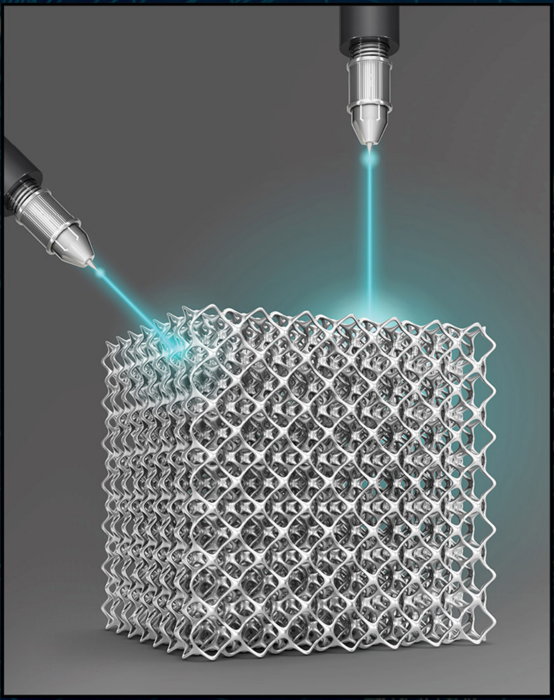
MATERIALS DEVELOPMENT AND PROCESSING FOR BIOMEDICAL APPLICATIONS



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Materials Development and Processing for Biomedical Applications

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Preface

It is our immense pleasure to introduce the book titled *Materials Development and Processing for Biomedical Applications*. This book is mainly focused on various methods of manufacturing, surface modifications, and advancements in biomedical applications for all kinds of readers. In particular, the fundamental aspects are discussed for a better understanding of the processing of various biomedical materials such as metals, ceramics, polymers, composites, etc. Besides, advancements in various fields of biomedical applications are emphasized. The book is basically focusing on five different aspects such as materials properties, development, processing, surface coatings, and future perspectives of advanced biomedical device fabrications.

The development and applications of various metallic and non-metallic materials are given importance in recent days and advancements in the development of new materials are highly appreciated. Biomedical materials from the micro-nano scale possess various properties which will significantly affect the resulting properties. The introduction to biomaterial and the properties of various biomedical materials are important to understand for the further development of biomedical materials with better biocompatibility and without any adverse effects. Authors have elaborated the various properties of biomedical materials at the beginning in several chapters which will enrich the fundamental knowledge of the readers. Furthermore, synthesis of nano materials, the properties of degradable and non-degradable (permanent) implant materials are discussed extensively. Following the materials properties part, the development of degradable and polymeric materials is discussed. Interestingly, Mg alloys have similar mechanical properties close to the natural bone; however, their chemical reactivity is much faster and a faster degradation rate limits them for implant applications. Ultra-pure Mg possesses a very low corrosion rate (~0.1 mm/y), yet mechanical properties are poor, and alloying and processing are necessary to enhance the properties. The degradable metallic implant materials, particularly of Mg-based alloys developments, processing through severe plastic deformation (SPD) processes are discussed for manufacturing degradable stent materials which shows the improvement in the required properties. Besides, the development of 2D materials and applications of 3D printing technology to fabricate polymeric materials for biomedical applications are discussed.

Laser processing is one of the precise techniques used for the fabrication of micro/nano functional surfaces and is attractive for biomedical applications. Surface laser texturing to fabricate the micro/nano surfaces and their biomedical applications are discussed. Laser powder bed fusion (LPBF) to fabricate Ti-based alloys are discussed in two parts. Part 1 discusses fabrication, the process details, and the influencing parameters of LPBF. Further, Part 2 discusses the characteristic properties of as-built and post-treated titanium alloys. These chapters comprehensively discuss the prospects of LPBF, and it is one of the promising topics for the fabrication of Ti-based alloys for biomedical applications and readers can get the benefits from these chapters. Online monitoring during laser processing is one of the interesting topics to understand and optimizing the processing condition are discussed. In particular, collaborative monitoring and artificial intelligence of optical signals, photoacoustic signals, image signals, temperature signals, etc., during high potential laser surgeries (such as orthopedic surgery, eye surgery, and so on) will be beneficial for the precise control of the process. It is one of the demanding technologies for the modern biomedical industries. Furthermore, laser processing and ablation as one of the rapid processes has also been focused on fabricating the nanoparticles for various biomedical applications. In this context, the laser-assisted production of calcium phosphate nanoparticles from marine origin has also been discussed, which will give the idea to the readers to expand the laser processing for nanoparticle synthesis for the applications in various scales for energy and environmental applications.

Surface treatments and modification of implant materials are beneficial to alter the surface-related properties such as surface energies, chemical composition, corrosion resistance, mechanical properties, and biocompatibility. Furthermore, surface treatments and subsurface modification in certain cases are advantageous for the implant to introduce porous structures without altering the bulk properties of implants. Surface treatments such as surface mechanical attrition treatments (SMAT), chemical conversion treatments/coatings, anodic oxidation, plasma electrolytic oxidation, polymeric coatings, ceramic coatings, composite coatings, vacuum deposition, plasma coatings, electrospinning, etc. are some of the techniques commonly used for metallic implants. The introduction to these techniques, processing conditions, and properties are emphasized by several authors and discussed in detail. The SMAT is a mechanical treatment used to refine the microstructure at the surface and subsurface levels to enhance the corrosion resistance. Anodic oxidation of titanium alloys results in the formation of ordered nanotubes and enhances the biocompatibility of implants. Further, control of process parameters such as anodizing environment, condition, and post-treatments result in porous to ordered surfaces and altered properties. A detailed discussion about the influencing parameters and results properties are explained. Electrospinning is one of the evolving techniques to coat polymeric and composite materials directly over implant surfaces; one of the studies on electrospinning of polymers on degradable implants is discussed for biomedical applications. A wide range of surface treatments covered in this book will be helpful for readers to understand the importance of surface treatments and their future perspectives.

At the end of this book, the chapters discuss the advanced techniques such as flexible electronics, biosensors, microfluidic devices, chips, etc. for advanced health care applications. An overview of the key advances in wearable, flexible, smart biosensors and their potential in sensitivity and reliability is discussed. In particular, materials/components used for advanced health care diagnostic devices, signal measurements, and exercise-based wearable devices, ocular wearable, internet-of-things-based biosensors for the biomedical field are explained. Various types of organs-on-a-chip (OOc), also called micro physiological systems, used in biomedical applications are also explained. Overall, the chapters present in the book are comprised of a wide range of topics for the benefit of the readers working in the area of biomedical applications. Therefore, the editors strongly believe that the resources given in this book from various authors will be helpful for researchers from basic to advanced levels.

