Synthesis, Properties of Graphene Oxide-Metal Oxide Mixed Nanocomposites and their Applications - Review

Pampi Majumder¹, Kakoli Dutta^{2*}, Partha Dutta^{3*}

¹University of Engineering and Management, New Town, Kolkata, India

²Institute of Engineering and Management, Salt Lake, Kolkata, India

³Maharaja Manindra Chandra College, 20 Ramkanta Bose street, Kolkata, India

ABSTRACT: Graphene oxide-metal oxide mixed nanocomposites have attracted extensive attention in recent days because of the large surface area of graphene moiety which offers sufficient space to accommodate different nanomaterials preventing agglomeration of nanocomposites. These composites can improve the unique properties of graphene and induce new properties such as high dye adsorption capacity, extended light absorption range, enhanced charge separation and transportation properties, photocatalytic performance, sensitivity in chemical and biological sensors etc. In this review, we will briefly discuss different synthetic strategies, properties and various applications of graphene oxide based metal oxide nanocomposites.

KEYWORDS: Graphene, Graphene Oxide, Metal Oxide, Graphene oxide-Metal oxide nanocomposites

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1. INTRODUCTION

Graphene was isolated in 2004 by Novoselov et al [1] of Manchester University, UK. It is a thin, tightly packed, monolayer allotrope of sp² hybridized carbon atoms that are bonded together in a hexagonal honey comb lattice. Graphene has attracted tremendous attention because of their novel properties like large surface area, high thermal conductivity, high electrical conductivity, and high mobility. Moreover, graphene is highly transparent and it is the strongest material ever known. In spite of all unique properties, graphene has limited application because it is hydrophobic in nature toward water, organic solvent, inorganic solvent and graphene sheets tend to form irreversible agglomerates due to Van Der Waals interaction. This issue drives the researchers to think of manipulation of graphene properties by introducing new functional groups on the surface of graphene sheets [2-6].

Graphene oxide (GO) provides an alternative path to overcome the situation. It is a single atomic layered carbon-based nanoscale material with different oxygen containing functional groups in the surface. These oxygen containing groups have high affinity to water molecules and thus hydrophilic in nature and it can be dispersed in water very easily. Moreover, by the study of the surface charge (zeta potential) of the GO sheets it was found that the GO sheets acquire negative charges when dispersed in water due to the dissociation of carboxylic acid and phenolic hydroxyl groups. That is why GO can form stable colloidal dispersions in water which attributed to electrostatic repulsion and hydrophilicity of GO sheets. In other solvents it is allowed to be uniformly deposited onto wide ranging substrates in the form of thin films or networks [7]. Structurally graphene oxide and graphene sheet are very close to each other. The edges of graphene

oxide are functionalized with hydroxyl, epoxy group and carbonyl groups. These groups disturb the aromatic regions in the basal planes, that is why the layer of graphene oxide consist of both aromatic regions and oxidized aliphatic six-membered rings, which leads to distorted sp³- hybridized geometry and results in the insulating property of Graphene oxide. Normally Graphene oxide is a poor conductor but treatment with heat, light or chemical reduction most of graphene's properties can be restored [8-11].

Metal oxide nanoparticles (NPs) plays appreciable role in many areas of chemistry and physics due to their unusual physical and chemical properties owing to their extremely small size, large specific surface area and number of promising applications. They exhibit larger surface-to-volume ratio that provides unsaturated and more reactive surface atoms. Nanocomposites have potential to combine desirable properties of different nanoscale building blocks to improve mechanical, optical, electronic or magnetic properties. Metal oxides have shown higher alkaline corrosion resistance compared to other materials due to the stabilization of higher oxidation state of transition metals. Most synthesis approaches of nanocomposites based on mechanical or chemical mixing and produce a random distribution of constitutive phases.

To overcome these problems several groups are investigated layer-by-layer deposition and other techniques to prepare layered nanocomposites with ceramics, clays and graphite oxide. Due to the large surface area and the unique properties, GO is selected as an attractive choice as the matrix for these kinds of nanocomposites. Also the incorporation of metal oxide NPs inhibits the aggregation of graphene layers. Metal NPs have excellent optical, catalytic, and electrical properties and for this reason it is a long-term desire to integrate

*Corresponding Author: kakoli.dutta@iemcal.com & par_dut@yahoo.com

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metal NPs into composite materials like graphene oxide to explore their properties and applications. These composites can improve the unique properties of graphene and induce new properties such as high dye adsorption capacity, extended light absorption range, enhanced charge separation and transportation properties, photocatalytic performance, sensitivity in chemical and biological sense etc [7, 12, 13].

