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## 2-Nitrophenol sensor-based wet-chemically prepared binary doped $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ nanosheets by an electrochemical approach†

Mohammed M. Rahman,<sup>ab</sup> M. M. Alam<sup>\*c</sup> and Abdullah M. Asiri<sup>ab</sup>

Herein, the wet-chemical process (co-precipitation) was used to prepare nanosheets (NSs) of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  in an alkaline medium (pH  $\sim$  10.5). The synthesized NSs were totally characterized by Fourier-transform infrared spectroscopy (FTIR), ultraviolet visible spectroscopy (UV/vis), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD). The synthesized NSs were deposited onto a glassy carbon electrode (GCE) to prepare a very thin layer with a conducting binder for detecting 2-nitrophenol (2-NP) selectively by a reliable electrochemical method. The proposed chemical sensor exhibits good sensitivity ( $54.9842 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ ), long-term stability, and enhanced chemical response by electrochemical approaches. The resultant current is found to be linear over the concentration range (LDR) from 0.01 nM to 0.01 mM. The estimated detection limit (DL) is equal to  $1.73 \pm 0.02 \text{ pM}$ . This study introduces a potential route for future sensitive sensor development with  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs by an electrochemical approach for the selective detection of hazardous and carcinogenic chemicals in environmental and health care fields.

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### 1. Introduction

Nitro-organic compounds (nitro-phenols) are well known as anthropogenic, toxic, inhibitory, and bio-refractory compounds and have vast industrial applications in the manufacture of a variety of useful products such as pharmaceuticals, industrial chemicals, pesticides, organic dyes, fungicides, insecticides, explosives, and aniline.<sup>1</sup> Therefore, the EPA (Environmental Protection Agency) and EU (European Union) have enlisted NPs as hazardous because of their highly toxic behavior towards the environment including human, animal, plants, aquatic life, and living organisms.<sup>2–4</sup> NPs may cause various harmful effects in human body, particularly cancer, generate poisoning, and tumors in the urinary tract.<sup>5,6</sup> The NPs are soluble in water, and due to the numerous manmade activities, they have not only been detected in industrial effluents, but also in fresh water and marine environment.<sup>7</sup> To protect the public health and the environment from harmful effects of NPs, it is obligatory to develop an efficient and sensitive portable device (chemical

sensor) that will be used to detect NPs in the working place, environment, and public health sector.<sup>8</sup> The existing typical methods, such as spectrophotometry,<sup>9</sup> fluorescence,<sup>10</sup> gas chromatography,<sup>11</sup> capillary electrophoresis,<sup>12</sup> and high performance liquid chromatography,<sup>13</sup> are applied to detect NPs. However, these traditional methods have several disadvantages such as being costly and time consuming, requiring heavy instrumentation, and are complicated to use outdoors. On the other hand, the electrochemical method has useful features including low cost, easy operation, short response time, portable simple instrumentation, and selectivity with high sensitivity.<sup>14</sup>

The transition metal oxides with multiple oxidation states such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{MnO}_2$ , and  $\text{CrO}_2$  are extensively applied as a successive electron mediators to detect NPs.<sup>15</sup> An efficient NP chemical sensor fabricated with  $\alpha\text{-MnO}_2$  nanotubes had exhibited the sensitivity of  $19.18 \mu\text{A} \text{mM}^{-1} \text{cm}^{-2}$  and detection limit of 0.1 mM.<sup>16</sup> Another NP chemical sensor based on  $\text{Mn}_2\text{O}_3/\text{ZnO}$  nanoparticles showed the sensitivity  $4.6667 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$  with the detection limit 0.83 nM.<sup>17</sup> In this decade, carbon nanotubes impregnated with transition metal oxides are extensively considered for the detection of environmental toxins, and this is becoming increasingly popular ever since the first invention.<sup>18–20</sup> It has been reported that the NP sensor fabricated with hydride components of carbon nanotube and phthalocyanine cobalt(II) shows an outstanding detection limit 0.2  $\mu\text{M}$  with a linear dynamic range from 1  $\mu\text{M}$  to 1.9 mM.<sup>21</sup> Besides this, another talented NP chemical sensor assembled

<sup>a</sup>Chemistry Department, King Abdulaziz University, Faculty of Science, P.O. Box 80203, Jeddah 21589, Saudi Arabia

<sup>b</sup>Center of Excellence for Advanced Material Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

<sup>c</sup>Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology, Sylhet 3100, Bangladesh. E-mail: mmalamsust@gmail.com; Tel: +880-821548976

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with a poly(diallyldimethylammonium chloride)-functionalized graphene composite has exhibited a dynamic result of detection limit 0.02  $\mu\text{M}$  with a wider linear dynamic range from 0.06 to 110  $\mu\text{M}$ .<sup>22</sup>

Due to the high toxicity of 2-NP, sustainable development of methods for its selective detection is urgently needed. Therefore, an initiative has been taken for efficient detection of 2-NP by an electrochemical sensor constructed with  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs. A thin layer of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs with a conducting binding agent (5% Nafion suspension in ethanol) was deposited on GCE to obtain a working electrode of 2-NP chemical sensor. The assembled  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/binder/GCE was applied successfully to detect 2-NP by a reliable electrochemical approach. To the best of our knowledge, the exploration of environmental toxin (2-NP) using a chemical sensor fabricated with active  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs has been reported for the first time herein. Therefore, it may be concluded that the 2-NP chemical sensor based on  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs onto GCE is a novel introduction in the field of sensor technology with promising applications in environmental toxin analysis.

