



Sol–gel synthesis of poly(o-toluidine)@Sn(II)silicate/CNT composites for ion selective membrane electrodes



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ARTICLE INFO

Available online xxx

Keywords:

Nanomaterials
Organic–inorganic
Cation-exchanger
Poly(o-toluidine)

ABSTRACT

Advanced poly(o-toluidine)@Sn(II)silicate/CNT nanocomposites were synthesized using sol–gel of Sn(II) silicate by varying the mixing volume ratio concentration of inorganic reactant with a fixed mixing volume ratio, i.e., 1:1, of organic polymer. Physico-chemical characterization was conducted using SEM, XRD, FTIR, UV–Vis and TGA. Ion-exchange capacity distribution studies were also conducted to determine the ion-exchange capabilities. The distribution studies revealed high selectivity for Hg^{2+} , which is an important environmental pollutant. Due to the selective nature of the composite, an ion selective membrane electrode was designed for determining $Hg(II)$ ions in solutions. The electrode potential remains unchanged within a pH range of 4.0–7.0 and at a working concentration range of 1×10^{-1} M to 1×10^{-6} M for Hg^{2+} ions and a Nerstian slope of 32.14 mV per decade change in Hg^{2+} ion concentration.

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1. Introduction

The widespread study of new materials are currently being studied worldwide, although the scope of commercial uses for new materials remains small and relatively few viable technologies have emerged from the laboratory proof-of-concept stage. Limitations in processability, such as low mechanical strength, poor flexibility and high cost, have prevented conducting polymers from making significant commercial impact. To improve the processability of conducting polymers, several approaches have been developed. Mixing nanoparticles with polymers to form composite materials has been practiced for decades. For example, clay-reinforced resin, known as Bakelite, was introduced in the early 1900s as one of the first mass-produced polymer–nanoparticle composites [1] and fundamentally transformed the nature of everyday household materials. Prior to the development of Bakelite, nanocomposites could be found in nanoparticle-toughened automobile tires prepared by blending carbon black, zinc oxide, and/or magnesium sulfate particles with vulcanized rubber [2]. Despite these early successes, the scientific community did not widely study nanocomposites until the early 1990s, when Toyota researchers revealed that adding mica to nylon produced a five-fold increase in the yield and tensile strength of the material [3,4].

Subsequent developments have further contributed to the surging interest in polymer–nanoparticle composites. Composites based on conductive or semiconductive nanoparticles are very attractive for electronic applications and can augment the use of conjugated organic polymers in flexible electronics, light-emitting displays, and photovoltaics. Organic–inorganic hybrid photovoltaics composed of polythiophene–quantum dot (or CdSe nanorod) composites exhibit enhanced performance with tailored ligand coverage, such as amine- and phosphonic acid-terminated polythiophenes [5]. The enhanced dispersion of particles or nanorods in the polythiophene matrix improves device performance characterized by significantly improved power conversion efficiencies that are ~3 times that of conventional blends but use only half the volume of nanocrystalline material. Conducting polymer–noble metal nanocomposites provides an exciting system for designing device functionality [6] and exhibit enhanced sensing and catalytic capabilities compared to pure conducting polymers [7–13].

Generally, the synthetic methodology of a nanocomposite depends on the chemical and physical properties of the host inorganic materials and the guest organic polymers [14,15]. It is believed that the guest species must be soluble in a solvent system, whether miscible or immiscible with water. To date, most polymer nanocomposites have been fabricated via the direct insertion approach, where the polymers are first dispersed in water or an organic solvent and then inserted into the layered structure. Another synthetic approach involves insertion of the monomer first, followed by treatment with an oxidant.

The design, fabrication and application of novel electrochemical sensors have been a topic of research in recent years [16–18]. The

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modification of membranes to provide suitable functionalities remains a topic of interest among researchers worldwide due to the potential of improving the ion transfer rate from substrates to the membrane [19, 20]. The modification of membranes with heteropolyacids (HPAs) has received much attention [21,22] owing to their attractive electronic and molecular properties, which has resulted in novel applications, such as in catalysis, materials science [23] and energy storage devices [24,25], etc. However, the high solubility of heteropolyacids in aqueous media limits the stability of such modified membranes, leading to the leaching of heteropolycations from the membrane surface and to the subsequent drop in their electrochemical features. However, entrapment into the conducting polymer matrix leads to the fabrication of molecular hybrid materials, which minimizes the leaching of the exchanger due to its interactions with the polymer matrix and the poor solubility of the conducting polymer in water. In addition, inorganic clusters maintain their integrity and activity while benefiting from the conducting properties and the polymeric nature of the hybrid structure. Further incorporation of metal nanoparticles into organic–inorganic hybrid materials offers enhanced performance due to the increases in conductivity and surface area. In this regard, we sought to fabricate membranes using a nano-incorporated organic–organic hybrid material for use as an ion selective electrode. In the present study, we developed a facile method for fabricating a CNT-incorporated organic–inorganic composite-embedded membrane, and we report its electrochemical properties.

