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 π-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 π-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 oxide 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. METHOD

2.1 Preparation of Zinc Oxalate (ZnC₂O₄)

14.74 g of ZnSO₄·7H₂O (Loba Chemie) was dissolved in 250 ml of deionised water by stirring. The oxalic acid solution was prepared by dissolving 63g of H₂C₂O₄·2H₂O (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 µl 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 µl of the paste was drop coated on to a glassy carbon electrode (GCE). The coated electrode was dipped in a 1 M H₂SO₄ solution containing 4-nitrophenol, uric acid, ascorbic acid, H₂O₂ 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 Kα 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.
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 20 values of 31.7°, 34.2, 36.2, 47.6, 56.6, 62.8 and 68.1° 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°, 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 3: FTIR Spectrum of the nanocomposite

FTIR spectrum of the nanocomposite (Figure 3) shows wurtzite Zn-O vibrations at 604 cm\(^{-1}\) and 436 cm\(^{-1}\) [16]. Functionalization of graphene is further indicated from the FTIR spectral bands at 1101 cm\(^{-1}\) and 1139 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 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 cm\(^{-1}\) [19]. The band centred around 3300 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 cm\(^{-1}\) [16].

Figure 4: Raman spectrum of ZnO/Graphene

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For the electrochemical/electronic applications of graphene, as already mentioned, the aromatic π-conjugative network of graphene has to be preserved. The presence of functionalities and other defective sites on graphene sheets, which will disturb the aromatic π-conjugation can be easily understood by Raman spectral analysis. In the Raman spectrum shown in Figure 4, the peak at 1347 cm\(^{-1}\) corresponds to the D band indicating defective sites of graphene [20-21]. The band at 1580 cm\(^{-1}\) indicates the G band which arises from the 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 π-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 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 cm\(^{-1}\). The spectral bands at 405 and 439 cm\(^{-1}\), characteristics of ZnO are of E\(_1\) (TO) and E\(_2\)\(^{\text{high}}\), respectively. E\(_2\) mode also corresponds to the peak at 99 cm\(^{-1}\). Other peaks represent the second-order Raman bands. Second-order scattering results in the band at 331 cm\(^{-1}\) whereas E\(_1\) (LO) mode gave a peak at 576 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 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 H\(_2\)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 H\(_2\)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.

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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) \(\rightarrow\) 4-nitrosophenol (peak a1) couple [25-26]. The different stages in electrocatalysis are also shown in Figure 7.

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.
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