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Fabrication of Ag doped $Ni_{1-X}Gd_xO$ Nanocomposite by Auto-Combustion Method and their Antibacterial Efficacy

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Abstract

The Nanoparticles with antibacterial activity attracts immense applications in biomedical devices, food processing and food packaging. The unique size and composition dependent properties of nanocomposites are attracting tremendous interest because they showed promising role in diagnostics and therapeutics. To stabilize the drug and to overcome the increasing drug resistance of the bacteria, there is an extreme need to develop novel antimicrobial agents. Here we have fabricated Ag doped $Ni_{1-X}Gd_XO$ nanocomposite by simple, fast, single step combustion method using water as solvent. Physiochemical properties of the nanocomposites were understood by X-ray diffraction (XRD), Transmission electron microscopy (TEM), selected area electron diffraction (SAED), Fourier transformation infrared spectroscopy (FTIR) and EDX. Well diffusion method was carried out to evaluate the antibacterial activity of the synthesized nanocomposites against pathogens Bacillus subtilis and Klebsiella pneumoniae. The synergistic effects of synthesized metal oxide nanocomposites lead to the superior antibacterial activity and showed as promising antibacterial agent.

Keywords: *Ag doped $Ni_{1-X}Gd_xO$; Combustion method; reactive oxygen species (ROS); antibacterial activity; pathogens.*

1. Introduction

Nanomaterials have attracted much more interest of the society because of the wide range applications in different fields. The nanosize materials represent a variety of size (Paresh Chandra Ray,2010; Aki Kutvonen et.al., 2010) and shape dependent properties which can be incorporated by controlling the sizes of the constituent components (Vicki H. Grassian,2008; Okkyoung Choi et.al., 2008; Ronald E Miller et.al., 2000). Due to their superior properties like optical (Xiaomin Li et.al., 2015; Abdullah Al-Sehemi et.al., 2013), electrical (Ameer Azam et.al., 2010), structural (Ghougali M., et.al., 2016), electrochemical (Xiong Wang, et.al., 2005), magnetic (Morteza Mahmoudia et.al., 2011) and catalytic (Sudarsanam Putla et.al., 2015) properties compared to their bulk counterparts, nanomaterials have vast applications in electronics, chemical engineering, nanowires, batteries, photocatalytic, solar cells, automotive sectors, sensors, memory storage devices, drug delivery, catalysis, and very recently in the treatment of cancer cells (André Venter et.al., 2011; Peiqi Cao et.al., 2015; Zijiong Li et.al., 2016; Abdel Aal A.et.al., 2009; Mukes Kapilashrami et.al., 2014). In recent years, there is an immense interest to synthesize nanoparticles of transition and inner-transition metals.

Transition metal oxides show excellent size dependent properties leading to a number of interesting applications. Due to excellent properties, metal oxides of transition and inner-transition metals are employed in various fields and one of the emerging fields is biomedicine (Wei Wu et.al., 2015; Daishun Ling et.al., 2015; Yan-Wen Wang et.al., 2014). There has been continuous research is going on to synthesize eco-friendly and non-hazardous metal oxide nanomaterials, for better applications. The higher adsorption ability of metal oxides than the bulk materials supports their cytotoxic activity through medium starvation (Costa, M. and J.D. Heck, 1984). Transition metal oxides nanoparticles such as

