Nanomaterials : Synthesis, Properties, and Applications

Dr. Archana R. Deokar,

Modern College of Arts, Science, and Commerce, Shivajinagar, Pune-411005

The modern era of nanotechnology has its seeds sown by renowned physicist Richard P. Feyman in 1959 with his famous talk "There's plenty of Room at the Bottom," In this speech he talked about manipulating and controlling things on a small scale.[1] The term "Nanotechnology" was introduced by a Japanese Scientist Norio Taniguchi. The further development of nanotechnology is mainly attributed to the work of German theoretical physicist K. Eric Drexler who used the word "nanotechnology" in his 1986 book "Engines of Creation: The Coming Era of Nanotechnology".

Nanotechnology is defined by National Nanotechnology Intiative of United States is the manipulation of matter with at least one dimension lying in the range of 1 to 100 nanometer Science underlying nanotechnology is called as nanoscience. Nanoscience is the study of structures and materials on the scale of nanometer. The term nano refers to 10^{-9} i.e. one billionth of something. It can be ascribed to any unit of measurement. Thus one nanometer (nm) means one billionth of a meter i.e. 10^{-9} m. One nanometer is on the scale of atomic diameter. Just to compare, human hair is about 100, 000 nm thick.[2]

Basically nanotechnology deals with both natural and artificial structures on nanometer scale. This is a technology which is capable of manipulating single atoms and molecules. Various fields of science such as surface science, organic chemistry, molecular biology, semiconductor physics, microfabrication etc. come under the umbrella of nanotechnology with wide applications e.g. in nanomedicine, nanoelectronics, biomaterials, energy production, and cosmetics etc. It has been developed at a fast pace due to the invention of many observational and characterizing tools particularly atomic tunneling microscope (STM) and atomic force microscope (AFM).[3,4,5]

There are two basic approaches used for synthesis of nanomaterials-top-down and bottom up. Conventional microtechnology is a top-down technology whereby microstructures are fabricated by manipulating a large piece/ bulk material typically a single crystal of silicon, using processes such as lithography, etching, and metallization etc. Top down methods of making nanostructures require large installations and are quiet expensive. They need huge amount of capital to be invested.

The invention of advanced instruments such as STM or AFM for observation and manipulation of individual atoms and molecules have led to a new approach to technology called bottom-up approach. In this method, instead of making small structures are made directly by assembling of molecules and atoms. This bottom-up approach of synthesis of nanostructures is supposed to work within all living systems since the very beginning of life on earth. Bottom up process does not require large installations to be out up and hence is a cost effective method.

Although synthesis of nanomaterials has been broadly classified into two categories, synthesis methods can be further classified into three more classes

1) Physical Methods: Nanoparticles may be synthesized using a number of physical methods such as arc discharge method, electron beam lithography, mechanical grinder, inert gas condensation, ion implantation, ball milling, spray pyrolysis, vapor-phase synthesis. These methods are of two types viz mechanical type and vapor deposition type. These methods work at high temperatures. The highest working temperature is usually greater than 350^0C.

2) Chemical methods: These are simple and inexpensive methods for synthesizing nanoparticles. Large quantities of materials can be prepared with variety of sizes and shapes of particles. Co-precipitation method, microemlusion method, electro-chemical method, chemical reduction of metal salts, pyrolysis, phytochemical method, solvothermal synthesis, sol-gel process, sonochemical method.

3) Biological Method: Biological methods are based on the use of micro-organisms (fungi, yeast, bacteria etc.) or plant extracts (and enzymes) or use of templates such as DNA and viruses. This type of synthesis is environment friendly and least toxic and therefore called green synthesis.

Emerging nanomaterials such as magnetic nanoparticle (MNPs), quantum dots (QDs), carbon nanotubes (CNTs), fullerene, and graphene has been explored in recent years owing to their excellent optical, electrical, and magentic properties, surface reactivity, and biocompatibility. This review will mainly emphasize on synthesis and applications of carbon based nanomaterials such as carbon nanotubes and graphene for biomedical applications.

