Original Article

Design and Preparation of a New and Novel Nanocomposite with CNTs and Its Sensor Applications

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\textbf{A B S T R A C T}

Inorganic–organic nanocomposite poly(o-toluidine) Ce(III)tungstate@CNT was prepared by sol–gel intercalation insertion method, later on it was mixed with CNTs that leads to the formation of CNT intercalated inorganic–organic hybrid nanocomposite. The polymerization of monomer was achieved by ammonium persulphate (APS) chemical oxidation, inside the inorganic matrices that leads insertion of polymer. Characterization of POTCe(III)Ce@CNT nanocomposite by various physicochemical studies as FT-IR, X-ray, UV–vis spectrophotometry, TEM, SEM/EDX, TGA and four probe conductivity measuring technique was done. On the basis of physicochemical properties as cation-exchange capacity as well as electrical conductivity, the advanced nanocomposite was utilized for the sensor application for environmental remediation. It was used for the preparation of POTCe(III)Ce@CNT ion selective membrane electrode.

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1. Introduction

Advanced organic–inorganic hybrid nanocomposite widely studied in the last decades and utilized widely in all fields of research [1–5]. The organic components are light organic molecules, organic polymers and organometallics while the inorganic counterparts are layered structures, zeolites and one dimensional polymers [6–8]. The properties of the hybrid are the results of the synergistically obtained from the individual components [9]. Also some interesting applications results by inserting guests into the host was found and with some different materials [10–16]. Conducting polymers as polyaniline, polypyrrole, oligothiophene and their derivative as poly o-toluidine are used in the composite preparations because of having high conductivity and low cost, easily oxidizable by solution method, anisotropic optical and electrical properties and polymers of this type are easy to process with other polymers and components that’s why now we have chosen poly-o-toluidine as a conducting component in our this work [17,18] have been used. It is obvious that the chemical and physical properties of the organic guest and inorganic host

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determine the synthetic methodology of a new nanocomposite [19].

CNTs have ultimate physical and chemical properties as such they have potential in many applications [20]. Its application as electrode material is attacking considerable interests lately, which among the reasons is the availability of reactive functional groups to enhance electron transfer. Also, the porosity with large surface, interfacial adsorption quality and more electrocatalytic activity are key properties. So many new designs of chemical sensors and biochemical sensors making use of this material have emerged. It has shown that electrode surface fouling was significantly minimized by CNTs. The nano-dimensions combined with the graphitic chemistry provide the electronic properties of CNTs that makes them a unique material for both bio and chemical sensing. In sensing devices CNTs may works as both anchorages for an electrochemical mediator as well as electro-active component. Adsorption of the mediator provides much wider potential window for the detection as a result much more stable material. MWCNTs have been used to incorporate copolymer composite material that conferred oxidation and reduction characteristic to the sensor material.

The main two disadvantages of CNTs is its insolvibility in common solvents as well as the tendency to aggregate. This prohibit the material from further processing tailor made for specific applications. It is now clear that the most promising approach to resolve this problem is to covalent functionalized by polymers. The tubes would dissolve in appropriate solvents because of the effect of the long polymeric chains as well as aggregation is decreased also by low degree of functionalization. In short, CNTs solubility and compatibility could be improved greatly by direct formation of composite. Generally, it can be done by esterification or amidation reaction of long alkyl chains with the composite components.

2. Experimental

2.1. Material and methods

The organic monomer o-toluidine; cerium nitrate; ammonium persulfate; multi-wall carbon nanotubes (MWCNTs, OD 20–30 nm and length 20 μm); acetone (Act); and ethanol (EtOH) were obtained from Sigma-Aldrich, and no further purification was done except for o-toluidine. The aniline was further purified by distillation before every use of the monomer. All the acids were used as received.

2.2. Preparation of POTCe(III)T@CNT composite membrane

100 ml 0.1 M acidic solution of Cerium tungstate was mixed in the 100 ml acidic solution of sodium tungstate, prepared in double distilled water, contained in the 250 ml conical flask and the mixture was stirred for 30 min. During stirring, 5 drop of CTAB (5 ml 0.01M) was mixed dropwise simultaneously CNTs in the mixture and heated for about 50 °C temperature. After stirring the mixture was sonicated on the sonicator for about 15 min. During this process the change of the mixture takes place from gray to black. Now, 100 ml 5% o-toluidine solution was prepared in standard flask in acidic medium and then mixed dropwise in the previously prepared inorganic mixture with the simultaneously 0.1 M APS solution to oxidize the monomer. The reaction was continued for 40 min. After 40 min the slurry was put over night for digestion in the temperature below 50 °C. Then, the mixture was filtered through a funnel with Whatman filter paper, washed repeatedly with double-distilled water and then ethanol to remove all remaining adhering impurities and unreacted reactant and dried over P2O5 at 45 °C in an oven for 24 h (Fig. 1).

