# Review Paper: Comparative Study of Conducting and Antimicrobial Behaviour of Graphene and Silver based Nano-Materials

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## Abstract

Instantaneous and ravid developments in nanotechnology stimulated innovative ideas across many fields of day-to-day life. Carbon-based nanomaterials have developed many platforms for an extensive range of applications due to their unique mechanical, electrical and biological properties. Nanoparticles of noble metals and their compounds are also playing an enormous role in many aspects of our life i.e. medical devices, pharmaceuticals, polymer industry, biomedical field, coating of kitchen appliances, food packing, clothes and gifts. Silver and carbon-based nanoparticles are being used diversely in food. fitness and health care, therapeutic, manufacturing and optical devices industries due to their distinctive chemical and physical characteristics.

This study provides a short review of antibacterial and conducting activities of graphene and silver nanoparticles (AgNPs) both.

These are well known conducting nanomaterials applied in many areas and a wide literature is available on these characteristics. Thermal conducting behaviour of both materials also has a noteworthy standing. Thus, it becomes interesting to utilize these features to create new composite materials with improved electrical, thermal and antimicrobial properties; comparative study is also an interesting field to do innovations. **Keywords**: Graphene, silver nanoparticles (AgNPs), antibacterial agent, conductivity.

#### Introduction

Antimicrobial activities of silver nana particles against bacteria, fungi, protozoa and certain viruses including antibiotic resistant strains<sup>11,110</sup> have been studied. AgNPs have been used since Roman time<sup>109</sup> and are greatly influenced by the dimensions (shape and size) of the particles. Size of the particles is inversely related to the antimicrobial behaviour<sup>87</sup>. Further, Yamanaka et al<sup>128</sup> showed antimicrobial effects of AgNPs on S. aureus and E. coli both. Antimicrobial polymers have tested against grampositive and gram-negative bacteria, viruses, yeast and fungi<sup>63</sup>. The AgNPs show electrical properties, optical properties, biological properties, thermal conductivity44 are effectively inactivate and kill a broad range of microbes<sup>51,102,103,104</sup>. The antibacterial activity represents the activity of the material that destroys or reduces bacterial growth, without employing toxicity to the tissues<sup>41</sup>.

Several investigations have reported that the parameters involved in the antibacterial activity of AgNPs are a combination of both physical and chemical features such as size, shape and surface-volume ratio of the nanoparticles, as well as their method of synthesis<sup>2,31</sup>. Numerous nanomaterials have been studied with respect to antimicrobial properties and the best-known example is AgNPs. Pictorial representation of some highly useful nanomaterials being used for antimicrobial treatment is given in figure 1. They are also being used in many other research and innovation fields for decay.



Figure 1: Pictorial representation of some very useful nanomaterials being used for antimicrobial treatment



Figure 2: a) Fullerene 0D, b) Carbon nanotube 1D, c and d) Graphene 2D, e) Graphite 3D, f) Diamond like carbon 3D and g) Graphane 3D<sup>1,13,33,66,71</sup>

Green synthesis of AgNPs is the main interest of researchers as it is considered an ecofriendly method. A study has demonstrated that *A. indica* juice can reduce silver nitrate to polydispersed spherical nanoparticles with a size range of  $5-25 \text{ nm.}^{101}$ 

Self-linking capacity i.e. catenation tendency is unique property of carbon, which is responsible to form many allotropes of carbon. Carbon nanostructures (CNSs) such as fullerene 0D, carbon nanotubes (CNTs) 1D, graphene 2D, diamond-like carbon 3D (DLC) and graphane 3D (figure 2) have been recognized to have antibacterial activities toward pathogens, excellent electrical conductivity, supreme strength, conductivity. mechanical high thermal extraordinarily high area and excellent surface photoluminescent properties.1,13,33,66,71

Among all the CNSs, graphene and its derivatives are broadly being used and applied in approximately every field of science, technology and engineering. Recent researches, innovations and applications are indicating that graphenebased materials have great effect on electronic and optoelectronic devices, chemical sensors, nanocomposites, energy storage and antimicrobial behaviour and achieving a great attention since 2004<sup>91</sup>. Graphene is a material composed of pure carbon, similar to graphite but with characteristics that make it extraordinarily light and strong. A sheet of one square meter of graphene weighs 0.77 milligrams. Its strength is 200 times greater than that of steel and its density is similar to that of carbon fibre<sup>45</sup>.

One of the best-known graphene derivatives of monocrystalline graphitic and monatomic thick films was synthesized and named graphane (sp<sup>3</sup> hybridized, three-

dimensional hydrogenated graphene). Graphene layer has thickness of only 0.34 nm and sp<sup>2</sup> hybridized covalently bonded one carbon atom attached to three other carbon atoms arranged in a hexagonal honeycomb lattice<sup>26,35,43,46,62,107,108</sup>. The applications in high carrier mobility<sup>80</sup>, chemical sensors<sup>90,21</sup>, nano electronic devices<sup>97</sup>, hydrogen storage systems<sup>18</sup> are due to the unique structural, mechanical and electrical properties of graphene.

