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Electrocatalysis of 2,6-Dinitrophenol Based on Wet-Chemically Synthesized PbO-ZnO Microstructures

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Abstract: In this approach, a reliable 2,6-dinitrophenol (2,6-DNP) sensor probe was developed by applying differential pulse voltammetry (DPV) using a glassy carbon electrode (GCE) decorated with a wet-chemically prepared PbO-doped ZnO microstructures’ (MSs) electro-catalyst. The nanomaterial characterizing tools such as FESEM, XPS, XRD, UV-vis., and FTIR were used for the synthesized PbO-doped ZnO MSs to evaluate in detail of their optical, structural, morphological, functional, and elemental properties. The peak currents obtained in DPV analysis of 2,6-DNP using PbO-doped ZnO MSs/GCE were plotted against the applied potential to result the calibration of 2,6-DNP sensor expressed by 

\[ i_p (\mu A) = 1.0171 C (\mu M) + 22.312 (R^2 = 0.9951; \text{regression co-efficient}) \]

The sensitivity of the proposed 2,6-DNP sensor probe obtained from the slope of the calibration curve as well as dynamic range for 2,6-DNP detection were found as 32.1867 \( \mu A \mu M \) and 3.23-16.67 \( \mu M \), respectively. Besides this, the lower limit of 2,6-DNP detection was calculated by using signal/noise (S/N = 3) ratio and found as good lowest limit (2.95 \( \pm \) 0.15 \( \mu M \)). As known from the perspective of environment and healthcare sectors, the existence of phenol and their derivatives are significantly carcinogenic and harmful which released from various industrial sources. Therefore, it is urgently required to detect by electrochemical method with doped nanostructure materials. The reproducibility as well as stability of the working electrode duration, response-time, and the analysis of real environmental-samples by applying the recovery method were measured, and found outstanding results in this investigation. A new electrochemical research approach is familiarized to the development of chemical sensor probe by using nanostructured materials as an electron sensing substrate for the environmental safety (ecological system).

Keywords: PbO-doped ZnO microstructures; differential pulse voltammetry; 2,6-dinitrophenol sensor; wet-chemical method; sensitivity; environmental safety

1. Introduction

For economic development, the industrialization is substantial approach to ensure the quality of life and it should be sustainable to conserve our environment free from toxic contaminations. Water is the most significant element of the environment and it is continuously polluted by toxic industrial wastes, especially phenolic compounds and its derivatives such as 2,6-dinitrophenol (2,6-DNP) from dyes, herbicides, photographic developers, pesticides, pharmaceuticals and explosives industries [1–4]. Our food chain is directly dependent on the environmental water and it is the major source of human exposures to toxic-like phenols. Therefore, 2,6-DNP can easily be absorbed by the gastrointestinal and respiratory
tract of human, which is led to cause the acute and chronic toxicity in humans. It has been reported that the acute toxicities of 2,6-DNP enhanced the basal metabolic rate, vomiting, nausea, headache, sweating, dizziness, and weight loss. Besides this, the chronic exposure of it might be caused the syndromes such as skin-lesions and effects on the central nervous system (CNS), bone marrow and cardiovascular system [5,6]. Moreover, 2,6-DNP has toxic effects in human such as mutagenesis, carcinogenesis, and teratogenesis and therefore, it is enlisted as hazardous toxic for human, and microorganisms by U.S.-Environmental Protection Agency (EPA) [7,8]. As a consequence, the early detection of this toxic substrate in the environmental water system can save thousands of lives from suffering and death. Up to date, some uncomfortable and traditional chromatographic methods with various drawbacks such as costly instrumentations, complicated samples preparation, long-analyzing time and un-portable for in situ detection are existed for this purpose [9–11].