2.3. Preparation of POTCe(III)T@CNT composite membrane

Ion-selective membranes were prepared on the basis of a method similar to one used before [21]. For the preparation of the best selective membrane, it is necessary to optimize the materials used in the composite membrane, THF (tetrahydrofuran) and PVC (polyvinylchloride). To 10 ml THF was added different amounts of the composite and PVC to make a suspension. This mixture of ingredients was poured into a glass tube with a diameter of 5 mm and a length of 10 cm, and the tube was allowed to sit for evaporation or drying overnight. Three sheets were prepared with different volume ratios to yield thicknesses of 0.40, 0.44 and 0.50 mm. The best smooth areas of the membranes were cut by a sharp-edged blade for subsequent experiments.

2.4. Characterization of membrane

The above-prepared membranes were characterized by important physical parameters such as thickness, porosity, and water content [22,23].

2.4.1. Water content (% total wet weight)

In this study, the membranes were dipped in water to elute the diffusible salt inside the membrane, then immediately removed from the water and wrapped in filter paper to remove the surface water moisture and weight. Then, the membrane was dried over P2O5 for 24 h and weighed again, and the water content was calculated on the basis of the following Eq. (1)

\[
\% \text{ Total wet weight} = \frac{W_w - W_d}{W_w} \times 100
\]  

In this equation, \(W_d\) and \(W_w\) represent the weight of the dry membrane and weight of the wet membrane, respectively.

2.4.2. Porosity

The water content of the membrane per unit volume of the cavities represented by the porosity (\(\varepsilon\)) was determined by Eq. (2) as follows:

\[
\varepsilon = \frac{W_d}{W_w} A L \rho_w
\]  

In Eq. (2), \(W_d\) and \(W_w\) represent the weight of the dry membrane and weight of the wet membrane, respectively; \(A\) and \(L\) are the area and thickness of the membrane, respectively; and \(\rho_w\) is the density of water.
2.4.3. Thickness and swelling
The swelling of the membrane was calculated on the basis of the absorption of salts by the membrane that was subjected to dry weight analysis; the membrane was dipped in salt in the form of 1 M NaCl for 24 h, and the difference in mass between the dry and wet membrane was calculated.

2.5. Fabrication of ion-sensitive membrane electrode
The best membrane, selected on the basis of the highest performance, was the 0.50 mm (M₃) membrane; a sample was cut in the form of the disc and mounted to the lower end of a Pyrex glass tube (Araldite). The tube had an o.d. of 0.8 cm and i.d. of 0.6 cm. After that, the tube was left to dry overnight. The tube was filled with 0.1 M metal ion solution for electrical contact. A saturated calomel electrode was inserted inside this tube, and now this is called as working electrode (Scheme 1) another one was used as a reference calomel electrode. Then, the electrode parameters such as the electrode response curve, response time, working pH range, and lower detection limit were determined to characterize the performance of the electrode. Metal ion solutions ranging in concentration from 10⁻¹ M to 1⁻¹⁰ M were prepared for the determination of electrode response. At the end, the external and membrane electrodes were connected to a potentiometer, and the readings were collected.

For electrode potential determination, the electrode was soaked for 5–7 days in the concentrated metal ion solution and dipped in 0.1 M Pb(NO₃)₂ for at least 1 h before use. The electrode also must be stored in a high-concentration solution of 0.1 M Pb(NO₃)₂. The potential results were plotted against the concentration of the respective metal ions. The solution pH was measured within a range of 1–10 at a constant ion concentration (1 × 10⁻³ M), and at each pH, the potential was recorded and plotted. For response time determination, the potential was first recorded for 1 × 10⁻³ M solution, then shifted a 10-times higher concentration (1 × 10⁻² M), the potentials were immediately recorded, and the time vs. potential was plotted.

