

Preface

The present monograph *Applied Spectroscopy and the Science of Nanomaterials* is a synergistic compendium of 11 informative and cutting-edge chapters written by leading researchers in the fields of spectroscopy and condensed matter physics as applied to a variety of materials at the nanoscale.

“[Raman Spectroscopy, Modeling and Simulation Studies of Carbon Nanotubes](#)” authored by Daniel Casimir, Raul Garcia-Sanchez and Prabhakar Misra focuses on carbon nanotubes (CNTs) that are allotropes of carbon and consist of a single layer of sp^2 -hybridized carbon atoms. CNTs have a hollow cylindrical shape and are of two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The majority of SWCNT have diameters of the order of ~ 1 nm and lengths of the order of microns to centimeters. MWCNTs are composed of concentric layers of SWCNTs nested inside one another, giving it a layered cylindrical shape. In this chapter, the authors provide a historical overview of CNTs and examine specifically their thermal properties and describe in-depth the use of Raman spectroscopy and Molecular Dynamics (MD) simulations to characterize and investigate the thermal characteristics of SWCNTs. Such investigations lead to a clearer understanding of the chirality of nanotubes through the visualization of rolled-up graphene sheets, and in turn provide insight into the versatility and myriad thermomechanical and electrical properties that make CNTs excellent candidates for a wide variety of applications in nanoelectronics and the semiconductor industry.

In “[Laser Optogalvanic Spectroscopy and Collisional State Dynamics Associated with Hollow Cathode Discharge Plasmas](#)” Michael Blosser, Xianming Han, Raul Garcia-Sanchez, and Prabhakar Misra discuss the laser optogalvanic effect in a discharge plasma environment, specifically associated with an iron–neon (Fe–Ne) hollow cathode lamp. The theoretical model behind the optogalvanic effect provides insight into the importance of laser optogalvanic spectroscopy as a tool for spectral characterization of plasma processes and enhanced understanding of the collisional state dynamics associated with the discharge species in hollow cathode lamps. The chapter focuses on transition states of neon in the Fe–Ne hollow cathode lamp and for illustrative purposes analyzes in detail the waveforms associated with

the optogalvanic transitions of neon: $1s_4-2p_3$ (607.4 nm), $1s_5-2p_7$ (621.7 nm), $1s_3-2p_5$ (626.6 nm), $1s_5-2p_8$ (633.4 nm) and $1s_5-2p_9$ (640.2 nm). A comparison between the experimentally recorded waveforms and the Monte Carlo fitting routine, along with a discussion related to the variation of the fitting coefficients as a function of the discharge current, illustrates the success of the theoretical model in elucidating collisional state dynamics associated with discharge species in a plasma environment. The authors also describe the potential applications of the optogalvanic effect at the nanoscale in fields such as graphene-based nanoelectronics and nanoplasmonics.

“[Applications of Fluorescence Anisotropy in Understanding Protein Conformational Disorder and Aggregation](#)” written by Neha Jain and Samrat Mukhopadhyay focuses on the applications of fluorescence anisotropy in protein conformational disorder and aggregation. Fluorescence spectroscopy is an ultrasensitive multiparametric technique that provides key insights into protein conformational dynamics and size changes simultaneously. Fluorescence polarization (anisotropy) is one of the parameters related to the rotational dynamics of a fluorophore either intrinsic to the molecule or attached to a biomolecule. The anisotropy measurements can be utilized to unravel the structural and dynamical properties of biomolecules. The advantage of fluorescence anisotropy measurements is that it is a concentration-independent parameter; it can be measured either in the steady-state or in the time-resolved format. Steady-state fluorescence anisotropy provides important information about the overall size/dynamics of biomolecules, whereas the time-resolved fluorescence anisotropy can distinguish between the local and the global dynamics of a fluorophore. Therefore, the time-resolved anisotropy measurements allow one to determine the conformational flexibility of biomolecules. In recent years, it has been demonstrated that fluorescence anisotropy can be effectively utilized to obtain structural and dynamical information about protein-based assemblies such as aggregates, protein-lipid complexes, etc. This chapter provides an overview of the applications of fluorescence anisotropy to study protein conformational disorder, misfolding, and aggregation, leading to the formation of nanoscopic amyloid fibrils that are implicated in a range of human diseases.

