COBALT DOPED ZnO–GRAPHENE NANOCOMPOSITE: SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY ON WATER BORNE BACTERIA

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Abstract

This work reports on successful one pot surfactant free *in-situ* synthesis of cobalt doped ZnO-chemically converted graphene (CCG) nanocomposite (CZG) by adopting a low temperature solution process utilizing zinc acetate dihydrate and graphene oxide with varying content of cobalt acetate tetrahydrate (upto 10% Co with respect to Zn) in the precursor medium. The materials properties were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), FTIR and Raman spectral analyses. The presence of ZnO nanoparticles (NPs) in the nanocomposites was confirmed by XRD and TEM studies. The TEM study revealed the uniform distribution of hexagonal ZnO in the CCG matrix. The existence of chemical interaction / complexation between CCG with ZnO/Zn^{2+} of the samples was confirmed by FTIR and Raman spectral analyses. The antibacterial activity was measured on *Escherichia coli and Staphylococcus aureus* as water borne bacteria to examine the efficiency of the nanocomposite towards killing the bacterial cells. Among the nanocomposites, 5% Co doped sample showed best antibacterial activity against the microorganisms. This synthesis strategy could open an avenue of Co doped other metal oxide-CCG nanocomposites for biomedical applications.

1. INTRODUCTION

Human beings always need fresh and pathogen free water for healthy and prosperous life. Pathogen free water has also utmost importance for animals and plants. However, the main concern is to make the water free from pathogen [1]. According to WHO, water borne pathogens are the main reasons for an estimation of more than 2.2 million deaths every year among them 1.4 million are of children [2]. The reason for these deaths is obviously the water borne bacterial infections which mainly caused by consumption of pathogen contaminated water [2]. There are several water disinfection techniques (such as chlorination, UV treatment and ozonization) for making large scale drinking water [1]. However, these techniques mostly require high temperature and pressure [3]. Use of organic acids, essential oils, bacteriocins and lysosomes has widely been investigated for this purpose also [3]. In this respect, inorganic nanomaterials that are not only stable against high temperature and pressure but also have strong antibacterial activity against water borne pathogens like *Escherichia coli, Vibrio cholerae, Pseudomonas aeruginosa, Staphylococcus aureus etc*.

Among the inorganic nanomaterials, nano metal oxides such as ZnO, Fe_2O_3, TiO_2, MgO, CaO, CuO, Al_2O_3 and Ag_2O have excellent

antibacterial activity [4]. In this respect, nano ZnO is widely regarded as biocompatible and antibacterial agent. It is generally used in healthcare products, food preservation and packaging systems, water purification, bio-imaging and drug delivery [1,3,4]. ZnO can disrupt cell membrane of bacteria. In this process, the growth of bacteria is slowed down and eventually died [5].

On the other hand, reduced graphene oxide (rGO) / chemically converted graphene (CCG) [6] has also been studied in many biomedical applications such as drug delivery, protein adsorption, biosensor, electrochemical detection of drug etc [7] for its unique physiochemical properties such as large surface area [8], easy to functionalize with other materials including metal oxides [9] and high biocompatibility. The rGO/CCG also has the unique property of directly killing bacterial cells. It also helps the nanoparticles for enhancing antibacterial activity in the form of nanocomposite with a metal oxide in nano regime [5]. Therefore, by coupling of CCG/rGO with suitable metal oxide nanoparticles in nanocomposite material can effectively kill bacterial cells which may not be possible by the individual component of the material [5].

Doping of metal oxide can also be a fruitful strategy for enhancing antibacterial activity of the material. In this case, Co^{2+} ions is a well-known dopant which can freely occupy at the Zn sites of ZnO matrix when ZnO is doped with Co. The Co doped ZnO can help to release Zn^{2+} ions from the ZnO matrix [1]. Subsequently, release of Zn^{2+} ions can destroy certain microorganisms by penetrating the ions into the cell membranes [1]. Moreover, there are plenty of reports on ZnO-graphene [10], Co doped ZnO [1] materials as promising antibacterial materials. However, there is scanty of report available in the literature on the antibacterial activity of Co doped ZnO-graphene nanocomposite [11].

