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 cm²) 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 ($2 \times 10^{-5} \mu A/\mu M$), LOD and sensitivity were calculated as 15.0 ± 0.1 pM and ~6.33 × 10⁻⁴ μA/(μM·cm) 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.

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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 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 aroylamines are widely used in the chemicals, dyes, pharmaceuticals, 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 an on a Kα spectrometer (Thermo scientific, Kα1 1066) with an excitation radiation source (AlKα1, 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 performed by using a JEOL JSM-7500F Field Emission Scanning Electron Microscope (FE-SEM), and Energy Dispersive X-ray Spectroscopy (EDS). The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu Kα1 radiation (λ = 1.5406 Å). The microstructure of NiO·CNT NCs were characterized using a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS) spectrometer using Al Kα excitation radiation source (1486.6 eV), pass energy: 200.0 eV, pressure: 10−9 Torr, excitation radiation source (A1Kα 1,1066) with an 10−6 beam size: 300.0 μm.
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).

1.2. Preparation of NiO-CNT nanocomposites by wet-chemical process

The wet-chemical process (Scheme 1) is a typical solid-state technique, widely used in the synthesis of doped or un-doped nanomaterials and the products will achieve smaller grains including shorter duration of phase formation. As reacting agents, nickel sulfate (NiSO₄·5H₂O), carbon nanotube (CNT), and sodium hydroxide (NaOH) were used in the synthesis of NiO-CNT NCs by simple and reliable method. On the basis of this procedure, CNT (1.0 wt %, 0.25 μg) was added with dissolved NiSO₄·5H₂O (0.1 mol/L, 2.73 g) in distilled water (100.0 mL) at an Erlenmeyer flask (250.0 mL) under continuous stirring; pH of the resultant mixture was adjusted to 10.27 with addition of NaOH and then placed for continuous stirring at 90.0°C. After 6 hr continuous stirring, the stirred solution was washed thoroughly with water and acetone respectively and kept for drying (12 hr) in open air at normal temperature.

In NiO-CNT NC growth method, initially NiO nucleus growth takes place by itself & mutual-aggregation, nano-crystal re-aggregated and formed aggregated NiO nanocrystal using Ostwald-Ripening method. Nanocrystal crystallized and re-aggregated with each other counter parts in presence of disperse CNT through Vander-Waals forces and NiO·CNT porous morphology had been reformed, which is presented in Scheme 2. The resultant light green products (NiO·CNT NCs) were dried in the oven for 24 hr at 60.0°C, grinding into powders, again dried at 60.0°C in the oven (24 hr) and then used for electrochemical characterizations and application. The NiO NPs without CNT were also prepared using the same method. The possible mechanisms of reactions for the formation of NiO-CNT NCs are as follows (Reaction (1) to (4)).

NaOH(aq) → Na⁺(aq) + OH⁻(aq) (1)
NiSO₄ → Ni²⁺(aq) + SO₄²⁻(aq) (2)
2 Na⁺(aq) + 2OH⁻(aq) + Ni²⁺(aq) + SO₄²⁻(aq) → Ni(OH)₂(aq) + Na₂SO₄(aq) (3)
2 Ni(OH)₂(aq) + CNT(dispersed) → NiO·CNT(s) + 2H₂O(aq) (4)

1.3. Fabrication of glassy carbon electrode with NiO-CNT NCs

A phosphate buffer saline (PBS, 0.1 mol/L, pH = 7) was prepared from Na₂HPO₄ (0.2 mol/L), NaH₂PO₄ (0.2 mol/L) and distilled water (100.0 mL). Ethanol and conducting binder, nafion were used to fabricate glassy carbon electrode with NiO-CNT NCs. The fabricated electrode was then kept for complete drying with uniform film formation at room temperature for 6 hr. As working and counter electrodes, the fabricated glassy carbon electrode (GCE) and platinum (Pt) were used respectively to measure the I–V responses.

