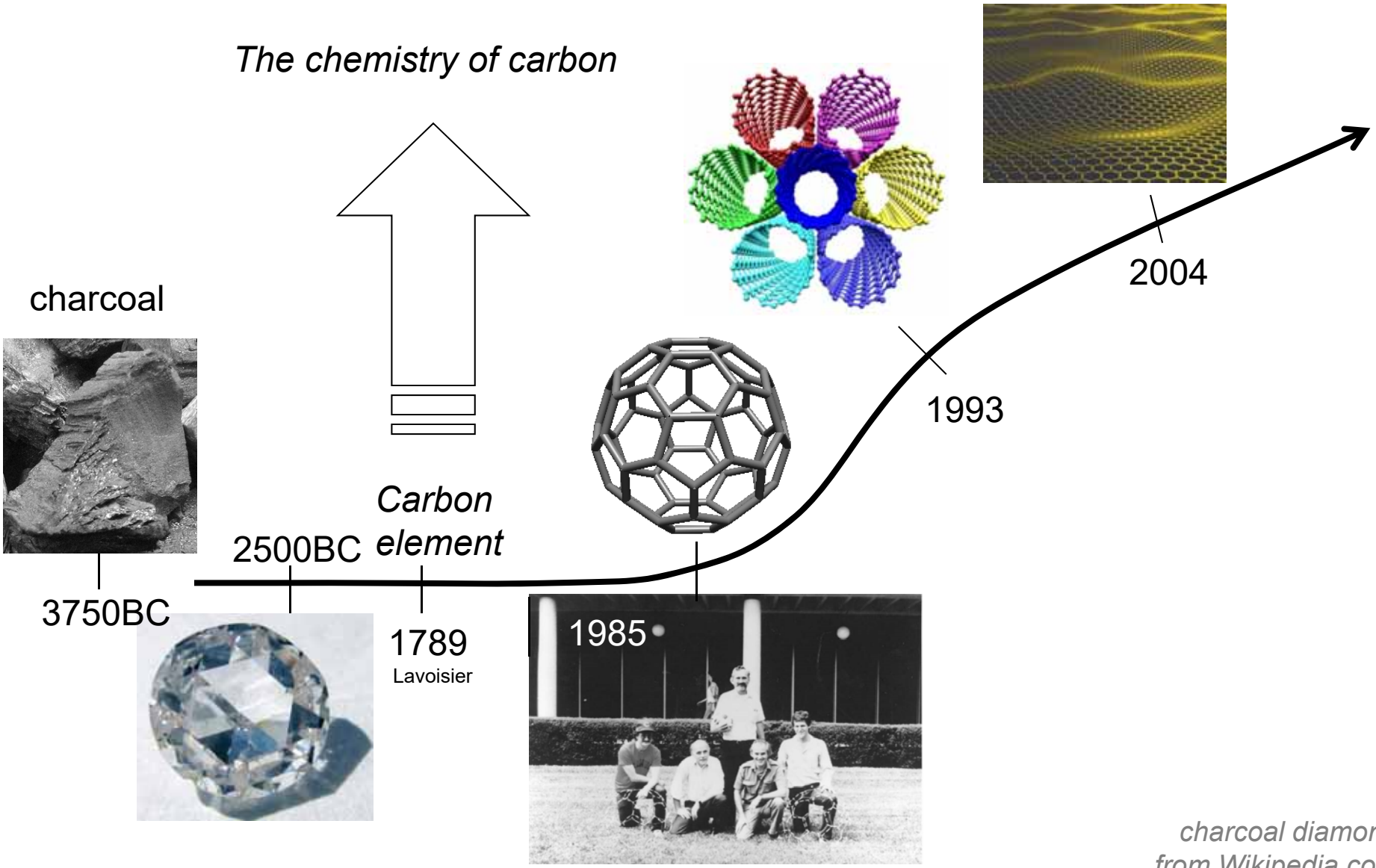
University of Tokyo. July 5, 2016

Molecularly Tunable Fluorescent Quantum Defects

YuHuang Wang
Department of Chemistry and Biochemistry
University of Maryland
yhw@umd.edu
http://www2.chem.umd.edu/groups/wang/


A Brief History of Carbon Materials



charcoal diamond from Wikipedia.com

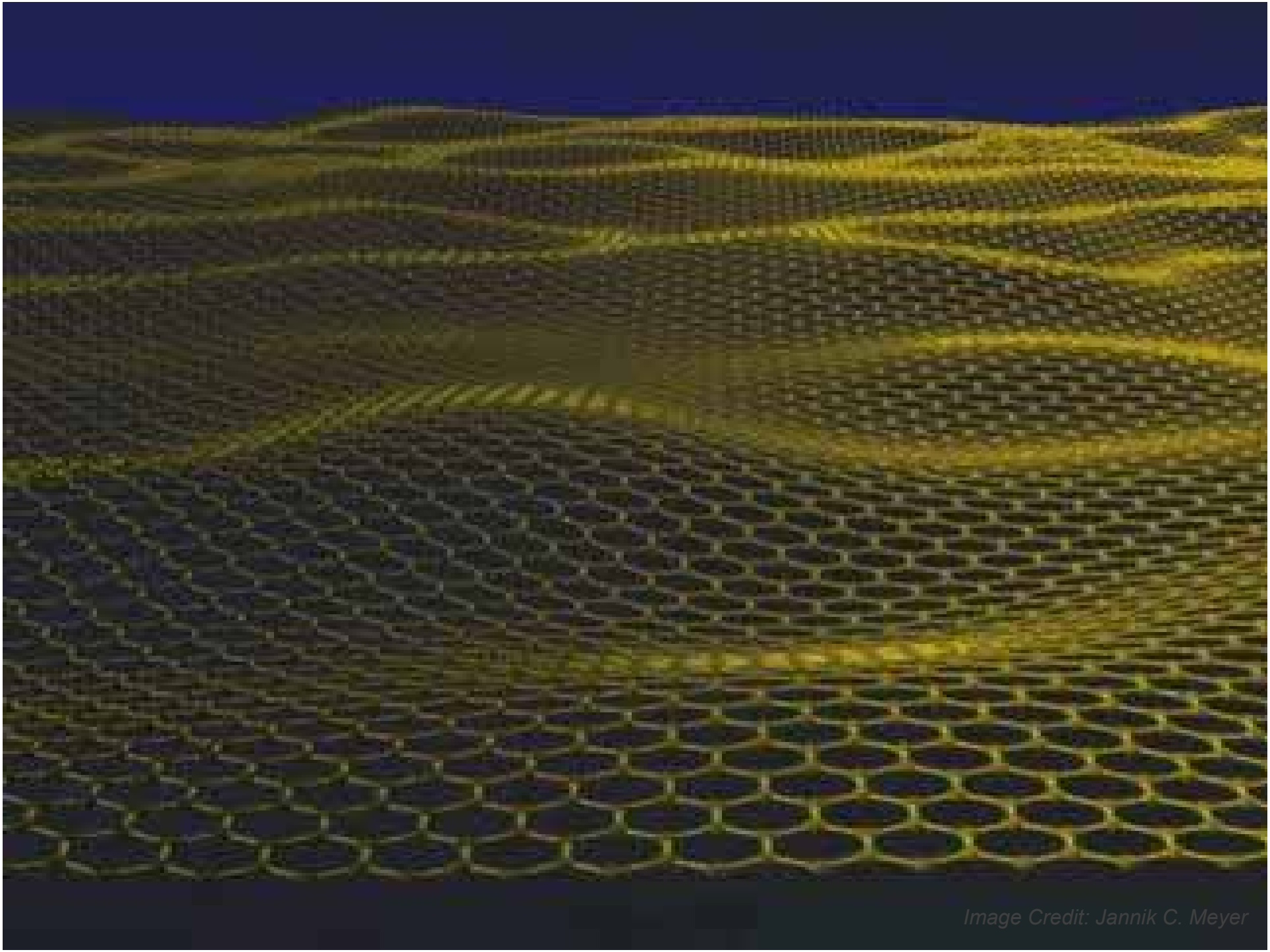
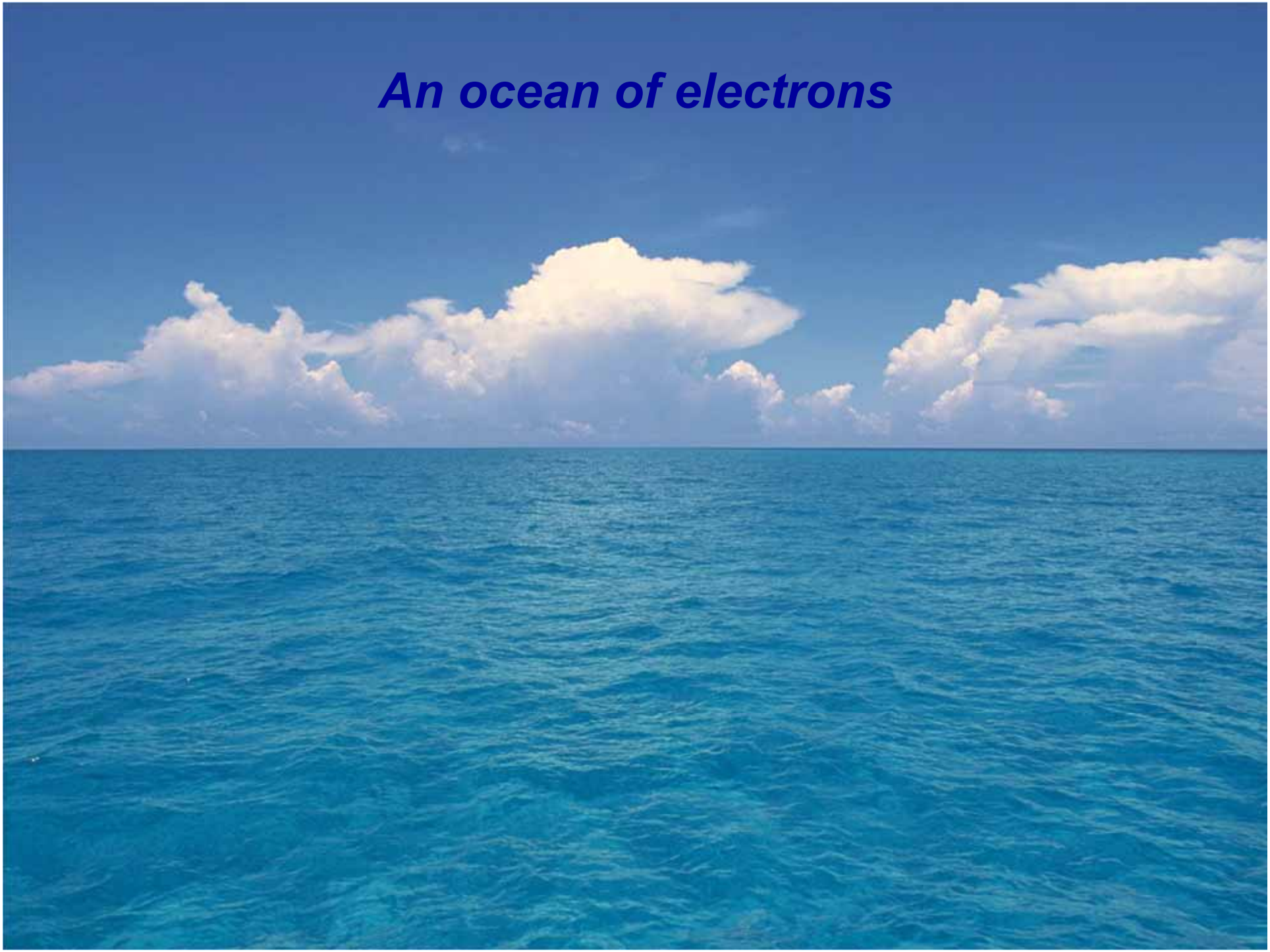


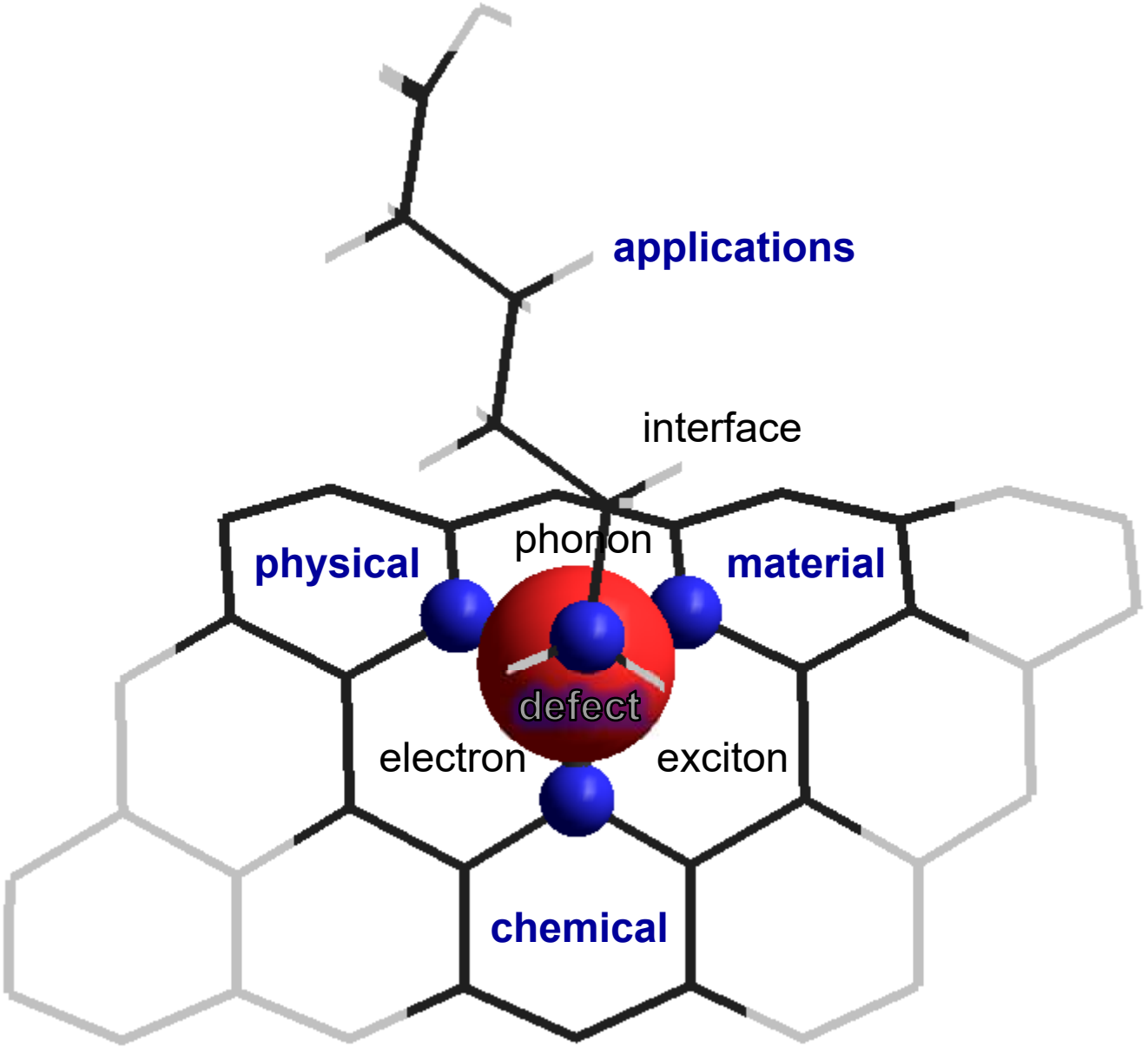
Image Credit: Jannik C. Meyer


An ocean of electrons

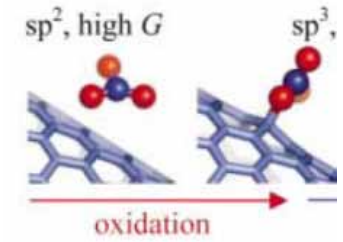

An island in the ocean of electrons?
21:02:02

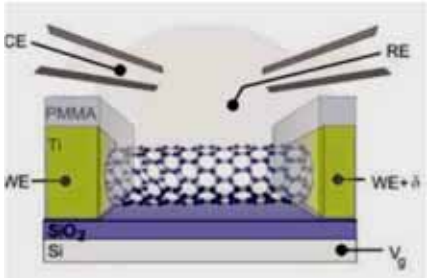
Diamond on graphene?

A Molecular Focusing Point of the Sea



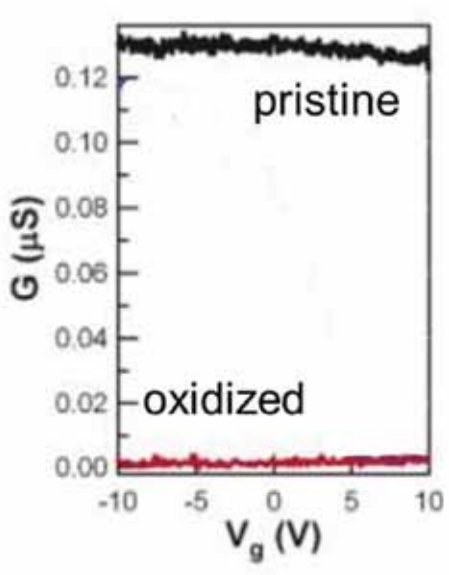
Inspiration: Point Oxidation





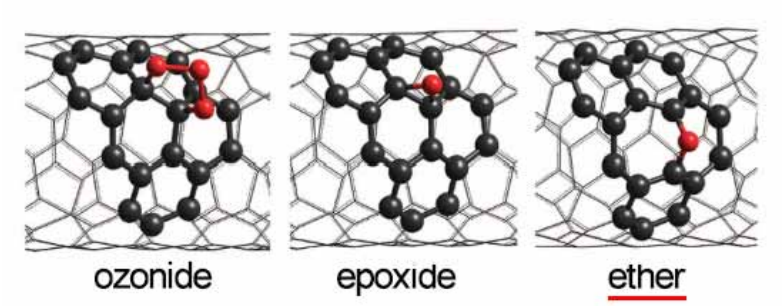
Point Oxidation

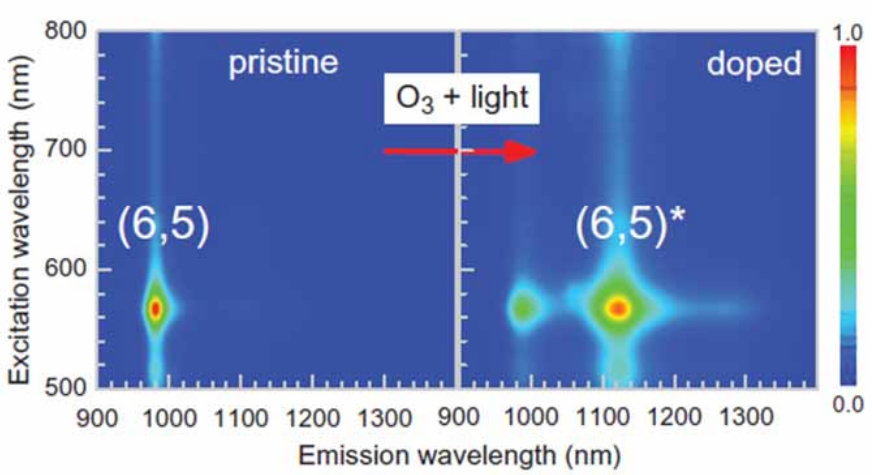
Collins et al, *Science* **2007**, *315*, 77.



"Oxygen Doping"

Weisman et al. *Science* **2010,** *330*, 1656-1659





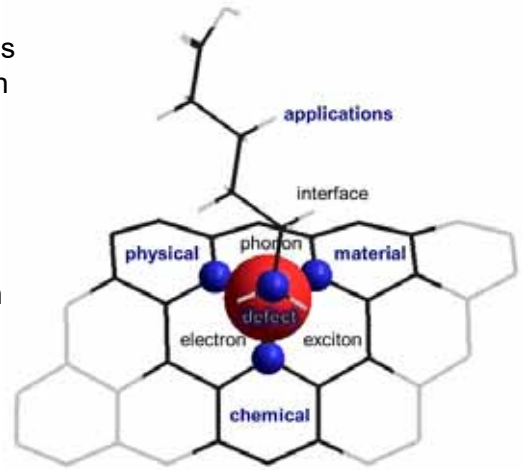
- Exposure of SWCNTs to O_3 and light induces a new emission feature, E_{11}*, which is red-shift from the native E_{11} emission.
- Also, Harutyunyan, Nagatsu, Kiliedna, Doorn, Matsuda et al.

Molecularly Tunable Fluorescent Quantum Defects

YuHuang Wang
University of Maryland
yhw@umd.edu; http://www2.chem.umd.edu/groups/wang/

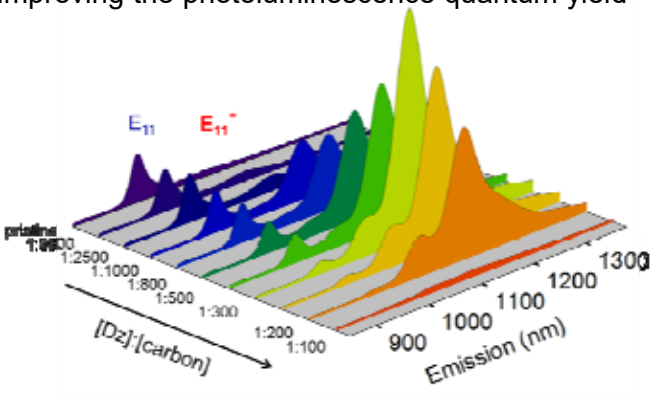
Defects can rule the properties of a crystal. This phenomenon is particularly intriguing in single-walled carbon nanotubes and graphene, where electrons, excitons, phonons, and spin can become strongly coupled with defects.

Collaborator: George Schatz



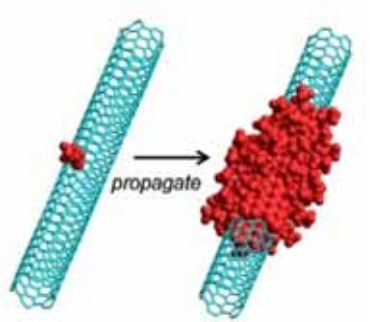
Defects that Brighten Dark Excitons

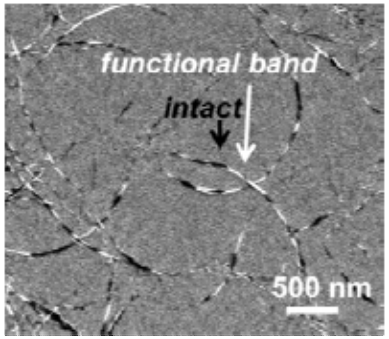
Controlled sp^3 defects brighten dark excitons in semiconducting carbon nanotubes, improving the photoluminescence quantum yield by up to 28 times.



Defects that Drive Chemical Propagation

Propagating from an implanted sp^3 defect, alkylcarboxyl functional groups are covalently attached to the sp^2 carbon lattice forming a band.

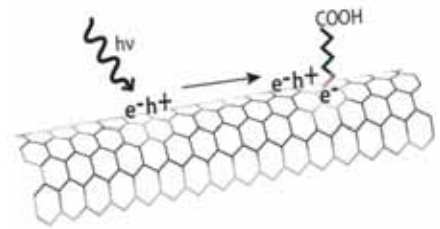


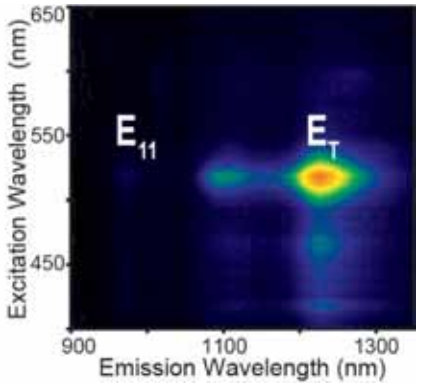


Nature Communications **2011**, *2*: 382. (also Collaborated w/ Rubloff)
J. Phys. Chem. Lett. **2011**, *2*, 885.
Chemistry Materials **2013**, *25*, 4487.

Defects that Stabilize Trions

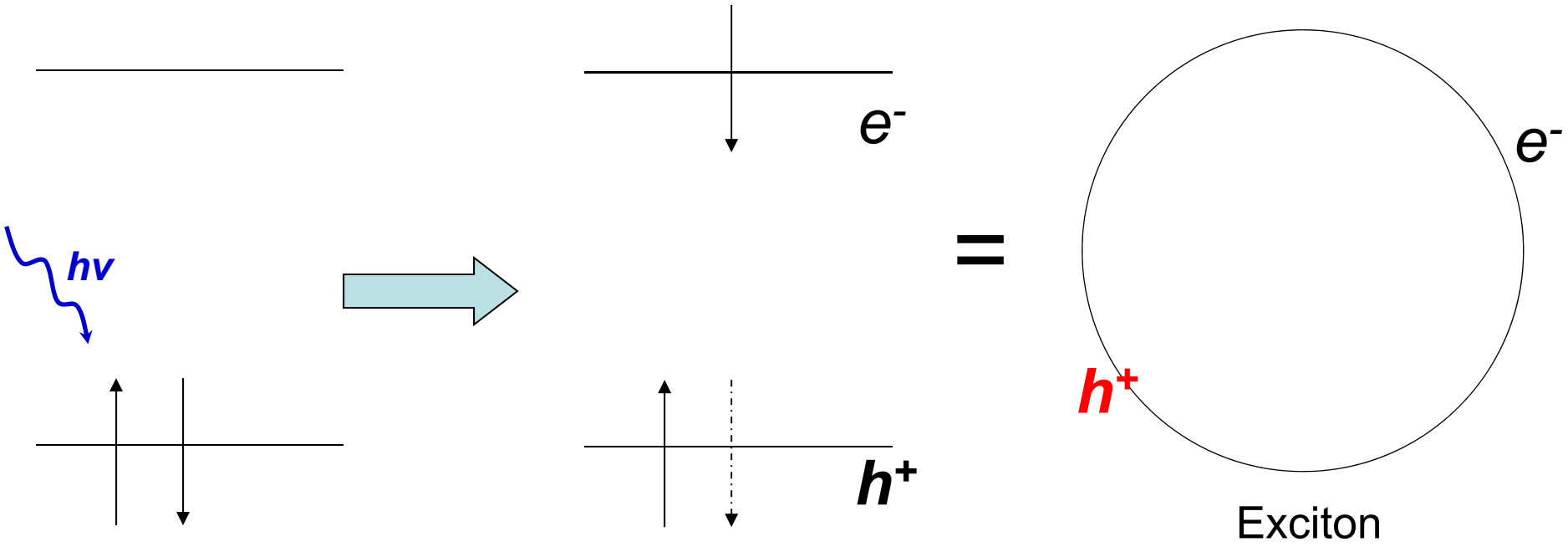
When exciton meets electron, trion—a H^- analog—luminesces brightly.



