Research Interests

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I. Overview of Research Plan: Computational Nanotechnology

Research in nanotechnology is undergoing a paradigm shift. A bottom-up or self-assembly approach is being investigated as an alternative to the current top-down approach. Most significantly, the shift from the exclusive use of lithography for device fabrication opens the field to not only novel fabrication schemes but the incorporation of diverse material systems. Combining organic and inorganic materials into self-assembled nanosystems is a dynamic area of research. Technology coupled with creative thinking offers us the ability to invent and probe at the molecular or atomic level. The development and/or combination of new materials with/without the currently used materials such as silicon holds promise to yield innovative devices with increased functionality that will impact electronic, chemical and biomedical applications.

In this context, we are also experiencing that the application of various computational methods to solve physical and chemical problems is accelerated at a prodigious rate and thereby these computational methods have become an essential engineering tool to design material and material processing at molecular level.

In this proposal, what I envision is “the Computational Nanotechnology” which provides us with another way to find treasures hidden in the field of nanotechnology, as shown in the following.

1. To develop integrated multiscale simulation solutions to properly handle the nanosystems that may have multiscale characteristics in time and space.

So far, lots of computational methodologies have been developed and validated in many fields of physics and chemistry. For example, rigorous quantum mechanical theory can provide useful information for electronic properties of material of our interest. To investigate a system with dimension of up to several nanometers, however, this quantum mechanical computation is still quite expensive to be used. Another category of computation is force field method, which allows us to investigate the structure and energetics of larger system with up to hundred-nanometer or even micrometer scale dimension. At this point, it should be noted that in many cases, the problems which we encounter are very complicated and multiscale: this is because the desired properties have quantum mechanical nature, and at the same time are realized through specific pattern of structures (or conformations) with the dimension of 1~100 nm. Thus, it seems to be very clear that just single method is not able to capture the whole picture of the problems. Furthermore, we meet exactly the same situation in the attempt to design and make any nanoscale devices. Therefore, the name of the game is about the methodology that can handle such phenomena in nanoscale system, which highly demands the development of the hierarchical multiscale computational nanotechnology (Figure 1).

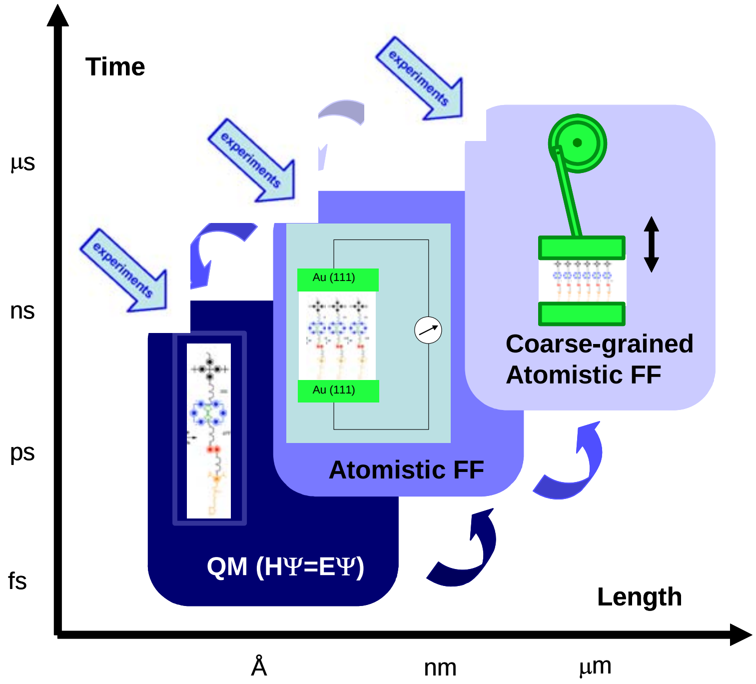


Figure 1. The hierarchical multiscale approach in computational nanotechnology

In this framework of computational nanotechnology, we start at the electronic (quantum) level that requires no input of experimental data (but is limited to several hundreds of atoms). These results are fed to the atomistic scale via parameters in the full atomistic force field (FF) that allow simulations with the size of 10^4~10^6 of atoms. The results of the atomistic MD calculations are used to derive lumped or coarse-grained models that can be used for systems having billions of atoms, which may be required for biosystems. *Thus, by integrating all these various methodologies in a consistent way to make them work cooperatively, we can establish a full set of methods to explore and create any specific nanosystems.*

