DEVELOPMENT OF SILVER-GRAPHENE OXIDE NANO-COMPOSITES FOR FABRICS AS AN ANTIMICROBIAL FINISH.

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Abstract : Present report discusses the silver decorated graphene oxide (Ag-GO) nano-composites and its antimicrobial activity on fabric. Nano silver (AgNPs) were pre-synthesized using clove extract as reducing agent. Biogenically prepared AgNPs were anchored on GO surface and characterized by X-ray diffractogram (XRD), and field emission scanning electron microscope (FE-SEM) that indicates the uniform decoration of GO with fine metallic AgNPs. Synthesized nano-composites of Ag-GO were investigated for their antimicrobial activity against Klebsiella pneumoniae and Staphylococcus aureus by AATCC 100-2012.

Keywords: Silver nanoparticles, Graphene oxide, Ag-GO nano-composites, Antimicrobial activity

I. INTRODUCTION

Bacterial contamination consequences the spreading of epidemic disease, infections, retreating material strength used in heat exchangers, medical tools and marine applications [1-6]. Therefore, control or avoid the growth of destructive microorganisms is challenging task in view of health and technological persistence. Several nano-structural materials like AgNPs, TiO_2, ZnO and CuO successfully showed their potential bactericidal role [7-16-17] AgNPs binds with sulfur containing binding site of DNA and blocks the DNA replication and hence restrict the bacterial growth [18]. However, AgNPs lacks with long term bactericidal activity due their aggregation. Many attempts have been made to overcome this difficulty by anchoring the AgNPs on rigid support to avoid the agglomeration. Notable examples of the support used included carbon nano tubes (CNTs), reduced graphene oxide/graphene oxide (rGO/GO), alluminosilicate clay, mesoporous silica [19-26]. Investigations further demonstrated that support extend the provision to tune the morphology and density of anchored AgNPs due to which antimicrobial activity found to be altered [27]. Among the aforementioned supports, GO is known to enhance bactericidal activity of resultant hybrid material. GO itself shows bactericidal activity that relies on its physico-chemical interaction with pathogens through many possible mechanisms as (1) atomically sharp edges of GO damage the cell membrane followed by RNA leakage that leads to death [28-31], (2) Wrapping of GO sheet around micro-organism colony restrict its growth [32-34], Liu et al (2011) demonstrated that functional groups on graphitic sheet create oxidative stress due to which it possesses antibacterial activity [35]. Later on Mangadlao et al (2015) illuminated that basal plane oxygen functionalities of GO damages the cell membrane of pathogens [36]. It has also been demonstrated that increase of defects in GO enhances the anti-bacterial activity [32]. It is worth to mention here that bactericidal activity of GO mainly relied on surface oxygenated functionalities. Therefore, combination of AgNPs and GO through composite formation leads to an enhanced bactericidal activity.

In this research work, we developed AgNPs by the green route with the help of clove extract, and AgNPs deposited on Graphene oxide. The prepared Ag-GO nanocomposites were coated on polyester fabric and studied the antimicrobial property of fabric.

II. EXPERIMENTAL

2.1 Material:

Graphite powder was purchased from Loba chemicals Pvt. Ltd. and Potassium paramagnet was procured from Qualigens fine chemicals. The required chemicals like Sulfuric acid, hydrogen peroxide, hydrochloric acid, ether and silver nitrate were procured from Merck Specialties Pvt. Ltd. Ethanol was purchased from Changshu Yangyuan chemical China.

2.2 Synthesis of Graphene Oxide:

Graphene oxide was prepared by chemical oxidation technique. [33]. Concentrated H_2SO_4/H_3PO_4 mixture was taken in 9:1 ratio in round bottom flask along with graphite flakes 3 gm and $KMnO_4$ 18 gm was added slowly in acid mixture of graphite flakes. The reaction mixture was heated upto 50 °C for 12 h. Reaction mixture was cooled to room temperature and poured in ice cool water (400 mL) containing H_2O_2 (3 mL). Filter the reaction mixture was filtered polyester cloth. Filtrate was centrifuged and washed the product with water, HCl, and ethanol and dried overnight at room temperature.