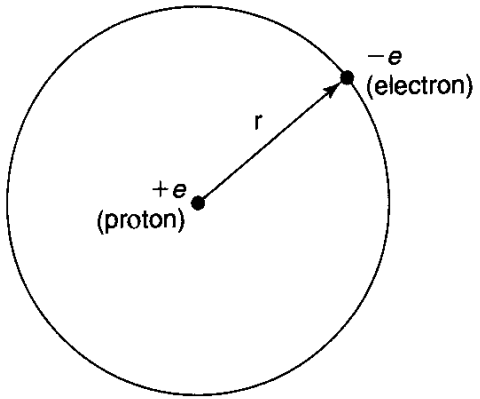


J. Phys. Chem. Lett. **2013**, *4*, 826.
Nature Chemistry **2013**, *5*, 840.
ACS Nano **2014**, *8*, 4239. (collaborated w/ Fourkas)
J. Phys. Chem. C **2015**, *119*, 3733.

What is an Exciton?

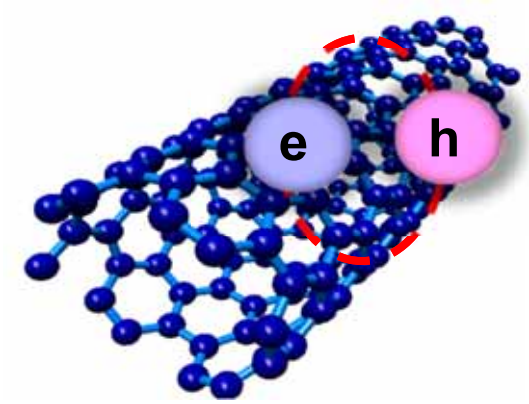


Exciton: an electron-hole pair bound by Coulomb interaction



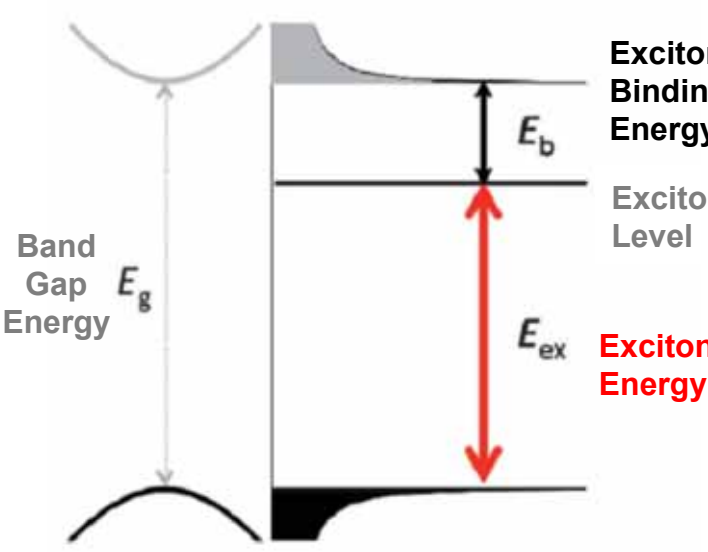
Hydrogen atom

Nanotube Excitons

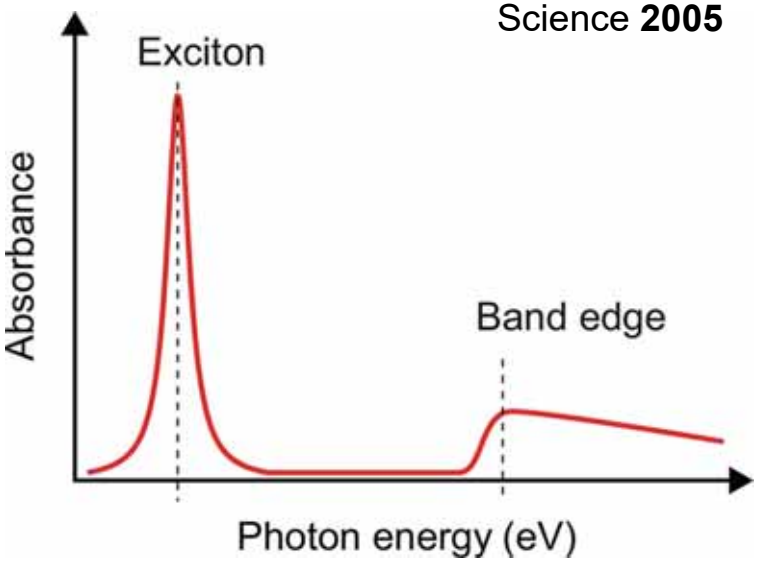


	Hydrogen	CNT Exciton
Binding energy	13.6 eV	100s of meV
Radius	0.053 nm	~1-3 nm

Also, Wang, F. et al. Science **2005**



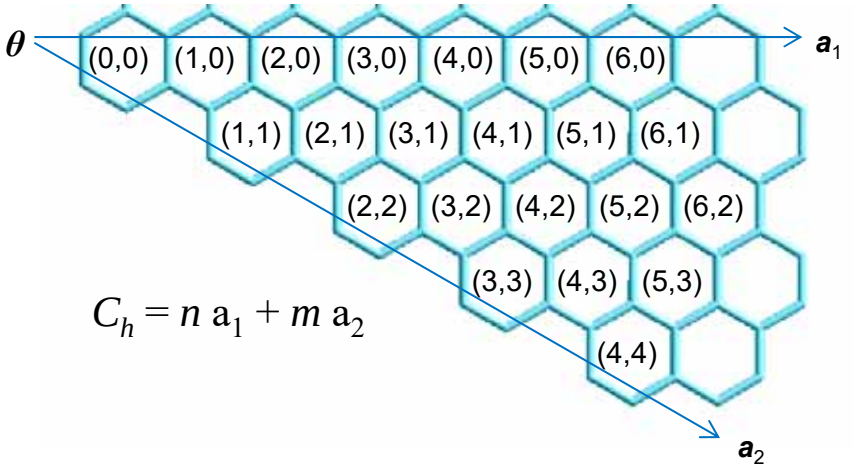
Miyauchi, *J. Mater. Chem. C*, **2013**, *1*, 6499.

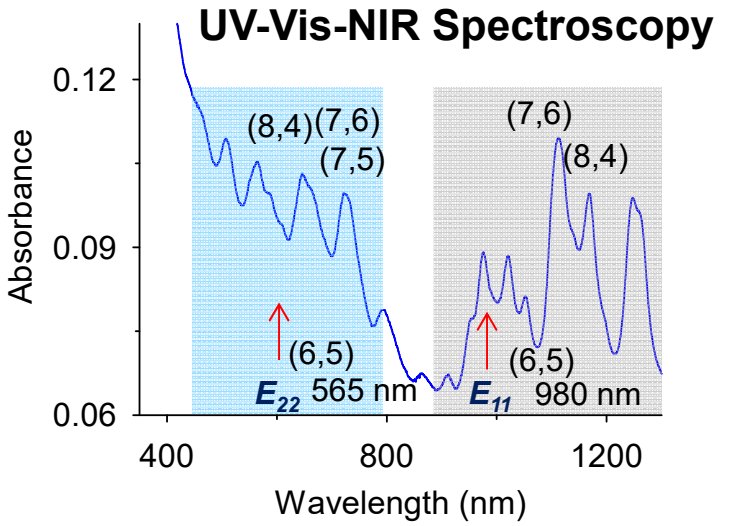


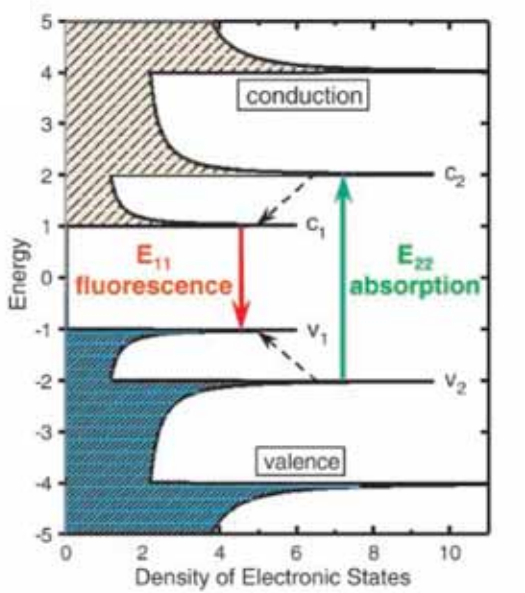
Kanemitsu *et al. SPIE Newsroom*, **2013**.

Carbon nanotube exciton has a strong binding energy, which is a significant fraction of the band gap energy.

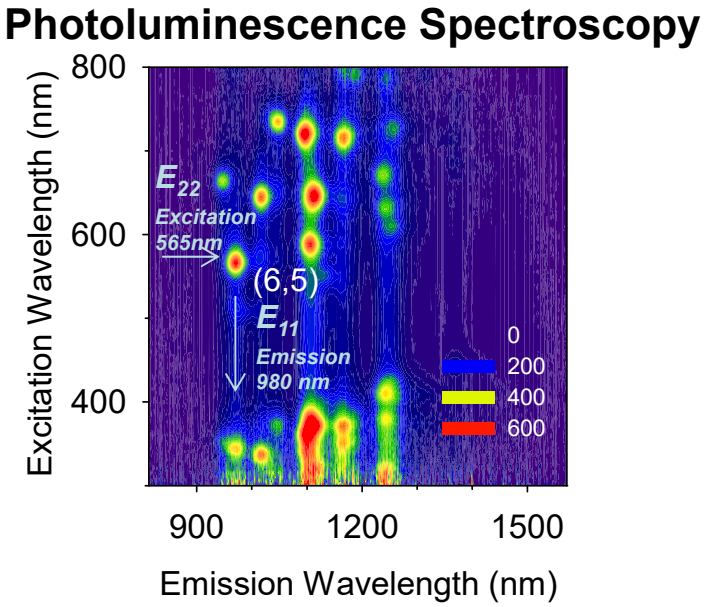
Optical Properties of SWCNT Excitons





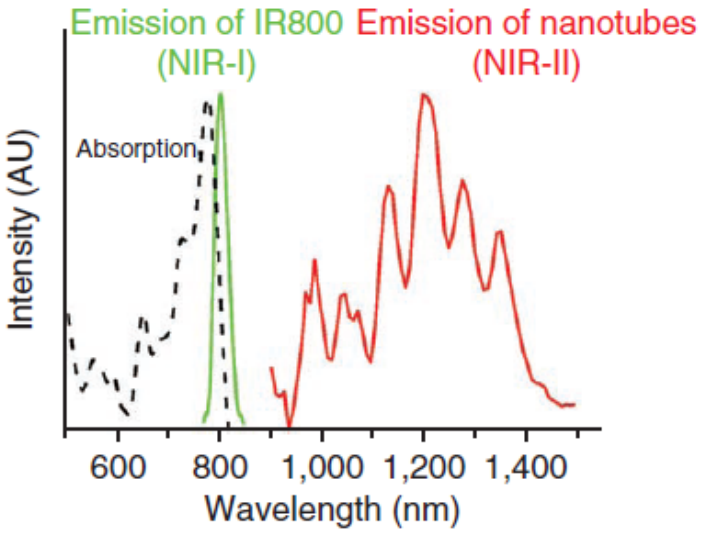


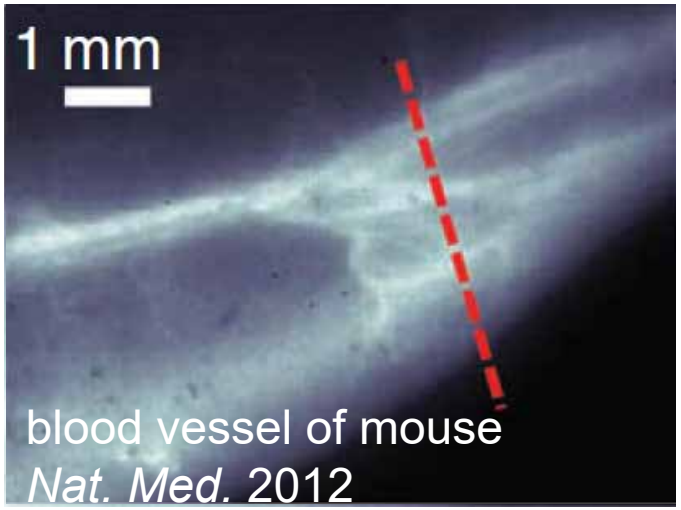
Bachilo *et al. Science* **2002**, *298*, 2361.



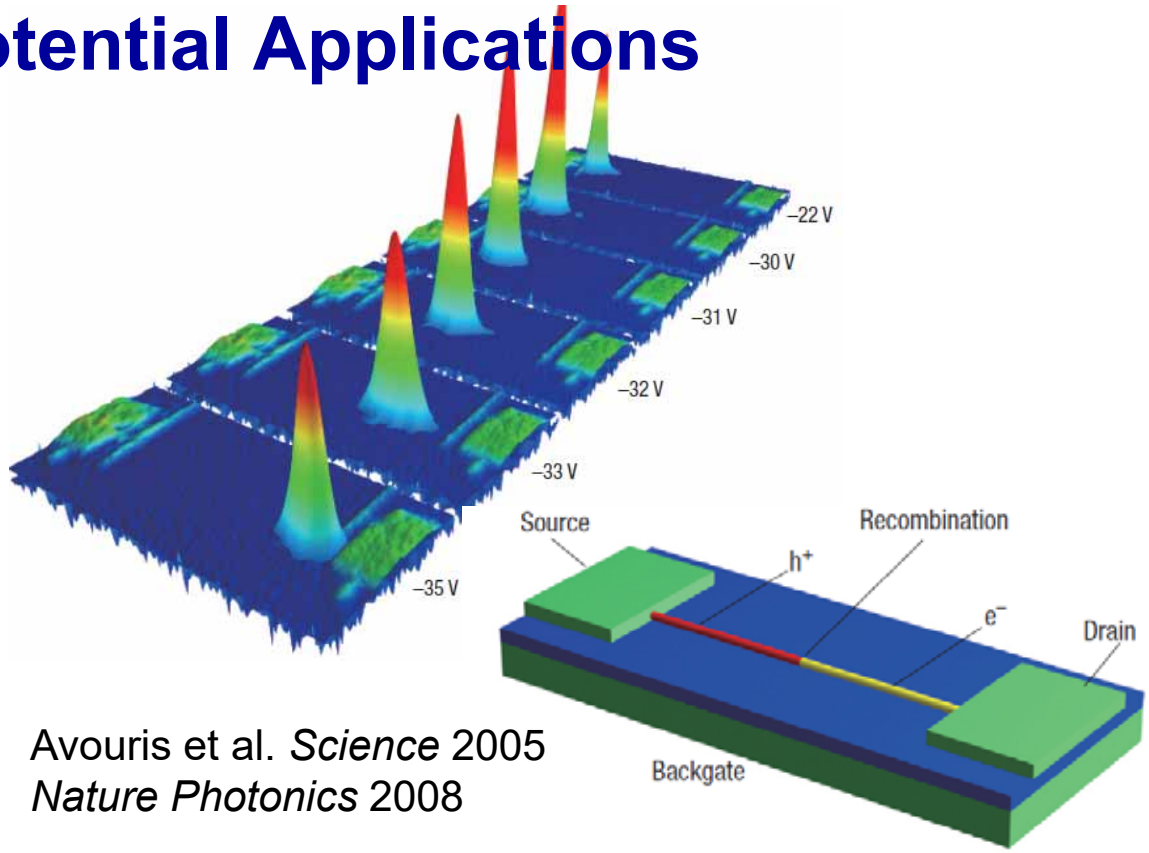
Excitonic energy states can be studied by optical spectroscopic methods.

Many Potential Applications





Dai, et al. (Also, Strano, Maruyama in biosensing, photovoltaics, …)



Avouris et al. *Science* 2005
Nature Photonics 2008

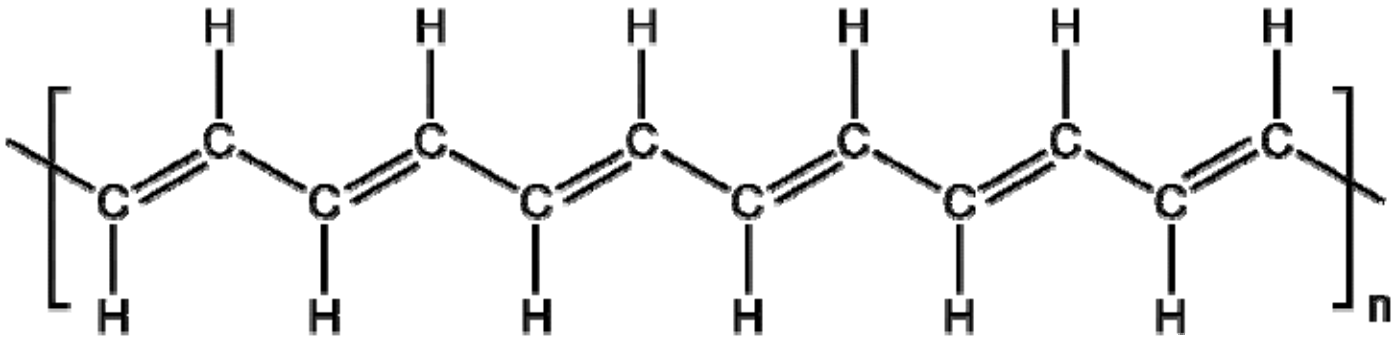
Pros:

- Occurs in near-IR where tissue scattering is minimal.
- Sharp peaks, non-blanking, tunable

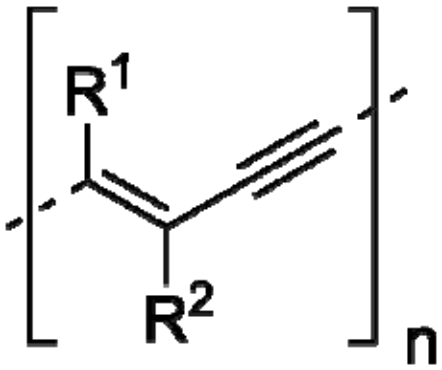
Cons:

- Quantum efficiency < 1 % (ensemble)

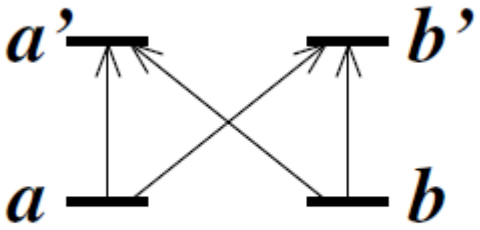
Finding Dark Excitons



***trans*-polyacetylene**

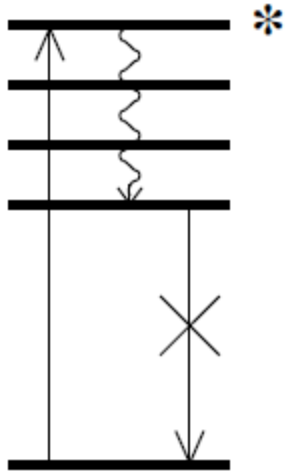


polydiacetylene



one-particle picture

e-e



Theoretical Predictions of Dark Excitons

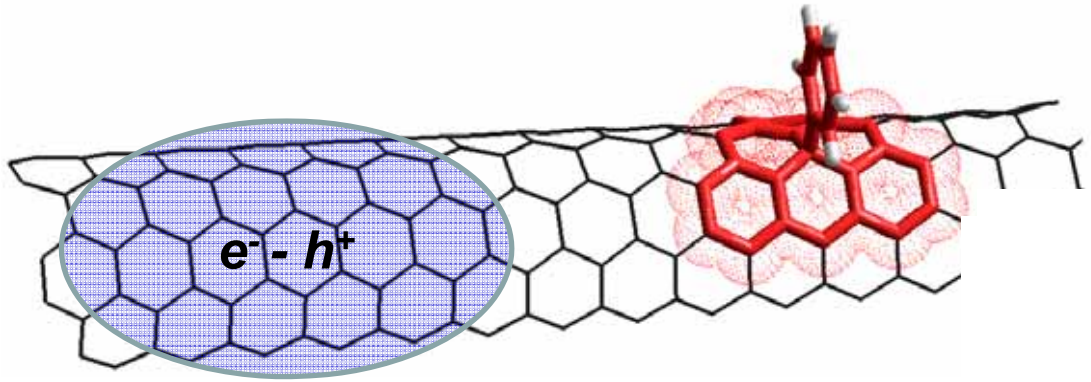
Zhao, Mazumdar. *PRL* 2004

Ando, *J Phys. Soc. Jpn.* 2007

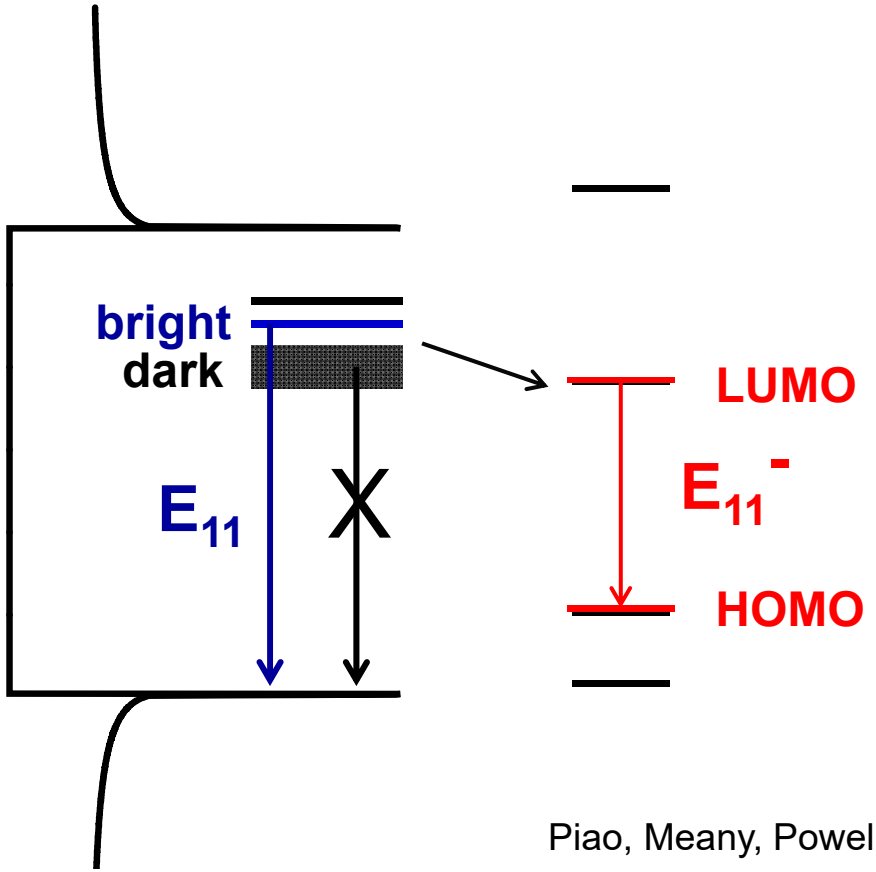
Louis et al. *PRL* 2005; Phys. Rev. B 2006

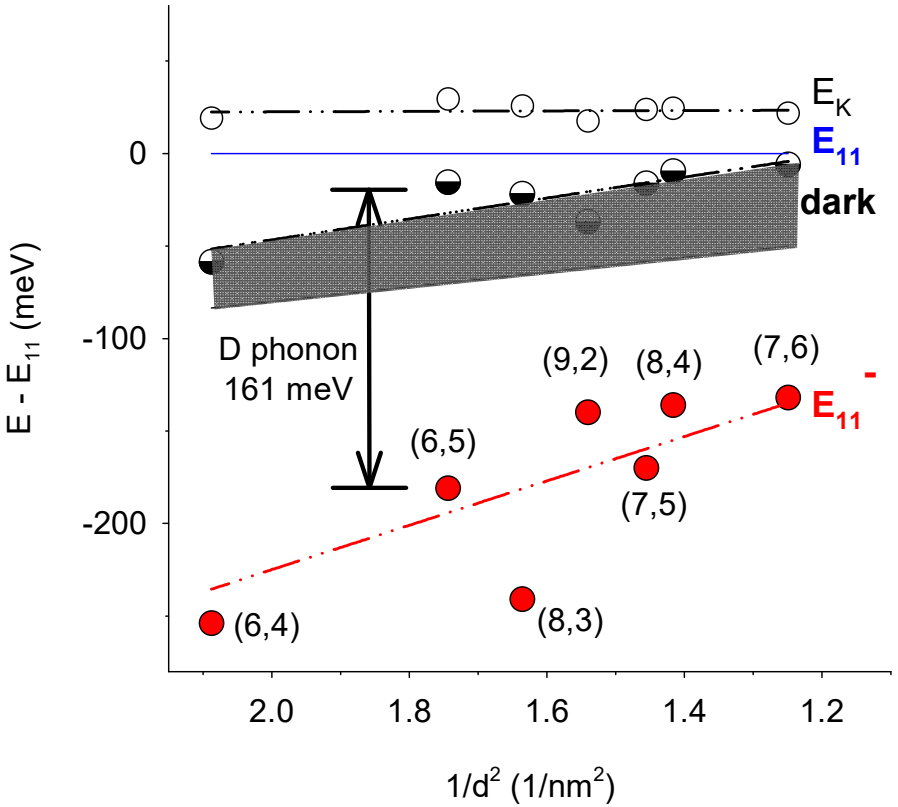
also Tretiak et al. *NL* 2012

Harnessing Dark Excitons



Yanmei Piao

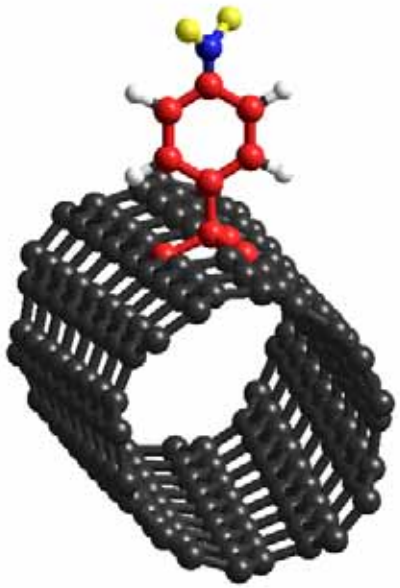




Piao, Meany, Powell, Valley, Kwon, Schatz, Wang*. *Nature Chemistry* (2013).