2. To establish guidelines of molecular architecture design to optimize the

properties/performance of nanosystem by elucidating the thermodynamic and kinetic driving forces in self-assembled nanosystems

One of the primary goals in the nanotechnology is to fabricate an ordered quantum structures with a designed pattern in a scalable process and at low cost. However, it is obvious that the nanosystems have nanometer-scale dimension in thickness and length, and thereby there may be no bulk phase of material. This implies that the given theories for bulk phase may not be good enough to describe them in most cases. Therefore, one necessity we are facing is to develop the nano-thermodynamics and nano-kinetics which has a correct language talking about nanosystems. Another necessity is about the interaction between atoms and between molecules. Basically, the key factor governing the atomic or molecular self-assembled structure is the non-bonded interactions such as van der Waals and electrostatic interaction. Because of these non-bonded interactions between the components, our nanosystem can explore the phase space (reversibly in most cases) at a given temperature and pressure condition until it reaches a thermodynamically favorable and stable state which is normally found in the self-assembled structure. Therefore, the most essential demand is to establish the rigorous criteria what kind of molecular architecture can maximize these non-bonded interactions among themselves and finally lead to the desirable nanostructure with optimal performances. Therefore, a part of my research will be to develop reliable thermodynamic and kinetic theories and to establish a guideline for molecular architecture design by investigating theoretically the relationship of nanostructures with their properties. *Summarizing, my research plan is to establish guidelines of molecular architecture design for nanosystems through the integrated multiscale simulations.* The fields I will make my research effort first are as follows, but not limited to.

II. Application in Nanotechnology

1. Nanoelectronics and Nanomechanics.

To design molecular electronics such as diode, transistor, switch, and even sensor, the correct quantum origin should be pursued and formulated mathematically. Single molecular system or self-assembled system will be simulated using the force field as well as the quantum mechanics in order to sample the most probable structure and its dynamics. From these simulations, all the statistical-mechanical/quantum-mechanical properties will be calculated and compared with the experimental observations.

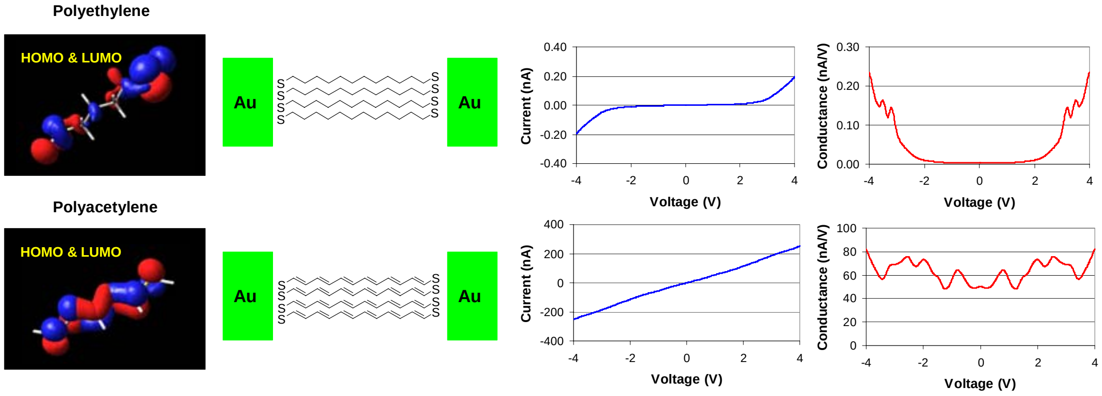


Figure 2. Current-voltage behavior of Polyethylene (C12) (upper) and polyacetylene (C12) (lower) calculated using the non-equilibrium Green's function theory.

Figure 2 shows the current-voltage relationship for the saturated hydrocarbon chain (polyethylene) SAM and for the conjugated chain (polyacetylene) SAM between Au electrodes, which is calculated by the non-equilibrium Green's function formalism (NEGF). However, besides this coherent tunneling current which would be dominant at low temperature, we need to develop a unifying theory to handle the thermal effect on electron transport through molecular or atomic vibration at certain temperature in order to properly describe various mechanisms in nanoelectronics, which will be pursued in my research program.

Another interesting topic I want to propose is the nanoelectromechanical system (NEMS). The system shown in Figure 3 is the self-assembled monolayer (SAM) of bistable [2]rotaxane on Au (111) surface in which the shuttling motion of cyclobis(paraquat-*p*-phenylene) (CBPQT) ring between tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) is controlled electrochemically or electrically. Amazingly, depending on this CBPQT ring position, the rotaxane molecule shows switching behavior. In other words, the conductivity of rotaxane is much higher when the CBPQT ring stays at DNP unit (ON state) than when the ring on TTF unit (OFF state). Thus, it should be very interesting and challenging to realize nanodevices using this electromechanical molecular switch.