Thank you.

Editorial Team

Editors

Savaş Kaya is Associate Professor of Inorganic Chemistry at Sivas Cumhuriyet University, Health Services Vocational School, Department of Pharmacy, Sivas/Turkey. He earned a doctorate degree in 2017 in the field of Theoretical Inorganic Chemistry. He does research in Theoretical Chemistry, Computational Chemistry, Materials Science, Corrosion Science, Physical Inorganic Chemistry and Coordination Chemistry. Savaş Kaya has published more than 180 papers in international journals indexed SCI and SCI expanded with h-index = 26. He is the editor of the book *Conceptual Density Functional Theory and Its Applications in the Chemical Domain*. He is the author of ten book chapters. Recently, he introduced the Kaya chemical reactivity approach and the Kaya combined reactivity descriptor and proposed some electronic structure principles.

Dr. Sasikumar Yesudass is currently working as Post-Doctoral Researcher in the School of Materials Science and Engineering, Tianjin University of Technology, China since 2018. He is presently working on the surface coatings of Mg alloys with a focus on improving bioactivity and is interested in advanced orthopedic implant devices. His major research areas include the electrochemical behavior of magnesium and titanium alloys for bio-implant applications and the corrosion inhibition studies of steels. Prior to joining Tianjin University in China, he received the CAPES Post-Doctoral fellowship award from the Brazilian government, at Central Federal Technical University, Rio de Janeiro, Brazil, and worked there 2017–2018. Besides, he has also received the National Research Fellow (NRF) Innovation Post Doctoral Research Fellowship award through the DST/National Research Foundation, at North West University, South Africa during 2014–2016. After his doctoral research, he worked as Assistant Professor in the Department of Physics, RRASE College of Engineering, Chennai, India 2012–2013. Dr. Sasikumar received his doctoral research (PhD) in surface modification and electrochemical behavior of titanium alloys for biomedical application' from the Department of Chemistry, College of Engineering, Anna University, India in the year 2012. He has published overall 22 peer-reviewed international publications in well-reputed SCI journals with an h-index of 12, written two book chapters and participated in various national and international conferences. In addition, he has delivered keynote lectures and invited talks at various international conferences. Besides, he has received research-oriented fellowships, like 'ICMR-Senior Research Fellowship' (2008) and 'CSIR-Diamond Jubilee Research Internship' (2006).

Dr. Srinivasan Arthanari has been a Researcher in the Chungnam National University, Daejeon, the Republic of Korea since 2021. His major research areas include the development of light metals, laser processing, surface treatments and corrosion studies. Previously, he received the Chinese post-doctoral fellowship at the School of Mechanical Engineering and Automation, Hefei Innovation Research Institute of Beihang University, Beijing, China in the year 2019–2021. He has also received Brain Korea (BK) fellowship and worked as a post-doctoral researcher at the School of Materials Science and Engineering, Seoul National University, South Korea during 2016–2018. Dr. Srinivasan earned his PhD in chemical surface treatment of Mg alloys for biomedical applications from the Department of Chemistry, College of Engineering Guindy, Anna University, India in 2015. Further, he has worked as Junior Research Fellow, and Senior Research Fellow in the Department of Science and Technology-Science and Engineering Research Board (DST-SERB), an Indian government-funded project during 2011–2013. As a recognition of his doctoral work, he earned the best PhD thesis award from the National Corrosion Council of India (NCCI) in 2016 and also received the Young Scientist Award-Runner Up I in 2015. He has published more than 35 peer-reviewed international publications, written book chapters, has been granted patents and has participated in various national/international projects. Dr. Srinivasan has also served as co-guest editor for a special issue in *MDPI-Crystals* journal, delivered webinars and keynote lectures in various international conferences and as a guest of honor in the national conference.

Dr. Sivakumar Bose has been a Postdoctoral Researcher in the Department of Biomedical Engineering, Pukyong National University, South Korea, since 2021. His present research work is focused on synthesis of nanomaterials for the bacterial disinfection (wound healing) applications using photo-induced methods. Previously he received a 'Chinese postdoctoral fellowship' in the School of Materials Science and Engineering, Hunan University, China during 2019–2020. Prior to joining Hunan University in China, he served as a National Postdoctoral Fellow in the Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai, India during 2017–2019. He completed his doctoral research in engineering (2017) at CSIR-National Metallurgical Laboratory, Jamshedpur, India under AcSIR University, India. His PhD thesis work is mainly focused on the 'Fabrication of boride coatings of titanium and Ti-6Al-4V alloy for the improvement of tribological properties'. Overall, his past and current research areas have expanded into various fields such as surface engineering, corrosion, bio-implants, synthesis of nanomaterials and bacterial disinfection. Dr. Sivakumar has published overall research articles in well-reputed SCI journals like (*Mat. Sci. & Eng. C*, *Applied Surf. Sci.*, *Nanoscale*, *Tribology International*, etc). He has presented and participated in many national/international conferences. Besides, he has received various research fellowships, such as 'National Postdoctoral Fellowship' (2019), 'CSIR-Senior Research Fellowship' (2013) and 'CSIR-Diamond Jubilee Research Intern' (2008). In addition, he has also delivered various keynote lectures to different institutions for the benefit of students and research scholars.

Dr. Goncagül Serdaroğlu is an Associate Professor at Sivas Cumhuriyet University (Math. and Sci. Edu. Department), Sivas, Turkey. Her main area of research is chemical reactivity behavior of the pharmaceutical important molecules by using the computational tools. Also, she is experienced with the computational prediction of the molecular spectroscopic properties (IR, NMR, UV) in addition to the electronic-related properties NBO (Natural Bond Orbital), FMO (Frontier Molecular Orbital) and NLO (nonlinear optic) of the molecular systems. Her master work was focused on the Statistical thermodynamics in calculation of the entropy and heat capacity and completed it from Sivas Cumhuriyet University, Department of Physicochemistry (Theoretical Chemistry) in 2003. Then, she earned a PhD degree from the same university in 2008. She has also worked as a post-doctoral fellow with Prof. Joseph Vincent Ortiz, Department of Chemistry and Biochemistry, Auburn University, Alabama, USA, during 2013–2014. She has also visited on scholarship, Instituto de Quimica Medica (CSIC), Madrid, Spain to work on the non-covalency effect and NMR chemical shifts properties of the organic-based compounds. Recently, she visited the University of L'Aquila, Italy for part of their research group work activities. So far, she has published over 60 papers in the Web of Science Core collections and has attended various international conferences which have mainly focused on Computational & Theoretical Chemistry and General Chemistry.