Small Window of Reactions

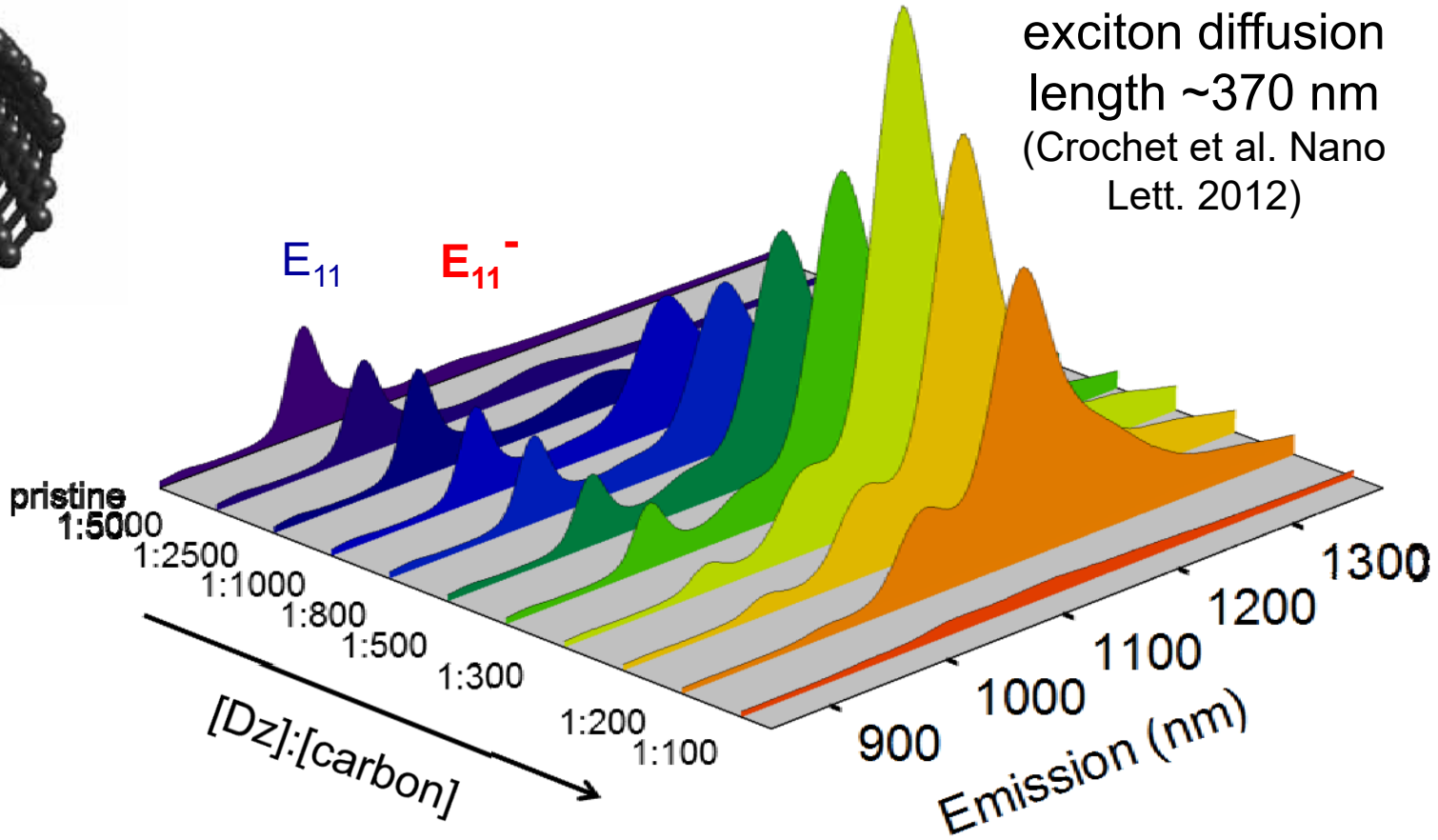
why unnoticed for more than a decade?



(6,5)-$C_6H_4NO_2$

1 functional group
per 20 nm length of SWCNT
on average

vs.
exciton diffusion
length ~370 nm
(Crochet et al. Nano
Lett. 2012)



CARBON NANOTUBES

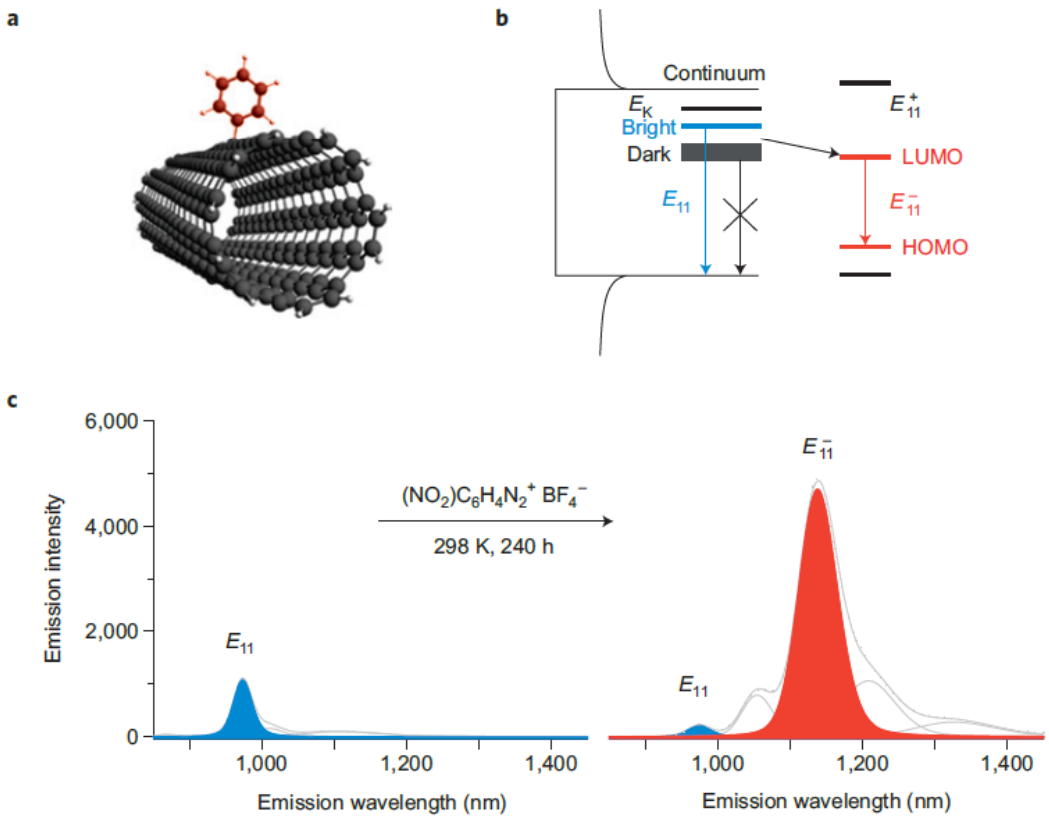
A bright future for defects

Covalently bonding groups to the walls of carbon nanotubes has been previously observed to quench their photoluminescence. Now, it has been shown that, if you get the chemistry just right, their photoluminescence can in fact be significantly brightened by introducing defects through functionalization.

Qing Hua Wang and Michael S. Strano

In crystalline materials such as metals and semiconductors, it is the defects rather than the perfect lattice structure that lead to the most interesting and useful properties. For example, line dislocations in metals allow them to be malleable by moving and sliding under mechanical stress; adding impurities to them can result in alloys with superior strength and corrosion resistance; and substituting lattice atoms with dopants in semiconductors allows the Fermi level to be precisely tuned for making transistors. In all of these examples, the careful incorporation of defects imparts very useful properties to crystalline materials[1]. It now turns out that adding a controlled concentration of defects can also have benefits for carbon nanotubes, which are cylindrical lattices of carbon atoms. Writing in *Nature Chemistry*, Wang and co-workers[2] describe an unexpected new effect by which defects in carbon nanotubes dramatically increase the intensity of their photoluminescence.

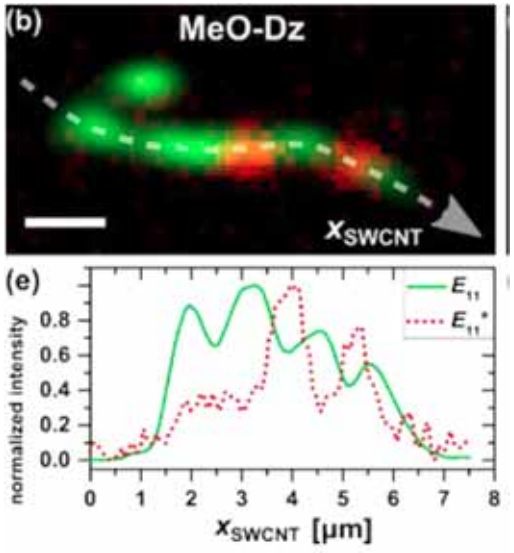
Single-walled carbon nanotubes



Wang, Q.-H.; Strano, M. S. *Nature Chemistry* **2013**, *5*, 812-813.

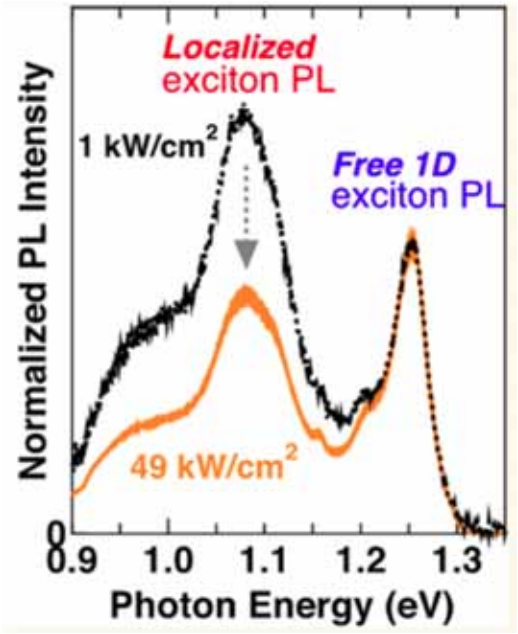
“A bright future for defects”? Indeed.

Exciton Localization



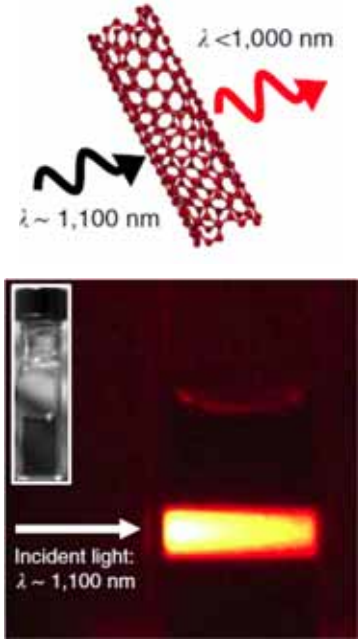
Doorn et al.
Nanoscale **2015**

Non-linear Effect



Matsuda et al.
ACS Nano **2014**

Near-infrared Up-conversion



Miyauchi et al.
Nature Communications
2015

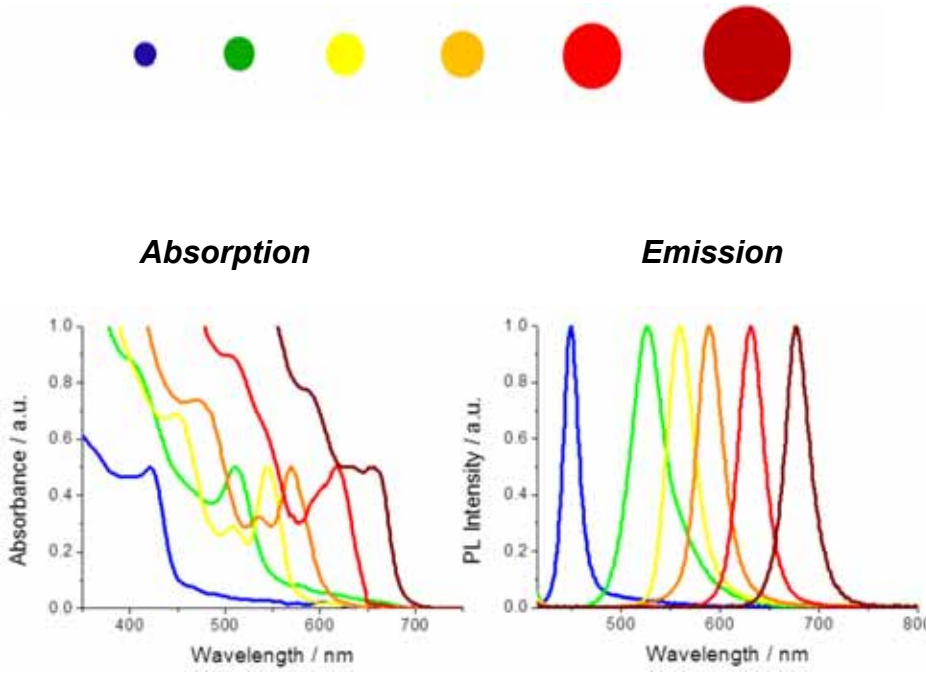
Coming soon:
fluorescent lifetime,
hyperspectral imaging, …

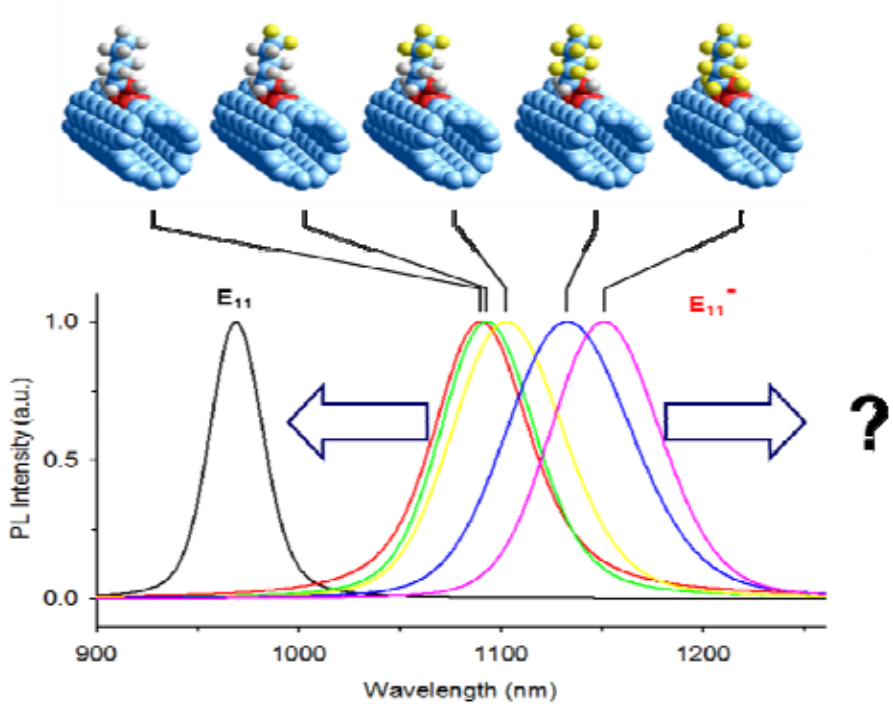
Also – 2D materials

Molecularly Tunable Quantum Emitters?

Quantum Dots ← *Size Engineering*

SWCNTs ← *Surface Engineering*

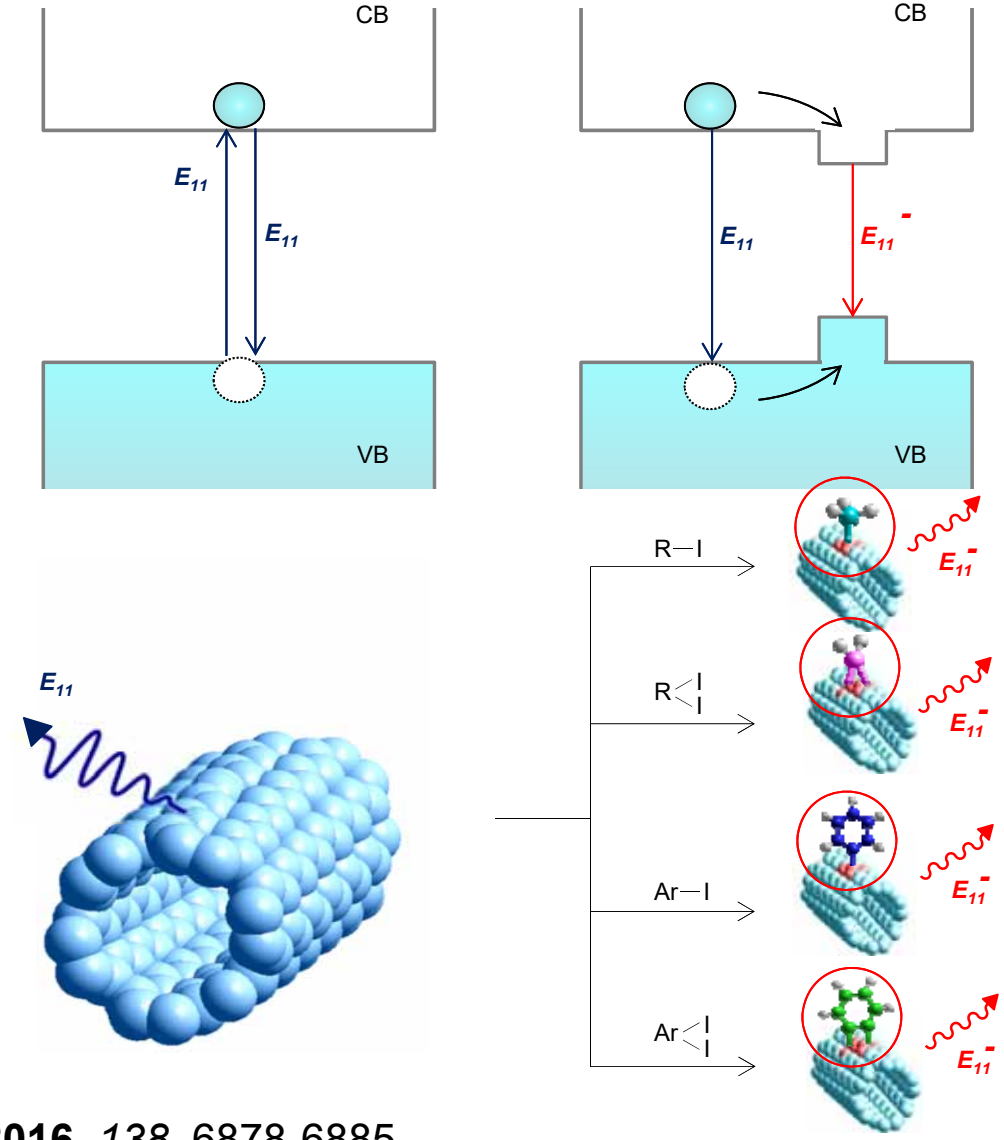


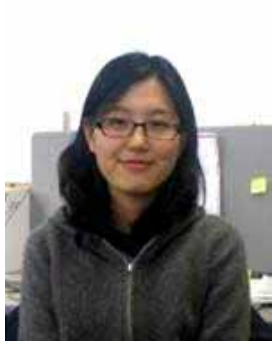


Yuan *et al. Polymers* **2012**, *4*, 1.

Can we chemically create a series of new quantum emitters from a single CNT crystal by varying the surface functional group?

A New Chemistry That Directly Tailors Excitons

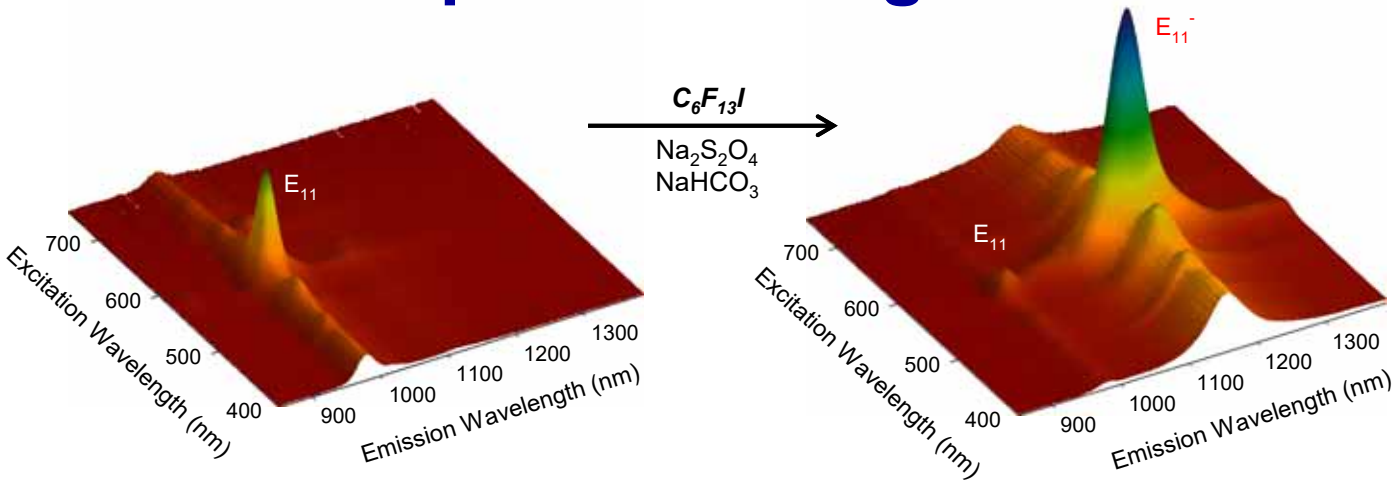


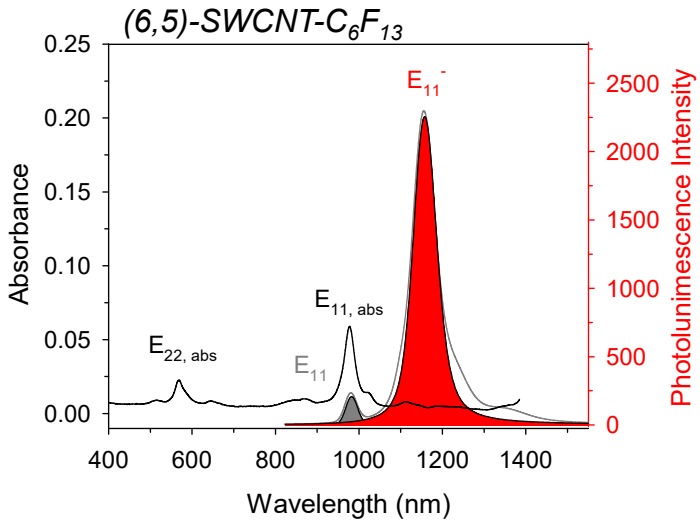


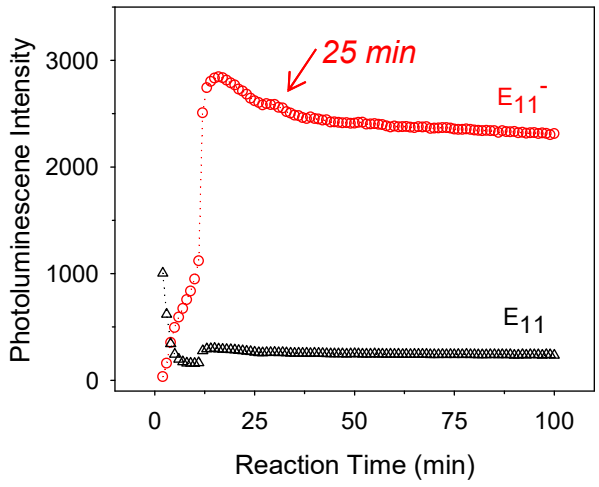
Hyejin Kwon

Kwon *et al. JACS* **2016**, *138*, 6878-6885.

Fast Development of Bright Defect PL



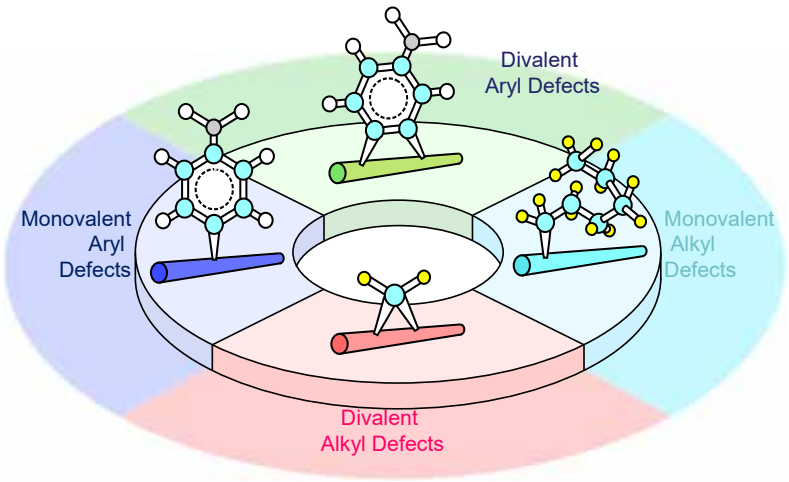


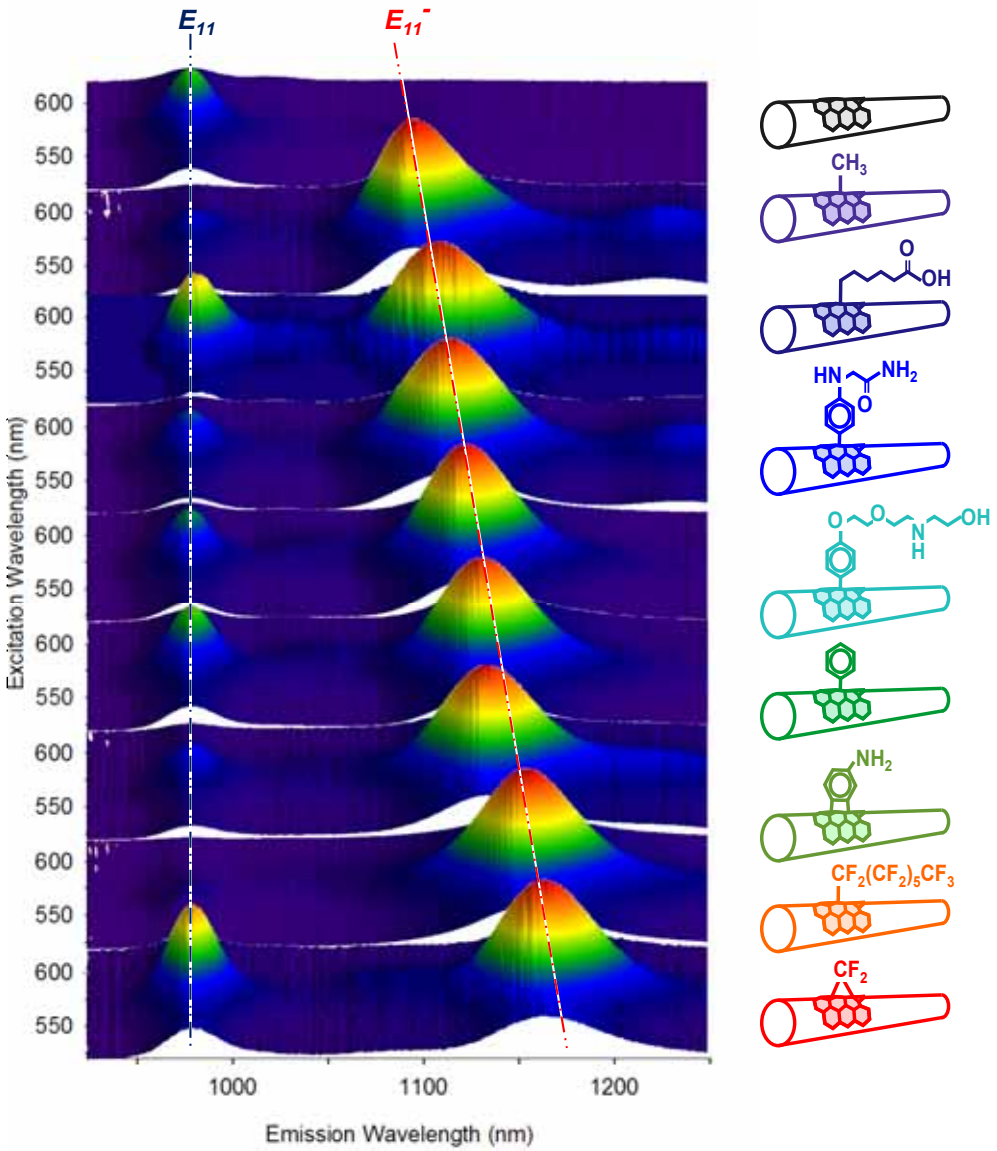


The reaction is 600 times faster and the induced defect PL is 1.25 times brighter than the brightest enabled by diazonium reactions.

