Electronic Structure and Transport in Biological Inorganic Hybrid Materials

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ABSTRACT

We present ab-initio and semi-empirical calculations of hybrid bio-inorganic structures and interfaces of carbon nanotubes, DNA, and Peptide Nucleic Acid (PNA) with either amide or glutamate linkers. Such structures are studied for bio-assembled nanoelectronic applications. Simulation results of single strand PNA are presented and compared to those of single-strand DNA. Calculations of self-energies for the non-equilibrium Green function formalism (NEGF) within the ab-initio FIREBALL code are described and demonstrated with a calculation of the transmission through a (10,0) CNT.

Keywords: ab-initio, semi-empirical, self-energy, NEGF, electron-transport, PNA, DNA, CNT

1 INTRODUCTION

Biologically self-assembled, hybrid, organic-inorganic nanostructures have a wide range of applications in engineering and biotechnology. Self-assembly methods include chemical self-assembly based on peptides, DNA and PNA (peptide nucleic acid) based self-assembly, antigen-antibody self-assembly, and virus based self-assembly. Materials assembled are metals, semiconductor nanocrystals and nanowires, and carbon nanotubes (CNTs). There is currently an intense interest in bio-assembled nanosystems bringing together disparate materials such as metals, semiconductor nanocrystals, DNA, PNA, proteins, peptides, and CNTs [1–3]. This interest is not only academic, but also shared and funded by the semiconductor industry through the MARCO Focus Center Research Program FENA [4]. Electrochemical, optical, and photochemical biosensor systems have resulted from the integration of metallic nanoparticles and semiconductor nanoparticles with enzymes [5,6], nucleic acids [7–9], and antigens/antibodies [10]. Biomaterials have the features of specificity and recognition in their binding that make them promising for directed assembly of nanoscale hybrid materials. Examples include the complementary base pairing of DNA [11–13], antigen-antibody binding [13], and the material specific binding of virus bound peptides [14].

One of the most advanced examples of bio-assembly of an electronic device is the bio-assembled carbon nanotube field effect transistor (CNTFET) demonstrated by Keren et al. [13]. This example uses both antigen-antibody binding and DNA recognition. The assembly of a CNTFET with metalized DNA leads is particularly auspicious. Metallization of DNA has been demonstrated with Pd, Pt, Ag, Au, Cu, and Ni [15], with workfunctions ranging from 4.1 to 5.6 eV compatible with the range found in CNTs [16]. This is synergistic with the discovery and advancement of ohmic contact technology for CNTFETs [17–20]. Most recently, metal patterning of DNA in a sequence specific manner while still retaining biological functionality opens the possibilities for complex, DNA templated, self-assembled circuits of CNTFETs [21].

2 PEPTIDE NUCLEIC ACID

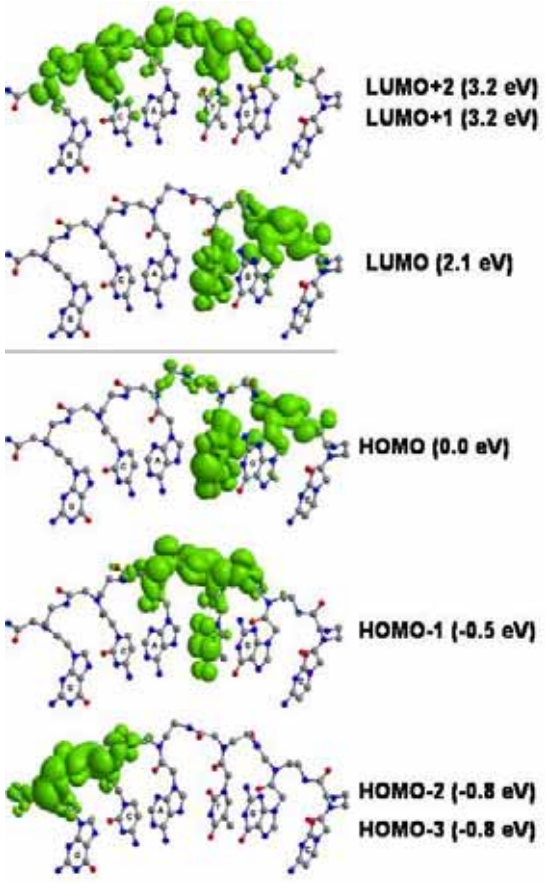

Figure 1: Nature of orbitals near the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a six base sequence (GCATGC) single strand PNA [22].

