This thesis is devoted to the investigation of mechanical properties and self-assembly process of materials at the nanoscale. Various nanostructured materials such as nanoparticles, nanotubes, nanowires and thin films are used as constituent elements of nanodevices. Hence, knowledge of the mechanical properties of materials at the nanoscale is extremely important for understanding their functionality in nanodevices. Mechanical properties of nanostructured materials may significantly differ from those of their bulk counterparts due to the high surface to volume ratio in nanostructures. We particularly focus on the role of the surface region on the stiffness of nanomaterials. We have shown that the stiffness of a nanomaterial can be tuned over a wide range by introducing appropriate coating on the nanostructure surface. We have also explored the effects of the surface region on the stability of various phases in a nanostructure.

In the second part of this thesis, we have described the self-assembly process of nanostructures mediated by drendrimers. Self-assembly techniques are frequently used to decorate nanostructures into specific networks. The motivation of this study is to investigate the mechanisms which control the effective interaction and the inter-particle distance between nanoparticle-dendrimer composites. Control over the inter-particle separation is very important since it has a strong influence on the electronic and optical properties of the nanostructures. In the following paragraphs, we summarize the results of our study.

We start with a brief introduction to the mechanical properties and self-assembly process of nanostructures in the first chapter. A brief review of the work done on these topics in the recent past is presented in this chapter. We discuss the results and conclusions of various experimental and numerical studies on these topics. We also mention the motivation for the studies we have carried out. At the end, we briefly describe the numerical methods (molecular dynamics (MD) and density functional theory (DFT)) which have been used in our investigations.

In the second chapter, we discuss the effects of the surface region on the mechanical properties of nanostructures. We have investigated the size and growth direction dependence of the mechanical properties of ZnS nanowires and thin films as a case study. We observe that the Young's modulus of nanowires and thin films strongly depends on their size and growth direction. This size

and growth direction dependence of the stiffness of nanostructured materials can be explained in terms of their surface modifications. Since the energy of the surface region is usually higher than that of the core region in a nanostructure, the surface atoms move their positions to minimize the surface energy. As a result, bond lengths at the surface region are usually different from their bulk values. We observe that in ZnS nanowires and thin films, the average bond length at the surface region is lower than that in the core region which remains unchanged from its bulk value. This decrease in the bond length (or equivalently increase in the bond energy) increases the effective stiffness of the entire nanostructure. As the size of the nanowire/thin film increases, the effect of the surface region gradually decreases and hence the Young's modulus value converges to the bulk value.

Since the surface region has a strong influence on the mechanical properties of nanostructures, the stiffness of a nanostructure can be tuned by modifying the surface region with other materials. In chapter three, we have shown that the stiffness of ZnS nanowires can be tuned by introducing a thin CdS shell on top of the ZnS surface. In general, the stiffness of a nanostructure can be increased (decreased) by coating the surface region with a stiffer (less stiff) material. However, the stiffness of the core/shell nanostructures strongly depends on the properties of the interface between the core and the shell. We observe that the binding energy between the core and shell regions is relatively low due to the lattice mismatch at the interface region of core/shell nanostructures. This lower binding energy strongly affects the stiffness of core/shell nanostructures. We have also shown that thermal properties such as thermal conductivity and melting temperature of core/shell structures can be tuned by changing the coating material.

In chapter four, we discuss the effects of the surface region on the stability of various phases in a nanostructure. The surface atoms may stabilize a particular phase in a nanostructure which is not a stable phase in the bulk material. In this chapter, we investigate the stability of the h-MgO phase, an intermediate structure found during the wurtzite to rock salt transformation, in CdSe nanostructures. We observe that this five-fold coordinated phase is more stable at lower temperatures and smaller sizes of the nanowires. The appearance of this phase has not been observed till now in experiments. We show that this phase is not stable for larger CdSe nanocrystals on which the experiments have been done.

In the rest of the thesis, we have presented the results of our studies of self-assembly of nanostructures mediated by DNAs and dendrimers. First we describe in chapter five the nature of the effective interaction between two PAMAM dendrimers. Dendrimers are frequently used to coat surfaces of nanoparticles to prevent the nanoparticles from aggregation. The interaction between such nanoparticle-dendrimer composites depends strongly on the nature of the effective interaction between dendrimers. We have used fully atomistic MD simulations to calculate the potential of mean force (PMF) between two PAMAM dendrimers. We show that the effective interaction strongly depends on the size (generation) and protonation level of the dendrimers. The PMF profiles of nonprotonated dendrimers show a global minimum which represents the attractive nature of the interaction between the dendrimers up to a certain center-to-center distance. On the other hand, the interaction between protonated dendrimers is repulsive throughout their interaction region. The PMF profiles are fitted very well by a sum of an exponential and a Gaussian function. This observation is in contradiction with some of the results of existing coarse-grained simulations which predicted the effective interaction between dendrimers to be Gaussian. Our atomistic simulation which includes all the local fluctuations is expected to give more accurate results.

Information about the effective interaction between two dendrimers helps in understanding how dendrimer molecules can be used to control the interaction strength and the preferred inter-particle distance between two nanostructures. In chapter six, we discuss the effective interaction between two dendrimer grafted gold nanoparticles. We observe that dendrimer molecules can get adsorbed spontaneously on the surface of a gold nanoparticle. These grafted dendrimers significantly alter the interaction between the gold nanoparticles. We have explored the effects of protonation level and the density of the grafted dendrimers on the effective interaction between two gold nanoparticle-dendrimer composites. We observe that these nanoparticle-dendrimer composites attract each other at low grafting density. However, the interaction strength and the inter-particle distance at the minimum of the potential are much lower and higher, respectively than those between two bare gold nanoparticles. Interestingly at higher grafting density, the nature of the interaction between the nanocomposites depends on the protonation level of the grafted dendrimers. Nanoparticles grafted with nonprotonated dendrimers still attract each other but with lower interaction strength and higher inter-particle distance compared to the values for low grafting density.

On the other hand, nanocomposites grafted with protonated dendrimers repel each other at high grafting density. Thus we show that the effective interaction and the optimal inter-particle distance between the nanostructures can be tuned over a wide range by using a suitable grafting density and protonation level of the dendrimers.

In the seventh chapter, we describe a strategy to assemble dendrimers with the help of single stranded DNA (ssDNA). We attach an ssDNA to one dendrimer and a complementary ssDNA to a second dendrimer. These two complementary ssDNAs bind with each other through base pair formation to assemble the dendrimers into a single structure. The complementary ssDNAs form a dsDNA which is rigid enough to maintain the inter-dendrimer distance almost the same as the length of the DNA. The inter-dendrimer distance can be tuned by changing the DNA length. However, this method strongly depends on the protonation level of the dendrimers. It works well only for nonprotonated dendrimers. Since the protonated dendrimers are positively charged, they strongly interact with the negatively charged ssDNAs through electrostatic interaction. As a result, ssDNAs wrap the dendrimer surface and hence the inter-dendrimer distance can not be controlled. We have also verified that this method works for multiple nonprotonated dendrimers as well.

In the final chapter of this thesis, we summarize the main results and conclude with a brief discussion of future directions of research on the problems considered in the thesis.