



Macromolecular Nanotechnology

High performance polyaniline/vanadyl phosphate (PANI–VOPO₄) nano composite sheets prepared by exfoliation/intercalation method for sensing applications



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ABSTRACT

A new class novel polyaniline/vanadyl phosphate (PANI–VOPO₄) composite was synthesized by exfoliation/intercalation method. The sol of polyaniline (PANI) into the gel of VOPO₄ by ranging mixing volume ratios concentration of inorganic reactant with a fixed mixing volume ratios i.e.(1:1) of organic polymer. The physico-chemical characterization was carried out by SEM, XRD, FTIR, UV–vis and simultaneous TGA studies. The analytical utility of this membrane was established by employing it as a sensor in electrometric titrations. Lead (Pb²⁺) is a serious carcinogenic and one of the most toxic heavy metals presents in the environmental contaminants. PANI–VOPO₄ onto flat-glassy carbon electrode (GCE; surface area: 0.0316 cm²) was fabricated with conducting coating agents to fabricate a sensitive and selective Pb²⁺ ions sensor in short response time in phosphate buffer phase. The fabricated cationic-sensor is exhibited higher sensitivity, large-dynamic concentration ranges, long-term stability, and improved electrochemical performances toward lead ions. The calibration plot is linear ($r^2 = 0.9798$) over the large Pb²⁺ concentration ranges (2.0 nM–2.0 mM). The sensitivity and detection limit is $\sim 2.105 \mu\text{A mM cm}^{-2}$ and $\sim 1.36 \pm 0.05 \text{ nM}$ (signal-to-noise ratio, at a SNR of 3) respectively. This novel effort is initiated a well-organize way of efficient cationic sensor development with conducting binder deposited GCE for toxic pollutants in environmental and health-care fields in large scales. Therefore, the PANI–VOPO₄/GCE sensor offers a cost effective material that can be considered as a viable alternative for effectively detecting and removing toxic Pb²⁺ from water samples.

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1. Introduction

Despite the promise of the new materials and their widespread study, the scope of commercial uses remains small and relatively few because of limitations of processability such as low mechanical strength, poor flexibility and high cost have prevented conducting polymers from making significant commercial impact. In order to improve the processability of the conducting polymers, several approaches have been developed over the years. Two-dimensional materials have been an ideal material platform for constructing electrochemical active offering great advantages to achieve higher energy densities

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materials. The mixing of nanoparticles with polymers to form composite materials has been practiced for decades. An effective combination of inherently conducting organic polymers with inorganic layered hosts results in a class of hybrid materials that has unique physical and chemical properties with wide potential application in diverse fields [1–4].

It has been shown that adding inorganic to polymers can enhance the mechanical, electrical, and thermal properties of the resulting nanocomposites. Conducting polymer based composite systems are interesting alternatives and have attracted substantial academic and industrial interest in recent years [5–10]. These composites are conducting polymers with thoroughly dispersed small inorganic filler particles. The physical, chemical and mechanical properties of the polymer composites are superior as compared to polymer alone because of the synergistic interaction between the conducting polymers and filler particles [11–18]. For example, the clay reinforced resin known as Bakelite was introduced in the early 1900s as one of the first mass-produced polymer-nanoparticle composites and fundamentally transformed the nature of practical household materials. Even before Bakelite, nanocomposites were finding applications in the form of nanoparticle-toughened automobile tires prepared by blending carbon black, zinc oxide, and/or magnesium sulfate particles with vulcanized rubber. Despite these early successes, the broad scientific community was not galvanized by nanocomposites until the early 1990s, when reports by Toyota researchers revealed that adding mica to nylon produced a five-fold increase in the yield and tensile strength of the material [19,20].