“[Nuclear Magnetic Resonance Spectroscopy in Nanomedicine](#)” authored by Ping-Chang Lin talks about the essentials of noninvasive measurements and deep penetration through living bodies using nuclear magnetic resonance (NMR) spectroscopy as a useful adjunct tool that complements *in vitro* and *in vivo* centered investigations in nanomedicine. This chapter introduces basic NMR principles and important NMR techniques that are especially relevant to the field of nanomedicine, followed by exploration of physicochemical characterization and metabolic profiles germane to the treatment and understanding of serious diseases. Conventional medicine generally relies on certain expression of disease symptoms (eg., metabolic responses, infections, and cancers) detected or diagnosed through the use of sophisticated and usually expensive medical instruments, devices, or implants, while appropriate therapy is subsequently developed based on clinical trials. On the contrary, nanomedicine, which focuses more attention on nanoscale interactions within biomolecules, cell organelles, and cells, is aimed at achieving early diagnosis and to ensure

accurate dosage for treatment at the molecular or cellular level, prior to the appearance of traditional symptoms. Two major challenges remain at the forefront of nanomedicine, namely: (1) how to reliably regulate the assembly of more than one active component in a nanoscale vector and (2) how well to control the forms and dosages of the active agents that are spatially and temporally released.

“[An Efficient Coupled Dipole Method for the Accurate Calculation of van der Waals Interactions at the Nanoscale](#)” is written by Hye-Young Kim and details the powerful and efficient coupled dipole technique for understanding van der Waals (VDW) interactions at the nanoscale. The VDW force arises from purely quantum mechanical charge fluctuations and is variously called a dispersion or London or Casimir force. This often considered as weak, yet ubiquitous, attractive interaction is important in many nanoscale systems. This chapter provides an overview of the Coupled Dipole Method (CDM), an atomistic and accurate computational method widely adopted to predict the VDW forces between dielectric nanomaterials. There is a concern about the burden of memory and computing time needed to solve eigenvalue problems by either diagonalization or iteration, which have hindered the implementation of CDM for large systems. Here, an efficient way, named trace-CDM (TCDM), is presented. TCDM uses the simple fact that the trace of a square matrix is equal to the sum of its eigenvalues and thus calculates the accurate VDW energies without solving for the eigenvalues. Four examples are presented to demonstrate the advantages of the method as a time and effort saver computational technique for complex eigenvalue problems in nanoscience.

“[Adsorption of Gases in Nanomaterials: Theory and Simulations](#)” by Mamadou T. Mbaye, Sidi M. Maiga and Silvina M. Gatica describes the theory and simulations associated with the adsorption of gases in nanomaterials. “Physical adsorption” (physisorption) is a term applied to atoms or molecules that are weakly bound to surfaces and has been extensively explored for more than half of a century because of interest in both potential applications and basic science. These applications include the separation of cryogenic gases, their storage, and their use as surface characterization tools, such as the measurement of surface area of porous media by nitrogen adsorption. The science of physisorption encompasses a wide variety of fundamental questions, including many related to phase transitions. The remarkable capability of physical adsorption to explore and analyze these diverse phenomena *quantitatively* derives from the weak binding energy <0.3 eV, which has several significant consequences. One is that the adsorbed film represents just a small perturbation of the underlying surface, simplifying theoretical analysis enormously. Often the substrate is assumed to be perfectly rigid, unaffected by the film. Another consequence is that the adsorbed gases are not significantly altered from their 3D gas phase electronic state, meaning that their mutual interactions are relatively well known. A particularly valuable consequence of the small binding energy is that a vapor coexists with the film (except at very low T), so that one can experimentally determine the chemical potential of both phases. This chapter focuses on adsorption in nanomaterials. In particular, the authors describe equilibrium properties of gases adsorbed in CNTs, graphene and Metal Organic Frameworks (MOFs). The behavior of adsorbed matter at the nanoscale is