Graphene is a one-atom thick two-dimensional sheet of carbon. Apart from other carbon allotropes, i.e., fullerenes, carbon nanotubes, and graphite, graphene exhibits a myriad of unique chemical and physical properties. Single-layer graphene is highly transparent toward visible light (~2.3% absorption). It possesses superlative mechanical strength with a Young's modulus of ~1.1 TPa. An unparalleled thermal conductivity (~5000 Wm K^{-1}) and large surface area (2630 m^2 g^{-1}) have also been reported. Owing to these unique chemical and physical properties and the unique biocompatibility, graphene has attracted much attention in the scientific community for numerous potential applications of graphene in biotechnology, including biosensing, disease diagnostics, antibacterial and antiviral materials, cancer targeting and photothermal therapy, drug delivery, electrical stimulation of cells, and tissue engineering. [6-11] Various approaches have been developed for the synthesis of graphene and its derivatives, including mechanical exfoliation, epitaxial growth, unzipping carbon nanotubes, exfoliation of GO, liquid phase exfoliation of graphite, etc.

In 1991, Iijima Sumio, a Japanese physicist accidentally invented CNTs during the synthesis of fullerene. The walls of CNTs are made up of hexagonal lattice of atoms and are capped at their ends by one half of a fullerene-like moiety. CNTs can be as thin as a few nanometers yet are as long as thins as a few microns. The chemical bonding of nanotubes is composed entirely of sp^2 bonds, which provide nanotubes with their exceptional strength. Generally, CNTs are categorized as either Single walled Carbon Nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). MWCNTs were discovered in 1991 whereas SWCNTs in 1993. Most SWCNTs have a diameter of close to 1 nm but they can be as long as 100 µm. MWCNTs area collections of nested tubes of continuously increasing diameters. Thus MWCNTs are nanotubes within nanotubes. Diameter of MWCNTs can be anywhere in between 2-100 nm and their lengths can be up to 20 cm. CNTs can be synthesized by electric arc-discharge method, laser ablation method, or chemical vapor deposition method.

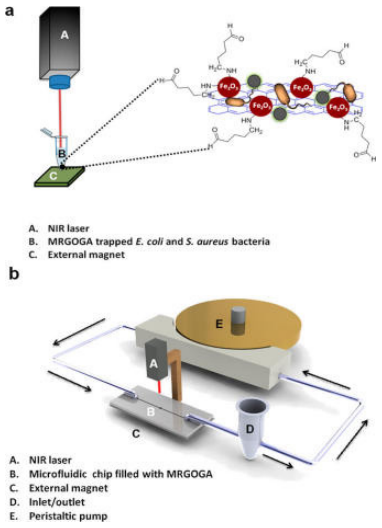

Figure 1: Schematic of (a) batch and (b) continuous operation mode for antibacterial photothermal treatment by MRGOGA. Reprinted with permission from *ACS Nano*, 2013, 7 (2), pp 1281-1290. Copyright 2013 American Chemical Society.[12]

Following section represents the literature survey on applications of graphene and CNTs in biomedical field.

In this work, we have synthesized a graphene-based photothermal agent, magnetic reduced graphene oxide functionalized with glutaraldehyde (MRGOGA) for efficient capture and effective killing of both gram-positive *Staphylococcus aureus* (*S. aureus*) and gram-negative *Escherichia coli* (*E. coli*) bacteria upon near-infrared (NIR) laser irradiation. Here, we took advantage of the excellent photothermal properties of reduced graphene oxide upon NIR laser irradiation and glutaraldehyde as an efficient capturing agent toward both bacteria. Its magnetic characteristic allows bacteria to be readily trapped in a small volume by the external magnet.The synergetic effects increase the heating extent by MRGOGA upon NIR laser irradiation and the killing of the captured bacteria. The survival rate and membrane integrity assay demonstrate that 80 ppm MRGOGA solution provided rapid and effective killing of up to 99% of both gram-positive and gram-negative bacteria in 10 min upon NIR laser irradiation under batch operation mode (Fig. 1a) Graphene demonstrated better photothermal antibacterial efficiency than carbon nanotubes. Furthermore, a microfluidic chip system under continuous operation mode (Fig.1b) demonstrates the reusability of MRGOGA and offers a biocompatible platform for online phothothermal sterilization.[12]

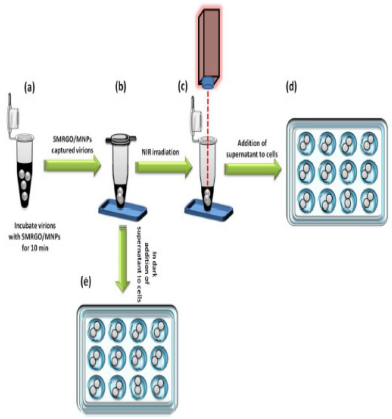

Figure 2: Photothermal antiviral assay for SMRGO/MNPs in the dark or following NIR irradiation (808 nm, 1.6 W/cm^2). Reprinted with permission from *Bioconjugate Chem., 2017, 28 (4), pp 1115–1122*. Copyright 2017 American Chemical Society.