In this work, we report a facile one pot surfactant free low temperature (95°C) solution process for the synthesis of Co doped ZnO-CCG (CZG) nanocomposite using optimized content of zinc acetate dihydrate, graphene oxide and

cobalt acetate tetrahydrate as precursor materials. Water borne bacteria such as, *Escherichia coli* and *Staphylococcus aureus* has been used to test the antibacterial activity of the synthesized nanocomposite materials. It is noted that the stable CZG nanocomposite shows an excellent antibacterial activity towards the water borne bacteria.

2. EXPERIMENTAL

2.1 Synthesis of Co doped ZnO-CCG (CZG) nanocomposite

Low temperature (95°C) solution process [12] was adopted for the synthesis of Co doped ZnO-chemically converted graphene (CZG) nanocomposite. Initially, the as-prepared GO was uniformly dispersed in dimethyl formamide (DMF, Merck) solvent (40 ml) by ultrasonication for 2 h duration. In an another container, 1 g of zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$, Sigma-Aldrich, ≥98%] and cobalt acetate tetrahydrate [$(CH_3COO)_2Co.4H_2O$, Merck] with varying contents (0, 2, 5 and 10 atomic percent, at.%; with respect to Zn) was uniformly dispersed in 200 ml of DMF by continuous stirring. Accordingly, the synthesized nanocomposite materials were labelled as ZG, CZG2, CZG5 and CZG10, respectively. After that the dispersed GO and the solution containing the metal salts were mixed together and stirred the aliquot for further 2 h. Then, the precursors were kept in an air oven at 95°C for 9 h [6]. In the later stage, the solid materials were separated out with the help of centrifugation using double distilled water and ethanol as washing solvents. Finally, the samples were dried in at ~60°C for 3 h duration an air oven. Without using GO, the pristine ZnO (ZO) was also synthesized by following the similar technique.

3. CHARACTERIZATIONS

3.1 Materials properties

X-ray diffraction (XRD) study of the samples was performed by using a X-ray diffractometer (Bruker D8 Advance with DAVINCI design X-ray diffraction unit) with nickel filtered CuK_α radiation source (λ = 1.5418 Å) in the 2θ range, 5°–80°.

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The transmission electron microscopy / high resolution transmission electron microscopy (TEM/HRTEM) along with TEM-EDS studies were carried out by FEI Company make (Tecnai G2 30.S-Twin, Netherlands) instrument at an accelerating voltage of 300 kV. In the measurement, carbon coated 300 mesh Cu grids were used for placement of samples. On the other hand, FTIR spectral study was performed by Thermo Electron Corporation, USA make FTIR spectrometer (Nicolet 5700). In each experiment, the number of scans was fixed at 100 (wavenumber resolution, 4 cm^{-1}). Raman spectra of the samples were recorded using micro-Raman (Renishaw inVia Raman microscope) with an argon ion laser of 514 nm incident wavelength as an excitation source.
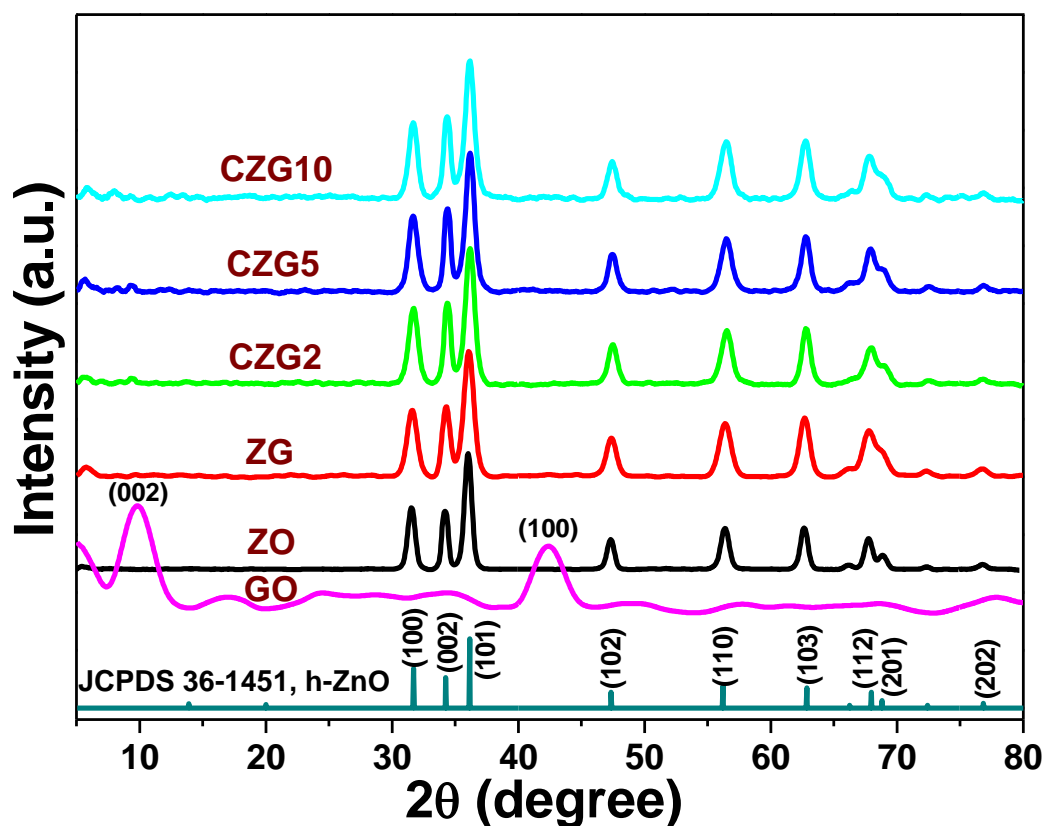

