

TABLE OF CONTENTS

	Page
TABLE OF CONTENTS	i
LIST OF TABLES	ii
LIST OF FIGURES	iv
LIST OF ABBREVIATIONS	ix
INTRODUCTION	1
LITERATURE REVIEW	7
METHODS OF CALCULATIONS	18
Perdew, Burke and Ernzerhof (PBE) Functional	18
Resolution of the Identity (RI) Technique	19
Computational Methods	20
Computational Models	21
RESULTS AND DISCUSSIONS	24
SWCNT/gold Complexes (Hybrid Assembling Nanosupports)	24
SWCNT/Gold/Adenine Complexes (DNA Sensor Probe)	33
DNA Probe Stability	39
Nucleic Acid Sensor Sensitivity	43
Prophecy for Thymine Hybridization	46
SWCNT/Gold/Adenine:Thymine Complexes (Target Capture)	49
Stability	49
Sensitivity	51
Preliminary Summarization	54
CONCLUSION	55
LITERATURE CITED	56
APPENDIX	60

LIST OF TABLES

Table		Page
1	Systematic evaluation of the suitable methods and basis sets for adenine-thymine base pair\	21
2	Symmetrical optimized geometries and calculated binding energies (E_b) of SWCNT(8,0)/Au and SWCNT(5,5)/Au complexes. The Au atom is altered deposited position on hexagonal of SWCNT (see picture) which consisting of Axial, Zigzag, Armchair; above C-C bond, Top; above the carbon atom and Hexagonal; above hollow center	25
3	Symmetrical optimized geometries and calculated binding energies (E_b) of SWCNT(8,0)/Au ₃ and SWCNT(5,5)/Au ₃ complexes. The basal of Au ₃ cluster is contacted on sidewall of SWCNT and defines this binding aspect as Apex-Up mode	27
4	Symmetrical optimized geometries and calculated binding energies (E_b) of SWCNT(8,0)/Au ₃ and SWCNT(5,5)/Au ₃ complexes. The apex Au atom of Au ₃ cluster is contacted on sidewall of SWCNT and defines this binding aspect as Apex-Down mode	28
5	Symmetrical optimized geometries and calculated binding energies (E_b) of SWCNT(8,0)/Au ₃ and SWCNT(5,5)/Au ₃ complexes. The planet of Au ₃ cluster is contacted on sidewall of SWCNT and defines this binding aspect as Horizontal mode	29
6	The geometrical parameters, calculated binding energies (E_b), energy gap and Mulliken population molecular charges of the Au/A:T, SWCNT(8,0)/Au/A:T, SWCNT(5,5)/Au/A:T and their fragments.	38
7	The geometrical parameters, calculated binding energies (E_b), energy gap and Mulliken population molecular charges of the Au ₃ (IP)/A:T ^a , SWCNT(8,0)/Au ₃ (ApD)/A:T, SWCNT(5,5)/ Au ₃ (ApD)/A:T and their fragments	40

LIST OF TABLES (Continued)

Table		Page
8	The geometrical parameters, calculated binding energies (E_b), energy gap and Mulliken population molecular charges of the Au ₃ (IP)/A:T, Au ₃ (PP)/A:T, SWCNT(8,0)/Au ₃ (ApU)/A:T, SWCNT(5,5)/Au ₃ (ApU)/A:T and their fragments.	42
9	The important geometrical parameters and Mulligen atomic charges of adenine (as reference) base and several adenine probes; Au/A, Au ₃ (IP)/A, Au ₃ (PP)/A, SWCNT(8,0)/Au/A, SWCNT(5,5)/Au/A, SWCNT/(8,0)Au ₃ (ApD)/A, SWCNT/(5,5)Au ₃ (ApD)/A, SWCNT(8,0)/Au ₃ (ApU)/A and SWCNT(5,5)/Au ₃ (ApU)/A.	45
10	The geometrical parameters, Mulligen atomic charges and calculated binding energies (E_b) of double hydrogen bond of original A:T base pair (as reference). and several target-probe systems	48
11	The Δq_{Mprobe} and $\Delta q_{Msupport}$ (au.) parameters of Au/A:T, Au ₃ (IP)/A:T, Au ₃ (PP)/A:T, SWCNT(8,0)/Au/A:T, SWCNT(5,5)/Au/A:T, SWCNT(8,0)/Au ₃ (ApD)/A:T, SWCNT(5,5)/Au ₃ (ApD)/A:T, SWCNT(8,0)/Au ₃ (ApU)/A:T, SWCNT(5,5)/Au ₃ (ApU)/A:T complexes	52

