

Directed Assembly of Nanostructures for Nanoelectronics

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Scaling Trend in Si – Moore's Law



Moore's law: Functionality per cost goes up 2x every 18 months

In 25 years: we will approach the inter-atomic distance

One has to pay for it: Moore's second Law: Every two generations, Fab cost goes up 2x Challenge: Reaching the physical limit; the excessive cost (what is the future of computing?) Opportunity: maneuvering and building things bottom-up

Nanopatterning...

1959 – Richard Feynman
 – "there's plenty of room at the bottom"

•C³ in the IC industry

CompetitivenessCost EffectivenessCollaboration and Co-development

•D³ in the Biotech industry

- •Detection of first diseased cell
- •Diagnosis of diseases
- •Delivery of targeted treatment



Scale of Natural and Artificial Structures

Engineered Micro/Nano Structures

Structures From Nature





Ozkan Research Group



Self Assembly

SELF-assembly involves the spontaneous and autonomous organization of disorganized interacting components into an organized pattern without direct human or mechanical interference.

RAINDROPS on a leaf illustrate thermodynamic self-assembly



The laws of thermodynamics require that a raindrop take the form that maximizes its energetic stability. The smooth, curved shape does so by minimizing the area of the unstable surface.

EMBRYO exemplifies coded self-assembly



The kind of self-assembly embodied by life is called coded self-assembly because instructions for the design of the system are built into its components.

Self Assembly and Intermolecular Forces: Molecular Recognition

Type of Force	Strength (kJ/mol)	gth (kJ/mol) Example	
Covalent	>210	CC bond	
Electrostatic	>190	Li+F-	
Dipole-dipole	5-40	H ⁺ -Cl ⁻ H ⁺ -Cl ⁻	
π - π interaction	10-20	CNTCNT*	
Hydrogen bonding	5-40	ssDNAssDNA**	
Dispersion	<5	$H^{+}-O^{=}-H^{+}Cl^{}Cl^{+}$	
Hydrophobic	5-40	H ₂ OMetal	
Dative	20-380	SAu	

OUR APPROACH: BOTTOM-UP ASSEMBLY



Heterogeneous Integration by Self Assembly









- Drop-in technology
- Biomolecules, nanowires, nanotubes
- Built into back-end processing
- Massively parallel integration?
- Compatibility issues?



A new paradigm for synthesizing devices and integrated circuits

Biological assembly of Devices Nanocrystals, carbon nanotubes, nanowires Linkers: Peptides, DNA, PNA, Viruses

CNT-peptide

complex



Synthesized inverter structure

Nano Letters (2003) Carbon (2004) Carbon (2006) PSS (2006) JNO (2006) Small (2006) nature nanotechnology (2006) JNO (2007) JNO (2008)

2-terminal device: Resonant tunneling diode

SWNT-DNA-SWNT

3-terminal device

Our vision

Cross-bar logic circuit on a DNA array

- Map bio-assembly onto a cross-bar architecture
- Gray grid represents DNA array.
- Gold is metallized DNA
 providing gating and contacts
- 2D topology

Other recent work...

- A. Dehon, ACM J. on Emerging Technologies in Computing Systems, **1**, 109 (2005)
- G. Snider, P. Kuekes, and R. S. Williams, *Nanotechnology*, **15**, 881 (2004)
- R. Beckman, E. Johnston-Halperin, Y. Luo, J. E. Green, and J. R. Heath, *Science*, **310**, 465 (2005)
- C. Dwyer, V. Johri, M. Cheung, J. Patwardhan, A. Lebeck, and D. Sorin, *Nanotechnology*, **15**, 1240 (2004)



Layout of cross-bar NOR gate bio-assembled on DNA tile array JNO (2006)

Our vision

CNT-Mol RTD Array

- Cellular automata type architecture.
- 2D array of non-linear elements



2D CNT-Mol RTD network to implement a cellular automata-type architecture

Design Considerations

What linkers to be used?

- How and where to start assembly process?
- What templates to use?
- How to solve poor conductivity between the components within the assembly?
- How to integrate to existing device platforms?

What linkers to use: Biological Linker Archive

•Protein: amino acids

•Virus: (a) Adenovirus (b) Rotavirus (c) Influenza virus (d) Vesicular stomatitis virus

(e) Tobacco mosaic virus (f) Alfalfa mosaic virus (g) T4 bacteriophage (h) M13 bacteriophage
 •Nucleic Acid: DNA, RNA, PNA*



Nanowires, Nanotubes, Combs, Spheres....



