Chapter 7

Concluding Remarks

Summary

In conclusion, we have shown that LbL assembly of Fe$_3$O$_4$ nanocrystals and nickel phthalocyanine (NiPc) molecules can be supplemented by orienting their magnetic-moments in each monolayer. In other words, we have shown that LbL films can be deposited via a combined effect of electrostatic and magnetic forces of attraction. That is, the oriented magnetic-moments of the monolayer of the magnetic materials on the substrate can supplement electrostatic adsorption process of the next and subsequent monolayers. The observation has been supported by optical absorption spectroscopy, thickness deduced from AFM topographies, and magnetic contrast imaging of the surface of the films by MFM. We have shown that the magnetic field-assisted LbL assembly has led to a compact film with fewer voids in each monolayer. Close-packing of NiPc molecules in the magnetic field-assisted LbL films has been supported by the results from conductivity and impedance measurements of sandwiched-devices based on the LbL films. MFM mapping of the films has confirmed that magnetic domains became oriented in the LbL films and remained so in the subsequently adsorbed layers. Such assembly of NiPc molecules formed by usual LbL electrostatic assembly and magnetic field assisted assembly are schematically shown in figure 7.1.

Because of the planar structure of the NiPc molecules, we have successfully formed multilayered LbL films with NiPc molecules in each layer lying (a) parallel to the substrate or (b) perpendicular to it with the molecular plane facing one particular direction via the magnetic field-assisted LbL assembly process. Formation of such molecular orientations was confirmed by (polarized) electronic absorption spectroscopy and magnetic force microscopy. Since such films are ideal to study anisotropy of physicochemical properties of the molecule
itself, we measured dielectric properties and conductivity of molecular films in the two orientations of the molecules. Ultrathin films with the molecules lying parallel to the substrate have a lower dielectric constant and a higher conductivity than that having the other orientation of the molecules in LbL films.

Figure 7.1. Assembly of NiPc molecules via (a) usual LbL electrostatic assembly and (b) magnetic field-assisted assembly, showing the orientation of the molecules along with their magnetic moments.

In studying the effect of molecular orientation on electrical bistability, we have characterized the monolayers of NiPc, oriented in parallel and perpendicular configurations on an electrode substrate with a STM tip. We have observed that the degree of bistability (On/Off ratio) is higher for the molecules in the monolayer lying perpendicular to the substrate as compared to that with molecules parallel to the electrode. From the current-voltage characteristics, we have observed that the electrical bistability is associated with a decrease in transport gap and an increase in the density of states. By varying the amplitude of voltage pulse, we could introduce multilevel conductance in the monolayer of NiPc molecules. The conductance switching to a high-state occurs due to decrease in transport gap of the molecules that correspondingly lowers the barrier height for carrier injection.

To investigate the effect of alignment of magnetization vectors cobalt-doped ZnO nanocrystals on electrical bistability, we have recorded tunneling current through scanning
tunneling spectroscopy. An electrically high-conducting state could be achieved by applying a suitable voltage, the threshold voltage, the magnitude of which has been determined for different doping concentration of cobalt-doped ZnO nanoparticles, ranging from 0 to 10 at. %. Magnetization vector of such (room-temperature) ferromagnetic nanostructures could be aligned to study the effect of alignment of their magnetic domains on electrical bistability. In the range of cobalt-doped nanocrystals, we have observed that electrical bistability or conductance-switching to a high-conducting state occurred due to a decrease in the transport gap. Upon alignment of the magnetization vectors of the nanocrystals in a monolayer, the transport gap further decreases primarily due to an increase in the valence band-edge energy. In the cobalt-doped ZnO nanocrystals, it has further been observed that the alignment of magnetization vectors and conductance switching both lead to a decrease in the transport gap. Schematic energy-band diagram of low- and high-conducting states for both unaligned and aligned monolayers of cobalt-doped ZnO is shown in figure 7.2.

In order to use the magnetic field as another parameter in the “write” and “read” processes of a memory device, we have fabricated electrically-bistable devices based on Fe$_3$O$_4$ nanoparticles. In the presence of magnetic field, the nature of bistability has changed completely. Current-voltage characteristics under a magnetic field showed that the initial state
was already a high-conducting one. From the comparison of current-voltage characteristics without and with magnetic field, we concluded that the conductance-switching (to a high-state) and orientation of magnetic domains of Fe$_3$O$_4$ nanoparticles occur concurrently.

To study the selective quantum confinement effect, we have grown a series of type-I core/shell nanostructures such as CdSe/CdS, CdSe/ZnSe, CdSe/ZnS etc. in order to selectively create a conduction or a valence band-offset. In all core/shell systems, CdSe quantum dots were in the core and a range of materials with varying and controllable thickness as the shell layer. From the tunneling spectroscopy and density of states of the isolated nanostructures recorded with a scanning tunneling microscope tip, we have observed that the change in the band-edge energy of the core in the core/shell systems was selective. The band-edge energy of the core in core/shell systems changes only when a band-offset was small enough allowing delocalization of that type of carriers up to the shell layer. A large valence and/or conduction band offset in the core/shell system confined the respective carriers in the core. In other words, we showed that the quantum confinement effect could be relaxed for a selective (type of) carriers in these core/shell systems. A schematic diagram explaining the selective quantum confinement effect is depicted in figure 7.3.

![Schematic diagram](image)

**Figure 7.3.** Schematic representation of energy band-diagram of CdSe/CdS and CdSe/ZnSe type-I core/shell nanoparticles along with their radial wave function for ground state electrons and holes of the core. The respective shifts in the conduction or valence band-edges upon selective delocalization of electron or holes are shown in $dI/dV$ spectrum.