# Preface

Self-assembled mesocrystals represent a fascinating class of materials with significant scientific importance due to their unique structure and properties. These mesocrystals are formed through the self-organization of nanocrystals into ordered three-dimensional architectures, often exhibiting intriguing hierarchical arrangements at multiple length scales. The scientific importance of self-assembled mesocrystals lies in their potential to bridge the gap between molecular-scale interactions and macroscopic material properties. Studying mesocrystals provides valuable insights into fundamental principles governing crystal growth and self-assembly processes in condensed matter physics and materials science. Moreover, these materials exhibit exceptional physical properties, such as enhanced mechanical strength, optical properties, and catalytic activity, which can be tailored by controlling the assembly conditions. Understanding the formation and behavior of self-assembled mesocrystals not only advances our fundamental knowledge of crystal engineering but also holds promise for the design and development of novel functional materials for a range of technological applications, including sensors, energy storage devices, and biomedical technologies. Therefore, investigating self-assembled mesocrystals contributes significantly to the advancement of both fundamental science and applied materials research.

The functional properties of these nanostructures could further be enhanced by combining them with polymer matrices resulting in truly multifunctional organic-inorganic hybrid nanocomposites. In recent years, the field of advanced materials science has seen remarkable progress in the development of multifunctional polymer nanocomposites, particularly in the realm of thin films for applications spanning optoelectronic and electronic devices. In addition to the excellent electric, magnetic, optical, and chemical properties bestowed by the inorganic phase, the hybrid nanomaterial would possess high flexibility, lightweight, dimensional stability, scratch and shock resistance, corrosion resistance, hydrophobicity arising from the organic matrix. Owing to the plethora of diverse functionalities, polymer nanocomposites establish themselves as one of the most technologically advanced nanomaterials for future nanoscale devices and applications.

One such significant application is the field of memory technologies and new age flexible electronics. Owing to the rise of high-performance computing applications such as AI, machine learning, and big data analytics there has been exponential growth in data creation and consumption in recent years. Traditional silicon-based electronics have been tremendously successful in these works but following Moore's law, the downsizing of electrical components will reach its physical limit very soon. Therefore, a new memory technology is urgently needed that could offer high-density storage, faster read/write speed, non-volatility, lower power consumption, higher endurance & retention, mechanical flexibility, and scalability. Among various emerging memory devices, resistive random access memory (RRAM) has gained significant attention due to its simpler structure such as cross-point arrays and vertical structure, which may lead to high-density memory storage over conventional flash and DRAM technology.

Until now a large number of attempts have been taken to develop high-performance resistive switch based memory devices by using different metal oxides like hafnium oxide (HfOx), titanium oxide (TiOx), nickel oxide (NiO), zinc oxide (ZnO), manganese oxide (MnOx), aluminum oxide (AlOx), zirconium dioxide (ZrO2) etc. where oxygen vacancy created a conducting channel due to the ionic movement of $O^{-2}$ due to the external bias. However, the deposition techniques of these metal oxides are mostly based on expensive physical vapor deposition methods like pulse laser deposition (PLD), atomic layer deposition (ALD), reactive sputtering etc. Additionally, inorganic layers are brittle and mechanically unstable and thus cannot be accommodated in new-generation flexible and portable microelectronics. To overcome this serious drawback, solution-processed polymer nanocomposite (PNC) based resistive switching layers are developed which combine the resistive switching ability of inorganic nanostructures with the mechanical flexibility of polymers. However, the reported operating voltages and On-to-Off current ratio ($I_{on}/I_{off}$ ratio) of PNC-based devices are still not favorable for practical device application, and detailed studies of different factors affecting the device performance are required to achieve their maximal potential.

The key challenge addressed by this research lies in the tailored design of polymer nanocomposite thin films capable of multifunctionality. Optoelectronic applications demand materials that can efficiently interact with light, exhibiting properties such as light emission, absorption, or modulation. Likewise, in the domain of flexible memory devices, materials must possess the ability to store and retrieve data reliably while enduring mechanical stresses associated with flexibility. To realize these objectives, the thesis will explore several critical aspects.

Chapter 1 opens up with an introduction to functional nanostructures, a brief discussion on the most studied nanostructures with their significant applications in different areas. It further introduces different types of nanocomposites, their design and properties and then concentrates on the key advantages and plethora of applications of polymer nanocomposites. In the latter part of the chapter we have given a detailed background of the research that constitutes this thesis. We have also discussed key fundamental concepts that are essential and necessary to the understanding of this research work. These topics include self-assembly of nanoparticles, oriented attachment crystal growth, zeta potential, quantum confinement in semiconductors, resistive switching mechanism, and conducting filament formation mechanism.