Kwon *et al. JACS* **2016**, *138*, 6878-6885.

Molecularly Tunable Quantum Emitters





- **Versatile groups**
  - Valency controlled: mono/divalent
  - Series of alkyl and aryl groups
  - Terminal moiety (e.g. -COOH, -NH_2, and -OH)
  - Tunable defect PL (64 meV in NIR II, two times larger tunability than the diazonium method)

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Inductive Effect on Alkyl Quantum Defects

(6,5)-SWCNT-**R**	E_{11} (nm)	E_{11} fwhm (meV)	E_{11}^- (nm)	E_{11}^- fwhm (meV)	Δ E (meV)	σ^* (calc)
Non-functionalized	979	37	-	-	0	-
$-CH_2CH_2CH_2CH_2CH_2CH_3$	981	45	1096	56	133	-0.774
$-CH_2CH_2CH_2CH_2CH_2CF_3$	980	45	1099	56	137	-0.462
$-CH_2CH_2CH_2CH_2CF_2CF_3$	980	38	1107	59	146	-0.127
$-CH_2CH_2CF_2CF_2CF_2CF_3$	983	40	1137	76	170	1.086
$-CF_2CF_2CF_2CF_2CF_2CF_3$	981	42	1155	69	190	4.867
$-CH_2CH_2CH_2CH_2CH_2CF_3$	980	45	1099	56	137	-0.462
$-CH_2CH_2CH_2CH_2CF_3$	979	40	1104	59	143	-0.287
$-CH_2CH_2CH_2CF_3$	980	42	1101	55	140	-0.034
$-CH_2CH_2CF_3$	980	42	1110	59	147	0.310
$-CH_2CF_3$	982	42	1114	67	150	1.244
$-CF_3$	980	45	1158	63	194	3.961

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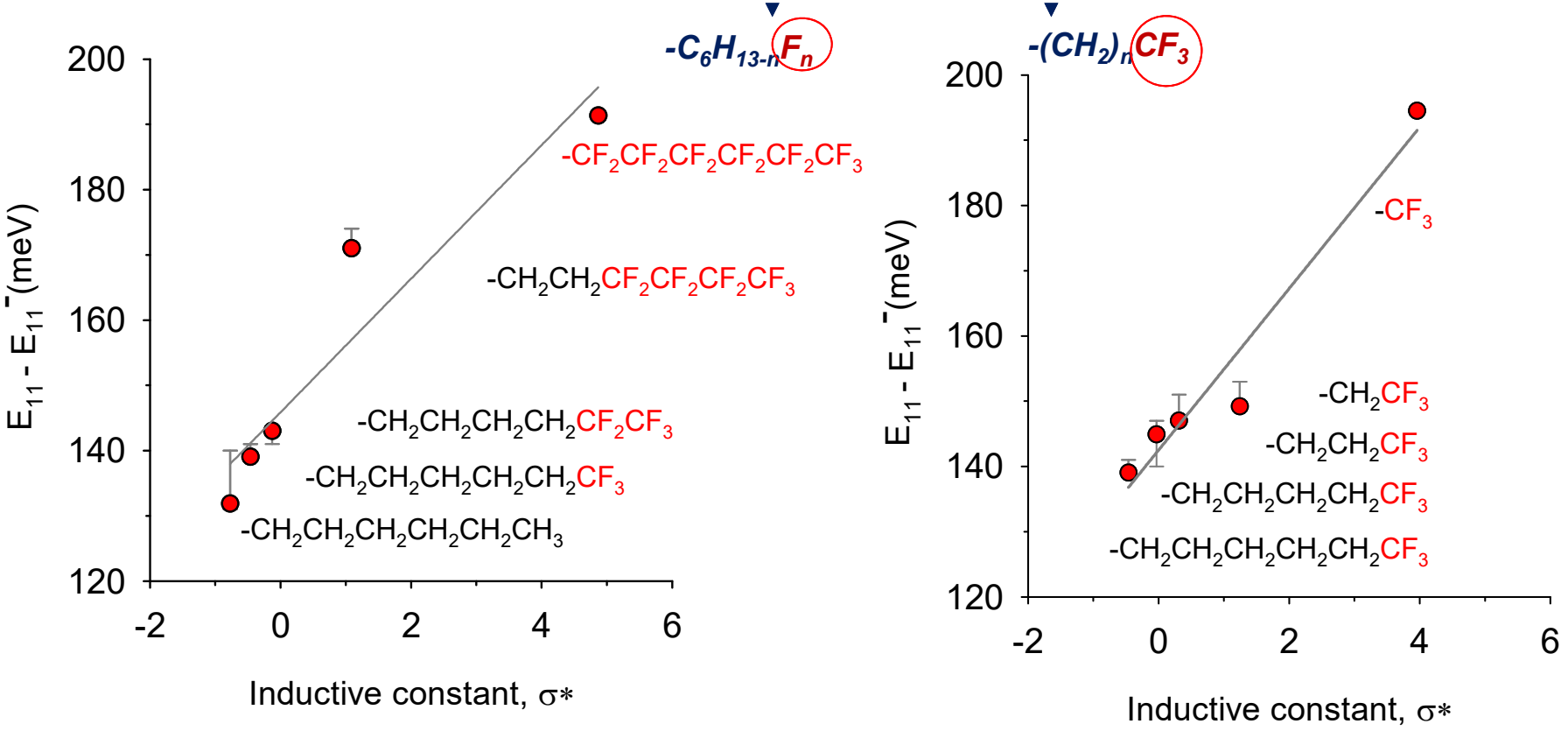
Inductive Effect on Alkyl Quantum Defects

$$\sigma^* = 7.840 \sum_i \Delta\chi_i R_i^2 / r_i^2$$

Electronegativity

Distance between A and B



Tunability originates from strong electronic couplings between excitons and alkyl defects.

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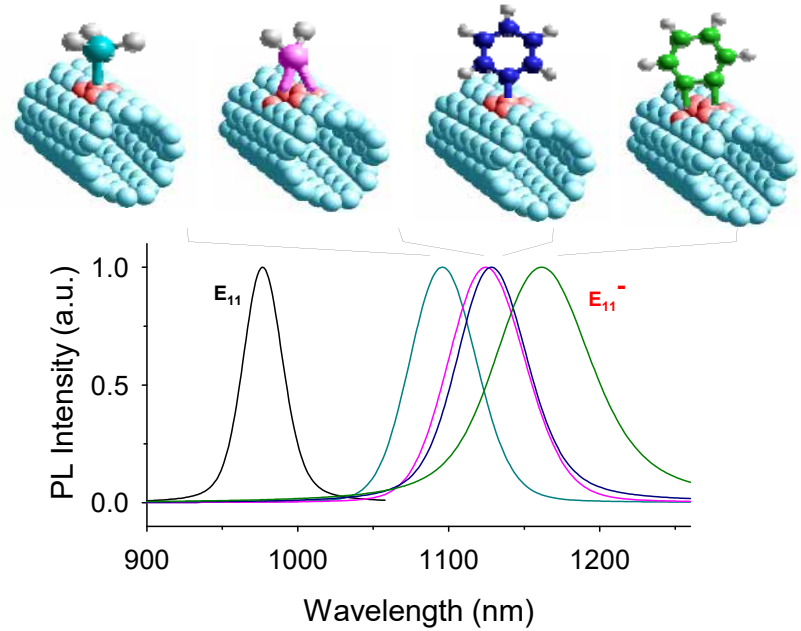
Valency Controlled Quantum Defects



	monovalent					divalent		
(6,5)-SWCNT-**R**	E_{11} (nm)	E_{11}^- (nm)	Δ E (meV)	(6,5)-SWCNT-**R**	E_{11} (nm)	E_{11}^- (nm)	Δ E (meV)
$-CH_3$	980	1094	**132**	$>CH_2$	980	1125	**163**
$-CF_3$	980	1158	**194**	$>CF_2$	980	1164	**200**
$-C_6H_5$	979	1129	**168**	$>C_6H_4$	986	1162	**190**
$-C_6H_4NH_2$	980	1121	**159**	$>C_6H_3NH_2$	980	1133	**171**

Can we control the local atomic configurations of quantum defects?

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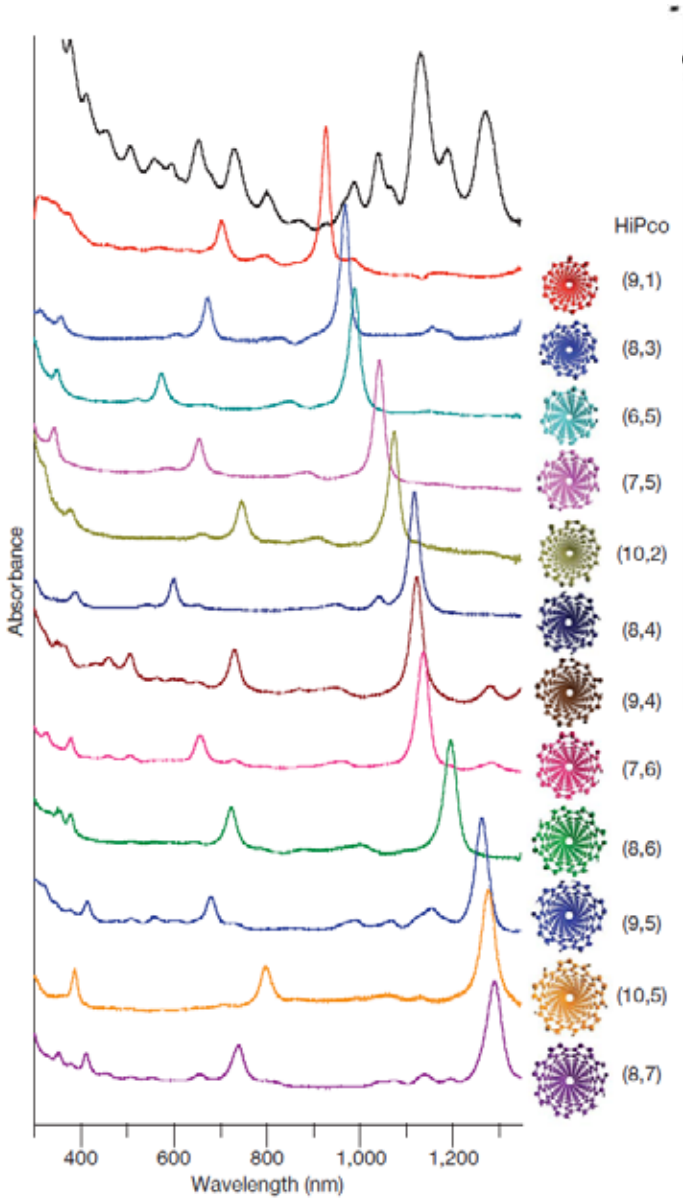
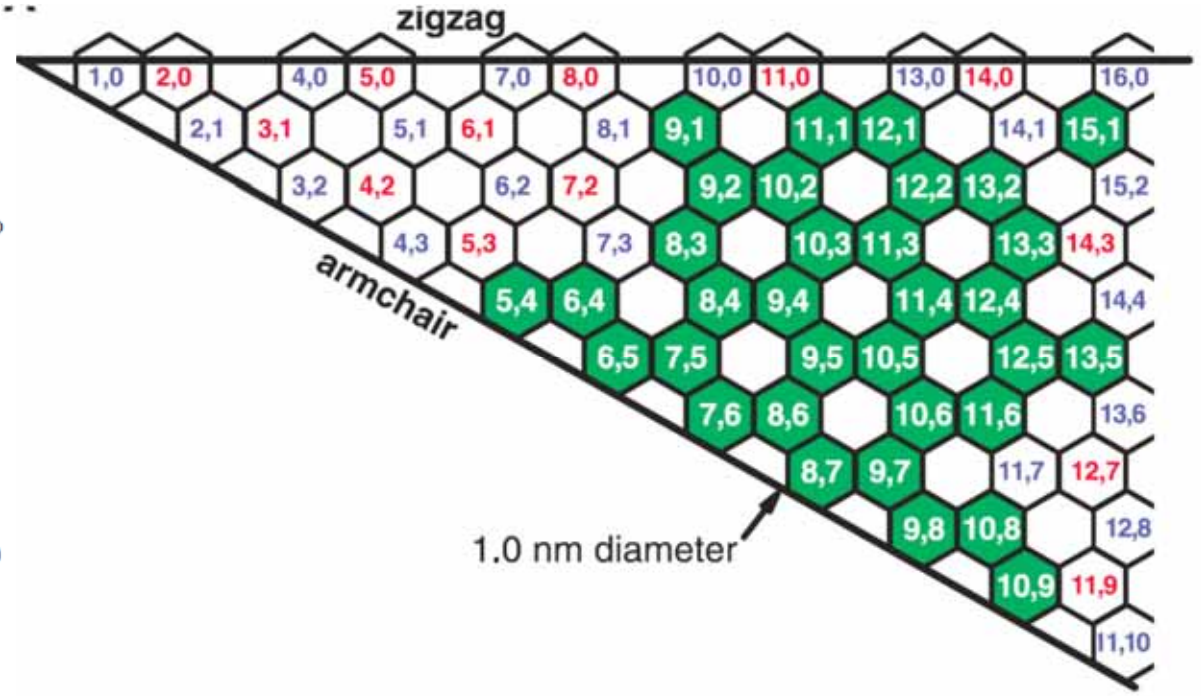
Conclusions: Part I

- Covalent incorporation of sp^3 defects into the sp^2 lattice of semiconducting carbon nanotubes creates fluorescent quantum defects. Emission from exciton trapped in these defects is significantly brighter, molecularly specific and features substantial vibrational reorganization.
- Molecularly tunable fluorescent quantum defects can be created in semiconducting carbon nanotubes through covalently bonded surface functional groups that are themselves non-emitting.
- By varying the surface functional groups, the same carbon nanotube crystal can be chemically converted to create more than 50 distinct quantum emitters with unique near-infrared photoluminescence.
- Our new ability to control nanostructure excitons through surface functional groups opens up exciting possibilities for post-synthesis chemical engineering of carbon nanomaterials.

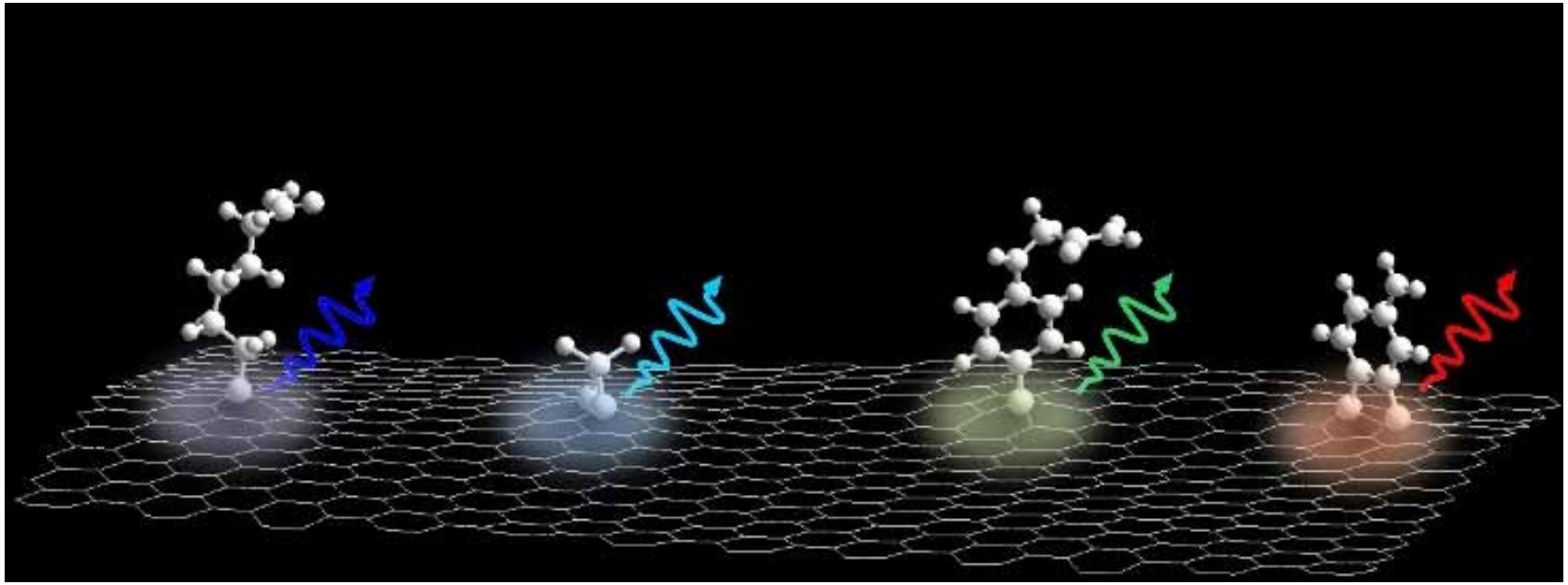
The Nanotube Chirality

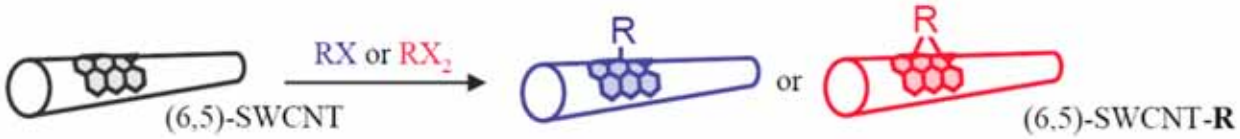


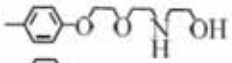
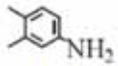
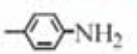
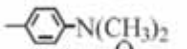
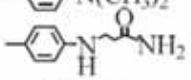


Bachilo et al. *Science* **2002**, *298*, 2361.
Zheng et al. *Nature* **2009**, *460*, 250.
Image courtesy of Mark Hersam

Fluorescent Quantum Defects:
A New Molecular Dimension?

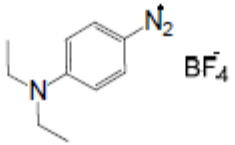
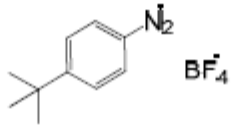
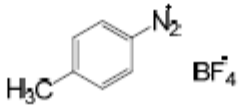
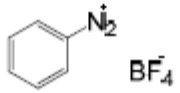
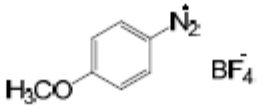
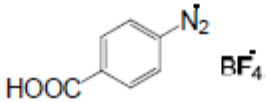
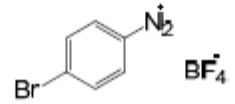
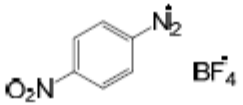
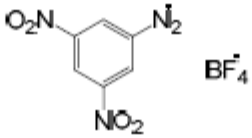




(6,5)-SWCNT-**R**	E_{11} (nm)	E_{11}^{-} (nm)	ΔE (meV)	Source of Precursor
Non -functionalized	979	-	-	-
$-CH_3$	980	1094	132	
$-CH_2CH_2CH_2CH_3$	984	1099	132	
$-CH_2CH_2CH_2CH_2CH_2CH_3$	981	1096	133	
$-CH_2CH_2CH_2CH_2CH_2CH_3$	980	1097	135	
$-CH_2CH_2CH_2CH_2CH_2CF_3$	980	1099	137	
$-CH_2CH_2CH_2CH_2CH_2COOH$	980	1102	140	
$-CH_2CH_2CH_2CF_3$	981	1101	140	
$-CH_2CH_2CH_2CH_2CF_3$	979	1104	143	$-CH_2CH_2CF_2CF_2CF_2CF_3$
$-CH_2CH_2CF_3$	981	1110	147	$-CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$
$-CH_2CH_2CH_2CH_2CF_2CF_3$	980	1107	146	$-CHF_3$
$-CH_2CF_3$	982	1114	150	
$-CH_2CF_2CF_2CF_3$	980	1114	152	$-CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3$
	980	1121	159	
	984	1127	160	$-CF_2CF_2CF_2CF_2CF_2CF_3$
	979	1121	160	$-CF_2CF_2CF_2CF_3$
$>CH_2$ (^{12}C)	979	1125	164	$-CF_3$
$>CH_2$ (^{13}C)	980	1125	163	$>CF_2$

979	1125	164	
979	1129	168	
980	1131	169	
980	1133	171	
983	1137	170	
983	1139	173	
979	1138	177	
980	1145	182	
979	1152	190	
986	1162	190	
981	1155	190	
979	1155	193	
980	1158	194	
980	1164	200	

Supplementary Table S1. Organic diazonium salts used in this study and their FT-IR and ^{1}H-NMR signatures.

Name	Abbreviation by Substituent Group	Molecular Structure	Chemical Shifts (ppm)[a]	Characteristic IR Features (cm^{-1})[b]	Source
4-diazo-N,N-diethylaniline tetrafluoroborate	$N(CH_2CH_3)_2$-Dz		δ 7.45 (ABq, *J* = 8.8 Hz, Δν = 419.2 Hz, 4H), 1.24 (t, *J* = 7.2 Hz, 6H), 3.60 (q, *J* = 7.2 Hz, 4H)	3122, 3084, 2980, 2940, 2135, 1579	MP Biomedicals
4-tert-butylbenzenediazonium tetrafluoroborate	$C(CH_3)_3$-Dz		δ 8.17 (ABq, *J* = 8.8 Hz, Δν = 176.8 Hz, 4H), 1.38 (s, 9H)	3106, 2972, 2903, 2275, 1574	Synthesized
4-methylbenzenediazonium tetrafluoroborate	CH_3-Dz		δ 8.55 (ABq, *J* = 8.8 Hz, Δν = 254.4 Hz, 4H), 2.64 (s, 3H)	3112, 3039, 2287, 1581	Synthesized
benzenediazonium tetrafluoroborate	H-Dz		δ 8.50 (d, J = 8.8 Hz, 2H), 8.34 – 8.25 (m, 1H), 7.97 (dt, J = 8.0 Hz, 2H)	3107, 3018, 2295, 1570	Synthesized
4-methoxybenzenediazonium tetrafluoroborate	OCH_3-Dz		δ 8.40 (dd, J = 9.4, 9.5 Hz, 2H), 7.34 (dd, J = 9.4, 9.5 Hz, 2H), 4.06 (s, 3H)	3122, 3106, 2250, 1583, 1572	Sigma Aldrich, 98%
4-carboxybenzenediazonium tetrafluoroborate	COOH-Dz		δ 8.49 (ABq, *J* = 9.0 Hz, Δν = 67.2 Hz, 4H)	3279, 3113, 3042, 2302, 1729, 1581	Synthesized
4-bromobenzenediazonium tetrafluoroborate	Br-Dz		δ 8.22 (ABq, *J* = 9.1 Hz, Δν = 98.4 Hz, 4H)	3106, 3092, 2286, 1554	Sigma Aldrich, 96%
4-nitrobenzenediazonium tetrafluoroborate	NO_2-Dz		δ 8.68 (ABq, *J* = 9.2 Hz, Δν = 58.5 Hz, 4H)	3104, 3023, 2306, 1614, 1537	Synthesized
3,5-dinitrobenzenediazonium tetrafluoroborate	3,5-(NO_2)-Dz		δ 9.78 (s, 1H), 9.69 (s, 2H)	3075, 3042, 2316, 1548	Synthesized

[a] CD_3CN was used as the solvent, [b] Monitored from 4000-400 cm^{-1}; the frequencies shown indicate O-H stretch (3279 cm^{-1}), sp^2 (3023~3122 cm^{-1}), sp^2-CH stretch (2903~2980 cm^{-1}), N≡N stretch (diazonium bond, 2135~2316 cm^{-1}), C=O stretch (1614 cm^{-1}) and aromatic C=C bending (1537~1614 cm^{-1}), respectively.