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1 Nanomaterials and Its Application as Biomedical Materials

G.S. Mary Fabiola, P. Dhivya and M. Anto Simon Joseph

CONTENTS

1.1 INTRODUCTION

Not all things that are big, are always beautiful. Tiny things make wonders. Nano—a unit prefix—meaning "one billionth"—an element of 10^{-9} or 0.000000001. The term "*nano*" has its root deep from the Greek term "*nanos*" or Latin "*nanus*", meaning "dwarf". Nanomaterials are exploited to designate the fabrication of materials stretching in size from 1–100 nm. Progressive and prospective research over a couple of decades has facilitated the development of hybrid materials via integrated design. The conceptualization of nanotechnology attracted more attention during the 1990's. However, the word nanotechnology was rediscovered and publicized in a lecture delivered by physics Nobel laureate Richard P. Feymann titled "There's Plenty of Room at the Bottom" on the eve of a

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gathering of the American Physical Society at Caltech on 29th December 1952. Nanotechnology has reformed the era of science and engineering over a span of two decades since the beginning of the 21st century. The tailor-made nanomaterials have initiated researchers to discover, design, develop, and manipulate the sole properties of constituents on nano scale. The fabrication of nanomaterials has rendered a tremendous contribution to material science. Nanomaterials possess certain unique physiochemical characteristics which make them unique and account for their vivid applications in comparison with the corresponding bulk material.

The incorporation of engineered materials in science and technology has quintessentially replaced the traditional metals to reach new horizons in therapeutics. The implementation of nanoparticles in the recapitulation of technologies is attributable to the nanoscale size of the reinforcing phase and the fact that the surface to volume ratio is expressively higher than conventional materials.

Nanomaterials are vibrantly used in medicine and therapeutics for the profound recognition of strategic biological molecules, specific and benign imaging of ailing tissues, and new forms of therapeutics. In the recent past, numerous nanoparticle-based therapeutic and diagnostic mediators have been established for the treatment of numerous diseases. The exploitation of nanoparticles in medicine provides exceptional choice to alter some essential properties of therapeutic carriers which include their solubility, diffusivity, bio-distribution, release characteristics, and immunogenicity. Accurate nanoparticle engineering has generated longer flow half-lives, enhanced bioavailability, and lower toxicity.

1.2 PROPERTIES OF NANOMATERIALS

Nanomaterials possess remarkable properties that make them distinct from their bulk counterparts as depicted in Figure 1.1. Materials when reduced to nano scale reveal properties exclusively diverse from their bulk material.

For instance, copper in its bulk state is opaque, whereas nano copper is transparent. Similarly, aluminum is stable even at a higher temperature, but nano-aluminum is combustible. Thus materials in their nano scale have significant changes in properties which are entirely different from the micro- and macroscopic materials. The distinctive size, shape, and structure of the nanomaterials justify the reactivity, sensitivity, mechanical, magnetic, optical, and thermal properties of nanomaterials. This accounts for the unique and ubiquitous properties of the nanomaterials, thereby inviting intense scientific research providing a prospective outlook into the future.

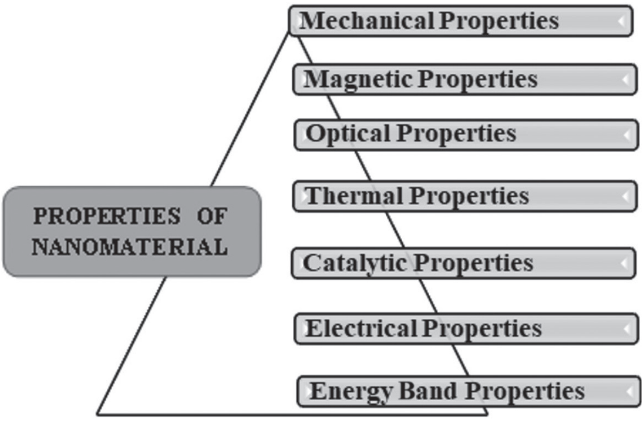

FIGURE 1.1 Materialistic properties of nanomaterials.

1.2.1 MECHANICAL PROPERTIES

Mechanical properties of metals are often associated with mechanical characteristics of metal which include strength, toughness, hardness, brittleness, plasticity, elasticity, rigidity, malleability, and ductility. The traditional inorganic metals are brittle, hard, and rigid but lack plasticity and elasticity. Alternatively, organic materials are flexible but are not rigid, brittle, and strong. These disadvantages are overcome by the nanomaterials which possess high surface area, volume, and quantum effects when compared to micro- and macroscopic materials. The influence of the selection of nanomaterials, the process of fabrication, grain size, and structure of the grain boundary has a noteworthy effect on the mechanical properties of nanomaterials. In comparison with the bulk, nanomaterials refine the grain size and form inter/intragranular structure, improving the grain boundary and thereby enhancing the mechanical properties of nanostructured materials. The flexural strength of nano-Al_2O_3 ceramics is comparatively stronger when compared with micro-scale monolithic alumina ceramics (Teng et al. 2007).

1.2.2 MAGNETIC PROPERTIES

Nanomaterials have properties entirely different from bulk material. The reduction in size or dimension of the nanomaterial introduces quantum confinement by reducing the symmetry of the system. The total energy of a ferromagnetic material is the summation of exchange energy, anisotropic energy, demagnetization energy, and energy due to the applied magnetic field. As in the case of nanomaterials, interaction among the exchange energy, anisotropic energy, and demagnetization energy is more pronounced. When the dimensions of the grain size become smaller, exchange forces dominate because of strong coupling and cause all the neighboring atoms to align in a particular spin. From the alignment, there exists a diameter called critical diameter that can be calculated. When the size of the particle more reduced than the critical diameter, magnetization becomes unstable and loses magnetization and the ferromagnetic material becomes superparamagnetic. The shrinkage in particle size increases the saturated magnetization and the reversal of magnetization becomes insignificant in nanomaterials. The structural and magnetic features of biocompatible Fe_3O_4 magnetic nanoparticles are used in labeling units of biomedical applications.