Graphane is reported much stable structure than graphene having C atom sp<sup>3</sup> -bonded to one H atom above and below<sup>125</sup>. Graphene to graphane formation indicates electrical conductor, to a semiconductor and electrical insulator transformation<sup>136</sup>. Graphene-based nanomaterials such as pristine graphene (pG), graphene nanosheets (GNS), graphite (Gt), multilayer graphene (MLG), graphene oxide (GO) and reduced graphene oxide (RGO) have been reported. Studies show that under similar conditions, GO shows the highest antibacterial activity toward *P*. *aeruginosa* followed by rGO, Gt and GtO. Antibacterial action of graphene oxide and reduced graphene oxide against *P. aeruginosa*, *E. coli* and *C. albicans* was also reported<sup>40,115,134</sup>.

Both graphene and silver nanoparticles are well known conductive nano materials previously applied in many areas and widely studied, although electrical properties in both materials show a significant difference and thus it becomes interesting to compare both and utilize their features to create materials with improved electrical properties. Electrical properties of graphene are utilized in areas like display technologies, energy storage devices, transistor technology, surface technologies etc.<sup>17</sup> Some toxic effects of AgNPs are also reported<sup>7,57</sup>. Although there is extensive debate on the toxicity of graphene, a comprehensive study of it was given by Lalwani et al<sup>61</sup>.

## **Electrical Conducting Behaviour of Graphene**

In graphene, the conduction and valance band meet at the dirac points, it has very high electrical conductivity thus making it a zero-gap semiconductor<sup>27</sup>. This 2D, one atom thick material shows high electronic quality since the mobility( $\mu$ ) of charge carriers is remarkably high and for single layer graphene at low temperature, values upto 20,000  $Cm^2/Vs$  have been raported<sup>35,83,133</sup>. It is also proved that electron mobility is nearly independent of temperature<sup>76</sup>. These electronic properties in graphene are due unique structure. In graphene, carbon atoms form a hexagonal lattice and keep a distance of 1.42Å from each other. Three neighboring carbon atoms are joined by three  $\sigma$  bonds with central carbon atom and fourth one is a  $\pi$  bond and each atom has one of these  $\pi$  bonds. The  $\pi$  band and  $\pi^*$  band are responsible for almost all electronic properties of graphene is formed by the hybridization of these  $\pi$  bonds.<sup>27</sup>



Figure 3: Hexagonal lettice of graphene monolayer with white and black circles indicating carbon atoms<sup>75</sup> (Copyright © 2011, Springer-Verlag Berlin Heidelberg)

2D honeycomb crystal structure of carbon atoms (figure 3) is a fair expression of monolayer graphene sheet<sup>75</sup>. Thus, electrical conductivity of graphene can be controlled by changing the availability of  $\pi$  bonds, we can see significant changes in conductivity when graphene is oxidised to form graphene oxide<sup>3</sup>. Electrical properties will also change

significandly with the number of graphene layers and crystal structure<sup>38,50</sup>. Different forms of graphene-nanomaterial like graphene-nanosheets, graphene-nanoribbons, graphene-nanoflakes etc. are proved to be effectieve to make composite materials with unique electrical properties<sup>17</sup>.

Electrical Conducting **Behaviour** of Silver **Nanoparticles:** Electrical conductance by silver nanoparticles is due to the availiability of free electrons since it is a mettalic atom. Conductivity in silver nanoparticles can be altered by changing the size ,structure, crystallinity and composition<sup>9,49</sup>. Nano sized metal particles show notably different physical and chemical properties compared to their bulk counterparts. This is mainly because of increased surface area and this leads to extensive uses mainly in the areas of catalysis and sensing<sup>64,69</sup>.

Conductive nature of silver-nanopowder is extremely useful since it is used to make conductive inks, pastes and adhesives for various electronic devices<sup>67</sup>. Experiments conducted by Park et al<sup>85</sup>, Chen et al<sup>23</sup> and Liu et al<sup>68</sup> proved the effectiveness of using silver nanoparticles in electronic applications. One dimensional silver-nanoparticles like silver-nanowires with size range 45nm–110nm in diameter and pitch of 500nm–1000nm are found to be extremely effective in optical electronic devices and similar conductive transparent applications due to its optical transmission upto 91%. Figure 4 shows (a) silver-nanowire networks, (b) SEM images of uniform network, (c) contact area of the wire network and the electrical contact pads and (d) AFM measurements.<sup>118</sup>

The electrical properties of silver nanoparticles can also be modified by making composites with other materials. The experiments conducted by Xin et al<sup>127</sup> proved that electrical conductivity of carbon nanotubes decorated with silver nanoparticles is more than normal materials. Similarl study was conducted by Nam et al<sup>78</sup> revealed the increase of electrical conductivity by 8 times after introducing silica to silver nanowire/polymer nanocomposites.



