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Facile Synthesis of Zinc Cobaltate Nano flakes: An enhanced Electrochemical detection of Organic Pollutant 4-Nitrotoluene

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The current work, we have demonstrate an electrochemical determination of 4-nitrotoluene (4-NT) based on zinc cobaltate nanoflakes ($ZnCo_2O_4$; ZnC Nfs) The ZnC Nfs was synthesized by simple Co-precipitation method and its physicochemical properties were systematically studied with various analytical and spectroscopic techniques such as XRD, FESEM and EDX. Moreover, the proposed ZnC Nfs modified with Screen-printed carbon electrode (SPCE) after that directly used for the electrochemical determination (4-NT). The ZnC/SPCE shows an excellent electrochemical activity for the (4-NT) detection. The as prepared ZnC Nfs provide a highly selective and sensitive electrocatalyst for the (4-NT) determination with good linear range response 0.05µM- 385.5µM and low detection limit 0.044µM. The ZnC/SPCE electrochemical sensor established the outstanding selectivity, well stability and reproducibility.

Keywords: Electrochemical sensor, Organic pollutant, Co-precipitation, $ZnCo_2O_4$ nanoflakes, 4-NT.

1. INTRODUCTION

4-nitrotoluene (4-NT) is one of the most important nitro aromatic compound, it have been applied in many industrial fields such as dye, paints, cotton, leather, pharmaceutical, and

petrochemical. Further, 4-NT act as a good explosive material because they are, widely used as explosive in army and several terrorist. This explosive behavior is lead to contaminate soil, groundwater, and plants. Moreover, the long term consumption of 4-NT can cause several health disease to human such as dizziness, intoxication, emphysema, shortness of breath, cardiovascular disease and central nervous system disease [1-11].

Due to these reason, detection of 4-NT is most important to human and environmental system. Up to date, various analytical methods have been used for 4-NT detection, such as surface enhanced Raman spectroscopy (SERS) [12] high performance liquid chromatography [13-15], chemiluminescence [16, 17], fluorescence [18,19] and electrochemical method [20,21]. Among the all, the electrochemical method have drawn a much more attention due to the simple operation, quick fabrication, high sensitivity, and less expensive. At the same, several chemical composites used for the 4-NT detection, for example, shuang yuan.et al. develop the iron-based metal-organic framework; ordered mesoporous carbon material for the electrochemical detection of 4-NT [22]. Although, binary metal oxides also one of the excellent electocatalytic material for the sensors applications.

Recently, transition metal cobaltate (ACo_2O_4 A=Mn, Fe, Ni, Cu, Zn, etc..,) have been widely used in various fields such as lithium-ion batteries, supercapacitor, photo degradation, oxygen evolution reaction (OER) electrochemical sensor and biosensor., because of the unique physical properties, low cost, and high cyclic stability [23-33]. Especially, ($ZnCo_2O_4$) have been extensively studied as advanced electrode material for the supercapacitor due to the excellent electrochemical performance [34-36]. In addition, $ZnCo_2O_4$ have two different active sites such as tetrahedral (Zn^{2+}) octahedral (Co^{3+}) thus, increasing the electrical conductivity and chemical stability. Therefore, many research groups are developed various $ZnCo_2O_4$ micro-nano structures have been synthesized by different methods. For example, hydrothermal method, electrospinning method, sol-gel method, solvothermal route, and co-precipitation method [37-41]. On the other hand, there is no literature report available for the synthesis of nanoflakes-like $ZnCo_2O_4$ (ZnC) via co-precipitation method and its application for the electrochemical detection of 4-NT.

In this current study, we have demonstrate a novel electrochemical sensor for the detection of 4-NT based on ZnC Nfs modified SPCE for the first time. The as-proposed ZnC/SPCE was employed as an excellent electrocatalyst for the detection of 4-NT. Compared to the bare (SPCE) electrode, the electrochemical activity of 4-NT in ZnC/SPCE has improved greatly. Numerous influential factors such as effect of pH and scan rate were examined. Also, the fabricated electrochemical properties of ZnC/SPCE electrode shows a very lowest detection limit, good selectivity and sensitivity towards 4-NT organic pollutant.