LIST OF FIGURES

Figure		Page
1	Properties of DNA-functionalized gold nanoparticles. A mixture of gold nanoparticles with surface-immobilized complementary DNA sequences (a, b) appears red in color and has a strong absorbance at 520 nm. When a complementary DNA sequence (a'b') is added to the solution, the particles are reversibly aggregated causing a red shift in the surface plasmon absorbance to 574 nm, thus, appearing purple in color	2
2	Electrical detection of DNA hybridization using Au nanoparticle labels. (a) Immobilization of capture probes in the gap between two electrodes. (b) Hybridization with target DNA and Au nanoparticle-labeled detection probe. (c) Reductive deposition of Ag, creating a bridge that decreases resistance	2
3	Electrochemical detection of DNA hybridization using Au nanoparticle labels. a) Immobilization of target DNA. b) Hybridization with Au nanoparticle labeled detection probe. c) Voltammetric detection of Au redox signal	3
4	Schematics of various strategies used to integrate CNTs in electrochemical sensors. DNA detection via labelling with CNT loaded a) with enzymes, b) with quantum dots and c) with intercalator	4
5	(a) Schematic illustration of self-assembly of thiolated oligonucleotides onto Au–CNT hybrid. The use of MCH assists the erection of ssDNA and facilitates hybridization of complementary oligonucleotides, which is detected via mediator $\text{Ru}(\text{bpy})_3^{2+}$. (b) UV–Vis absorption spectrum of MWNT bound with gold nanoparticles. The inset shows the TEM image of a MWNT coated with gold nanoparticles	5

LIST OF FIGURES (Continued)

Figure		Page
6	The four bases of DNA showing their complementary binding properties and DNA nucleotide	7
7	General DNA biosensor design. Target DNA is capture at the recognition layer, and the resulting hybridization signal is transduced into a usable electronic signal for display and analysis	8
8	Key interactions between fields of biology and nanotechnology	9
9	The dimensions of wires used in conventional CMOS technology, together with as-grown nanowires and carbon nanotubes. While the cross-section of nanofibers and inorganic nanowires is comparable to the size of typical proteins, single wall carbon nanotubes (hollow cylinders of carbon) have a diameter comparable to DNA	9
10	Schematic depiction of thiol-modified oligonucleotides self-assembling on the gold electrode and hybridizing with gold-nanoparticle-supported DNA sequences	10
11	Schematic of the honeycomb structure of a graphene sheet (A). SWCNTs can be formed by folding the sheet along the shown lattice vectors leading to armchair (B), zigzag (C), and chiral (D) tubes, respectively. The graphene sheets rolled up into concentric cylinders form MWCNT (E)	11
12	Schematic mechanism for nucleic acid sensing via an inlaid multi-walled carbon nanotube combined with Ru(bpy) ₃ ²⁺ -mediator) amplified guanine oxidation	12

LIST OF FIGURES (Continued)

Figure		Page
13	Representative HRTEM micrographs showing (a) low-magnification and (b) high-magnification views of Au nanoparticle supported on a carbon nanotube	13
14	The four possible planar (N1, N3, N7) and nonplanar (N6) binding sites of the gold cluster Au ₃ to adenine. Also shown is the NH ₂ anchored complex A: Au ₃ (N6). The bond lengths are given in Å and bond angles in deg	15
15	The stable [A-Au ₃]:T pairs. The WC intermolecular H-bonds of the A:T pair are characterized by the following geometrical parameters: R(N6-H6(A)) = 1.023 Å, r(H6(A)···O4(T)) = 1.926 Å, ∠N6H6(A)O4(T) = 174.1°; R(N3-H3(T)) = 1.044 Å, r(H3(T)···N1(A)) = 1.822 Å, ∠N3H3(T)N1(A) = 178.5°; R(C2-H2(A)) = 1.087 Å, r(H2(A)···O2(T)) = 2.937 Å, ∠C2H2(A)O2(T) = 131.9°. The bond lengths are given in angstroms and bond angles in degrees	16
16	Illustration of studied configurations and their systematic labels of a) SWCNT/Au/A:T, b) SWCNT/Au ₃ (ApU)/A:T and c) SWCNT/Au ₃ (ApD)/A:T	23
17	A schematic description of different binding sites (H, hollow; A, axial; Z, zigzag; T, top; Ar, armchair) of individual atoms adsorbed on a SWCNT(8,0) and SWCNT(5,5). Filled circles denote adatoms	24
18	Fully optimized geometries, calculated binding energies (E_b) and deposited distances of the most stable structure of a) SWCNT(8,0)/Au and b) SWCNT(5,5)/Au complexes. From a) and b) demonstrate that the Au atom prefers deposition on SWCNT with top site binding	26

LIST OF FIGURES (Continued)

