

# Ball-Mill Assisted Green One-Pot Synthesis of ZnO/Graphene Nanocomposite for Selective Electrochemical Sensing of aquatic pollutant 4-nitrophenol

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**Article Info****Article history:**Received Jun 16<sup>th</sup>, 2021Revised Aug 17<sup>th</sup>, 2021Accepted Oct 19<sup>th</sup>, 2021**Keywords:**

ZnO/graphene

Ball-milling

Metal oxalate

Electrochemical sensing

4-Nitrophenol

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**ABSTRACT**

ZnO, having good transparency, high electron mobility and lower electrical noise, is an excellent material for electrochemical studies. Due to its high surface area and electrical conductivity, graphene is well suitable for the good dispersion of metal oxides for electronic/electrochemical applications. Graphene prevents particle agglomeration, whereas the addition of metal oxide prevents layer restacking in graphene. The bulk preparation of graphene via cost-effective and green methods are preferred. The aromatic conjugated  $\pi$ -network along the whole surface is not attained in large scale graphite oxide assisted production due to the defects and functional groups introduced during the hazardous synthetic procedure. Here, less defective graphene is synthesised via ball milling of graphite using metal oxalate as an exfoliating agent for the first time. Calcination of metal oxalate inserted graphite leads to the enormous evolution of gases thereby sliding the graphitic layers, leading to the formation of graphene sheets decorated with ZnO spherical nanoparticles' bunches. The layer exfoliation and metal oxide incorporation are achieved here via a one-pot synthesis strategy. The use of ZnO/graphene in the selective sensing of 4-nitrophenol is investigated using cyclic voltammetric measurements in the presence of interfering compounds such as glucose, uric acid, ascorbic acid and H<sub>2</sub>O<sub>2</sub>.

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**1. INTRODUCTION**

Graphene, the one-atom-thick, planar sheet of hexagonal aromatic carbon network is gaining enhanced attention due to its fascinating properties and thus derived wide applications [1]. The high conductivity and fast electron mobility over the conjugated aromatic  $\pi$ -network can make it highly suitable for electronic applications [2]. In addition, the high surface area is an attractive feature of graphene which allow the distribution of a variety of materials over graphene sheets forming effective hybrid nanocomposites and thereby creating enhanced material properties [3].

There are various means of graphene preparation, among which CVD, epitaxial growth etc. are beneficial for the production of less defective graphene sheets with the retention of the aromatic conjugative  $\pi$ -network making them suitable for electronic applications [4-5]. High cost is the major limitation of these techniques for their bulk production. Hazardous oxidizing conditions during preparation introduces lots of defects and functionalities to the derived graphene in the high yielding graphite oxide assisted method of graphene preparation, limiting its use for applications where electron mobility and migration is of prime importance [6-8]. Ball-mill assisted exfoliation of graphite is an intelligent technique for the large-scale production of the less defective graphene, which uses a suitable milling agent for the shear force dominated exfoliation [9-11]. The additional merit of this method is the introduction of edge functionalities to the produced graphene, making them dispersible in various solvents in addition to the benefits in composite formation via those edge functionalities [12]. Both wet and dry ball milling is available. The reported milling agents in graphite exfoliation are oxalic acid, carbohydrates, melamine, dry ice, inorganic salts etc. [13].

Graphene in combination with metal oxides can show synergistic properties unattainable from the individual ones. But in most of the reported metal oxide-graphene nanocomposite preparation, initially graphene is prepared by any means which itself is a multistep process in many procedures and then the metal oxide or its precursor is added to the graphene dispersion, demanding further steps in the nanocomposite formation [14]. One-pot metal oxide - graphene preparation is a rarely successful method [8]. Inspired from the oxalic acid assisted ball-milled exfoliation of graphite, here a green and novel metal oxalate assisted graphite exfoliation is reported [12]. The green means of one-pot preparation of ZnO/graphene nanocomposite is performed by a ball-mill assisted zinc oxalate exfoliation of graphite. The prepared nanocomposite is characterized and used in the selective electrochemical sensing of 4-nitrophenol (4-NP), a common aquatic pollutant.