## 2. Experimental

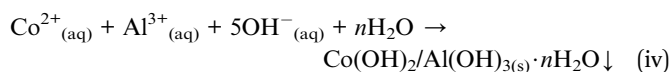
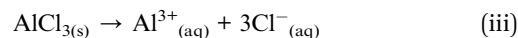
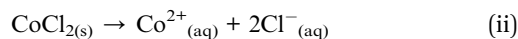
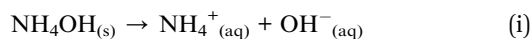
### 2.1 Materials and methods

The analytical grade chemicals cobalt(II) chloride ( $\text{CoCl}_2$ ), aluminum chloride ( $\text{AlCl}_3$ ), and ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) were obtained from the Sigma-Aldrich company and used as received to prepare  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs. To execute this study, M-tolylhydrazine (M-THyd), 2,4-dinitrophenol (2,4-DNP), 2-nitrophenol (2-NP), methanol (M), 3-methylaniline (3-MA), 3-chlorophenol (3-CP), ammonium hydroxide (AH), 3,4-diaminotoluene (3,4-DAT), 3-methoxyphenylhydrazine (3-MPHyd), bisphenol A (BPA), Nafion (5% Nafion suspension in ethanol), monosodium phosphate, and disodium phosphate were purchased from Sigma-Aldrich company. To explore the FTIR and UV-vis spectra, the produced  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs were analyzed using a Thermoscientific NICOLET iS50 FTIR (Madison, WI, USA) and 300 UV/visible spectrophotometer (Thermoscientific), respectively. The binding energies of Co, Al, and O and the corresponding oxidation states were measured by XPS analysis using a K- $\alpha$ 1 spectrometer (thermo scientific, K- $\alpha$ 1 1066) with a radiation source (A1K $\alpha$ 1, Beam spot size = 300.0  $\mu\text{m}$ , pass energy = 200.0 eV, and pressure  $\sim 10^{-8}$  torr). The optical properties, such as the arrangement of molecules, analysis of elements, morphological structure, and particle size, of synthesized NSs were investigated by implementation of FESEM (JEOL, JSM-7600F, Japan) and XEDS. Besides this, the phase (crystallinity of nanoparticles) identification was carried out by the execution of XRD analysis on the prepared  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs under ambient conditions. A slurry of NSs was used to coat the GCE with a conducting binder, and the resulting working electrode was implemented successfully to detect 2-NP in an aqueous medium. The electrochemical measurement was executed by a Keithley electrometer (6517A, USA) under room condition.

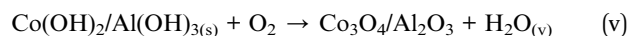
### 2.2 Preparation of $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ NSs by a wet-chemical process

The wet-chemical process (co-precipitation) is an extensively used technique to prepare doped nanomaterials at low temperatures. This method involves three successive steps: (i) precipitation of two or more metal hydroxides in aqueous media, (ii) drying of separated precipitate, and (iii) calcination of dried precipitate in a high temperature muffle furnace. For the execution of this study, the predetermined weights of cobalt chloride ( $\text{CoCl}_2$ ) and aluminum chloride ( $\text{AlCl}_3$ ) were dissolved in 100.0 mL de-ionized (DI) water in a 250.0 mL conical flask. Then, a 0.1 M solution of  $\text{NH}_4\text{OH}$  was added to the resultant solution dropwise under continuous magnetic stirring, and the pH of the solution was adjusted to around 10.5. Under this condition, the metal ions were precipitated out quantitatively in the form of  $\text{Co}(\text{OH})_2/\text{Al}(\text{OH})_3$ . The precipitate was separated out from water and then dried in an oven at 105  $^\circ\text{C}$ . Subsequently the dried sample was calcined at 500  $^\circ\text{C}$  for 6 hours in a high temperature furnace for the metal hydroxides to transform into the metal oxide form  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  in presence of atmospheric oxygen. The calcined sample in the oxide form was ground in a mortar into nanosized particles. The reaction scheme is supposed to be as follows:

In aqueous medium:



In the muffle furnace:



In the wet-chemical process, the precipitation of metal ion in the form of metal hydroxide is dependent on the value of  $K_s$  (solubility product constant) in an aqueous medium. At the pH 10.5, the  $K_s$  values for  $\text{Al}(\text{OH})_3$  and  $\text{Co}(\text{OH})_2$  are  $3 \times 10^{-34}$  and  $5.92 \times 10^{-15}$ , respectively.<sup>34</sup> As 0.1 M ammonium hydroxide solution is added dropwise to the resultant solution, the  $\text{OH}^-$  concentration increases gradually. Consequently, with the lower  $K_s$  value of  $\text{Al}(\text{OH})_3$ , aluminum hydroxide starts to precipitate first and forms nuclei of crystals.<sup>23</sup> Then, with an increase in the  $\text{OH}^-$  ion concentration, the crystallites of aluminum hydroxide start to aggregate. Due to the addition of ammonium hydroxide in the resulting solution, the pH continues to increase for the adjustment of the reactor during preparation of nanomaterials. Then, cobalt hydroxide also starts to precipitate, which is adsorbed on crystallites of aluminum hydroxide. This similar tendency of growth pattern of nanomaterials has been reported elsewhere.<sup>24–26</sup> Subsequently, the obtained crystals of metal hydroxides are sequentially washed with water, ethanol, and acetone and dried overnight at 105  $^\circ\text{C}$  in an oven. After this, the



