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Research Paper

EDA modified PANI/SWNTs nanocomposite for determination of Ni(II) metal ions

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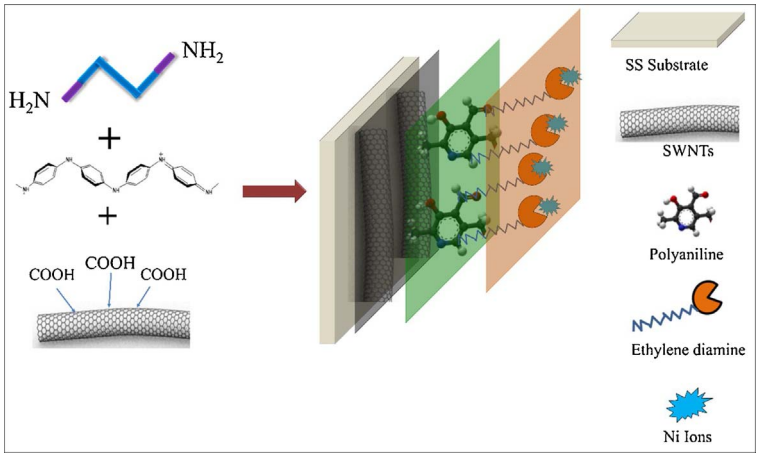
GRAPHICAL ABSTRACT



Scheme 1 Representation of the formation of ethyleendiamine modified PANI/SWNTs nanocompsite based electrochemical sensor for sensitive and selective detection of Ni(II) ions.

The formation of EDA modified PANI/SWNTs nanocomposite for detection of Ni(II) ions is shown in Scheme 1. The PANI/SWNTs nanocomposite structure was deposited on stainless steel (SS)-304 substrate through electrochemical route. Further the nanocomposite was modified with ethylenediamine via dip coating technique at room temperature.

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Keywords:
Ethylenediamine
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ABSTRACT

Present communication deals with demonstration of a simple and facile approach towards electrochemical synthesis of single walled carbon nanotubes (SWNTs) and polyaniline (PANI) nanocomposite by electrochemical method and its application for the detection of Ni(II) metal ion from aqueous media in presence of ethylene-diamine (EDA) chelating ligand. The modification of PANI/SWNTs nanocomposite with EDA was done through simple dip coating technique at room temperature. Polyaniline (PANI) and single walled carbon nanotubes (SWNTs) nanocomposite considered as a sensing backbone. EDA served the purpose of selective detection of Ni

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Nickel ion (II) metal ion from aqueous media due to its ring-like structure. Ethylenediamine functionalized PANI/SWNTs nanocomposite (EDA-PANI/SWNTs) properties are evident from Electrochemical, Fourier transform infrared spectrometer (FTIR), Raman Spectroscopy, X-ray diffraction (XRD) and Atomic force microscope (AFM) analysis. Differential Pulse Voltammetry (DPV) technique was applied for the electrochemical analysis of Ni(II) ion. All recorded observations revealed that EDA modified PANI/SWNTs nanocomposite is suitable for the detection of Ni(II) ion.

1. Introduction

Contemporary carbon nanotubes (CNTs) and organic conducting polymer (OCP) based nanocomposite materials are grasping the attention of research communities due to their nanometer-sized structures and excellent properties [1–5]. High surface to volume ratio of nanocomposite materials is a key factor for the catalytic activities. The nanocomposite materials also show outstanding magnetic, optical, electronic, chemical, and electrochemical properties. In fact CNTs were first time discovered in 1991 by Sumio Ijjima [6]. CNTs have excellent electrical properties as well as large surface area compared to other carbon based materials. CNTs shows improved mechanical properties like high tensile strength, flexibility due to its Sp^2 bonded carbon structure [7,8]. CNTs are insoluble in water due to their polar nature [9] and likely advisable for the most of the analytical applications. CNTs can be functionalized covalently and non-covalently with a variety of materials to form the modified and composite electrode materials for plenty of applications with improved properties [10,11]. The extraordinary properties of CNTs, such as ease of functionalization ability, high surface to volume ratio, unique thermal, chemical, electrical and mechanical properties make them most preferred material for plenty of applications [12,13].