Figure 4: (a) Sketch of silver nanowire networks. (b) SEM image of the  $\Lambda = 500$  nm, w = 55 nm network showing the uniformity of the network over a large area. (c) SEM image showing the contact area of the wire network and the electrical contact pads. (d) Height profile (colour bar) of the  $\Lambda = 500$  nm, w = 55 nm network obtained from AFM measurements, (© 2012 American Chemical Society)<sup>118</sup>.

Electrical properties of silver nanoparticles are also suitable for applications in various types of sensors<sup>120</sup>. Studies conducted by Rivero et al<sup>92</sup> revealed the high efficiency of sensors created by incorporating silver nanoparticles. Human breathing sensor is created and silver-nanoparticles got synthesized *in situ* in the layer-by-layer coating of the polymeric matrix. AFM figures ( $20\mu m \times 20\mu m$ ) in tapping mode of height and phase represented in figure 5.<sup>92</sup>

Flexible films of polyvinylpyrrolidone (PVP)/ nanofibrillated cellulose (NFC)/Silver nanoparticles (AgNPs) were prepared and analysed for improved flexibility, microscopic structure, mechanical properties, tensile properties and electrical conductivity by Khalil et al<sup>53</sup> with *in situ* formation of AgNPs in PVP matrix conformation by TEM and UV–Vis techniques. NFC isolated from rice straw pulp is used to make ecofriendly films; the reduction of AgNPs is represented in figure 6. Preparation of nano-fibrillated cellulose (NFC) is obtained by pulp of rice straw. The bleaching of pulp was done according to Wise et al.<sup>126</sup> Determination of chemical composition was according to Browning<sup>19</sup> and oxidised according to Hassan et al<sup>42</sup>. Standard polyvinylpyrrolidone (PVP) purchased from Alfa Aesar was used for this study.

Nanocomposite films of PVP/ NFC /AgNPs in the ratio of 25/75/2 at 30°C temperature showed electrical conductivity within the range of  $2.36 \times 10^{-10}$  S/cm– $1.5 \times 10^{-6}$  S/cm. This is the best range to prepare sensitive electronic packing components, antistatic and electrostatic dissipative materials<sup>53</sup>.



Figure 5: Random distribution of synthesized AgNPs inside polymeric coating, AFM figures (20µm X 20µm) in tapping mode of height and phase<sup>92</sup>



Figure 6: Synthesis of reduced AgNPs from AgNO<sub>3</sub><sup>53</sup>.

**Antimicrobial Behaviour of Silver Nanoparticles** (AgNPs): Shahverdi et al<sup>100</sup> have synthesized AgNPs from novel strain of *Streptomyces sp.*; zone of inhibition seems extremely upright showing a relatively large zone of inhibition in both gram positive (*S. aureus, S. epidermidis*) and gram negative (*E. coli, S. typhi, P.aueroginosa, K. pneumonia, P. vulgaris*) by well diffusion method shown in table 1 and proved that the silver nanoparticles synthesized

from *Streptomyces species* seem to be promising and effective antibacterial agent against the multidrug resistant strains of bacteria<sup>105</sup>.

Although AgNPs synthesized from *B. subtilis* by Tariq et  $al^{112}$  showed the potential to act against pathogenic *B. substilis*strains. Size and an ideal peak at 426 nm were analyzed by SEM and UV. Additionally, size distribution analysis has confirmed the single population of the particle with size around 80 nm. These particles were much effective against various pathogenic drug-resistant strains table 1.

The electro-spun PAN nanofiber membranes were successfully coated with AgNPs through *in situ* reduction of Ag<sup>+</sup> ions by a successive wetting process in AgNO<sub>3</sub> and NaOH solutions under physiologically mild conditions. Antibacterial activity against both gram-positive and gramnegative bacteria for the formed PAN-AgNP<sub>s10</sub> membrane was confirmed best and can be used for antibacterial masks, chemical and biological protection and biomedical devices as depicted in table  $2^{54}$ . By bio-reduction methods (Ag<sup>+</sup> to Ag<sup>o</sup> from AgNO<sub>3</sub> solution within 30 min) using aqueous leaves extract of *Hibiscus Rosa-Sinensis (HRS)* and confirmed by UV–Vis. spectroscopy and FTIR, AgNPs were synthesized.