Recently, the nano-metal oxides/hybrid nanocomposites as electrons mediator on sensing working electrode are coming popular to the researchers due to its potential applications as sensors. Applying the fluorece technique, the novel functional polymer [12], thiazol-substituted pyrazoline nanoparticles [13], and metal-organic frameworks [14] have been used as fluorescent substrates to the development of 2,6-dinitrophenol sensors and exhibited wider detection range with a lower detection limit of 2,6-dinitrophenol reliably, which are appreciable. Besides this, the metal-organic framework [15] and graphene quantum dots [16] have been used as luminescent nanomaterials for the detection of 2,6-dinitrophenol. The cyclic voltammetry is another reliable method for researchers for sensor development. The cathodically pretreated boron-doped diamond [17] and polycongo red decorated glassy carbon electrode [18] have been tested as potential 2,6-DNP sensors and exhibited a dynamic range of 0.0312 µM–3.12 mM and 0.5 µM–65 µM with a lower limit of 9.16 nM and 0.1 µM, respectively, for 2,6-DNP detection. Moreover, Bismuth Bulk Electrode [19] and silver solid amalgam electrode [20] have implemented to construct 2,6-DNP differential pulse voltametric electrochemical sensor and exhibited reliable outcomes.

Generally, ZnO and PbO are well-known as sensing substrates individually for the development of sensor. As a gas sensor, ZnO as single/composites has been reported to sense ethanol [21], oxygen [22], H2S [23], NO2 [24], CO [25], and NH3 [26], respectively. ZnO is an n-type semi-conductive metal-oxide with direct and wider optical bandgap and having the unique piezo-electric characteristic. These physio-electrochemical properties of ZnO are well suited as electrons sensing substrates to develop the electrochemical sensors of various bio-chemicals and chemicals [27–32], as reported previously. On the other hand, the PbO has wider optical bandgap and attractive electro-chemical properties and used potentially to develop of sensors such as humidity [33], ethanol [34], and methanol [35]. Therefore, ZnO and PbO have already applied as sensing substrates separately to the development of sensors. On the other hand, the synergic electro-catalytic characteristic of individual metal oxide in the binary nanocomposites can be promoted in the detection performance of analytes [36]. Here, PbO-doped ZnO MSs have employed a great deal of consideration owing to their chemical, structural, physical, and optical properties in terms of large-active surface area, high-stability, high porosity, high activity, and permeability, which directly dependent on the structural morphology prepared by reactant precursors in these doped materials in basic medium at low-temperature. Here, the MS materials were wet-chemically synthesized by using reducing agents at ambient conditions. This technique has several advantages including facile preparation, accurate control of the reactant temperature, easy to handle, one-step reaction, and high surface area as well as high porosity. Optical, morphological, electrical, and chemical properties of PbO-doped ZnO MSs are of huge significance from the scientific aspect, compared to their undoped counter parts. Non-stoichiometry, mostly oxygen vacancies, conduct nature in the doped nanostructure materials. The formation energy of oxygen vacancies and metal interstitials in the semiconductor is very low, and thus these defects form eagerly, resulting in the experimentally elevated conductivity of PbO-doped ZnO MS materials compared to other PbO and ZnO nanomaterials. PbO-doped ZnO MSs have also attracted considerable interest due to their potential applications in
fabricating opto-electronics, electro-analytical, selective detection of assays, sensor devices, hybrid-composites, electron-field emission sources for emission exhibits, biochemical detections, and surface-enhanced Raman properties, etc. PbO-doped ZnO MSs material offers improved performance due to the large-active surface area which increased conductivity and current responses of PbO-doped ZnO MSs/Nafion/GCE assembly during electrochemical investigation. This fabricated doped PbO-doped ZnO MSs/Nafion/GCE is very active and electro-oxidized the 2,6-DNP in respect of current against applied potential compared to other chemicals. In addition, the doped nanomaterials have lower optical band-gap energy and higher reactive surface area compared to the single metal oxides, which might be influenced by the electrochemical sensing performances [37–39]. For this reason, PbO-doped ZnO MSs have been prepared applying the wet-chemical method to enhance the electrochemical sensing of target 2,6-DNP in phosphate-buffered solution.