1.2.3 OPTICAL PROPERTIES

The surface morphology has a great effect on the optical and semiconducting properties of nanomaterials. The general optical properties of materials include reflection, refraction, transmission, absorption, and emission. The origin of the color of materials is caused by the surface plasmons. The surface plasmon is a natural phenomenon of oscillation of an electron at the junction of the material. The optical properties are largely dependent on the electronic structure—nanosphere in particular, which in turn varies with the morphology as it depends on the surface atoms. When the sphere is small in comparison with the wavelength of the incident light, and the frequency is quite close to that of the surface plasmon, then the surface plasmon absorbs more energy. Because of reduced dimensionality, the drift of electrons is restricted in nano scale when related to its bulk counterpart. The smaller the magnitude of the particle, the wider will be the optical band gap and shorter will be the wavelength and hence will be blue shifted. For example, spherical gold nanomaterial of 25-nm diameter appears in the region of green whereas gold nanomaterials of 100 nm appear orange. The factors that govern the size-dependent optical properties in nanomaterials are augmented energy level spacing—quantum effect and Surface Plasmon Resonance. When the dimension of the nanomaterial is confined to the nanometer range, with its characteristic wavelength approaching either closer to or less than the de Broglie wavelength of the respective charge carriers, which may be electrons or holes or the wavelength of the light, the periphery of the crystal gets ruptured in case of crystalline solids, whereas the atomic density of amorphous solids changes in the nanometer range.

1.2.4 Thermal Properties

The thermal properties involve the transfer of heat in nanomaterials. The thermal properties of materials in nanoscale dimensions largely depend on the surface properties, classical or quantum size, interfacial structure, which is usually insignificant in bulk materials. The thermal properties could be accounted for the conduction of electrons as well as phonons which causes lattice vibrations. In nanostructured materials, the size of the nanomaterial becomes comparable to the mean free path of phonons through phonon scattering, phonon confinement, and quantization effects of phonon. Nanoscale thermal management suffers a slow progression because of the difficulties experimental setup and a controlled thermal transportation feature in the nanoscale dimension.

1.2.5 Catalytic Properties

Nanomaterials have been used as a catalyst in enormous chemical reactions. Nanocatalyst stands as a perfect boundary between the homogeneous and heterogeneous catalyst. Nanocatalyst embarks supreme efficacy in terms of its high activity, selectivity, sensitivity, efficiency, and stability. The catalytic activity of nanomaterials is confined to the structural, quantum size and electronic effects. It is a well-known fact that a decrease in the dimension of the particles increases the surface area thereby enabling more and more reactant molecules to get adsorbed on the nanomaterials, eventually resulting in enhanced catalytic activity. The existence of a greater quantity of surface atoms creates more active sites for the adsorption of reactant molecules. These phenomena cause a greater dissociation of the binding energy of the reactants and a pronounced catalytic activity of the nanomaterials resulting in the formation of the products.

1.2.6 Electrical Properties

The electrical conductivity of nanomaterials can be expressed in terms of conductivity or resistivity. The electrical conductivity is justified by the band structure of solids. Unlike nanomaterials, the conductivity of bulk material is independent of measurements like diameter, area of cross-section, twist of conductivity, etc. When a material is condensed to nano size, the electron is restricted for movement to a confined particular dimension and there is an increase in surface scattering. Hence the electrical conductivity drops down with reduced dimensions. However, the electrical conductivity may be altered due to the establishment of a well-ordered microstructure when the particle size is diminished to the nm range. The nanomaterials are associated parallel to the axis, which contributes to the conduction through the tunneling effect. The smaller the diameter, the better alignment of nanomaterials, which results in higher electrical conductivity. The conductivity of a multi-walled carbon nanotube is very much different from the single-walled carbon nanotube of the same dimensions.

1.2.7 Energy Band Conduction Properties

Semiconductor nanomaterials often refer to a variety of compounds of group II–VI, III–V, or IV–VI of the periodic table into which these elements are formed. For example, silicon and germanium occupy group IV, gallium and indium constitute group III–V, while those compounds of zinc and cadmium form II–VI semiconductors. The semiconducting properties are associated with the electronic structure and as discussed in the previous section, electrical property. The precise surface area and surface-to-volume ratio considerably increase as the size of the material decreases. Factors such as size, shape, and surface characteristics can be changed to control their properties for exclusive applications of interest. A decrease in the particle size towards the nanometer range causes an escalation in the bandwidth between the valence band and conduction band. In other words, the confinement of an electron restricts the transition of an electron from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. This eventually results in the blue shift of the absorbed light, which is towards the high energy region. The transfer of electrons and holes in semiconductor nanomaterials is predominantly directed by the distinguished quantum confinement, and the means of transport of phonons and photons are essentially varied by the size and geometry of the materials.

1.3 CLASSIFICATION OF NANOMATERIALS

1.3.1 Classification Based on Spatial Dimension

According to Richard W. Siegel (Siegel 1993), based on the spatial dimensions, nanomaterials are classified into zero dimensional (0D) nanomaterials, one dimensional (1D) nanomaterials, two dimensional (2D) nanomaterials, and three dimensional (3D) nanomaterials.

1.3.1.1 Zero Dimensional (0D) Nanomaterials

When all the three dimensions are confined to one particular point and thus the movement of electron is restricted in all the three x,y,z directions, it is called zero dimensional. Example: nano dots, nanoparticles, quantum dots.

1.3.1.2 One Dimensional (1D) Nanomaterials

In case of one dimensional nanomaterials, two dimensions are reduced to nm range; only one dimension remains large and the electron is permitted to move in this one dimension. Example: nanowires, nanotubes, nano rods.

1.3.1.3 Two Dimensional (2D) Nanomaterials

Two dimensional nanomaterials have one dimension restrained to nm range and the electron is permitted to move freely in the remaining two dimensions which remains large. Example: nanowells, nanofilms, nanocoatings, nanolayers, nanoflakes, nanoplatelets.

1.3.1.4 Three Dimensional (3D) Nanomaterials

Three dimensional nanomaterials have no confinement in the nm range and the electron is permitted to move in all the x,y,z directions. They possess an arbitrary dimension above 100 nm. Example: bulk nanomaterials, nanopowders.

1.3.2 Classification Based on Composition

On the basis of composition, nanomaterials can be classified as organic nanomaterials, inorganic nanomaterials, and hybrid nanomaterials.

1.3.2.1 Organic Nanomaterials

Organic nanomaterials entail carbon-based nanomaterials taking different forms of spheres, cylinders, ellipsoids, or tubes. There exist non-covalent interactions like hydrogen bonding, pi staking, and electrostatic interactions. Organic nanomaterials are assembled upon either natural or synthetic organic molecules. Example: fullerenes, carbon nanotubes (CNTs), single-walled and multi-walled carbon nanotubes (SWCNTs and MWCNTs) and electrospun nanofibers.