2. HISTORY OF SYNTHESIS OF GRAPHENE OXIDE

In 1859, Brodie [14] had discovered a method to prepare graphitic acid by treating graphite with a strong acidic mixture containing potassium chlorate and fuming nitric acid. This Graphitic acid is insoluble in acids and saline solution but dispersed well in pure water and alkalines. While oxidising the graphite, Brodie found that the final substance form as a peculiar compound of carbon with higher weight than graphite and it changed its colour to light yellow composed of transparent plates after fourth or fifth times of treatments.

As a result of these experiments his initial interest to study the structure had changed to molecular formula and molecular weight of graphite. Then investigation had revealed that the product so obtained consists of mainly carbon, hydrogen and oxygen with a molecular formula of $C_{2.19}H_{0.80}O_{1.00}$ and the atomic weight of graphite is 33. Brodie found that carbon in the form of graphite functions as a distinct element but it is different when it forms a distinctive system of combination. Brodie finally gave the name of the substance as graphon, thus becomes the starting point that led to the current research of graphene.

Staudenmaier [15] in 1898 used concentrated sulphuric acid and nitric acid with Potassium chlorate to oxidize the graphite flakes. In this method a gradual increase amount of potassium chloride accelerated the rate of oxidation of graphite resulting the degree of oxidation of graphite similar to as of Brodie's method. This method is more practical but it is very much hazardous. In 1958, this method is modified by Hummers and Offeman [15]. They developed a safety procedure to oxidize graphite flakes within two hours. In this method graphite flakes were treated with a water free mixture of concentrated sulphuric acid, sodium nitrate and Potassium permanganate, resulting in the similar level of oxidation. In this method during oxidation process potassium permanganate is used to replace potassium chlorate to avoid spontaneous explosion while sodium nitrate replaced fuming nitric acid to eliminate fog of acid produced. In Hummers method more amount of oxygen is produced than Brodie's method. However, in this method toxic gas such as NO_2 and N_2O_4 are produced [11, 15, 16].

Graphite oxide is actually a group of graphene oxide. Graphene oxide is produced by exfoliation of graphite oxide. There are so many methods to exfoliate graphite oxide to graphene oxide. Among them sonication of graphite oxide into wafer or organic media is most used method because it is faster than other method. In older method rapid heat of graphite oxide at $100^\circ C$ in inert atmosphere was happened causing explosive thermal reduction of material, production of large amount of CO_2 and H_2O between spaces of graphite layers [15].

Finally Marcano [15] had made a complete study on Hummer's method, Modified Hummer's method and improved Hummer's method without $NaNO_3$. During oxidation when $NaNO_3$ is used, toxic gases are evolved. So, improved Hummer's method replaced the use of $NaNO_3$ with H_2SO_4 H_3PO_4 and doubled the amount of $KMnO_4$. The advantages of this method are production of more hydrophilic carbon material, equivalent conductivity, no emission of toxic gases and finally the large production of graphene oxide [15, 17].

3. SYNTHESIS OF GRAPHENE OXIDE-METAL OXIDE MIXED NANOCOMPOSITES

Metal oxide NPs can be integrated in GO to form mixed nanocomposites. Ehab Salih et al [18] described the synthesis procedure of GO-ZnO mixed NPs. In this process 10 mg GO is dispersed in 10 ml dimethylformamide (DMF) by sonication for 4 min, then added with stirring to 50ml Zinc acetate dihydrate dissolved in 0.02(M) DMF. The mixture is then heated to $90^\circ C$ for 5hrs. The grayish-white powder of ZnO/GO thus obtained is subjected to repeated washing with ethanol and water. The pure ZnO/GO powder is obtained after drying the product overnight at $50^\circ C$. Synthesis of magnetite-GO NPs was reported by Manuel Alejandro Perez Guzman [19]. They prepared the mixed composites by co-precipitation. GO was prepared in usual method. Then Fe(II) and Fe(III) solutions were prepared. Then 4 mL iron (III), 1 mL iron (II) solutions and 50 ml distilled water was continuously stirred, the solution then turned to orange color at a pH=1, then 50ml ammonium hydroxide was added. Then the solution turned to black color when pH=9 reached. The black product was precipitated by magnet aid and washed several times with distilled water and freeze-dried. Linlin Zhong and Kyusik Yun [20] describe modified preparation method of ZnO/GO. They first prepare ZnO nanoparticles, graphene oxide sheets and then fabricate them.

