Synthesis of ZnO-Graphene Nanocomposite by Chemical Co-Precipitation Method and Its Structural Characterizations

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Abstract. A series of ZnO-Graphene nanocomposites were synthesized by a simple and low-cost chemical co-precipitation method. GO was synthesized by using modified Hummers method. Zinc salt and graphene oxide (GO) of different mass ratios (3:1, 3:2 and 3:3 GO to Zn) were used as precursors in de-ionized water. Further the structural characterizations of the prepared samples were done by X-Ray Diffraction (XRD), UV-Visible Spectrophotometry, Fourier Transform Infrared Spectroscopy and Raman spectroscopy. FTIR studies confirmed the formation of graphene oxide with different oxygen containing functional groups. Raman studies confirmed that the samples have characteristic Raman modes D band, G band and 2D band in the range of 1340-1358 cm\(^{-1}\), 1577-1583 cm\(^{-1}\), and 2717-2722 cm\(^{-1}\) respectively. The XRD analysis has revealed that the synthesized ZnO-graphene nanocomposites have the typical peaks at \(\sim\)26° and \(\sim\)43° of graphene. UV-vis spectrum studies showed a slight increase in the energy band-gaps of ZnO-Graphene nanocomposites calculated by using Tauc plot.

INTRODUCTION

In recent years, metal oxides and carbon allotropes are the two most fascinating materials for the scientific researchers. Due to its superior properties such as anti-oxidation, large excitation binding energy (60 meV), higher electron mobility (115-155 cm\(^2\)V\(^{-1}\)s\(^{-1}\)) and chemical stability, ZnO is the most explored material over other metal oxides. Being an II-VI compound semiconductor, ZnO has been recognized to have potential applications in optoelectronics due to its direct bandgap of 3.37 eV at room temperature. Because of its fabulous properties, ZnO has been used in the applications for optical detector, gas sensor, solar cell, short-wavelength UV laser, photocatalysts, microsensors, blue or green optoelectronic devices and so forth [1-4].

Carbon has showed its significance in boundless field of applications. It basically exists in three forms–amorphous, graphite and diamond, depending upon the carbon atom arrangement and their properties. Graphene is the most recent member of carbon family having remarkable properties, making it the most desirable candidate for potential applications. Graphene is a single layer of carbon atoms arranged in sp\(^2\) bonded aromatic configuration. It is regarded as the building block of all the sp\(^2\) graphitic materials, such as graphene sheets can be stacked together to form graphite with interlayer spacing of 0.334 nm [5,6]. The sp\(^2\) hybridized structure give rise to many unique properties like a high theoretical specific surface area, remarkable electronic properties and electron transport capabilities, high thermal conductivity, high transparency and high mechanical strength. In spite of excellent properties, graphene has some limitations such as it is highly hydrophobic in nature and graphene sheets get agglomerated due to strong interactions between them which limits its use in different applications [7].

Thus, the focus of research is turned over to Graphene Oxide (GO), a precursor in preparation of graphene, due to its high hydrophilicity. It is a 2D layer of sp\(^2\) and sp\(^3\) hybridized carbon atoms having oxygen containing functional groups (such as carboxyl, epoxy, hydroxyl functional groups) attached onto its edges and basal planes which make it chemically active [8].
GO has many advantages over graphene such as large scale and cost-effective production, easy processing etc. it has many excellent properties due to the attached oxygen containing functional groups which act as active site for any modification as per the requirements of particular application fields such as energy storage, solar cells, photocatalysis, drug delivery, oil-water emulsion separation and in bio-medical applications [9-16]. Since the single component of graphene or graphene oxide may have a limit in their uses in certain applications, so their functional modification is important to expand their applicability areas. For the functional modifications, the metal oxides are the preferred choice as they are advantageous of suppressing agglomeration and subsequent sedimentation when dispersed into solvents. In addition, graphene/graphene oxide metal oxide nanocomposites showed enhanced electron conductivity, shortened ion paths and the surface area increased significantly as compared to the single component graphene/graphene oxide [17].

Thus, attaching ZnO onto the graphene sheets has overcome the limitations of both the components. Besides the superior properties of ZnO, it has some limitations, such as quick recombination of charge carriers. By forming composites with graphene-based materials this recombination slows down and improved the performance of the devices. Also, due to the formation of nanocomposites of graphene with metal oxide nanoparticles, the degree of restacking of graphene sheets has been reduced resulting the enhanced performance of graphene-based materials [18,19].