1.3.2.2 Inorganic Nanomaterials

Inorganic nanomaterials include metals based, oxides of metal based, and quantum dots—nanomaterial metalloids in nano dimensions. They may extract the form of the oxide or hydroxide or phosphate or sulphide or chalcogenide of the metal. Example: gold nanoparticles, zinc oxide nanoparticles, mesoporous silica nanoparticles.

1.3.2.3 Hybrid Nanomaterials

Hybrid nanomaterials are composite nanomaterials and are a combination of organic-organic nanomaterial, organic-inorganic nanomaterial and inorganic-inorganic nanomaterials. They are unique chemical conjugates of organic and inorganic nanoparticles; as a result, multifunctional hybrid materials are obtained, which possess immense applications. Example: lipid-polymer hybrid nanoparticle, hybrid silica particles.

1.4 BIOMEDICAL APPLICATION OF NANOMATERIALS

The rise of inventive and fabricated nanomaterials is at the forefront in emergent areas of biomedical applications. The exploitation of rationally designed nano biomaterials in clinical applications has surpassed traditional therapeutic modalities. Nanomaterials have invoked engrossment among researchers because of their unique physicochemical properties, biocompatibility, and desired functionalization modification, size- and shape-dependent optical and magnetic properties. Nanomaterials scale well in biomedical applications which include diagnosis, targeted drug delivery, prostheses, and implants. A multifunctional framework centered around metal, carbon, polymer, biological moieties, and lipid-based nanomaterials is associated with biomedical imaging, diagnostics, and/or therapeutics and serves as a synergistic combinational platform in biomedical applications.

1.4.1 Biomedical Imaging

Early detection and diagnosis offer a quintessential role in biomedical studies. Fluorescence imaging is vividly used for the characterization of novel drugs or of new formulations of prevailing drugs exclusively at the preclinical level. Integrating photo luminescent imaging analytics and molecular probes over the preceding years have been used in imaging of cell/tissue in diagnostics. Photo luminescent imaging constitutes the preliminary stage in the drug development process for the translation phase from *in vitro* assays to preclinical systems, as well as to evaluate their ADME. Functional imaging will provide a detailed picture of the local and real time biological activity of the drug. The technique involves the radioactive labeling of the fluorescent material which can be applied in the early progress of a drug and transform the applicability, *in vitro* on cells, then *in vivo* in small animals and finally rendered into the clinic with restrictions. It is not appropriate to use this method for small drugs due to the large size of the fluorophores. But this can be applied for a nanoparticle, on the basis of the assumption that the labeling should not intensely modify the corresponding property of the nanoparticles or that the fluorophore could be a fragment of the final formulation.

Prominent advances of recent times include the application of optical nanoprobes, such as persistent luminescent nanoparticles (PLNPs) which are developed to replace the usage of long-lasting near infrared (NIR) luminescence capability. The added advantage to the usage of determined luminescence nanoparticles is optical imaging without constant excitation and autofluorescence. The most common and extensively used nanoparticles in biomedical imaging and cancer therapy include nanoparticles, nano rods, nanospheres, nano shells, and nano stars. Nanoparticles aid as drug carriers, imaging contrast agents, photothermal agents, photoacoustic agents, and radiation dose enhancers. Nanoparticles continue to be potential candidates in biomedical imaging for the major imaging techniques Magnetic Resonance Imaging (MRI), Positron Emission Tomography (PET), Single Photon Emission Computed Tomography (SPECT), Magnetic Particle Imaging (MPI), Nuclear Medicine, Ultrasound (US) imaging, Computed Tomography (CT), and Optical Imaging in particular. The breakthrough in the advances of NPs includes the use of iron oxide NPs (Pellico et al. 2017), the design of radio isotope chelator free particles for PET (Dash et al. 2019), and the development of fluorescent NPs such as carbon dots and up-converting nanoparticles (Siddique et al. 2020).

1.4.2 Targeted Drug Delivery and Controlled Drug Release

Drug delivery often refers to the design, construction, engineering technologies and transport of a particular therapeutic compound to attain the desired therapeutic effect. Drugs can be directed into several routes into the human body which may be buccal, oral, pulmonary, transdermal, ocular, sublingual, vaginal, and anal. These conventional approaches of drug delivery involve the transportation of the drug through the blood to the target of interest. The major setback of the traditional method is the damage caused to the normal cells. Hence, research is intensified in seeking a selective and targeted drug delivery where the drug is being delivered to the target without affecting the healthy cell. Another aspect of concern is the advance of biodegradable nanoparticles as drug delivery devices (Idrees et al. 2020). Various morphologies involving large surface-area-to-volume ratios such as nanoparticles, nanospheres, nano-encapsules are used as drug delivery systems. The small size of the nanoparticles penetrate through the smaller capillaries, being effortlessly taken up by the cells, and the biodegradability of the nanomaterial allows efficient and controlled drug accumulation and controlled drug release to the target site over a duration of time. Nanomaterials also defend the captured drug from gastrointestinal interferences. The formulations of targeted drug delivery of nanoparticles and controlled drug release involve drugs to be dissolved, entrapped, adsorbed, attached, and encapsulated into the nanomaterial matrix (Yetisgin et al. 2020).

Each nanomaterial has its own characteristic way of targeted drug delivery. For instance, nano capsules are a vesicular system with the drug bounded by a polymer membrane, whereas nanospheres are matrix types of structures where the drug is physically and uniformly spread. As in the case of nanospheres belonging to the matrix type of system, the drugs are adsorbed at their surface, entrapped or dissolved within the particle. Drug delivery systems are in general polymeric and nano sized and the different forms of drug delivery systems include nanoparticles, ceramic nanoparticles, micelles, polymeric micelles, dendrimers, and liposomes. Polymeric nanoparticles such as PLGA (poly(lactide-co-glycide)), PLA (polylactic acid) is largely used for the drug delivery of estradiol. The degradation of the polymer can be modified by changing the block of the copolymer composition and the molecular weight of the polymer and thus the release of the encapsulated therapeutic agent from the polymeric nanoparticle can be transformed from days to months (Masood 2016).