To prepare ZnO nanoparticles 0.125 M Zinc acetate and 0.25M Sodium hydroxide solution is dissolved in succession into methanol heated to $65^\circ C$ under continuous stirring. Then, 10 mL of the sodium hydroxide-methanol solution was injected into 10 mL zinc acetate by a 20 ml syringe maintaining the flow rate at $330 \mu L/\text{minute}$ and the solution was stirred at 800 rpm at a temperature of $65^\circ C$. Again 10 ml sodium hydroxide solution was added to the mixture drop wise and stirred for 30 minutes. The obtained white precipitate of ZnO particles separated by centrifugation and washed three times with anhydrous ethanol in ultrasonication bath and dried in a hot air oven at $60^\circ C$ for 24 hours. GO was synthesised by modified Hummer method with graphite powder as a precursor. The prepared ZnO was dissolved in dimethylsulfoxide (DMSO) and ultrasonicated for 1 hour. Then 10 ml 3-aminopropyltriethoxysilane (APTS) was added to the solution and again sonicated for 2 hours. After that amino-functionalized ZnO was separated by centrifugation, washed with ethanol and dried in an oven. The powder of ZnO-APTS and GO were dissolved in dimethylformamide. The mixed solution was sonicated for 2hrs to reach uniform dispersion. Finally ZnO/GO mixed nanocomposites were recovered by centrifugation, washed with alcohol, dried in an oven [20]. In few reports

GO used as a template for directly synthesizing metal NPs and directly fabricating metal NPs-GO composites on substrates. Xiaozhu Zhou et al [21] reported a simple method to synthesis of Ag Nps on GO without any surfactant or reducing agent. The prepared Ag NPs then simply immersed in HAuCl₄ solution and AuNPs-GO mixed nanocomposites were obtained. Chao Xu et al [22] prepared Co₃O₄-GO nanocomposites. Co₃O₄ nanoparticles (average size of 100nm) were exfoliated and decorated into GO sheets by the intercalation and adsorption of cobalt ions into the layered GO sheets followed by the nucleation and growth on Co₃O₄. Williams et al [23] synthesized TiO₂-GO nanocomposites.

Ethanol solution of suspended GO undergoes reduction by accepting electrons from UV irradiated TiO₂ suspensions. The reduction is happened by changes in the absorption of the GO. In a recent study by Yadong Li et al [24] preparation method of GO-CuO is discussed. They dissolved 40mg GO powder in 40ml distilled water and flaked into a homogeneous suspension of GO by sonication for 30minutes. To this GO suspension 2g cupric chloride was added and stirred for 30 minutes. After that 1ml ammonia water was added quickly and vigorously stirred for 1hour. Finally the samples produced were washed three times by distilled water and dried in vacuum [24].

4. PROPERTIES OF GRAPHENE OXIDE-METAL OXIDE NANOPARTICLES

Due to large surface area and 2D flexibility of graphene nanosheets it can offer sufficient space to accommodate different nanomaterials and also prevent their agglomeration. But graphene is hydrophobic in nature and has strong tendency to agglomerates due to van der Waals attraction between graphene layers which limits its application. So, to overcome this problem graphene oxide was prepared. Oxygen containing groups present in graphene oxide makes it hydrophilic in nature and can be easily dissolved in water and other solvents. Graphene oxide has good superficial characteristics, so solid -air contact efficiency increases with the increase amount of oxygen adsorption. Metal oxide nanostructures have several advantages like exceptional electrical, optical and molecular properties. There are possibilities to insert more functional groups on the surface for the immobilization of other biological catalysts. Metal oxides are generally poorly conductive and suffer from dissolution and aggregation during electrochemical reactions. The main advantages of association of Graphene oxide with the metal oxide nanoparticles are –

- a) The growth of nanoparticles is limited and their stability is improved.
- b) The attached nanoparticles enlarge the interplanar spacing of GO in solid state and avoid the aggregation of GO sheets.
- c) High surface area of GO prevents the aggregation of nanoparticles.