nickel oxide, titanium oxide, zinc oxide, manganese oxide, cobalt oxide, have proven their effectiveness against infectious diseases, in-vitro and animal cells (Maryam Banoee et.al., 2010; Samarpita Senapati et.al., 2012; Shahanavaj Khan et.al., 2015; Yi Chen et.al., 2015; Khashan KS et.al., 2016). Nickel oxide (NiO) is one of the important transition metal oxide p-type semiconductor nanoparticles owing cubic lattice structure with a band gap from 3.6 to 4.0 eV (Angel Ezhilarasi A et.al., 2016). Nanostructured NiO is important because of its uniform morphology and crystallinity. NiO is an abundant and commercially important semiconducting oxide nanoparticle. NiO nanoparticles are mainly used in catalysis, electrochromics, batteries, sensors, supercapacitors, solar cells (Kuhlenbeck H et.al., 2013; De-Long Sun et.al., 2017; Dawei Su et.al., 2012; Yingqiu Zhang et.al., 2012; Gayatri Natu et.al., 2012; Changzhou Yuan et.al., 2009). NiO nanoparticles have drawn lot of interest in recent research, because of high chemical stability, electro catalysis, super conductance characteristics and electron transfer capability (Sasi B., et.al., 2003). Because of anti-inflammatory properties they are employed in the field of biomedicine (Catherine C Berry et.al., 2003). Due to the potential of inducing oxidative stress and the tendency to release nickel ions (Ni^{2+}) inside the cell, NiO nanoparticles was found to possess toxic effects over bacteria. Because of unique properties like surface area and adsorbing ability NiO have positive tendency for their cytotoxic effects (Schrand et.al., 2010; Latvala S et.al., 2016). Since physical, chemical and biological properties depend on their size and shape, tuning the size, shape and structure of metal oxides is one of the important research areas (Sattarahmady N. et.al., 2014). Also the combination of two or multiple metals can therefore offer synergistic advantages over any modality alone. Thus the incorporation or doping of metals to the host material will impart changes in their chemical and physical properties of nanoparticles (Anshu Singhal et.al., 2009; Maddahi P et.al., 2014).

There has been significant interest in inner transition metals as their unique 4f electron structure confers unique properties, ideal for bioanalysis as probes and bioimaging agents. Gadolinium has seven unpaired electrons and it shows paramagnetic behaviour. Gadolinium in particular offers many attractive characteristics for the diagnosis and therapies for cancer (Zhang, G. et.al., 2015; Dutta RK et.al., 2015; Stephane Roux et.al., 2010). Gadolinium shows good catalytic activity due to its large specific surface area and nanometre (nm) size (Caio Luis Santos Silva et.al., 2013). The incorporation of gadolinium into nickel deposit is expected to improve the electrocatalytic activity of nickel. These characteristics make gadolinium an ultimate candidate in the development of multifunctional nanocomposites for both therapeutic and diagnostic purposes. Silver is a promising material in the field of medicine. Many studies (Muhammad Akram Raza et.al., 2016; Shanmugam Rajeshkumar et.al., 2016; Xuesen Hong et.al., 2016) showed that silver nanoparticles were good and efficient antibacterial agents.

Furthermore, we need a suitable method to synthesize the nanocomposite and to get a reduction in the crystal size to only a few nanometres (nm) which modify the electronic, optical, catalytic, magnetic and biological characteristics properties. Various techniques like thermal decomposition, electro deposition, sol-gel chemistry, ball milling, vapour deposition, co-precipitation method, solution combustion (SC) etc., are employed to synthesis various nanocomposites. Solution combustion method is one of the efficient synthetic methods for the synthesis of nanocomposites. Solution combustion method is facile, rapid, low-cost and efficient method. In this method, synthesis of nanocomposites carried out by self-sustained exothermic reaction between oxidizer (usually nitrates) and fuel (glycine, urea, citric acid etc.,) (Singanahally T. Aruna et.al., 2008). The basic principle of the combustion method is that once the reaction is initiated at a chosen ignition temperature, a self-sustaining exothermic reaction takes place within a short time interval. Many important parameters, such as generation of flame, ignition temperature, liberation of gas, background atmosphere and fuel–oxidant ratio, play an important role in the combustion method (Alves et.al., 2013; Umadevi M et.al., 2013). Because of the importance and enhanced properties of NiO, gadolinium and silver nanoparticles in this work we made an attempt to synthesize nickel and gadolinium nanocomposites doped by silver with small particle size and large surface area with good antibacterial properties.

2. Materials and Methods

Samples of pure NiO, $Ni_{1-X}Gd_XO$ and Ag doped $Ni_{1-X}Gd_XO$ nanocomposites were prepared using simple solution combustion method, which allows efficient synthesis of nanosized materials. Glycine acts as a fuel material and metal nitrate was served as an oxidiser.

2.1 Materials Used:

Nickel nitrate ($Ni(NO_3)_2.6H_2O$ - Merck), Gadolinium nitrate ($Gd(NO_3)_3.6H_2O$ - Alfa aesar), Silver nitrate ($AgNO_3$ - Alfa aesar) and Glycine

($C_2H_5NO_2$- Merck). All the precursors/materials were obtained from commercial suppliers and used as received. Deionised water was used throughout the synthesis.

