



Structural, electrical, optical and analytical applications of newly synthesized polyaniline based nickel molybdate composite



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ABSTRACT

The synthesis of polyaniline based nickel molybdate nano composite cation exchanger was described by sol-gel method and was explored to study the electrical, optical and analytical applications. The nano composite material was characterized by Fourier Transform Infrared (spectrometer), X-ray diffraction, particle size analyzer, scanning electron microscopy and tunneling electron microscopy. The XRD of nano composite material confirmed the semi-crystalline nature while as particle size analysis as well as TEM depicted average particle size of 76 nm. The partition coefficient studies of different metal ions in the composite were performed in demineralised water and sodium dodecyl sulfate surfactant, and it was found to be selective for Pb(II), Hg(II) and Th(IV) ions. To implement the use of polyaniline Ni(II) molybdate nano composite as adsorbent, some important binary separations of metal ions were performed. SEM analysis showed that the nano composite has random non-preferential orientation with no visible cracks and appeared to be composed of dense and loose aggregation of small particles. The UV-vis spectrum of the nano composite indicated a band gap of about 3.44 eV showing a weak blue shift compared to 3.37 eV for the bulk. Due to their optical and electrical properties, nano composite is promising candidate for use as selectivity of different cations.

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1. Introduction

Organic-inorganic composites have attracted considerable attention as they can combine the advantages of both components and may offer special properties through reinforcing or modifying each other [1]. Polyaniline (PANI) has been the subject of many studies due to its oxygen and moisture-stability and potential applications in many fields [2]. PANI can also provide good network for inorganic components and modify properties and stability of the latter [3]. Nickel oxide has received considerable attention due to potential applications in many fields such as electrochromics, electrocatalysis and supercapacitor [4–7]. Chemically synthesized PANI and NiO composite by Song and coworkers produced PANI/NiO nanoparticle, nanobelt and nanotube in the presence of sodium dodecylbenzenesulfonate (SDBS). The materials showed improved conductivity and thermostability [8–10]. Generally, PANI is synthesized by anodic polymerization of aniline in acidic aqueous solution [2] hence the electrochemical synthesis of organic-inorganic composites based on PANI and metal oxides are mostly conducted by selecting oxides which can be

electrodeposited in low pH media [11–13]. However, most oxides can only be electrodeposited from high pH media, which limits the formation of such PANI composites. Recently, we have demonstrated that it is feasible to form electroactive PANI in aqueous solutions of pH 2–12 [14]. PANI-SiO₂ and PANI-MnOx composites were hence obtained [15]. Nickel oxide was reported to be electrodeposited either at a fixed potential between 0.7 and 1.2 V or by dynamic potential cycling in the potential range of 0–1.2 V vs. SCE from Ni²⁺ in neutral to weak basic solutions [16–21]. It is therefore likely that PANI and nickel oxide can be co-deposited to form an organic-inorganic composite film.

In addition to above applications, polyaniline based composite materials have been at the forefront of the global search for commercially available conducting polymers because of their unique proton dopability, low cost, ease of synthesis, excellent redox recyclability, variable electrical conductivity and their thermal and chemical stability [22,23]. In continuation of our previous work [24,25], here we report the synthesis of polyaniline Ni(II) molybdate (PNM) nano composite and simultaneously study its optical as well as electrical properties. The morphological and structural studies were carried by XRD, SEM, TEM and particle size analysis techniques. The optical properties of nano-composite were studied UV-vis measurements while as the electrical properties were studied by LCR meter.

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2. Experimental

2.1. Materials and reagents

Reagents for the synthesis include aniline, sodium molybdate and Nickel chloride which were purchased from E-Merck and Sigma–Aldrich with purity of 99.90% and used without further purification. All other chemicals were of analytical grade. Solutions of Nickel chloride (0.25 M) and sodium molybdate (0.25 M) solutions were prepared with demineralised water (DMW), whereas a 10% solution (v/v) of aniline and 0.10 M potassium persulfate was prepared in a 1 M HCl solution.

2.2. Apparatus

The IR spectra were recorded on KBr pellets with Perkin Elmer RXI Spectrometer and values are given in cm^{-1} . The XRD analysis was determined by Rigaku Diffractometer (2400) using graded d -space elliptical side-by-side multilayer optics, monochromatic Cu $K\alpha$ radiation $\lambda = (0.15406 \text{ nm})$ in 2θ range from 20° to 80° and an imaging plate (R-Axis IV) while as the particle size was analyzed by using laser diffraction during which sample was mixed with distilled water using Ultrasonic treatment. The scanning electron microscopy (SEM) was studied by instrument (SEM; LEO, 435 VF). SEM images provided information about the preparation of well-ordered precipitates, composite pore structure, micro/macro porosity, homogeneity, thickness, cracks and surface texture/morphology. The particle size was also studied by Transmission electron microscopy (TEM) analysis, performed on Jeol H-7500 microscope. Dielectric and impedance spectroscopy measurements were carried out in the frequency range 1 kHz to 1 MHz using LCR meter (Agilent 48). The optical properties of polymer matrix nano composite were studied by UV–vis measurements and the instrument used was Beckman DU 40 Spectrophotometer (USA).