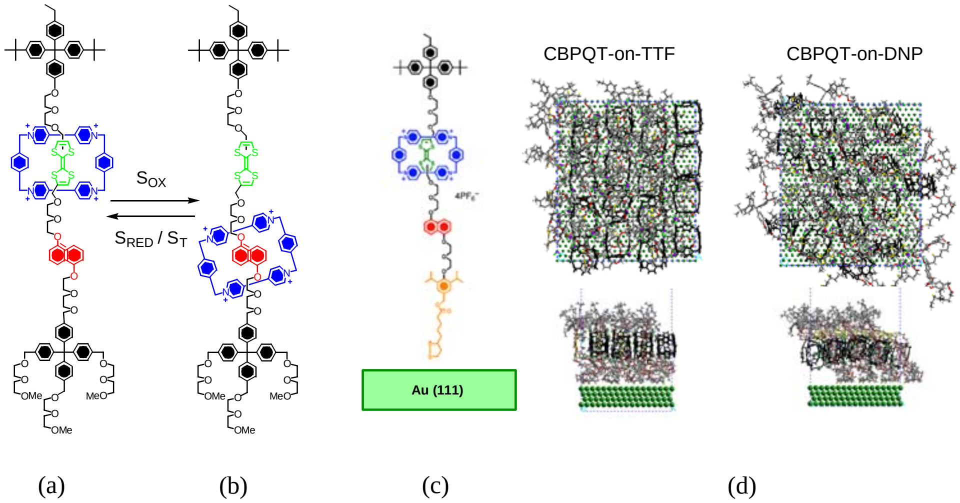


Figure 3. Electromechanical displacement of cyclobis(paraquat-*p*-phenylene) (CBPQT) ring along backbone between tetrathiafulvalene (TTF) (a) and 1,5-dioxynaphthalene (DNP) (b) station; chemical structure of bistable [2]rotaxane on Au (111) surface (c); self-assembled monolayer (SAM) of rotaxane on Au (111) surface.

Besides, a rotaxane-based molecular machine such as muscle, actuator, valve, and motor would also be feasible by designing a molecular architecture utilizing dimensional change. At this point, again, we can ask which molecular architecture is the best to optimize the target property. *Therefore, through the computational investigation by my integrated multiscale computational solution, I will be able to suggest the molecular architecture for desirable properties.*

2. Energy Technology: Self-Assembled Nanostructured Fuel Cell.

Fuel cell technology became one of the most important technologies of the 21st century because fuel cells are more efficient and environmentally friendly than conventional combustion engines. Especially, Polymer electrolyte membrane fuel cells (PEMFC) operating at low temperatures (70-90^{o}C) are prime candidates for use in the next generation of electric vehicles as well as in any mobile electric device. Fuel cells contain complex heterogeneous structures, with chemical, electrochemical, and physical phenomena spanning length scales from nanoscale (nanophase-segregation in membrane and electrocatalyst), to micron scale (three-phase interfacial region of reactant/electrolyte/electronic conductor), to mesoscale (e.g., membrane-electrode assembly), and macroscale (e.g., solid, fluid and gas interfaces and associated flow fields). To enable the development of high performance fuel cells having the multiscale structures above-mentioned, the integrated approach with lots of interdisciplinary knowledge should be applied.

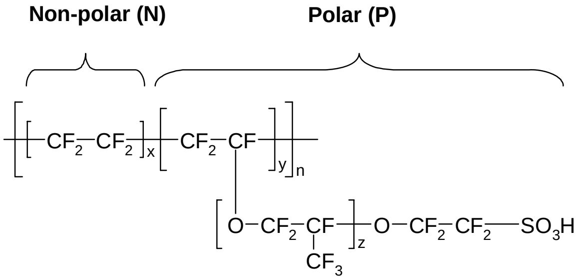
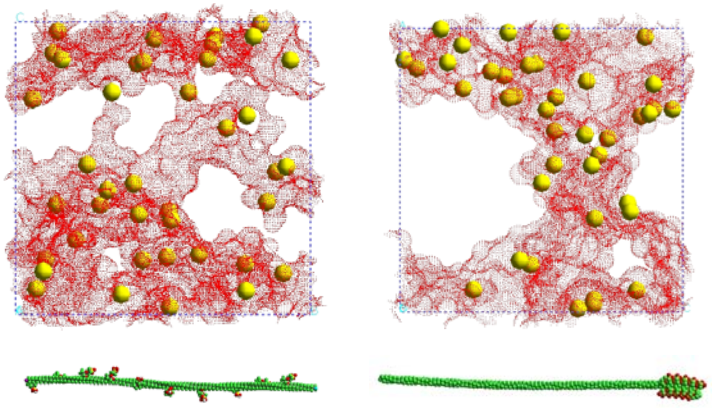


Figure 4. Chemical structure of Nafion. x=6.5 (~7), y=1, and z=1 corresponds to Nafion 117.