dried sample is subjected to calcination at higher temperatures in a furnace (Barnstead Thermolyne, 6000 Furnace, USA) at 500 °C for 6 hours. The schematic of the formation mechanism of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs is presented in Scheme 1. To obtain the nano-sized particles, the calcined  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs were ground in a mortar. The prepared NSs were applied for the detection of 2-NP by an electrochemical approach under ambient conditions.

### 2.3 Fabrication of GCE with $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ NSs

A slurry of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs was prepared in ethanol and coated on a GCE as a very thin layer. To enhance the physical binding strength between NSs and GCE, a drop of Nafion (5% Nafion suspension in ethanol) was added. The assembled  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/binder/GCE was kept inside an oven at 34.0 °C for enough time to dry the conducting film entirely. The desired electrochemical cell was organized with the  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/binder/GCE and a Pt-wire (diameter 1.5 mm) as the working electrode and the counter electrode, respectively. To execute the sensor analytical performances, a series of 2-NP solutions based on the concentration ranging from 0.01 nM to 0.1 mM was prepared and used as a target analyte. The sensitivity of the anticipated chemical sensor was estimated from the slope of the calibration curve accomplished as resultant-current *versus* applied-concentration of 2-NP. The linear dynamic range (LDR) was measured from the maximum linearity (regression coefficient,  $r^2$ ) of calibration curve, and detection limit was obtained from the signal to noise ratio of 3. The used electrometer is a simple two-electrodes system. The volume of the buffer solution (PBS) in the measuring electrochemical cell was maintained constant at 10.0 mL during the execution of this study.

## 3. Results and discussions

### 3.1 Structural analyses

The XRD (powder X-ray diffraction) patterns are able to provide detailed information about unit cell dimensions (phase crystallinity), and this technique was implemented on  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs with the radiation source Cu-K $\alpha$ 1 ( $\lambda = 1.54178$  Å) in the range of 10–80°, and the corresponding scanning speed was 2° min<sup>-1</sup>. According to the XRD spectrum presented in Fig. 1, the synthesized  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs contain well-assorted phases of  $\text{Co}_3\text{O}_4$  and  $\text{Al}_2\text{O}_3$ . As observed from the Fig. 1, the reflected peaks of  $\text{Co}_3\text{O}_4$  indices as  $\beta$  are (111), (220), (222), (400), (533), (622), (440), and (511), having great similarities with the previous reports.<sup>27–30</sup> Beside this, the observed diffracted peaks

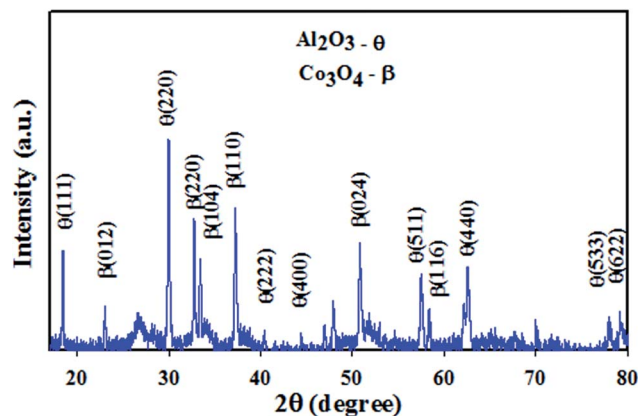


Fig. 1 Powder XRD pattern of the  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  nanostructures for the structural analysis.

for  $\text{Al}_2\text{O}_3$  indices as  $\theta$  are (012), (104), (024), (220), (110), and (116), which have been identified by previous authors<sup>31–35</sup> and JCPDS no. 29-0063 to be belonging to  $\text{Al}_2\text{O}_3$ . Based on the Scherrer equation, the crystal size of the nanoparticles can be calculated from the XRD diffraction pattern.

$$D = 0.91\lambda/(\beta \cos \theta) \quad (\text{vi})$$

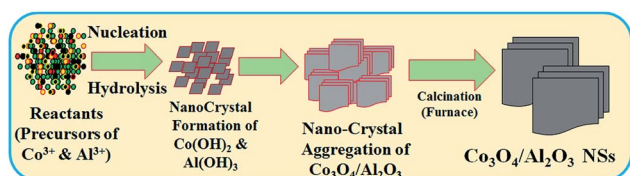
Herein,  $\lambda$  represents the wavelength (X-ray radiation = 1.5418 Å) and  $\beta$  is full width at half maxima (FWHM), corresponding to most intense peak, and  $\theta$  is the diffracting angle.<sup>36</sup> From the eqn (vi), the calculated crystal size (following the Scherrer equation) is equal to 30.86 nm. The optical analysis of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs is also performed and presented in the ESI section (Fig. S4†).