2. EXPERIMENTAL SECTION

2.1 Materials

Zinc sulfate ($ZnSO_4$), Cobalt chloride ($CoCl_2$), urea, ethylene glycol, 4-nitro toluene ($CH_3C_6H_4NO_2$), 4-nitro-phenol, 4-chloro-nitrobenzene, 4-bromo-nitrobenzene, 4-nitro-benzoicacid, cadmium nitrate, lead nitrate, calcium chloride, mercury and all other chemicals were received from

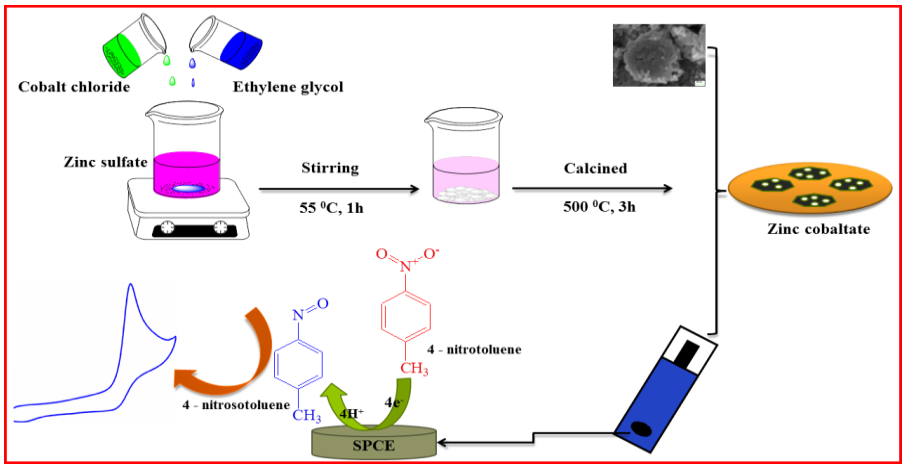
Sigma-Aldrich chemical Co., (USA), Alfa-Aeser (USA) and Fluka chemicals (Switzerland) companies and used without further purification. The phosphate buffer solution (PBS) was prepared by monosodium dihydrogen phosphate (NaH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4).All required solutions were prepared by double distilled (DD) water.

2.2 Characterizations

The Morphological studies of ZnC Nfs were carried out with field emission-scanning electron microscopy (FE-SEM, Quanta 250, FEG, Hitachi, Japan operated at 15 kV).The X-ray diffraction patterns compound were examined in a XRD, XPERT-PRO spectrometer (PANalytical B.V., The Netherlands) with Cu Kα radiation λ = 1.5406.All the electrochemical studies of 4-NT detection such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using CHI 705A and CHI 900 (CH Instruments, USA) electrochemical workstation. A conventional three-electrode system was used for the electrochemical studies, where the modified ZnC Nfs screen-printed carbon electrode (SPCE) was used as a working electrode (working area = 0.07 cm^2) and Ag/AgCl (sat. KCl) and platinum wire are used as reference and counter electrode, respectively. All the electrochemical measurements were carried out at room temperature.

2.3 Preparations of Zinc cobaltate nanoflakes ($ZnCO_2O_4$) Nfs

The synthesis of zinc cobaltate was carried out by simple co-precipitation method. In a typical procedure, 35 mL of 0.2M of ($CoCl_2$) was dissolved in 250mL beaker and allowed to stirring at room temperature, then 35 mL of 0.1M of $ZnSO_4$ solution was added to above solution with and allowed to constant stirring for 1 hour. After that, (light purple color) precipitate ($ZnCo_2O_4$) was cleaned with plentiful amount of distilled water followed by ethanol and dried at 50°C for overnight. Finally, $ZnCo_2O_4$ Nfs was calcined at 500 °C for 3 h. Then the calcined $ZnCo_2O_4$ Nfs was used for further physicochemical characterization.



Scheme 1. The synthesis and fabrication of ZnC Nfs/ SPCE and its electrochemical applications towards 4-NT detection.

2.4 Fabrication of Zinc cobaltate nanoflakes (ZnC Nfs) modified electrode

Prior to electrode surface modification process, the bare SPCE was washed with DI water and ethanol to remove the adsorbed impurities on the electrode surface. The synthesized ZnC Nfs was re-dispersed in DI water at a concentration of 5 mg/mL with the help of ultrsonication for 15 min to get a block suspension. After that, 6µL (optimized concentration) of ZnC Nfs homogeneous suspension was drop casted on the cleaned SPCE surface was dried at ambient temperature. Later, the dried electrode was gently washed with DI water to remove the loosely attached molecules. The obtained electrode was represented as ZnC/SPCE and it was used for all electrochemical studies. The synthesis and fabrication of Zinc cobaltate nanoflakes on the SPCE and its electrochemical applications are shown in Scheme 1.