Figure 1: XRD patterns of ZO, ZG, CZG2, CZG5 and CZG10 samples along with as-synthesized graphene oxide (GO)

3.2 Bacterial strains

Gram-positive bacteria - *Staphylococcus aureus* (S. aureus, ATCC 25923) and Gram-negative bacteria - *Escherichia coli* (E. coli, MTCC 2939) were used to study the antibacterial activity of CZG nanocomposites. Bacterial colonies were grown by Mueller-Hindon-Broth (MHB) medium. A single colony of bacteria (*Staphylococcus aureus, Escherichia coli*) was transferred to MHB medium and incubated it at 37°C until the density of the broth (containing the suspended organisms) reached a desired standard (0.5 McFarland standards) [5] using sterile distilled water. The organism suspension was used for further application within 30 min of preparation.

3.3 Determination of minimum inhibitory concentration (MIC) of CZG nanocomposites

An approximately 10^7 CFU ml^{-1} E. Coli / S. aureus bacteria cells were grown in 15 ml liquid MHB medium supplemented with different

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concentrations (1.5625, 3.125, 6.25, 12.5, 25, 50, 100, 200 µg ml^{-1}) of the samples (ZO, ZG, CZG2, CZG5 and CZG10) and incubated at 37°C for 24 h. After that the bacterial growth rate was investigated by measuring optical density (OD) where the OD of the treated and untreated bacteria (i.e. control) was measured at 600 nm using UV-Visible spectrophotometer (SpectraMax M5). Then, the results were further analysed to check the antibacterial activity or the MIC value of the individual samples.

4 RESULTS AND DISCUSSION

4.1 Materials properties

4.1.1 Phase structure

X-ray powder diffraction (XRD) study is usually used to realize crystallinity and to confirm the crystal phases of samples. In the present work, XRD were measured for as-synthesized GO, pristine ZnO (ZO), ZnO–CCG (ZG) and Co doped ZnO–CCG (CZG) nanocomposites (Figure 1). The Figure 1 clearly reveals that the XRD peaks of GO located at ~10.1° and ~42.4° along the crystal planes (002) and (100), respectively are found to be disappeared completely in graphene oxide incorporated ZG, CZG2, CZG5 and CZG10 samples after 9 h of reaction time [5]. The disappearance of these peaks indicated the transformation of GO to CCG took place in the nanocomposites [6].