Biological self assembly of carbon nanotubes

- Biological Linkers (e.g. DNA, PNA, Streptavidin)
 - Specificity unique labeling of CNTs for assembly on conventional substrates
 - Insulators for engineering purposes
 - Metallization for conducting interconnects
 - Demonstrated with Pd, Pt, Ni, Cu, Au, Ag

Where and How to Start Assembly: Lock and Key Lithography[™] assembly of nanostructures



Collaboration with J. Hartley (University of Albany) and M. Ozkan (UCR)

TECHCON, 2007 Austin, TX NIST, 2007, Gaithersburg, Maryland

Where and How to Start Assembly: Lock and Key Lithography[™] assembly of nanostructures



Carbon Nanotubes and Quantum Dots FOR SELF ASSEMBLY



Ravindran et al, Nano Letters, 3, 4, 447 (2003)



Purification and shortening of nanotubes is achieved via strong acid axidation

Liu et al, Science, 280, 1253 (1998) Rinzler et al, Appl. Phys. A, 67, 29 (1998) Rao et al, Phys. Rev. Lett., 86, 3895 (2001)



Ends of carbon nanotubes can be functionalized with a variety of groups, -COOH, $-NH_2$, etc. which provides flexibility for their utilization in assembly with other organic and inorganic materials.

Chemical Self Assemby of CNT-QD Hybrids



Introduction of carboxyl-terminal groups via acid treatment (Oxidation)



Water stabilization of CdSe/ZnS QDs via aminoethane thiol treatment



Heterojunction formation via Ethylene carbodiimide reaction

Biological Assembly of Carbon Nanotubes



- deoxyribonucleic and peptide nucleic acid fragments are used as linkers
- EDC coupling is used to connect SWCNTs through DNA and PNA

•SWCNT-DNA-SWCNT •SWCNT-PNA-SWCNT

- Conjugation with DNA and PNA linkers have been demonstrated
- Electrical characterization of bioconjugates have been carried out
- Three terminal device fabrication is the next step...

Carbon (2007) Small (2006) Nanotechnology (2006)

QD end-conjugation for short and long CNTs





(A) CNT ~500 nm in length with QD conjugation at both the ends. (B) QD conjugation only at CNT ends for overall length larger than $4\mu m$

Nano Letters (2003)

Molecular Linkers: DNA and PNA



tu

CNT-DNA-CNT Resonant tunneling diode

The comparison between DNA and PNA: > The bases (G,C,A,T) in DNA and PNA are the same. DNA has sugar phosphate backbone, while PNA has a synthetic peptide backbone usually formed N-(2-amino-ethyl)-glycine units.

Biological Self Assembly of Nanostructures F Ċ R P ssDNA used as the linker



- EDC coupling is used to connect **SWCNTs**
- •SWCNT-DNA-SWCNT bioconjugates are formed
- Conjugation confirmed with FTIR



Biological Self Assembly of Nanostructures



- ssPNA used as the linker (neutral backbone)
- EDC coupling is used to connect SWCNTs
- •SWCNT-PNA-SWCNT bioconjugates are formed
- Conjugation confirmed with FTIR





Molecular Modeling of the Conjugates

(b)

3.6 eV LUMO / CNT

Homo-Lumo gap: ~3.6 eV
Homo orbital is confined on glutamate
Lumo orbital is located on the CNT
Good possibility for hole transport across the conjugate

<u>0 eV</u> HOMO / glu

<u>-1.1 eV</u> HOMO-1 / glu

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-1.7 eV HOMO-2
HOMO-3 / CNT
HOMO-4
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CNT-Mol RTDs

Amide Linker

- CNT end functionalization completed with EDC reaction results in an amide group (-CONH-) linking to molecule of interest
- Simulated 2 CNTs terminated with an amide group linked to C₂H₄ using FIREBALL and NEGF codes



(A) Schematic of CNT-amide- C_2H_4 -amide-CNT. (B) Relaxed structure with H passivation

R. Pandey, N. Bruque, K. Alam, and R. Lake, Phys. Stat. Sol. (a), 203, R5 (2006)

CNT-Mol RTDs

CNT-Molecule-CNT RTD

 Molecular linkers can act as functional electronic elements, not just mechanical linkers



Relaxed CNT-amide-C₂H₄-amide-CNT structure



Experimental Demonstration CNT-amide-DNA-amide-CNT



Measured current-voltage response of a Au-CNT-ssDNA-CNT-Au nanostructure

PSS (2006) JNO (2006) Small (2006)

CNT-Mol RTDs

Simulation CNT-ssDNA-CNT CNT-amide-GCCG-amide-CNT



(A) Symmetric ss-DNA connected to 2 (10,0) CNTs with amide linkers. (B) Transmission of CNT-ssDNA-CNT superimposed on transmission of ideal (10,0) CNT (dashed).