Incorporation of metal oxide on Graphene oxide increases their distinct properties. For example Linlin Zhong et al [20] prepared ZnO/GO in which GO has large surface and ZnO has wide band gap and resulting mixed Composites show enhanced electrochemical property compared to ZnO or GO alone. Ehab Salih et al [18]

prepared GO/ZnO mixed composites and by the conjugation of GO with ZnO NPs enhanced the electron transfer. GO plays role as a wire transfer for bridging the electron between ZnO and the electrode surface. It shows higher surface area and electrocatalytic activity than GO and ZnO alone. Yadong Li et al prepared CuO-GO mixed composites which is very effective against *Pseudomonas syringae* pv. *Tomato* (Pst) bacteria which is responsible for bacterial speck disease of tomatoes [24].

Xiaozhu Zhou et al [22] synthesised Ag NPs on GO surface without using any reducing agent. Obtained Ag NPs were immersed in HAuCl₄ Solution and AuNPs -GO mixed nanocomposites were obtained. Co₃O₄-GO and TiO₂-GO NPs [23]. Composite materials showed more catalytic activities than the metal oxide NPs in catalysis applications. Karolina Urbas et al. [25] synthesized magnetic functionalized graphene oxide to enhance its biocompatibility. Kirankumar et al [26] prepared GO embedded with copper oxide and made electrochemical sensors to detect Dopamine and paracetamol and by using the mixed composites enhanced antimicrobial and anti cancer activity was shown.

5. STRUCTURAL CHARACTERIZATION OF GRAPHENE OXIDE-METAL OXIDE NANOCOMPOSITES

Structural characterization of graphene oxide-metal oxide nanocomposites is of great importance for understanding the correlation between their structure and various properties. The fundamental knowledge about the structural features of nanocomposite is very essential for the building up of catalysts with optimal electrocatalytic activity. These features offer helpful clues for the further modification of the catalysts [4]. For determining the elemental composition of sample Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, X-ray diffraction (XRD) and Thermogravimetric analysis (TGA) can be used. TGA can also be used to study the amount of weight loss over certain temperature.

The morphologies and dimension of nanocomposites can be determined by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Atomic force microscopy (AFM), High resolution transmission electron microscopy (HRTEM).

For example Yadong Li et al [24] observed morphologies of GO and GO-CuO nanoparticles by TEM. They found GO as a thin and semitransparent sheet and after the reaction many dark spots on GO sheets confirm the presence of CuO nanoparticles. The lattice fringes of dark spots on GO were measured by HRTEM and got the value of 0.209 nm which assigned to the (111) lattice plane Cu NPs. The size of Cu NPs as measured by TEM was approximately 21.28 nm. Due to this small size of nanoparticle antibacterial properties increased as the chances of interaction with bacteria increased. Linlin Zhong et al [20] characterized ZnO nanoparticles by SEM and found that 170 nm sized particles uniformly dispersed and assemble to form a round particle. Smrutirekha [27] characterised CuO nanoparticles at different temperature by SEM having different resolution. In the images of CuO nanoparticles without annealed having resolution 5000x

and 7000x the particles are seen spherical in shape and their surface is not smoother but the size of particle lies within the nano range which confirms that the particles are in nano scale. When CuO nanoparticles annealed at 500°C the SEM images showed that the particles are getting agglomerated, thus the size increases and the surface becomes smooth and good electrical properties are expected. When CuO nanoparticles are annealed at 800°C due to heat treatment on sample atomic diffusion happens resulting more agglomeration. Hence more electrical properties are expected that that of without annealing CuO nanoparticles.

In the SEM images of CuO/GO nanocomposites prepared by two different concentration i.e. 5 ml and 10 ml of CuO with 50 ml of GO with two different resolution of 5000x and 7000x it is clearly shown that CuO is covering on the basal plane of GO and agglomeration is stopped in case of 5ml CuO containing nanocomposites whereas 10 ml of CuO containing nanocomposites showed the agglomeration of CuO.

Manuel et al [19] used TEM to characterize Fe₃O₄ nanoparticles and Fe₃O₄-GO nanoparticles. Mean size of agglomerated nanoparticles obtained is 18 nm which is near to the value obtained by XRD. The agglomeration was considerably reduced when CuO incorporated with GO. Xiaozhu Zhou et al [21] synthesized Ag nanoparticles on GO without using any surfactant or reducing agent and characterized its morphology by AFM and SEM. They observed that lots of nanoparticles were sitting on GO surface. The size of nanoparticles is 6.0±3.6 measured by TEM analysis.