## 2. METHODS

### 2.1 Preparation of Zinc Oxalate ( $ZnC_2O_4$ )

14.74 g of  $ZnSO_4 \cdot 7H_2O$  (Loba Chemie) was dissolved in 250 ml of deionised water by stirring. The oxalic acid solution was prepared by dissolving 63g of  $H_2C_2O_4 \cdot 2H_2O$  (Loba Chemie) in 200 ml of deionised water by heating. The oxalic acid solution was added from a separating funnel drop by drop into the zinc sulphate solution with constant stirring using a magnetic stirrer. Stirring was continued until the precipitation was completed. Allowed to stand and the precipitated zinc oxalate was filtered and washed. Dried in an air oven at 90 °C for 16 hours to obtain zinc oxalate.

### 2.2 Preparation of Zinc Oxide/Graphene Nanocomposite

Zinc oxide - graphene composite was prepared by ball milling method followed by heat treatment. 5g of graphite (Sigma Aldrich) and 65g of zinc oxalate were mixed well in a mixer grinder and transferred into a one-litre ball mill cylinder with 14 balls out of which 7 is having a diameter of one centimetre and the remaining having a diameter of 0.5 centimetres. Milling was performed for 48 hours with a speed of 80-120 rpm. The resulting composite was calcined at 400 °C for 3 hours and further designated as ZnO/Graphene.

### 2.3 Electrochemical Sensing of 4-Nitrophenol

About 9 mg of the ZnO/Graphene was dispersed in a mixture of 1.1 ml of double-distilled water, 1.4 ml of IPA and 5  $\mu$ l Nafion (5%, Alfa Aesor) by sonicating in a bath sonicator (6.5 L, PCI Analytics Ltd.) for 1 hour. Then a paste of this dispersion was made in a mortar. 5  $\mu$ l of the paste was drop coated on to a glassy carbon electrode (GCE). The coated electrode was dipped in a 1 M  $H_2SO_4$  solution containing 4-nitrophenol, uric acid, ascorbic acid,  $H_2O_2$  and glucose. Cyclic voltammogram is measured in a CHI1210C electrochemical analyser (CH Instruments USA) in the potential range of +1.1 to -1.0.

### 2.4 Characterization of The ZnO/Graphene Nanocomposite

The prepared ZnO/Graphene nanocomposite system was characterized using different techniques such as Transmission Electron Microscope (TEM, JEOL JEM-2100 microscope operating at 200 kV), X-ray diffraction (XRD, Bruker AXS Advance powder X-ray diffractometer with  $Cu K\alpha$  radiation at a wavelength of 0.15406 nm), Raman spectroscopy (JASCO NRS-4100 spectrometer using a Raman microprobe with 532 nm wavelength laser) and Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer spectrum two L1600300 FTIR spectrometer by KBr pellet method).

## 3. RESULTS AND DISCUSSION

In the preparation of ZnO/graphene, metal oxalate acts as the milling agent for the layer separation of graphite during ball-milling by itself inserting into the layers during the ball-milling process. By calcination of the ball-milled mixture, the zinc oxalate is converted into ZnO and during the process, oxalate introduces edge functionalities to the graphene resulting in its effective dispersion in polar solvents. During heat treatment, enormous gas evolution also occurs that can slide the layers and also forming bunches of spherical particles of ZnO on graphene sheets. The material formation and the exfoliation strategy are revealed from various characterization results. The schematic of material formation is picturized in figure 1.