Mercury is responsible for the cause of poisoning through water, food and smoking. Mercury contamination in drinking water inhibits the function of certain enzymes necessary for the formation of heme in bone marrow, the pigment that combines with protein to form hemoglobin. Upon inhalation, its vapor enters the brain via the blood stream and causes severe damage to the central nervous system. Inorganic mercuric compounds primarily attack the liver and kidney. Mercuric chloride is corrosive and, when ingested, precipitates proteins of mucous membranes, causing ashen appearance of the mouth, pharynx and gastric mucus. Organic mercurial are the most toxic substances. CH_3Hg^+ can pass through the placental barrier and enter fetal tissues. $\text{Hg}(\text{II})$ is therefore a dangerous pollutant in the environment. Heavy metal ion removal from water has been the subject of extensive technological research [26].

Ion-exchange membranes obtained by embedding ion-exchangers as electroactive materials in a polymer binder, such as epoxy resin PVC, have been extensively used as potentiometric sensors, ion sensors, chemical sensors, or more commonly, ion-selective electrodes. In the present study, we sought to fabricate a new heterogeneous precipitate-based membrane electrode using the poly(*o*-methoxyaniline) Sn(II) silicate CNTS composite, a nanocomposite cation-exchanger as an electroactive material, for determining $\text{Hg}(\text{II})$ ions present in a solution.

2. Experimental procedures

2.1. Reagents and instruments

The main reagents (*o*-toluidine monomer; E. Merck, stannous chloride from CDH and sodium metasilicate from Loba Chemie) were used. All other reagents (hydrochloric acid, nitric acid, sulfuric acid, sodium nitrate, potassium nitrate, mercuric nitrate, lead nitrate, etc.) and chemicals were of analytical grade. The following instruments were used in this study. All potentiometric (emf) and pH measurements were performed using a pH/ion meter model 720A (Orion, USA) with a saturated calomel electrode as the reference electrode, an electronic balance (digital, Sartorius-210S, Japan), and an automatic temperature controlled water bath incubator shaker (Elcon, India). Aqueous solutions of different concentrations were prepared by diluting standard salt solutions in deionized water ($18.6 \text{ M } \Omega \text{ cm}^{-1}$) from a Milli-Q plus (Millipore, USA). A Jeol JSM 6300 scanning electron microscope (SEM)

with a Link-Oxford-Isis X-ray microanalysis system (EDX) was used for surface studies. An FTIR spectrophotometer model 2000 (PerkinElmer, USA) was used for functional group analysis.

2.2. Preparation of poly(*o*-toluidine)@Sn(II)silicate/CNT composites

The poly(*o*-toluidine)@Sn(II)silicate/CNT composites were prepared via sol–gel mixing of oxidized *o*-toluidine by ammonium persulphate, an organic polymer, into the dispersed FCNTs mixed directly to the dispersed FCNTs in situ and sonicated for 24 h at 40 °C. Inorganic Sn(II) silicate precipitates (prepared by mixing of 1 M HCl stannous chloride in an aqueous sodium meta silicate at different mixing ratios) was mixed via sol–gel methods and stirred for more than 2 h. The reaction mixture was stirred for an additional 24 h under the same conditions. The resultant powder was precipitated in methanol, filtered using a Buchner funnel, and then carefully washed with methanol, hydrochloric acid (0.1 M), distilled water and acetone. The obtained garnish black powder was dried under a vacuum dryer at room temperature for 24 h.

The samples were converted to the H^+ form by maintaining in a 1 M HNO_3 solution for 24 h with occasional shaking and intermittent replacement of the supernatant liquid. The excess acid was removed by washing several times with dematerialized water (DMW). Finally, the samples were dried at 40 °C. Hence, a number of nanocomposite samples were prepared, and samples were selected for further studies based on their Na^+ ion exchange capacity (IEC) (1.10 meq/g) and physical appearance.

2.3. Ion-exchange capacity (IEC)

The ion-exchange capacity, which is generally taken as a measure of the hydrogen ions liberated by neutral salt that flow through the composite cation-exchanger, was determined using a standard column process. One gram of the dry cation-exchanger sample in the H^+ -form was added to a glass column with an internal diameter of ~1 cm and fitted with a glass wool support at the bottom. The bed length was approximately 1.5 cm long. As eluents, 1 M alkali and alkaline earth metal nitrates were used to completely elute the H^+ ions from the cation-exchange column, maintaining a very slow flow rate ($\sim 0.5 \text{ mL min}^{-1}$). The effluent was titrated against a standard 0.1 M NaOH using a phenolphthalein indicator.

2.4. Selectivity (sorption) studies

The distribution coefficients (K_d values) of the various metal ions on the PTh-SnP nanocomposite were determined using a batch method in various solvent systems. The distribution coefficient (K_d) was determined using the following equations:

$$K_d = \frac{\text{m moles of metal ions / gm of ion-exchanger}}{\text{m moles of metal ions / ml of solution}} (\text{ml g}^{-1}) \quad (1)$$

$$\text{i.e., } K_d = [(I-F)/F] \times [V/M] (\text{ml g}^{-1}) \quad (2)$$

where, I is the initial amount of metal ion in the aqueous phase, F is the final amount of metal ion in the aqueous phase, V is the volume of the solution (ml), and M is the amount of the cation-exchanger (g).

2.5. Preparation of poly(*o*-toluidine)@Sn(II)silicate/CNT composite cation-exchange membrane

Ion-exchange membrane of the nanocomposite was prepared according to the method reported by A.A. Khan and A. Khan [27]. To determine the optimum membrane composition, various amounts of the composite material were ground into a fine powder and mixed

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