### 3.2 Morphological and elemental analyses

The morphological and elemental analysis of synthesized  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs were investigated by FESEM and EDS analysis, as illustrated in Fig. 2. The typical FESEM images with high to low magnification are presented in the Fig. 2(a and b), and it is clearly visible that the synthesized  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  materials are nanosheets in terms of shape.<sup>37–39</sup> The FESEM investigation is similar with the results of EDS analysis, as shown in Fig. 2(c and d). According to the EDS analysis, the composition of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs is O 46.95%, Al 19.74%, and Co 33.3%. Besides these, any other peak is not visible; therefore, it can be concluded that the prepared  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs consist of cobalt, aluminum, and oxygen only.<sup>40–42</sup>

### 3.3 Binding energy analysis

The synthesized NSs were subjected to XPS investigation with an X-ray beam. The XPS spectrum is obtained when the atoms of the sample absorb the kinetic energy of X-ray beam and the electrons of outer spin orbital jump from lower to higher energy level. The atomic composition with the corresponding chemical formula and the oxidation state of the species present in the nanomaterial can be scrutinized efficiently by this practice.<sup>43–45</sup> The core level XPS spectra of Co 2p, Al 2p, and O 1s are presented in Fig. 3. The high resolution of Co 2p spectrum shows



Scheme 1 The growth mechanism of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs produced by the low-temperature wet-chemical method.





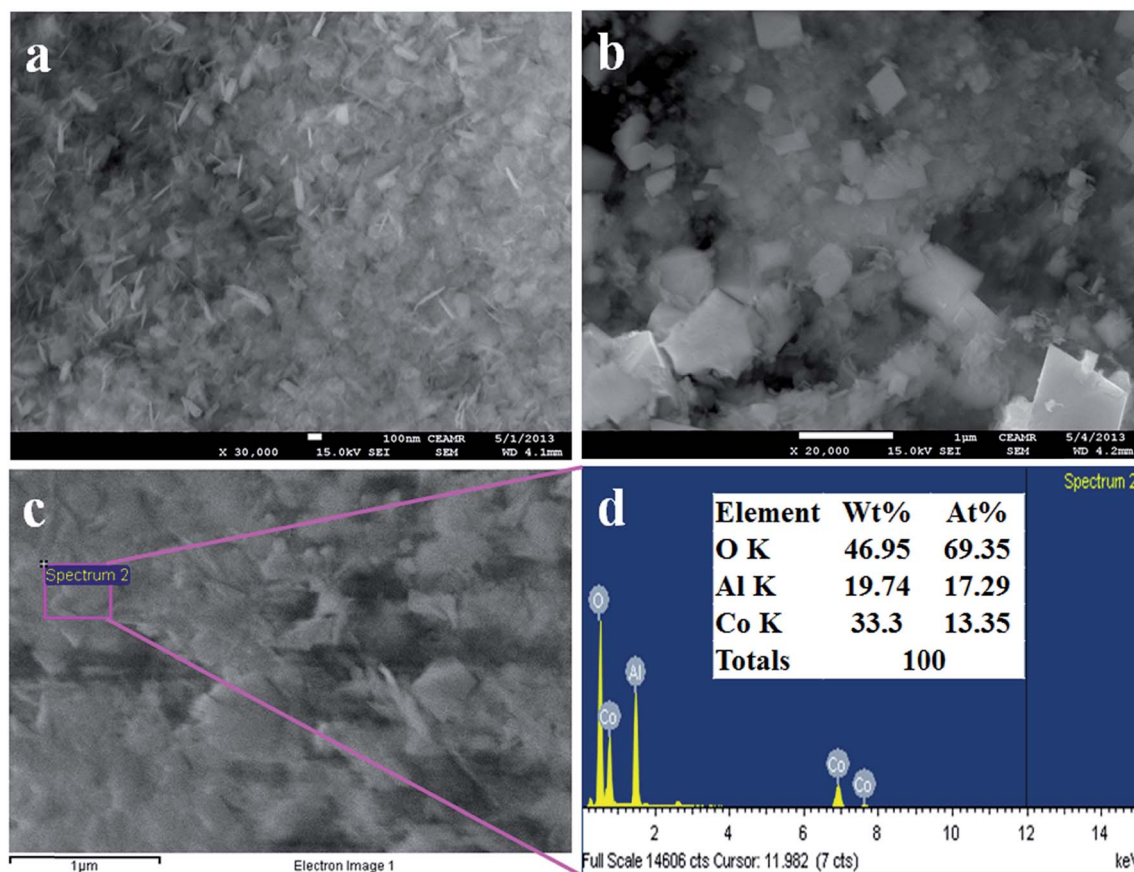


Fig. 2 Morphological and elemental analyses (a and b) FESEM analysis from high to low magnified images and (c and d) elemental analysis of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  nanostructures.