1.4.3 Tissue Engineering

Tissue engineering deals with the art of creating, restoring, replacing, and maintaining tissues and organs using biological substituents, which have a very close resemblance to the body's native tissues/organs. It is a connecting discipline of integrated biology, engineering, material science, and medicine. Traditional bone substituents in the biomedical industry include bioceramics like alumina, zirconia, hydroxyapatite, tricalcium phosphates, owing to their low density, biocompatibility, chemical stability, and high wear resistance (Eliaz et al. 2017). The implementation of nanotechnology in tissue engineering has evolved as evolutionary and revolutionary changes. The most common feature of tissue engineering is the fabrication of a three dimensional porous scaffold which serves as a substrate and support for tissue growth and directs the cells to grow in the correct anatomical shape, thereby possessing biocompatibility to avoid inhibition of cell growth. Nanotechnology fabricates biomaterials of nanometer size like nanofibers, nanopatterns, and controlled-release nanoparticles to mimic native tissues/organs engineering.

Tissue engineering involves functionality-dependent design and construction of nanostructures. For instance, the design and construction of neural tissue require electrical conductivity, while bone and cartilage tissues necessitate enhanced mechanical properties (Achachelouei et al. 2019). The fabrication of scaffolding material that reiterates the cellular environment on a nano scale has raised great interest in recent years. Carbon nanotubes are vividly used in tissue engineering as they are chemically stable, conduct electricity, and mechanically strong to be employed as scaffolds. Filamentous carbon nanotubes possess a structural alignment that is analogous to the extracellular environment which supports surrounding cells. Thus the carbon nanotubes may have the capability to kindle cell function in the same way as the extracellular matrix (Huang 2020). The biocompatibility tests of carbon nanotubes in suspension and carbon nanotubes confined in a structure exposed that the loose carbon nanotubes suspended in cell culture were found to decline in cell viability. The cells that are directly attached to carbon nanotube-containing structures created cell growth and demonstrated excellent biocompatibility of carbon nanotubes with living cells.

1.4.4 ARTIFICIAL IMPLANTS

The influx of nanoparticles in medicinal devices is an upcoming field. Devices or materials that are positioned within the body superficially are called artificial implants. They are intended to convey suppositories, monitor body functions, and deliver sustenance to organs and tissues. Earlier implants were made of skin, bone, or other body tissues. Later, metals, ceramics, polymers and their composites were designed and largely employed to support, enhance, or to even replace a fraction. Artificial implants can be used permanently as in the case of stents or hip implants, while chemotherapy ports or screws to repair broken bones are temporary and are removed after healing. But the safety and potential side effect remain a question, though the artificial implants possess good dimensional tolerance, high fracture toughness, good fatigue resistance, comparable strength, and modulus close to the bone, high wear resistance of tissue, biocompatibility, high purity, and reproducibility.

The interaction between the artificial implants and cells has facilitated nanotech research towards the frame of nanomaterials towards artificial implants. The norm of nano-engineered quantum dots and magnetic nanoparticles for stem cell tracking and the enrichment of material properties with carbon nanotubes and graphene are in progress (Zhao et al. 2020). The biocompatibility of the nanomaterials in artificial implants includes promoting biological tissue for implant integration, promoting cell adhesion, providing pathways for vascularization, non-carcinogenesis, non-pyrogenicity, non-toxicity, and non-allergic response (Velu et al. 2020). The ability to undergo sterilization, autoclave and dry heating, ethylene oxide gas, and radiation account for the sterilizability. The primary functionality of nanomaterials in artificial implants is the entrenchment of modulus of elasticity for the stiffness of the material, ultimate tensile strength to withstand a load and dimensional accuracy on an economical fabrication process. The ease of molding, extrusion process, machinability, and ability for fiber forming elucidate the usage of nanomaterials in manufacturing artificial implants. Nanostructures provide antibacterial properties to prevent implants against postoperative infections proposed for bone and implants. Nano-sized silver particles widely aid in the exploration of suitable size, shape as well as a novel method of surface modifications such as SDP technology for orthopedic implants (Qing et al. 2018).

1.4.5 GENE THERAPY

Despite of the blooming advances in the field of medicine, cancer remains with a high mortality rate, especially in developing and underdeveloped countries. One of the leading causes for such a high mortality rate is the limitation of actual treatments based on drugs and radiation. These confines include lack of specificity, reduced drug bioavailability, drug rapid blood clearance, poor drug solubility, patient resistance, and disease relapse. Traditionally used chemotherapeutics which include cisplatin or taxol have been favored over other therapies due to the selective killing of cancer cells preferentially by inhibiting replication or inducing apoptosis. Certain chemotherapeutics produce adverse effects as well. Chemotherapeutics with anthracyclines and cyclophosphamide cores cause serious side effects in patients, killing healthy cells and tissues like bone marrow, epithelial cells, and hair follicles. Hence, the development of alternate and more efficient treatments that may offer fewer side effects in comparison to the actual therapies remains a challenge to researchers.

Novel technologies for cancer treatment have been employed in the recent past based on the research and application of nanotechnology and molecular biology. The targeted level treatment remains the limelight of treatment in the recent past and near future. The advance of molecular biology permits the manipulation of nucleic acid in the management of numerous genetic diseases like cancer. Gene therapy comprises the transmission of genetic material into a target cell nucleus for healing concerns with comparatively negligible side effects. This genetic material could be DNA or RNA, the complete gene sequence, gene segments, or an oligonucleotide.

With the development of genomic technologies, nanoparticles owing to their greater penetrating power play a critical part in incorporating all the desirable characteristics of modification into a single gene delivery system (Rodrigues et al. 2020). Lipid and polymer-based gene delivery vectors are paved to be sophisticated delivery systems in gene therapy. Polymeric nanoparticles are largely employed for gene therapy and protein delivery.

1.4.6 Photodynamic Therapy

Photodynamic therapy is emerging to be a remedial modality for early detection and localized cancers. The three key components in photodynamic therapy include: photosensitizer, light, and molecular oxygen. The photosensitizer is administered either by intravenous injection or by local application depending on the part of the body to be treated. Once the drug is absorbed by the pathologic tissue, light is exposed. The photosensitizer gets activated by light and forms Reactive Oxygen Species (ROS), which in turn kill cancer directly. A major issue faced by prolonged photodynamic therapy is the increased selective accumulation of the photosensitizers within the tumor thereby leading to a lower effective dose of the drug. To improve the efficacy of photodynamic therapy, efforts were laid to bind the photosensitizer itself by ligands such as monoclonal antibodies or low-density lipoprotein (LDL) or via carrier system such as liposomes and micelles (Gibot et al. 2020).