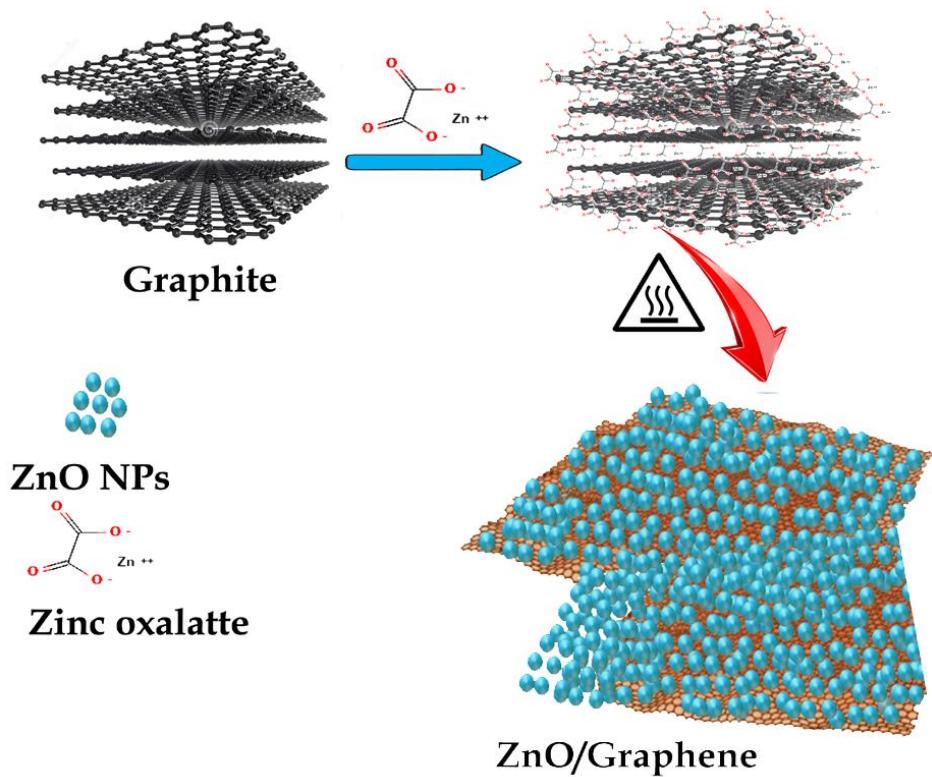


Figure 1: Schematic representation of ZnO/graphene nanocomposite formation

### 3.1. Material Characterization

Figure 2 shows the XRD pattern of the nanocomposite. Formation of crystalline hexagonal Wurtzite phase of ZnO is well evident from the peaks at  $2\theta$  values of  $31.7^\circ$ ,  $34.2^\circ$ ,  $36.2^\circ$ ,  $47.6^\circ$ ,  $56.6^\circ$ ,  $62.8^\circ$  and  $68.1^\circ$  corresponding to diffraction from (100), (002), (101), (102), (110), (103) and (112) planes respectively (JCPDS card no.36-1451). A slightly broad, less intense graphitic peak is also present in the composite at  $26.5^\circ$ , indicating well exfoliation and edge functionalization of graphitic sheets [15]. In addition to the peaks of ZnO and graphene, some less intense impurity peaks are also found to be present in the composite. These contaminants in the nanocomposite can be eliminated by increasing the calcination time or with repeated washing using dilute mineral acids.