Fig. 1 shows the nature of orbitals near the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a six base sequence (GCATGC) single strand PNA. The calculations were done using the PM3 semi-empirical package [23] implemented in Gaussian03 program suite [24]. The HOMO-LUMO bandgap in the given PNA sequence is 2.1 eV. The HOMO and LUMO orbitals are relatively localized, confined on the thymine base, its backbone, and the backbone of its two nearest neighbors. Comparing with similar calculations for ss-DNA, we find for states close to the HOMO and LUMO, a significantly larger fraction of the molecular orbitals are on the peptide backbone of the PNA than on the sugar backbone of the DNA. This suggests that ss-PNA may be more suitable for metallization of the backbone compared to ss-DNA [25].

3 HYBRID BIO-INORGANIC SYSTEMS

The structure in Fig. 2 consists of one unit of back-bone plus base (Guanine) segment of a single-strand PNA connected to a (10,0) CNT with a Glutamate (Glu) linker. This is the standard experimental procedure for functionalizing a CNT with PNA [26, 27]. We modeled the structure using GAUSSIAN03 to determine the energy levels and orbital locations as shown in Fig. 2. The hybrid density functional theory method B3LYP [28] was used to carry out a full geometry optimization of the single unit PNA attached to glutamate using the 6-31G* basis set. This optimized geometry was linked to an optimal 2 unit cell (10,0) zig-zag CNT and this assembly was used as a computationally cost effective model to investigate the PNA-Glu-CNT system. The molecular energies and orbitals are calculated using the PM3 method [23].

Fig. 2 shows that the HOMO of the PNA-Glu-CNT model is located on the Glu bridge between the CNT and the PNA, and the LUMO is located on the CNT. The HOMO-LUMO gap is 3.6 eV. For comparison, the HOMO-LUMO gap of the bare CNT is 3.2 eV. The large gap is the result of the short length (2 unit cells) of the modeled CNT. For an extended (10,0) CNT, the bandgap is 0.98 eV, and for a (13,0) CNT, the bandgap is 0.7 eV. The HOMO on the Glu sits in the energy gap of the CNT. The HOMO-1 orbital at -1.1eV (with respect to the HOMO) is also on the Glu. The HOMO-2 through HOMO-4 orbitals, lie on the CNT. They are closely spaced in energy 200-300 meV and begin at -1.7eV.

The relative alignment of the Glu states with respect to the the CNT states suggests that for a longer CNT for which the gap is close to its extended value of under 1eV, the Glu state will align closely with the valence band of the CNT enabling good hole transfer across the Glu bridge for p-type CNTs. The large band-gap seen here is due to the truncation of the CNT, that artificially increased the HOMO-LUMO gap by over a factor of 3 from 1 eV to 3.2 eV.

A second, similar example is the (10,0) CNT connected to a single unit of a guanine base, single-strand DNA with an amide linker shown in Fig. 3. The HOMO-LUMO gap of 3.1 eV is slightly less than the 3.2 eV gap of the bare 2 unit cell CNT. The HOMO orbital is confined on the CNT and pushed away from the amide linker at the interface. In contrast, the LUMO orbital extends across the linker suggesting good electron transfer across the amide bridge for n-type CNTs.

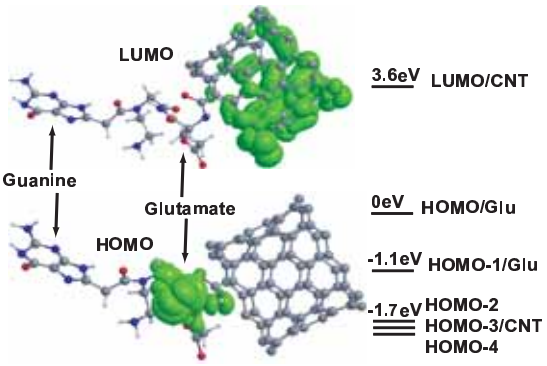

Figure 2: Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the CNT-Glu-PNA assembly [29].