2. Results and Discussion

2.1. Binding Energy and Ionization States of PbO-Doped ZnO MSs

Figure 1 represents the XPS analysis report of PbO-doped ZnO MSs consisting of O1s, Zn2p, and Pb4f orbitals of existing elements only. As shown in Figure 1a, the Zn2p orbital is split in two spin-orbitals such as Zn2p\textsubscript{3/2} and Zn2p\textsubscript{1/2} located at 1022 and 1045 eV detached with 23.0 eV, which is characteristic value for 2+ ionization state of Zn\textsuperscript{2+} in PbO-doped ZnO MSs [40,41]. The O1s orbital as revealed in Figure 1b presents a peak located at 531 eV indicating O\textsuperscript{2−} ion associated with the Zn-O bond in the PbO-doped ZnO MSs [42,43]. Besides this, Pb4f orbital shows two spin orbitals of Pb4f\textsubscript{7/2} and Pb4f\textsubscript{5/2} located at 138.6 and 143.2, respectively, and separated by 4.2 eV, which is recognized for oxidation of Pb\textsuperscript{2+} in PbO-doped ZnO MSs [44,45].

![Figure 1. XPS spectrum of synthesized PbO-doped ZnO MSs. (a) The spin orbitals of Zn2p level, (b) O1s level, (c) Pb4f orbital, and (d) full spectrum.](image-url)
2.2. Crystallinity, Functional Groups and Optical Bandgap of PbO-Doped ZnO MSs

The XRD analysis of PbO-doped ZnO MSs performed at $2\theta = 20$–$80^\circ$ as perceived in Figure 2a. As appearing in Figure 2a, the resultant X-ray pattern is shown the crystalline phases of ZnO and identified plans are (100), (002), (101), (102), (110), (103), and (200), respectively, which are recognized by JCPSD no 01-007-2551 and reported articles on ZnO [46,47]. The PbO is another imported metal oxide existing in PbO-doped ZnO MSs and X-ray pattern as in Figure 2a is illustrated (001), (101), (110), (002), (112), (211), (103), and (310) plans of PbO approved by JCPSD no. 0038-1477 and previously authors [48,49]. The grain size of PbO-doped ZnO MSs is calculated by applying the Scherrer equation \[D = \frac{0.89 \lambda}{\beta \cos \theta}\] and the produced particle size is equal to 28.53 nm.

![Figure 2](image-url)

**Figure 2.** Structural, functional and optical analyses of PbO-doped ZnO MSs. (a) X-ray diffraction analysis of PbO-doped ZnO MSs, (b) FTIR and (c) UV-vis. spectrums.

Here, $\lambda = $ wavelength (Cu K$\alpha$), $\beta = $ full width at the half- maximum (FWHM) of the PbO (110) line and $\theta$ is the diffraction angle.

As illustrated in Figure 2b, the peaks due to photo-absorption positioned at 400 and 590 cm$^{-1}$ are acquired for transverse optical stretching-modes of Zn-O and Pb-O individually in PbO-doped ZnO MSs and confirmed the existence of ZnO and PbO in the prepared MSs sample [50,51]. The appeared peak at 680 cm$^{-1}$ which is assigned for Pb–O–Pb results from the asymmetric bending vibrations [52]. The absorption peaks perceived at 1120 and 1450 cm$^{-1}$ are recognized for C-O and H-O bonds, respectively [53,54]. Besides this, the optical bandgap energy of PbO-doped ZnO MSs is calculated from optical absorbance of ultra-violet visible light (UV-vis) as shown in Figure 2c. The bandgap energy is calculated from Tauc relation \[\alpha h\nu = A(h\nu − E_g)\] and obtained value is 3.4 eV [55].

Here, $\alpha = $ absorption coefficient, $h\nu = $ photon energy (eV).
2.3. FESEM and EDS Analysis of PbO-Doped ZnO MSs

The structural configuration (shape, size and arrangement) of PbO/ZnO was investigated by FESEM analysis as shown in Figure 3a,b. As seeming in Figure 3a,b, the low and high magnifying images are illustrated that the PbO/ZnO are aggregated each other to form a flower-like shape but not a complete flower, and it is really difficult to identify its morphological shape. Therefore, the synthesized PbO/ZnO can be considered as PbO/ZnO microstructures (MSs) in shape. The similar observation is perceived from Figure 3c. The perceived elemental compositions of PbO/ZnO (MSs) as in Figure 3d obtained from EDS analysis consist of O 27.2%, Zn 63.14%, and Pb 9.67% as weight. Assuming the elemental composition of PbO/ZnO (MSs), it looks similar to PbO-doped ZnO MSs.