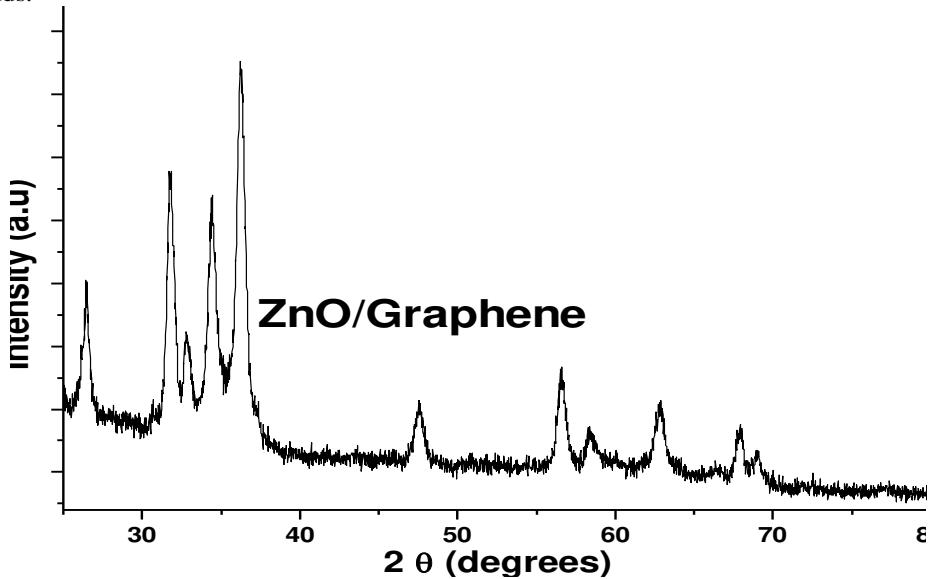


Figure 2: XRD pattern of the nanocomposite

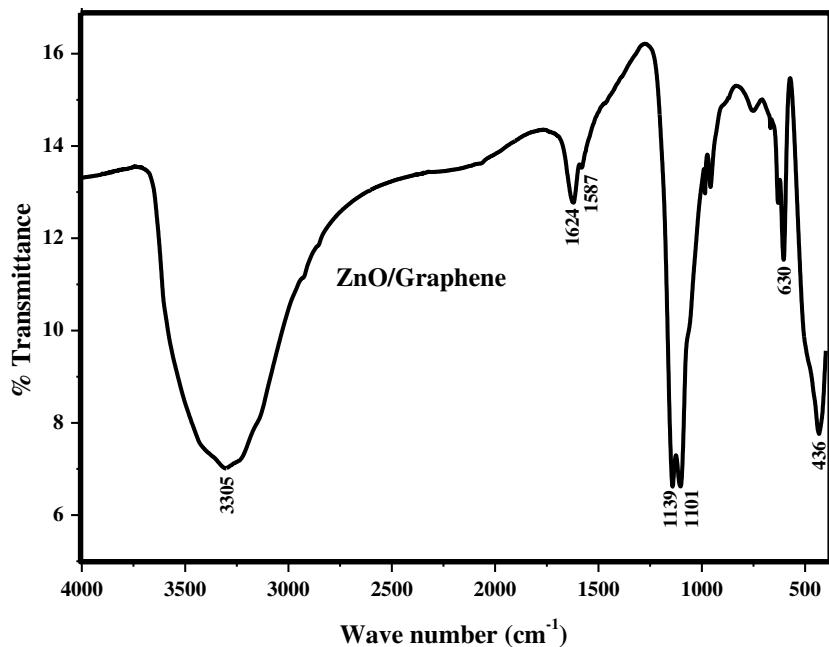


Figure 3: FTIR Spectrum of the nanocomposite

FTIR spectrum of the nanocomposite (Figure 3) shows wurtzite Zn-O vibrations at  $604 \text{ cm}^{-1}$  and  $436 \text{ cm}^{-1}$  [16]. Functionalization of graphene is further indicated from the FTIR spectral bands at  $1101 \text{ cm}^{-1}$  and  $1139 \text{ cm}^{-1}$  showing the presence of epoxy and hydroxyl groups [17-18]. No carboxyl or carbonyl functionalities are visible in the FTIR spectrum, this additionally ratifies the exfoliation during heating with the enormous evolution of gases such as  $\text{CO}_2$ . Oxalic acid assisted exfoliation of graphite reported edge functionalization with carbonyl moieties too. Aromatic C=C stretching in graphene is observed at  $1587 \text{ cm}^{-1}$  [19]. The band centred around  $3300 \text{ cm}^{-1}$  indicates O-H stretching bands of graphene, surface hydroxyl groups of ZnO and adsorbed water [16]. The bending vibration bands of adsorbed water is visible at  $1624 \text{ cm}^{-1}$  [16].