In this study, antibacterial activity against *S. aureus* was better than *E. coli*<sup>106</sup>. AgNPs of different size were

synthesized by sodium borohydride as a reducing agent in ultrasonic field and tested against *S. aureus*, *B. subtilis*, *S. mutans*, *E. coli* and *P. aeruginosa*. AgNPs were most effective against *E. coli* and *B. subtilis*. They seemed to be much sensitive towards size of AgNPs as in table 3a and 3b.<sup>117</sup>

Copolymer membranes of PAN having AO (amidoxime) content were immobilized with NS particles. UV-Vis data showed the wavelength rage of 380-450 for the synthesis of AgNPs. TEM analyses the morphological characteristics i.e. size and shape of NS. The antimicrobial activities of virgin as well as various NS containing samples were examined against gram positive bacteria *S. aureus* and gram-negative bacteria *E. coli* by the estimation of the number of viable colonies. This indicated that the NS penetrates within the swollen AO membranes and stays back. It can be seen that on an average, number of viable *S. aureus* and *E. coli* colonies decreased by 95% for both cases as compared to virgin AO 3.5 membrane as in figure 7 and 8<sup>111</sup>.

Silver nanoparticles obtained using *Pinus thunbergii* (Japanese black pine) cone extracts exhibit antibacterial activity against various gram-positive and gram-negative agricultural pathogens such as *Pseudomonas syringae*, *Xanthomonas oryzae*, *Burkholderia glumae and Bacillus thuringiensis*<sup>119</sup>. Crystalline AgNPs as having various uses in nanomedicine were synthesised by utilizing the root extract of *Helicteresisora*. Yellow to reddish brown colour transformation was observed during the synthesis. Capping of oxidized polyphenols and carboxyl proteins were responsible for the extended stability of nanoparticles. Morphology and size were also determined. The techniques used for the confirmation were UV–visible spectroscopy, TEM, X-ray diffraction and FTIR.

Zone of inhibition (mm) of pathogenic microbes <sup>112</sup> .			
S.N.	Organism	Zone of	
		inhibition (mm)	
1	S. typhi	40	
2	S. epidermidis	38	
3	S. aureus	36	
4	Pseudomonas	35	
	aeruginosa		
5	Proteus vulgaris	34	
6	E. coli	34	
7	Klebsiellapneumoniae	30	

 Table 1

 Zone of inhibition (mm) of pathogenic microbes<sup>112</sup>.

Table 2The characterization of formed PAN-AgNPs nanofiber membranes54.

	PAN-	PAN-	PAN-
	AgNPs1	AgNPs10	AgNPs100
Diameter of nanofibers	$293.37 \pm$	$279.25 \pm$	$285.48\pm49.26$
(nm)	54.65	42.94	
Size of AgNPs (nm)	$25.37 \pm 8.54$	$21.35\pm4.83$	$20.27\pm3.84$
Amount of AgNPs (wt%)	$8.40\pm2.60$	$11.27\pm3.53$	$14.22\pm3.22$

	a)			
Organism	m Zone diameter (mm)			
	15 µL/disc	20 µL/disc	25 µL/disc	
S. aureus	Not found	Not found	Not found	
B. subtilis	7	9	11	
S. mutans	7	9	9	
E. coli	Not found	7	9	
P. aeruginosa	Not found	Not found	7	

Table 3Antimicrobial efficacy of AgNPs of diameter a) 32 nm b) 20 nm<sup>117</sup>.

<b>b</b> )					
Organism	Zone diameter (mm)				
	15 µL/disc	20 µL/disc	25 μL/disc		
S. aureus	Not found	7	7		
B. subtilis	12	13	14		
S. mutans	7	9	11		
E. coli	9	11	13		
P. aeruginosa	Not found	Not found	7		



Figure 7: Particle size distribution histogram of NS<sub>R60</sub> evaluated from TEM images<sup>111</sup>



(a) (b) Figure 8: a) TEM image of NS<sub>R60</sub> b) UV-vis absorption spectra of NS solutions<sup>111</sup>.

Additionally, antioxidant and antibacterial behaviour were observed and it was concluded that potential antioxidant and antibacterial AgNPs can be produced for commercial and medicinal application<sup>16</sup>. Silver-nanoparticles were synthesised using aqueous extract of *Morus alba* (mulberry) leaves by Das et al<sup>28</sup> and reported as potential antibacterial and antioxidant agent. SPR peak in the range of 423–450 nm confirmed the formation of nano-species. Spherical shaped and 12-39 nm sized, (SEM, TEM and HR-TEM), possible reducing and capping compounds (FTIR), desirable crystalline orientation (XRD) and zeta potential of + 37.4 mV (DLS) were analysed.

Bactericidal effect was analysed for gram positive (*B. megaterium ATCC 14581, S. aureus ATCC 11632* and *B. subtilis ATCC 11774*) and gram negative (*E. coli ATCC 11229* and *S. typhimurium ATCC 25241*) both. However, highest behaviour was against *S. typhimurium* with MIC 40  $\mu$ g/ml. Additionally, dose dependent antioxidant behaviour of AgNPs against DPPH, ABTS<sup>+</sup>, superoxide and nitric oxide free radicals and significant metal chelating behaviour was performed<sup>28</sup>.