3. Results and discussion
3.1. Characterization
Here, OT was polymerized on the surface of Ce(III)T with the help of the APS redox reaction to provide a pure conduction environment. The reaction of CNTs with the already prepared Ce(III)T was simplified because the dispersion capability of the CNTs increased due to the presence of the additional functional groups on the surface. This is the process that makes CNT more accessible to other moieties, as well as another property: in this composite POTCe(III)T®CNT, CNT presents nucleation behavior that assists conduction in the composite (Fig. 1).

SEM micrographs of the composite (POTCe(III)T®CNT), shown in Fig. 2a–d, were taken at different magnifications. A different solid and thicker area appeared in the lower-resolution image; also, there were some thickness in the image that were not visible at other magnifications. The presence of metal in the composite was revealed by the visible luster in the image. Here, the appearance of thicker CNTs was clear on the basis of morphology structure and coating of the polymer happened on the surface. All these morphological characteristics result from the porosity, increased area and flakiness of the material, which helps to enable the diffusion of ions through the material.

It is obvious from the thermogravimetric curve of the composite that the initial weight loss was negligible, as is clear from Fig. 3. However, as the temperature increased to 500°C,
Scheme 1 – Schematic diagram for ion selective membrane electrode.

Fig. 2 – Scanning electron micrographs of poly(o-toluidine) Ce(III)tungstate@CNT nanocomposite at different magnifications.
the weight loss shown by the curve was only 10%, which may be due to the moisture removal, as well as the possible decomposition of the organic part of the material. Again, there was a large feature in the curve that showed a large weight loss to 20% as the temperature increased from 500 to 900 °C, the formation of metal oxides means the decomposition of the inorganic part of the material. Another DTA curve also revealed further information about the reaction nature of the material and showed two broad peaks, one at approximately ~400 °C and another at approximately ~800 °C, which indicated exothermic weight loss during heating.

POTCe(III)T@CNT was characterized by the presence of different functional groups and the change in bonds after formation, as shown in Fig. 3. FT-IR spectra of POTCe(III)T@CNT, POTCe(III)T and CNTs are given. There is a strong peak at approximately 1574 cm⁻¹, which is probably indicative of the presence of C=N and C=C quinoid and benzenoid stretching vibrations. Because of in-plane deformation, other peaks may also be involved in this region. The peak for CNT in the spectra is clear at approximately 1500 cm⁻¹.

For W metal, the main region for IR bands by number and by position is at approximately 600–3200 cm⁻¹. Polaron–polaron interactions happened between the planar poly(o-toluidine) and tungsten metal; these interactions caused the shifting of the ring deformation mode of the material and resulted in the incomplete interaction of some of the metal with the poly(o-toluidine) due to the bulky nature of the metal. All the above results confirm the considerable amount of POT in the composite. The substituted benzene showed the out-of-plane bending deformation of C—H. This is indicated by the presence of the band at approximately 800 cm⁻¹. The presence of metal in the composite resulted in the broadening of the same peak (Fig. 4).

One big lump sum peak in XRD of the composite showed the presence of the moisture and the nano size presence in the current composite. Remaining phase of the composite shows the CNTs (Fig. 5).

TEM (transmission electron micrograph) images of the composite at different magnifications are shown in Fig. 6 at different magnification that is showed the presence of the polymer coating with the inorganic matrices on the CNTs.

### 3.2. Preparation of a Pb²⁺ ion-sensitive membrane electrode

A heterogeneous ion-selective electrode was also prepared with POTCe(III)T@CNT. It is a necessary condition of ISE that the electroactive material be sensitive and selective for a particular species; furthermore, selectivity is determined by the physicochemical properties of the material and the composition of the membrane that is used in the formation of the ISE. POTCe(III)T@CNT was used for the preparation of various membrane samples with different ratios of PVC, and the best sample membrane was selected on the basis of thickness, uniformity, cracks, and mechanical strength, as well as the uniformity of material distribution, etc. As shown in Table 1, membrane sample M3, with a 0.50 mm thickness and 33% PVC ratio (w/w), was selected for subsequent study.
Table 1 – Characterization of the membrane of poly(o-toluidine) Ce(III)tungstate@CNT(POTCe(III)T@CNT) composite.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness of the membrane (nm)</th>
<th>Water content of % weight of wet membrane</th>
<th>Porosity</th>
<th>Swelling of % weight of wet membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1</td>
<td>0.40</td>
<td>0.04651</td>
<td>0.0500</td>
<td>Swelling</td>
</tr>
<tr>
<td>M-2</td>
<td>0.44</td>
<td>0.06383</td>
<td>0.0682</td>
<td>Swelling</td>
</tr>
<tr>
<td>M-3</td>
<td>0.50</td>
<td>0.07272</td>
<td>0.0800</td>
<td>Swelling</td>
</tr>
</tbody>
</table>

