed to C-O stretching. A prominent peak at 1465 cm⁻¹ is ascribed to $-CH_2$ scissoring. The bands in the region 690–900 cm⁻¹ are due to C–H, out of plane bending vibrations (Nabi et al. 2009).

The ¹H-NMR spectrum of n-butyl benzoate is shown in Fig. 9: ¹H-NMR (400 MHz, CDCl₃): 8.0337 (2H, t, ArH), 7.4065 (1H, t, ArH), 7.5165 (2H, tt, ArH), 4.3072 (2H, t, OCH₂), 1.7134 (2H, m, CH₂), 1.4309 (2H, m, CH₂), 0.99 (3H, t, CH₃) (Guilbault 1980). The disappearance of the singlet due to –OH group of n-butyl alcohol (1H, s, OH) at 2.37 δ in the ¹H-NMR (Figure S13) spectrum of the product confirms the formation of ester.

Conclusion

In brief, nano-composite based on multiwalled carbon nanotubes-doped tin zirconium molybdophosphate (MWC-NTs–SnZrMoP) was found to be distinctly selective for barium ions, and was exercised for the construction of barium ion-selective electrode (ISE). The fabricated sensor displays quite good detection ability for Ba²⁺ compared to different interfering cations. The electrode displayed near Nernstian response over the barium ion concentration range of 1.0×10^{-7} – 1×10^{-1} M, with an average slope of 23.3 mV per decade change of concentration. The response time of the proposed electrode was 11 s, with the lower detection limit (LOD) for barium ions being 1.78×10^{-8} M under optimized experimental conditions. The proposed ISE was also applied as an indicator electrode in potentiometric titrations. The nano-composite was also used successfully as a



Fig. 9 ¹H-NMR spectrum of n-butyl benzoate

heterogeneous catalyst for the esterification of benzoic acid with n-butyl alcohol, and the obtained results were compared with those using conventional homogeneous liquid catalyst.

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