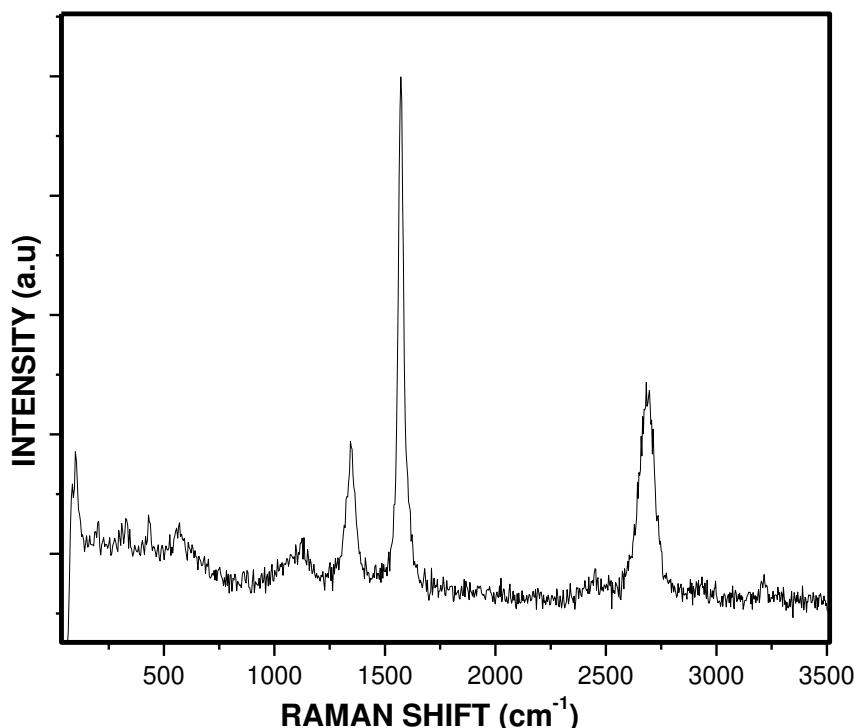


Figure 4: Raman spectrum of ZnO/Graphene

For the electrochemical/electronic applications of graphene, as already mentioned, the aromatic  $\pi$ -conjugative network of graphene has to be preserved. The presence of functionalities and other defective sites on graphene sheets, which will disturb the aromatic  $\pi$ -conjugation can be easily understood by Raman spectral analysis. In the Raman spectrum shown in Figure 4, the peak at  $1347\text{ cm}^{-1}$  corresponds to the D band indicating defective sites of graphene [20-21]. The band at  $1580\text{ cm}^{-1}$  indicates the G band which arises from the  $\text{sp}^2$  carbon in the aromatic network [20].  $I_D/I_G$  value is a measure of defects on graphene and thus it indicates aromatic  $\pi$ -conjugative network disruption [21]. In the ZnO/graphene nanocomposite of our investigation, the value is found to be low (0.2) whereas, in the case of graphene oxide-based samples it comes around 1. This further supports the suitability of our nanocomposite for applications where electron migration and its transfer are the performance determining factors. The 2D band is observed to be symmetric and the value indicates ( $2696\text{ cm}^{-1}$ ) layer exfoliation of graphite [21].

ZnO bands are also well evident in the Raman spectrum with peaks at 99, 295, 331, 439, 405, 576 and  $1134\text{ cm}^{-1}$ . The spectral bands at 405 and  $439\text{ cm}^{-1}$ , characteristics of ZnO are of E1 (TO) and E2<sup>high</sup>, respectively. E2 mode also corresponds to the peak at  $99\text{ cm}^{-1}$ . Other peaks represent the second-order Raman bands. Second-order scattering results in the band at  $331\text{ cm}^{-1}$  whereas E1 (LO) mode gave a peak at  $576\text{ cm}^{-1}$ . The results obtained are in good agreement with the previously reported ZnO nanoparticles' Raman spectral bands [22-23]. The morphology of the nanocomposite is analyzed using TEM images shown in Figure 5. Formation of the composite, sheet-like nature of graphene and assembly of spherical ZnO particles on graphene sheets are well visible from the TEM images. The lattice fringes of Wurtzite ZnO at  $0.25\text{ nm}$  corresponding to the (101) plane is visible from the HRTEM image [24].