Saxena et al<sup>95</sup> reported the synthesis of AgNPs (33.6 nm average mean size) by using *Allium cepa* extract, characterisation was done by UV-vis, DLS (Dynamic Light Scattering) and TEM. The studies for *E. coli* and *S. typhimurium* were in  $50\mu$ g/ml concentration of AgNPs reported to be effective against bactericidal effect.

Mycosynthesis of AgNPs was reported byAzmath et al<sup>8</sup> *Colletotrichum sp.* ALF2-6 is a endophytic fungi inhabiting Andrographis paniculata shrub used as a reducing and capping agent and showed antibacterial effect (human pathogen). AgNPs were synthesised by using leaf and stem extract of *Piper nigrum* (black pepper) and examined for agricultural plant pathogens<sup>88</sup>. Antibacterial and cytotoxic effects of AgNPs were examined by using *Chrysanthemum indicum* (Indian chrysanthemum) by using a simple, cost-effective and ecofriendly method.<sup>6</sup>

Antimicrobial nature of AgNPs towards construction materials was determined with minimum concentration (9–10.7 ppm) for fungi *P. variotii*, *P. pinophilum*, *C. globosum*, *T. virens* and *A. brasiliensis*, bacteria *P. aeruginosa*, *S. aureus* and *E. coli* and yeasts *C. albicans* and *Y. lipolytica*. The size of antimicrobial nature of AgNPs towards construction materials was determined with minimum concentration (9–10.7 ppm) for fungi *P. variotii*, *P. pinophilum*, *C. globosum*, *T. virens and A. brasiliensis*, bacteria *P. aeruginos3a*, *S. aureus and E. coli* and yeasts *C. albicans* and *Y. lipolytica*.

However, the total inhibition of P. variotii growth was determined at very low concentration, 4.28 mg/l of AgNPs. In eukaryotes the entered AgNPs aggregated in larger particles, this was reported by Żarowska et al<sup>130</sup> during the study of *A. brasiliensis*.

Antimicrobial Behaviour of Graphene and Graphene based NanoMaterials: GO shows the highest antibacterial activity toward *P. aeruginosa* followed by rGO, Gt and GtO. FTIR, Raman, XRD, FESEM, EDX and VSM characterised GrO/Fe<sub>3</sub>O<sub>4</sub>/Ag nanocomposite with the 3:1 ratio of Gr and Fe<sub>3</sub>O<sub>4</sub> showing highest efficiency towards the removal of COD,  $PO_4^{3-}$  and total nitrogen.

It was reported for water decontamination and disinfection purposes. In this study, *C. Operculatus* leaf extract was used for the synthesis and antibacterial (*S. aureus*, *S. enteric* and *C. albicans*) and antifungal activity were also reported.

However, removal of 100% of *E. coli* was reported by GF31A (0.1 g/100 mL)<sup>65</sup>. Green synthesised Ag/GrO nanocomposite was studied against *P. aeruginosa*, *S. Aureus*<sup>30</sup> and Gr/CS/Fe<sub>3</sub>O<sub>4</sub> nanocomposites prepared by hydrothermal method reported antibacterial behaviour against *P. aeruginosa* and *K. Pneumoniae*<sup>73</sup>.

Published literature shows significant antimicrobial activities of graphene and graphene-based materials. Due to the existence of the outer layer in the structure of gramnegative organisms; graphene sheets showed more resistant to the cell membrane damage than gram-positive bacteria<sup>4</sup>. Although, some bacterial species were found to live in the presence of graphene such as the *Shewanella* family, which is capable to reduce GO into graphene under ambient conditions with no inhibition of bacterial growth<sup>121</sup>.

In some cases, E. coli bacteria attached to GO films were able to grow faster and develop denser biofilms than cultures without graphene, suggesting that GO not only lacks bactericidal activities, but that it basically enhanced bacterial proliferation<sup>93</sup>. Noteworthy, numerous researches were based on antibacterial behaviour of GO and GO-based materials carried out on eukaryotic cells and many are still going on<sup>132</sup>. Studies showed that GO can act as antibiotic as well as growth promoter; giving the surprising possibility to modified GO effects on bacteria is responsible to the versatile applications in the environmental and medical sciences. At low concentrations, GO clustering forms floating scaffolds able to enhance bacterial growth, while at high concentrations, GO forms scaffolds able to inhibit the bacterial growth. The GO can be used for treatments against multidrug resistant bacteria. water remediation/ desalination/purification, phar-maceuticals and probiotic therapies<sup>84</sup>.

**Thermal Conducting Behaviour of Graphene:** Materials having high thermal conductivity hold extreme importance since it has a wide range of applications, such as high amount of heat formed in modern electronic circuits required suitable materials, hence are in more demand. Graphene exhibits an excellent thermal conductivity which is very interesting since it increases the potential use of graphene and graphene-based materials in a wide range of technological applications<sup>56</sup>.