3. RESULTS AND DISCUSSION

3.1 Characterization of Zinc cobaltate nanoflakes (ZnC) Nfs

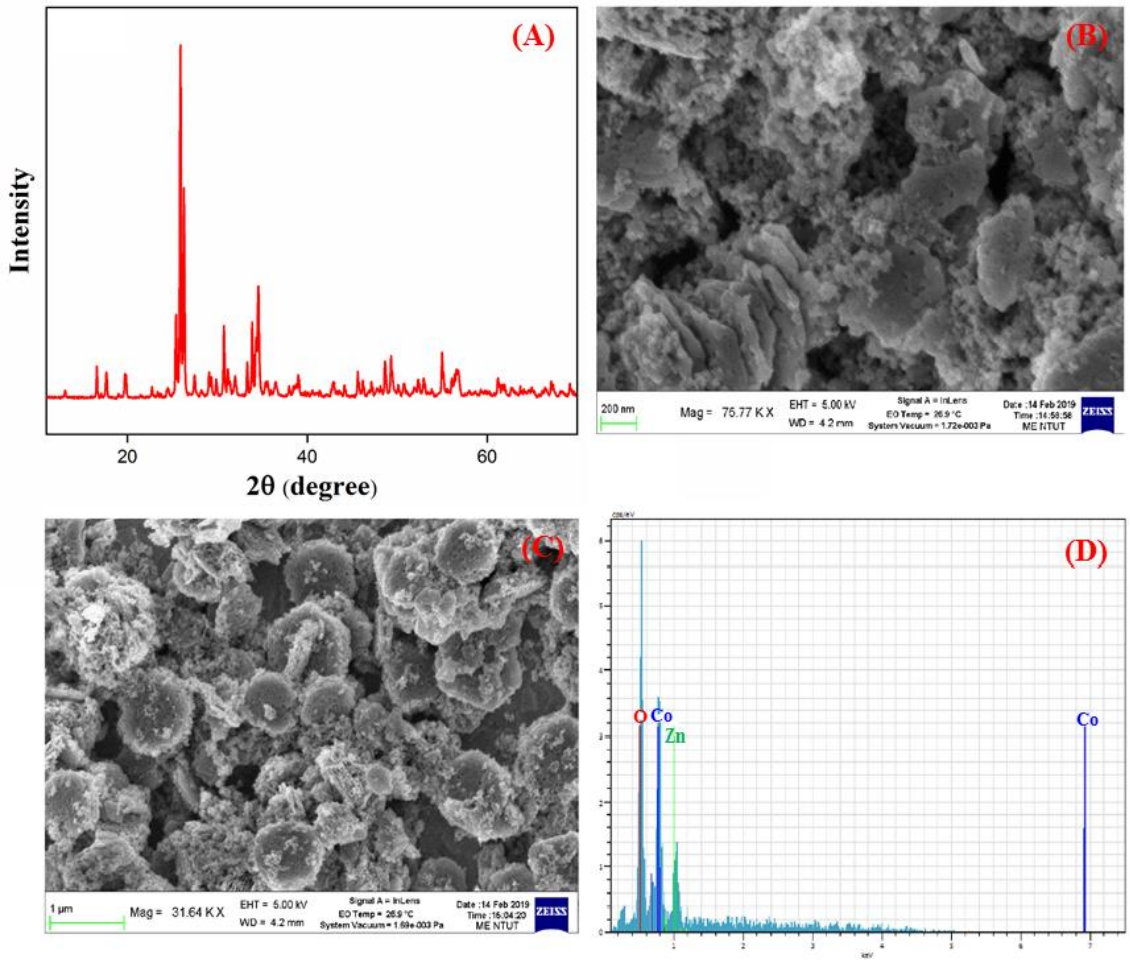


Figure 1.(A) XRD, (B, C) FE-SEM images of ZnC Nfs and (D) EDX spectrum of ZnC Nfs.

The crystalline structure of the as-prepared sample was identified by XRD analysis and shown in Fig.1A. The major planes (111), (220), (311), (400), (331), (511), (440) and (533) were corresponding to the cubic phase of $ZnCo_2O_4$ Nfs and is good consistent with the JCPDS No. 23−1390. No other notable peaks correspond to the impurities were observed suggested that the high purity of $ZnCo_2O_4$ Nfs. The morphology of the as-prepared $ZnCo_2O_4$ was investigated by FE-SEM. The FE-SEM images of $ZnCo_2O_4$ in Fig.1B-C, clearly demonstrate the nanoflakes like structure, and the average diameter and length of nanoflakes like ZnC is to be 200nm and 1µm, respectively. Furthermore, the elemental compositions are clearly investigated by EDX spectrum. The EDX results in Fig.1D clearly exhibit the presence of Zinc (Zn), Cobalt (Co) and Oxygen (O) elements without any other impurity.