Ehab Salih et al [18] examined synthesized GO and ZnO/GO nanocomposites by FESEM. In the images basic shape of GO sheet was exfoliated and looked like pieces of leaves with a dimension of several hundred nm to several microns and images of ZnO/GO indicates that ZnO NPs are closely anchored at the surface of GO. In the TEM images of GO surface looked smooth and integrated and in the images of ZnO/GO nanocomposite, a large number of ZnO nanocrystals with average diameters 21.7± 2.3 nm were uniformly observed on the surface of GO. ZnO nanocrystals are seen almost spherical in shape by high magnification TEM. By HR-TEM image of ZnO nanocrystals a clear lattice fringe is seen which indicates a high degree of crystallinity of the ZnO. Yadong Li et al [24] Using energy-dispersive X-ray spectroscopy (EDS) analyzed the elemental composition of prepared GO-Cu NPs and found that the GO-Cu NPs is made of carbon, oxygen, chlorine and copper (copper content accounted for 57.46 wt %). The weight and atomic ratio of C, O, Zn elements of ZnO-GO composites were detected by Linlin Zhong et al. [20] They found no other elements from ZnO-GO composites except coating elements Pt and substrate component Si.

Yadong Li et al [24] used X-ray diffraction for analysing microstructures of GO and GO-Cu NPs. A peak concerning at $2\theta = 10.43^\circ$ found in the crystal structure of GO, which disappeared in case of CuO-GO NPs indicating that CuO NPs changed the surface structure of GO. Linlin Zhong et al [20] used XRD to determine interlayer distances and crystalline structure in the powder form of ZnO and

showed the appearance of characteristic diffraction peaks for pure ZnO particles corresponding to the (100), (002), (101), (102), (110), (103), and (112) planes. All these peaks confirm the hexagonal wurtzite structure of crystalline ZnO. In case of graphene oxide a sharp diffraction peak appears at $2\theta = 11.6^\circ$. The XRD pattern of ZnO/GO composites is found to be similar to that of ZnO. The (001) reflection of graphene oxide disappeared in the XRD pattern of ZnO/GO composites which confirm the intercalation of ZnO particles that damages the regular stack of graphene oxide. Manuel et al [19] reported XRD pattern of Fe₃O₄ nanoparticles and Fe₃O₄-GO nanocomposites and found diffracted peaks at $2\theta = 30.1, 35.5, 43.2, 53.5, 57.1$ and 62.7° , corresponded to the (200), (311), (400), (422), (511) and (440) planes of magnetite. The crystal size of magnetite and nanocomposites calculated by Scherrer was 20 nm and 12 nm respectively. The decrease in size may occur due to the presence of GO that prevent the growth of nanoparticles.

Smrutirekha [27] reported XRD pattern of CuO nanoparticles annealed at different temperatures and their composites with GO. It was found that the phase of CuO nanoparticles matched with the International Centre for Diffraction Data (ICDD) card No 80-1268. From the XRD peaks it was concluded that CuO nanoparticles exhibited monoclinic crystalline structure having lattice constant $a=4.6833 \text{ \AA}$, $b=3.4208 \text{ \AA}$ and $c=5.1294 \text{ \AA}$. To investigate the effect of temperature on CuO nanoparticles when material were annealed at 500°C and 800°C it has been clearly found that the intensity of peaks increases with the increase in annealing temperature which further indicates that the crystallinity of CuO NPs increases with the increase of annealing temperature.

Simultaneously, with the increase in annealing temperature the peaks become narrower resulting the increase of crystallite size from 26.865 nm at 500°C to 35.2963 nm at 800°C. The XRD pattern of GO is almost flat having a small peak at 11° which indicates that GO is exfoliated and the small peak occurs due to over stacked few layers GO with more than the interlayer distance ($0.335 \text{ \AA}$). In case of CuO-GO mixed composites annealed at 200°C the crystallite size of GO-CuO (5 ml) was 50.567 nm which is more than that of GO-CuO (10 ml) having crystallite size of 41.7374 nm.