Therefore, ZnO-graphene nanocomposites have been expected to show enhanced performances in various applications like in optoelectronic devices, solar energy conversion, energy storage, optoelectronic, gas sensing and photocatalysis [20]. In this paper, we report the successful synthesis of ZnO-graphene nanocomposites by using a simple chemical co-precipitation method. X-ray diffraction (XRD), FTIR and Raman spectroscopy were utilized for structural characterization of samples. UV-Visible spectroscopy was used to obtain the band gap energy.

**EXPERIMENTAL**

**Materials Required**

Graphite fine powder (Central Drug House, min assay 99.5%), sodium nitrate (Fisher Scientific), potassium permanganate purified (CDH), phosphoric acid, sulfuric acid, hydrogen peroxide (30%), zinc acetate dihydrate extra pure (Sisco Research Laboratory Pvt. Ltd. min assay 99.5%), hydrazine hydrate (CDH), sodium hydroxide. Millipore water is used throughout the synthesis procedure. All the chemicals were of analytical grade and used without any purification.

**Synthesis of Graphitic Oxide**

Graphitic oxide was synthesized using modified Hummers method and ZnO nano particles were synthesized by a simple chemical route as discussed in our earlier work [21]. In general, graphite powder and sodium nitrate were mixed with sulfuric acid and phosphoric acid and stirred in an ice bath. Then potassium permanganate was slowly added to the mixture maintaining the temperature below 5°C. The suspension was reacted and stirred in different temperature conditions while adding water. Then hydrogen peroxide was added. Then the product undergoes centrifugation and washing with hydrochloric acid several times and was dried at 60°C.

**Synthesis of ZnO-Graphene Nanocomposites**

ZnO-graphene nanocomposites (GZ composites) were synthesized by a chemical route [21,22]. In the process, 0.1g Zinc Acetate was added to a GO suspension (0.3g in 90ml water and sonicated for 30 minutes) and stirred for 3 hours. Then 20μl of N₂H₄ was added to the mixture while stirring for another 3 hours at 80°C. Then the precipitate was centrifuged (3000rpm, 30 minutes) and washed with water and alcohol several times. The obtained product was dried at 100°C in water bath for 2 hours followed by annealing the dried powder at 450°C for 4 hours. The final powder was designated as GZ-1. The process was repeated with varying mass of Zinc Acetate as 0.2g and 0.3g and the product were designated as GZ-2 and GZ-3 respectively.

Fig. 1 shows the process and samples prepared in the laboratory.
Characterizations

Powder XRD patterns of the prepared sample were recorded by Rigaku Ultima in single phase as 40kV with Cu- \( \alpha \) (1.54 Å) Radiation. FTIR of the sample was recorded by Bruker instrument. UV-Vis spectroscopy was recorded on a Systronics double beam UV-Vis Spectrophotometer:2202. Raman mapping measurements were performed at room temperature in 180 back scattering geometry using excitation wavelength 532 nm.

RESULTS AND DISCUSSION

ZnO nanoparticles decorated on graphene sheets were obtained by the chemical reaction between \( \text{Zn}^{2+} \) and \( \text{OH}^- \) ions in aqueous solution via electrostatic force. Zinc acetate when dissolved into GO suspension, \( \text{Zn}^{2+} \) ions will be adsorbed onto the surfaces of GO sheets because of their bonding with the O atoms of the negatively charged oxygen containing functional groups present on GO sheets [23,24]. After the addition of hydrazine hydrate solution \( \text{Zn(OH)}_2^2^- \) and \( \text{ZnO}^2- \) may bond with the functional groups such as carboxyl and hydroxyl groups of GO sheets by intermolecular hydrogen bonds and GO will be reduced to graphene simultaneously [25]. After annealing ZnO-graphene nanocomposites were obtained. The obtained products were characterized by several techniques to ensure the formation of GZ composite.