2.3 Preparation of Silver Nanoparticle:

Silver nanoparticles was prepared by green route synthesis by using pure clove extract which act as reducing agent. Clove extract solution was made by drenched 5 g of clove in 100mL distilled water, red color solution obtained was filtered and filtrate was used for the synthesis of silver nanoparticles. The freshly prepared clove extract 1 ml was added into freshly prepared 100ml $AgNO_3$ solution (0.5mM) and kept untouched for 1hr. The color of the solution was gradually converted from colorless to reddish brown.

2.4 Preparation of Ag-GO Nano-composite:

Aqueous disperson of Graphene Oxide was prepared by dispersing 0.5 g in 100ml distilled water through stirring and sonication. The prepared silver nanoparticles solution 10 ml was added drop-wise to GO dispersion using pressure equalizing funnel with continuous stirring and sol was stored at room temperature.

2.5 *Preparation of Ag-GO Nano-composite coated fabric:*

The aqueous dispersion of Ag-GO Nano-composite was prepared by dispersing 1 gram per liter with acrylic binder. The fabric was kept in Ag-GO Nano-composite dispersion for seconds and padded and cure at 70ºC. The pure also AgNPs were coated on fabric same above stated procedure.

2.5 Antimicrobial activity:

2.5.1Antibacterial Finishes test on Textile Materials:

Sample swatches were stacked and placed into sterile containers. The number of swatches to be tested was determined by the number of swatches that could absorb 1.0 ± 0.1 mL of inoculums without leaving any free liquid. One (1.0) mL of the 105 CFU/mL inoculum was placed onto the top swatch and allowed to wick through the sample stack. The inoculated swatches were incubated for a specified contact time. At the appropriate contact time, neutralizing broth was added to each container and the containers were shaken for 1 minute to release the inoculum from the test swatches and into the neutralizing broth. Serial dilutions were made and the plates incubated. After incubation, colonies of recovered are counted and used to determine percent reduction.

Fabric sample preparation: The samples were cut in circular swatches 4.8 ± 0.1 cm in diameter, from the coated fabric. The number of swatches to be used is dependent on the fiber type and fabric construction.

2.6. Characterization:

The synthesized of AgNPs and Ag-GO nano-composites were observed by recording the UV-Visible spectra using spectrophotometer (Cary60 UV-VIS spectrophotometer) on respective sol. The Crystallization nature of products was determined using Bruker, D8 ADVANCE (Bruker Corporation, Tokyo, Japan) make X-ray powder diffractometer (XRD). The Surface morphology was observed using Scanning Electron Microscope. The The functional moties of prepared composite material was investigated using Fourier Transform Infra-red (FTIR) spectroscopy.

III. RESULTS AND DISCUSSION:

AgNPs using clove extract reduction and its subsequent deposition on GO surface was observed by UV−Vis spectra and depicted in figure 1. Representative UV- visible spectra AgNPs sol and its addition to GO suspension displayed well resolved absorbance band *ca*. 434 nm which suggests the presence of AgNPs in both the sols. Symmetrical shape of SPR indicates the small and

uniform size of AgNPs. The absorbance was increased with increase in concentration of Ag^+ ions used during synthesis of AgNPs and attributed to an increase in particle density on GO surface.