Ehab Salih [18] reported XRD of GO, ZnO nanocrystals and GO/ZnO nanocomposites. In the image of GO a peak at 10.6° was observed due to the presence of oxygen carrying group on the GO surface. In case of GO/ZnO nanocomposite due to the exfoliation of GO sheet on ZnO nanocrystals surface loading the peak was decreased. A coincidence of diffraction peaks of ZnO nanocrystals and ZnO/GO was observed at $31.7^\circ, 34.4^\circ, 36.2^\circ, 47.4^\circ, 56.6^\circ, 62.9^\circ, 65.5^\circ, 68.0^\circ, 69.1^\circ$ which corresponds to (100), (002), (101), (102), (110), (103), (200), (112), (201) lattice planes respectively indicates the formation of well crystalline structure of ZnO nanocrystals on GO surface.

Xiaozhu Zhou et al. [21] synthesized the component of nanoparticles by XRD in which it is clearly shows that Ag NPs are obtained on GO surface. The size of Ag NPs depends on the reaction time. When the reaction happens in 10min the Ag NPs formed on GO surface will show

lower density and smaller diameter (2.7 ± 0.8) compared to AgNPs obtained in 30min which is characterized by AFM. As synthesized Ag NPs on GO are very active substrate for Surface Enhanced Raman Spectroscopy.

Elemental composition of sample can be determined by Fourier transform infrared spectroscopy (FT-IR). The FT-IR analysis of ZnO shows peaks at $1,050\text{ cm}^{-1}$, $1,150\text{ cm}^{-1}$, $1,200\text{ cm}^{-1}$, $1,450\text{ cm}^{-1}$, and $3,260\text{ cm}^{-1}$. The peak at $1,000\text{ cm}^{-1}$ indicated the presence of C-O vibrations of graphitic domains. The peak at $1,150\text{ cm}^{-1}$ indicated the presence of C-OH group. Peaks at $1,650\text{ cm}^{-1}$ and $1,750\text{ cm}^{-1}$, represents C=C groups and C=O groups came from carboxylic acid respectively. The peak at $3,350\text{ cm}^{-1}$ occurs due to the presence of O-H groups came from water remaining in graphene oxide. Complete removal of water from graphene oxide is impossible because graphene oxide is hydrophilic in nature and it absorbs water from air [20].

Yadong Li et al [24] used FT-IR to detect changes in functional groups. In the FTIR spectrum of GO, numerous functional groups peaks are observed including peaks of O-H (3427 cm^{-1}), C=C (1655 cm^{-1}), C-O (1286 cm^{-1}), and the asymmetric stretching vibration of C-H bonds in -CH₃ and -CH₂ (2924 cm^{-1}) and the in-plane bending vibration of C-H (1425 cm^{-1}). After the reaction between GO and CuO NPs, the FT-IR spectrum of mixed composites showed changes in the functional groups – strong peak at 3427 cm^{-1} was divided into two adsorptions peak of O-H stretching vibration at 3446 cm^{-1} and 3354 cm^{-1} and adsorption band of C=C at 1655 cm^{-1} drifted to 1624 cm^{-1} . The adsorption peaks at 2924 cm^{-1} , 1425 cm^{-1} and 1286 cm^{-1} disappeared and some new peaks appeared including the O-H stretching vibration at 1385 cm^{-1} , the C-H out-plane bending vibrations at 987 , 920 , and 847 cm^{-1} and Cu-O stretching vibrations in monoclinic CuO below 600 cm^{-1} . These changes suggested that Cu NPs successfully immobilized on GO surface.

Manuel et al [19] used FT-IR to characterize Fe₃O₄ and Fe₃O₄-GO. In both cases, bands appeared around 570 cm^{-1} and the bands are associated to the stretching vibration modes of the magnetite Fe-O bonds. In FT-IR spectrum of Fe₃O₄, C=O stretching vibrations at 1720 cm^{-1} and O-H stretching vibrations at 3300 cm^{-1} were found. In case of Fe₃O₄-GO spectrum prominent O-H and C=O signals were found due to the presence of functional groups at GO sheets.

Ehab Salih et al [18] used FT-IR spectra for functional analysis and found O-H stretching vibrations ($3240 - 3300\text{ cm}^{-1}$), C=O stretching vibration ($1720-1740\text{ cm}^{-1}$), C=C from un-oxidized sp² C-C bonds ($1590-1620\text{ cm}^{-1}$) and C-O vibrations (1250 cm^{-1}). When the spectra of ZnO/GO nanocomposite was compared with that of GO, a slight shift with a reduction in the intensity of the O-H peak (at 3240 cm^{-1}). The peak of C=O stretching vibration at about 1740 cm^{-1} was disappeared in ZnO/GO nanocomposite.