2.1 Polymer Electrolyte Membrane. The most well-known polymer for PEMFC is Nafion which consists of hydrophobic and hydrophilic segment (Figure 4). Such molecular architecture leads to its own self-assembled structure through phase-segregation. Figure 5 shows that this self-assembled nanostructure can be controlled by changing monomeric sequence along chain. The protonic current can flow through the percolated water channel associated with hydrophilic polar part of Nafion in such nanostructure in membrane.

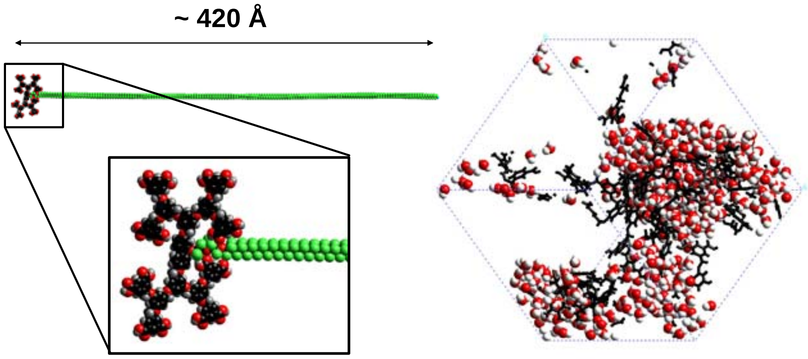
In order to improve the performance of fuel cell, it seems to be very obvious that we should control such self-assembled feature of nanostructure. Here, I present an example based on this structure-performance relationship in Figure 6.



(a) degree of randomness =1.1 (b) degree of randomness =0.1

Figure 5. Self-assembled nanostructure of Nafion in membrane, depending on the monomeric sequence. Red part is Connolly surface of hydrophilic phase incorporated with water phase; yellow balls are sulfurs in sulfonate groups. White part is occupied by Nafion backbone chain which was made invisible for clear view.

An interesting molecular architecture here is to combine a water-soluble hydrophilic dendrimer together with hydrophobic PTFE (polytetrafluoroethylene) and its nanostructure. In this concept, the nanophase-segregation of membrane is intrinsically endowed by the molecular architecture because the spherical shape of hydrophilic dendrimer would efficiently form a bicontinuous phase in the membrane in the presence of water. The characteristic dimension of such nanophase-segregation can be controlled by changing dendrimer size (its generation) and kinds of end functional group such as sulfonic acid, phosphonic acid and so on. This is very promising way to tune the performance of fuel cell because the transport property of water or proton in such nanostructure depends on such characteristics of nanophase-segregation.



(a) (b)

Figure 6. Water-soluble dendrimer-hydrophobic PTFE diblock copolymer (a) and its self-assembled nanostructure in membrane (b). White part in (b) is occupied by PTFE backbone.

2.2 Hydrated Polymer Electrolyte/Electrode Interface. A great challenge in understanding of the PEMFC performance is to characterize the interface between the hydrated polymer electrolyte (Nafion) and the cathode (carbon-supported Pt nanoparticles) as in Figure 7. And it is essential to understand how the protons are transferred across the membrane-cathode interface, particularly, how this is affected by the distribution of water at this interface. Although a connected (percolating) water structure existing throughout the Nafion membrane has been simulated, no atomistic structural model has been proposed to explain the distribution of water and O_2 to the Pt-Nafion interface. Therefore, as a first step, the most probable structure at this interface will be predicted. On the basis of such predicted structural features of the interface, the dynamics of protons, O_2 molecules, and water entering the interface will also be characterized. Thus the important chemistry may occur at the interfaces between these regions and the catalysts. Indeed understanding the distribution and dynamics of these important species in these regions may be most important to improve the performance of a PEMFC, allowing us to optimizing the interface between the cathode and membrane.