3.2 Electrochemical characterization of 4-NT with different electrode

The electrochemical sensing behavior modified ZnC/SPCE and the unmodified bare SPCE were studied by CV and DPV for the detection of organic pollutant 4-NT (200µM) in (PBS; pH 07) at the 50mV/s scan rate. Fig.2A displays the CV response of ZnC/SPCE, bare SPCE in the absence (a, b) and presence (c, d) of 200µM of 4-NT 50mV/sat scan rate. The ZnC/SPCE and bare SPCE reveals that there is no electrochemical signal was observed in the absence of 200µM of 4-NT.

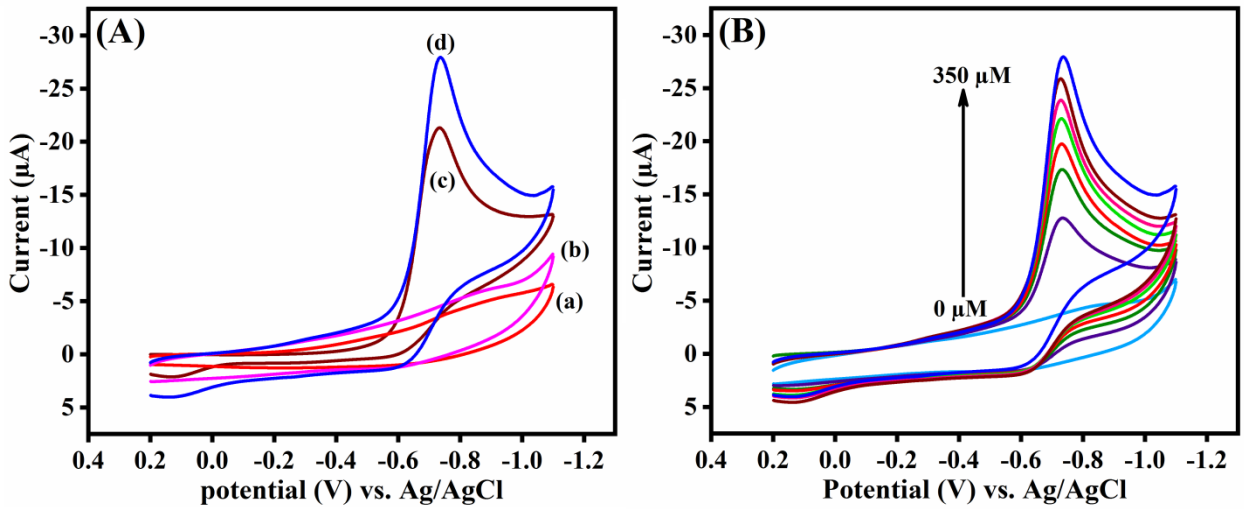


Figure 2. (A) The CV response of bare SPCE (a), modified ZnC/SPCE (b) in the absence (a,b) and presence of (c,d) of 200 µM 4-NT in 0.05 M PB Solution (pH 7.0) at scan rate of 50 mVs^{-1}. (B) CVs behavior of ZnC/SPCE in the presence of 4-NT for different concentration range (0-350 µM) in 0.05M PBS.

Interestingly, presence of (200µM) of 4-NT is a sharp and well-defined reduction peaks were observed for both electrode ZnC/SPCE(Fig.1A(d)) and bare SPCE (Fig.1A(c)), however, comparatively ZnC/SPCE has an enhanced reduction peak current than the bare SPCE which appeared at the potential of -0.72V. Further, one oxidation peak was observed corresponding to the reduction peak during the reverse scan which confirms that the reduction reaction of 4-NT is reversible process

with four electron ($4e^-$) transfer reaction. At the same, the unmodified bare SPCE was given a low electrocatalytic activity comparatively lower then modified ZnC/SPCE. However, the observed cathodic peak current is ascribed to the reduction of 4-nitro toluene to 4-hydroxylaminotoluene (4-HAT) whereas, the anodic peak is due to the oxidation of 4-HAT to 4-nitrosotoluene. The possible electrochemical reaction mechanism of 4-NT on the ZnC/SPCE is shown in Scheme 2. The obtained results are clearly suggested that the ZnC Nfs as a better electrode material for the 4-NT detection.