Many studies have shown superior thermal conductivity of graphene although specific conductivity value for graphene is not specified as shown in figure  $9^{20,24}$ . Thermal conductivity in the range  $\sim (4.84\pm0.44)\times10^3$  to  $(5.30\pm0.48)\times10^3$  W/mk is obtained for suspended single layer graphene by the study conducted by Baladin et al<sup>10</sup>. These studies also proved that graphene has high thermal conductivity than carbon nanotubes.



Figure 9: (a) SEM image of the suspended graphene on Au coated SiNx porous membrane. (b) Raman spectra of the suspended graphene showing the G and 2D peaks features characteristic of single layer graphene. (c) Schematic of the experimental setup of thermal transport measurement of suspended graphene. (d) Temperature dependence of the 2D peak frequency for monolayer graphene. The inset shows the relationship between the G and 2D peak shifts<sup>24</sup>.

The thermal conductivity of graphene is assumed due to presence of phonons<sup>82</sup> and electrons, here electronic contribution to thermal conductivity of graphene is negligible<sup>37</sup>. Carbon based materials such as graphene which has metal like properties, exhibit high thermal conduction mainly because of phonons, lattice vibrations enabling efficient heat transfer due to strong covalent sp<sup>2</sup> bonding which is responsible for this nature<sup>58</sup>. Thermal conductivity of graphene decreases, as the number or layers of graphene increase until it become graphite. It has been assumed due to multilayer lattice.

Further, as the number of layers of graphene increases, phonon scattering and dispersion increase leading to decrease of thermal conductivity<sup>36</sup>. Graphite is made up of multiple layers of graphene and due to the interactions between these layers, thermal conductivity decreases significantly<sup>15</sup>. Pristine carbon-nanotubes have been used for the synthesis of conductive polyaniline<sup>14</sup>. Structure of graphene nanoparticles also influences its thermal properties, as there are many nano structures of graphene available and are being used for variable eco-friendly purposes. Studies done by many researchers have shown that graphene nanoribbons with perfect edges have high thermal conductivity than graphene nanoribbons with rough edges<sup>32,77,94</sup>. Different methods such as Raman electrical, optical pump and probe and electrical 3w are used to thermal measure conductance along graphene materials<sup>25,34,59,74</sup>

One of the important parameters for the thermal application of any material is its thermal coupling properties. Thermal energy transfer of graphene with other materials like SiO<sub>2</sub> is widely studied<sup>89</sup>. The main factors affecting these kinds of thermal transfers are the suspended regions in graphene layers, methods of preparation of graphene and type of surface i. e. roughness or smoothness<sup>60,96</sup>. Since graphene has better heat transfer properties while mixing with different materials and very high temperature stability of up to 2600K<sup>55</sup>, its application as thermal interface material is studied and liquid phase exfoliated graphene is found to be suitable for industrial applications<sup>70,98</sup>.

The thermoelectric effects of graphene are also an interesting topic of research. Peak value for thermoelectric power of graphene is at ~  $80\mu$ VK<sup>-1</sup> at room temperature<sup>22</sup>. Making composites with graphene or changing the lattice structure by various methods like electron beam irradiation or by charged impurities can potentially create materials for efficient thermoelectric conversions<sup>114,122</sup>. These thermal properties of graphene can be controlled by making graphene derivatives or composite materials for various applications<sup>72</sup>. Due to these unique thermal properties of graphene, a lot of studies are still going on and we can expect more results in the future.

**Thermal Conducting Behaviour of Silver Nanoparticles:** Generally metallic nanoparticles exhibit a decrease in thermal conductivity as the size of the particles decreases and this is mainly because of the method of thermal conductivity in metallic particles<sup>48,79,86</sup>. In metals, heat conduction is mainly because of the lattice vibrations<sup>116</sup> because of this as the size decreases, effectively transfer heat decreases. Thermal conductivity is measured for silver nanoparticles with three different sizes during the study conducted by Warrier et al<sup>123</sup> and results are in good agreement with general theory as shown in figure 10.

The thermal conductivity varies by changing the conditions of medium and surrounding in which nanoparticles exist as studied by Iyahraja et al<sup>47</sup> and explained that polyvinylpyrrolidone coated silver nanoparticles in distilled water exhibit increased thermal conductivity as particle size decreased. This behaviour was based on the brownian motion of the nanoparticles and high specific area. However, heat transfer increases, as surface area as well as brownian motion increase. Both these properties provide an additional route for heat transfer, therefore it can be assumed that thermal conductivity of silver nanoparticles in liquid medium can be increased by decreasing particle size. Metallic nanoparticles especially silver nanoparticles are widely used to increase the conductivity of colloidal materials and composites<sup>39,99</sup>. Literature shows that as the amount of silver nanoparticles varies, thermal conductivity also changes significantly.





nanoparticles. Points (1% black square 2% black circle) represents experimental data of this work. Dashed (1%-----, 2%.....) and solid lines represent calculated values assuming size dependence and without size dependence respectively (© nanoscale research letters) reference<sup>123</sup>

The study conducted by Seyhan et al<sup>99</sup> revealed that rate of thermal conductivity decreases as the concentration of nanoparticles keeps on increasing. Thus, by varying particle size, surrounding materials and concentration, the thermal conductive nature of silver nanoparticles can be controlled. This was explained by the occurrence of agglomeration of silver nanoparticles at high concentrations. A strong thermally conductive nature of nano sized silver particles makes it an attractive material to be used in various field of electrical and mechanical sciences.