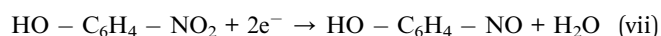
two obvious dominated peaks centered at 781.0 and 796.0 eV. These two sharp peaks can be ascribed to  $\text{Co } 2p_{3/2}$  and  $\text{Co } 2p_{1/2}$  orbits and obviously verify the presence of  $\text{Co}^{3+}$ . The projected two satellite peaks of  $\text{Co } 2p_{3/2}$  and  $\text{Co } 2p_{1/2}$  are at 787.0 and 803.0 eV, respectively. These two peaks can be attributed to the presence of  $\text{Co}^{2+}$  in the synthesized NSs, as illustrated in Fig. 3(c).<sup>46–50</sup> Therefore, the presence of dominant and satellite peaks of  $\text{Co } 2p$  spin orbitals indicate the co-existence of  $\text{Co(II)}$  and  $\text{Co(III)}$  on the surface of synthesized  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs. The O 1s exhibit a peak at 531.3 eV, which is presented in Fig. 3(b) and attributed to  $\text{O}^{2-}$  in  $\text{Al}_2\text{O}_3$ .<sup>51–55</sup> The XPS spectra of Al 2p is concentrated at 73.3 and 75.1 eV, and the peaks of Al 2p at 75.1 eV are ascribed to  $\text{Al}^{3+}-\text{O}^{2-}$  bonds in  $\text{Al}_2\text{O}_3$ , as illustrated in Fig. 3(d).<sup>56–59</sup> The different states of O 1s, Al 2p, and Co 2p are also quantified and presented in the ESI section (Fig. S5†).

### 3.4 Applications: sensing of 2-NP by $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ NSs

The selective detection of 2-NP was executed in the optimized buffer system, and this performance was carried out by the implementation of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/binder/GCE as the working electrode. To enhance the binding strength between NSs and GCE, a drop of Nafion was added. Nafion not only enhances the binding strength, but also increases stability, conductivity, and electron transfer rate of the electrode.<sup>60,61</sup> Thus, the prepared

electrode exhibited the advantages of high stability in air as well as in chemical environment, enhanced electrochemical performance during the detection of target analyte (2-NP), and can be easily subjected to performances, assembling, and fabrication, and above all, safe chemo-characteristics. Therefore, the proposed chemical sensor  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/binder/GCE was successfully used to detect 2-NP in an aqueous medium. During the performance of 2-NP chemical sensor, applied  $I$ - $V$  was measured on thin-film of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/binder/GCE, and the holding time in the electrometer was set as 1.0 s. A possible reduction mechanism of 2-NP is illustrated in Scheme 2. As observed from Scheme 2, the electrons are accepted from the applied current to reduce 2-NP into 2-AP (2-aminophenol). Therefore, the species of reactive 2-NP are adsorbed on the  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS surface and reduced to 2-aminophenol, as shown in reaction (vii) to (ix). Since the electrons are required to reduce 2-NP, the electrochemical response ( $I$ - $V$ ) is inversely proportional to the corresponding concentration of 2-NP.<sup>62–65</sup> A schematic of the detection process of 2-NP based on  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/binder/GCE sensor is demonstrated in Scheme 2.

The possible suggested reduction mechanism of 2-NP is presented in the reaction (vii) and (ix).



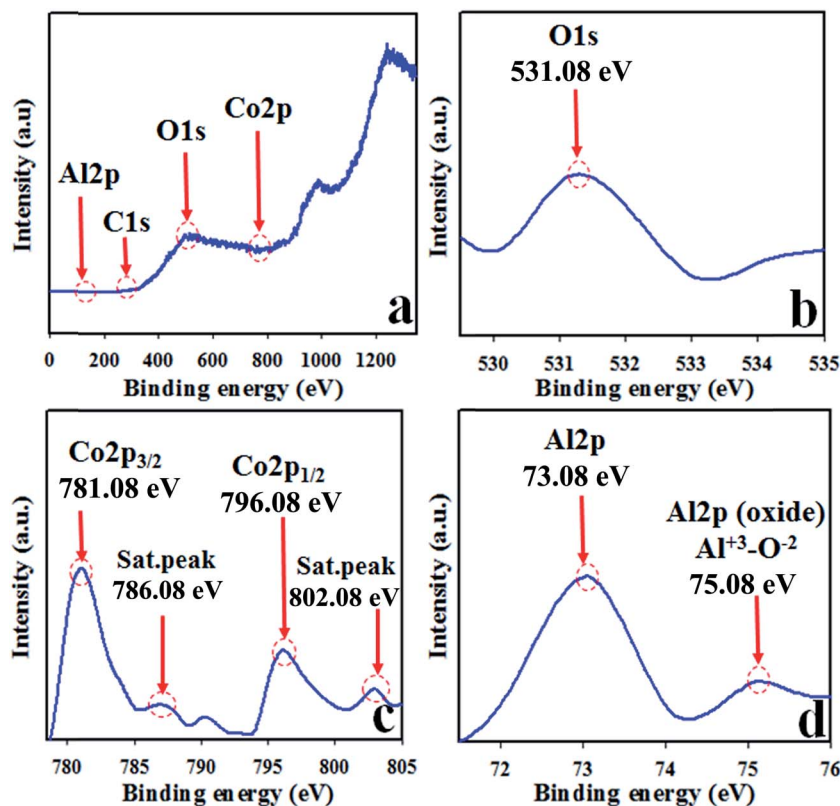
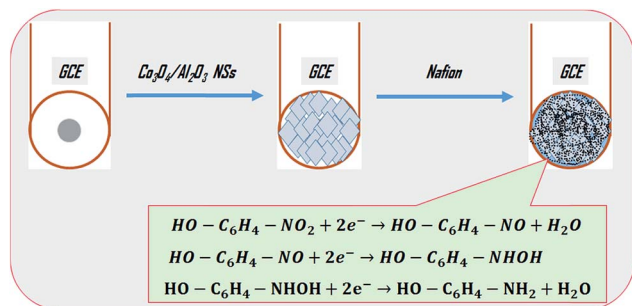
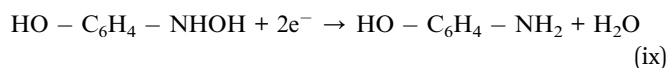
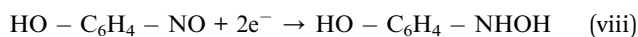