Simulate electronic transmission function

- 3 major resonances in valence band
- 1 double resonance in conduction band.
- Major peaks lie 0.5 1.0 eV above and below the E_c and E_v.
- Consistent with experimentally observed plateau in I-V around 0-bias.

Self-Synthesized Functional Devices

Bio-assembled CNTFETs – DNA assembly
 First simulations of the CNT-ssDNA-CNT system.



FIREBALL / NEGF calculations of transmission and spectral functions at transmission peaks a and b.



-L-GCATCTACG-L-

Au pad

0.6

0.2

-0.2

Au pad

Current (µA)

- The spacing of the major transmission peaks is consistent with the experimentally observed plateau around zero bias.
- The base pair types dictate the voltage of the resonant peaks in the I-V
- Spectral function indicates the spatial extent of energy states of charge carriers for a given system
- C. Ozkan et al, Small (2006)



SWNT-ssDNA-SWNT Resonant Tunneling Diode



Experimental system is more complex: may have 10-100 SWNTs in a bundle, and each SWNT is functionalized with n>1 oligomers

Assume n=2 with 20 SWNTs \rightarrow Max. current of 0.4 μ A

In the 9-base and 24-base configurations \rightarrow plateau region in I-V curves is also 2 eV wide...

Assume on-current for 9-base device 0.4 μ A \rightarrow divide by 20 (or 100) \rightarrow 20 (or 4) nA per SWNT

If $n=4 \rightarrow$ roughly 1-5 nA per DNA strand, so similar order of magnitude

C. Ozkan et al, Small (2006)

INTEGRATION APPROACH

Example

- Code unique nodes with
 DNA linkers
- Metallized DNA backbone as conducting linkers



Ag, Au, Cu, Pt, Pd



Self-synthesized inverter

DNA conductivity improvement via metallization

1.The adsorption of metal (II) complexes prior to their reduction to the metal2.Electrostatic interaction of the negatively charged DNA with positively charged particles

Pt nanowire templated by DNA



Michael Mertig, et al, Nano Lett., Vol. 2, No. 8, 2002

Pd metallized DNA by chemical reduction



Au nanowire templated by DNA

μμη

C. Ozkan et al, Nanotechnology (2005), JNO (2006)

Au NP bound to DNA electrostatically



Metallization of PNA fragments



wavenumber 1/cm

Ozkan et al, Nanotechnology (2006)



Initial Lock and Key Lithography™ Tests

Engineered Tethers



Signal Detection from 18 Engineered DNA Sequence

NW1 Wash @30 C



Au Nanowires functionalized with key1 sequence are addressed to the

Experimental Results

pads.

NW2 Wash @30 C

Au Nanowires functionalized with key2 sequence are addressed to the pads.

NW3 Wash @30 C



Au Nanowires functionalized with key3 sequence are addressed to the pads.

Virus-based memory device

• *Tobacco Mosaic Viruses* (TMV) functionalized with platinum nanoparticles attached to their outer surfaces could be used as nanoscale memory devices that can be switched on and off electronically.

•The hybrids are embedded in a conductive polymer, and sandwiched between two metallic electrodes.

•By applying an electrical potential between the two electrodes, a marked increase in current is observed at 3 volts. In this 'on' state, electrons were able to tunnel through a seemingly impenetrable barrier because of their quantum nature.

nanotechnol

•The 'on' state remained stable unless the voltage went below –2.4 volts, when it switches off.