2.2 Synthesis of Nickel oxide (NiO) nanoparticles:

In a typical synthetic procedure the stoichiometric proportions of the nickel nitrate and glycine in 100ml distilled water were weighed and sonicated for 15 minutes to get clear solution. Then the solution was stirred continuously for 30 minutes to get homogeneous solution. The obtained sample mixture was then kept in a pre-heated muffle furnace maintained at 400°C. Primarily the gel was formed and the gel gets ignited to give a porous NiO nanoparticles. The samples were washed and dried in an oven at 100°C. The obtained NiO nanoparticles were annealed for 2 hours maintained at 600°C using muffle furnace.

2.3 Synthesis of $Ni_{1-X}Gd_XO$ nanocomposites:

In the synthesis of $Ni_{1-X}Gd_XO$ nanocomposites, stoichiometric proportions of the nickel nitrate, gadolinium nitrate and glycine in 100 ml distilled water were weighed and carried out the same procedure similar to the synthesis of NiO nanoparticles.

2.4. Synthesis of Ag doped $Ni_{1-X}Gd_XO$ nanocomposites:

In the synthesis of Ag doped $Ni_{1-X}Gd_XO$ nanocomposites stoichiometric proportions of the nickel nitrate, gadolinium nitrate, silver nitrate (8 wt %) and glycine in 100ml distilled water were weighed and carried out the same procedure similar to the synthesis of NiO nanoparticles. A highly porous black sample was obtained.

2.5 Antibacterial Activity:

The synthesized pure and doped nanocomposites were tested for antibacterial activity by well-diffusion method against pathogenic gram-positive and gram-negative organisms such as bacillus subtilis and Klebsiella pneumoniae. The pure cultures of organisms were subcultured on Müller-Hinton broth at 37 °C on a rotary shaker at 150 rpm. Wells of 6mm diameter were made on Müller-Hinton agar plates using gel puncture. Each strain was swabbed uniformly onto the individual plates using sterile cotton swabs. The 50 µL (50µg/1ml) of sonicated nanoparticles were poured onto each of wells on plates using micropipette and incubated at 37 °C for 16 hours. Ampicillin was used as control.

3. Characterization

Characterization of nanoparticles is necessary to establish the understandings of nature of the material, morphology, their size dependent properties and utilization of these nanocomposites in different applications. Hence the synthesised NiO, $Ni_{1-X}Gd_XO$ and Ag doped $Ni_{1-X}Gd_XO$ nanocomposites were characterised through different electroanalytical techniques viz., X-ray diffraction (XRD), High resolution Transmission electron microscopy (HRTEM) measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan), selected area electron diffraction (SAED), Fourier transformation infrared spectroscopy (FTIR), Energy-dispersive X-ray spectroscopy (EDX).

4. Results and Discussion

The XRD studies gives information about the structural and crystallinity of the synthesised nanocomposites. The Figure 1 shows the XRD pattern of the synthesized nanocomposites.

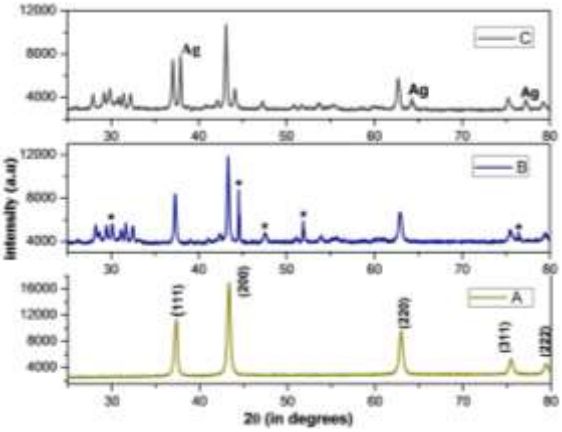

Figure 1: XRD Spectra of (A) Pure NiO (B) $Ni_{1-X}Gd_XO$ and (C) Ag doped $Ni_{1-X}Gd_XO$ nanocomposites.