2. Results and discussion

2.1. Evaluation of optical and structural properties

The optical property is one of the vital properties for the assessment of photo-catalytic-activity of the light-green NiO-CNT nanocomposites. According to the principle of UV/Vis, the outer electrons of the atoms can be shifted to the high energy level after adsorption of radiant energy. Due to the optical adsorption of radiant energy, the spectrum including band-gap energy of the metal oxide could be achieved. The UV/Vis spectra of the NiO NPs and NiO-CNT NC solution were recorded in the visible range (400–800 nm) and a broad

absorption band at around ~299.0 and ~330.4 nm were found respectively (Fig. 1a, c). On the basis of the maximum level band absorption, the band-gap energies of the NiO NPs and NiO-CNT NCs were calculated using Tauc’s equation (ν) (Silva et al., 2013).

\[
(\alpha h\nu)^{1/r} = A (h\nu - E_{bg})
\]

where, \(\alpha\) is the absorption coefficient, \(A\) is the constant related to the effective mass of the electrons, \(r = 0.5\) (Direct transition), \(h\) = Plank’s constant, \(\nu\) = Frequency, and \(E_{bg}\) = Band-gap energy.

According to the direct band-gap rule, \((\alpha h\nu)^{2} = A (h\nu - E_{bg})\), curve of \((\alpha h\nu)^{2}\) vs \(h\nu\) were plotted and then extrapolated to the axis. From the extrapolated curve, the band-gap energies for NiO NPs and NiO-CNT NCs were calculated as 2.1 and 1.9 eV respectively (Fig. 1b, d). No additional peaks associated with impurities and structural defects were observed in the spectra that indicated the crystalline characteristics of the prepared NiO nanoparticles and NiO-CNT NCs.

The light-green NiO NPs and NiO-CNT NCs were also examined in point of atomic and molecular vibrations to signify the functional nature of the NPs and NCs, and FT-IR

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**Fig. 1** – (a–c) UV/Vis spectra and (b–d) band-gap energy plot of NiO nanoparticles and NiO-CNT nanocomposites. UV/Vis: ultra-violet visible; NiO: nickel oxide nanoparticle; NiO-CNT NCs: nickel oxide nanoparticles decorated carbon nanotube nanocomposites.
spectra were recorded in the region of 4000–400 cm$^{-1}$ under normal condition in this purpose. The FT-IR spectrum of the NPs and NCs showed peaks at 3285, 2136, 1565, 1378, 1104, 842, and 607 cm$^{-1}$ which indicated the presence of O–H (stretching), –C≡C= (stretching), –C≡C– (stretching), C–H (rocking), Ni–O–Ni (stretching), C–H and Ni=O (stretching) in the NPs and NCs respectively (Fig. 2). The observed peak at 1104 and 607 cm$^{-1}$ denoted the formation of metal-oxide (Ni=O) bond which recognized the configuration of the NiO NPs and NiO-CNT NCs (Ali et al., 2013).

The crystalline nature is the indication of metal-oxygen framework. XRD analysis was conducted in the range (2$\theta$) of 10–80° to identify the crystalline pattern of the synthesized NiO NPs and NiO-CNT NCs. The potential peaks with indication for 2$\theta$ values were observed at 18.0 (002), 36.0 (111), 38.0 (200), 62.5.0 (220), 71.0 (311), and 78.0 (222) (Fig. 2). The peak at 18.0 (002) is denoted for carbon that was present in the NCs. All the observed peaks in the spectra were assigned by using the JCPDS file (No: 75-1621 and 14-0117). The strong peak indicated the crystalline pattern and purity of the NCs. From the XRD analysis it can be suggested that a big amount of crystalline NiO was present in the synthesized NCs (Yuan et al., 2009).

2.2. Evaluation of morphological and elemental characteristics

FESEM is one of the well recognized methods to evaluate the morphology of nanocomposite and nanomaterials. The morphology and elemental nature of the synthesized light green NiO NPs and NiO-CNT NCs were examined using FESEM and XEDS respectively. Using FESEM, the typical shapes of light green NiO NPs and NiO-CNT NCs were recorded at low to high magnified range. The observed magnified images denoted that NiO NPs (Fig. 3a, b) were aggregated with a bright contrast including well dispersed on the surface of CNT (Fig. 3c). The average size (diameter) of the aggregated NiO NPs is 60.0 nm. The conductance of CNT may be increased with the addition of NiO NPs which correlated the calculation of band-gap energy ($E_{bg}$) of two materials.