2.3. Synthesis of PNM

The polymerization of aniline was initiated by adding 0.1 M potassium persulfate into 10% solution of aniline in 1:1 ratio while maintaining the temperature below 10°C under constant stirring for 1 h [26] a dark green gel of polyaniline was obtained. The inorganic precipitate of Ni(II) molybdate was prepared by sol–gel method [27] by mixing 0.25 M solutions of sodium molybdate and nickel chloride steadily with continuous stirring at 25°C for 1 h whereby gel type slurry was obtained. The pH of the solution was maintained by adding a dilute solution of HCl or HNO_3 . The resulting precipitate formed was kept overnight in the mother liquor for digestion. The polyaniline Ni(II) molybdate composite was prepared by mixing of inorganic precipitate and polyaniline gel (in 1:1 volume ratio) with continuous stirring for 1 h at 25°C . The resultant dark green gel obtained was kept for 24 h at room temperature for digestion. The supernatant liquid was decanted and the gel was filtered under suction. The acidic traces or any other inorganic impurities were removed by washing with DMW and the material was dried in an oven at 50°C . The dried material was grounded into small granules, sieved and converted into H^+ form by treating with 1.0 M HNO_3 solution for 24 h with occasional shaking and replacing the supernatant liquid with fresh acid. Further traces of acid were removed after several washings with DMW and finally dried in oven at 50°C .

2.4. Ion-exchange capacity

The ion uptake capacity was determined by taking one gram composite (in H^+ form) into a glass column (0.5 cm. internal diameter) plugged with glass wool at the bottom. The counter ions (H^+) of the composite were released by passing NaNO_3 solution (0.1 M) at a flow rate of 2.0 mL min^{-1} . The H^+ ion content of the effluent was then determined by titrating against a standard solution of sodium hydroxide (0.1 mol L^{-1}).

2.5. Distribution (sorption) studies

The distribution coefficients (K_d values) of the metal ions in DMW and different concentration of sodium dodecyl sulfate (SDS) solvents were determined by Batch method. Under set conditions, the K_d values were used to access the overall ability of the composite, NM and PANI to eliminate the ions of interest. Various portions (500 mg) of each of the composite (in H^+ form) were taken and mixed with 50 mL of different metal nitrate solutions in the required medium and subsequently shaken for 8 h in a temperature controlled shaker at 25°C to attain equilibrium. The EDTA titration was used to determine the concentration of metal ion before and after equilibrium. The values of distribution coefficient were calculated using the equation:

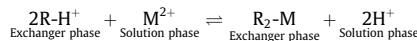
$$K_d = \frac{\text{Amount of metal ion retained in one gram of the exchanger phase (mg g}^{-1}\text{)}}{\text{Amount of metal ion in unit volume of the supernatant solution (mg mL}^{-1}\text{)}}$$

$$K_d = \frac{(I - F)/500 \text{ mg}}{F/50 \text{ mL}}$$

where I is the volume of EDTA used before the treatment of metal ion exchanger and F is the volume of EDTA consumed by metal ion left in solution phase.

The sorption of metal ions involves the ion-exchange of the H^+ ions in exchange phase with that of metal ions in solution phase.

For example:



where R = Polyaniline Ni(II)molybdate.

2.6. Quantitative separations of metal ions in synthetic binary mixtures

Quantitative separations of some important metal ions were achieved on polyaniline Ni(II) molybdate columns. One gram of composite was packed in a glass column (0.5 cm internal diameter) with a glass wool support at the end of the column. The column was washed thoroughly with DMW, and the mixtures of two metal ions (each with 0.1 M concentration) were loaded onto the column. The mixture was allowed to pass through the column at a flow rate of 2.0 mL min^{-1} . The process was repeated two or three times to ensure the complete absorption of metal ions onto the composite. The separation of metal ions was achieved by collecting the effluent in 10 mL fractions and titrating against the standard solution EDTA (0.01 M).

2.7. Electrical conductivity measurements

The sample of composite material was treated with HCl solution (0.1 M), washed repeatedly with DMW to remove excess acid, and dried at 50°C in the oven. For the conductivity measurement, 300 mg of material was finely ground, and pellets were made at a pressure of 25 kN. The thickness of the pellets was measured by a micrometer. Thus, the electrical conductivity measurements of treated (0.1 M HCl solution) and untreated samples of polyaniline Ni(II)molybdate composite were performed by increasing the temperature (between 30°C and 200°C) using LCR meter.

The pre-requisite for understanding the performance of a composite is its complete physico-chemical characterization, which involves the determination of all such parameters like thickness, porosity, swelling, water content which affects its electrical properties (Table 1).

3. Result and discussion

3.1. Structural characterizations

The suspended particle had been measured by laser. The average particle size was found to be 71 nm, 76 nm and 81 nm. The reason for such a uniform and smaller particle size is the sol–gel preparation mode (Fig. 1). SEM surface image of the nano composite of nickel molybdate and polyaniline was taken at 60 MPa pressure and are shown in Fig. 2(A) and the cross-sectional SEM micrograph of the surface is shown in Fig. 2(B). Composite had random non-preferential orientation with no visible cracks and appeared to be composed of dense and loose aggregation of small particles. The composite is macroscopically uniform in thickness and porous in nature. The pores are evenly distributed and are modeled as uniform capillaries that extend throughout the material. The thickness is still large as compared to the pore radius and it is assumed that the composite material and adjacent solution (interface) are in equilibrium. The distribution of charge density and mobile species within the pores are assumed to be uniform. The particle size as evidenced from TEM (Fig. 3) image is in the nano range.

The peak position of the sample at 44.31° and 55.71° shows the presence of nickel molybdate in composite which was confirmed from the ICDD card no. 070356 and the presence of peak position of polyaniline at 21.7° in composite was confirmed from the

Table 1
Characteristics of nano composite.

Thickness (cm)	0.075
Water content as % weight of wet composite material	0.074
Porosity	0.113
Swelling of %weight wet composite	No swelling

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