Raman spectroscopy has a high sensitivity to the electronic structures so it is widely used to characterize ordered and disordered crystal structures of carbon materials. It can reveal the characteristic information about the defects /disorders and about the bonds of the individual components and composites. Defects of sample

are represented by D- peak while the G-peak and 2D peaks give the information of the sp² hybridized carbon network and presence of impurities in graphene respectively. The Raman peaks of graphene correspond to D- peak at $\sim 1323\text{ cm}^{-1}$, G-peak at $\sim 1573\text{ cm}^{-1}$ and 2D-peak at $\sim 2657\text{ cm}^{-1}$. [8]

Karolina Urbas et al [25] reported Raman spectra of GO, B-GO-Fe₃O₄ (43 wt% of GO-Fe₃O₄) and N-GO-Fe₃O₄ (40% of GO-Fe₃O₄). Peaks at 1318 and 1602 cm^{-1} were found which corresponded to D and G band respectively. D band occurred due to amorphization of graphite during the oxidation process and G mode originated from the in-plane vibration of sp² carbon atoms. In case of GO-magnetite the ratio of I_D/I_G increased which indicates the successful functionalization of the starting material. In the spectra of B-GO-Fe₃O₄ and N-GO-Fe₃O₄ due to presence of magnetite nanoparticles additional peaks in the range of $200-300\text{ cm}^{-1}$ were observed.

Kudin et al [28] described the Raman spectra of GO and functionalized graphene sheets (FGSs). They found that the G- band initially shifted to higher frequencies during graphite amorphization and gave the possible explanations of this shift. Finally they experimentally observed that the presence of double bonds is the most plausible explanation of the blue shift of G - band. UV-Vis spectra: - The optical properties of the samples can be determined by UV-Visible spectrometer (UV-VIS).

Linlin Zhong et al [20] used to characterize the absorption spectrum of ZnO nanoparticles by UV-VIS spectrum. A strong absorption maximum at a wavelength of 352 nm was found in the spectrum of ZnO particles. In case of graphene oxide an absorption peak centered at 235 nm and a shoulder at $\sim 300\text{ nm}$, were observed which assigned to the $\pi - \pi^*$ transition of aromatic C-C bonds and the $n - \pi^*$ transitions of C=O bonds respectively. In case of mixed composites an absorption peak at 352 nm was observed that attributed to the absorption of surface-attaching ZnO particles and the absorption peak of graphene oxide at 235 nm shifted to 225 nm . Shifting of peak occurs due to the close conjugation of the ZnO particles and graphene oxide sheets that resulted in rapid electron transfer and increased transition energy.

Smruti Lekha Rout [27] studied optical properties of CuO NPs by UV-VIS Spectrum in which the absorption spectra edge is absorbed at wavelength 850 nm which corresponds to energy band gap $E_g = 1.4953\text{ eV}$. A temperature dependency with the UV-VIS Spectra of CuO nanoparticles annealed at different temperature was observed i.e. the absorption spectra edge for CuO NPs annealed at 500°C and at 800°C is absorbed at wavelength 866 nm and at 854 nm respectively which corresponds to energy band gap $E_g = 1.43\text{ eV}$ and $E_g = 1.45\text{ eV}$.

Thus an increase in energy band occurs with an increase in annealing temperature of CuO nanoparticles. On the other hand energy band increases from 1.06 eV to 1.34 eV with the increase of concentration of CuO from 5 ml to 10 ml in case of CuO/GO nanocomposites and the absorption band edge corresponding to 5 ml and 10 ml CuO with 50 ml GO is at wavelength 1169 nm and 921 nm respectively.