Nanoparticles are proving to be an emerging paradigm in photodynamic therapy. The foremost lead application of nanoparticles in photodynamic therapy is large surface area with a varied functional group for modified biochemical processes, large surface volume, controlled release of drugs, and easy transportation of hydrophobic drugs in blood, high permeability and retention effect. Nanoparticles encompassing inorganic oxide, metallic, ceramic and biodegradable polymer nanomaterials have successfully been in use in photodynamic therapy in the recent past (Chen et al. 2020). Nanoparticles used in photodynamic therapy can be broadly classified into active and passive nanomaterials depending on the mechanism of activation of photosensitizer nanoparticles. The role of the mechanism of active nanoparticles can be sub-classified as activation of photosensitized nanoparticles, up-conversion nanoparticles, and self-lighting nanoparticles. In the case of active nanoparticles, materials for photosensitizers like CdSe/CdS/ZnS cause indirect excitation of photosensitizers through a Fluorescence Resonance Energy Transfer (FRET) mechanism from the nanoparticle to the photosensitizer. Fullerene aids in the transfer of energy from incident light directly to surrounding oxygen.

Based on material composition, passive nanoparticles can be classified as biodegradable and non-biodegradable nanoparticles. Biodegradable nanoparticles include alginate, chitosan, cyclodextrin, albumin, PLA, PLGA, wherein the drug is delivered by micelles, dendrimers, liposomes, or polymeric nanoparticles, ensures the controlled release of the encapsulated photosensitizer through biodegradation. Fabrication of non-biodegradable nanomaterials includes polyacrylamide in which the two-photon dye is encapsulated by microemulsion, silica which assists in the absorption of photosensitizer by covalently bonding through a porous shell, gold nanoparticles act as pure carriers, and magnetic iron oxide nanoparticles in which a drug is carried directly or co-encapsulated in a micelle or polymeric nanoparticle. The added advantage of magnetic iron oxide nanoparticle is the achievement of target delivery by an external magnetic field (Yang et al. 2019).

1.4.7 SONODYNAMIC THERAPY

Sonodynamic therapy has been considered as a safe alternate to the conventional as SDT uses ultrasound at relatively low intensities (ranging from 0.5 to 4 W/cm^2) when thermal or mechanical effects cannot be induced to living cells (Wan et al. 2016). Porphyrin-based molecules or Xanthene dyes are employed in the sonodynamic therapy, as the same were earlier used in photodynamic therapy (Buck et al. 2017). These molecules present a Reactive Oxygen Species (ROS)–mediated cytotoxic effect when stimulated by ultrasound. The major disadvantage of most of the sonosensitizing agents is they are strongly hydrophobic and aggregate easily in the physiological environment, thereby decreasing the efficacy and producing a retarding effect in the pharmacokinetic behavior. These molecules would indeed be toxic and show low selectivity towards tissues.

The evolution of nanoparticle-mediated sonodynamic therapy has made a major stride forward in overcoming the challenges faced by deleterious side effects caused by chemotherapy and radiotherapy (Canavese et al. 2018). Nanomaterials may serve as nano sensitizers or active carriers of sonosensitizers. Titanium dioxide nanoparticles are the most widely used nano sensitizers in SDT. Because of their semiconducting property, they are employed as photosensitizers in photodynamic therapy as well to obtain ROS. The therapeutic enhancements obtained with TiO_2 NPs, an enriched and favored binding and internalization of NPs toward cancer cells and functionalization with targeting molecules make nanoparticles auspicious for the advance towards targeted therapy (Kim et al. 2020). The sonodynamic therapy (SDT) of semiconductor metal oxide nanoparticles, for example TiO_2 and ZnO_2, can provide a therapeutic platform in the future (Bogdan et al. 2017). As termed, the significant role played by the NPs in inducing the cytotoxic effects, as initiators of the SDT process, is tremendous.

1.4.8 CRYOSURGERY

Cryosurgery is a unique technique when extreme cold derived from liquid nitrogen or argon gas is used in surgery to terminate unusual or damaged tissues. Cryosurgery is otherwise called freezing therapy, cryotherapy, or cryoablation and has been increasingly used due to the controlled annihilation of tumor tissue. But a major setback of cryosurgery is when the gases undergo deficit or inappropriate freezing as it fails to destroy the target tumor tissues, and the probability of regenesis of tumor is high and the rate of treatment often a failure. Another major drawback is that the surrounding healthy tissues/cells may suffer from serious injury due to the extreme coldness. Hence, a new strategy of inculcating nanomaterials—nano cryosurgery is invoked in biomedical applications to overcome the freezing efficiency of the traditional cryosurgical procedure.

The primary protocol of nano cryosurgery is to carry a functional suspension of nanoparticles into the target tissues, which then helps as adjuvant or drug carrier either to maximize the freezing heat transfer process, standardize freezing scale, alter ice-ball formation orientation, or avert the surrounding healthy tissues from being frozen (Hou et al. 2018). Furthermore, the introduction of nanoparticles in the course of cryosurgery with potential challenges and future prospects aid in the better imaging of the edge of a tumor as well as the margin of the ice ball. The nano cryosurgery is anticipated to move horizons emerging frontline of nano-biomedical engineering. Typical nanoparticles (NPs), which are nontoxic, biodegradable, and possess excellent thermal properties with a few side effects, produce an accelerated and enlargement of ice-ball formation and enhance cryoinjury, thereby promoting the generation of ice nuclei. The applicability of magnetic nanoparticles with high thermal conductivity and good biological compatibility improves nucleation with increased kinetic and thermodynamic parameters. Polymeric NPs change the morphology of ice crystals and improve thermal conductivity (Stewart et al. 2020). TNF α—conjugated Au NPs causes contraction of the tumor without systematic toxicity and destroys tumor cells within the ice ball efficiently with minimal side effects (Hou et al. 2018). Nanoparticle-encapsulated doxorubicin (nDOX) achieves nearly complete eradication of the cancer stem-like cells (CSCs) with fewer side effects and enhanced targeting.

1.4.9 MAGNETIC HYPOTHERMIA

Over the era, cancer is still considered a deadly disease and most forms of human cancer are not curable. The reasons may be multifactorial. But the chief and primary limiting factor remains in the lack of understanding of the mechanism by which the tumor grows and the therapeutic intervention. The most common and principal types of cancer therapies include chemotherapy, radiation therapy, and surgery. Magnetic hyperthermia is an additional modality to cancer therapy but is yet to be considered as a standard-of-care therapy.

