Near Infrared-II Imaging, Plasmonic Platforms, Graphene Nanoribbons & Novel Materials for Energy

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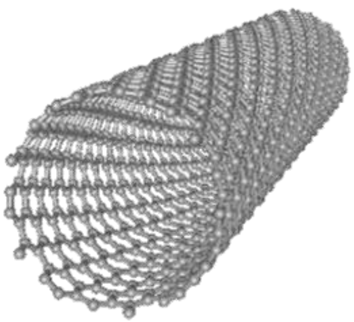
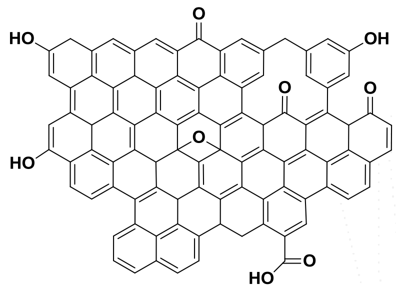
Department of Chemistry, Stanford University

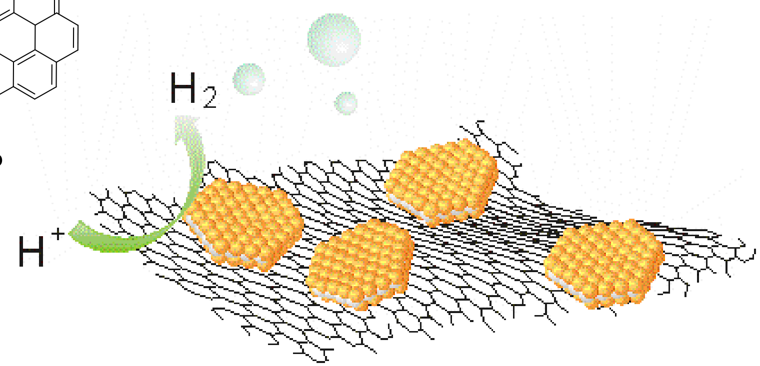
Our Current Research

Carbon Nanotube (CNT) & graphene



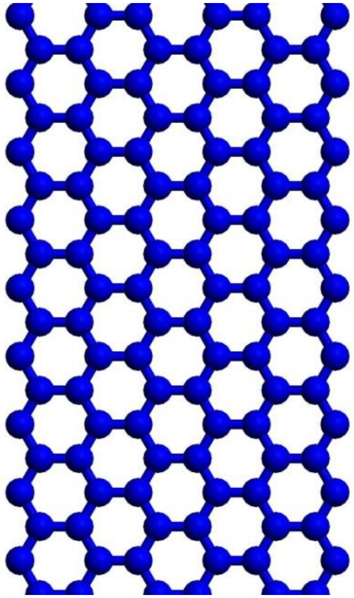


NanoCarbon-Inorganic Hybrid materials



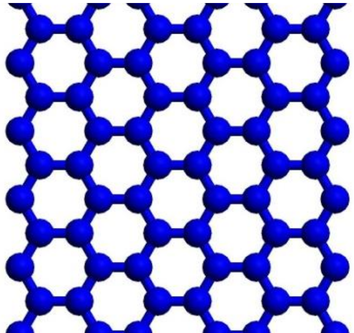
ENERGY

Graphene Nanoribbon