Fig. 3 Binding energy analysis by XPS study of  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs (a) full spectrum, (b) O 1s level, (c) spin orbit Co 2p level, and (d) spin orbit of Al 2p level.



Scheme 2 The expected sensing mechanism for the determination of 2-NP by  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs on sensor probe.



The synthesized NSs are not responsive equally in all buffers to applied  $I$ - $V$ . Therefore, for obtaining the maximum output of the  $I$ - $V$  responses, the pH of the measuring buffer system was necessary to be optimized for the  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/binder/GCE. Fig. 4(a) represents the  $I$ - $V$  response of pH ranging from 5.7 to 8.0. Obviously, among the tested buffer system, the best  $I$ - $V$  response was attained at pH 6.5. Then, a number of environmental toxins have been investigated at the concentration level of  $1.0 \mu\text{M}$  and pH =

7.5 with the proposed chemical sensor. The electrochemical responses of M-THyd, 2,4-DNP, 2-NP, methanol, 3-MA, 3-CP, AH, 3,4-DAT, 3-MPHyd, and BPA are illustrated in Fig. 4(b). Obviously, the electrochemical response of 2-NP has the highest intensity under experimental conditions. The reproducibility test of a chemical sensor provides the evidence of reliability. Therefore, this test was performed at  $0.1 \mu\text{M}$  concentration of 2-NP, and the resulting data is represented in Fig. 4(c). As seen in the Fig. 4(c), the replicated six runs are practically indistinguishable under an identical condition. The electrochemical responses are unchanged even after washing of electrode in each trial. Therefore, this test provides the evidence of reliability, and the projected 2-NP chemical sensor can be applied in the real field successively. The relative standard deviation of the reproducibility performances (RSD) is estimated, and it is found to be 1.54 at an applied potential of +1.5 V. The response time is another tool to measure the efficiency of a chemical sensor, and this test has been performed using a  $0.1 \mu\text{M}$  solution of 2-NP. As illustrated in Fig. 4(d), steady response is achieved in about around 10.5 s, and the obtained result may be considered highly satisfactory.

Fig. 5(a) presents the  $I$ - $V$  response of 2-NP for various concentrations ranging from  $0.01 \text{ nM}$  to  $0.1 \text{ mM}$ . Evidently, this is a very wide range, and the applied potential is higher than +1.0 V. As shown in Fig. 5(a),  $I$ - $V$  responses are distinguishable from lower to higher concentration of 2-NP. To evaluate the analytical performance of the projected chemical sensor, the current data at an applied potential of +1.5 V has been obtained



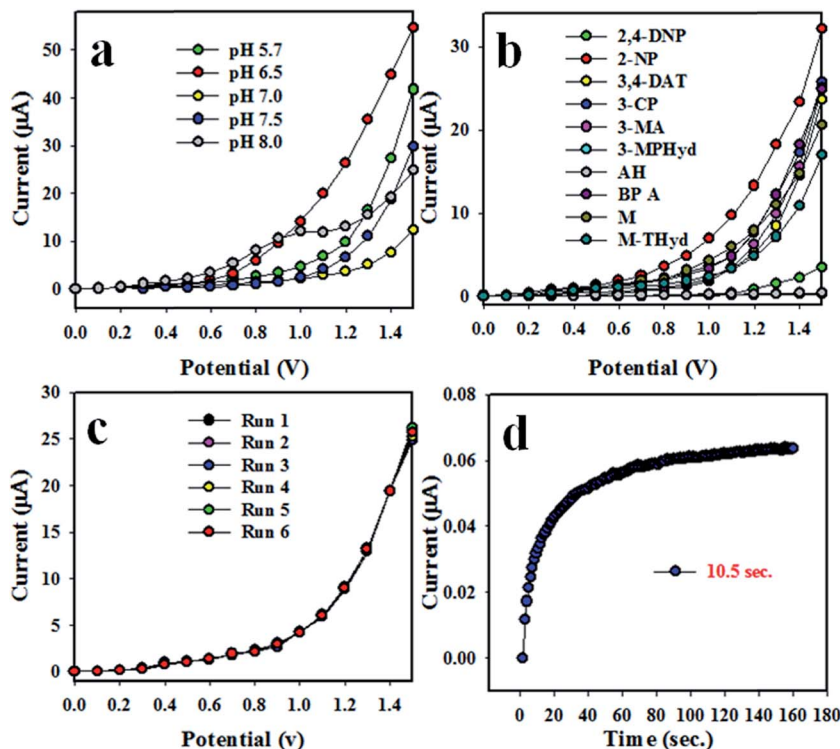


Fig. 4 Optimization of 2-NP with  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs. (a) pH optimization, (b) selectivity, (c) repeatability, and (d) response time.