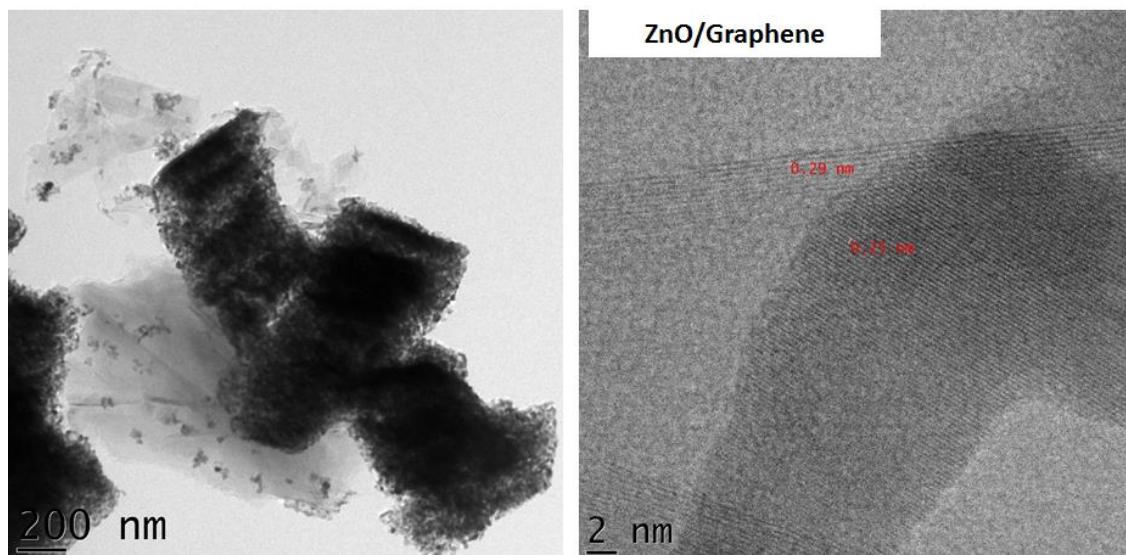


Figure 5: TEM and HRTEM images of ZnO/Graphene

### 3.2. Electrochemical Selective Sensing of 4-Nitrophenol

Selective electrochemical sensing of 4-NP is investigated by cyclic voltammetric (CV) measurements of the nanocomposite coated glassy carbon electrode in the  $\text{H}_2\text{SO}_4$  electrolyte. One of the major requirements of any sensing measurement is the selectivity towards the target molecule among mixtures containing other electroactive compounds. To investigate the selectivity towards the sensing of aquatic pollutant 4-NP, we have conducted the measurements in the presence of other molecules such as glucose, uric acid, ascorbic acid and  $\text{H}_2\text{O}_2$ . The composite solely sensed the presence of 4-NP among the studied molecules. The addition of other molecules could not produce any oxidation/reduction peaks which usually enable the sensing. Further studies in the sensing of 4-NP such as finding out the lower detection limit, linear concentration range, repeatability, reproducibility and stability of the sensor have to be performed to project the nanocomposite for its commercial use in the selective sensing of 4-NP.

