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Ultrasensitive and selective 4-aminophenol chemical sensor development based on nickel oxide nanoparticles decorated carbon nanotube nanocomposites for green environment

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ABSTRACT

Nickel oxide nanoparticles decorated carbon nanotube nanocomposites (NiO·CNT NCs) were prepared in a basic medium by using facile wet-chemical routes. The optical, morphological, and structural properties of NiO·CNT NCs were characterized using Fourier transformed infra-red (FT-IR), Ultra-violet visible (UV/Vis) spectroscopy, field-emission scanning electron microscopy (FESEM), X-ray energy dispersed spectroscopy (XEDS), X-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD) methods. Selective 4-aminophenol (4-AP) chemical sensor was developed by a flat glassy carbon electrode (GCE, surface area: 0.0316 cm^2) fabricated with a thin-layer of NCs. Electrochemical responses including higher sensitivity, large dynamic range (LDR), limit of detection (LOD), and long-term stability towards 4-AP were obtained using the fabricated chemical sensors. The calibration curve was found linear (R^2 = 0.914) over a wide range of 4-AP concentration (0.1 nmol/L–0.1 mol/L). In perspective of slope (2×10^{-5} μA/μM), LOD and sensitivity were calculated as 15.0 ± 0.1 pM and ~6.33×10^{-4} μA/(μM·cm^{-1}) respectively. The synthesized NiO·CNT NCs using a wet-chemical method is a significant route for the development of ultrasensitive and selective phenolic sensor based on nano-materials for environmental toxic substances. It is suggested that a pioneer and selective development of 4-AP sensitive sensor using NiO·CNT NCs by a facile and reliable current *vs* voltage (I–V) method for the major application of toxic agents in biological, green environmental, and health-care fields in near future.

Introduction

Nanostructure materials have been attracted more attention due to their exceptional characteristics and significant applications in sciences (Kumar and Singhal, 2007). Self-aggregation is the easy synthetic method of nanomaterials, in which ordered aggregates may be formed in a spontaneous process (Whitesides and Boncheva, 2002). It is still a big challenge to design a simple and reliable technique for low-dimensional metal oxide having chemical components and controlled morphologies with conjugated organic or inorganic molecules, which strongly affect the properties of doped nanocomposite materials (Dale and Huber, 2009). Nanomaterials may be utilized in different technological field such as catalysis, drug targeting, medical imaging, and refrigeration systems (Kesavan et al., 1999). Enhancing the surface area and reducing the crystal dimension of the

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nano-particles are the optional approach to improve the responses of sensing materials (Galatsis et al., 2003). The protection of environment and health is a great concern of study for the determination of poisonous materials through a well-recognized method using a chemical sensor. Nanostructure material semiconductor is very efficient and sensitive because of their high active surface area and spherical size to volume ratio in comparison with traditional nano-materials at the micro to nano-ranges. Nickel oxide (NiO) electrode has high resistivity, which is a serious drawback to apply for practical applications to super-capacitors. It is crucial to enhance the electrode conductivity in order to improve the energy density and power density of electrodes. Moreover, the specific surface area of electrodes is directly related to the specific capacitance. However, the specific surface area of the NiO is in general not high enough for high capacitance. The carbon nanotube has been known to yield high conductivity and large specific surface area adding carbon nanotube (CNT) in NiO electrode is therefore expected to provide a chance to improve the performance of the NiO and super-capacitors. In this report, we propose a nanocomposite consisting of NiO and CNT and apply it to an electrode material for super-capacitors. The nanocomposite was prepared by a simple chemical precipitation followed by thermal annealing. This approach is easy to control and straightforward, which is suitable for production in large quantity. We find that the conductivity of the nanocomposite is greatly improved by an addition of NiO with CNT for higher capacitance, higher power-density, and long-cycle life.