6. APPLICATION OF GO-METAL OXIDE MIXED NANOCOMPOSITES

There are so many instances of the varieties of applications of graphene based materials or metal oxide nanoparticles. Some of the examples are discussed below. Graphite has large lithium storage capacity so it is used as an anode material for Lithium but this is not sufficient for requiring high energy capacity. Graphene due to its excellent structural, electrical, and chemical properties acts as a very suitable material for all types of chemical sensor and has more lithium storage capacity than graphite. But the applications of graphene are limited because of the expensive nature of its mass production and the main problem is graphene has the tendency to stack due to vander- Waals interactions between its layers. This problem can be overcome by hybridising Graphene with metal oxide nanoparticles [10, 11]. GO is used as a starting material for fabrication graphene-based field effect transistor (FET). It is used as electrode materials in batteries, for high capacity energy storage in lithium ion batteries. It is able to store hydrogen which may, in the future, be very useful for the storage of hydrogen fuel in hybrid cars [29]. GO is a very good antibacterial agent because it has the ability to induce oxidative stress by Reactive Oxygen Species (ROS) and peroxidation. [30],

Kotchey et al. [31] showed the disruption of bacterial membrane by superoxide anion generated by GO. In recent research by Arnab Halder et al [16] found that an aqueous dispersion of modified GO exhibits a broad fluorescence in the UV region. In another report by Arnab

Halder et al [32] interesting luminescence behavior and electronic characteristics of polyaniline (PANI) grafted GO was shown at low pH. As GO is a fluorescent material it is successfully used in fluorescent-based biosensors for the detection of DNA and proteins with a promise of better diagnostics Applications of Graphene and Graphene-Oxide Based Nanomaterials for HIV. It is also used for bio sensing applications, for early disease detection, and for assisting in finding cures for cancer and detecting biologically relevant molecules. GO is particularly used in the drug-delivery systems in biomedical field. GO is mostly used for making many anticancer drugs because it does not target healthy cells, it targets only tumors, and has a low toxicity. GO can be used in water purification system. It enables a water penetration path between individual GO layers. Multilayer GO films consist of millions of randomly stacked flakes, leaving nano-sized capillaries between them and they are optically transparent and impermeable under dry conditions. When exposed to water (or water vapor), the films allow passage of molecules smaller than a certain size [33].

So many works have been done on Graphene based materials, Graphene oxide based materials and metal oxide nanoparticles, but few works have been done on Graphene oxide-metal oxide mixed nanocomposites. For example, Ahmed Kamal et al reported that Copper Oxide-Graphene Oxide mixed nanoparticles act as a catalyst in synthesis of ligand free Aryl sulphides [34]. In another work; GO based CuO NPs composite electrode is used for highly enhanced non enzymatic glucose detection [35].

Kiran Kumar et al [26] applied this modified nanocomposites electrode to detect Dopamine and Paracetamol and it is found to enhance biological activity (antimicrobial and anticancer activity). In recent research on GO-CuO nanoparticles, Yadong Li et al show that they are very efficient agents against bacteria. They applied the composites on *Pseudomonas syringae* pv. Tomato bacteria which is responsible for bacterial speck disease of tomato. The tomatoes treated by GO-Cu NPs had shown no phytotoxicity and they concluded that these nanocomposites showed 16-times higher antibacterial activity than Kocide 3000 at a very low concentration. Some research works on Silver based nps loaded with GO shows excellent antibacterial activity against *Escherichia coli* and *Xanthomonas oryzae* pv. *Oryzae* [24].

Another important mixed nanocomposite is ZnO-GO NPs. Linlin Zhong and Kyusik Yun have worked on this composite and reported the excellent antibacterial activity by micro dilution method in which minimum inhibitory concentrations of 6.25 µg/mL for *Escherichia coli* and *Salmonella typhimurium*, 12.5 µg/mL for *Bacillus subtilis*, and 25 µg/mL for *Enterococcus faecalis* [20].

Ehabsalih et al have worked to identify the possibility of direct electrochemical uses of Zinc oxide-Go nanocomposite and they found that due to catalytic properties of Graphene oxides the mixed ZnO-GO composites enhanced the electron transfer. At 10% (w/w) concentration ZnO-GO has shown the highest electrochemical properties. They have high electrical conductivity, electrocatalytic activity and provide a direct electrochemical detection of superoxide and used for electrochemical sensor [18] Co₃O₄-GO [22] and TiO₂-GO NPs [23] composite materials showed more catalytic activities than the metal oxide nanoparticles in catalysis applications.

7. CONCLUSION

In this review we have discussed in detail the strategies of formation of GO-metal oxide mixed nanocomposites, their properties, characterization and possible applications in catalysis, energy storage, electrochemical biomedical, bio sensing and pharmaceutical fields. Moreover the properties of GO-metal oxide mixed nanocomposites were compared with that of GO and GO based nanostructures based on recent reviews.

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