The presence of hexagonal ZnO (h-ZnO) in ZO, ZG, CZG2, CZG5 and CZG10 samples was also confirmed by the observation of XRD peaks in all the samples [JCPDS 36-1451] [5]. Another important observation is that there is a slight shifting (~ 0.16°) in 2θ values towards higher diffraction angles for all the Co doped samples (CZG2, CZG5 and CZG10). This observation can be explained on the basis of substitution of Zn site by Co. It is possible due to smaller ionic radius of Co^{2+} (0.61 Å) compares to Zn^{2+}(0.74 Å). The Co^{2+} ion can easily replace Zn^{2+} in ZnO crystal lattice of hexagonal zinc oxide [13]. Further confirmation of incorporation Co^{2+} ions into ZnO lattice is also evidenced from the observation of average crystallite size (D) measured along (101) plane of ZnO in ZO, ZG,

CZG2, CZG5 and CZG10 samples from their XRD patterns [14]. The calculated 'D' values of ZnO in pristine ZnO (ZO), ZG, CZG2, CZG5 and CZG10 nanocomposites are ~ 15 nm, ~ 11 nm, ~ 10 nm, ~ 9.6 nm and ~ 9.1 nm, respectively. Therefore, with increasing Co doping concentration, a gradual decrease of crystallite size is seen in cobalt doped ZG nanocomposites (CZG) compares to ZO and ZG. The reason for this decrease can be attributed to the substitution of Zn^{2+} ions by Co^{2+} ions in h-ZnO crystal lattice. Moreover, the coupling of CCG with ZnO in ZG nanocomposite can prevent the grain growth of ZnO which might be resulted in decrease of crystallite size of ZnO in ZG sample compares to pristine ZnO in ZO sample [6]. The small crystallite size can result in increasing surface area of the particles which might contribute to enhance antibacterial activity towards biomedical application [5] (to be discussed later).

4.1.2 Microstructural property

The TEM microstructure of a representative CZG5 sample is shown in Figure 2a which shows well distributed ZnO NPs in CCG layers. The corresponding HRTEM image of the sample is shown in Figure 2b. The figure clearly shows distinct lattice fringes with an interplanar distance of 0.28 nm, corresponds to (100) plane of hexagonal ZnO. This observation fully supports the XRD data (Figure 1) of the sample. On the other hand, the TEM-EDX curve of CZG5 is shown in Figure 2c. As revealed from the EDX curve, the presence of C and Cu can be originated from the carbon coated Cu grid used for the TEM study. Another source of carbon can be the CCG matrix, the organic part of the organic-inorganic (ZnO/Zn^{2+}) hybrid CZG nanocomposite. However, the existence of ZnO and CCG can show the signals for Zn and O elements in the sample. The particle size distribution of CZG5 is shown in the histogram (Figure 2d) obtained from the TEM image (Figure 2a) of the sample. An average particle size of ~10.2 nm is obtained from the histogram. This data is also supported the crystallite size of ZnO measured by XRD study (Figure 1).

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4.1.3 FTIR spectra

To investigate the chemical bonding of the nanocomposites, the FTIR spectra of ZO, ZG, CZG2, CZG5 and CZG10 nanocomposites are measured (Figure 3). The FTIR peaks appear at 1730, 1624, 1207 and 1048 cm^{-1} in GO, attribute to COOH stretching vibration in carboxylic acid groups, skeletal vibration of unoxidized graphitic domains as well as for the vibrations of C–O stretching, and C–OH stretching, respectively [5]. The presence of Zn–O stretching vibration of h-ZnO is revealed by a prominent vibration appeared at ~465 cm^{-1} for ZO, ZG, CZG2, CZG5 and CZG10 nanocomposites [9]. This observation strongly supports the XRD result