XRD and UV-Visible Spectroscopy

XRD and UV-Visible spectroscopy results were already discussed in our previous work [21]. XRD results confirmed the formation of ZnO on Graphene nanocomposites. In XRD spectra of samples, typical (002) and (101) peaks at ~26° and ~42° of graphene were present. In addition to that in GZ series the peaks at 31.8° (100), 34.4° (002), 36.1° (101) 56.85° (110) were also appeared with increasing concentration of ZnO precursor. From the UV-Visible spectra it was concluded that all the samples show good absorbance in visible region. The as calculated band gaps of prepared samples are shown in table.

<table>
<thead>
<tr>
<th>Samples</th>
<th>ZnO (eV)</th>
<th>GO</th>
<th>GZ-1</th>
<th>GZ-2</th>
<th>GZ-3</th>
</tr>
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<tbody>
<tr>
<td>Band Gap</td>
<td>3.71</td>
<td>2.76</td>
<td>2.76</td>
<td>2.82</td>
<td>2.99</td>
</tr>
</tbody>
</table>

FTIR Spectroscopy

Fig. 2 shows the FTIR spectrum of the samples. FTIR spectroscopy was employed for investigating the structure and functional groups in the ZnO-graphene nanocomposites samples. The FTIR spectrum shows broad peaks 3649 cm\(^{-1}\), 3735 cm\(^{-1}\), 3854 cm\(^{-1}\) in the high wavenumber area are assigned to the stretching and bending vibrations of hydroxyl groups(O-H) of absorbed H\(_2\)O molecules on the samples. These hydroxyl groups, results in the formation of hydrogen bonds between graphite and water molecules. Therefore, it can be inferred that the samples have strong hydrophilicity. The peak at 2361 cm\(^{-1}\) is due to the CO\(_2\) molecules on the surface of the samples which can be seen in both GO and GZ-3 samples. The characteristic peak present at 2180 cm\(^{-1}\) in GO is attributed to the alkyne C≡C
group which is absent in GZ-3 sample. The presence of the peak at 1652 cm\(^{-1}\) observed in the medium wavenumber area in the spectrum of both the samples can be attributed to the stretching vibrations of C=C alkene groups. The peak at 1558 cm\(^{-1}\) is attributed to the aromatic C=C group. The peak at 669 cm\(^{-1}\) of GZ-3 is similar to that of pure ZnO, which is due to the stretching modes of Zn-O [26]. The presence of these oxygen-containing groups reveals that the graphite has been oxidized and both the GO and GZ-3 are hydrophilic in nature.

![FTIR Spectra of samples prepared.](image)

**FIGURE 2.** FTIR Spectra of samples prepared.

**Raman Spectroscopy**

Raman spectroscopy is a powerful tool to characterize carbon-based nanostructures. The presence of G and D bands in the Raman spectrum describes the features of nanostructures. The G band arises due to first order scattering of the E\(_{2g}\) mode representing the in-plane stretching motion of sp\(^2\) C-C bond. The D band, considered as the disorder peak, originated from sp\(^3\) defect-based breathing mode phonons of A\(_{1g}\) symmetry caused by introduction of oxygen containing functional groups. The D band to G band intensity ratio (I\(_D\)/I\(_G\)) is generally used as a measure of defect density and quality of graphene. The 2D band is the overtone of D band attributed to double resonance transitions due to the production of two phonons with opposite momentum. The D band is Raman active in presence of defects while the 2D band can be active even in absence of defects. Bands originated from the two phonon processes in the range \(\approx 2200–3500 \text{ cm}^{-1}\) are termed as 2D, \(D + D'\), \(2D'\) and so on. For higher wave numbers, they are due to third order processes, etc. The intensity is generally diminished when increasing the order of the process, because of the cross section which becomes less and less probable. Considering the less intense bands, the \(D''\) band is present in the shoulder of the D band of very defective samples [27-30]. Other bands at \(~2450 \text{ cm}\)\(^{-1}\) has been attributed recently to a \(D + D''\) band, the \(D + D'\), the \(2D'\) bands and the \(2D + G\) band [31,32].