Reduction of AgNO<sub>3</sub> to produce AgNPs as a nanofluid by polyol method was reported by Zeroual et al<sup>131</sup>. Ethylene glycol and aqueous emulsion of latex copolymer with fixed amount of AgNO<sub>3</sub> were used during this synthesis. UV-Vis, TEM, EDS and dynamic viscosity are the experimental techniques used for the determination. Enrichment of about 3% in thermal conductivity without rise in viscosity of the produced ethylene glycol silver-based nanofluids than the latex copolymer was analysed, hence ethylene glycol silverbased nanofluids are applicable as circulating heat transfer fluids<sup>131</sup>.

Comprehensive operation of environmental approachable and renewable energy resources is one of the basic needs of present circumstances; solar energy-based set-ups are providing an optimistic courage for this purpose. Such systems are made by photo-thermal (PT) or photovoltaicthermal (PVT) nanofluids having high heat transfer ability. Highly luminescent organic components, AgNPs dispersed within a base fluid, were tested by Walshe et al<sup>124</sup>. AgNPs' inclusion fluid complex has increased total solar energy conversion into thermal energy and minimizes the losses in the electrical power component. Numerous fluorescent imidazo-phenanthroline molecules were dispersed in ethylene glycol with AgNPs for this purpose.

**Electrical Conducting Applications of Graphene and Silver Nanoparticle Composite Materials:** Different combinations of silver nono particles and graphene resulted in significant changes in the electrical conductive properties of material. These materials have wide range of applications. For example conducting transperent thin films can be prepared by using graphene multilayers. The major problem faced was the aggregation and restacking of graphene nanosheets.

Tien et al<sup>113</sup> solved this problem by iducing silvernanoparticles between graphene layers.Here,AgNPs are functioning as a good nano spacer and conductor. Overall the combination showed impoved electrical conductivity than individual materials. Zhong et al<sup>135</sup> also explained similar structural composition to explore the possibility to make better conductive inks, where they confirmed increased electrical conductivity of graphene silver nanoparticle system than pure graphene. Field of wearable technology is one of the important areas where the potential application of graphene- silver nanoparticle composites can be introduced. Conductive inks with antimicrobial property that can be applied to fabrics and related materials have enormous potential to do furthur research.

Karim et al<sup>52</sup> succesfully concluded that graphene–silver nanoparticle composite ink is well suited for conductive ink printing for wearable e-textile applications.

Antimicrobial Applications of Graphene and Silver Nanoparticle Composite Materials: Sandwich-like nanomaterial films of Ag/halloysite nanotubes (HNTs)/rGO show increased antibacterial (*E. coli and S. aureus*) (figure 9 B) and antimicrobial behaviour than individual AgNPs, rGOnanosheets or their composites. Curve of GO represented a considerable FTIR peak around 1720 cm<sup>-1</sup>of carboxyl group(C=O) of GO showing the synthesised Ag/ HNTs/rGO. Reduction of GO is shown by peaks around 2930 cm<sup>-1</sup> and 2840 cm<sup>-1</sup> (figure 12 A)<sup>129</sup>.

By the reduction of  $AgNO_3$  in a graphene oxide (GrO) suspension, AgNPs are produces followed by the study of antimicrobial activity against the *E. coli* and *P. aeruginosa*.

According to the study of growth kinetics, *P. aeruginosa* is considered more sensitive to the AgNPs–GrO suspension. Growth delay of these two bacteria at different concentration of AgNO<sub>3</sub> is represented in figure 13a (*P. aeruginosa*) and 13b (*E. coli*.). More is the concentration of the AgNPs, more is the growth delay of *P. aeruginosa* and *E. coli*.<sup>29</sup>

Aqueous extract of Colocasiaesculenta leaf was used to synthesise Ag-rGO composite which has reduced graphene

oxide, here antimicrobial behaviour was increased. The minimum inhibitory concentration (MIC) of the Ag-RGO was resolute using micro-dilution technique.<sup>81</sup>

Table 5 indicates that the Ag-rGOnanohybrid system has better antimicrobial behaviour than the individual nanomaterials of silver and graphene oxide.