(Figure 1). Moreover, a broad vibration appears at ~3430 cm^{-1} in all the nanocomposites, implies the presence of hydroxyl groups. A new peak observed at ~1564 cm^{-1} suggests the transformation of CCG from GO in GO loaded samples (ZG, CZG2, CZG5 and CZG10). It is also noted that the ~1564 cm^{-1} vibration peak is absenting in pristine graphene oxide. This confirms the formation of CCG in the nanocomposite. It is worthy to note that the FTIR vibrations responsible for oxygen functional groups of GO become very weak or nearly disappeared in the ZG, CZG2, CZG5 and CZG10 nanocomposites, also emphasized the transformation of GO to CCG in the nanocomposites.
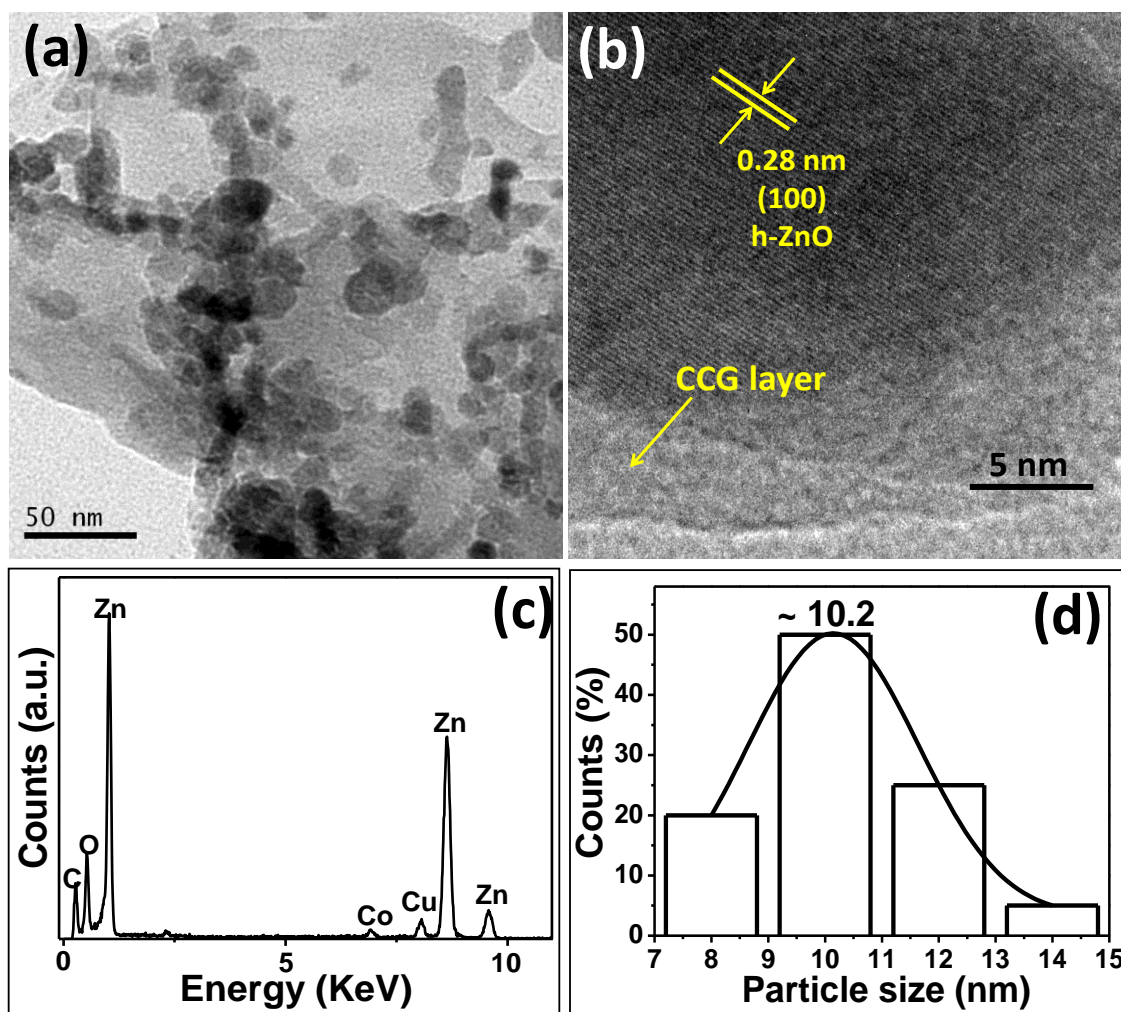