In this work, we have designed and synthesized sulfonated magnetic nanoparticles functionalized with reduced graphene oxide (SMRGO) to capture and destroy herpes simplex virus type 1 (HSV-1). Figure 2 represents the schematic of photothermal antiviral assay for SMRGO/MNPs in the dark or following NIR irradiation. Graphene sheets were uniformly anchored with spherical magnetic nanoparticles (MNPs) of varying size between ~5-20 nm. Fourier-transform infrared spectroscopy (FT-IR) confirmed the sulfonation and anchoring of MNPs on the graphene sheets. Upon irradiation of the composite with near-infrared light (NIR, 808 nm, 7 min), SMRGO (100 ppm) demonstrated superior (~99.99%, Figure 3) photothermal antiviral activity. This was probably due to the capturing efficiency, unique sheet-like structure, high surface area and excellent photothermal properties of graphene. In addition, electrostatic interactions of MNPs with viral particles appear to play a vital role in the inhibition of viral infection. These results suggest that graphene composites may help to combat viral infections including, but not only, HSV-1.

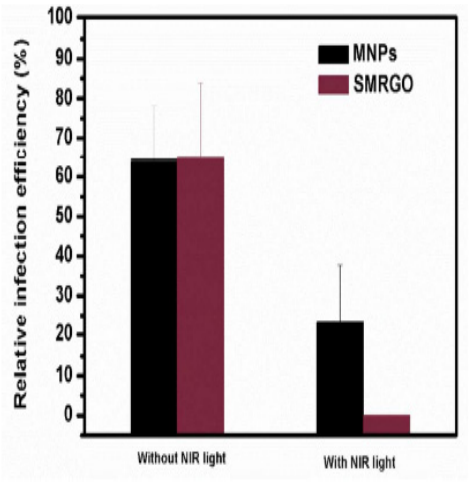

Figure 3: Relative percentage of cell infection before (dark) and after (light) photothermal treatment with MNPs and SMRGO. Reprinted with permission from *Bioconjugate Chem., 2017, 28 (4), pp 1115–1122*. Copyright 2017 American Chemical Society.[13]

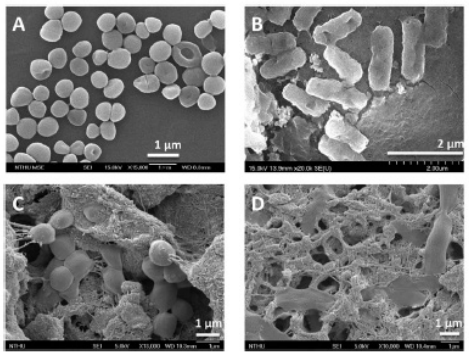

Fig. 1 SEM images of control group (A) *S. aureus* and (B) *E. coli* incubated with UP for 1 h; experimental group (C) *S. aureus* and (D) *E. coli* incubated with SP for 1 h.

Figure 4: SEM images of control group (A) *S. aureus* and (B) *E. coli* incubated with UP for 1 h; experimental group (C) *S. aureus* and (D) *E. coli* incubated with SP for 1 h. Reprinted with permission from *Journal of Material Chemistry B., 2013, 1, 2639–2646*. Copyright 2013 Royal Society of Chemistry.[14]

Figure 4 represents the SEM image of interaction of gram-positive and gram-negative bacterial species with SWCNTs coated paper. Upon interaction with SWCNTs coated paper both bacteria losses its integrity. In this study, the antibacterial activity and mechanism of acid-functionalized single-walled carbon nanotube (AFSWCNT) coated paper was assessed for gram-positive *Staphylococcus aureus* and gram-negative *Escherichia coli* models of bacteria. Better activity towards gram-positive bacteria was observed, whereas the presence of an outer membrane makes gram-negative bacteria more resistant to cell membrane damage caused by AFSWCNTs. Based on measured cytoplasmic efflux materials of bacteria, X-ray photoelectron spectroscopy, and scanning transmission electron microscopy combined with electron energy-loss spectroscopy imaging studies, we found that the better antibacterial activity of AFSWCNTs toward gram-positive bacteria is attributed to not only direct physical contact and piercing action, but also molecular-scale interaction with surface functional groups of bacteria. The novel antibacterial mechanism of AFSWCNTs might bring a promising strategy to design new antibacterial materials against drug-resistant bacteria species.

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