Figure 12: (A) FRIT spectra of a) natural graphite b) GO and c) Ag/HNTs/rGO (B) bacterial colonies formed by (a), (b) *E. coli* and (c), (d) *S. aureus*: (a), (c) control groups, (b), (d) treated with Ag/HNTs/ rGO<sup>129</sup>.



Figure 13: Comparative bacterial growth kinetics graphs of a) *P. aeruginosa* and b) *E. coli* in nutrient broth at different conditions<sup>29</sup>.

MIC of the nanonybrid of selected microbes.					
Name of the Organism	RGO (µg/mL)	AgNPs (µg/mL)	Ag-RGO (µg/mL)	Antibiotic (µg/mL)	
S. aureus	16	20	12.5	8	
E. coli	21	25	20	10	
C. albicans	19	20	16	6	

 Table 4

 MIC of the nanohybrid of selected microbes

Table 5						
Antimicrobial acti	Antimicrobial activity (zone of inhibition).					

Name of the organism	RGO	AgNPs	Ag-RGO	Antibiotic
S. aureus	17.42±0.18	12.79±0.3	23.82±0.18	32.1±0.2
E. coli	17.06±0.23	13.88±0.06	$18.84 \pm 0.06$	33.6±0.1
C. albicans	18.18±0.14	12.48±0.17	21.73±0.13	35.55±0.15



Figure 14: Antimicrobial activity of RGO, AgNPs, Ag-RGO, DMSO and Antibiotics against a) *S. aureus*, b) *E. coli* and c) *C. Albicans*<sup>12</sup>.

Zones of inhibition of the selected microorganism were determined. The MIC values of our samples are shown in table 5 (figure 14). Zone of inhibition was compared with individual nanomaterials and Ag-rGO showed higher than the other. There are three main peaks shown in FTIR of GO at 228 nm, 302 nm and 429 nm. Peak at 228 nm is due to the  $\pi$ -  $\pi^*$  and n-  $\pi^*$  transition of the aromatic carbon bonds present. Peak at 302 nm represents C=O bonds. Peak at around 429 nm indicates the formation of silvernanoparticles (UV-visible spectroscopy). A red shift (265 nm) shows the formation of rGO. Percentage of Ag in the Ag-rGOnanohybrid was determined by EDX study. Carbonyl, carboxylic, epoxy and hydroxyl groups of GO are shown by the bands at 1049, 1224, 1720  $cm^{-1}$  and 3400  $cm^{-1}$ respectively in the FTIR spectra. Reduction of GO is shown by the broad band at  $3400 \text{ cm}^{-1}$ .

The ratio of ID/IG of Raman spectroscopy is useful to calculate the degree of disorder in organic molecules. AgrGO shows less ID/IG ratio than GO i.e. 0.8 which is 0.15 less. Reduction and restoration of carbon based sp<sup>2</sup> hybridised species are confirmed. XRD technique is used to show the presence of silver nanoparticles emerged in the membrane<sup>12</sup>. Damage of cell membrane, extraction of phospholipids and separation of microorganisms are showing mechanism of antibacterial behaviour of graphene-based materials<sup>1</sup>. Thus, researches on AgNPs–Gr

composites are still going on and possibility of other combinations is also getting explored.

#### Conclusion

Nanoscience is playing an important and versatile role in the present research. Graphene and silver-nanoparticles are two of the many nanomaterials being used in nanotechnology and nanoscience. In the recent research, graphene and graphene-based nanomaterials are utilised in electronics, photonics, capacitors/supercapacitors, biosensing, energy storage systems, chemical sensors, optoelectronics, nanocomposites. LEDs. solar cells. drug and pharmaceuticals in catalysis, reduction of dyes, selective oxidation of benzene, synergistic oxidation of carbon monoxide, chemotherapy, antimicrobial agent, coating of medical equipment and household goods etc. Conducting and antimicrobial behaviour of both are two highly used qualities and are playing a huge role at industrial, commercial, domestic, research and innovation fields.

Literature indicates that among all the nanometalparticles, silver-nanoparticles are considered as most effective and widely used towards antibacterial activity due to their various green synthesis and cost effectiveness. The antibacterial behaviour of AgNPs depends on the shape, size and charge of the AgNPs and is found inversely related to the size and positively charged AgNPs. It is more effective to kill bacteria than other microbes. AgNPs are effectively and innovatively being used for decades in field of water purification by membranes based on the coating or composite of AgNPs and still have a wide interest of researchers.

Graphene is a good antimicrobial agent and is being used for two decades for the same purpose. Graphene and graphenebased nanomaterial are more effective towards gram negative bacteria. Graphene-based nanocomposites are widely being used for antimicrobial purposes. Composites of silver and graphene nanomaterial are also showing effective antimicrobial behaviour.

Conducting behaviour is also a common character of both and literature shows future innovative ideas of forming a composite material of nanomaterial of silver and graphene in many fields of science and technology.

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