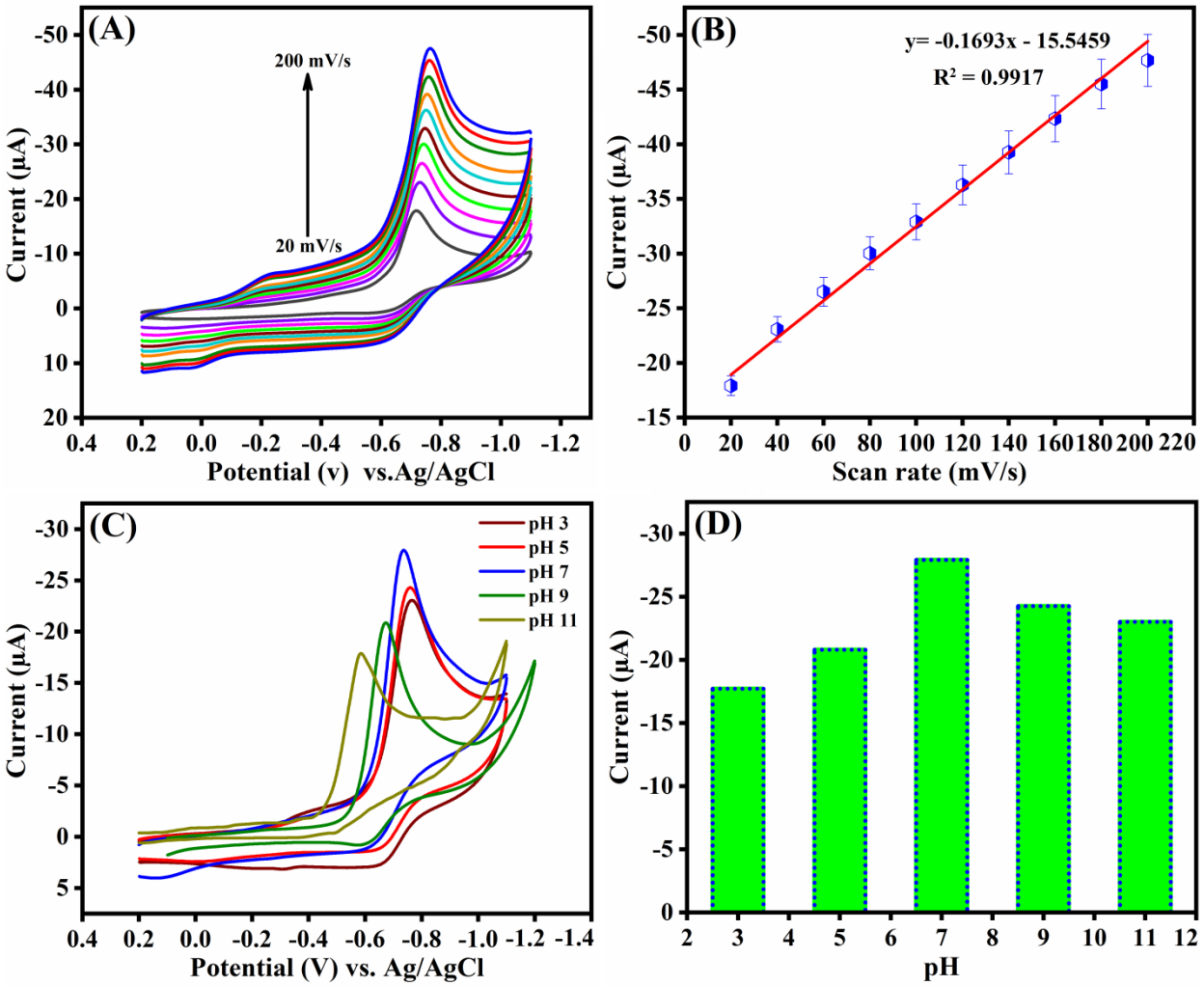


Figure 3. (A) The CV behavior of modified ZnC/SPCE in the presence of 200 µM 4-NT in 0.05 M PBS (pH 7.0) at different scan rate (20-200) mVs^{-1}. (B) The calibration plot for the cathodic peak current vs. different scan rate. (C) CV response of 200 µM 4-NT at ZnC/SPCE with different pH ranges from 3.0 to 11.0 at a scan rate of 50 mVs^{-1}. (D) The bar diagram for the cathodic peak current vs. pH.