Figure 2: TEM result of CZG5 nanocomposite. (a) TEM image, (b) corresponding HRTEM image, (c) TEM-EDS curve and (d) histograms for the particle size distributions
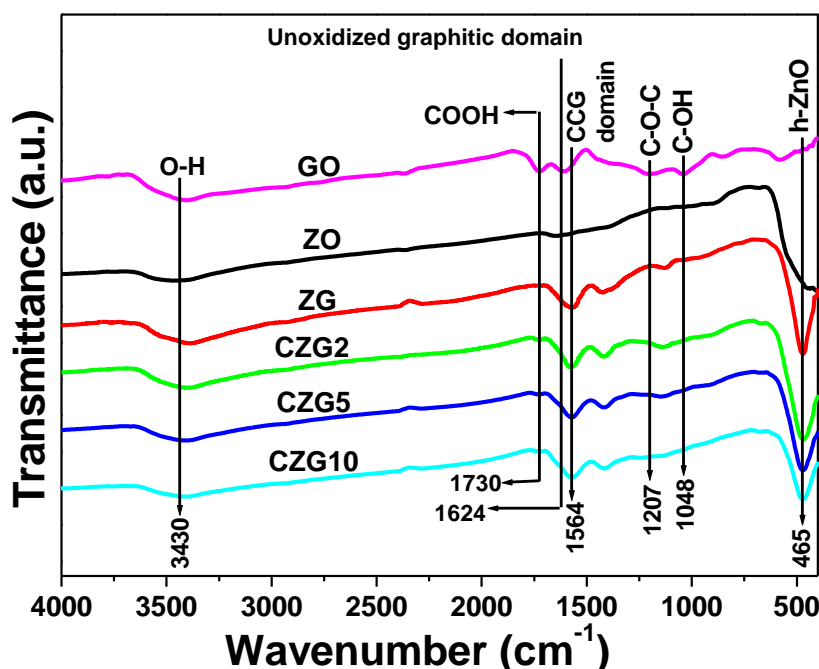
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Figure 3: FTIR spectra of ZO, ZG, CZG2, CZG5 and CZG10 samples along with as-synthesized graphene oxide (GO)

4.1.4 Raman spectra

Micro-Raman spectral study (Figure 4) has been performed especially on GO and GO loaded ZG and CZG5 samples to understand the changes in structural defects and/or layer by layer exfoliation in graphene moiety that are present in the nanocomposites. In each sample, two distinct Raman peaks are seen, one at ~1350 cm^{-1} and another at ~1597 cm^{-1}, assign to D band (defect) and G (graphene) band, respectively. The exfoliation and/or breaking of graphene layers can be the reason for the appearance of the D band whereas the G band (graphene) can originate due to the existence of E_{2g} phonon in sp^2 carbon atoms in graphene moiety. The intensities of D and G bands are denoted as I_D and I_G, respectively. In this regard, the ratio of I_D/I_G value is proved to be an important factor regarding the knowledge of chemical interaction that happened between the CCG and the inorganic moiety (Co doped ZnO/Zn^{2+}) of the nanocomposite. It can be seen from the figure that the I_D/I_G value is much higher in ZG compare of ZO. This relative increase in I_D/I_G value can be attributed to decrease of in-plane sp^2 domain size of graphene. That result

could imply the layer by layer exfoliation and/or breaking of graphene layers due to chemical interaction/complexation with the inorganic moiety [6]. The reduction of GO to CCG due to the removal of oxygen functional groups can also be a valid reason for the increase in I_D/I_G ratio. The doping of Co ions into ZnO lattice can also be confirmed by a further increase in I_D/I_G value in CZG5 nanocomposite. This phenomenon would indirectly link to the decrease of crystallite size of ZnO as obtained from the XRD result (Figure 1). The interaction between Co doped ZnO/Zn^{2+} ion and CCG can help to enhance antibacterial activity of the nanocomposite sample (discussed in the later section).

4.2 Biomedical properties

4.2.1 Minimum inhibitory concentration (MIC) of nanocomposites

Gram-positive bacteria - *Staphylococcus aureus* and Gram-negative bacteria – *Escherichia coli* were used as model water borne bacteria (microorganisms). Figure 5 shows the effect of ZO, ZG, CZG2, CZG5 and CZG10 samples with different concentrations on