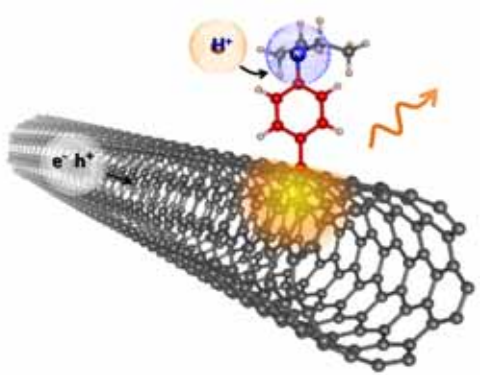
An

(n,m) × molecules = nm^2

opportunity*?*

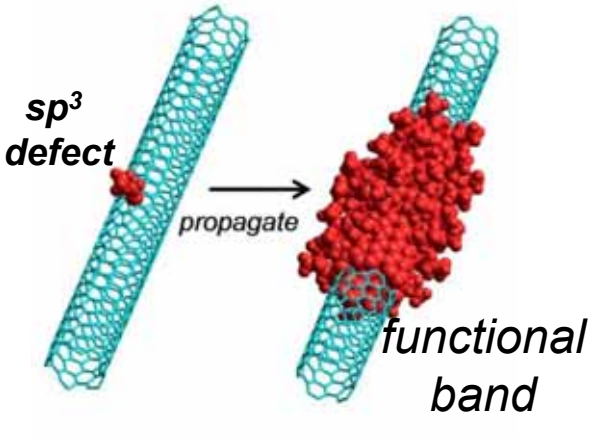
So why is this important? A new toolbox

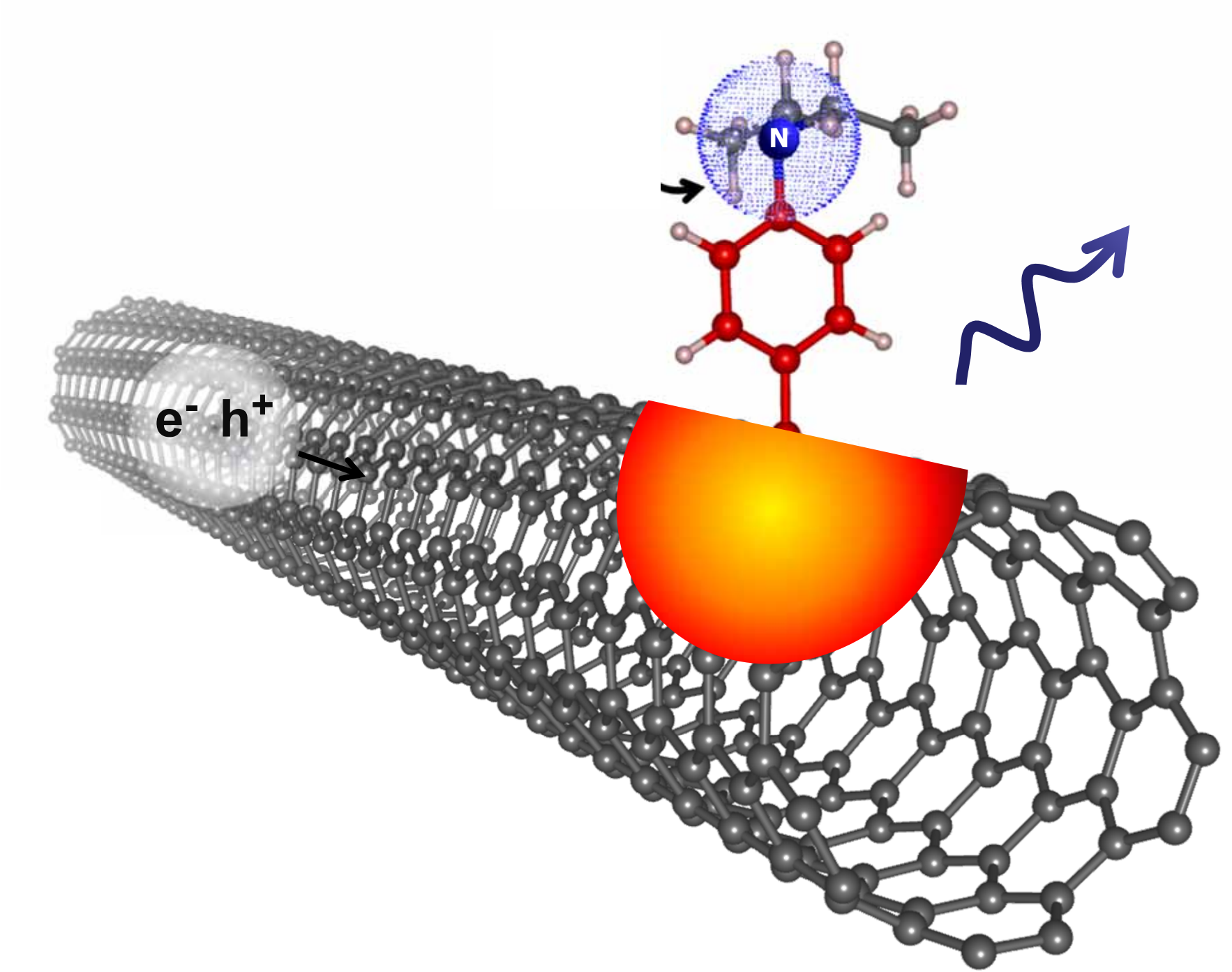
- **Optical Probing of pH and Temperature in Complex Fluids Through Semiconducting Carbon Nanotubes**
  - *Is it possible to probe local chemical events through fluorescent quantum defects?*



- **Probing quasi-particles**
  - *Can we probe fundamental physical phenomena through defect-bound quasi-particles (e.g., excitons and trions)?*

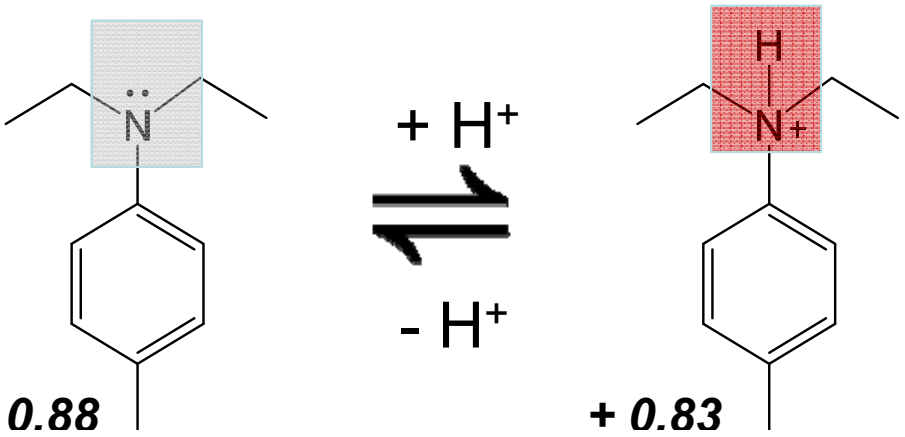
- **Chemical Propagation in an "Electron Sea"**
  - *How can we separate "growth" from "nucleation" in covalent nanochemistry and use that new capability to design functional materials?*



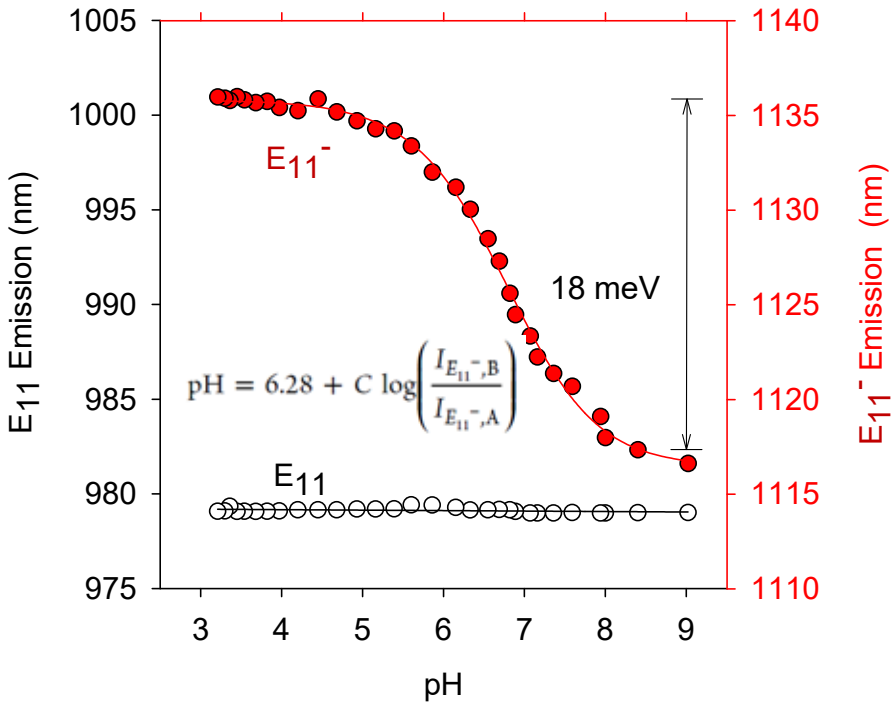

N
e- h+

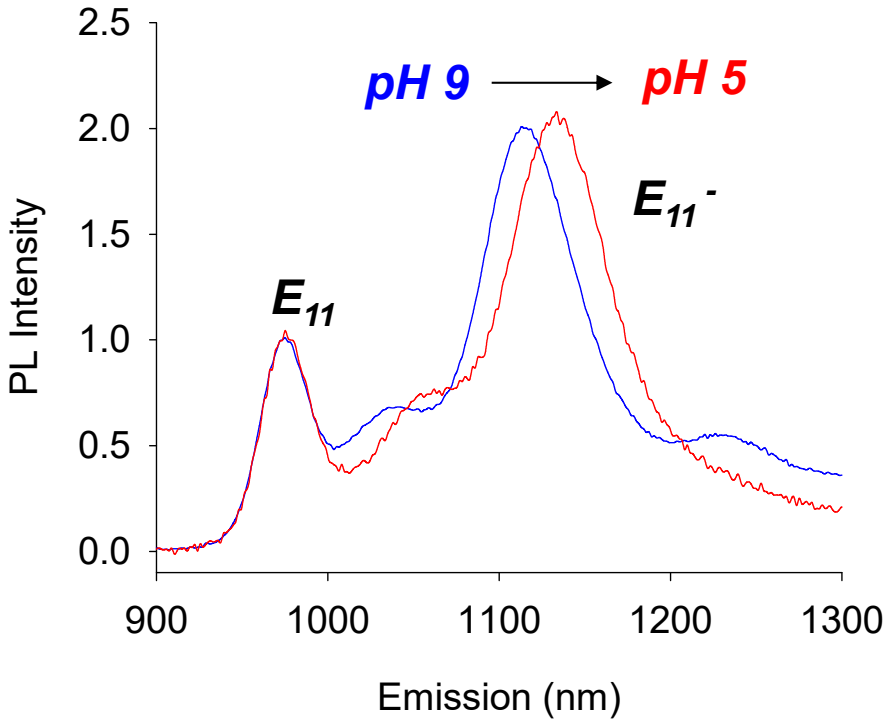
A pH Sensor?

Hyejin Kwon Mijin Kim



J. Phys. Chem. C **2015**, *119*, 3733.





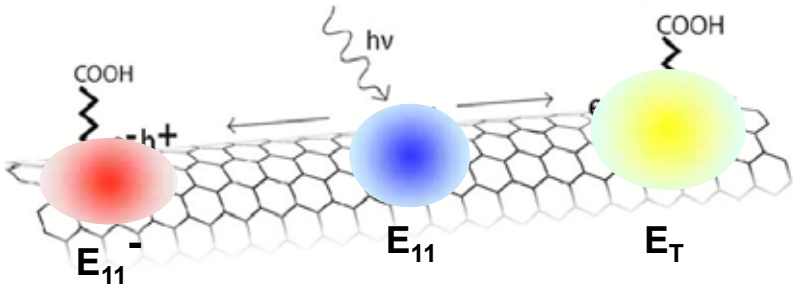
Only aminoaryl defects respond to pH changes

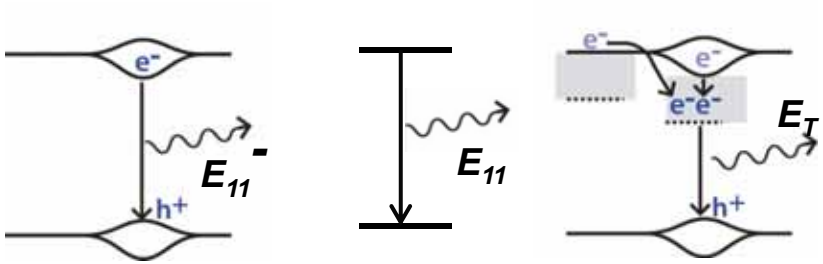
(6,5)-ArX	E_{11} (nm)	E_{11}^{-} (nm)		E_{11}^{-} shift (meV)
		pH 9.0	pH 4.0	
Pristine	971	-	-	-
$-N(CH_2CH_3)_2$	975	1116	1134	18
$-N(CH_3)_2$	975	1116	1134	18
$-OCH_3$	973	1116	1116	0
-COOH	976	1124	1124	0
-Br	973	1125	1125	0
$-NO_2$	973	1137	1137	0
$-3,5-NO_2$	973	1145	1145	0

* due to small difference (0.43) in Hammett constant between the protonated and deprotonated forms of carboxylic acid.

J. Phys. Chem. C **2015**, *119*, 3733.

Trion Photoluminescence: When Exciton Meets Electron

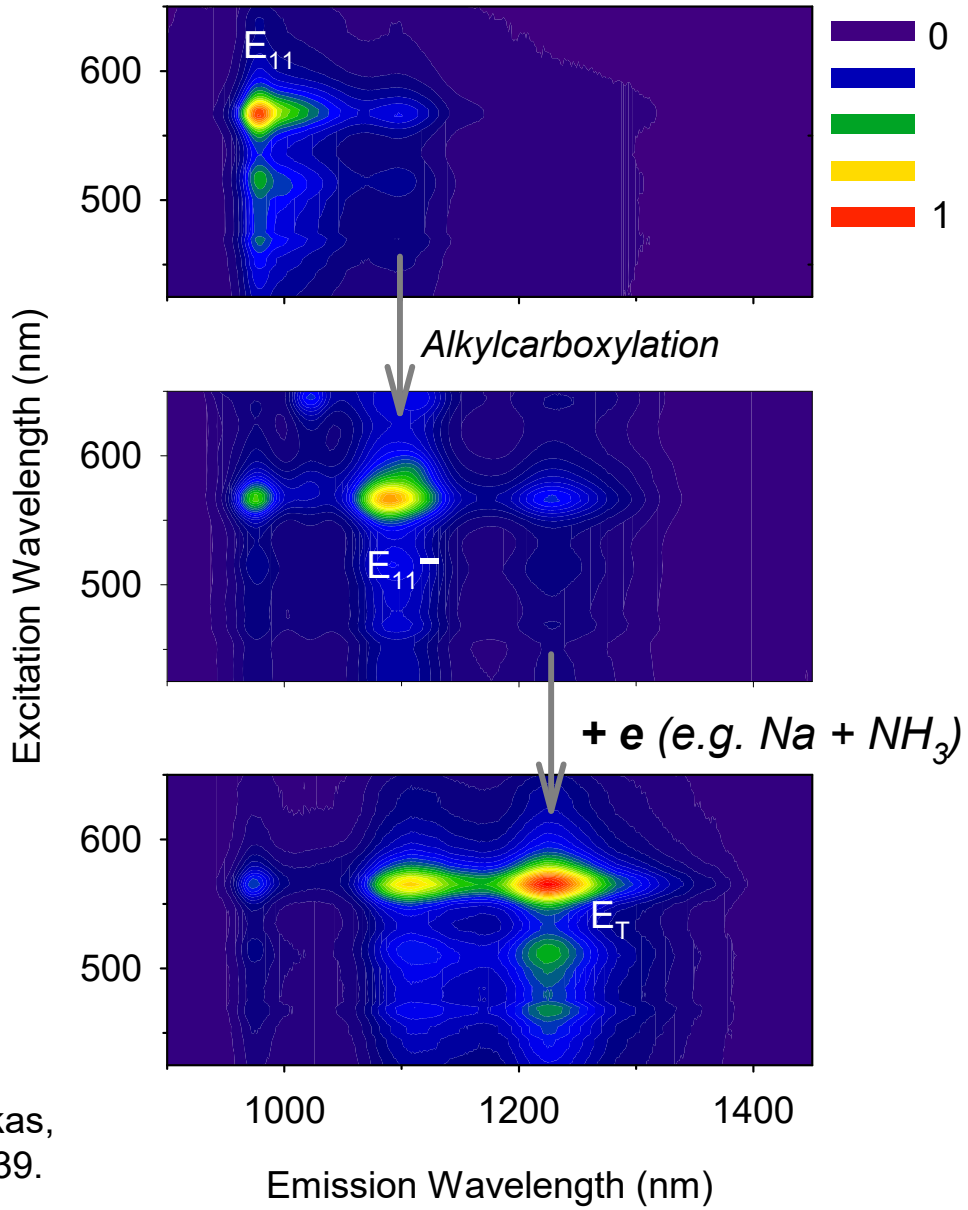




Alex Brozena

- Almost as bright as parent exciton.
- High binding energy (262 meV vs. ~170-190 meV for unbound trions in (6,5) and 1-20 meV in quantum wells and quantum dots).

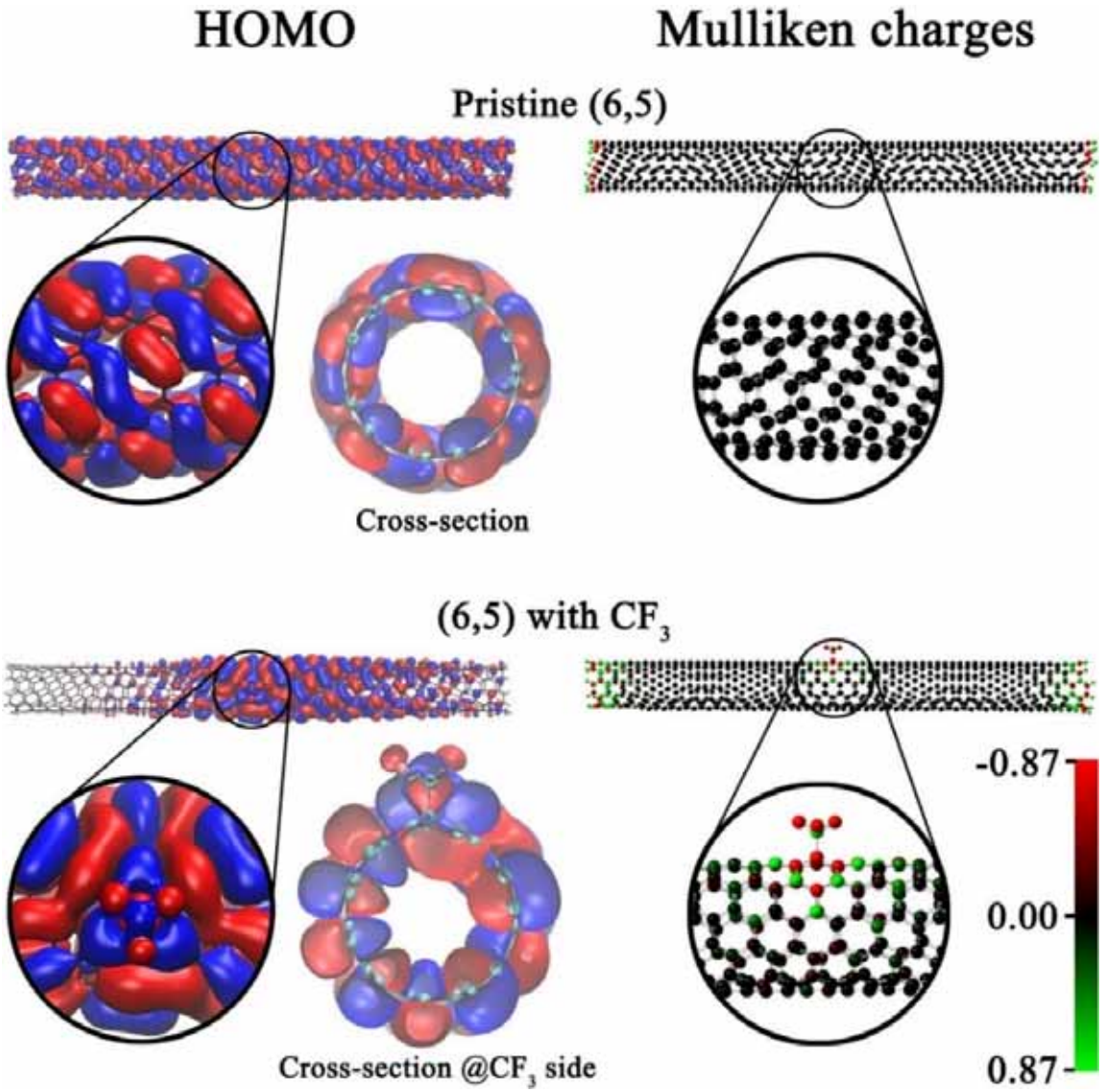
Brozena, Leeds, Zhang, Fourkas, Wang, *ACS Nano* **2014**, *8*, 4239.



Defect-Induced Localization Effects

- DFT: B3LYP/6-31G*
- Charges and frontier orbital wave functions are strongly localized around a defect.
- Excitons respond sensitively to functional defects due to localization?

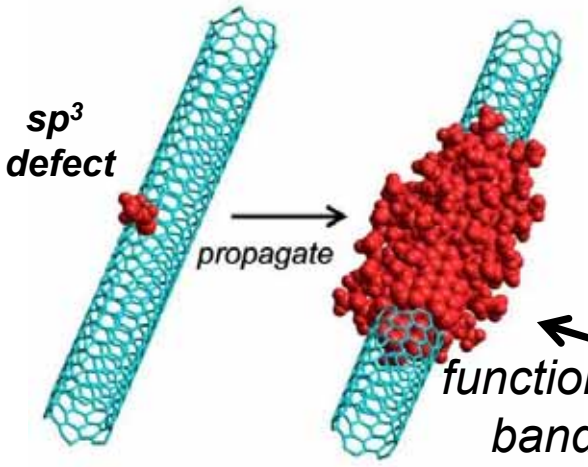
Dr. Al'ona Furmanchuk
(Schatz Group)



Kwon *et al. JACS* **2016**, *138*, 6878-6885.

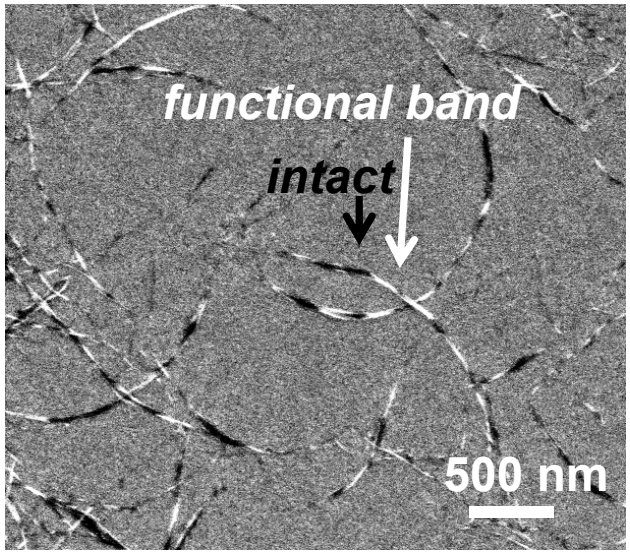
Confined Propagation of Covalent Chemical Reactions on Single-Walled Carbon Nanotubes

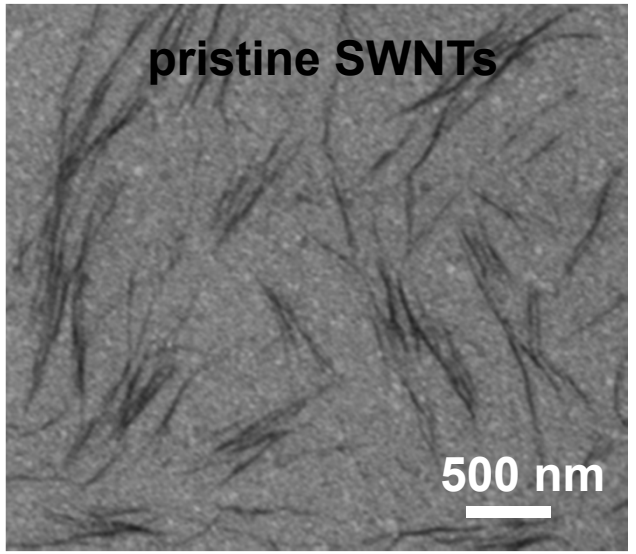
Dr. Shunliu Deng

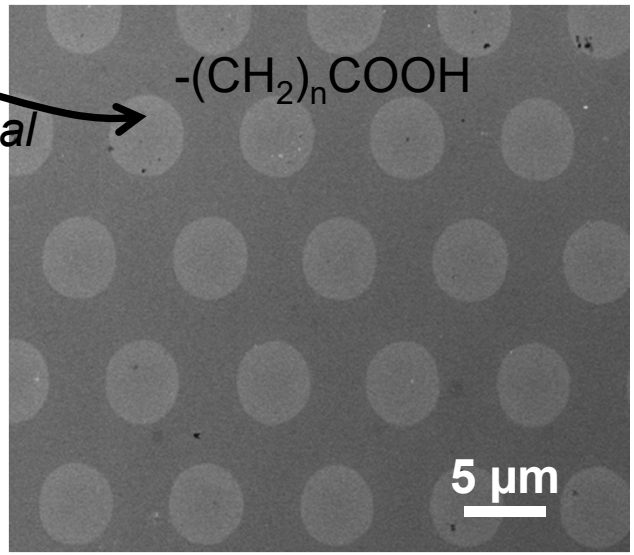


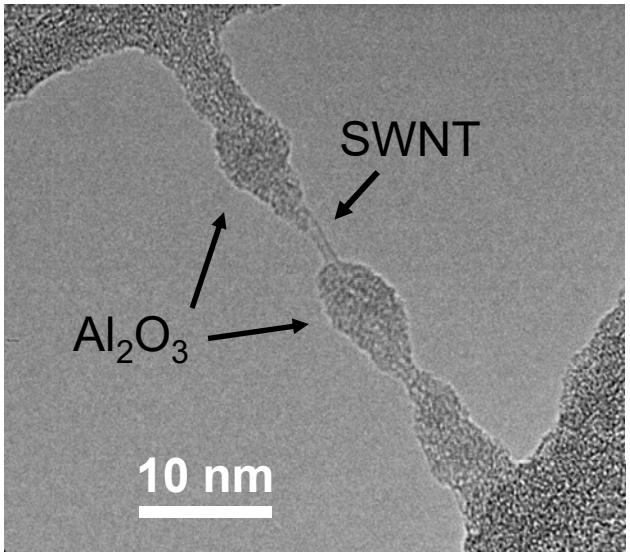
Billups-Birch Reactions:

- Soak nanotubes in solvated electrons (Li/Na in liquid NH_3).
- Add $Br(CH_2)_nCOOH$.
- Repeat.





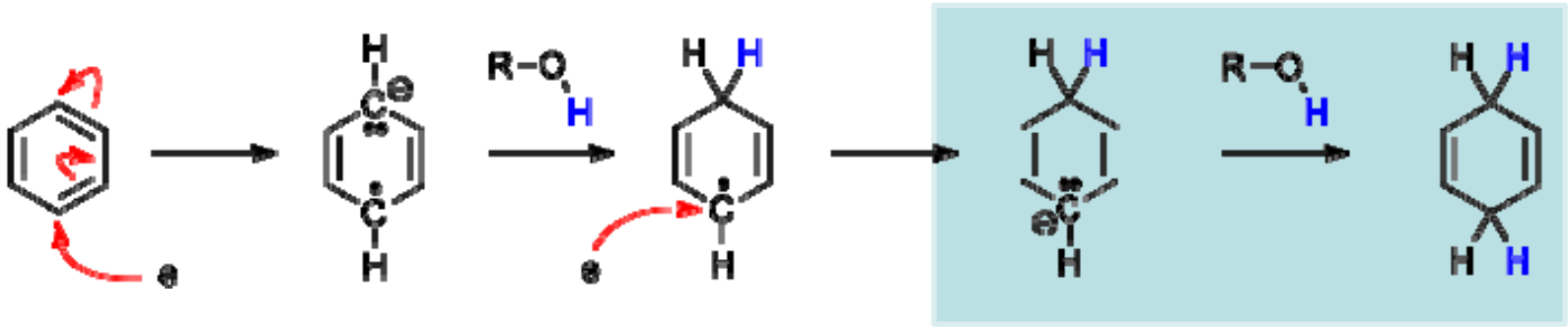




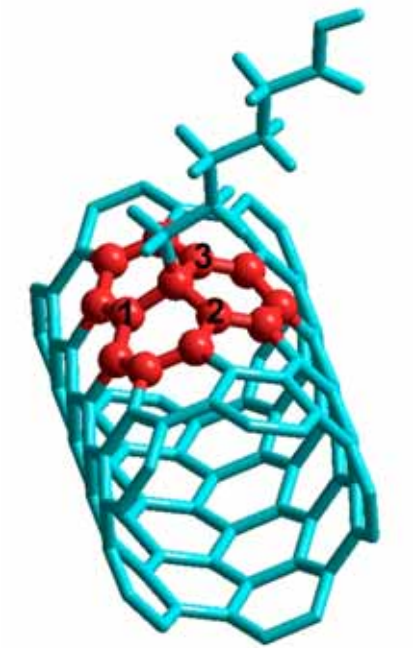
Deng, Zhang, Brozena, Mayes, Banerjee, Chiou, Rubloff, Schatz, Wang*
Nature Communications **2011** 2:382.

Why Does the Reaction Propagate Exclusively from (sp^3) Defects?

Birch Reduction: follow the electron



Localization of electrons around an sp^3 defect



(5,5)-$(CH_2)_5COOH$

Table 1 | Net atomic charges around a sp^3 defect site from Mulliken population analysis of a SWNT with a covalently bonded $-(CH_2)_5COOH$ group.