The methodology based on the insertion of monomeric precursors into two-dimensional inorganic host structures with high oxidative property (FeOCl, V_2O_5 xerogel, and $VOPO_4 \cdot nH_2O$, for instance) has led to the design and preparation of nanocomposites [21]. Several allotropic structural modifications of vanadyl phosphate have been extensively studied due to its ability to intercalate various guests into the inter-layer space [22,23]. Vanadyl phosphate ($VOPO_4$) has seen tremendous advances for layered materials with higher electrochemical performance [24–26]. The intercalation of guest species (molecules, ions, and polymers) occurs via an acid–base process or involves the reduction of vanadium (V) to vanadium (IV) with concomitant intercalation of cations, in order to counterbalance the induced negative layer charge [27]. Further, owing to mixed ionic–electronic conducting property, vanadyl phosphate has proven to undergo electrochemical intercalation. Park and co-workers reported that the sono-chemically synthesized polycrystalline $VOPO_4$ exhibits a high specific energy, comparable to that of commercial $Lix-CoO_2$. Besides, fast insertion and extraction characteristics were verified for this compound with respect to lithium ions when polycrystalline vanadyl phosphate was used as a cathode in a nonaqueous electrochemical cell [28]. Dupre and co-authors have found that the introduction of a VV/VIV mixed valency induces an increase in the electronic conductivity. In addition to this, in order to facilitate the ionic diffusion, ‘pillaring species have been introduced into the inter-layer space. These same authors also observed that sodium ion insertion into the inter-layer space leads to an improvement of the intercalation kinetics as well the cyclability [29]. In another work, it was demonstrated that the introduction of inter-layer species such as HCOOH and CH_3COOH within the $a-VOPO_4$ structure induces an increase in the ionic diffusion coefficient [30].

In this context, investigation of the electrochemical properties of $a-VOPO_4 \cdot 2H_2O$ /intrinsic conductive polymers hybrid materials is interesting, because it would enable one to explore their potentiality as constituent elements in cathodes for lithium ion battery and it would help describe the mechanism through which the introduction of polyaniline into the host structure affects cyclability. Thus, our interest is to investigate the effect on conductivity and sensitivity after insertion into $VOPO_4 \cdot 2H_2O$ /polyaniline and to investigate the electrochemical properties along with their potential application as a sensing electrode.

The lead(II) ion (Pb^{2+}) attained substantial importance as one of the most toxic heavy metallic pollutants in drinking water as well as soil surfaces, which may cause serious damage to the intelligence quotient and body organ of infants and young children through the respiratory system, digestive system, skin and deposits inside the body [31]. Although there are many traditional methods to detect Pb^{2+} accurately, such as spectrophotometry [32], atomic absorption spectrometry [33] and inductively coupled plasma atomic emission spectrometry [34], they have some disadvantages, such as complicated processes or high-cost equipment and low sensitivity. Hence, it is an important issue to establish a highly sensitive and selective analytical method for the trace detection of Pb^{2+} in the environment. It is one of the most poisonous heavy metals which could have a serious impact on the environment and human organs [35,36]. The accumulation of lead in the human body could induce toxic effects on kidneys, liver, the reproductive system and nervous system [37]. Based on the International World Health Organization and Environmental Protection Agency, the maximum permitted concentration of Pb^{2+} in drinking water is 10.0 mg/L and 50.0 mg/L, respectively [38]. The maximum acceptable level of Pb^{2+} in blood is 10.0 mg dL⁻¹, according to the Center of Disease Control and Prevention [39]. Multivalent transition metals exist in natural and contaminated environments and cannot be easily detoxified via degradation, resulting in their persistence in the environment [40]. Pb^{2+} ion, a multivalent transition metal, is a longstanding environmental contaminant since it can be taken into the body through the pulmonary system via the digestive system through contaminated water or food [41]. Recent improvements in technologies offer a noble method for the sensitive detection of small molecules, proteins, and even cells based on the affinity and specificity of aptamers, which are nucleic acid ligands selected from random sequence pools in vitro [42]. Based on a Pb^{2+} -dependent DNzyme which can serve as a biosensing recognition element, many highly sensitive and selective fluorescent [43], electrochemical [44], resonance Rayleigh scattering, electrogenerated chemiluminescence (ECL) [45] and colorimetric [46] sensors have been developed for Pb^{2+} detection in recent years. Atomic absorption spectrometry and inductively coupled plasma mass spectrometry are also the conventional analytical techniques for lead ions detection. These methods are time-consuming and need specialized operator and sophisticated equipment [47,48]. So, selective, sensitive, low-cost and simple methods for determination of Pb^{2+} are in great demand. Concerns over toxic exposure to Pb^{2+}

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