dramatically different from the corresponding bulk material, due in part to the reduced dimensionality. The chapter describes the main results of simulations of adsorbed gases in nanomaterials and predicts novel phases that have not been observed yet, presenting challenges and opportunities to make significant breakthroughs in understanding intriguing phenomena linked with the behavior of adsorbed molecules at the nanoscale.

“[Atom-Precise Metal Nanoclusters](#)” penned by Anu George and Sukhendu Mandal looks at the world of atom-precise metallic nanoclusters. Nanoscale metals are generally classified based on three length scales into nanoparticles, nanocrystals, and nanoclusters. Nanoparticles are broadly defined as nanoscale particles in the range 1–100 nm, while the term “nanocrystal” is defined as a nanoscale crystallite of size >2 nm and nanoclusters (NCs) are those noncrystalline nanoparticles that are typically very small and composed of a specific number of metal atoms in the metal core, which are protected by shell of ligands. NCs are noncrystallographic in nature due to lack of translational symmetry. Optical properties of large metal nanoparticles to external electromagnetic fields depend on their sizes, free-electron density, and therefore their nearly bulk-like dielectric function relative to that of the surrounding medium. When particle size approaches the subnanometer size regime, the optical, electronic, and chemical properties of metal NCs differ dramatically from the other two size regimes. The ultra-small size of these NCs induces distinctive quantum confinement effects, which result in discrete electronic structure and molecular-like properties, such as HOMO–LUMO electronic transition, enhanced photoluminescence, intrinsic magnetism, to name a few. These NCs bridge small organometallic complexes and larger crystalline metal nanoparticles. Understanding the evolution as a function of cluster size is one of the grand challenges in chemistry and physics at the present time. In this chapter, the authors discuss the bridging roles of metal NCs between molecular chemistry and nanotechnology. Fundamental understanding of the evolution of the structure, electronic, and optical properties, as the materials evolve from the atomic state to NCs to fcc-structured nanocrystals, is of paramount importance and constitutes a major task in nano and materials science research. The evolution across length scales holds promise to yield fundamental insights into correlation between structure and the important quantum mechanical properties of NCs.

“[Plasmonic Properties of Metallic Nanostructures, Two Dimensional Materials, and Their Composites](#)” is authored by Lauren Rast and describes the intense and highly tunable optical field enhancement provided by nanomaterials supporting plasmon resonances, which has diverse applications in the areas of biophotonics, terahertz spectroscopy, and subwavelength microscopy. This chapter compares plasmon resonance behavior and tunability in noble metal nanostructures with that of two-dimensional and quasi-two dimensional materials including graphene, silicene, germanene, and transition metal dichalcogenides. Plasmonic optical behavior and related advancements in two-dimensional materials functionalized by metallic nanostructures are discussed, as well as possibilities for new directions for work on similar composite plasmonic systems are outlined.

“[Application of Graphene Within Optoelectronic Devices and Transistors](#)” written by F.V. Kusmartsev, W.M. Wu, M.P. Pierpoint, and K.C. Yung talks about how scientists are always yearning for new and exciting ways to unlock graphene’s true potential. There are reports that suggest this two-dimensional material may possess some unique properties that make it a viable candidate for use in optoelectronic and semiconducting devices. Although graphene is highly transparent due to its atomic thickness, the material does exhibit strong interaction with photons, which provides clear advantages over existing materials when used in photonic devices. Moreover, the material can be used to *trap* light and alter the incident wavelength, forming the basis for a plasmonic device. The authors highlight graphene’s nonlinear optical response to an applied electric field and the phenomenon of saturable absorption. Within the context of logical devices, graphene has no discernible band-gap. Therefore, generating one will be of utmost importance. Among many others, some existing methods to open this band-gap include chemical doping, deformation of the honeycomb structure, or the use of CNTs. The authors also discuss various designs of transistors, including those which incorporate CNTs, and others which exploit the idea of quantum tunneling. A key advantage of the CNT transistor is that ballistic transport occurs throughout the CNT channel, with short channel effects being minimized. The authors go on to discuss recent developments associated with the graphene tunneling transistor, with emphasis being placed upon its operational mechanism. Kusmartsev and colleagues also discuss the incorporation of graphene within high frequency devices that do not require a predefined band-gap.