Chapter 2 sheds light on the various synthesis and characterization techniques utilized in this research. The synthesis of polymer nanocomposites involves precise control over the dispersion of nanoparticles within the polymer matrix. This research investigates novel methods to achieve uniform dispersion, ensuring optimal interaction between the polymer and nanoparticles. The synthesis methodologies include sol gel method, solvothermal method, modified hummers method and solution mixing via ultrasonication. Advanced characterization techniques such as XPS, AFM, UV-Vis, PL, FTIR, Raman, Electron microscopy (e.g., TEM, SEM), and X-ray diffraction are employed to elucidate the structural, optical, chemical and electrical properties of the nanostructures and nanocomposite thin films. Understanding these properties is fundamental to tailoring materials for specific applications.

In chapter 3, we implement nature-inspired biomimetic growth of anisotropic, hierarchical nanostructures that could offer insight into new and exciting crystalline properties for advanced multifunctional applications. Our study demonstrates diethanolamine-mediated mesoscopic self-assembly of semiconducting ZnO Quantum Dots (3-5 nm) into lattice-aligned, symmetrical nanoclusters (40-50 nm) via non-classical Oriented Attachment crystal growth observed in various biomineralization processes. The oriented attachment (OA) process resulted in precisely aligned quantum dots possessing preferential orientation along <100> plane. Owing to the unique structure and surface engineering, the colloids exhibited excellent long-term physico-chemical stability as evident from the DLS and Zeta potential studies. The final nanoclusters, even though 40-50 nm in size, retained the quantum characteristics of individual quantum dots and displayed size-dependent, tunable optical properties such as the wavelength of PL emission, blue shift of absorption shoulder and band gap energy which is a unique observation, characteristic of mesocrystal morphology and cannot be obtained in bulk nanostructures Surface morphology of mesocrystals implied a porous microstructure with highly enhanced effective surface area compared to bulk nanoparticles of similar size range. A large number of surface defects were induced in the nanoclusters owing to the unique crystallization mechanism which was experimentally confirmed by the sharp green PL emission peak with a narrow bandwidth.

Chapter 4 explores and surface and interfacial properties of engineered polymer nanocomposite thin films. Multifunctional nanocomposite thin films of self-assembled nanostructures and polymethyl methacrylate were spin-coated onto plasma-treated Si wafers and the surface and interfacial properties were rigorously studied. Preferential orientation of the thin films along <100> direction was evident from the XRD data. Diethanolamine, due to its dual functionality radically enhanced the chemical interaction between polar ZnO and non-polar PMMA matrix resulting in highly stable thin films (Class II hybrids) with enhanced surface and interfacial properties as evident from the extremely low surface roughness and homogenous nanofiller dispersion observed in AFM and FE-SEM studies. Chemical interactions at the interface were also established quantitatively by XPS binding energy measurements which suggested hydrogen bonds and covalent bonds between organic-inorganic phases promoted via diethanolamine surface engineering. The thin films exhibit excellent absorption characteristics ranging from 300nm to 360 nm which spans both the UV-A and UV-B spectrum which is considered harmful for both humans and natural resources such as plantations, water bodies, etc . Additionally, the nanocomposite films exhibited remarkable transparency in the visible region lying between 85-90 %, rendering them suitable for application as transparent conductive electrodes, UV shielding windows, active layer in energy conversion devices, etc.

Chapter 5 and 6 further extends the application of polymethyl methacrylate nanocomposite thin films to flexible memory devices which form an inseparable part of the next generation flexible and wearable electronic devices, displays, sensors, etc. In contrast to the self-assembled ZnO mesocrystals utilized in Chapter 3 & 4, this section deals with nanocomposite thin films embedded with Graphene/ZnO heterostructures. Chapter 5 elucidates the synthesis methodology of these heterostructures i.e. modified hummers method followed by solvothermal synthesis. Furthermore, the structural, morphological, chemical and optical properties of these advanced nanomaterials have been studied in depth using methods such as XRD, AFM, FESEM, HRTEM, UV-Vis, PL, Raman and FTIR spectroscopy.

Chapter 6 details the fabrication methodology of 0D-2D heterostructure based flexible non-volatile resistive memory devices. The device structure consists of an ITO-coated flexible PET substrate as the bottom electrode and PMMA-embedded reduced-graphene/ZnO nanoparticle (NP) (rGO/ZnO NP) heterostructure as the flexible active layer. Besides, a rGO/PMMA-based device was also fabricated as reference. The operating voltage of this device is limited within ±2 V whereas the ON-to-OFF state is ~$10^6$ which is ~$10^3$ times higher than the reference device. The device also exhibited excellent endurance and retention characteristics with no significant degradation for more than 50 cycles. Besides, the retention time of this device is ~$10^4$ s which is several times more than the reference device. These electrical performance enhancements were attributed to the multifunctionality introduced by the rGO/ZnO NP heterostructures. A model based on the energy band of the components of this composite material has been proposed for better understanding of this mechanism. Flexibility studies exhibited a stable device performance for an extreme bending radius of 6 mm. The resistance of the device in ON-to-OFF states did not show any significant change even after 1000 bending cycles thus establishing the device as an excellent memory candidate for flexible and portable electronics.

Chapter 7 constitutes concluding remarks on our thorough studies and also provides a brief glimpse of future research endeavors.