![Figure 3. FESEM analysis of PbO-doped ZnO MSs (a,b) low and high magnifying images, (c) EDS image, and (d) EDS elemental compositions of existing atoms as wt% and At%.](image)

2.4. Electrochemical Characterization of PbO-Doped ZnO MSs as Sensing Substrates on GCE

The electrons movement ability on PbO-doped ZnO MSs/GCE was evaluated by cyclic voltammetric study of 0.1 mM [Fe(CN)₆³⁻]/[Fe(CN)₆⁴⁻] couple in 7 pH phosphate buffer as shown in Figure 4a. The sharp peaks located +0.3 V and +0.2 V are identified for the oxidation and reduction in ferrocyanide, respectively, on the coated GCE by PbO-doped ZnO MSs. On the other hand, the bare GCE is exhibited a broad peaks separation potential (+0.3 V) for oxidation to reduction in ferrocyanide compared to coated GCE (+0.10 V). Therefore, the high oxidation and reduction current obtained from coated GCE having smaller (∆Ep) potential for oxidation to reduction peaks separation is confirmed the advanced electron movement of the modified GCE with PbO-doped ZnO MSs. This observation has been demonstrated previously in the toxin detection by electrochemical approach elsewhere [55]. The conductance of a modified GCE with PbO-doped ZnO MSs is an important observation, which is assessed its capability to the oxidation/reduction in an analyte. Therefore, the electrochemical impedance spectroscopy (EIS) was performed.
by using 0.1 mM solution of Fe(CN)$_6^{3−/4−}$ in phosphate buffer of pH 7 based on PbO-doped ZnO MSs/GCE, which is illustrated in Figure 4b. From the resultant EIS as in Figure 4b, the semi-circle diameter representing the resistance of charge transfer (Rct; 205.0 Ω) is smaller for PbO-doped ZnO MSs/GCE compared to bare GCE (Rct; 521.0 Ω). Thus, it is observed that the GCE modified PbO-doped ZnO MSs has improved the charge-transfer capacity in electrochemical reaction. This concept has been demonstrated from the previous study [56,57]. Therefore, there is significance changed in redox system with GCE and without MSs/GCE in identical conditions.

As perceived in Figure 5a, the assembled sensor based on PbO-doped ZnO MSs/GCE is explored the scan rate (SR) of electrochemical (cyclic voltametric) analysis of 0.1 mM solution of Fe(CN)$_6^{3−/4−}$ in 7 pH buffer. As shown in Figure 5a, the oxidation and reduction peaks positioned at +0.3 V and +0.2 V, respectively, are increased/decreased linearly at a range of SR of 25−325 mVs$^{−1}$. The peak points current (ip) of oxidation and reduction were plotted as square roots of SR$^{1/2}$ versus ip shown in Figure 5b and expressed by ip = 7.58 (SR)$^{0.5}$ − 15.646 (R$^2 = 0.9908$) and ip = −5.4739(SR)$^{0.5}$ + 15.162 (R$^2 = 0.9905$) corresponding to oxidation and reduction process. As presented in Figure 5b, the linearity is perceived for both plots (oxidation/reduction), and suggested for a good diffusion control in oxidation and reduction reactions of Fe(CN)$_6^{3−/4−}$ (0.1 mM) in 7 pH phosphate buffer phase.

Figure 4. Electrochemical analysis of PbO-doped ZnO MSs fabricated GCE electrode. (a) The cyclic voltammetry of Bare and PbO-doped ZnO MSs modified GCE in 0.1 mM solution of Fe(CN)$_6^{3−/4−}$ in 7 pH buffer phase, and (b) Electrochemical impedance spectroscopy (EIS) for bare and PbO-doped ZnO MSs modified GCE using 0.1 mM solution of Fe(CN)$_6^{3−/4−}$ in 7 pH buffer phase.