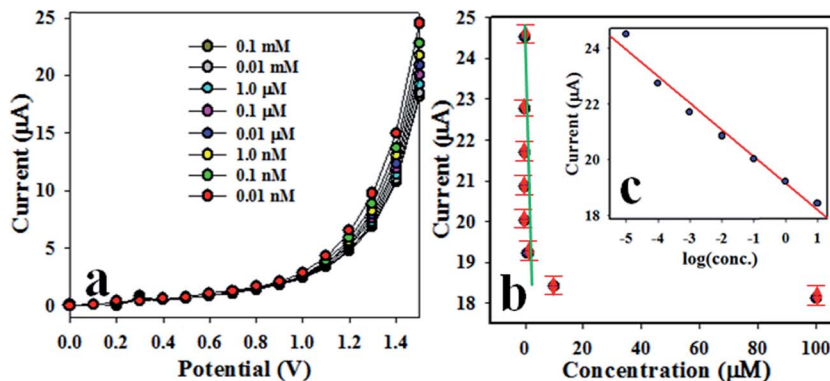


Fig. 5 Performance of 2-NP sensor. (a) Concentration variation of 2-NP based on  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs/GCE by  $I$ - $V$  method, (b) calibration curve (inset:  $\log[2\text{-NP conc.}]$  vs. current).

from Fig. 5(a) and plotted as current vs. concentration of 2-NP in the Fig. 5(b), which is known as a calibration plot. This calibration plot is found to be linear with the regression co-efficient value  $r^2 = 0.99$  along the x-axis in logarithmic scale. The sensitivity of 2-NP chemical sensor is estimated from the slope of calibration curve, and it is equal to  $54.9842 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ . The linear dynamic range (LDR) is found to be from 0.01 nM to 0.01 mM. At a signal to noise ratio equal to 3, the limit of detection (LOD) and limit of quantity (LOQ) were calculated to be  $1.73 \pm 0.02 \text{ pM}$  and  $5.77 \pm 0.02 \text{ pM}$ , respectively. Obviously, the  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/binder/GCE electrode could be used to determine 2-NP in an aqueous medium in a wide concentration range. The stability performance of electrode based on  $\text{Co}_3\text{O}_4/$

$\text{Al}_2\text{O}_3$  NSs has been evaluated in the detection of 2-NP under identical conditions for intra-days and inter-day, as presented in Fig. S1 and S2,<sup>†</sup> respectively, in the ESI section.<sup>†</sup> Therefore, it can be concluded from Fig. S1 and S2<sup>†</sup> that the fabricated electrode is able to perform efficiently in long-term. The reliable measurement of 2-NP with other toxins such as 3-CP and 4-NP According to this figure, the toxin 3-CP and 4-NP have not shown any remarkable interference effect on the projected chemical sensor during the sensing of 2-NP.

As observed from Fig. 5(a), the electrochemical response of 2-NP chemical sensor based on active  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/GCE increases with a decrease in the concentration of 2-NP.



Therefore, the highest  $I$ - $V$  response is found at lowest concentrations of 2-NP. During the sensing of 2-NP by  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/GCE electrode, a small surface coverage due to the adsorption of few 2-NP molecules on surface of electrode occurs in the initial stage, and corresponding reduction reaction of 2-NP starts progressively. With enrichment of analyte (2-NP), the rate of reaction is increased, and the higher surface coverage is obtained. With further enrichment of 2-NP concentration in the sensing medium, the reduction reaction comes to equilibrium, and the surface coverage approaches its saturation state. With an additional increase in the analyte concentration, a steady state equilibrium  $I$ - $V$  response is observed, and a saturated

surface coverage is accomplished. Therefore, it can be summarized that the proposed 2-NP chemical sensor based on the  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/GCE assembly can be applied for efficient detection of the targeted toxin (2-NP). As indicated, the proposed 2-NP chemical sensor exhibits reasonable short response time of around 10.5 s, and it should be mentioned that 10.5 s is needed by the 2-NP chemical sensor to attain steady state saturation. Since the proposed 2-NP chemical sensor demonstrates a high sensitivity of  $54.9842 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ , it can be accredited that it has very good adsorption capacity and active catalytic decomposition ability.<sup>66–70</sup> The interference effect is studied in the presence of different phenolic compounds and their derivatives, such as 2-NP, 2,4-DNP, BPA, and 3-CP, under identical conditions, as presented in Table 1.

