Chapter 3

Characterization of Gr, GZ and GCZ

Summary: This chapter deals with the characterisation studies of pristine graphene, graphene – ZnO hybrid nanocomposite and graphene – ZnO – CuS hybrid nanocomposite. The high resolution transmission electron microscopy (HRTEM) has been employed to investigate the shape, thickness and interplanar distance of the synthesized graphene and hybrid nanocomposites. X-ray diffraction (XRD) technique has been used for evaluate the structure, composition of the synthesized graphene and hybrid nanocomposites. The hybridisation and particle - particle interactions exist in the synthesised graphene and hybrid nanocomposites have been evaluated by using Raman spectroscopy. The specific surface area, pore size and pore volume of the synthesized graphene and hybrid nanocomposites have been analysed by the Brunauer – Emmett – Teller (BET) method. The results show that the interplanar distance between thin, silk like graphene sheets are 0.34 nm with prominent sp² hybridisation. Additionally, the presence of ZnO nanotubes and CuS – ZnO hybrid nano fillers significantly increased the interplanar distance between the graphene sheets without changing its sp² moiety. The results confirmed that addition of ZnO nanotubes and CuS - ZnO hybrid nano fillers is a suitable method to prevent the self – agglomeration of graphene layers.
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3.1 Introduction

Recently, various nanomaterials have been fabricated and studied their properties for different applications. The discovery of graphene has widely explored a new dimension in the modern research field. The excellent properties and cost effective synthesis have proven to be focus on the synthesis of graphene based materials\textsuperscript{1-3}. The major drawback of graphene as a nano filler is its self-agglomeration due to the strong van der Waals forces and \pi-\pi interactions between graphene sheets\textsuperscript{4-7}. The functionalisation of graphene layers is an attractive target to overcome this drawbacks\textsuperscript{8-12}. The studies showed that the non - covalent functionalisation is the suitable technique to prevent the self - agglomeration of graphene layers without changing its sp\textsuperscript{2} moiety. The non – covalent functionalisation mainly focused on the doping of nano materials into the graphene layers\textsuperscript{13-16}. However the combination of graphene and other nano material via the non-covalent functionalisation provides the hybrid nanomaterial with the synergistic properties\textsuperscript{17-18}. Several studies have been reported so far on the synthesis and characterisation of graphene based hybrid nanocomposites via non – covalent functionalisation. From the literature review, it is understand that the limited work regarding the synthesis of graphene based ternary nanocomposites i.e., graphene doped with ZnO - CuS hybrid nano materials have been reported.

The present work reported the characterisation techniques for the analysis of synthesised graphene (Gr) graphene-ZnO hybrid (GZ) nanocomposites and graphene – ZnO – CuS hybrid (GCZ) nanocomposites. The morphology of graphene and hybrid nanocomposites has been investigated by TEM analysis. The XRD and Raman techniques have been used to evaluate the nature of graphene and the bonding interaction of the hybrid nanocomposites. The BET technique has been used to measure the specific surface area, pore size and pore volume of the synthesized graphene and hybrid nanocomposites.

3.2. Results and Discussion

3.2.1 XRD Analysis

XRD analysis is used to determine the structure, composition and particle size of the nano materials. The inter planar distance between layers of the nano materials can be analysed by Bragg’s equation.
\[ n\lambda = 2d \sin \theta \]  \hspace{1cm} (3.1)

Where \( n \) is an integer, \( d \) is the interlayer spacing, \( \lambda \) is the wavelength and \( \theta \) is the diffraction angle.

Figure 3.1 shows the XRD patterns of Gr, GZ and GCZ. The results shows that Gr exhibited a major characteristic peak at \( 2\theta = 26^\circ \) corresponding to the (002) reflection. Another peak observed at \( 2\theta = 45^\circ \) corresponding to the merging of (100) and (101) reflections. In the case of GZ, the characteristic diffraction peaks of ZnO nanotubes are observed in addition to the characteristic peaks of graphene. The observed diffraction peaks at \( 2\theta = 31.6^\circ, 34.4^\circ, 36.35^\circ, 47.38^\circ, 56.53^\circ, 62.52^\circ \) and \( 68.53^\circ \) corresponding to the (100), (002), (101), (102), (110), (103) and (112) reflections of ZnO nanotubes. The results confirmed that the strong bonding interaction existed in between ZnO nanotubes and graphene layers. In the case of GCZ, the characteristic graphitic diffraction peak is also present. The characteristic reflection planes of CuS nanoparticles at (006), (103), (108), (110) and (116) are also present in GCZ. In addition, the other reflection planes at (002), (101), and (102) are also observed due to the presence of hexagonal wurtzite phase of ZnO nanotubes. The results confirmed that the ZnO - CuS nanoparticles strongly bonded with the graphene layers.
3.2.2 Raman Spectra Analysis

The hybridisation present in the synthesized samples and the interaction between graphene and semiconductors is analysed by Raman spectroscopy. The Raman spectra of Gr, GZ and GCZ are shown in Figure 3.2 (a). In graphene the characteristics peaks are present at 1350, 1582 and 2700 cm\(^{-1}\) corresponding to the D band, G band and 2D band. The D band and G bands represented the sp\(^3\) and sp\(^2\) moiety present in the graphene\(^{20}\). The 2D band is the overtone of D band.