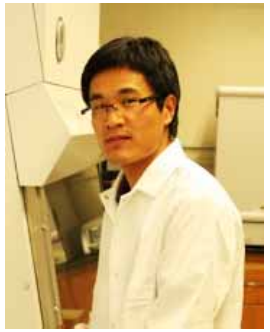
	Neutral	−1 Charge	−2 Charge
(5,5)-$(CH_2)_5COOH$			
Defect site	0.12	0.13	0.13
C1	−0.04	−0.07	−0.08
C2	−0.02	−0.05	−0.06
C3	−0.02	−0.05	−0.06
(10,0)-$(CH_2)_5COOH$			
Defect site	0.12	0.13	0.13
C1	−0.04	−0.06	−0.07
C2	−0.01	−0.02	−0.02
C3	−0.04	−0.06	−0.07

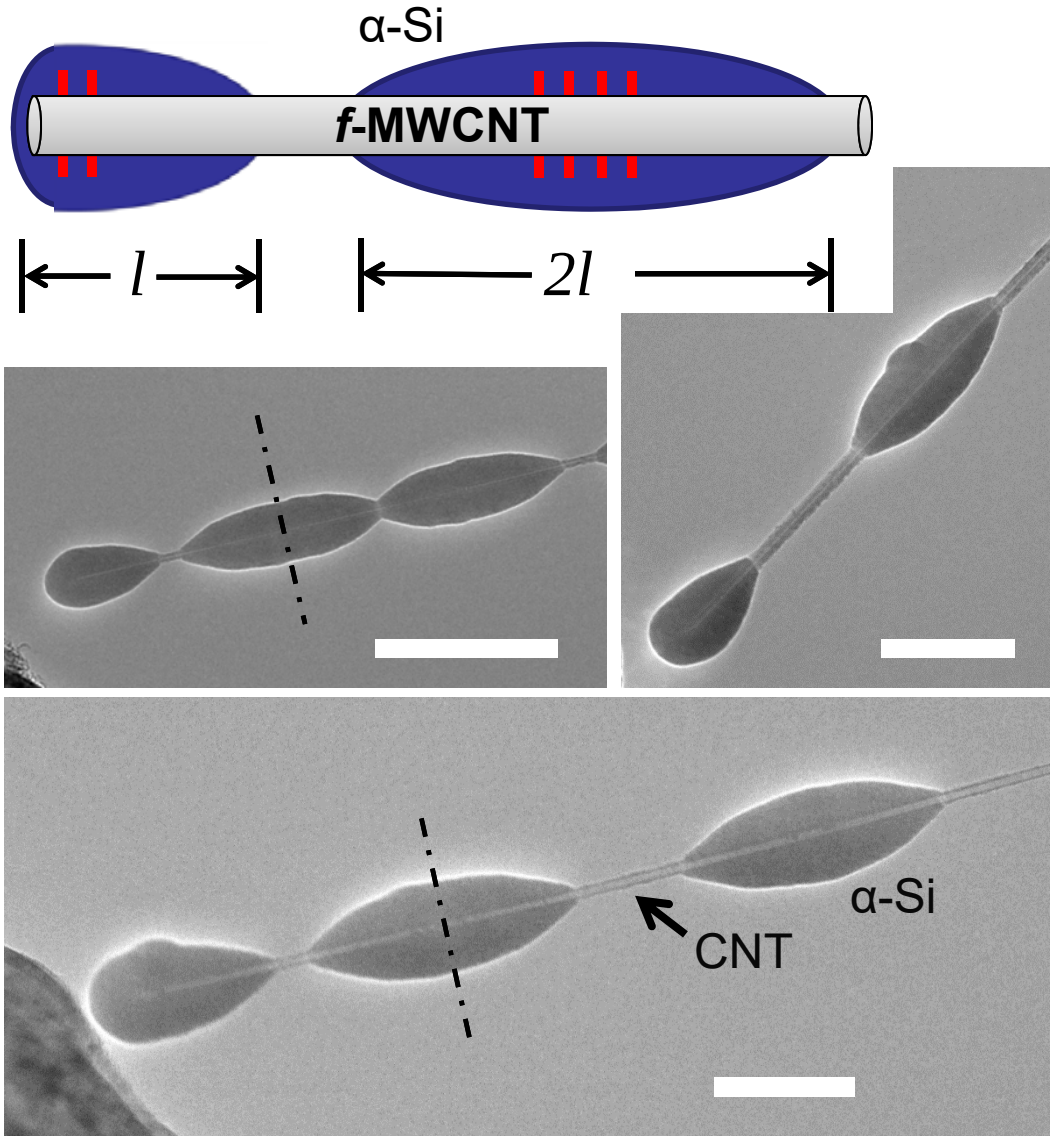
Carbon atoms not listed have a charge close to zero, being as high as −0.01 e, and −0.02 e charges for neutral, −1 and −2 charged carbon nanotubes. For the complete set of atomic charges, see Supplementary Tables.

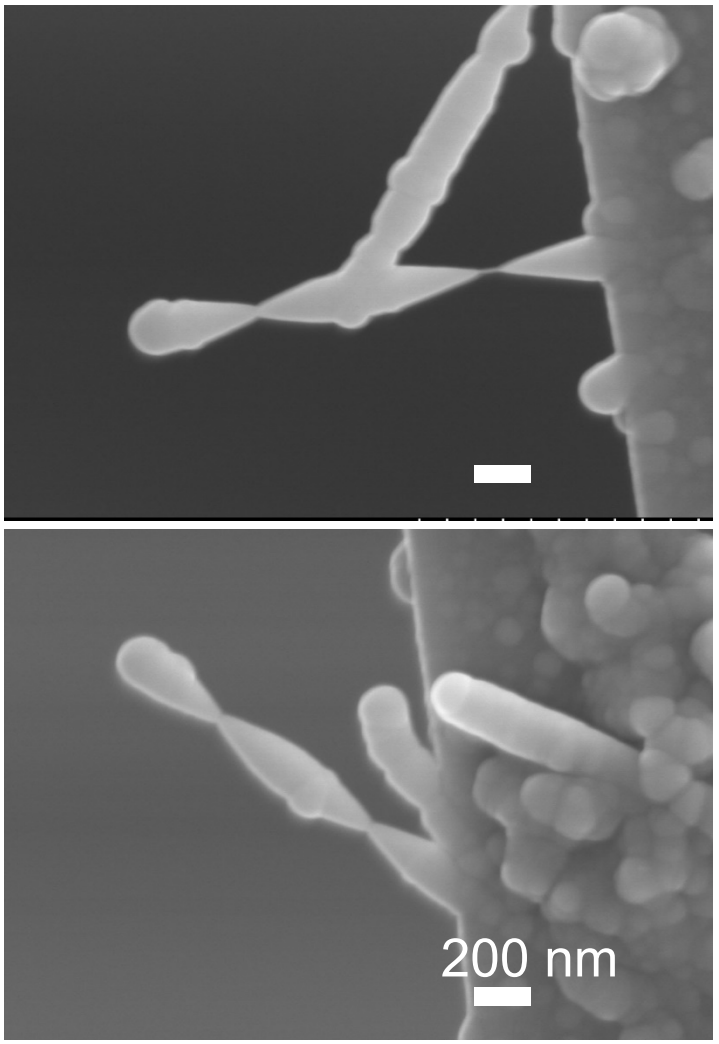
Mulliken Population Analysis

Maricris Mayes
George Schatz

Silicon Beads on a String



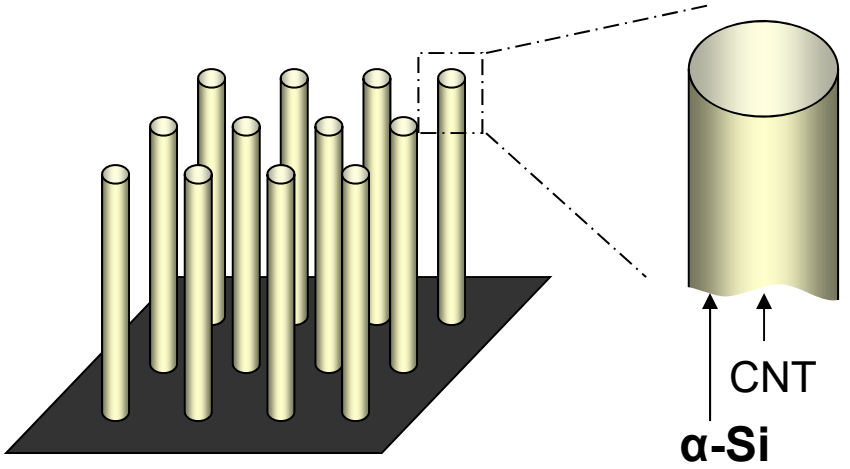




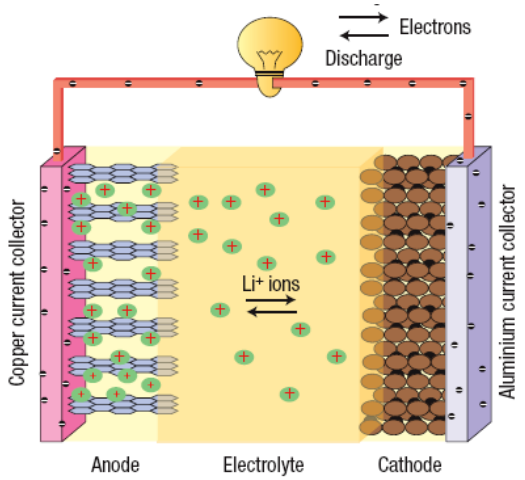
Sun, et al. *ACS Nano*, **2013**, *7*, 2717-2724.

Why Si-C?

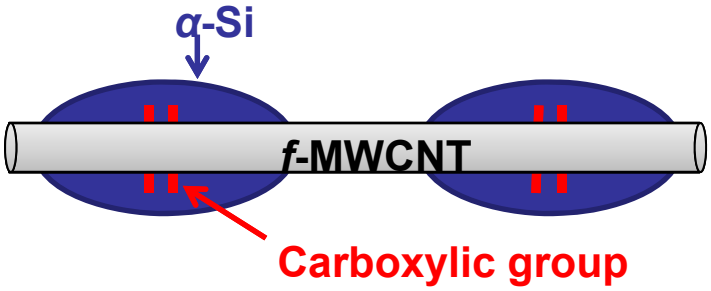
- α-Si maximizes Li^+ storage capacity.
- CNT core improves structural stability and electrical conductivity?
- Core-shell structure shortens Li^+ diffusion paths, accelerating diffusion kinetics?

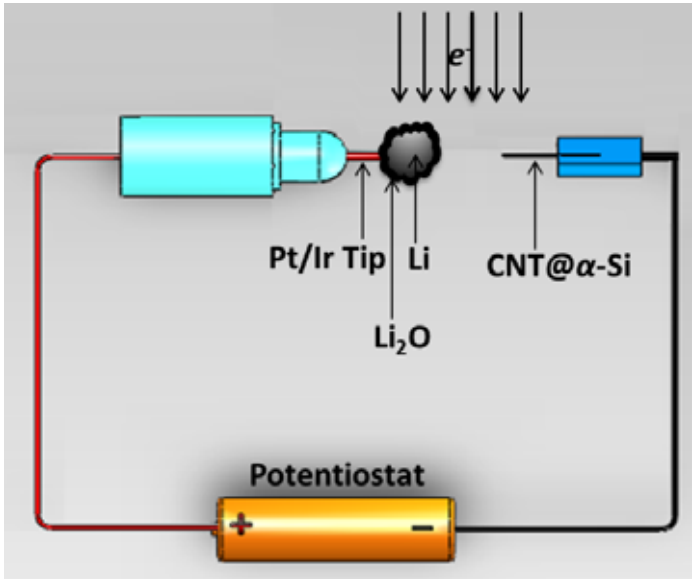


Anode Material	Storage Capacity ($mA•h•g^{-1}$)	Electrical Conductivity ($S•cm^{-1}$)	Pulverization
α-Silicon	4,200 ($Li_{4.2}Si$)	$\leq 10^{-4}$	Yes
CNTs	~1,000	$>10^4$	No
Graphite	372 (LiC_6)	$\sim 10^3$	No

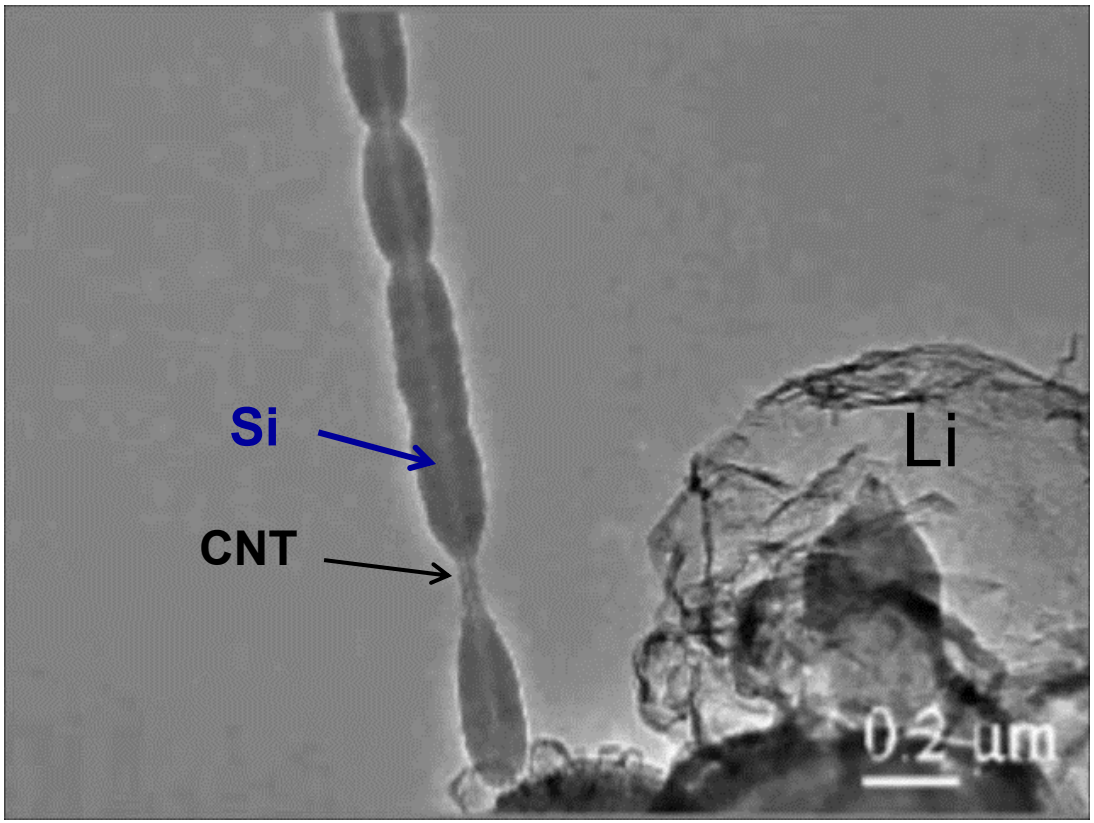


A Beaded-String Silicon Anode



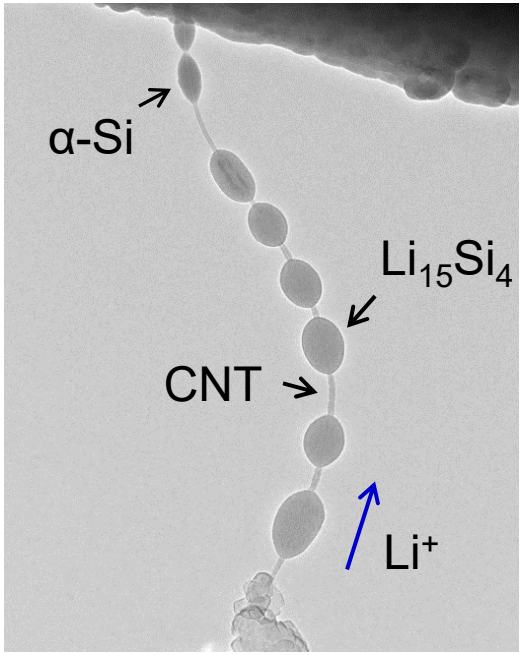


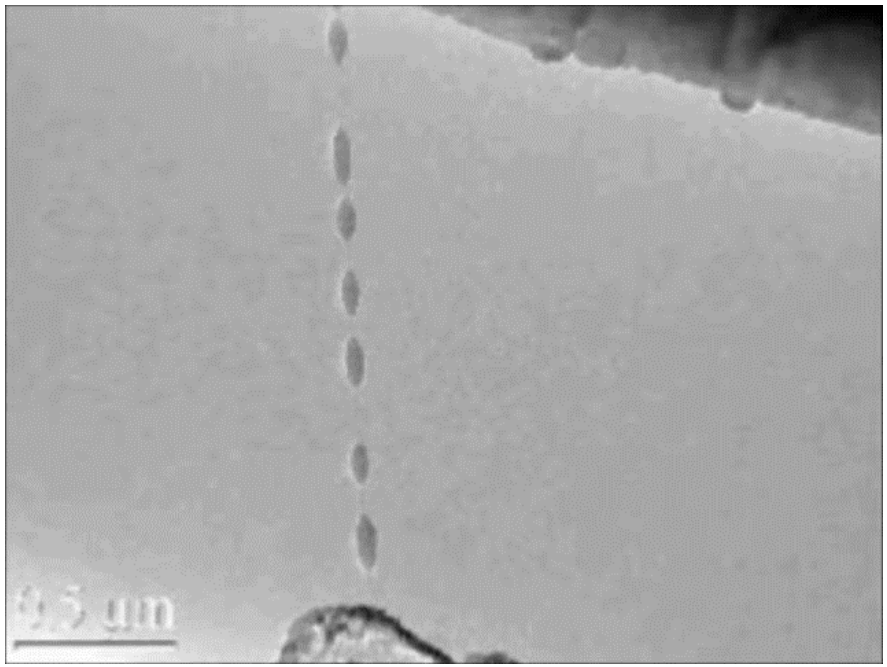
$xLi^+ + Si + x\ e^- \leftrightarrow Li_xSi$



Collaboration w/ J. Cumings

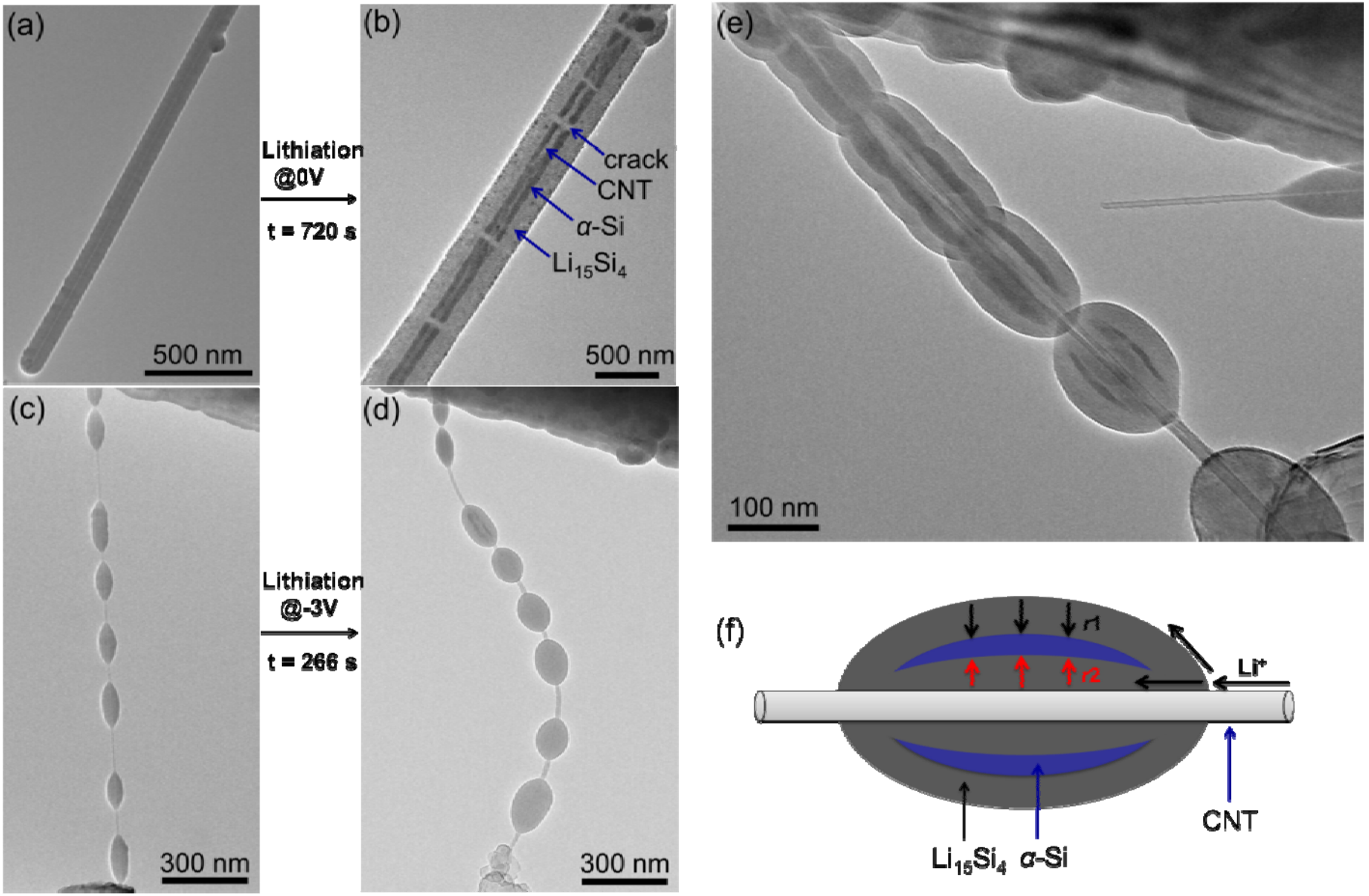
Silicon beads “breathe” radially on a string



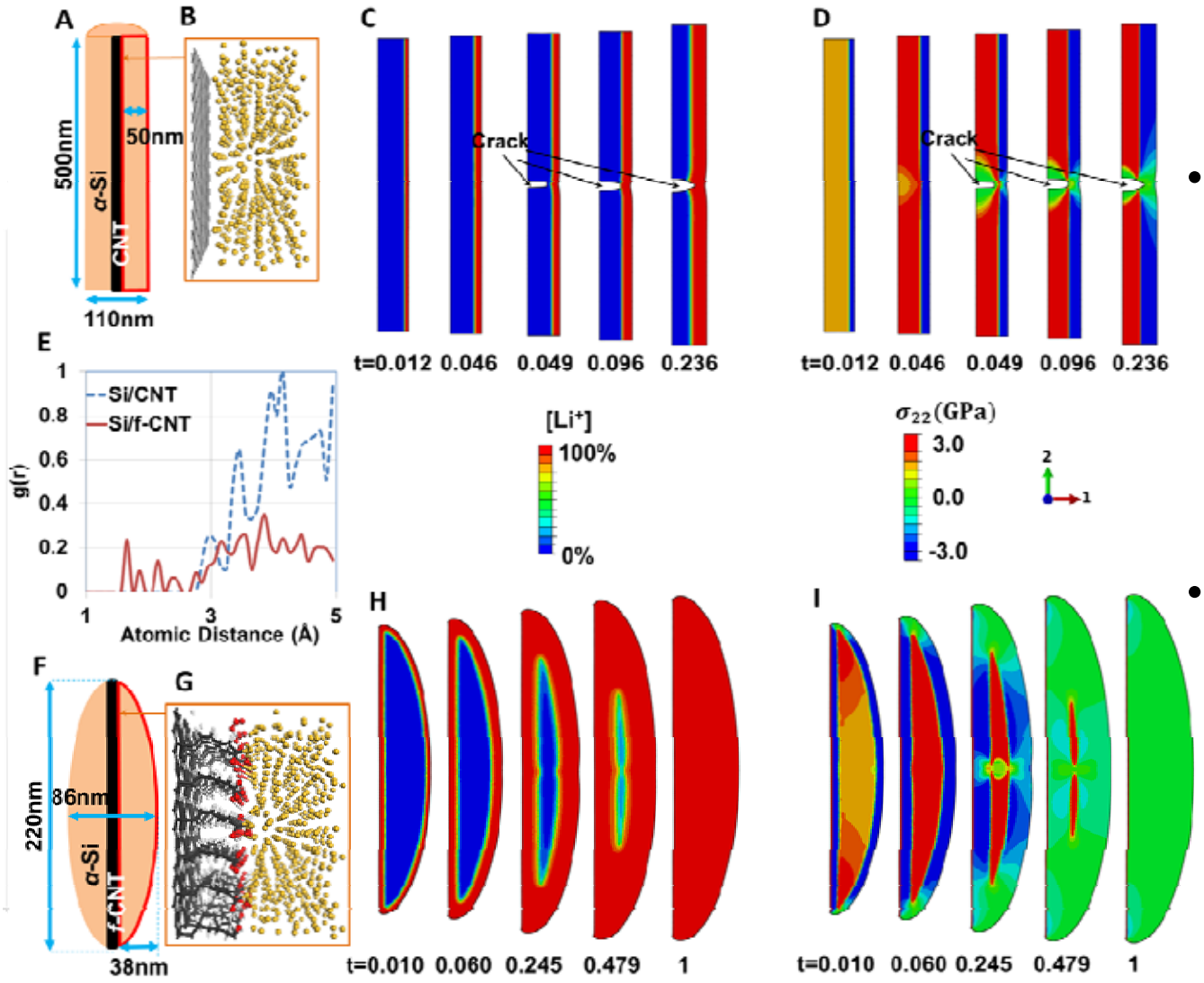


Movie played at 40x speed
lithiation at -3V

Microstructural Evolution



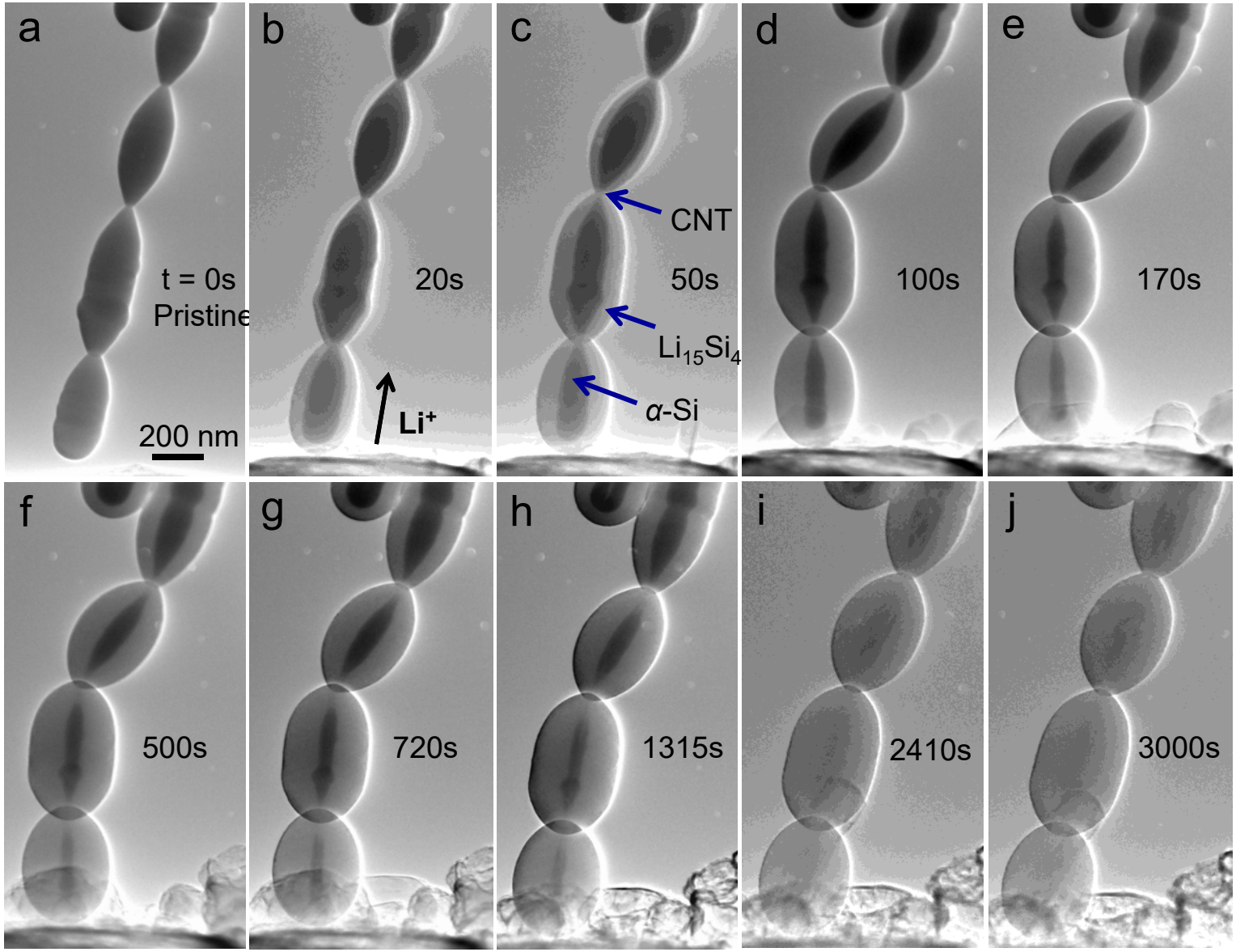
Interfacial Bonding Averts Fracture of Silicon



- Formation of Si-C and Si-O covalent bonds increases interfacial bonding by 4 times, based on DFT calculations.
- Finite element simulations suggest that the chemically tailored Si-C interface constrains the Si bead to breathe symmetrically.