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Staphylococcus aureus, and *Escherichia coli* for the study of antibacterial activity of the materials. The bacterial growth inhibition would directly depend on the concentration of cobalt doping as revealed from the Figure 5. In this context, the CZG5 nanocomposite can be seen as a better antibacterial agent than ZO, ZG and CZG2 samples. The MIC value for gram negative bacteria (*Escherichia coli*) and gram-positive bacteria (*Staphylococcus aureus*) after the treatment of CZG5 nanocomposite are 3.125µg/ml and 6.25µg/ml. Moreover, CZG5 and CZG10 nanocomposites show similar antibacterial activity. Therefore, the CZG5 nanocomposite can be taken as an ideal candidate for obtaining effective antibacterial activity. The ZG nanocomposite seems to have greater antibacterial activity than ZO implying that the CCG incorporation might have influenced the antibacterial activity. The disruption of the bacterial cell wall by oxidative and membrane stresses with the help of the sharp edges of graphene sheets can be the reason behind the enhanced antibacterial activity of CCG [5]. The CCG can also help the ZnO nanoparticles for enhancing antibacterial activity via uniform distribution [5]. The cobalt doping further enhanced the antibacterial activity of ZnO nanoparticles. That's why it is confirmed that the antibacterial activity also dependent on cobalt doping concentration.

Although, a plenty of research has already been done on the antibacterial activity by nanoparticles but the mechanism behind it is yet to be clearly known till date. Several known concepts can be attributed behind the antibacterial activity like cell wall disruption, protein synthesis inhibition and disruption of DNA replication of bacteria cells etc. The incorporation of Zn^{2+} into the bacterial cell membrane and the accumulation of nanoparticles can be the reasons for the death of microorganism [5]. The activity of Zn^{2+} ions might also be considered for cell wall disruption. In this regard, the disruption of cell wall can effectively cause leakage of intracellular material which in turn causes the bacterial cell death. The inhibition of protein synthesis and DNA replication can also possible by Zn^{2+} ions [5]. The Zn^{2+} ions generally help to modify the DNA by interacting with sugar phosphate group of gene which can inhibit the DNA replication process of bacteria. The interaction between Co ions, ZnO and CCG (Figure 4, Raman spectra) can also be given as a reason for the enhanced antibacterial activity because it would create more reactive oxygen species (ROS) generation and eventually causes more bacterial cell death. The successful substitution of some Zn^{2+} ions by Co^{2+} ions into ZnO crystal lattice would help Zn^{2+} ions at the interstitial position to release of more Zn^{2+} ions form ZnO crystal lattice. Therefore, it is no doubt that the release of Zn^{2+} ions would result in enhancing the antibacterial activity [1]. The reduced crystallite size of CZG nanocomposites due to the Co^{2+} ions incorporation would also have an effect on antibacterial activity. Moreover, the inhibition of DNA replication and protein synthesis seems to be affected due to the presence of smaller nanocomposite particles.

5. CONCLUSION

In summary, we have synthesized a highly effective antibacterial agent of Co doped ZnO-chemically converted graphene (CCG) nanocomposite (CZG) in dimethyl formamide solvent by low temperature solution process without using any surfactant in the precursor. The formation of ZnO and the conversion of graphene oxide to CCG took place *in situ*. A series of Co doped-ZnO-CCG nanocomposites was synthesized by changing the doping concentration in the precursor. As-synthesized nanocomposite (CZG5) derived from 5% Co doped precursor showed the best antibacterial activity of water borne bacteria at 6.25 and 3.125 µg/ml for Gram-positive bacteria - *Staphylococcus aureus* and Gram-negative bacteria - *Escherichia coli,* respectively. Therefore, Co doping in ZG nanocomposites seemed to have enhanced capability of inhibiting the growth of water borne bacteria compare to pristine ZG nanocomposite. This synthesis strategy could open an avenue of Co doped other metal oxide-graphene nanocomposites for biomedical applications.