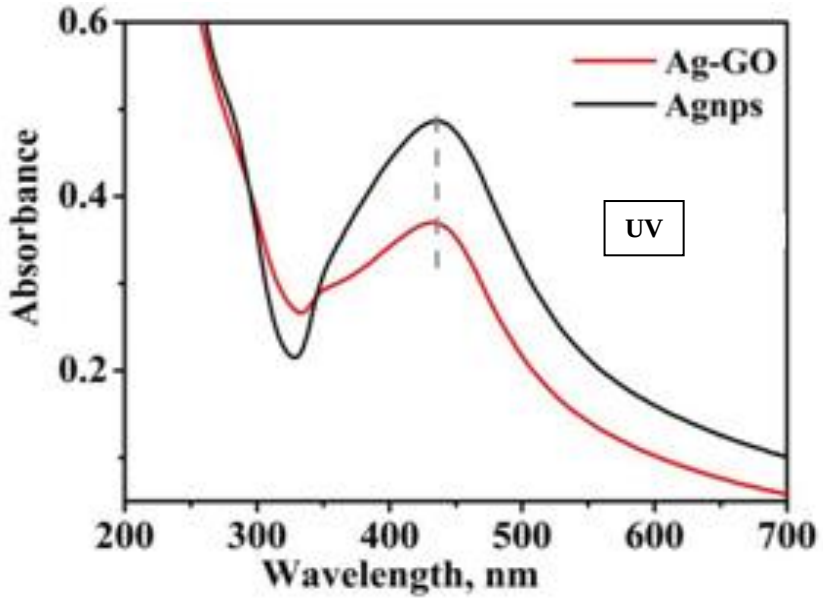

Figure 1: UV-Visible spectra of AgNPs and GO-AgNPs nano-composites

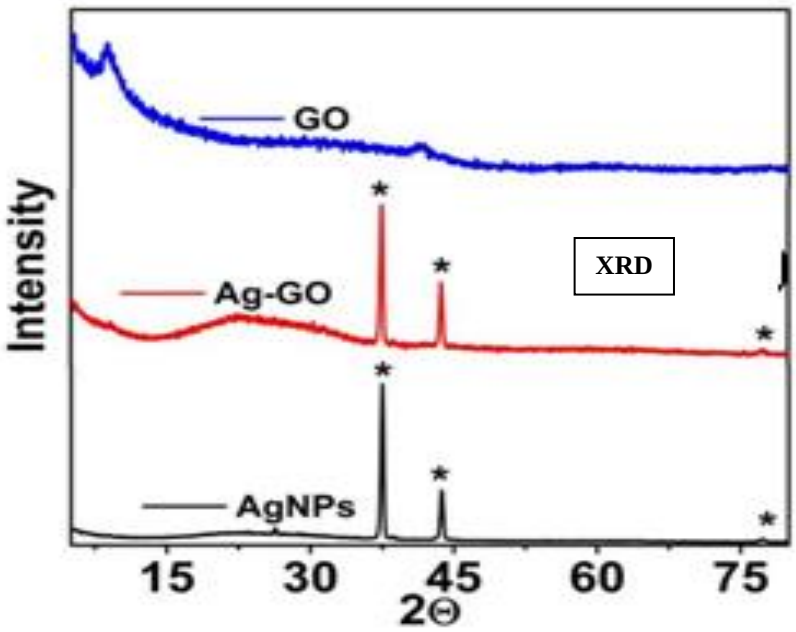

Figure 2. X-ray diffractogram of AgNPs, Ag-GO nano-composites and GO.

Crystallization nature of synthesized GO, AgNPs and Ag-GO nanocomposite was evaluated by XRD and depicted in Figure 2. For GO, broad diffraction pattern at $2\Theta = 8.4^o$ is indexed to [001] plane corresponds to *d*-spacing ~1 nm. Presence of oxygen-containing functional groups and defects induced roughness on graphene sheets causes the broadening of diffraction peak of the GO [34]. In case of AgNPs and Ag-GO, observed diffraction patterns at 37.5^o, 43.7^o and 77.1^o are indexed to the [111], [200] and [311] planes of cubic phase metallic Ag (JCPDS No. 04-0783) and confirmed the presence of silver. Feeble pattern at higher diffracting angle suggests the fine size AgNPs. An absence of diffraction peak of GO for nano-composite attributed to an increase in exfoliation of GO sheet due to incorporation of AgNPs.

Figure 3 depicted the representative SEM images of Graphene Oxide and GO-AgNPs. Sheet like structure of GO with curled, corrugation due to flexibility of GO sheet and approximate dimensions of few tens of um^2 is observed. Very fine AgNPs uniformly distributed on GO sheet is observed in FE-SEM image of Ag-GO. Approximate particle size obtained from image is ~ 10-12 nm. Few bigger particles are also seen, which may be due to the agglomeration of pre-formed AgNPs during deposition. Formation of AgNPs can be described based on reduction of Ag^+ by eugenol, major ingredient of clove and also known for its anti-oxidant property [35].