Figure 5. Electrochemical characterization. (a) Scan rate of assembled working electrode based on PbO-doped ZnO MSs/GCE subjected to analyze of 0.1 mM solution of Fe(CN)$_6^{3−/4−}$ in buffer medium of pH = 7, and (b) V$^{0.5}$ versus ip (oxidation/reduction).
2.5. Detection of 2,6-DNP Applying DPV Method

Among the various voltammetric electrochemical analysis, the DPV for the detection of toxins is well-known and reliable. In this study, the DPV was applied to analyze 2,6-DNP in a buffer medium of distinct pH values in a range of 5.7~8.0 at 9.09 µM 2,6-DNP shown in Figure 6a,b, and the highest peak-current is obtained at pH 7 for the reduction in 2,6-DNP as demonstrated. Due to the doping of PbO, the resultant current is improved for PbO-doped ZnO MSs compared to undoped materials. Thus, the buffer solution of pH 7 is denoted as optimum to the detection of 2,6-DNP using differential pulse voltammetric method. Next, a wide range of 2,6-DNP (3.23~21.05 µM) was subjected to analysis electrochemically using this method as the obtained results are explored in Figure 6c. The peak point currents are decreased at increasing 2,6-DNP concentration in the pH 7 buffer solution. As observed in Figure 6c, the current-density is reduced at the increasing of 2,6-DNP concentration and it can predict that the electrochemical reduction in the analyte occurs. To establish the calibration of 2,6-DNP sensor, the obtained peak-currents of 2,6-DNP reduction as in Figure 6c are plotted as current versus concentration of 2,6-DNP as explored in Figure 6d, which known as calibration curve. The resulting calibration curve in the range of concentration of 3.23~16.67 µM is expressed by an equation of line as i\text{p} (\mu A) = 1.0171 C(\mu M) + 22.312 fitted with the regression co-efficient of R^2 = 0.9951. Therefore, the concentration range (3.23~16.67 µM), in which the proposed 2,6-DNP sensor responses linearly, defines as a detection range (LDR) of 2,6-DNP. Obviously, it is a wider detection range. The sensor parameter sensitivity is calculated from the slope of LDR as in Figure 6d and active surface area of GCE (0.0316 cm^2) and it is found to be 32.1867 µAµM^{-1}cm^{-2}, which might be considered to be good sensitivity. The low limit of detection (LOD) is obtained considering signal/noise = 3 and an appreciable LOD at 2.00 ± 0.10 µM is perceived.

The steadiness of 2,6-DNP DPV sensor in the performance is necessary to establish the reliability of this method. The analyzed results with repeating values is known as reproducibility and this test was performed with PbO-doped ZnO MSs/GCE sensor using 9.09 µM concentration of 2,6-DNP in buffer medium of pH 7 shown in Figure 7a,b and this experiments were conducted in the consecutive seven hours. As perceived, the seven replicated analyzed data points are undistinguished and not possible to identify separately. Therefore, the outcomes of this test convey the information regarding the reliability of 2,6-DNP sensor. The sensor-performing stability for longer duration is important for this study. This stability test of this 2,6-DNP sensor was executed by analyzing 0.1 mM solution of Fe(CN)_6^{3-}/4^- in pH 7 buffer applying cyclic voltametric electrochemical approach at 20 cycles as illustrated in Figure 7c and resultant outcome confirms the long-term stability of 2,6-DNP in buffer phase. The performing efficiency of the sensor is calculated by response time, and this performance was tested at 9.09 µM 2,6-DNP as shown in Figure 7d. The resulting 20 s response time of the 2,6-DNP sensor is confirmed to have good efficiency.

A controlled experiment was executed with GCE modified by PbO-doped ZnO MSs, ZnO NPs and PbO NPs in differential pulse voltametric analysis of 2,6-DNP (9.09 µM) perceived in Figure 8 with identical conditions. It is shown that PbO-doped ZnO MSs/GCE electrodes are performed and exhibited the highest peak current at potential +1.10 V compared with their single oxide. This happened for the large reactive surface-area of binary oxides as well as higher conductivity (higher electrochemical activity) compared to their single oxides (ZnO and PbO). As it is shown in Figure 3d, the elemental analysis of prepared MSs is consist of around 10% Pb (wt%), whereas the dominating element is Zn with 63% (wt%). Therefore, it can be assumed that PbO is doped into the dominating ZnO. As known, the reactive surface area is increased due to doping in nanomaterials. Therefore, the surface area of PbO-doped ZnO MSs is higher that the pure ZnO. As shown in Figure 8, the reduction peak current of 2,6-DNP has little higher for pure ZnO compared to pure PbO modified GCE. When, ZnO is doped with PbO (around 10%), its reactivity is increased very high. Thus, it can be concluded that doping is increased the reactive surface area of ZnO. PbO-doped ZnO MSs material offers improved performance due to the large-active surface area which increased of conductivity and current responses of PbO-doped ZnO
MSs/Nafion/GCE assembly during electrochemical investigation. This fabricated doped PbO-doped ZnO MSs/Nafion/GCE is very active and electro-oxidized the 2,6-DNP in respect of current against applied potential compared with other chemicals. Therefore, PbO doped-ZnO MS has exhibited the highest electrochemical performance compared with the undoped counterpart.