Microtubules as 1-D templates for Au nanowires



- •Long filamentous proteins that are found in eukaryotic cells
- •Play a crucial role in positioning organelles and guiding intracellular movement
- •Rigid hollow cylindrical tubes 25 nm in diameter and several microns in length
- •Self-assembled from noncovalently associated heterodimer proteins called $\alpha\beta$ -tubulins
- •Covalently linked with colloidal Au through surface primary amine groups, followed by photochemical reduction of a gold ions from HAUCl₄ (Tetrachloroauric Acid)
- Tunneling AFM (TUNA): a Pt/Ir coated Si tip is placed on a single MT-Au nanowire. I-V measurements were taken transversely across the nanowire
- •Bistable behavior: A low conductivity state (OFF state) is present until an applied voltage surpasses a
- ~ 4.5 V threshold → material switches to a high conductivity, current increases by two orders of magnitude (ON state)
- By applying a reverse bias: MT-Au nanowires return to their original low conductivity state (erasing process)

Collaboration with Bruce Dunn (UCLA)

Other Research Areas

Electron transport through molecular-nanotube and bio-inorganic interfaces and nano architectures

- Virus templates for hierarchical nanoengineering
 Hybrid memory Device
 Thenenutics (Tracing Probe
 - Therapeutics/Imaging Probe
- Electrochemical nanoengineering of structures
 Nanowire solar cell and battery applications
 Nanopatterning (vertical and lateral arrays)
 Multisegment nanowires for sensors

□ Imaging for cell biology (live cell imaging and micro/nano bubble imaging in the NSOM and the AFM)

Integration of block-co-polymer patterning with DNA assembly

Electron Transport through Molecular-Carbon Nanotube Interfaces: Alternative Routes for End-Functionalization of Carbon Nanotubes



Reaction pathways for different linkers

SWNT-L-R-L-SWNT Nano Architectures

No	Molecule (R)	Linker (L)					
		Amide	Thioester	Ester	Imino	Ketone	
т						_	
1	disubstituted oligomeric olefine						
11	disubstituted oligomeric alkane						
TTT							
111	polyaromatic						
				_		_	
1 V	${\it Dimercapt}$ odiphenylacetylene						
V	CNT - L - CNT n (=1 or 3)					_	
v	2,5-disubstituted oligothiophene						
371		_		_	_	_	
V1	Terthiophene-dithioester						
VII	3,7-disubstituted Flourene						
VIII							
VIII	1, 1-disubstituted Ferrocene						

Cengiz Ozkan, FENA Center



Virus based nanoassembly -novel devices and therapuetics

CPMV-Fe₂O₃ NP hybrids



TAFM and MFM imaging of single CPMV-IO hybrids. (A) TAFM topography. (B) TAFM phase detection and (C) MFM phase detection of two adjacent CPMV-IO hybrids and their corresponding cross-sections (insets). Nominal size for nanoparticles and nanoclusters are ~ 12 nm and 30 nm respectively.

In collaboration with M. Ozkan (UCR), G. Budak (GU, Turkey), E. Ozbay (Bilkent, Turkey)

Electrochemical nanoengineering of structures for nanoelectronics, sensing and solar cell applications



I maging Methods for Cell Biology (NANOTUMOR Center, NCI-NIH)

Light microscopy

- Resolution of several hundreds of nanometers
- Non invasive

Electron/x-ray microscopy

- Resolution of several nanometers
- Not possible live cell imaging

AFM/NSOM

• Resolution of several tens of nanometers



Veeco Multimode V AFM / MFM / TUNA system



The Nanonics Multiview 1000 AFM/NSOMsystem

Advantanges of AFM:

- Surface morphologies
- Accurate size measurements
- Higher forces can be used to probe mechanical response of cell

Advantages of NSOM:

- Can see inner details of cells
- Increase resolution of optical microscope from ~200nm far-field to ~30nm near-field
- Can use fluorescence to mark specific parts of cell
- Simple sample preparation: No need to coat or extract a thin slice. Live cells can be used.



AFM and NSOM Image for a MCF10A cell Experiencing Telophase of Mitosis









MCF10A Normal Cell Incubated for 24 hours 8 nm Iron Oxide Nanoparticles

AFM Image

NSOM Image



We can see iron oxide nanoparticles inside the cell by NSOM

AFM can give complementary information to decide the particles' position.

AFM/NSOM hybrid technique together provide more detailed information for nanoparticles and cells

We observed endocytosis of iron oxide nanopartles

Recent Addition



-Massively parallel array of nanowires -Multi-segment nanowires -Core-shell nanowires

Summary

- Functionalized carbon nanotubes serve as 1-D building blocks for self-assembled electronic architectures
- Bio-molecular linkers can provide both binding and electrical functionality
- Virus and microtubule 1-D templates are also promising for device applications
- Electrochemical nanostructures for a variety of applications
- Massively parallel arrays of 1D templates are needed for large scale nanopatterning

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