At present, the nanostructure of metal oxide is a great deal of attention due to their many properties such as fabrication of chemical sensor, high active surface area, high porosity, permeability, quantum confinement effect and stability. Sensor-based metal oxide conjugated carbon nanotube nanocomposites are widely used for the monitoring of chemical process, air-water contamination and toxic materials in the environment (Brown et al., 1998). Identification and removing of hazardous materials from industrial waste water is one of the vital issues in the environmental field. Various techniques were reported for the detection and separation of toxic materials from the industrial waste water but some issues are still unsettled that are removing of hazardous compounds in efficiently and re-usability of the NCs materials and synthesis of the green NCs at a facile and low cost. The meso-porous nature of the NCs material allows facile recycling without major loss of sensor efficiency and potentiality. Having the properties of absorption and adsorption capability, the hybrid NC is a suitable sensor for the detection and removing of target toxins from environmental and industrial wastes. Many uses of nickel oxide have been reported in the previous study such as sensor of hydroxide ions (Hallam et al., 2010), super-capacitors (Wu and Wang, 2010; Lee et al., 2005), pseudo-capacitance materials (Sun et al., 2011), sensor (Wang et al., 2013), electro-catalyst (Basharat et al., 2015), photo-electrodes (Zhang et al., 2015a, 2015b), and enzymatic biosensors (Karimi-Maleh et al., 2013, 2014, 2015; Shahmiri et al., 2013; Sanati et al., 2014). The chemicals of arylamines are widely used in the chemicals, dyes, pharmaceuticals, photographics, and rubber industries (Nohynek et al., 2005). Substituted and unsubstituted phenols are common bi-products of industrial process, and contaminants of food including water (Nissim and Compton, 2014). 4-AP is an acute nephrotoxin (Gartland et al., 1989) and metabolite of many chemicals such as acetaminophen, aniline, and phenacetin (Hallman et al., 2000). Due to the many disadvantages of phenol, it is very important to develop an appropriate analytical technique which is a cheap, reliable, and effective for the accurate quantification and identification of 4-AP. Different sensing techniques including electrochemical methods, HPLC, and spectrometry have been reported earlier to detect phenolic compounds. The electrochemical I–V method is a cheap, easy to operate and portable technique compared with other detection procedures. Numerous chemically modified electrodes have been developed for the detection of 4-AP based on different nanostructure materials, semiconductor, doped or undoped nanomaterials, transition metal oxides, and electrocatalytic moieties (Rahman et al., 2015a). The purpose of this study was to synthesis of NiO·CNT NCs using a simple wet-chemical method having a potential chemical sensing ability to confirm the electrical properties as well as the development of frequent electronic and optoelectronic materials (Al-Mashat et al., 2010; Xu et al., 2010). NiO·CNT NCs permit very sensitive transduction of the liquid-surface interactions to modify the chemical properties. A cheap, portable and reliable phenolic sensor is needed for the current network of chemical sensor monitoring, detection of local concentrations, and controlling of the pollution in liquid phase. NiO·CNT NCs have been used to fabricate a simple and efficient chemical sensor and evaluation of the sensing performance towards 4-AP at normal conditions. To the best of our knowledge, this is the first report for the detection of target 4-AP with prepared NiO·CNT NCs using simple, convenient, and reliable I–V technique in short response time.

1. Experimental section

1.1. Materials and methods

The used chemicals of the analytical grade such as sodium hydroxide, nafion (5% ethanolic solution), 2-nitrophenol (2-NP), 3-methoxyphenol (3-MP), 4-aminophenol (4-AP), 4-methoxyphenol (4-MP), acetone (Ac), benzaldehyde (Ben), ethanol (EtOH), hydrazine (Hy), ammonium hydroxide (AH), n-hexane (n-Hx), pyridine (Py), tetrahydrofuran (THF), and xanthine (Xn) were purchased from Sigma-Aldrich company and used without further purification. FT-IR and UV/Vis spectra of the dried light green nickel oxide nanoparticles (NiO NPs) and nickel oxide nanoparticles decorated carbon nanotube nanocomposites (NiO·CNT NCs) were recorded on a Thermo scientific NICOLET iS50 FTIR spectrometer (Madison, WI, USA) and 300 UV/Visible spectrophotometer (Thermo scientific) respectively. The XPS examination was performed for the calculation of binding energies (eV) among C, Ni and O on a Kα spectrometer (Thermo scientific, Kα1 1066) with an excitation radiation source (A1Kα1, Beam spot size: 300.0 μm, pass energy: 200.0 eV, pressure: *ca.*10^{-8} Torr). The morphology and elemental analysis of NiO NPs and NiO·CNT NCs were recorded using FESEM (JEOL, JSM-7600F, Japan) and XEDS respectively. XRD experiment was also conducted under ambient conditions to detect the crystalline pattern of NiO NPs and NiO·CNT NCs. I–V experiment was performed to detect 4-AP at a selective point by fabricated NiO·CNT NCs using Keithley electrometer (6517A, USA).

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