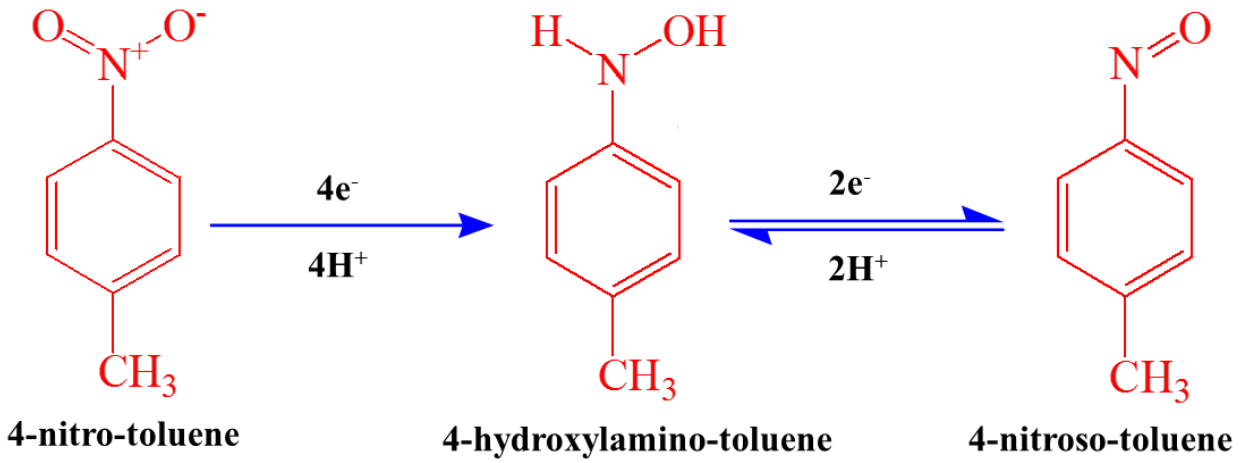
3.3 The effect of scan rate

The influence of scan rate of 4-NT detection was studied with ZnC/SPCE in the presence of 200µM of 4-NT in 0.05M PB Solution at different scan rate of 50 mVs^{-1}. Fig.3A revealed that cathodic peak current response of 4-NT gradually increased with increasing scan rate from 10 to 200mVs^{-1}.

Further, the resultant peak current was plotted with scan rate, which gives a good linearity (Fig.3B), the matching linear regression equation can be expressed as I_{pc} (μA) = -0.1693-15.5, and correlation coefficient R^2 = 0.9917. Therefore, we have confirmed the reduction of 4-NT is adsorption controlled process.

3.4 The influence of pH on the electrochemical reduction of 4-NT

The electrolyte pH influences the analytic parameter in electrochemical studies, which can affect electrochemical peak current response for the proposed sensor. Hence, we have studied the 4-NT reduction in various pH range (3-11). Fig.3C indicate that CV response of ZnC/SPCE (presence of 200μM 4-NT) the well-defined reduction peak current was appeared and the peak potential was shifted to the cathodic side while increasing the pH 3 to 11. The cathodic peak current of 4-NT was gradually increased with the increasing of pH 3-7 after that peak current response was decreased when increasing of pH 7 to 11 (Fig.3D). So that, we have chosen a pH 7 for supporting electrolyte for the all-electrochemical studies.



Scheme 2. Possible electrochemical reaction mechanism of 4-nitrotoluene

3.5 Determination of 4-NT on ZnC/SPCE

DPV technique is highly sensitive tool to quantitative detection of 4-NT. Hence, we have chosen a DPV for 4-NT determination. Fig.4A reveals that electrochemical investigation of 4-NT reduction at modified ZnC/SPCE in 0.05M PBS with lower to higher concentration of (0.05-1440μM) 4-NT.The sharp and well defined cathodic peak current was appeared while increasing the 4-NT concentration from lower to higher.