Figure		Page
19	<p>C_S (symmetry applied) optimized geometries, calculated binding energies (E_b), deposited distances and Mulliken population charges of a) the most stable structure of SWCNT(8,0)/Au₃ b) the most stable structure of SWCNT(5,5)/Au₃ c) the most stable structure of SWCNT(8,0)/Au₃ that holding the Au₃ cluster with PD-ApD binding mode and d) the most stable structure of SWCNT(5,5)/Au₃ that holding the Au₃ cluster with AL-ApU binding mode</p>	31
20	<p>Fully optimized geometries^a and Mulliken population atomic charges of the a) Au/A and b) Au/A:T. C_S (symmetry applied) optimized geometries and Mulliken population atomic charges of c) Au₃(IP=inplane)/A, d) Au₃(IP)/A:T, e) Au₃(PP=perpendicular plane)/A and f) Au₃(PP)/A:T</p>	34
21	<p>C_S (symmetry applied) optimized geometries and Mulliken population atomic charges of the a) SWCNT(8,0)/Au b) SWCNT(8,0)/Au/A c) SWCNT(8,0)/Au/A:T d) SWCNT(5,5)/Au e) SWCNT(5,5)/Au f) SWCNT(5,5)/Au/A:T. The SWCNT/A:T system are construct from the most stable of each SWCNT/Au complex (see Figure 19)</p>	35
22	<p>C_S (symmetry applied) optimized geometries and Mulliken population atomic charges of the a) SWCNT(8,0)/Au₃(ApD) that holding the Au₃ cluster with PDAX-ApB binding mode b) SWCNT(8,0)/Au₃(ApD)/A c) SWCNT(8,0)/Au₃(ApD)/A:T d) the most stable structure of SWCNT(5,5)/Au₃(ApD) that holding the Au₃ cluster with PDAX-ApT binding mode e) SWCNT(5,5)/Au₃(ApD)/A f) SWCNT(5,5)/ Au₃(ApD)/A:T. The b and c complexes are constructed from a complex and e and f complexes are constructed from d complex</p>	36

LIST OF FIGURES (Continued)

Figure		Page
23	<p>C_S (symmetry applied) optimized geometries and Mulliken population atomic charges of the a) the most stable structure of SWCNT(8,0)/Au₃(ApU) that holding the Au₃ cluster with ALAx-ApH binding mode b) SWCNT(8,0)/Au₃(ApU)/A c) SWCNT(8,0)/Au₃(ApU)/A:T d) SWCNT(5,5)/Au₃(ApU) that holding the Au₃ cluster with ALAx-ApT binding mode e)) SWCNT(5,5)/Au₃(ApU)/A. The b and c complexes are constructed from a complex and e complexes are constructed from d complex. The e complex is unstable so the f) SWCNT(5,5)/Au₃(ApU)/A:T complex is ignored</p>	37
24	<p>The geometry of double hydrogen bond of original A:T base pair (as reference) and calculated binding energies (E_b). The arrows show the trend of changing N3-H3...N1 and O4...H6'-N6 hydrogen bonds after binding with gold or SWCNT/gold complexes</p>	47

LIST OF ABBREVIATIONS

A	=	Adenine
Å	=	Angstrom
a.u.	=	Atomic Unit
ALAx	=	Along Axis
ApD	=	Apex-Down
ApH	=	Apex-Hollow
ApH	=	Apex-Bond
ApT	=	Apex-Top
ApU	=	Apex-Up
Au	=	Gold
Au NPs	=	Gold Nanoparticles
B3LYP	=	Becke 3-Parameter (Exchange), Lee, Yang and Parr (Correlation); Density Functional Theory
BsB	=	Basal-Bond
BsH	=	Basal-Hollow
BsT	=	Basal-Top
C	=	Cytosine
C	=	Carbon
cc-pVDZ	=	Correlation Consistence Polarized Valence Double Zeta
cc-pVTZ	=	Correlation Consistence Polarized Valence Triple Zeta
CMOS	=	Complementary Metal-Oxide Semiconductor
CNTs	=	Carbon Nanotubes
DFT	=	Density Functional Theory
DNA	=	Deoxy-ribo Nucleic Acid
Eb	=	Binding Energy
ECP	=	Effective Core Potential
eV	=	Electron Volt

LIST OF ABBREVIATIONS (Continued)

G	=	Gaunine
H	=	Hydrogen
HRTEM	=	High-Resolution Transmission Electron Microscopy
IP	=	In Plane
kcal/mol	=	kilocalorie per mol
MCH	=	Mercaptohexanol
MWCNTs	=	Multiwall Carbon Nanotubes
N	=	Nitrogen
nm	=	Nanometer
O	=	Oxygen
PBE	=	Perdew, Burke and Ernzerhof
PDA _x	=	Perpendicular Axis
PP	=	Perpendicular Plane
qm	=	Mulliken Charge
RECP	=	Relativistic Effective Core Potential
RI	=	Resolution of the Identity
Ru(bpy) ₃ ²⁺	=	Tris(2,2'-bipyridyl) ruthenium(II)
SWCNTs	=	Single-wall Carbon Nanotubes
T	=	Thymine
TDP	=	Temperature-Programmed Desorption
TEM	=	Transmission Electron Microscopy
UV-Vis	=	Ultraviolet Visible
WC	=	Watson-Crick