“[The Versatile Roles of Graphene in Organic Photovoltaic Device Technology](#)” authored by S. Jayalekshmi and Sreekanth J. Varma builds on the wonder material graphene’s potential applications in the realization of efficient and stable organic optoelectronic devices, especially flexible solar cells, and assesses the prospect of realizing all carbon photovoltaic devices. The combination of uniqueness and fine tuning of electrical and optical properties of graphene, makes it a highly sought after candidate for various technologically important applications in optoelectronics. Graphene has been identified as a suitable replacement for the highly expensive, brittle and less abundant indium tin oxide, as the transparent electrode material for optoelectronic device applications. The absence of energy band-gap in graphene had originally limited its applications in optoelectronic devices. This problem has since been solved with the advent of functionalized graphene and graphene nanoribbons (GNRs). Functionalized graphene and GNRs have extended its use as hole and electron transport layers in organic/polymer light emitting diodes and organic solar cells by appropriate tuning of the band-gap energy. Blending dispersions of functionalized graphene with the active layers in photovoltaic devices has been found to enhance light absorption and to enable carrier transport efficiently. Graphene layers with absorption in the entire visible region can be fine-tuned to be incorporated into the active layers of organic solar cells. Realization of optimal conditions for the synthesis of GNRs and functionalized graphene hold promise for achieving the requisite structural, optical and electrical properties for the development of all carbon-based cost-effective organic solar cells with improved efficiency in the not-too-distant future.

“Nanomaterials in Nanomedicine” written by Francis Mensah, Hailemichael Seyoum, and Prabhakar Misra focuses on the applications of nanomaterials in nanomedicine. Nanotechnology has led to the construction of new devices for diagnostics and therapeutics, which permits early detection and treatment of malignant tumors and other serious diseases. It has also led to the improvement and efficiency of drug, gene, and protein delivery. Nanoparticles are being used to target the central nervous system (CNS), which can be challenging because of the necessity to cross the blood–brain barrier (BBB). They are also used in the treatment of Alzheimer’s Disease (AD), which is a neurodegenerative disorder prevalent in the aging population. It is characterized by severe neuronal loss and proliferation of plaques composed of β -amyloid peptide (A_β) and τ -protein deposits. An imbalance between production and clearance leads to the aggregation of A_β peptides, especially in neurotoxic forms, and may be the initiating factor in AD. Nanobiotechnology forms the basis of many new devices being developed for medicine and surgery, such as nanorobots. It has applications in most branches of medicine, such as: nanooncology—concerning cancer research; nanoneurology—the study of neurological disorders; nanocardiology, which studies cardiovascular disorders; nanoorthopedics, which studies diseases of bones and joints; nanoophthalmology, which studies eye’s diseases; and also for other infectious diseases. This chapter illustrates the use of nanoparticles as effective drug carriers for localized treatment of tumors via the use of liposomes, which are viscoelastic and deformable materials, akin to red cells. In this chapter, the authors also present an overview of the viscoelastic properties of liposomes in connection with the use of red blood cells evolution equation in mathematical biology. Recent advances have shown that liposomes can be used to incorporate red blood cells for delivery in the human body, and understanding rheological properties of liposomes is vital to their effective therapeutic utilization.

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I would like to dedicate this book in fond memory of younger brother, Dr. Sudhakar Misra, who passed away prematurely on December 15, 2013.

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