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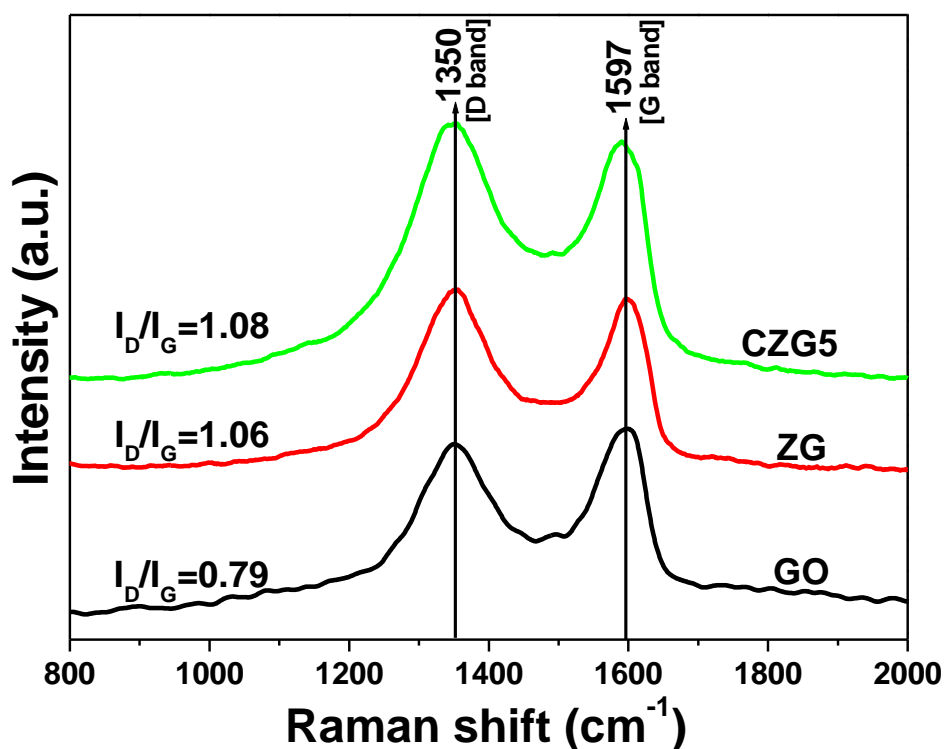Cobalt doped ZnO-graphene nanocomposite: synthesis, characterization and antibacterial activity

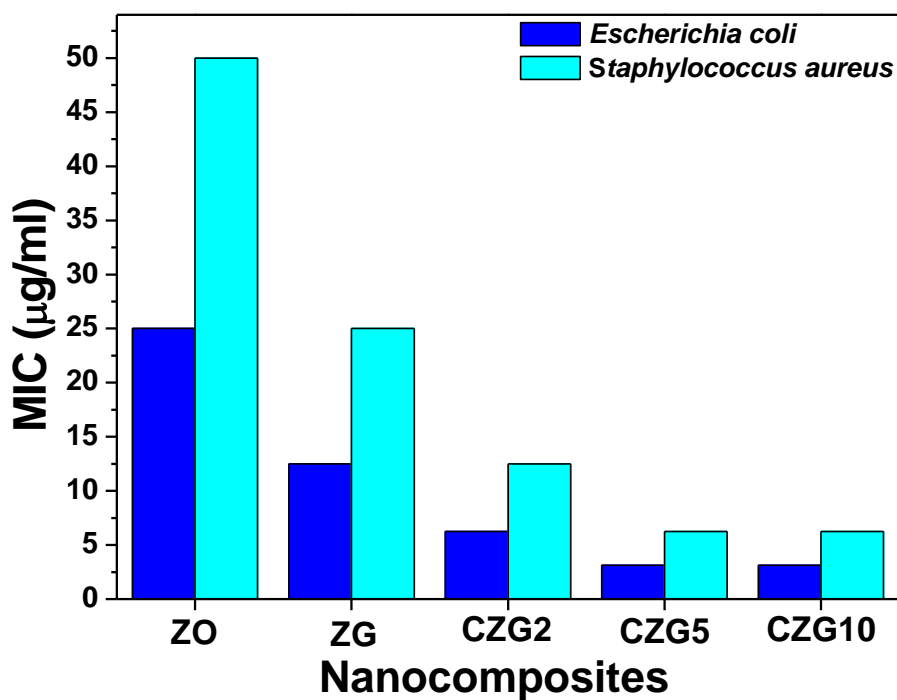**Figure 4: Raman spectra of GO, ZG and CZG5 samples. Respective I_D/I_G values are embedded**

Figure 5: Antibacterial activity of ZO, ZG, CZG2, CZG5 and CZG10 on *E. coli* and *S. aureus* bacteria

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