In Figure 1(A) the diffraction peaks at 2θ = 37.35°, 43.37°, 63.01°,75.47° and 79.49° associated with the (111), (200), (220), (311) and (222) crystal planes are accounted for the presence of pure cubic NiO phase with lattice parameter a = 4.168 Å, which is in agreement with the reported value (JCPDS Card No. 47-1049).Thus obtained XRD pattern confirms the formation of pure cubic NiO and since there was no other diffraction peaks, it also confirms the purity of NiO phase. The average crystallite sizes (D in nm) of nanocomposites were determined from the XRD pattern using the Scherrer's equation i.e.

$$D = K\lambda / \beta\cos\theta$$

(Where, K is a constant equal to 0.89, λ is the X-ray wavelength equal to 0.154nm, β is the full width at half maximum and θ is the half diffraction angle). In Figure 1(B), we have observed some extra peaks which indicate the impurity-related diffraction peaks (marked with asterisk), signify the presence of

monoclinic Gd_2O_3phase, (JCPDS Card No. 42-1465) distorted the crystal structure of NiO lattice. Since the ionic radii of the Gd^{3+} ion (0.938A˚) is larger than that of the Ni^{2+} ion (0.69A˚), the increased concentration of Gd^{3+} ions brought the expansion of crystal lattice and consequently the peaks shifted towards lower 2θ values. In Figure 1(C) we observed extra peaks at 37.98^0 and 64.26^0compared to Figure 1(B), these peaks were characteristic peak of cubic metallic silver (JCPDS Card No. 04-0783) which indicates that silver get attached to the surface of the nanocomposites. And also we can observe from Figure 1(C) that the diffraction peaks were markedly broadened upon the addition of the RE-oxides and silver, thus resulting in the decrease in particle size. Moreover, the XRD pattern shows the existence of low intensity peaks below 35°, which could be related to the presence of the rare earth (RE) oxides in smaller amounts (Bahaa M. et.al., 2016). The EDX confirms the presence of silver nanoparticles in the synthesized nanocomposites. The average crystallite size, d-spacing, strain were calculated and tabulated in Table 1.

Table 1: Particle size, d-spacing and strain calculated from XRD pattern of Pure NiO, $Ni_{1-X}Gd_XO$ and Ag doped $Ni_{1-X}Gd_XO$ nanocomposites.

Sl. No	Sample	Particle Size in nm	d-spacing in A˚	Strain
1	**Pure NiO**	30.9536	2.0974	0.0030153
2	**$Ni_{1-X}Gd_XO$**	24.5422	2.0858	0.0037821
3	**Ag doped $Ni_{1-X}Gd_XO$**	19.7833	2.0861	0.0046924

The particle surface morphology and also size of the synthesized Ag doped $Ni_{1-X}Gd_XO$ nanocomposites were analyzed from TEM images. Figure 2(A) and 2(B) shows the TEM images of the synthesized nanocomposites. The images revealed that the obtained nanocomposites were polycrystalline in nature with spherical shaped nanocomposites and slightly agglomerated due to high temperature annealing (600°C), with the average particle size of 5-20nm, which is in good agreement with the particle size of the XRD pattern. The d-spacing value of the crystal planes was found to be 0.24 nm from the HRTEM image shown in Figure 2(C) and this also accord with the XRD values.

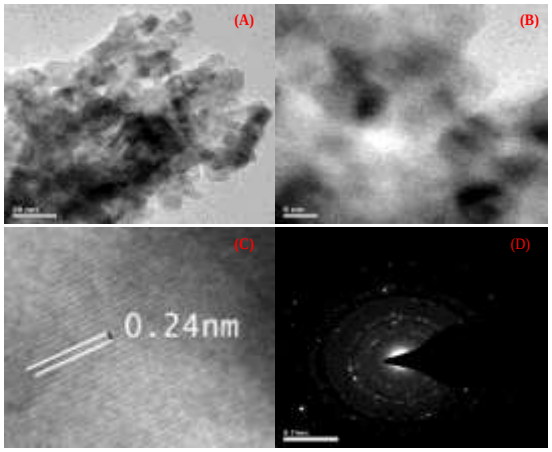

Figure 2: (A), (B) TEM Images (C) HRTEM Image and (D) SAED Spectra, of Ag doped $Ni_{1-X}Gd_XO$ nanocomposites.

Hence the as-synthesized nanocomposites, with small particle size, high dispersity and large specific surface area were promising material for biological applications (Okkyoung Choi et.al., 2008). A typical selected area electron diffraction (SAED) pattern of Ag doped $Ni_{1-X}Gd_XO$ nanocomposite is shown in Figure 2(D). The presence of concentric ring pattern in SAED is very much consistent with the (111), (200), (220) (311) and (222) planes of fcc-NiO structure and these SAED pattern results were in good agreement with the XRD studies.