The term hyperthermia involves the mild elevation of temperature to induce the death of cancer cells and to enhance the effect of radiotherapy and chemotherapy. Heat treatment is used as a chief aspect to destroy cancer cells. The principle behind magnetic hyperthermia involves the magnetic nanoparticles being activated by an alternating magnetic field being reconnoitered by targeted heating of the tumors. The basis of heat generation under alternating magnetic fields both for *in vivo* and *in vitro* studies for biomedical applications has been a subject of intense research (Chang et al. 2018). The efficacy of nanomaterials for magnetic imaging-guided hyperthermia, thermal cancer therapy, magnetically actuated drug delivery, and biofilm eradication is research of the recent past. A gradual increase in the temperature around the cancerous region to 40–43 °C induces significant cancer cell death in addition to the cytotoxic effect of radiotherapy and chemotherapy. The magnetic nanoparticles act as intermediaries for cancer therapy. A steady increase in the temperature of the cells above 40 °C produces pronounced effects in the membrane and the interior of the cells. Multifunctionalized hybrid nanocomposites involving the combination of magnetic nanoparticles with materials like graphene oxide (GO), photoactive materials, mesoporous nanoparticles, and polymeric nanoparticles—polymer matrix—embedded with active nanomaterials have been widely investigated (Kim et al. 2018).

1.4.10 ANTIMICROBIAL AND WOUND HEALING

The largest organ in the human body—skin—covers and integuments the entire body and provides protection against pathogens, toxins, and trauma and receives sensory stimuli from the external environment. The rupture of the skin leads to a wound, and the wound is often associated with infections. The healing of a wound is the extremely synchronized progression of restoring damaged tissue encompassing four sequential, yet overlying biological stages: hemostasis, inflammation, proliferation, and remodeling. A disconcertion in the previously stated wound-healing phases due to both external and internal factors may prolong the wound-healing stage and may lead to a disappointing outcome, causing a chronic wound status. The colonization of pathogens over the wound retards the healing process and infection control remains crucially important. In the emerging scenario of biomedical applications, nanomaterial-based wound-healing tactics have emerged as an effective tool against bacterial infections for their cell specificity, which was not earlier attainable with conventional wound-dressing materials or present therapies. The constructive use of metal and alloy nanoparticles have minimal concomitant and enhanced curative activity as compared to its ionic counterpart, which is well documented by *in vivo* excision wound-healing activity of silver (Ag), gold (Au), and Ag/Au alloy nanoparticles. It was evident that Ag NPs and Ag/Au NPs actively inhibited the growth of gram-negative bacterial pathogens and opportunistic *Candida spp.* (Shanmugasundaram et al. 2017). Nanomaterials with their large surface-to-area volume ratio, stability, and tunable properties are designed as drug delivery vehicles or the drug may itself be formulated to the nanoscale. These physicochemical properties enable the nanomaterial to penetrate through the layer of skin and interact efficiently at the wounded site with a continuous and controlled release of therapeutics. Nano-based approaches for wound-healing applications include micelles, polymeric nanocomposites, dendrimers, nanoemulsions, liposomes, cyclodextrins, lipid nanoparticles, magnetic nanoparticles, silica nanoparticles, nanographene oxide scaffolds, and metal nanoparticles. The applicability of nanomaterials as core antibacterial agents and as vehicles for the transportation to wound-healing therapeutic agents will be explored in the future.

1.5 CONCLUSIONS

This chapter summarizes the critical role of nanomaterials in biomedical applications. The portfolio set forward by the nano effects anticipate the evolution of stemming growth towards the advancements in biomedicine with engineered structures with novel functionalities. The distinctive properties of nanomaterials such as size, shape, chemical composition, surface structure and charge, biocompatibility, aggregation and agglomeration, and solubility, can prominently stimulate the interactions with biomolecules and cells, and can be exploited in a multifaceted spectrum of biomedical utilities ranging from drug delivery and biosensors to nanorobots. The revolutionary innovations—programmable and precise delivery of nanomaterials—impart a positive impact rendered by the biomedical applications, minimizing the adverse effects of traditional therapeutics and practices on human health and the environment. The key concerns and encounters in nanotechnology-based approaches provide a futuristic scope and vision of inculcating nanomaterials in biomedical applications.

TABLE 1.1
Nanodrug Carries Approved in Recent Past in Clinical Trials [17]

Drug Name	Delivery Material	Condition	Therapeutic Delivered	Clinical trials. Gov. Identifier	Status
Genexol PM	Amphilic diblock copolymer forming micelle	Non-small cell lung cancer	Paclitaxel	NCT01023347	Completed
Docetaxel-PNP	Polymeric nanomaterials (active nanocomponents loaded/entrapped in polymeric core)	Advanced solid malignancies	Docetaxel	NCT01103791	Completed
CYT-6091	Au NP	Unspecified adult solid tumor	TNF	NCT00356980	Completed
Kogenate FS	PEG-liposome	Hemophilia A	Recombinant factor VIII	NCT00629837	Completed
Long circulating liposomal prednisolone disodium phosphate	Liposome	Rheumatoid arthritis	Prednisolone	NCT00241982	Completed
LE-DT	Liposome	Pancreatic cancer	Doxetaxel	NCT01186731	Completed
Cisplatin and Liposomal Doxorubicin	Liposome	Advanced cancer	Cisplatin and Doxorubicin	NCT00507962	Completed
Liposomal doxorubicin and bevacizumab	Liposome	Kaposi's sarcoma	Doxorubicin and bevacizumab	NCT00923936	Completed
AP5346	Drug polymer conjugate	Head and neck cancer	AP5346 and Oxaliplatin	NCT00415298	Status Unknown

1.6 CHALLENGES AND FUTURE SCOPE OF NANOMATERIALS IN BIOMEDICAL APPLICATIONS

The convergence of science and technology has provided a quintessential hope of developing nanostructured materials in the field of medicine. The widespread opportunities of nanomaterials in therapeutics have gained the attention of researchers from multidimensional aspects ranging from medical practitioners to health experts working in government, industries, and academia. Recent clinical trials of nanomaterials in therapeutics are enumerated in Table 1.1. However, the biocompatibility of nanomaterials is a major concern because of adverse effects extending from cytotoxicity to hypersensitivity. Hence, prior to human exposure, all nanomaterials are imperiled to toxicological studies to meet the regulatory standards. In addition to designing, identifying, and validating a nanomaterial down the lane of the pipeline of drug designing, the toxicological analysis, route of exposure, coating material and sterility of the nanomaterial, economic viability have to be considered with utmost care. The futuristic scope of nanomaterials in the bio-medicinal field involves a perfect blend of nanotechnology and Computer-Aided Drug Designing (CADD). Nanorobots skilled in intruding biological system to identify cancer cells is the recent lead of nanomedicine. The potential of applying nanomaterials in this pandemic situation to arrive at more effective vaccines against COVID 19 is always a subject of major concern.

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