According to analytical performance, such as selectivity, detection limit, and dynamic linear range, of the chemical sensor, the proposed 2-NP chemical sensor fabricated based on  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/GCE showed a reasonably qualified performance as compared to the chemical sensors based on the various transition nanostructured metal oxides, and a comparison is illustrated in Table 2. In brief, the fabricated 2-NP chemical sensor is simple and efficient to detect 2-NP by applying current *versus* potential electro-chemical approaches. The sensing performance, such as detection limit (LD), linear dynamic range (LDR), and sensitivity, of earlier tested 2-NP

**Table 1** Measurement of interference effect by  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NS/GCE

Toxins	Observed current <sup>a</sup> ( $\mu\text{A}$ ) at +1.5 V					RSD <sup>c</sup> (%)
	$R_1$	$R_2$	$R_3$	$R_4$	Average <sup>b</sup> ( $\mu\text{A}$ )	
2-NP	26.756	26.298	25.839	26.347	26.310	1.42
2,4-DNP	3.699	3.613	3.527	3.643	3.621	1.98
BPA	22.839	23.137	22.410	21.981	22.592	2.23
3-CP	23.688	22.875	23.525	24.175	23.566	2.28

<sup>a</sup> Mean of four repeated ( $R$ ) determination (signal to noise ratio 3) with  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs/GCE at 0.1  $\mu\text{M}$  concentration. <sup>b</sup> The average observed current of the corresponding toxin. <sup>c</sup> Relative standard deviation value indicates precision among four repeated determinations.

**Table 2** Comparative performances of various nanomaterials or nanocomposites fabricated electrode for the detection of 2-NP by electro-chemical approaches<sup>a</sup>

Materials	LOD	LDR	Sensitivity	Ref.
$\text{Ag}_2\text{O}$ NPs/AuE	0.19 $\mu\text{M}$	1.0 $\mu\text{M}$ to 0.5 mM	$0.0474 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$	70
CuO nanohybrids	0.67 nM	1.0 nM to 1.0 mM	$0.045 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$	71
Spinel $\text{ZnMn}_2\text{O}_4$	20.0 $\mu\text{M}$	50.0 $\mu\text{M}$ to 0.05 M	$1.5 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$	72
B-doped diamond electrodes	8.4 mM	—	$0.3943 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$	73
$\text{Mn}_2\text{O}_3$ -ZnO NPs/AgE	0.83 nM	100 pM to 50.0 $\mu\text{M}$	$0.6667 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$	74
$\text{Ce}_2\text{O}_3$ CNT NCs	60 pM	100 pM to 100 $\mu\text{M}$	$0.0016 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$	75
$\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ NSs/GCE	$1.73 \pm 0.02$ pM	0.01 nM to 0.01 mM	$54.9842 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$	This work

<sup>a</sup> DL (detection limit), LDR (linear dynamic range), nM (nanomole), pM (picomole).

**Table 3** Measured concentration of 2-NP analytes in real environmental samples

Sample	Added 2-NP concentration	Determined 2-NP concentration <sup>a</sup> by $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ NSs/GCE	Recovery <sup>b</sup> (%)	RSD <sup>c</sup> (%) ( $n = 3$ )
Industrial effluent	0.100 $\mu\text{M}$	0.0991 $\mu\text{M}$	99.1	2.11
	0.100 $\mu\text{M}$	0.1032 $\mu\text{M}$	103.2	
	0.100 $\mu\text{M}$	0.1022 $\mu\text{M}$	102.2	
Plastic baby bottle	0.100 $\mu\text{M}$	0.1019 $\mu\text{M}$	101.9	0.83
	0.100 $\mu\text{M}$	0.1032 $\mu\text{M}$	103.2	
	0.100 $\mu\text{M}$	0.1035 $\mu\text{M}$	103.5	
	0.100 $\mu\text{M}$	0.1053 $\mu\text{M}$	105.3	
Sea water	0.100 $\mu\text{M}$	0.1059 $\mu\text{M}$	105.9	1.02
	0.100 $\mu\text{M}$	0.1074 $\mu\text{M}$	107.4	

<sup>a</sup> Mean of three repeated determinations (signal to noise ratio 3) with  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  NSs/GCE. <sup>b</sup> Concentration of 2-NP determined/concentration taken. <sup>c</sup> Relative standard deviation value indicates precision among three repeated determinations.





chemical sensors are associated and summarized in Table 2.<sup>70–75</sup>

### 3.5 The analysis of a real sample

The proposed 2-NP chemical sensor based on Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> NSs was employed for validation to detect and quantify 2-NP in real samples to test its applicability in practical field. The samples were obtained from various sources such as industrial effluent, extracts from PC baby-bottle, and seawater. The results of the analyses are presented in Table 3 and seem quite satisfactory.

## 4. Conclusions

The reliable wet-chemical process was used to prepare NSs of Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> at low temperature. Later, a thin layer of NSs was deposited onto GCE with a conducting binder to fabricate the working electrode for the 2-NP chemical sensor development. The calcined NSs were characterized by FESEM, EDS, XPS, FTIR, UV/vis, and XRD and applied to successively detect 2-NP in an aqueous medium. The proposed 2-NP chemical sensor based on Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> NSs displayed higher sensitivity, lower detection limit, broad linear dynamic ranges, and selectivity towards 2-NP by reliable *I*–*V* method. The applied current to concentration of 2-NP is linear over the concentration range from 0.01 nM to 0.01 mM with a detection limit of  $1.73 \pm 0.02$  pM, LOQ of  $5.77 \pm 0.02$  pM, and sensitivity of  $54.9842 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ . This approach introduced a well-organized route of efficient chemical sensor development for environmental pollutants in a broad scales.

## Conflicts of interest

There are no conflicts to declare.

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