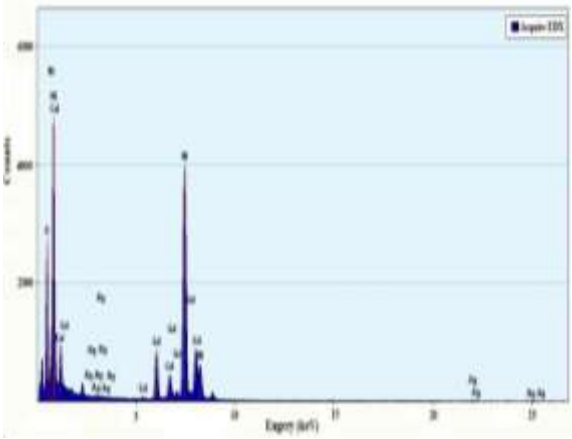

Figure 3: EDX Spectra of Ag doped $Ni_{1-X}Gd_XO$ nanocomposites.

The information about elemental composition of the synthesized nanostructures were analysed by EDX pattern. The Figure 3 shows the Energy-dispersive X-ray spectra of Ag doped $Ni_{1-X}Gd_XO$, which confirms the presence of Ni, Gd, Ag and O. There were no other impurity peaks which specify high purity of the synthesized nanocomposites. Thus EDX also confirms the formation of Ag doped $Ni_{1-X}Gd_XO$ nanocomposites.

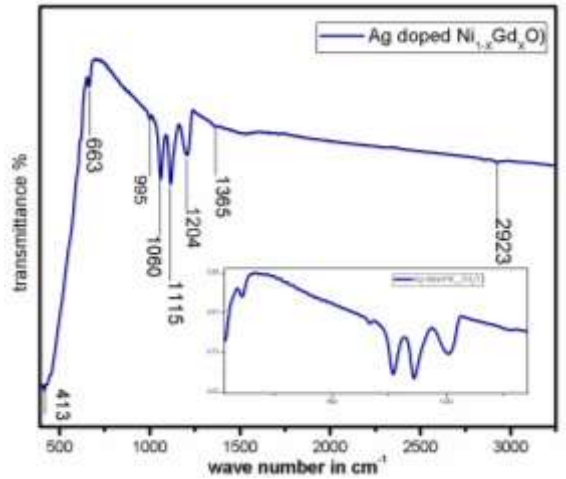

Figure 4: FTIR Spectra of Ag doped $Ni_{1-X}Gd_XO$ nanocomposites

Furthermore the formation and purity of the samples were confirmed by FTIR spectroscopy. FTIR analysis has been carriedout to determine the modes of vibrations of chemical bond and surface chemistry present in the prepared samples. Figure 4 shows the FTIR spectra of prepared nanocomposites. These spectra, illustrates an absorption peak at 413 cm^{-1} which was attributed to Ni-O phase, other peaks at 663 cm^{-1} and 995 cm^{-1}, corresponds to the metal–oxygen stretching. Two peaks at 1060 $cm^{-1}$and 1115 cm^{-1}, which could be attributed to the C–O stretching (Angel Ezhilarasi A.et.al., 2016) and another two absorption peak at 1210 cm^{-1} and 1365 cm^{-1}, is related to the metal carbonate structures (BeatrizCela et.al., 2011). The higher intensities of these peaks in rare earth containing nanocomposites could be due to their high ability to form surface carbonate structures (Bahaa M. et.al., 2016). And since there was no other absorption peaks in the FTIR it was confirmed that the prepared sample were free of the nitrate-group (2213–2034 cm^{-1}) (Dhananjaya N. et.al., 2012). These spectra confirm that combustion method is one of the efficient synthesis processes to fabricate impurity free nanocomposites.