On the basis of XEDS analysis, carbon (C), oxygen (O) and nickel (Ni) were present in the synthesized light green NiO NPs and NiO-CNT NCs (Fig. 4a, c). The NiO NPs contains O (90.49), Ni (9.51), and NCs consists of C (51.88), O (41.08) and Ni (7.04) wt.% respectively (Fig 4b, d). According to the elemental analysis, carbon was absent in NPs but present in the NCs that meant NiO NPs were properly dispersed with bright contrast on CNT. No other peaks related with impurities were observed on FESEM coupled with XEDS spectra which denoted that the NCs are composed of C, O, and Ni only.

2.3. Evaluation of binding energy

XPS is a quantitative spectroscopic method which could be used to identify the chemical nature of the elements present in the NCs. XPS spectrum might be recorded by irradiating of a X-ray beam with a nanocomposite material and the kinetic energy including electrons number of the sample have to be determined simultaneously (Rahman and Asiri, 2015b). Based on the XPS spectrum, carbon, oxygen and nickel were present in the synthesized NiO-CNT NCs (Fig. 5a). The C1s and O1s spectra showed the main peak at 290.2 and 532.5 eV which indicated that carbon (C) and oxygen (O$^2$\-) were present in the NCs (Fig. 5b, c). The spin orbit of nickel, Ni 2p$^{1/2}$ and Ni 2p$^{3/2}$ denoted the peaks at 876.0–882.5 eV which signified that nickel (Ni$^{2+}$) was also present in the prepared NiO-CNT NCs (Fig. 5d) (Alammar et al., 2012; Salvadori et al., 2014). Therefore, it is concluded that the wet-chemically prepared NiO-CNT NCs materials have NPs phase contained two materials (NiO and CNT). Also, this conclusion is reliable with the XRD data noticeably.

2.4. Application and determination of 4-AP by NiO-CNT NCs

Advancement of the fabricated electrode with NCs is the primary stage of using as a chemical sensor. The important application of NiO-CNT NCs assembled as a chemical sensor onto GCE has been examined for the identification and determination of target analyte, 4-AP in the buffer medium. The NiO-CNT NCs/GCE sensors bearing good number of positive points such as chemically inert, easy to fabricate, non-toxic, simple to assemble, stable in air and safe. Based on

Fig. 2 – FT-IR spectra and XRD analysis of NiO nanoparticles and NiO-CNT nanocomposites.
the I–V method, the current responses of NiO·CNT NCs/GCE considerably changed during the adsorption of 4-AP. The NiO·CNT NCs/GCE was used as chemical sensor for the detection of the 4-AP. The fabricated surface of NiO·CNT NCs/GCE was made uniform with nafion which is presented in Scheme 3a. The simple and possible reaction mechanism is generalized in Scheme 3b in the presence of 4-AP on NiO·CNT NC sensor surfaces by the I–V method. Probable I–V responses of 4-AP as chemical sensor can occur due to the NiO·CNT NCs/GCE on thin-film as a function of current-potential (Scheme 3c). The resultant electrical signals of 4-AP were implemented by simple and reliable I–V method using NiO·CNT NCs/GCE (Scheme 3d). In the presence of NiO·CNT NCs, the electrons were released from 4-AP by adsorbing reduced oxygen, which improved and enhanced the current responses against potential during the I–V measurement at room conditions. An extensive amplification of the current responses with applied potential was confirmed in noticeably having the holding time of electrometer was 1.0 sec.

The significant application of NiO·CNT NCs assembled onto an electrode as a chemical sensor has been engaged for the identification of compounds that are biologically and environmentally hazardous. The current responses (potential range = 0.1–1.5 V) for the uncoated bare GCE and coated with NiO·CNT NCs on the working electrode surface were presented in Fig. 6a. The differences of the current responses between bare and coated GCE happened due to the fact that current signals were increased by being coated compared with bare GCE (Fig. 6a). The selectivity was performed with different chemicals such as 2-NP, 3-MP, 4-AP, 4-MP, Ac, Ben, EtOH, Hy, AH, n-Hx, Py, THF, and Xn. 4-AP exposed maximum current responses to NiO·CNT NCs fabricated electrode and therefore...
it was clearly reported that the sensor was more selective towards 4-AP compared with other chemicals (Fig. 6b). The current signal without analyte (green-dotted) and with analyte (blue dotted) was recorded (Fig. 6c). An increment of current responses appeared in the case of the modified NiO·CNT electrode with 4-AP which exhibited a higher surface area with better coverage in absorption and adsorption potentiality onto the porous NCs surfaces of the target molecule (4-AP).