The large HOMO-LUMO gap seen in both of these simulations is due to the truncation of the CNT. The system of real interest has an effectively semi-infinite CNT with a bulk band-gap of 1 eV. One can simulate the system with longer and longer sections of CNT so that the CNT states begin to more closely resemble the continuum of band states; however this approach uses more and more cpu and memory resources to model the large CNT.

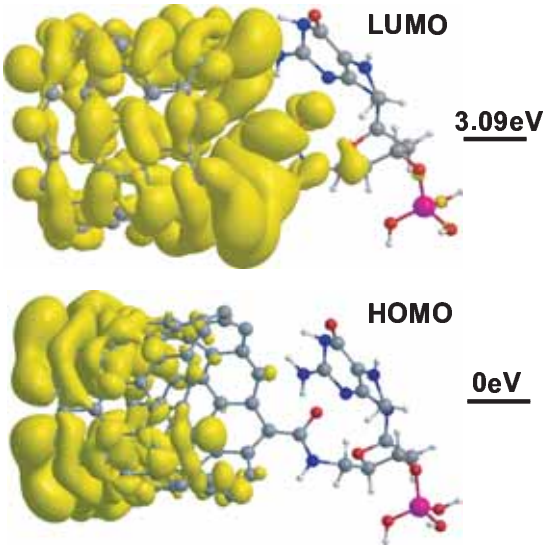

Figure 3: Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the model DNA-amide-CNT assembly [25].

A second approach is to terminate the CNT with a surface-self-energy matrix which exactly models the effect of the semi-infinite CNT extending to the left in Fig. 3. This is the NEGF approach to including the effect of semi-infinite regions via self-energies constructed from the surface Green functions. In this approach, the matrix size representing the system of Fig. 3 does not increase. It is simply modified at the end by the self-energy matrix representing the semi-infinite CNT. This modified matrix will then allow us to calculate the energy line-up of the molecular states with the band-states of the CNT.

4 NON-EQUILIBRIUM GREEN FUNCTIONS

We are implementing the NEGF approach within the FIREBALL code [30, 31]. The device Hamiltonian, the overlap matrix and the device-to-contact coupling matrices for an infinite (10,0) CNT are formed using the FIREBALL Hamiltonian matrix elements. The spatial extent of the non-zero matrix elements is determined by the pseudopotential cutoff limits and the FIREBALL orbital radii. The matrix elements extend 4 atomic layers which is exactly one unit cell of the (10,0) CNT. We label the unit cells such that cells $\{-\infty, \ldots, 0\}$ lie in the left contact, cells $\{1, \ldots, N\}$ lie in the "device," and cells $\{(N+1), \ldots, \infty\}$ lie in the right contact. The matrix elements of the Hamiltonian group into intra-cell subblocks $\mathbf{D}_{i,i}$ and inter-cell subblocks $\mathbf{t}_{i,i\pm1}$. We define effective off-diagonal matrix elements $\tilde{t}$ as $\tilde{t}_{i,j} = t_{i,j} - (E + i\eta)S_{i,j}$ where $S_{i,j}$ is the overlap matrix element between non-orthogonal orbitals i and j, E is the energy, and η is a convergence factor that is non-zero only in the leads.

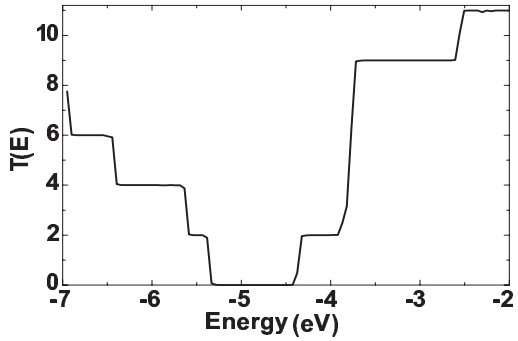

Figure 4: Transmission of a (10,0) CNT calculated with the matrix elements extracted from FIREBALL.