The GCE modification process is illustrated in the Scheme 1a and as perceived in Scheme 1b, the molecules of 2,6-DNP are contracted on the modified GCE surface. Due to the applied potential through assembled sensor, 2,6-DAP molecules are reduced to 2,6-diaminophenol (2,6-DAP). In this reduction process of 2,6-DNP, the data are recorded as decreasing the peak point current with increasing the concentration of 2,6-DNP as in Scheme 1c. The similar 2,6-DNP reduction has been described by previous authors [58,59].

Figure 6. Analysis of sensor performance for the detection of target analyte. (a) The pH effects on the DPV analysis of 2,6-DNP, (b) the bar diagram of pH effect in electrochemical analysis of 2,6-DNP, (c) the DPV analysis of 2,6-DNP in pH 7.0 based on the concentration variation from low to high, and (d) the calibration of 2,6-DNP sensors.
DNP, (c) the DPV analysis of 2,6-DNP in pH 7.0 based on the concentration variation from low to high, and (d) the calibration of 2,6-DNP sensor.

The steadiness of 2,6-DNP DPV sensor in the performance is necessary to establish the reliability of this method. The analyzed results with repeating values is known as reproducibility and this test was performed with PbO-doped ZnO MSs/GCE sensor using 9.09 µM concentration of 2,6-DNP in buffer medium of pH 7 shown in Figure 7a,b and this experiments were conducted in the consecutive seven hours. As perceived, the seven replicated analyzed data points are undistinguished and not possible to identify separately. Therefore, the outcomes of this test convey the information regarding the reliability of 2,6-DNP sensor. The sensor-performing stability for longer duration is important for this study. This stability test of this 2,6-DNP sensor was executed by analyzing 0.1 mM solution of Fe(CN)$_6^{3-}$/4$^{-}$ in pH 7 buffer applying cyclic voltammetric electrochemical approach at 20 cycles as illustrated in Figure 7c and resultant outcome confirms the long-term stability of 2,6-DNP in buffer phase. The performing efficiency of the sensor is calculated by response time, and this performance was tested at 9.09 µM 2,6-DNP as shown in Figure 7d. The resulting 20 s response time of the 2,6-DNP sensor is confirmed to have good efficiency.

**Figure 7.** PbO-doped ZnO MSs/GCE sensor reliability. (a) Reproducibility of 2,6-DNP sensor, (b) reproducibility in bar-diagram, (c) the stability of 2,6-DNP sensor and (d) response time.

A controlled experiment was executed with GCE modified by PbO-doped ZnO MSs, ZnO NPs and PbO NPs in differential pulse voltammetric analysis of 2,6-DNP (9.09 µM) perceived in Figure 8 with identical conditions. It is shown that PbO-doped ZnO MSs/GCE electrodes are performed and exhibited the highest peak current at potential +1.10 V compared with their single oxide. This happened for the large reactive surface-area of binary oxides as well as higher conductivity (higher electrochemical activity) compared to their single oxides (ZnO and PbO). As it is shown in Figure 3d, the elemental analysis of prepared MSs is consist of around 10% Pb (wt%), whereas the dominating element is Zn with 63% (wt%). Therefore, it can be assumed that PbO is doped into the dominating ZnO. As known, the reactive surface area is increased due to doping in nanomaterials. Therefore, the surface area of PbO-doped ZnO MSs is higher that the pure ZnO. As shown in Figure 8, the reduction peak current of 2,6-DNP has little higher for pure ZnO compared to pure PbO modified GCE. When, ZnO is doped with PbO (around 10%), its reactivity is increased very high. Thus, it can be concluded that doping is increased the reactive surface area of ZnO. PbO-doped ZnO MSs material offers improved performance due to the large-active surface area which increased of conductivity and current responses of PbO-doped ZnO MSs/Nafion/GCE assembly during electrochemical investigation. This fabricated doped PbO-doped ZnO MSs/Nafion/GCE is very active and electro-oxidized the 2,6-DNP in respect of current against applied potential compared with other chemicals. Therefore, PbO doped-ZnO MS has exhibited the highest electrochemical performance compared with the undoped counterpart.