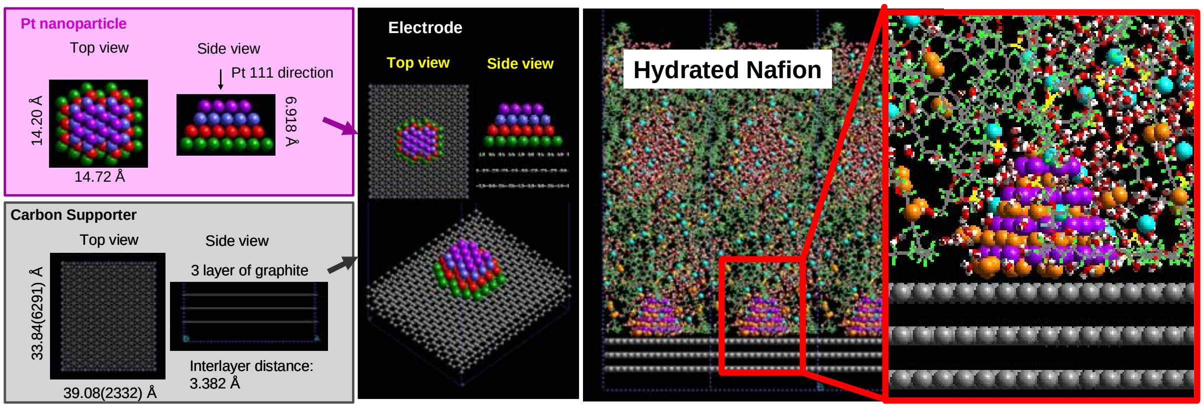


Figure 7. Atomistic model of cathode (a) and interface (b). The orange balls are O_2 molecules and the light blue balls are oxygen in hydronium (H_3O^+).

Summarizing, my research plan in this field is to improve/develop an integrated multiscale simulation solution navigating this energetic world and thereby to suggest a brand new molecular architecture making it more energetic. I am quite sure that this kind of theoretical effort will share the fruit of technology with the experimental pursues.

3. NanoBiotechnology.

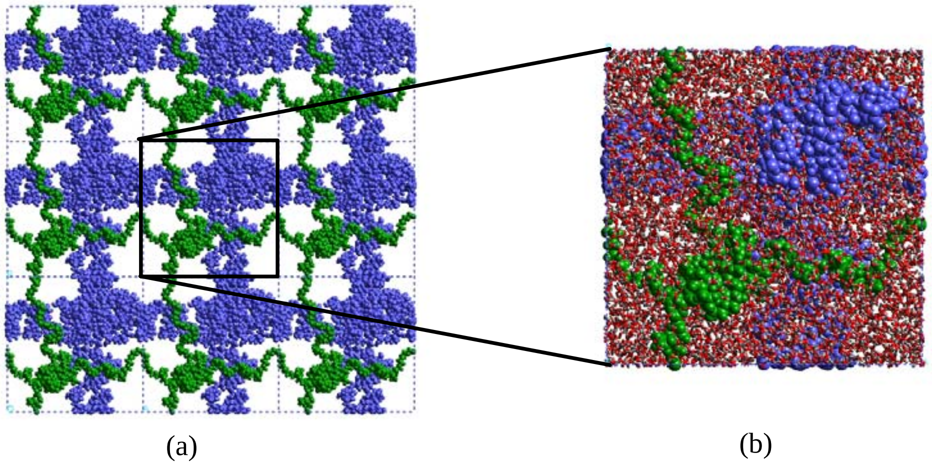


Figure 8. (a) Interpenetrating network consisting of PEG and PAA; (b) its hydrogel state with 80 wt % water content. Green and blue polymer corresponds to PEG and PAA, respectively.

3.1 Nanostructured Material for Bio-Applications. In addition to biologically-driven materials, so far, various synthetic materials have been used for the bio-applications (e.g., PMMA in dentistry, polyester in vascular graft, polyurethane in artificial heart etc.). Although these given materials have helped a lot of people enjoy lives in a better state, there are still strong demands for better materials which have better properties such as biocompatibility, mechanical properties, sensitivity, and smart responsiveness and so on. In order to obtain better materials, we may think various ways to do: to redesign given synthetic materials, to hybridize synthetic materials with biologically-driven materials, and to modify given biologically-driven materials. An example here (Figure 8) is a hydrogel system for replacing tissue, especially cornea, which is a three-dimensional nanostructured interpenetrating network of polyethylene glycol (PEG) and polyacrylic acid (PAA). Although the hydrogel made of only PEG or PAA is good at both transparency and nutrition permeability, they have not been used for replacing human cornea because of their poor mechanical strength. As shown in Figure 8, a perfect network structure can be prepared in the presence of water and then be modeled how much mechanical strength it can achieve without a significant loss of any other good aspects (transparency and nutrition permeability). It has been just classically explained in that the mechanical properties of this kind of network structure are due to the change of conformational entropy. However, there is no such theory that can predict the quantitative properties as a function of molecular variables such as chemical structures, molecular weight between cross-linking points, and amount of water and so on. <u>*At this situation, through the computational nanotechnology, we will be able to design the molecular architecture and its self-assembled nanostructure to obtain any desirable properties.*</u>