The calculation of the self-energy representing the semi-infinite CNT, begins with the calculation of the surface Green function. The surface Green function of the semi-infinite lead on the left $\mathbf{g}^R_{0,0}$ is calculated from the self-consistent expression:

$$\mathbf{g}^R_{0,0} = \left[(E + i\eta)\mathbf{S}_{0,0} - \mathbf{D}_{0,0} - \tilde{\mathbf{t}}_{0,-1}\mathbf{g}^R_{0,0}\tilde{\mathbf{t}}_{-1,0}\right]^{-1} \quad (1)$$

The convergence of this self-consistent calculation depends on the energy E. When the energy lies within a band-gap of the lead material, Eq. 1 converges quickly within 5 iterations. When the energy E lies in a band, convergence can be quite slow, taking up to 500 iterations with $\eta = 10$ meV and a convergence criteria of a percent difference change less than 0.0001. We update by taking the average of the old and new value of $\mathbf{g}^R_{0,0}$.

The non-zero blocks of the self-energy matrices are calculated using $\mathbf{\Sigma}^R_{1,1} = \tilde{\mathbf{t}}_{1,0}\mathbf{g}^R_{0,0}\tilde{\mathbf{t}}_{0,1}$ and $\mathbf{\Sigma}^R_{N,N} = \tilde{\mathbf{t}}_{N,N+1}\mathbf{g}^R_{N+1,N+1}\tilde{\mathbf{t}}_{N+1,N}$, where $\mathbf{g}$'s are the surface green functions calculated using iterative approach and $\tilde{\mathbf{t}}_{1,0} = t_{1,0} - (E+i\eta)S_{1,0}$ and $\tilde{\mathbf{t}}_{N,N+1} = t_{N,N+1} - (E+i\eta)S_{N,N+1}$.

One of the best tests of the self-energy matrices is to calculate the transmission through an ideal periodic structure of the same material, in this case the (10,0) CNT. The transmission should turn on in integer steps at the valence band maximums and conduction band minimums.

The transmission coefficient shown in Fig. 4 was calculated from [32]

$$T(E) = \mathrm{tr}\left\{\mathbf{\Gamma}^B_{1,1}\left[\mathbf{A}_{1,1} - \mathbf{G}^R_{1,1}\mathbf{\Gamma}^B_{1,1}\mathbf{G}^A_{1,1}\right]\right\} \quad (2)$$

where $\mathbf{\Gamma}^B_{1,1} = i\left(\mathbf{\Sigma}^{RB}_{1,1} - \mathbf{\Sigma}^{AB}_{1,1}\right)$, $\mathbf{A}_{1,1} = i\left(\mathbf{G}^R_{1,1} - \mathbf{G}^A_{1,1}\right)$, $\mathbf{\Sigma}^A = \left[\mathbf{\Sigma}^R\right]^\dagger$, and $\mathbf{G}^A = \left[\mathbf{G}^R\right]^\dagger$.

The integer turn-ons of the transmission matched the band maxima and minima of the E-k band diagram provided by FIREBALL as they should. We are now in the process of applying the NEGF/FIREBALL code to simulate the line-up of the CNT band states with the molecular states of the DNA, PNA, and linkers shown in Figs. 2 and 3.

5 SUMMARY

Ab-initio and semi-empirical calculations of hybrid bio-inorganic clusters have been presented. The results for the PNA-Glu-CNT cluster indicate that the Glu state will align closely with the valence band of the CNT enabling hole transfer across the bridge for p-type CNTs. For the DNA-amide-CNT cluster, the HOMO is localized away from the interface on the CNT, but the LUMO is extended across the interface suggesting good electron transfer across the amide bridge for n-type CNTs. An ab-initio, DFT, NEGF approach has been described to model the semi-infinite CNT - biomolecule electronic structure.

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