Molecular Dynamics Simulations of the Nucleotides and Metallic Nanoparticles Interaction on a Carbon Nanotube Matrix

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We simulated the interaction of the small nucleotide chain (NC) with gold nanoparticles (NPs) inside carbon nanotube (CNT) of an open ended boundary. Such system represents a great interest in many aspects of today biochemical and nanotechnological research (diagnostic applications, drug delivery in cell, nanorobotic design and related manipulations). The entire system (the NC chain, gold NPs and CNT) were allowed to interact with each other by the Van der Waals (VdW) forces only. The CNT was described through a quantum-chemistry potential, though the trajectory calculation for the whole NC-NP-CNT model was performed via the classical molecular dynamics (MD) approach. The Lennard-Jones short-ranged interaction is assumed between the NC, NP and CNT. We have carried out a series of MD simulations on different NC-NP-CNT configurations to investigate the peculiarities of NC-NP bonding and structural formation along with dynamical behavior inside a CNT matrix under rather a weak VdW interaction. [doi:10.2320/matertrans.MA201565]

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1. Introduction

The understanding of the DNA interaction and binding mechanism with metallic nano-particles and metallic surfaces embedded by the CNT environment represents a great interest in many aspects of today biochemical and nanotechnological research (diagnostic applications, drug delivery in cell, nanorobotic design and related manipulations).1-12 Recent experimental and simulation studies involve the DNA interaction with highly localized proton beams or metallic NPs (such as Ag, Au, etc.), aimed on targeted cancer therapy through the injection of metal micro- or nanoparticles into the tumor tissue with consequent local microwave or laser heating.

Along with DNA-NP also the DNA-CNT system represents a great interest in today biomedicine applications due to diagnostic and treatment of oncology diseases. Cancer, in which cells grow and divide abnormally, is one of the primary diseases with regards to how it responds to CNT drug delivery. Representing a revolutionally potential for the biochemical and medicine the use of CNTs in drug delivery has based on the enhancing of sufficient solubility and allowing of efficient tumor targeting. These aspects prevent CNTs from being cytotoxic and altering the function of immune cells. For today, cancer therapy involves surgery, radiation therapy, and chemotherapy. Recent experimental and simulation studies involve the interaction of DNA with highly localized high power beams and various nanoparticles (Ag, Au, etc.). These studies are aimed on targeted cancer therapy through the injection of metal micro- or nanoparticles into the tumor tissue with consequent local microwave or laser heating. Due to their good heat conductivities of NPs (Ag, Au, and so on) the experiments reveal that the only tumor cells to destroy, remaining normal cells undamaged. Nevertheless, such kind treatment methods are usually painful and kill normal cells in addition to producing adverse side effects.1-9

CNTs as drug delivery vehicles have shown a potential interest due to a targeting of specific cancer cells with a lower dosage rather than conventional drugs have. With regard to the different aspects of the DNA interaction and carbon nanotubes (CNTs) there has also been a great discussion for today nano- and biotechnological innovation and application. For example, the use of the DNA-CNT system in DNA nanotechnology have intensively been discussed in molecular recognition processes, as a candidate material in cell drug delivery, as nucleic acid selection method (DNA aptamer) in SELEX (Systematic Evolution of Ligands by Exponential enrichment), so on. The conformational transition of aptamers (single chain DNA or RNA molecules that possess specific spatial structure) around CNT may cause some modification of the charge distribution on the CNT surface. It is worth noting that CNT surface has extremely sensitive to even a small change of the electrical charge of its environment. The replacement of even a single nucleotide for the DNA or RNA structure can modify, on the other hand, the charge environment around CNT. As a result, the CNT charge conductivity will be changed as well. So far, the DNA or RNA interactions with CNT could result to an essential modification for the charge distribution and consequent charge transfer through by the CNT surface. In the physics measurement the DNA-CNT charge distribution can be estimated trivially. This simple scheme from the point of view of application and diagnostic purposes has considered being one of the promising technologies in the DNA-CNT interaction processes with target proteins (say, of blood cells in human body).5-12

In this work, the molecular dynamics (MD) simulations were performed on a small nucleotide chain (one purine and one pyrimidine) to investigate its interaction and binding processes with gold nanoparticles that happen inside of a carbon nanotube. The small NC model interacting with a NP-CNT system one believe is an important stage in the understanding of the interaction mechanism of a full DNA or RNA molecule with NP and CNT.

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2. Models and Simulation Method

We have simulated a three component molecular system consisting of a two nucleotide chain (NC), gold nanoparticles (NPs) and a carbon nanotube (CNT) under different temperature conditions ($T = 100, 200$ and $300$ K). Two nucleotides (one pyrimidine and one purine) as in the primary structure of DNA were relaxed in the vicinity of gold particles. A primary DNA or RNA structure consists of a linear sequence of nucleotides that are linked together by phosphodiester bonds. Nucleotides consist of 3 components: (1) Nitrogenous base - A (Adenine), G (Guanine), C (Cytosine), T (Thymine, present in DNA only) and U (Uracil, present in RNA only); (2) 5-carbon sugar which is called deoxyribose (found in DNA) and ribose (found in RNA); (3) One or more phosphate groups. The nucleotide chain was located from gold atoms at distances ($5 - 10$ Å), i.e. within a range of Van der Waals (VdW) forces. It should be stressed out that the NC-NP distance, as shown below, represents a larger distance between the nucleotide’ phosphorus (P) and gold (Au) atoms. All other NC-NP interatomic distances lie within $d[\text{NC(P)--NP(Au)}]$ values and are smaller than $d[\text{NC(P)--NP(Au)}]$ (Figs. 1–3). The molecular system NC-NP-CNT was built up as the cell size $95 \times 95 \times 65$ Å$^3$, containing of the 63 atoms of NC, 1–3 gold atoms of NP and 800 C atoms of CNT, with the CNT both open-ended and periodic boundary conditions.