**Figure 8.** Control experiment is performed by DPV analysis of 2,6-DNP detection in 9.09 µM based on various binary or single metal oxides modified GCE.
Scheme 1. Schematic representation of sensor. (a) GCE modification by PbO-doped ZnO MSs, (b) Assembled of instrument for differential pulse voltammetric analysis of 2,6-DNP to 2,6-DAP, (c) Analyzed data in instrument.

To establish the reliability of this study, comparison of similar work has been presented in Table 1 [1,7,16] by considering the reliability measuring parameters including LOD, LDR, and sensitivity. As shown, parameters obtained from this study are satisfactory.

Table 1. The analytical parameters of 2,6-DNP for various modified electrode.

| Modified GCE                | *LOD   | #LDR       | Sensitivity               | Ref.  |
|-----------------------------|--------|------------|---------------------------|-------|
| PCR/GCE                     | 0.1 µM | 0.5–65 µM  | —                         | [1]   |
| Functional PVC              | 23.0 nM| 2.5 µM–mM  | —                         | [7]   |
| GQDs                        | 0.091 µM| 0.1–15 µM | —                         | [16]  |
| PbO/ZnO MSs/GCE             | 2.0 µM | 3.23–16.67 µM| 32.1867 µAµM⁻¹cm⁻² | This work |

*LOD (detection limit), #LDR (linear dynamic range), µM (micromole), mM (millimole).

2.6. The Recovery Method to Real Samples Analysis

For the validity of PbO-doped ZnO MSs/GCE sensor probe, the real environmental samples such as mineral water, sea water, and tap water were analysed by electrochemical approach. After collecting the real samples, they were filtered with filter paper and directly injected in the electrochemical cell for analysis. The concentration of the spike sample was taken at 2.09 µM. Applying the DPV method, the environmental samples were analyzed using the recovery method as presented in Table 2, which shows the satisfactory outcomes.
Table 2. The collected real samples analyzed by PbO-doped ZnO MSs/GCE electrochemical sensor.

| Real Samples       | Added 2,6-DNP Conc. (µM) | Measured 2,6-DNP Conc.\(^a\) by PbO-ZnO MSs/GCE (µM) | Average Recovery\(^b\) (%) | RSD\(^c\) (%)  
\((n = 3)\) |
|--------------------|--------------------------|-------------------------------------------------------|-----------------------------|---------------------|
| Mineral water      | 2.09                     | R1: 2.97, R2: 2.99, R3: 2.95                           | 98.68                       |                     |
| Sea water          | 2.09                     | R1: 2.94, R2: 2.96, R3: 2.98                           | 98.53                       |                     |
| Tap water          | 2.09                     | R1: 2.97, R2: 2.00, R3: 2.93                           | 98.64                       |                     |

\(^a\) Mean of three repeated determination (signal to noise ratio 3) with PbO-doped ZnO MSs/GCE. \(^b\) Concentration of 2,6-DNP determined/Concentration taken. (Unit: µM). \(^c\) Relative standard deviation value indicates precision among three repeated measurements (R1, R2, and R3).

3. Experimental

3.1. Materials and Methods

The PbO-doped ZnO MSs was synthesized by old co-precipitation technique from analytical grade ZnCl\(_2\) and PbCl\(_2\) obtained from Merck Germany. Besides this, Nafion 5% in ethanol, concentrated ammonia, 2,6-dinitrophenol (2,6-DNP), mono and disodium phosphate were acquired from Sigma-Aldrich (Boston, MA, USA). The XPS instrument of Thermo-Scientific was implemented using Al\(_{1-k\text{-}}\) radiation sources with size of 300 functioned at applied potential of 200 eV, and pressure of 10\(^{-8}\) Torr on the microstructure materials to investigate the oxidation states and binding energy of the atoms in synthesized PbO-doped ZnO MSs. The structural morphology (shape, sizes and arrangements) and atomic mass were evaluated by FESEM and EDS analysis by JEOL (JSM-7600F, Tokyo, Japan). Moreover, the Thermo-scientific FTIR was used to evaluate the metal-oxygen bonds as well as other functional groups presented in the prepared nanostructure materials. The nanoparticles size and crystallinity of prepared MSs were evaluated by X-ray diffraction (XRD) analysis. Furthermore, UV-vis spectrometer was applied to identify the average optical bandgap of PbO-doped ZnO MSs. The potentiostats/galvanostats (Metrohm Autolab Modules) was used as the source of constant potential supply.