5. Antibacterial Studies

All The Antibacterial resistivity studies of fabricated pure and doped nanocomposites were carried out using well-diffusion (Sondi I et.al., 2004; Ivask A et.al., 2014) method against gram-positive and gram-negative pathogens bacillus subtilis and Klebsiella pneumoniae. After the addition of nanocomposites to the agar plates containing pathogens, it was incubated at 37 °C for 16 hours, the different levels of zone of inhibition which emerges as a clear area around the wells was measured using a meter ruler, and the mean value for each organism was recorded and expressed in millimetres (mm). Here the zone of inhibition not only dependent on the nature of the nanocomposites used but also depends on the size and morphology of the nanocomposites. Smaller nanoparticles exhibit greater toxicity toward pathogens, as these nanoparticles expected to diffuse more easily relative to those of larger size (Sondi I et.al., 2004). Hence smaller the size of the nanocomposites higher will be the zone of inhibition, since it facilitates the nanocomposites to pass through the cell wall of the pathogens efficiently and resulting in formation of ROS. The negative charge on the cell wall interacts with the positively charged metal nanoparticles resulting in the formation of ROS (Ivask A et.al., 2014), which will responsible for damage of cell membrane resulting in the death of the bacteria and correspondingly shows the antibacterial activity..

Figure 5: Antibacterial activity of (A) Pure NiO, (B) $Ni_{1-X}Gd_XO$, (C) Ag doped $Ni_{1-X}Gd_XO$ nanocomposites and control (ampicillin) against (a) Bacillus subtilis and (b) Klebsiella pneumoniae.

Table 2: Zone of inhibition in millimetre (mm) of Pure NiO, $Ni_{1-X}Gd_XO$ and Ag doped $Ni_{1-X}Gd_XO$ nanocomposites against (a) Bacillus subtilis and (b) Klebsiella pneumoniae.

Name of the compound	Concentration	Organism used	Zone of inhibition (mm)
Pure NiO (E-2 A)	(50μg/ 1ml)	(a) B.Subtilis	10±0.8
		(b) K.pneumoniae	9±0.5
$Ni_{1-X}G_XO$ (E-2 B)	(50μg/ 1ml)	(a) B.Subtilis	11±1.0
		(b) K.pneumoniae	10±0.7
Ag doped $Ni_{1-x}G_XO$ (E-2 C)	(50μg/ 1ml)	(a) B.Subtilis	12±1.2
		(b) K.pneumoniae	10±0.8
CONTROL Ampicillin	(50μg/ 1ml)	(a) B.Subtilis	17±0.4
		(b)K.pneumoniae	17±0.3

The Figure 5 and Table 2, shows the zone of inhibition of the synthesized pure NiO, $Ni_{1-X}Gd_XO$ and Ag doped $Ni_{1-X}Gd_XO$ nanocomposites. Here all the synthesized nanocomposites showed good antibacterial zone of inhibition over the pathogens Bacillus subtilius and Klebsiella pneumonia. But compared to pure NiO nanoparticles and $Ni_{1-X}Gd_XO$

nanocomposites the Ag doped $Ni_{1-X}Gd_XO$ nanocomposites showed highest zone of inhibition (12±1.2 mm) on Bacillus subtilius, it may be due to smaller size and composition of the nanocomposites which facilitates to diffuse through the cell wall to induce toxicity**.** Thus Ag doped $Ni_{1-X}Gd_XO$ emerged as a good antibacterial agent.

6. Conclusions

The Ag doped $Ni_{1-X}Gd_XO$ nanocomposites have been synthesized by auto-combustion route and this synthesis method played a vital role in controlling size and to maintain purity of the nanocomposites. The synthesized nanocomposites were characterized by XRD, TEM, EDX and FTIR analytical techniques. XRD confirms the fcc phase and formation of metallic silver. The average particle size is found to be 5-20 nm and the composites were polycrystalline in nature. The TEM showed slightly agglomerated spherical shaped nanocomposites and d-spacing value was found to be 0.24 nm. The EDX and FTIR studies confirmed the purity of the synthesized nanocomposites. Antibacterial activity was performed using well diffusion method. The Ag doped $Ni_{1-X}Gd_XO$ nanocomposites showed an efficient antibacterial activity over the pathogens Bacillus subtilis and Klebsiella pneumoniae. Enhanced antibacterial activity of Ag doped $Ni_{1-X}Gd_XO$ nanocomposite was attributed to the active formation of reactive oxygen species (ROS) by reacting with cell wall. This confirms that these nanocomposites have potential to interact with cell wall of the bacteria and by synergistic effect can cause damage to cell membrane, resulting in death of the pathogens. Thus these nanocomposites were efficiently reduced bacterial growth and played vital role as antibacterial agent. In future, these nanocomposites can be further analysed for cancer therapy and as contrast agents in MRI techniques.

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