The resistance value of the NiO·CNT NCs modified GCE chemical sensors could be decreased with increasing active surface area which is an important property of the nanocomposites (Faisal et al., 2011; Zhou et al., 2015). These reactions might happen in bulk-system/air–liquid interface/neighboring atmosphere owing to the small carrier concentration that increases the resistance. For increment of the oxygen adsorption, the sensitivity of 4-AP towards NiO·CNT NCs could be achieved due to higher-oxygen lacking conducts. Larger amount of oxygen adsorbed on the NiO-doped nanocomposite-sensor surface, more oxidizing potentiality and faster oxidation of 4-AP. The activity of 4-AP would have been extremely more as contrast to other hazardous chemical with the surface under indistinguishable conditions (Liu et al., 2010; Zhang et al., 2015a, 2015b).

The current–voltage responses of the 4-AP with different concentration towards NiO·CNT NCs modified electrode were performed with indication that the change of current of the fabricated electrode was a function of 4-AP concentration under normal condition and it was also recorded that the current responses increased gradually from lower to higher concentration of the target molecule (Fig. 7a). A good range of the analyte concentrations (0.1–10.0 mol/L) was examined from the lower to higher potential (0.1–1.5 V) to observe the possible analytical limit. The linear calibration curve at 0.5 V was plotted from the various concentrations of 4-AP (Fig. 7b). The linear dynamic range (1.0–0.1 mol/L), regression co-efficient ($R^2 = 0.914$), sensitivity ($6.33.0 \times 10^{-4} \mu A/(\mu M \ cm^2)$), and LOD (15.0 ± 0.1 pM) at signal to noise ratio ~3 were calculated from the calibration curve. Limit of dynamic range (1.0 nmol/L–0.1 mol/L) including response time of the electrode sensor were also calculated from the practical concentration variation graph.

The sensitivity of the NiO·CNT NCs coated electrode sensor was performed up to two weeks for observation of the stability and reproducibility of sensors. It was revealed that the current–voltage responses did not extensively change after washing of each experiment of the fabricated NiO·CNT NCs electrode, and relative standard deviation was found to be 5.0% (Fig. 7c). The sensitivity remained almost same as the initial response up to two weeks and after that the responses of the fabricated electrode become decreased gradually. A series of

![Fig. 5 – Study of XPS for NiO-CNT nanocomposites. (a) full spectrum; (b) C1s level; (c) O1s; (d) Ni$^{2+}$ 2p$_{1/2}$ and Ni$^{2+}$ 2p$_{3/2}$ level of acquired with MgK$_\alpha$1 radiations. X-ray beam-spot size: 400.0 μm; pass-energy: 200.0 eV; pressures: <10$^{-8}$ Torr. XPS: X-ray photoelectron spectroscopy; NiO-CNT: nickel oxide nanoparticles decorated carbon nanotube.](image-url)
seven successive measurements of 4-AP solution (1.0 μmol/L) yielded good reproducible responses with the NiO·CNT NC electrode at different conditions. A control experiment was also performed at analyte concentration (0.1 μmol/L) with different fabricated electrodes and a remarkable increased of current responses were found for the NiO·CNT NCs/GCE compared with NiO NPs/GCE and CNT/GCE (Fig. 7d). The responses of NC sensor were determined with respect to storage time for measurement of long term storage ability. The storage ability determination of the NiO·CNT NCs electrode sensor was carried out under normal condition and the sensitivity remained almost 90% as the initial response for several days. It was clearly reported that the fabricated sensor could be used without any major loss of sensitivity up to few weeks.

For a low concentration of 4-AP in liquid medium, there is a smaller surface coverage of 4-AP molecules on NiO·CNT NCs/GCE film and hence the surface reaction proceeds steadily. By increasing the 4-AP concentration, the surface reaction was increased significantly (gradually increased the response as well) owing to large surface area contacted with 4-AP molecules. Further increasing of 4-AP concentration on NiO·CNT NCs/GCE surface, it was exhibited a more rapid increased the current responses, due to larger surface covered by 4-AP chemical. Usually, the surface coverage of 4-AP molecules on NiO-CNT