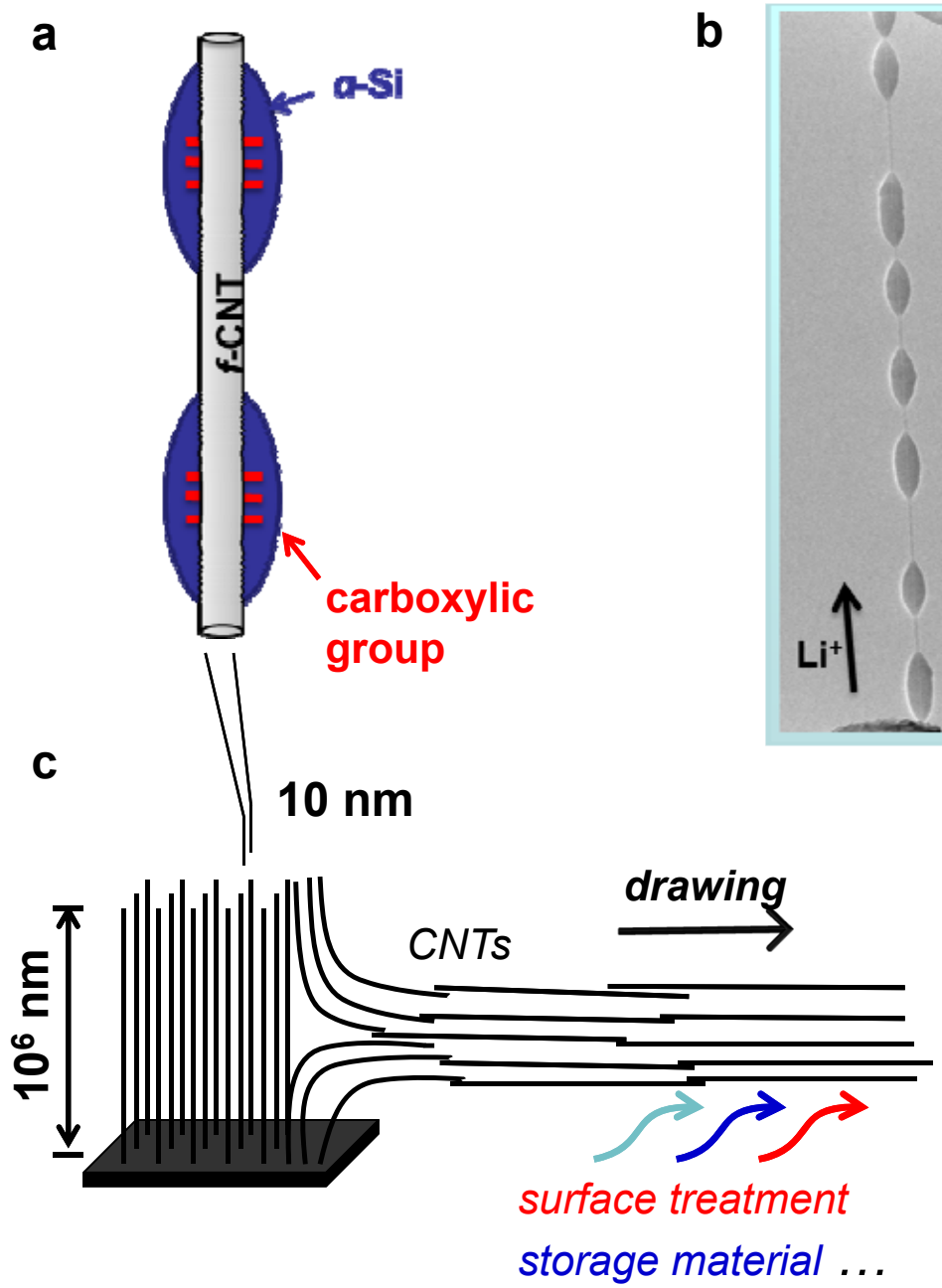
Yue Qi (GM, now MSU); Teng Li (UMD)

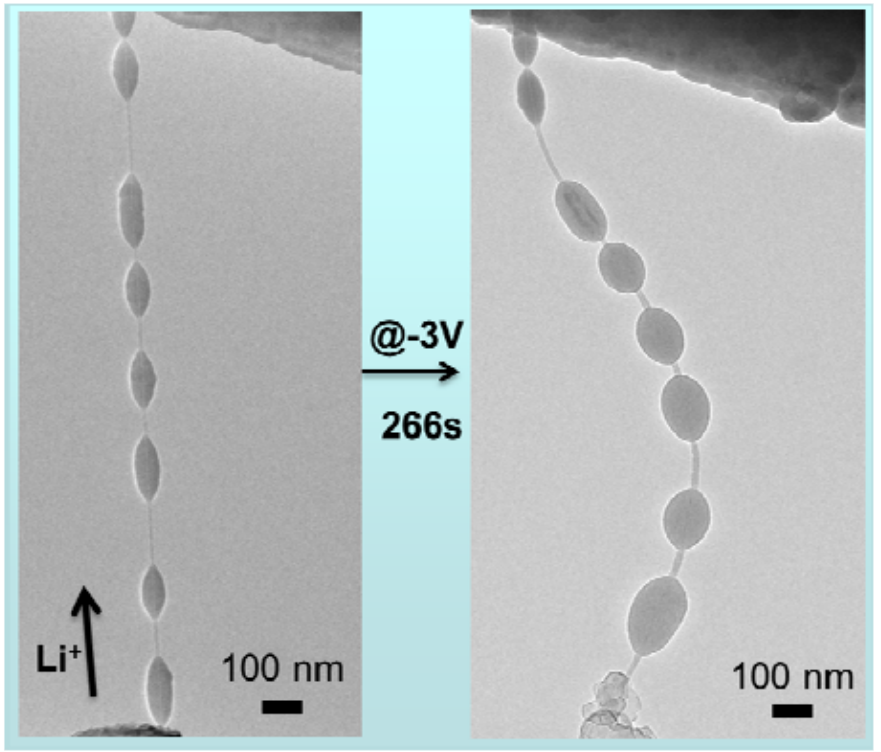
Lithium Ions Propagate along a String of Merging Silicon Beads

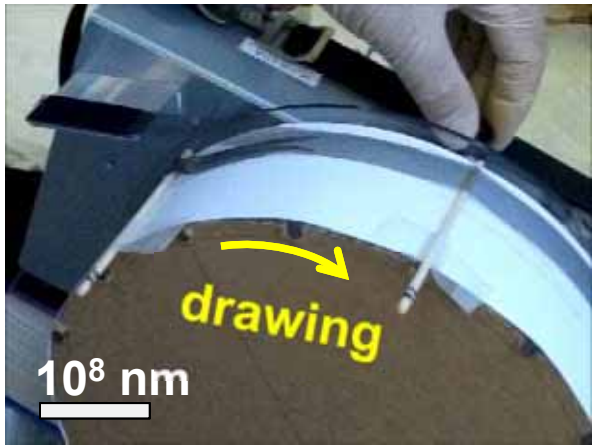


How can one translate “nano” into “macro”?

Spinning “Nano” into “Macro”?

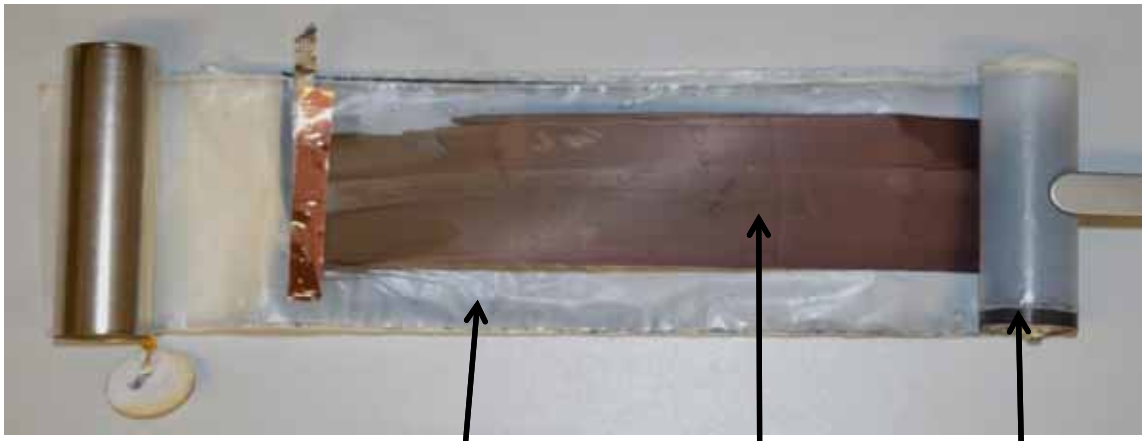






Roll and Pack

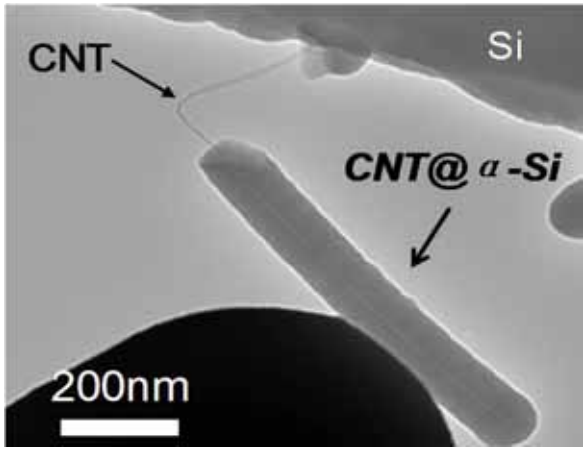
f-CNT@Si Thin Film



18650 Full Cell

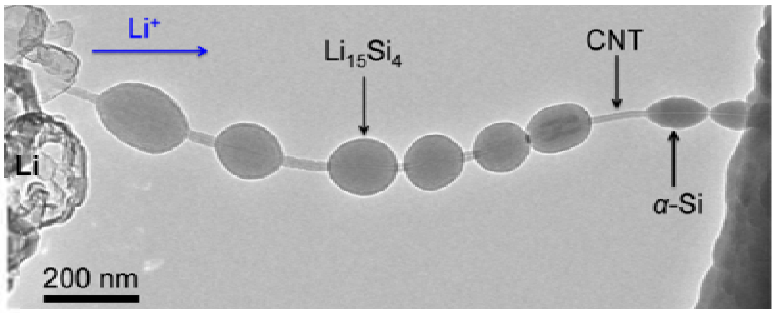
Chemically Tailored Interface

Intrinsically Weak



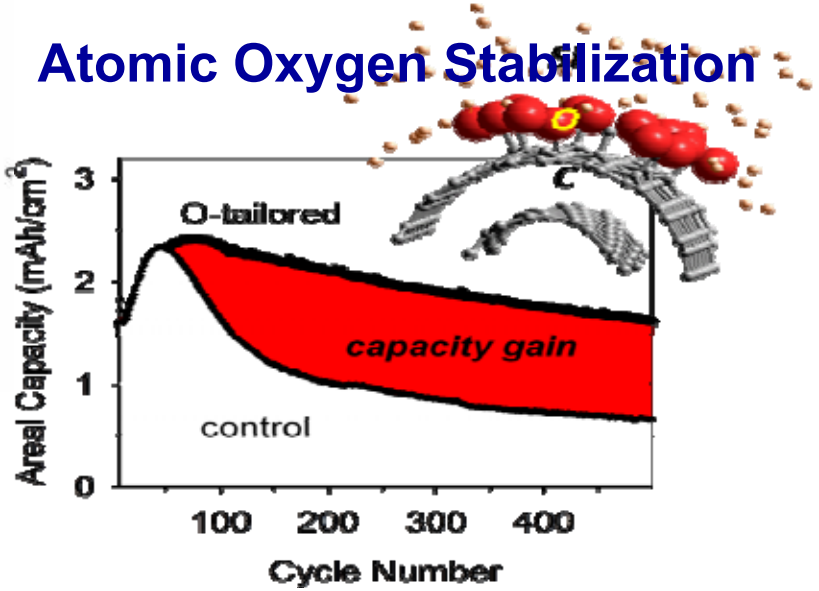
Liao, *et al. Adv. Mater.* **2011,** *23*, 4318.

Beaded Strings



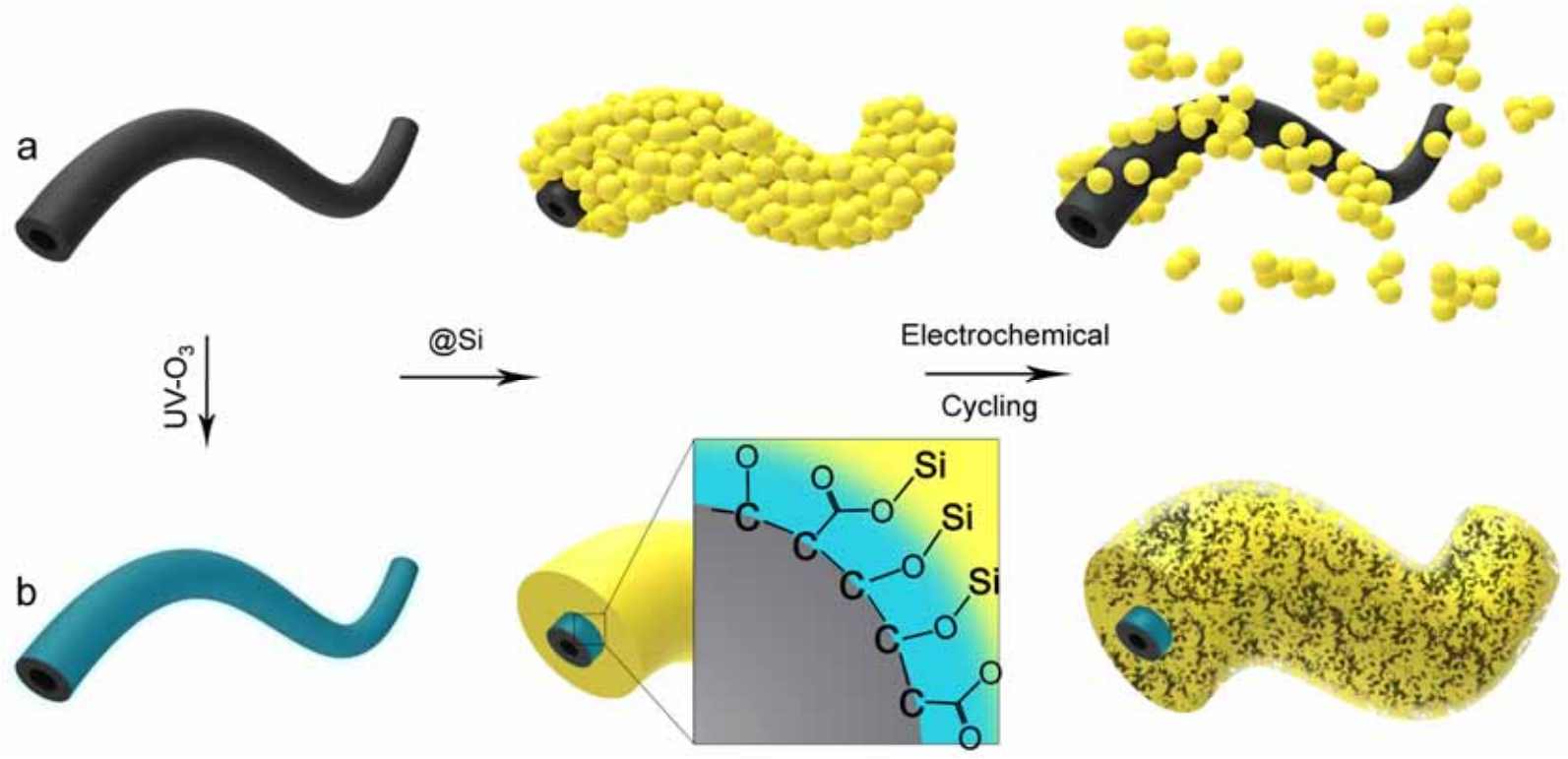
Sun, *et al. ACS Nano.* **2013,** *7*, 2717.

Atomic Oxygen Stabilization



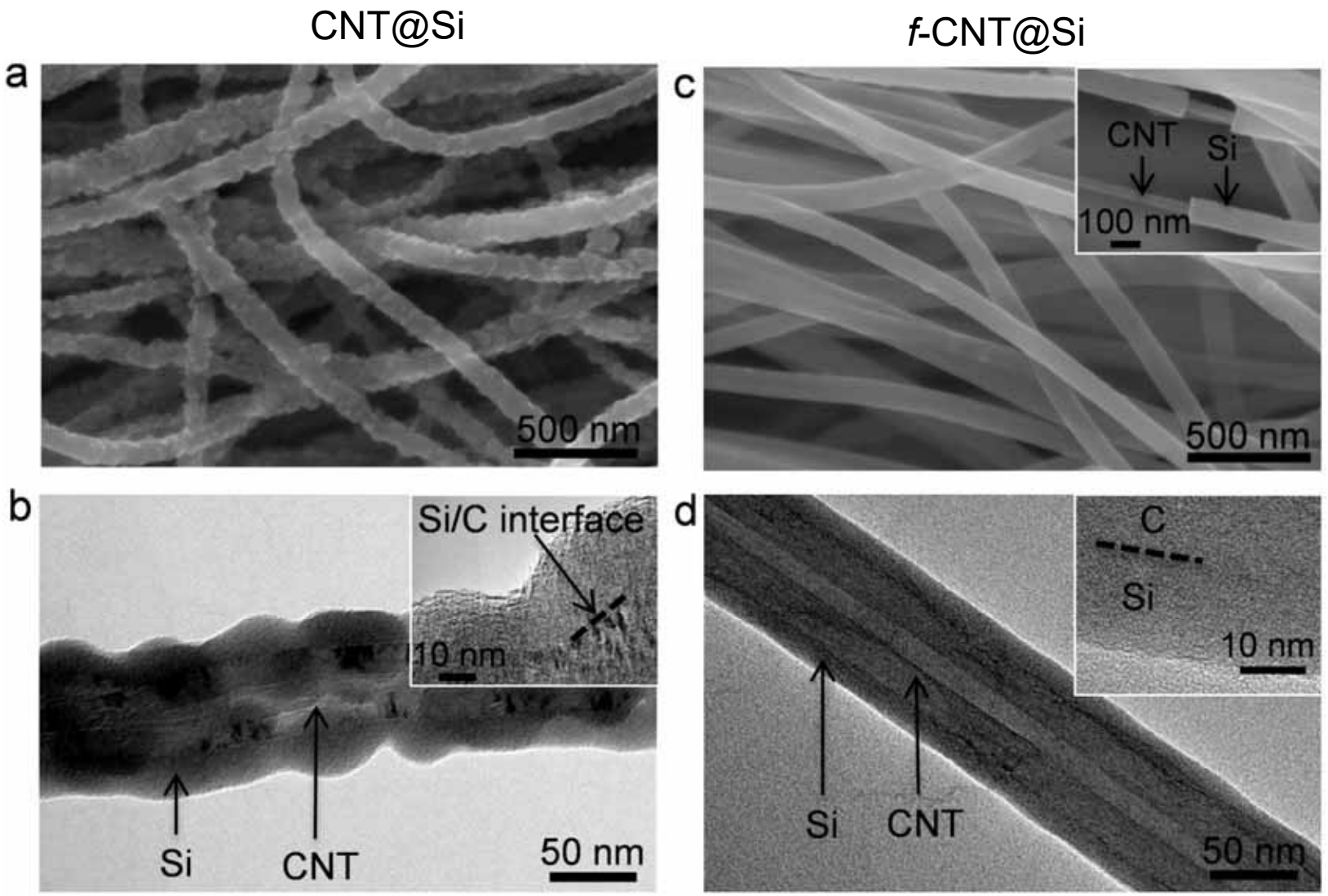
Sun, *et al. Nano Lett.,* **2015**, *15*, 703.

Stabilizing Si-C Interface by Atomic Oxygen



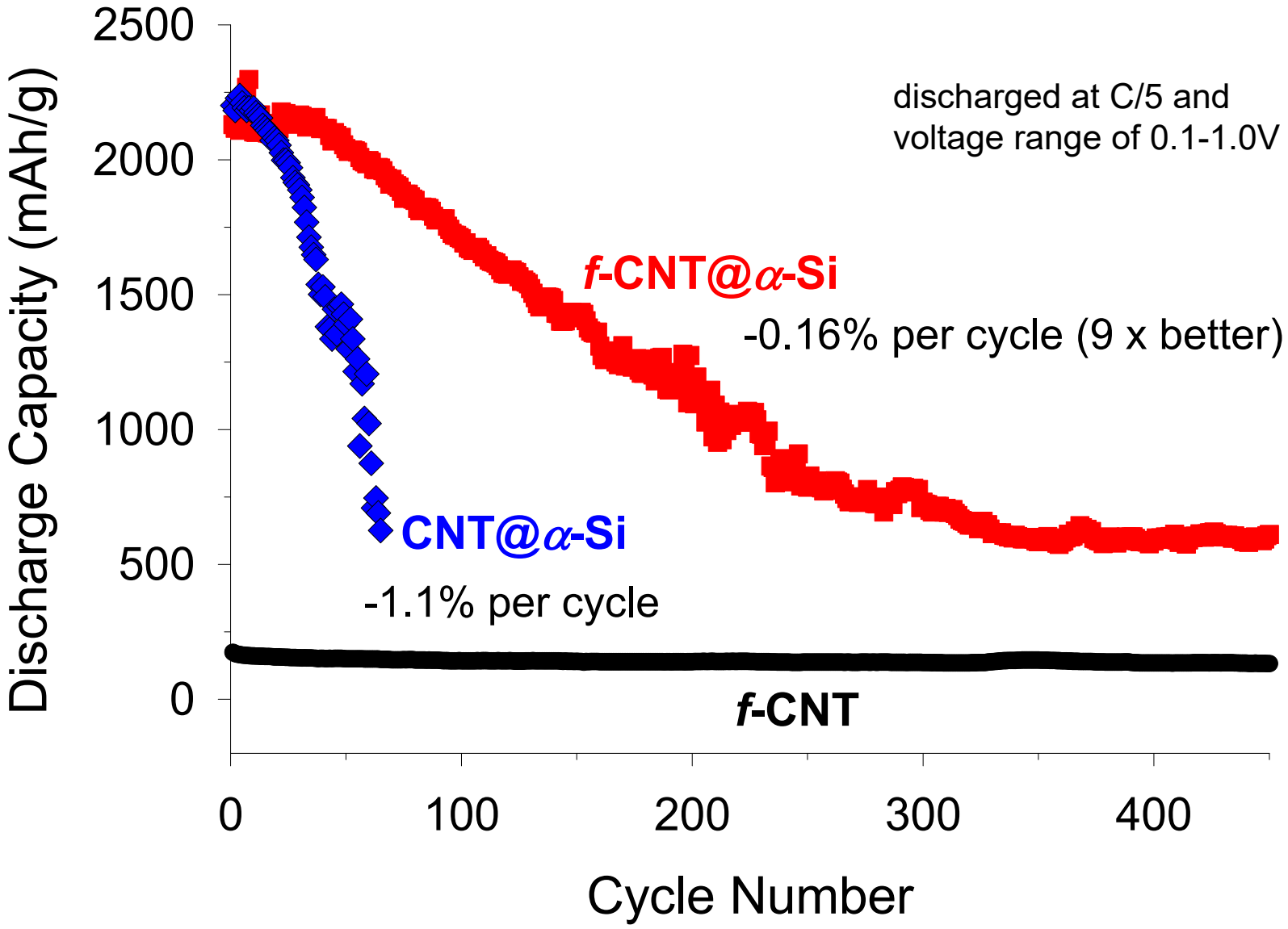
Sun, *et al. Nano Lett.,* **2015**, *15*, 703.