A classical molecular dynamics study was performed using the DL\_POLY-2.20$^{13,14}$ general-purpose code. The NVT ensemble with a Berendsen thermostat and a Verlet leapfrog scheme were employed. The integration time step of the dynamical equations of motion was 1 fs. The entire system (the nucleotide chain, gold atoms and carbon nanotube) were allowed to interact with each other via the VdW potential only. For describing of VdW interactions we used Lennard-Jones (LJ) potential, which is commonly in use for simulation of liquids and condensed phases. The LJ potential looks like:

$$V(r) = 4\varepsilon \left[ \frac{(\sigma/r)^12}{(\sigma/r)^6} \right].$$

where $\varepsilon$, $\sigma$ are LJ interaction parameters and the cross-section interaction parameters were defined using the Lorentz-Berthelot mixing rule: $\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{\frac{1}{2}}$ and $\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$.

The force field parameters for the NC (nucleotide chain) and CNT (carbon nanotube) molecules were chosen from the DL\_FIELD database.$^{14}$ The intramolecular interactions for the NC chain were described using the LJ, combined with angular and dihedral bonding potentials. The LJ, cross-interaction and bond parameters for the NC-NP-CNT system were the same as in our paper.$^{13}$

For the describing CNT we have employed the quantum chemistry Tersoff potential, so far a co-called hybrid approach (the combination of quantum chemistry potential and classical trajectory calculations) has been realized to investigate the NC interaction with with CNT. In CNTs we have chemical bonding is hybridization sp$^2$ (as graphite), which is stronger than sp$^3$ bond (of diamond). The nature of chemical bonding in CNTs is described by quantum chemistry, through the process of orbital hybridization. The Tersoff potential in hybrid MD simulations correctly describes the nature of covalent bonding in carbon nanotube; it allows the breaking and formation of chemical bonds, that is associated with hybridization process. Tersoff potential is pair wise potential, but coefficient in attractive term depends on local environment, thus, Tersoff potential possesses a many body nature (see, Ref. 13 and references therein).
3. Results and Discussion

The MD simulation results indicate on the formation of contacts (bonding) for the nucleotides during their collective interaction with gold atoms. Under the similar condition and being relaxed inside the same CNT matrix, the NC-NP interaction may produce a different scenario of a bond formation. Here we present the MD results for the only NC-2NP-CNT system. More graphical and configuration data, regarding the systems NC-1NP-CNT (model 1) and NC-3NP-CNT (model 3), to be reported elsewhere in details. In Fig. 3 the NC-2NP distance distributions at the temperatures $T = 100, 200$ and $300$ K are presented for the model NC-2NP-CNT. As it is noted above, the NC-NP distance represents a larger distance between the nucleotide’ phosphorus (P) and gold (Au) atoms. (All NC-NP interatomic distances lie within the values of $d[NC(P)-NP(Au)]$ and are smaller than $d[NC(P)-NP(Au)]$). Figure 4 show the MD simulation snapshots for this two gold particle NC-2Au (NC-2NP) system at the temperatures $T = 100, 200$ and $300$ K, respectively. In Figs. 5 (left and right) the average NC dihedral (torsion) and angular energies for the model NC-2NP-CNT are shown at the temperatures $T = 100, 200$ and $300$ K.

The observations show that for the NC-NP-CNT system the formation of the NP-NC bond is overestimated in the confined environment given by CNT matrix. For the same NC-2NP system, under the similar temperature and thermodynamic conditions, we observe a different scenario of the bond formation (weak, strong or intermediate bonding), where a correlation effect between the NC intramolecular internal vibrations and a weak VdW NC-NPs interaction has to remain a key factor. With the temperature grows the NC intramolecular oscillations have essentially modified the picture of the NC-NPs bonding. We observe more fluctuation in the NP-NC bonding processes, which is true not only for a single gold atomic case (model 1, NC-1NP-CNT), but also for the two (model 2, NC-2NP-CNT) and three (model 3, NC-3NP-CNT) gold particle ones. The NC chain can form with a particular gold atom a close contact, while with another, under the same positional and temperature conditions, a resultant weak bond.

4. Conclusion

In conclusion, the small NC-NP-CNT system simulated in this study represents an important stage in the understanding of the interaction mechanism of a full DNA or RNA molecule with NPs and CNT. We have carried out a series of MD simulations with different NC-NPs-CNT molecular models to investigate the peculiarities of VdW interactions, bond and structural formations along with the dynamical behaviour. The NC intermolecular motions were estimated from MD data thereby building the distance distributions, the angular and dihedral (torsional) bond energy graphs versus simulation time. The analysis of the MD data has shown that the NC-NPs bonding are overestimated by the CNT matrix playing a role of a confined environment. The correlation effect between the NC intramolecular internal vibrations and a weak VdW NC-NPs interaction is a key feature of the NC-
NPs bonding that to be taken into account in the related design of the DNA-CNT devices. One has to mention the enhancement of the DNA-CNT nanorobotic devices for the purposes of the diagnostic applications, in the chemical and drug delivery inside of living cells and other important application in today DNA nanotechnology.

REFERENCES