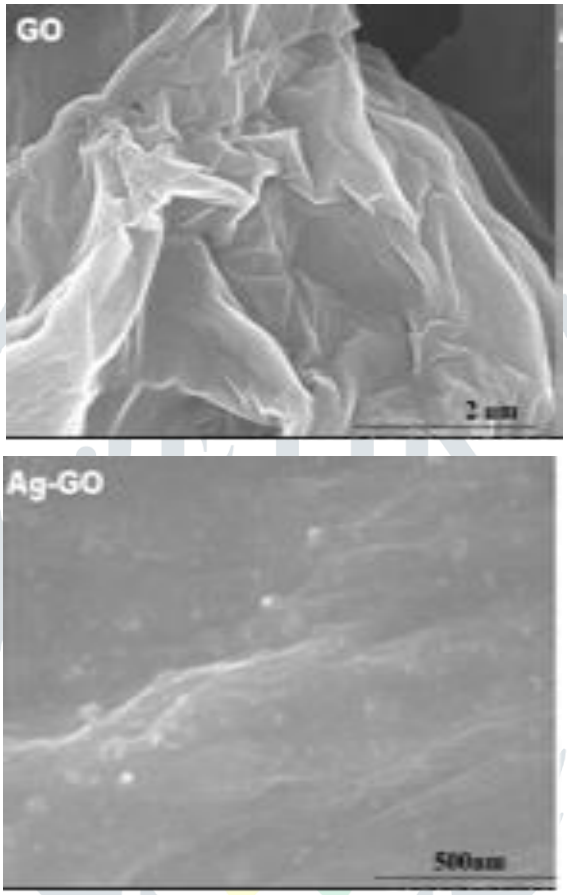

Figure 3: SEM images of GO and GO-AgNPs nano-composites.

GO was studied by FTIR spectroscopy and depicted in Figure 4. GO shows characteristics vibration bands at 3400 cm^{-1}, broad peak at 1715 cm^{-1}, 1510 cm^{-1} and 1145 cm^{-1} for hydroxyl, C=O of carboxylic acid and carboxylic ester, respectively. In case of Ag-GO hydroxyl peak disappeared with emergence of new band at 3130 cm^{-1}, which we attributed to the C-H (aromatic) stretching frequency of eugenol.

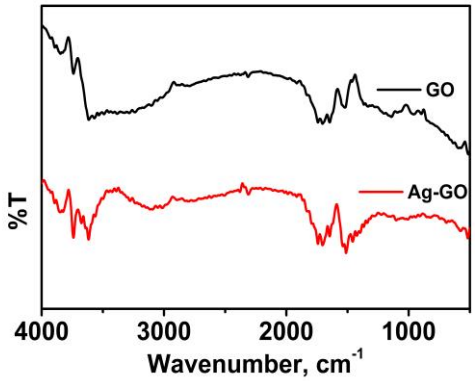

Figure 4: FTIR spectra of GO and GO-AgNPs nano-composites.

However, presence of weak vibration band C=O in Ag-GO suggest the perseverance of oxygenated functionalities after deposition of AgNPs. Based on above results it is concluded that fine AgNPs are uniformly anchored on the GO sheet through interaction with oxygenated functionalities present on GO.

Antimicrobial Study:

The antimicrobial study of fabric was carried out by AATCC 100-2012, polyester fabric sample was coated with AgNps and Ag-GO nanocomposite. The results showed Ag-GO nanocomposite coated fabric was have enhanced antimicrobial property than AgNps coated fabric.

Bacterial reduction % calculated by formula

100(B-A)/B= R

R= % Reduction

A = no. of bacteria recovered from the inoculated treated test specimen fabric in the jar incubated over the desired contact period. i.e 24 hrs

B = no. of bacteria recovered from the inoculated treated test specimen fabric in the jar incubated immediately after contact (0 period)

The results have been made after 24 hrs. of incubation.

Sample	Bacterial Reduction,(%)	
	Klebsiella Pneumoniae ATCC 4352	*Staphylococcus aureus ATCC6538*
Neat Fabric	0.00	0.00
Fabric coated with AgNPS	79.88	76.72
Fabric coated with Ag-GO nanocomposite	99.60	99.56

Table1. Antimicrobial performance of fabric

IV. CONCLUSION:

Ag-GO nano-composites were prepared through green rout synthesis. AgNPs were biologically prepared by ex-situ reduction using clove extract and deposited on GO surface. Surface oxygen functionalities on GO provides the anchoring sites for the AgNPs. Ex-situ synthesis technique helps for perseverance of the surface oxygenated Antimicrobial activity of Ag-GO nano-composites coated fabric was studied against the *Klebsiella Pneumoniae* and *Staphylococcus aureus* which showed an enhanced activity than AgNPs.

V. ACKNOWLEDGEMENT:

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