In the case of hybrid nanocomposite, the position of G and 2D bands are significantly blue shifted. The enlarged 2D band image of Gr, GZ and GCZ is displayed in Figure 3.2(b). This is due to the electrons transfer from semiconductor to Gr layers. In addition, the enhanced intensity of G band is also observed in Raman spectra\(^{21-23}\). The increased intensity of the G band again confirmed that the addition of GZ and GCZ on the Gr layers without cause any changes in the exact sp\(^2\) hybridisation of Gr layers. The results again show that the intensity of the D band in the hybrid nanocomposites is also increased. This is due to the presence of stronger interaction existed in between the semiconductors and Gr.

![Figure 3.2(a): Raman spectra of Gr, GZ and GCZ (b): Enlarged 2D band of Gr, GZ and GCZ](image-url)
3.2.3 Morphological Analysis

The morphological analysis of the synthesized samples are analysed by Transmission Electron Microscopy (TEM). The TEM and HRTEM image of the synthesized Gr is displayed in Figure 3.3 (a) – (b). The TEM image showed that thin, silky, wave like sheets are obtained which is randomly separated. Furthermore, the HRTEM image showed that the interplanar distance between the individual Gr layers is 0.34 nm.

![Figure 3.3(a): TEM image of Gr (b): HRTEM image of Gr](image)

The TEM and HRTEM image of synthesized GZ is shown in Figure 3.3 (c) – (d). From this result, it is confirmed that individually separated ZnO nanotubes is homogeneously anchored on the surface of Gr layers. The size and shape of the ZnO nanotubes is also measured by the TEM analysis. It is cleared that ZnO nanotubes with thickness 4 -12 nm are uniformly decorated on the surface of Gr layers. From the HRTEM images, the observed interplanar distance of GZ is 0.281 and 0.26 nm corresponding to the (100) and (002) d spacing of ZnO.

The TEM and HRTEM image of the one of the dopants, CuS – ZnO hybrid is displayed in Figure 3.3 (e) – (f). From this image the average particle size of the spherical shaped CuS nanoparticle is ranging from 2 - 8 nm. In addition, the CuS
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A nanoparticle is uniformly decorated on the ZnO nanotubes is also observed in TEM analysis. The HRTEM analysis indicated that the interplanar distance of the spherical CuS nanoparticle on the ZnO nanotubes is 0.303 and 0.271 nm corresponding to the (102) and (006) d spacing of CuS.

Figure 3.3(c): TEM image of GZ (d): HRTEM image of GZ

Figure 3.3(e): TEM image of CuS-ZnO hybrid nanocomposite (f): HRTEM image of CuS-ZnO hybrid nanocomposite
The TEM and HRTEM image of GCZ is shown in Figure 3.3 (g) – (h). The TEM image showed that the dopant (CuS-ZnO hybrid) is homogeneously dispersed on the surface of Gr layers. The interplanar distance of GCZ analysed from HRTEM image showed that 0.271, 0.303 and 0.281 nm corresponding to the (102) and (006) d spacing of CuS and (100) plane of ZnO nanotube. The results clearly proved that the stronger interaction existed between Gr layers and the CuS-ZnO hybrid nanomaterial.

![Figure 3.3(g): TEM image of GCZ (h): HRTEM image of GCZ](image)

3.2.4 Analysis of Surface Area, Pore Volume and Pore Size

Brunauer –Emmet – Teller (BET) method is used for measuring the surface area, pore volume and pore size of Gr and hybrid nanocomposites. The nitrogen adsorption – desorption isotherms of Gr, GZ and GCZ is displayed in Figure 3.4(a). According to IUPAC classification, the shapes of the isotherm are included in type IV shape. This indicates the fact that the slit shaped pores are also present in the samples. From this analysis the observed surface area of Gr, GZ and GCZ is 154, 350 and 635 m²/g. The results confirmed that Gr layers are more randomly dispersed due to the presence of CuS – ZnO hybrid.
The pore size distribution curve of Gr, GZ and GCZ is shown in Figure 3.4(b). It is observed that the pore size distribution of the samples ranging between 1 to 5 nm. This indicates that mesoporous voids also present in the samples. The results clearly confirmed that the presence of ZnO nanotubes and CuS- ZnO hybrid materials also promote the increased pore size distribution of Gr.

Figure 3.4(a): BET adsorption desorption isotherm curves of Gr, GZ and GCZ

Figure 3.4(b): Pore size distribution curves of Gr, GZ and GCZ
3.3 Conclusions

- The TEM and HRTEM analysis show that thin, silky, wave like Graphene sheets with interplanar distance 0.34 nm is obtained by this method.
- The ZnO nanotubes and CuS- ZnO hybrid nano materials are homogeneously anchored on the surface of Gr layers.
- The interplanar distance of Gr layers is significantly enhanced by the presence of ZnO nanotubes and CuS - ZnO hybrid nano material.
- The XRD analysis show that ZnO nanotubes and CuS - ZnO hybrid nanomaterials are strongly bonded with Gr layers.
- Raman spectra measurements show that electrons are transferred from semiconductor to Gr layers.
- The anchoring of semiconductors on the surface of Gr layers without cause any changes in the sp² moiety of the graphene layers.
- From the BET analysis, the specific surface area of Gr, GZ and GCZ is 154, 350 and 635 m²/g.
- The mesoporous voids are present in the synthesized samples
- The pore distribution of Gr is significantly increased with the presence of semiconductors.
- The prevention of the self- stacking properties and tuning the properties of graphene is effectively done by the presence of most efficient, cheaply synthesized and eco-friendly nano materials such as ZnO nanotubes and CuS - ZnO hybrid nanocomposites.

3.4 References

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