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**Scheme 3** – Schematic view of (a) NiO-CNT NCs coated rod-shape round-disk GCE electrode with conducting binder, (b) proposed detection mechanism of 4-AP onto NiO-CNT NCs/GCE electrode, (c) expected I–V curve, (d) observed I–V response. Surface area of GCE = 0.0316 cm²; Method: I–V. Delay time = 1.0 sec. NiO-CNT NCs: nickel oxide nanoparticles decorated carbon nanotube nanocomposites; GCE: glassy carbon electrode.
NCs/GCE surface reached to saturation based on the regular enhancement of current responses. The 4-AP sensing mechanism of the NiO·CNT NCs/GCE fabricated film is explained and presented below. Initially, oxygen (dissolved) is chemisorbed on the NiO·CNT NCs/GCE surfaces, when the porous-fabricated-film was immersed in buffer-phase system. During the chemisorption, the dissolved oxygen was transferred into ionic species such as $\text{O}_2^{\text{ads}}$ and $\text{O}^{\text{ads}}$ which gained electrons from the conduction band. The reaction kinetics is as follows according to Eqs. (6) to (8).

$$\text{O}_2^{\text{ads}} \rightarrow \text{O}_2^{\text{ads}}$$  \hspace{1cm} (6)

$$\text{O}_2^{\text{ads}} + e^- \rightarrow \text{O}_2^{\text{ads}}$$  \hspace{1cm} (7)

$$\text{O}_2^{\text{ads}} + e^- \rightarrow 2\text{O}^{\text{ads}}$$  \hspace{1cm} (8)

The reaction between 4-AP and ionic oxygen species can take place in Eq. (9). Here, the reaction in Eq. (9) depends on the presence of 4-AP chemical in reaction medium. On NiO-CNT NCs/GCE surfaces, the analyte was oxidized and then electrons were released into the conduction band, therefore decreasing the resistance (increasing the conduction current) of the NiO-CNT NCs/GCE film upon presence of 4-AP.

$$\text{4-AP}^{\text{ad-ox/NiO·CNT NCs}} + n\text{O}^{\text{ads}} \rightarrow \text{4-AP}^{\text{de-red/NiO·CNT NCs}} + n\text{e}^-$$  \hspace{1cm} (9)

The enhanced sensitivity of the fabricated NiO-CNT NCs/GCE can be accomplished to the excellent absorption (porous surfaces in NiO-CNT NCs/bindners/GCE) and adsorption ability as well as higher catalytic decomposition activity of the NiO-CNT NCs. The estimated sensitivity and LOD of the fabricated sensor were relatively higher and lower respectively compared with the previously reported chemical sensors based on other nanocomposites or nanomaterials modified electrodes measured by electrochemical approaches (Jordan et al., 2006; Rahman, 2012, 2014; Rahman and Asiri, 2015a, 2015b, 2015c, 2015d, 2015e; Rahman et al., 2011, 2012, 2013a, 2013b, 2013c, 2014a, 2014b). Due to high specific surface area, NiO-CNT NCs provides a favorable nano-environment for the 4-AP detection with good quantity. The high sensitivity of NiO-CNT NCs/GCE provides high electron communication features which enhanced the direct electron transfer between the active sites of NiO-CNT NCs and coated GCE. The NiO-CNT NCs/GCE system is demonstrated a simple...
and reliable approach for the detection of toxic chemicals. It is also revealed that the significant access to a large group of chemicals for wide-range of ecological and biomedical applications in environmental and health-care fields respectively. Table 1 shows some selected application of nanocomposites for sensing organic molecules (4-AP) using different electrochemical methods.

### 3. Conclusions

NiO-CNT NCs were synthesized using a wet-chemical procedure in alkaline medium that was economical, easy, efficient and simple to operate. Characteristic features of NCs were conducted including UV/Vis, FT-IR, FESEM, XEDS, XPS, and XRD techniques. A simple fabrication method was applied to fabricate NiO-CNT NCs/GCE electrode at room conditions. The selective and sensitive 4-AP sensor were prepared successfully on the basis of electrode embedded with NiO-CNT NCs using conducting coating nafion binder. The electrochemical performances of the fabricated 4-AP sensor were excellent in terms of LOD, LDR, sensitivity, selectivity, reproducibility, and stability in short response time. The NiO-CNT NCs electrode was exhibited good sensitivity (6.33 x 10^{-4} μA/(μM·cm^{-2})) and lower LOD (15.0 ± 0.1 μM). A well-organized method could be introduced of this novel approach for the development of effective chemical sensors for ecological and green environment in broad scales.

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