Fig. 3(a) shows the Raman spectra of GO, GZ-1, GZ-2 and GZ-3 samples in the spectral range 1000-3500 cm\(^{-1}\). The characteristic Raman bands D band, G band and 2D band, in graphene, are positioned at \(~1350 \text{ cm}^{-1}, ~1580 \text{ cm}^{-1}\) and \(~2690 \text{ cm}^{-1}\) and in graphite at \(~1334 \text{ cm}^{-1}, ~1575 \text{ cm}^{-1}\) and \(~2676 \text{ cm}^{-1}\) respectively [33]. In the GO spectra the G band, D band, 2D band, were positioned at 1356, 1581, 2717 cm\(^{-1}\) respectively. Other bands like D' band \(D + D''\) band and \(D + D'\) band were also visible at 1356, 1581, 2717 cm\(^{-1}\) respectively. The I\(_D\)/I\(_G\) and I\(_G\)/I\(_{2D}\) were calculated as 0.14 and 2.084 respectively (see Table 2). The prepared GZ samples showed a blue shift in D and G bands could indicate that the interaction of graphene sheets and ZnO nanoparticles generate surface hybridization. The Raman intensities of ZnO are not seen on the Raman spectrum of ZnO-graphene samples, which indicates that the Raman peak intensity of ZnO is weak. Although the structural defects are more in the graphene lattice (D/G ratio of GO), these defects act as helpful nucleation sites for ZnO. This results in less aggregated ZnO particles due to their strong interaction with defect sites of graphene sheets.
The relative intensity ratio between the 2D and G bands was also found to be dependent on the number of layers: \( I_G/I_{2D} \) is greater than 1 is for multilayer graphene, and falls down to 0.5 for monolayer. In the prepared samples it was found to be around 2 that indicates that the prepared samples should have multi-layered structure. The value

\[
I_d/I_g < 1
\]

for all the synthesized samples were found to be less than 1. It suggests the presence of more isolated graphene domain (sp² hybridized carbon atom structure) in the synthesized samples. The in-plane sp² cluster size \((L_a)\) can be calculated using the formula [34]:

\[
L_a = 2.4 \times 10^{10} \lambda^4 (I_d/I_g)^{-1}
\]

where, \(\lambda\) denotes the wavelength of the laser light. This showed that there was an increase in the in-plane sp² cluster size. The increase in the cluster size may be due to the conversion of C atoms from sp³ to sp² bonded domains [30,35].

<table>
<thead>
<tr>
<th>Samples</th>
<th>D Band (cm⁻¹)</th>
<th>G Band (cm⁻¹)</th>
<th>D' Band (cm⁻¹)</th>
<th>D+D'' Band (cm⁻¹)</th>
<th>2D Band (cm⁻¹)</th>
<th>D+D' Band (cm⁻¹)</th>
<th>(I_d/I_G)</th>
<th>(I_G/I_{2D})</th>
<th>In-plane cluster size (L_a) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1355.5</td>
<td>1581.1</td>
<td>1616.67</td>
<td>2445</td>
<td>2717.5</td>
<td>3242</td>
<td>0.140</td>
<td>2.084</td>
<td>137.32</td>
</tr>
<tr>
<td>GZ-1</td>
<td>1347.4</td>
<td>1577.3</td>
<td>1617.7</td>
<td>2446</td>
<td>2717.7</td>
<td>3229</td>
<td>0.181</td>
<td>2.925</td>
<td>106.21</td>
</tr>
<tr>
<td>GZ-2</td>
<td>1356</td>
<td>1582.4</td>
<td>1617.7</td>
<td>2461</td>
<td>2722</td>
<td>3247.6</td>
<td>0.099</td>
<td>1.712</td>
<td>194.19</td>
</tr>
<tr>
<td>GZ-3</td>
<td>1357.7</td>
<td>1581.1</td>
<td>1618.8</td>
<td>2460</td>
<td>2721.1</td>
<td>3248</td>
<td>0.073</td>
<td>2.516</td>
<td>263.35</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

ZnO-Graphene incorporated with different mass ratios (3:1, 3:2 and 3:3 GO to Zn) were prepared by a simple chemical route. The structural analysis was done by different characterization techniques. The formation of graphene oxide and presence of different functional groups was confirmed by FTIR Spectroscopy. The XRD results show the graphene like peaks at 26 and 43 degree in all samples and the peaks were sharp showing the crystalline nature of the samples. Raman spectroscopy confirmed the presence of characteristic D band G band and 2D band in
all the prepared samples. Analysis of UV-Visible spectroscopy concludes the increased band gap from 2.76 eV to 2.99 eV and the samples showed good absorption in the visible range offering good materials for the potential applications in photocatalysis.

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