The response observed for the prepared heterogeneous Pb(II) ion-sensitive membrane electrode had a linear range from $\sim 1 \times 10^{-3}$ M to $1 \times 10^{-6}$ M. As shown in Fig. 7, the appropriate concentration area of the curve was selected for a sloping portion of the linear curve. The standard detection limit of the ISE was observed to be approximately $4 \times 10^{-4}$, while the lower limit of detection was approximately $1 \times 10^{-6}$ M, as determined by the response curve obtained by the intersection of an extrapolated segment of the graph. It is clear from Fig. 7 that the working range was $1 \times 10^{-3}$ M to $1 \times 10^{-7}$ M (Fig. 7) and the Nernstian response of the POTCe(III)T@CNT embedded Pb(II)-selective heterogeneous membrane electrode was 27.29 mV/decade.

Another important property of the ISE, the effect of pH, was also determined at constant conc. solutions of $1 \times 10^{-3}$ M with different pH values. The working pH range for the Pb(II) ion-selective membrane electrode in the present study was found to be 2.0–6.0, as it is clear from Fig. 8 that the potential is stable in this range but deviates elsewhere.

The time at which the potential become stable in the measurement of ISE electrodes is one of the important features of the membrane and is called the readiness of response [24].
Fig. 7 – Calibration graph of poly(o-toluidine) Ce(III)tungstate@CNT embedded membrane electrode showing selectivity for Pb²⁺ selectivity.

Fig. 8 – pH studies of poly(o-toluidine) Ce(III)tungstate@CNT embedded ion selective membrane electrode.

Fig. 9 – Response time curve of poly(o-toluidine) Ce(III)tungstate@CNT modified membrane electrode.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Selectivity coefficient values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn²⁺</td>
<td>0.002</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>0.003</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>0.011</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.009</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>0.016</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.021</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.017</td>
</tr>
</tbody>
</table>

The time was determined, as is clear from Fig. 9, and the value was ~20 s.

Another important parameter of the membrane is the lifespan. The lifespan of the current membrane was also observed and was found to be 72 days without any change in potential of ±1 mV per concentration decade. It was also necessary to re-equilibrate the electrode in 0.1 M metal solution after four to five days when we noticed any drift in potential.

The selectivity coefficient of different metal ions was determined by the mixed solution method on POTCe(III)T@CNT for the Pb(II) ion-selective composite membrane electrode. The selectivity coefficient is the indicator of the interference of foreign ions (M⁺⁺) in the selectivity for the primary ion (Pb(II)). On the basis of the selectivity coefficient results shown in Table 2, the electrode is selective for Pb(II). The important part of this study is the use of this ion-selective membrane as the indicator electrode for the determination of Pb(II) ions against EDTA. The potential drop that occurred as we added EDTA to the salt solution indicated the complexation of the metal ion with the EDTA. It is affirmed that the measurement of Pb(II) ions is easily determined from this titration graph, which supports that the titration graph ought to increase sharply for the purpose of identification. As per the hypothesis, if the slope is near the standard Nernstian incline (29 ± 3) value, as in the present examination, the electrode is more precise than other electrodes with less consistent values [25–29].

4. Conclusions

In this study, a POTCe(III)T@CNT nanocomposite was prepared by the incorporation of CNTs into a conducting polymer and the incorporation of POTCe(III)T to work as an electrical conductivity enhancer. The polymerization of a monomer, toluidine, was performed on the surface of the CNTs, and afterward, Ce(III)T was added to complete the composite. On the basis of characterization results, the composite was highly thermally, mechanically and chemically stable. The composite was used for the preparation of ion membranes that were characterized by various parameters, viz., porosity, swelling, and wettability. On the basis of its selectivity, a membrane was also subjected to the preparation of an ion-selective membrane electrode and was found to be selective for the ions of highly hazardous transition metal Pb(II). The electrode showed a good Nernstian slope, wide pH range and long lifespan. The prepared membrane electrode was used as the indicator
Acknowledgments

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