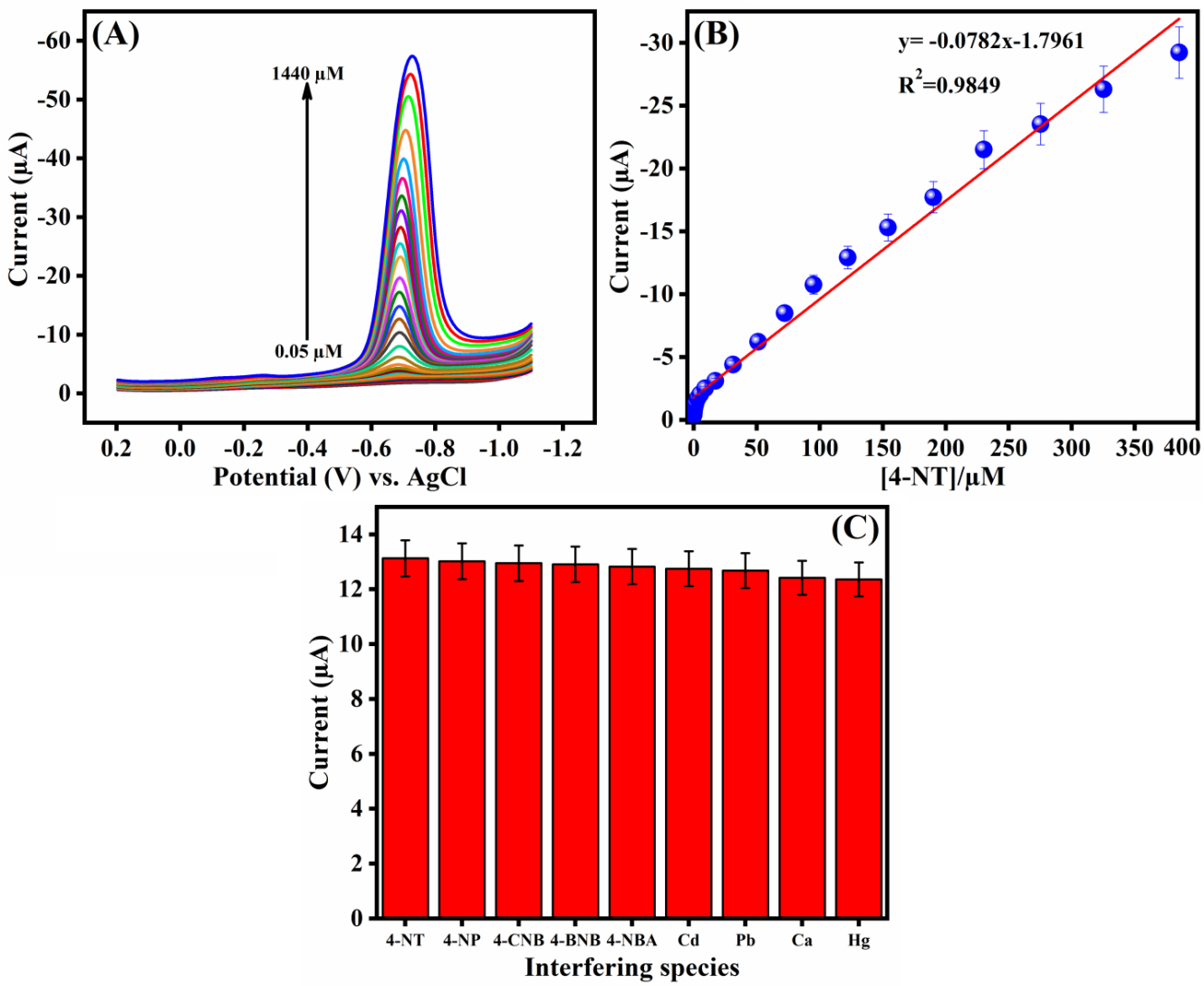


Figure 4. (A) DPVs of 4-NT at ZnC/SPCE in0.05M PBS with different concentration from 0.05µM to 1440µM. (B) The calibration plot for cathodic peak current vs. concentration of 4-NT. (C) The calibration plot for 4-NT reduction in the presence of potentially co-interfering compounds: 4-NP, 4-CNB, 4-BNB, 4-NBA, Cd, Pb, Ca and Hg containing of 0.05M PBS.

Fig.4B shows that linear relationship between cathodic peak current, with concentration of 4-NT. The linear concentration of proposed sensor is 0.05µM- 385.5µM. The corresponding linear relation equation is I_{pc} (µA) = -0.0782 (µM) - 1.79; correlation coefficient is be R^2= 0.9849. From, calibration plot and limit of detection and sensitivity was calculated as 0.044µM and 1.11µA$\mu M^{-1}cm^{-2}$. Moreover, the occurred limit of detection, linear range, and sensitivity of modified ZnC/SPCE were associated with previously reported other 4-NT sensors and the results are shown in table 1. From the results of Table 1, the proposed ZnC/SPCE has an excellent analytical performance compared with other modified 4-NT sensors. Therefore, the prepared ZnC/SPCE possesses a very lower LOD, wide linear response range and good current sensitivity for the determination of 4-NT.