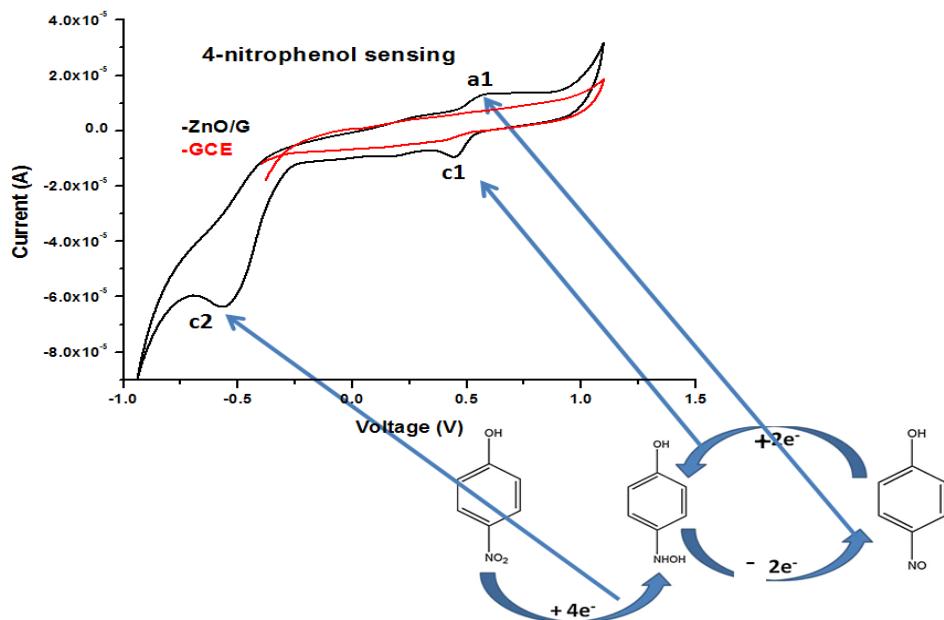


Figure 6: CV and different compounds formed during electrocatalysis of 4-NP

The CV curves of the nanocomposite displayed the peaks of an intense irreversible reduction peak and a pair of redox peaks (Figure 6). The electrocatalytic reduction process involves the following steps, the irreversible  $4e^-$  transfer reduction of 4-NP, which results in the formation of 4-hydroxyaminophenol (peak c2) and a two-electron redox process due to the 4-hydroxyaminophenol (peak c1)  $\rightleftharpoons$  4-nitrosophenol (peak a1) couple [25-26]. The different stages in electrocatalysis are also shown in Figure 7.

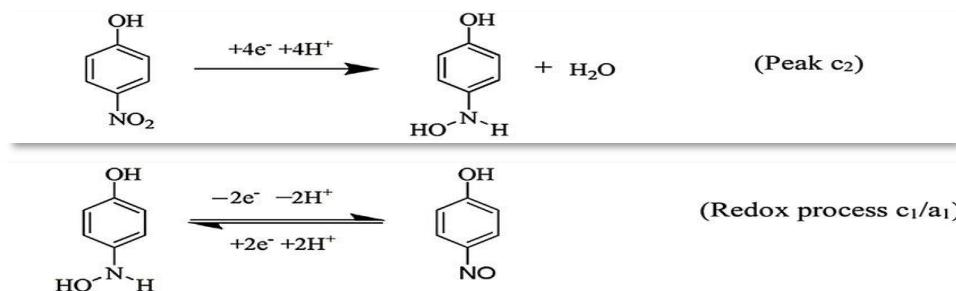


Figure 7: Different stages in the electrochemical sensing of 4-Nitrophenol

#### 4. CONCLUSION

In conclusion, a novel facile and green method of graphite exfoliation using metal oxalate as the milling agent and subsequent metal oxide - graphene nanocomposite formation via calcination is well established in the present investigation via the preparation of ZnO/graphene nanocomposite using zinc oxalate and graphite. Material characterization studies indicated the less defective nature and edge functionalization of graphene sheets as well as the formation of Wurtzite ZnO. The prepared ZnO/graphene nanocomposite is found to be highly selective in the electrochemical sensing of 4-nitrophenol.

#### ACKNOWLEDGEMENTS

The authors acknowledge Sree Neelakata Government Sanskrit College Pattambi and the University of Calicut for providing the facilities. Department of Science and Technology, New Delhi, India is acknowledged for Instrumental support via the FIST-2016 program. SAIF, Kochi, India is acknowledged for XRD, and TEM analyses. PSGIAS, Coimbatore is acknowledged for RAMAN spectral analysis.

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