3.2. Synthesis of PbO-Doped ZnO MSs

The co-precipitation technique has extensive used to prepare doped nanomaterials of metal oxides with distinct structural morphology in the form of doped/un-doped materials. The analytical grades of reactant precursors (ZnCl\(_2\) and PbCl\(_2\)) were used for this co-precipitation preparation. 0.1 M solutions of ZnCl\(_2\) and PbCl\(_2\) were prepared using di-deionized water separately in two 100.0 mL conical-flask in this typical synthesis process. Then, another 200 mL beaker, the solution was taken as 50.0 mL of prepared each salt solution. To accomplish the co-precipitation of metal ions as metal-hydroxides, the beaker was kept heating at 80 °C using a hot-plat heating facilitated by continuous mechanical stirring system and added 0.1 M NH\(_4\)OH drop-wisely. For alkaline solution addition, the pH of solution was raised, and it was assumed that all the soluble metal ions were precipitated out as white metal-hydroxides quantitatively at pH around 10.5. Then, the resultant co-precipitated mass of Zn(OH)\(_2\)/Pb(OH)\(_2\)/nH\(_2\)O was subjected into muffle furnace.
at 500 °C around 6 h to calcine in presence of air-flow. At this high temperature, all the meal-hydroxides were oxidized to metal-oxides as shown in the reaction (5).

\[ \text{Zn(OH)}_2 \cdot \text{Pb(OH)}_2 \rightarrow \text{ZnO/PbO} + 2\text{H}_2\text{O} \]  

(5)

3.3. GCE Modification by PbO-Doped ZnO MSs

The working electrode (WE) of proposed sensor was obtained by the modification of a GCE which was the most important and sensitive task of this study. To deposit a layer of prepared PbO-doped ZnO MSs on GCE, an ethanoic slurry (1.0 mL) of MSs was used to coat on GCE and followed by drying at the laboratory ambient conditions. As the necessary requirement for this investigation, 5% Nafion-suspension (5.0 µL) was added on the modified dry GCE-surface and followed drying again by keeping inside an oven at 35 °C for an 1 h to execute the drying completely. Then, the working electrode (PbO-doped ZnO MSs/GCE), reference electrode (Ag-AgCl column electrode), and Pt-wire (performed as counter electrode) were joined with Metrohm-Autolab to fulfill sensor assembly. The 2,6-DNP was dissolved in deionized water to result 2,6-DNP solutions with a range of concentration (3.23 to 21.05 µM), which were applied for the electrochemical characterization of the assembled sensor probe. Sodium phosphates (mono and di form) were used to dilute in deionized water for the formation of the buffer having the distinct pH value of 5.7 to 8.0. For electrochemical analysis, 30.0 mL of buffer was used from 2,6-DNP having a range of 3.23–21.05 µM.

4. Conclusions

Here, binary PbO-doped ZnO MS is wet-chemically prepared in alkaline medium and then fully characterized by conventional method for the optical, structural, functional and morphological analyses. The 2,6-DNP electrochemical sensor probe was fabricated by using prepared PbO-doped ZnO MSs coated onto GCE. The assembled 2,6-DNP sensor probe was subjected to the detection of 2,6-DNP in 7.0 pH by applying DPV method. The sensor probe was perceived as reliable in-terms of LOD, LDR, reproducibility, selectivity, sensitivity, response time, and long-time stability in a room condition. Additionally, a satisfactory result was found in analyzing real samples for the sensor validation. Thus, this process to the development of sensor would a reliable method for the detection of carcinogenic chemicals by using doped microstructure materials for the safety of environmental ecology, as well as the healthcare sector.

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