Table 1. Comparative studies of ZnC/SPCE for the 4-NT detection with other previous reported electrodes.

Electrode	quantitative method	Linear range (µM)	LOD (µM)	Reference
α-MnO_2	CV	0.2 -0.8	0.144	[42]
MWCNTs	CV	0.54-7.29, 7.29-43.75	0.044	[43]
Pn- MWCNTs/ Po- MWCNTs	SWASV	0.5-4, 0.2-1.2	0.4420 0.2822	[44]
NH2-Fe-MIL-88B@OMC-3	DPV	20-225, 225-2600	8	[22]
ZnC/SPCE	DPV	0.05-385.5	0.044	This work

3.6 Selectivity, stability, and repeatability studies

To explore the selectivity and anti-interference properties of ZnC/SPCE in the presence of co-interfering electroactive species such as 4-NP, 4-CNB, 4-BNB, 4-NBA, Cd, Pb, Ca and Hg, in 0.05M PBS containing of 4-NT by DPV analysis. The DPV response of 4-NT was studied in the presence of 10-fold higher concentrations of co-interfering compounds. The reduction peak current did not affect the peak current and peak potential of 4-NT even in the presence of 10-folds higher concentration of co-interfering compounds, suggest that the proposed ZnC/SPCE has a well anti-interference capability. The bar diagram of Fig.4C, suggested that the prepared ZnC modified SPCE has an excellent selectivity for the detection of 4-NT.

The stability of the ZnC/SPCE modified electrode was studied in the presence of 100 µM 4-NT containing 0.05M PBS (pH 7.0) by DPV technique. The 4-NT reduction peak current response was slightly decreased (3.9 %) after 15^{th} cycles. After the 15^{th} cycles, there is no further reduction peak current decrement was noticed at ZnC/SPCE, which confirms that the proposed ZnC/SPCE has an appreciable stability for the 4-NT sensor. The repeatability was evaluated through the consecutive measurements under 4-NT for five times at a single ZnC/SPCE with RSD of less than 6%, suggesting a good repeatability of the proposed sensor. These results revealed that the ZnC/SPCE has a good stability, and repeatability for the 4-NT sensor.

3.7 Real sample analysis

To evaluate the performance of ZnC/SPCE by real sample analysis, the determination of 4-NT was carried out in tab water and river water samples. The water samples are investigated by under optimized experimental conditions, certain amount of river water sample were directly added into the 0.05M PBS and calculated the amount of 4-NT. The recovery results of water samples can be seen in Table 2. The average recovery ranges of water samples varied from 98.1%, to 99.3% indicating that is no matrix effect observed in the results. These results suggest that as prepared ZnC/SPCE can be used for the 4-NT determination in river and tab water samples.

Table 2. The obtained results for the Determination of 4-NT in water samples

Samples	**Added (µM)**	**Found (µM)**	**Recovery (%)**
River water	0.00	0.00	-
	2.0	1.98	98.1
	4.0	3.98	98.9
	6.0	5.95	98.7
Tab water	0.00	0.00	-
	2.0	1.96	96.8
	4.0	3.92	97.5
	6.0	5.95	99.3

4. CONCLUSION

In this current work we have successfully synthesized a $ZnCo_2O_4$ Nfs by simple co-precipitation method and fabricated as an electrode material used for electrochemical detection of organic pollutant 4-NT. The synthesized material was characterized by XRD, FE-SEM and EDX. The electrochemical activity of ZnC/SPCE studied by CV and DPV. Significantly, the ZnC Nfs modified SPCE displayed an excellent electrocatalytic activity towards 4-NT determination with numerous advantageous features such as simple preparation procedure, larger surface area, superior electron transfer rate and strong adsorption towards 4-NT. Furthermore, the proposed sensor have outstanding analytical behavior with a wide linear range (0.05µM- 385.5µM), low limit of detection (0.044µM), and good sensitivity towards 4-NT detection. The electrode displayed satisfactory tremendous selectivity, stability, and repeatability for the 4-NT detection. Hence, the ZnC Nfs materials are well suitable for use in the electrochemical sensor and possible industrial applications.

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