Defect-Controlled Nucleation

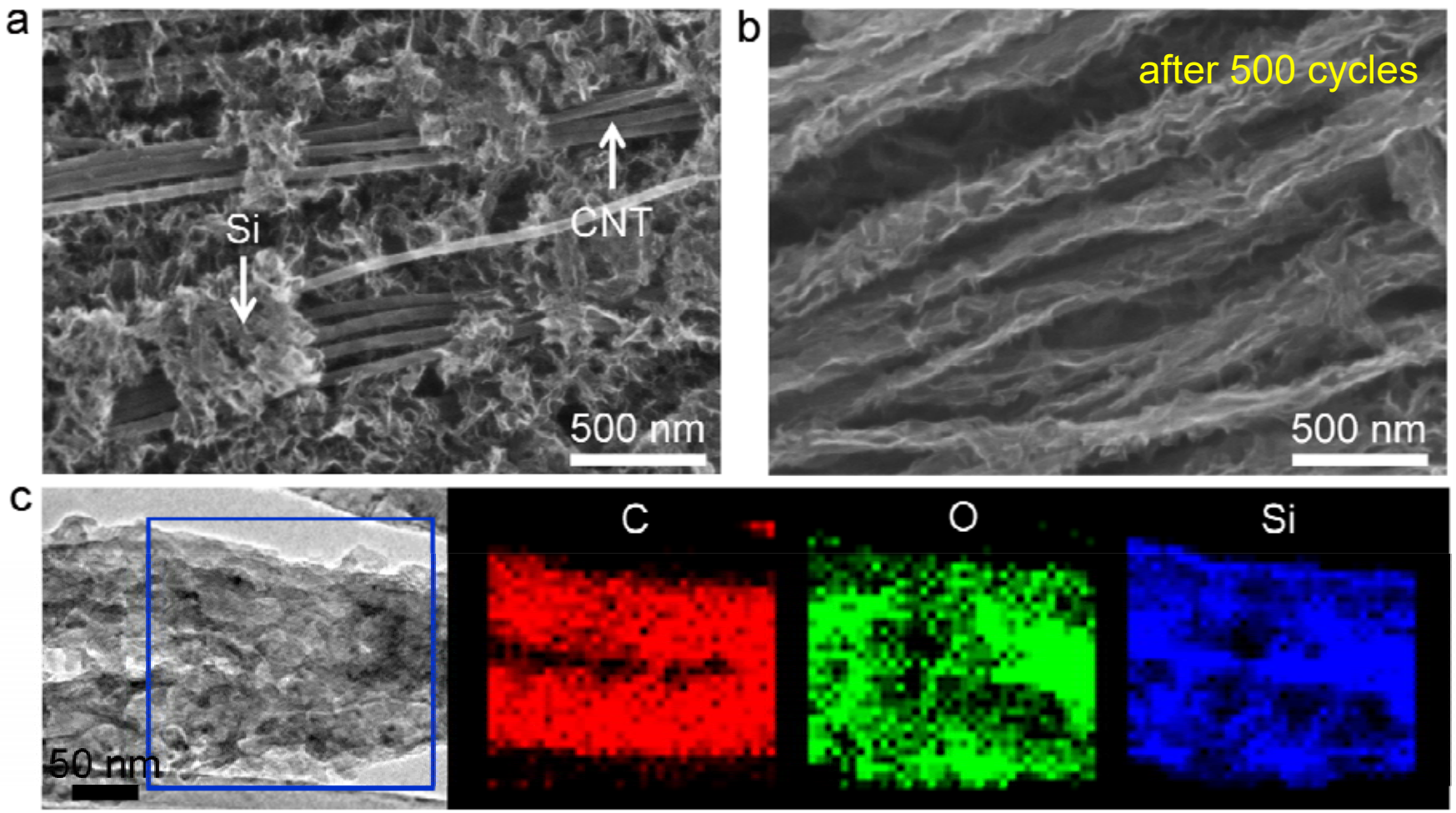


Sun, *et al. Nano Lett.*, **2015**, *15*, 703.

Chemically tailored interface slows down capacity loss

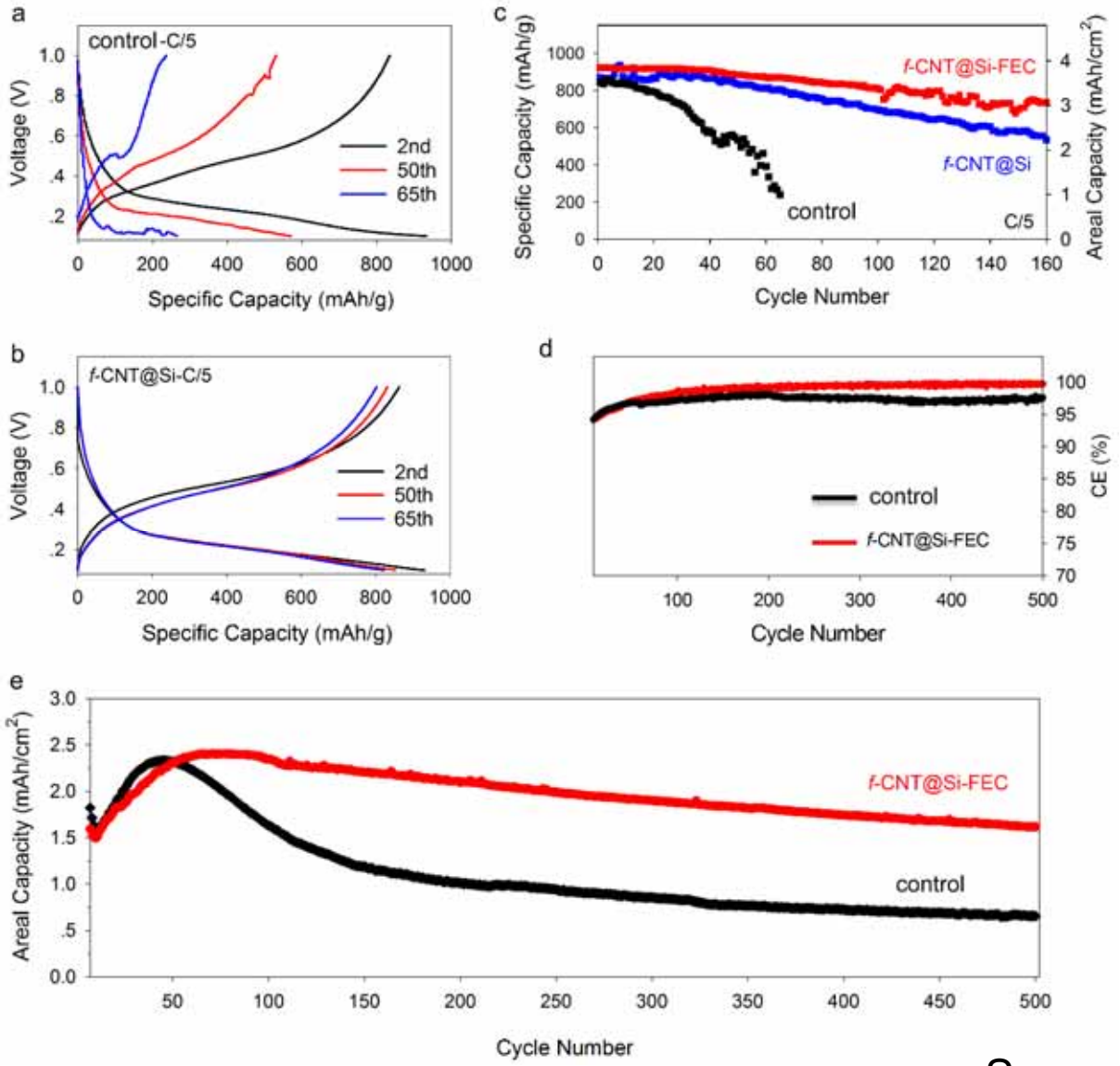


CNT@Si *versus* *f*-CNT@Si



Sun, *et al. Nano Lett.*, **2015**, *15*, 703.

Interfacial Oxygen Stabilizes Composite Si Anodes

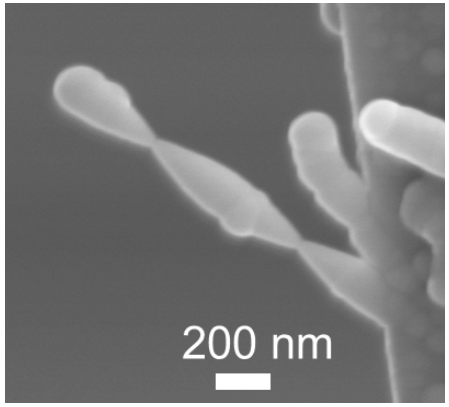


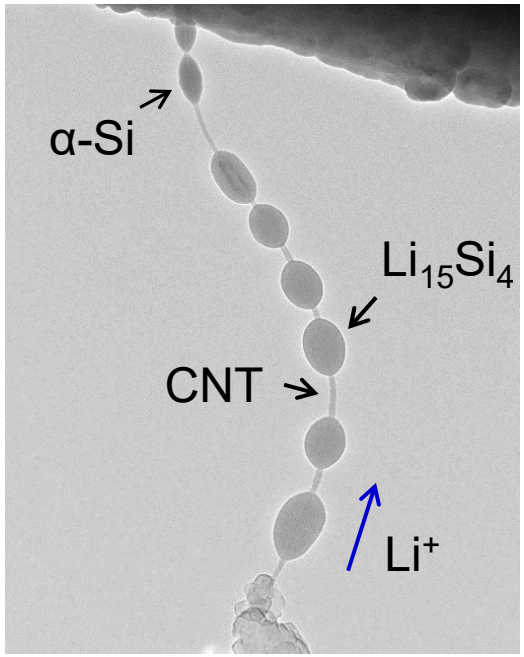
- High areal capacity (3.86 mAh/cm^2), high specific capacity (922 mAh/g based on the mass of the entire electrode), and good cyclability (80% retention of capacity after 160 cycles) are simultaneously attained.
- At 1C, the areal capacity approaches 1.61 mAh/cm^2 at the 500th cycle.

Sun, *et al. Nano Lett.*, **2015**, *15*, 703.

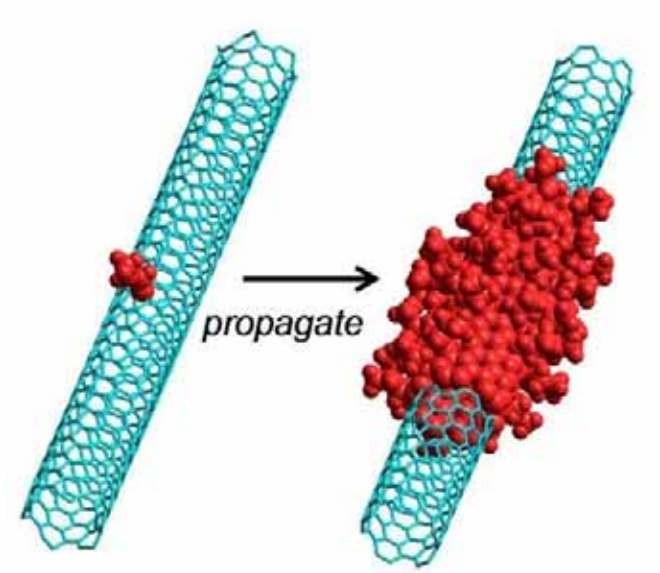
Summary: Part II

A Beaded-String Silicon Anode

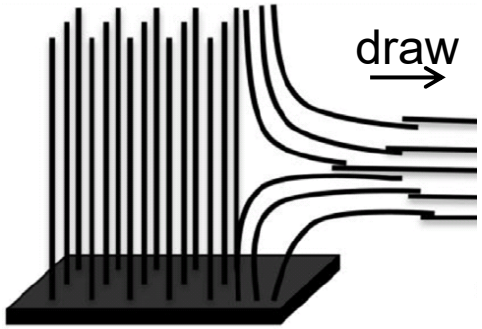


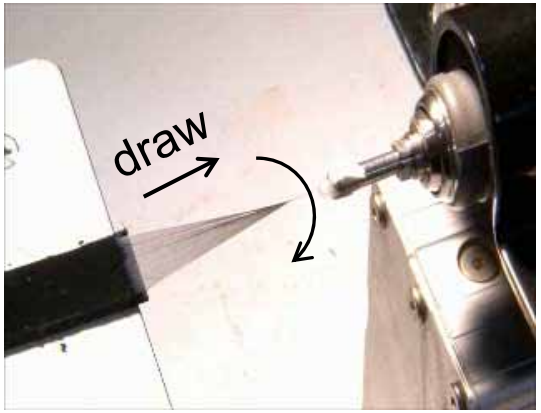


- Silicon beads on a CNT string "breathe" during lithiation
- Efficient Li^+ transport
- High electrochemical reversibility
- Spinning "Nano" to "Macro"



Initiation vs. Propagation





CARBON NANOTUBES

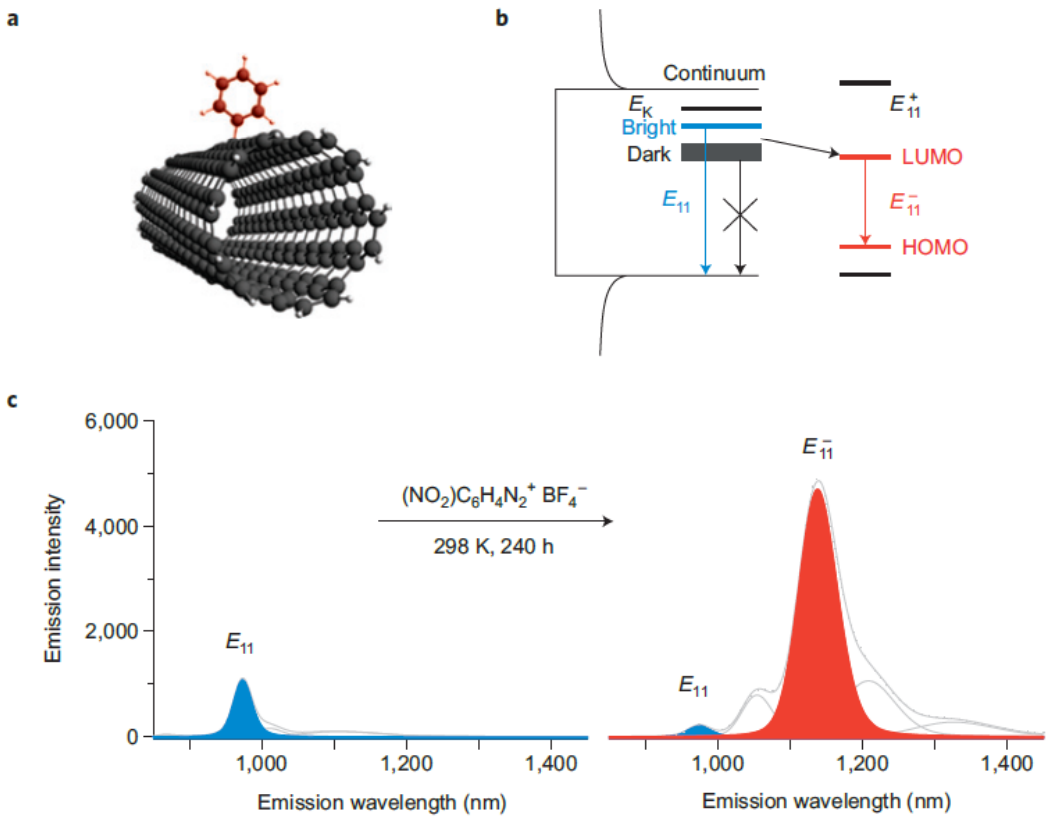
A bright future for defects

Covalently bonding groups to the walls of carbon nanotubes has been previously observed to quench their photoluminescence. Now, it has been shown that, if you get the chemistry just right, their photoluminescence can in fact be significantly brightened by introducing defects through functionalization.

Qing Hua Wang and Michael S. Strano

In crystalline materials such as metals and semiconductors, it is the defects rather than the perfect lattice structure that lead to the most interesting and useful properties. For example, line dislocations in metals allow them to be malleable by moving and sliding under mechanical stress; adding impurities to them can result in alloys with superior strength and corrosion resistance; and substituting lattice atoms with dopants in semiconductors allows the Fermi level to be precisely tuned for making transistors. In all of these examples, the careful incorporation of defects imparts very useful properties to crystalline materials[1]. It now turns out that adding a controlled concentration of defects can also have benefits for carbon nanotubes, which are cylindrical lattices of carbon atoms. Writing in *Nature Chemistry*, Wang and co-workers[2] describe an unexpected new effect by which defects in carbon nanotubes dramatically increase the intensity of their photoluminescence.

Single-walled carbon nanotubes

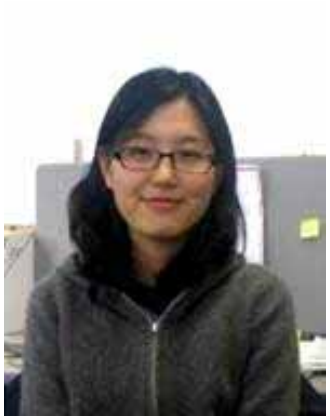


Wang, Q.-H.; Strano, M. S. *Nature Chemistry* **2013**, *5*, 812-813.


Humanity's Top Ten Problems
for next 50 years
1. ENERGY
2 WATER
3 FOOD
4 ENVIRONMENT
5 POVERTY
TERRORISM
DISEASE
WAR
EDUCA
DEMO
10 POP
2003 6.3 Billion People
2050 8-10 Billion People

Acknowledgements

Fluorescent
Quantum Defects



Dr. Hyejin Kwon
(Ph.D. ‘16)

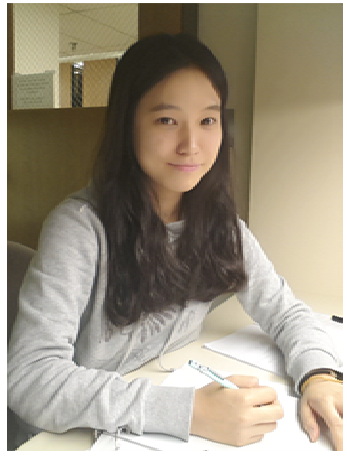
Lyndsey Powell

Dr. Alex Brozena
(Ph.D.’13, DOE
Graduate Fellow,
inaugural class)

Dr. Yin Zhang
(Ph.D. ’14)

Dr. Yanmei Piao
(Ph.D.’14)

Brendan Meany



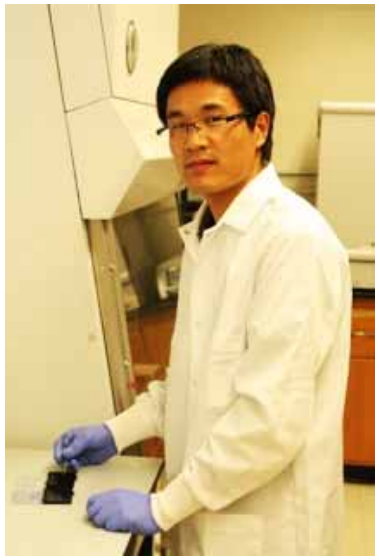
Mijin Kim

Acknowledgements

Beaded String

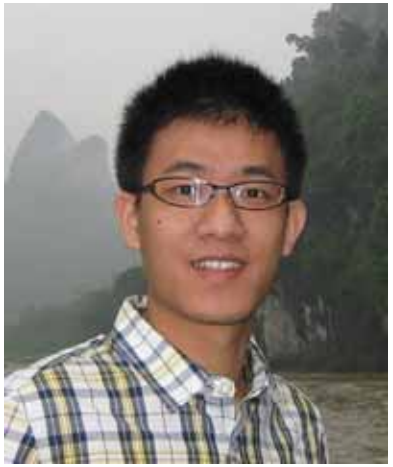
Dr. Shunliu Deng

Dr. Hongwei Liao
(joint w/ Cumings)



Dr. Chuanfu Sun

Kim Karki (Cumings)



Peng Wang

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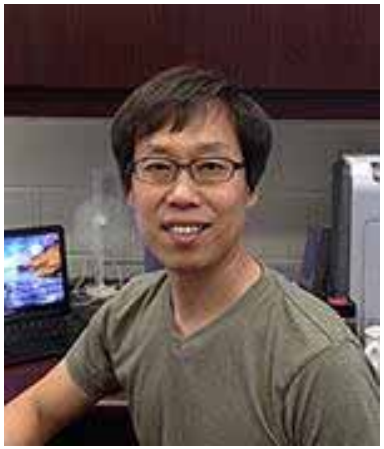
Gary Rubloff

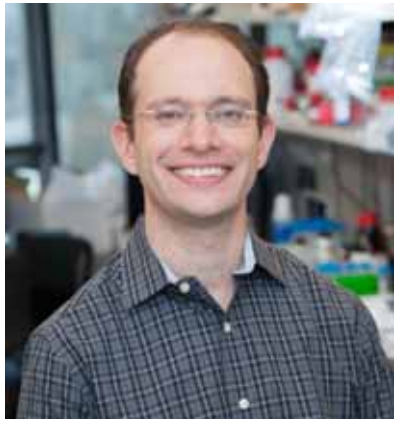
John Fourkas

Yue Qi



Sang Bok Lee

Morihiro Okada



Daniel Heller

George Schatz

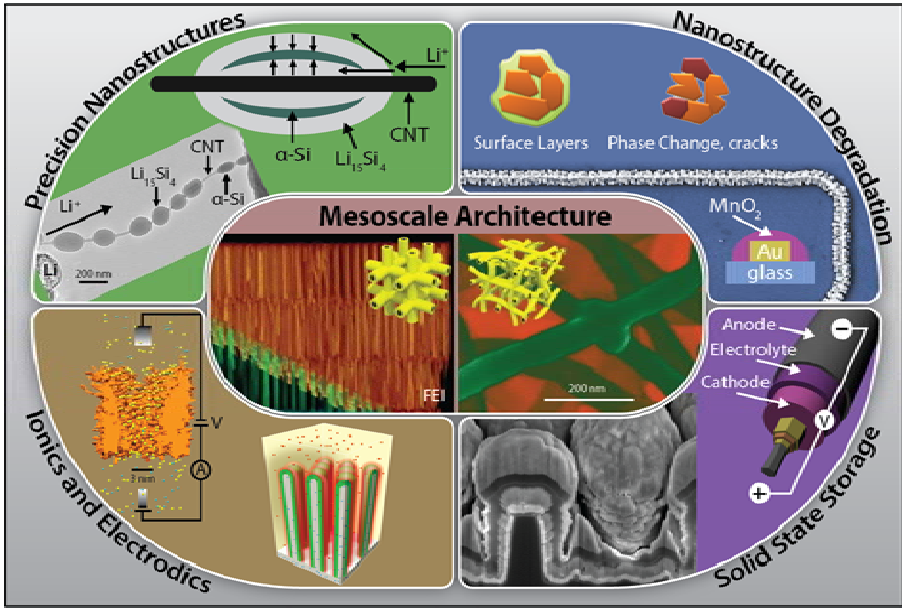
John Cumings

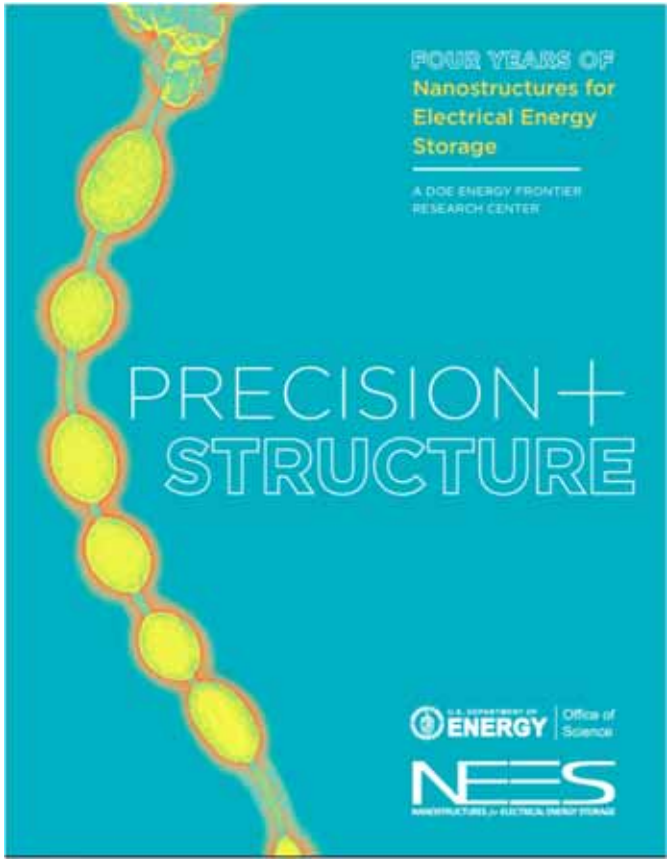
Stephen Doorn

…and many others who have inspired our thoughts and encouraged/helped us in various ways…

NANOSTRUCTURES *for* ELECTRICAL ENERGY STORAGE

An Energy Frontier Research Center
Director: Gary Rubloff
Deputy Director: Sang Bok Lee





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UCI Yale UF UNIVERSITY of FLORIDA THE UNIVERSITY OF UTAH MICHIGAN STATE UNIVERSITY UCLA

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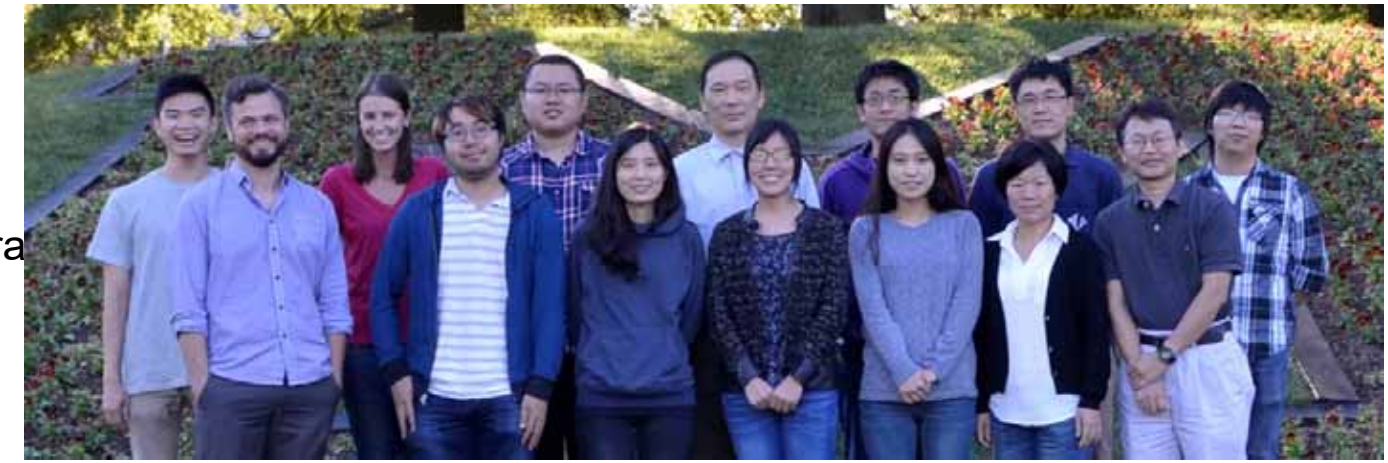
Wang Group

Xiyuan Cheng
Mijin Kim
Hyejin Kwon
Anna Lieberman (undergra
Brendan Meany
Jasper Mok (undergrad)
Allen Ng
Lyndsey Powell
Peng Wang
Dr. Shunliu Deng
Dr. Zhongjie Huang
Dr. Morihiro Okada
Dr. Zhiwei Peng
Dr. Chuan-fu Sun



Former Group Members

Dr. Yanmei Piao (PhD'14, NIST)
Dr. Alex Brozena (PhD '13. DOE graduate fellow)
Dr. Jarrett Leeds (PhD '13. HP)
Prof. ChienFu Chen (National Chung Hsing Univ.)
Prof. Shunliu Deng (Xiamen Univ.)
Prof. Pingli He (China Agricultural University)
Prof. Jia Huang (Tongji Univ., 1000 Young Talents)
Dr. Hongwei Liao (NanoSynthesis, Inc.)
Prof. Cai Shen (Chinese Academy of Sciences)
Dr. Yongxin Wang (VF Corporation)
Dr. Yin Zhang (Xi'an Jiaotong Univ.)…

Collaborators

Dr. Stephen Doorn (LANL)
Dr. Daniel Heller (MSKCC)
Prof. Mark Hersam (Northwestern)
Prof. Matteo Pasquali (Rice)
Prof. George Schatz (Northwestern)
Dr. Ming Zheng (NIST)
…and many on campus

Funding

Never Too Many Cooks

Positions Open

http://www2.chem.umd.edu/groups/wang/