OCPs have enormous chemical, mechanical, optical and electrical properties and these properties as a result OCPs have been explored for various applications [14–17]. OCPs are enough flexible to make reversible changes in conductivity, color, mass and volume via doping, owing to their unique conjugated p-electron system [18–20]. Thus, OCPs Viz., polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) are having great deal of interest and widely applicable for electrode materials due to their high conductivity, high pseudo capacitance, low cost, environmental stability, and ease of synthesis [21–24]. However, in spite of all these suitable properties, OCPs have some limitations in their use due to the considerable volume change during the repeated intercalation and depletion of ions during charge and discharge process which is responsible for the largely decrease in mechanical stability of OCPs [25]. In this context, CNTs are promising materials to incorporate with OCPs to facilitate and improve the performance of OCPs for various applications due to their high surface area and high mechanical strength, electrical conductivity and chemical stability [26,27].

In 1994 Ajayan et al., has first reported the great advantage of the composite structure of CNTs-OCPs utilizing their individual countless profitable properties [28,29]. The combination of CNTs and OCPs based composite materials can achieve improved synergistic effect which means to achieve an efficient electro catalysis [30,31].

Thus, CNTs-OCPs composite structure have a wide range of applications in quite large number of fields such as, biomedical [32], orthopedic implants [33], treatment of periodontal diseases in dentistry [34], VOC sensors [35] etc.

In this regard, herein we have synthesized a single walled carbon nanotubes (SWNTs) – polyaniline (PANI) composite with ethylenediamine (EDA) as modifier chelating ligand for the detection of Ni(II) ion from the aqueous phase. PANI can interact with SWNTs via π-π stacking which corresponds to non-covalent bonding. In the composite formation, SWNTs will act as a backbone of the structure surrounded by PANI molecules. EDA molecules will bind to the surface of PANI molecules and can firmly attach through π-π interaction which gives the ethylenediamine modified PANI-SWNTs nanocomposite for the selective and sensitive detection of Ni (II) ions.

2. Experimental

2.1. Materials and reagents

Aniline of reagent grade was purchased from Sigma Aldrich (Bangalore, India); Dodecyl benzene sulphonic acid sodium salt (DBSA) was procured from Kemphasol (Bombay, India) and it was used as surfactant and organic solvent to form fine suspension of SWNTs. H_2SO_4 of HPLC grade acquired from Rankem (Bombay, India), SWNTs functionalized with carboxyl groups (-COOH) were purchased from Nanoshel LLC. Ethylenediamine (EDA) was procured from Fisher Scientific, 1-ethyl-3(3 (dimethyl amino) propyl)-Carbodiimide (EDC) was procured from Sigma Aldrich (Bangalore, India). Phosphate buffer with pH 7, and other chemicals were reagent grade quality and they were used as received. Stainless Steel (SS type 304, 0.5 mm thick and area 1 × 1 cm^2) purchased from MTI (Korea). Metal salt of $Ni(NO)_3$ was procured from Fisher Scientific. All processes were performed in aqueous media and the preparation of the aqueous solutions were carried out using ultra-pure quality of water.

2.2. Synthesis of PANI/SWNTs nanocomposite

PANI/SWNTs nanocomposite was synthesized by an electrochemical method using cyclic voltammetry technique. Briefly, 0.25 M of aniline monomer and 0.5 M of H_2SO_4 were added in distilled water (100 ml). It was 12% wt. of SWNTs in distilled water with respect to the concentration of aniline monomer. DBSA was added as a surfactant in the SWNTs + DI (Deionized water) solution to make fine suspension of the SWNTs with the ratio of 10:1 (DBSA:SWNTs) sonicated for 6 h Resulting suspension of SWNTs was added slowly to the aniline + H_2SO_4 solution, stirred for 20 min at room temperature using magnetic stirrer. The final electrolyte of aniline + H_2SO_4 + SWNTs was utilized for the electrochemical synthesis of PANI/SWNTs nanocomposite.

Cyclic Voltammetry technique was used for electrochemical synthesis of PANI/SWNTs nanocomposite. SS substrate was used as a working electrode, Platinum plate as a counter electrode and Ag/AgCl as a reference electrode for synthesis of composite. The potential was scanned between 0.1–1.0 V for 20 cycles at the scan rate of 0.1 V/s. The composite formation on working electrode was observed by dark green colored coating with respect to the applied potential and cycles. The deposited dark green colored film was washed thoroughly with DI water to remove the excess monomer on a substrate surface and further dried at room temperature.

2.3. Preparation of EDA modified PANI/SWNTs nanocomposite

For the preparation of chelating ligand solution, 0.1 M of EDC (crosslinking agent) was added to the 0.01 M of EDA in 100 ml of distilled water and stirred for 20 min at room temperature. The electrochemically prepared PANI/SWNTs nanocomposite thin film was dipped in the EDA solution for 5 h at room temperature. After completion of dipping period the EDA modified nanocomposite film was rinsed through distilled water to remove the loosely bound EDA particles on