3.2 DNA- and Protein-based Nanotechnology. In terms of the self-assembled supramolecular system, our nature often provides us with various ideal materials as well as interesting concepts. A double-stranded DNA is a good example for this. From its spring-like shape and dimension (2 nm diameter and 3.4 nm repeating unit), it may be reasonably expected that this structure have good elastic properties which can be useful for nanoscale machines.

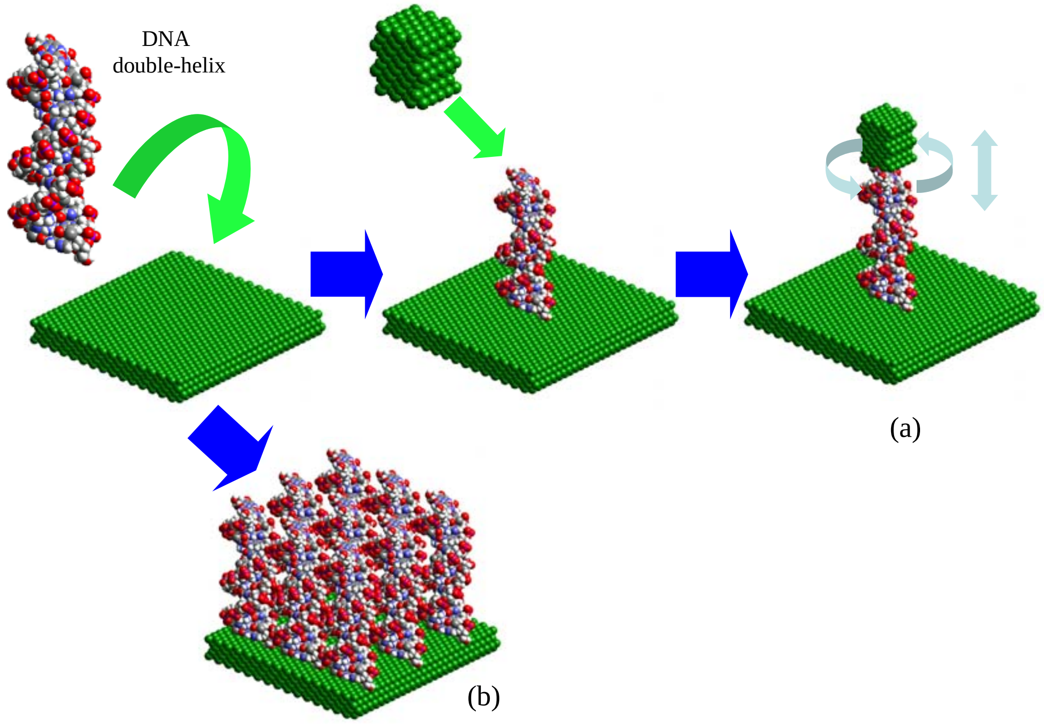


Figure 9. Simulation of DNA: (a) single double-helix and (b) self-assembled monolayer.

Indeed, such mechanical properties have been investigated experimentally. Besides, this DNA can have some selective affinity for specific chemicals which can be used for nanoscale devices such as sensors and bioinformatics processors. One more interesting property of DNA is that this secondary structure of DNA can have certain level of conductivity, meaning that the electron can transport through DNA. This feature opens new possibility for DNA-based electric circuits. It is very clear that these topics show the multiscale faces of DNA. In order to realize all these fancy ideas, therefore, what we need is to understand the DNA (structures and properties) and then to manipulate the structures and thereby to obtain the desired properties. *As a part of my research plan, I propose to study the properties of individual building block (single or double-stranded DNAs and natural or non-natural proteins as Figure 9a) and of their self-assembled systems (Figure 9b) using the computational nanotechnology in the perspective of making nanoscale machines and devices.*