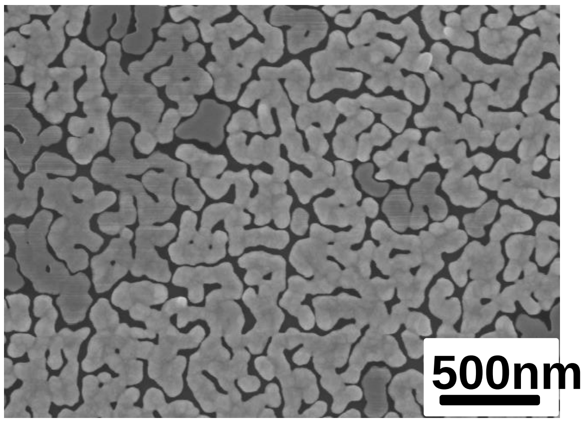


NOVEL

1D SYSTEMS



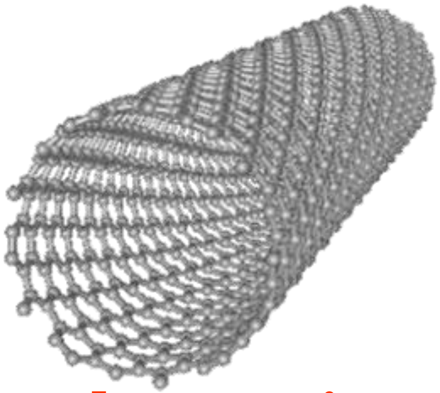
Plasmonic Gold Films

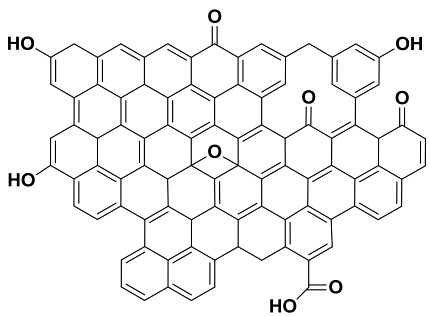


NANO-BIO

Interface Nanomaterials with Bio-Systems

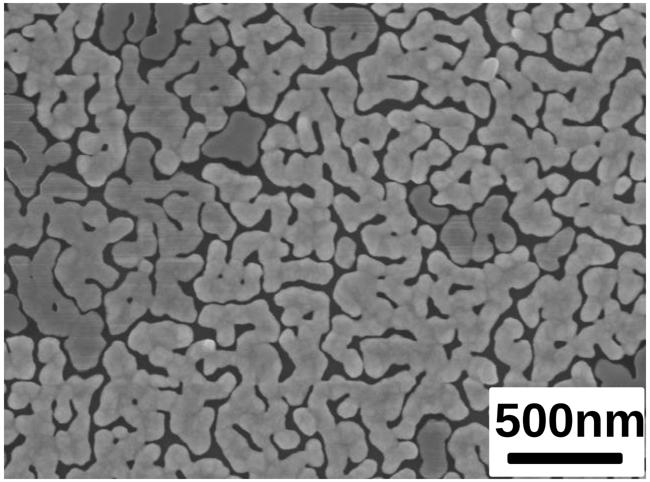
Carbon Nanotube (CNT) & Nano-graphene





- Utilization of the physical (electrical, optical…) properties of nanomaterials for imaging, detection, diagnosis and treatment of diseases (cancer, heart disease...)

Plasmonic Gold Films



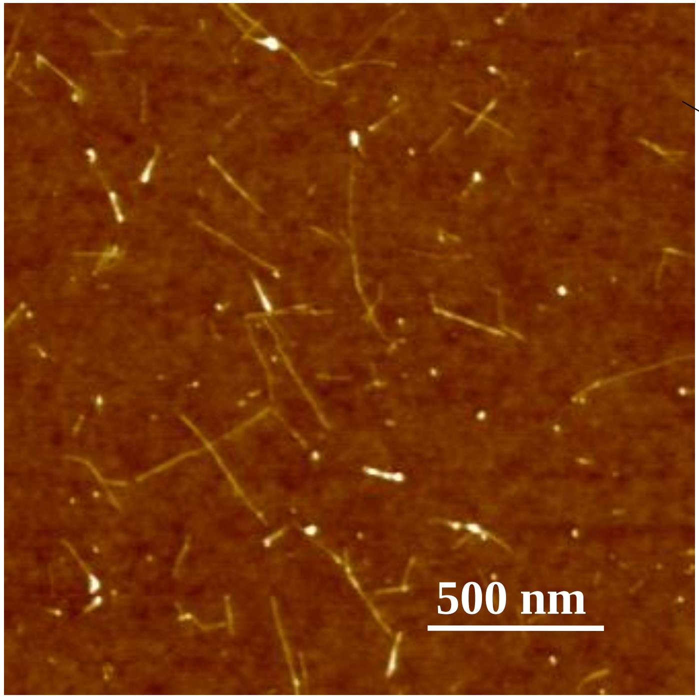
Top Fatal Diseases:

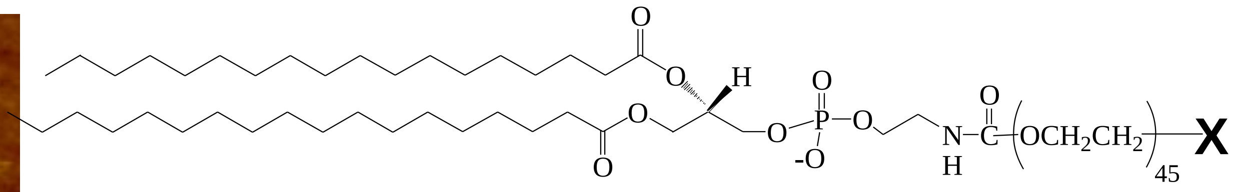
1. Ischaemic heart disease
Annual deaths: ~ 7,200,000
2. Cancers
Annual deaths: ~7,100,000
3. Cerebrovascular disease (Stroke)
Annual deaths: ~ 5,500,000

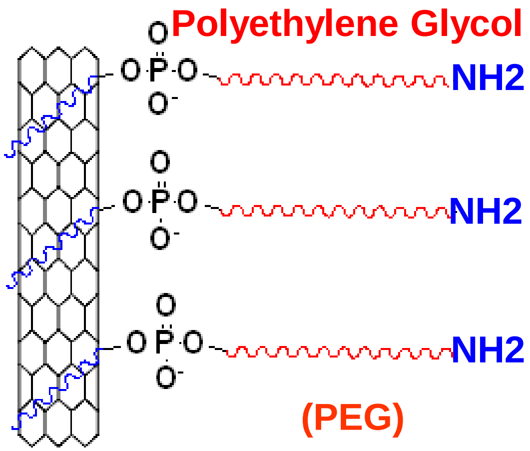
Vessel diseases: #1 killer

Making CNTs Biocompatible and Non-Toxic

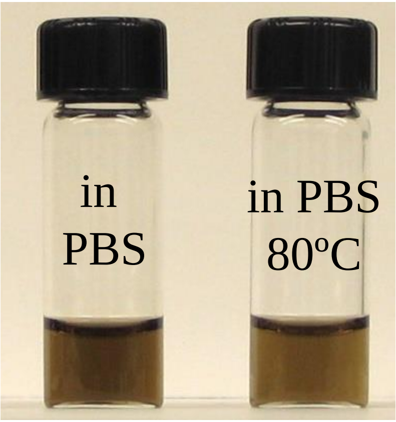
(Kam, N.W.S. et al. **PNAS** 2005, *102*, 11600.)





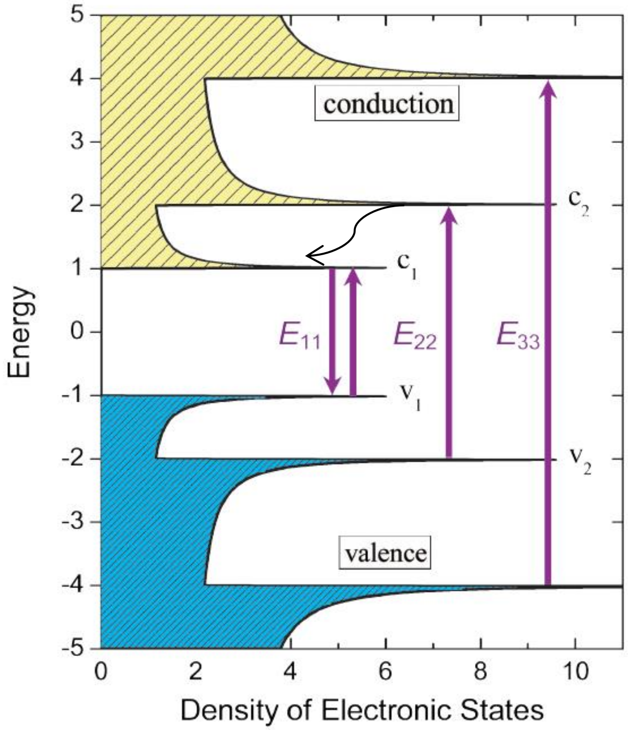


SWNT/Phospholipid-PEG

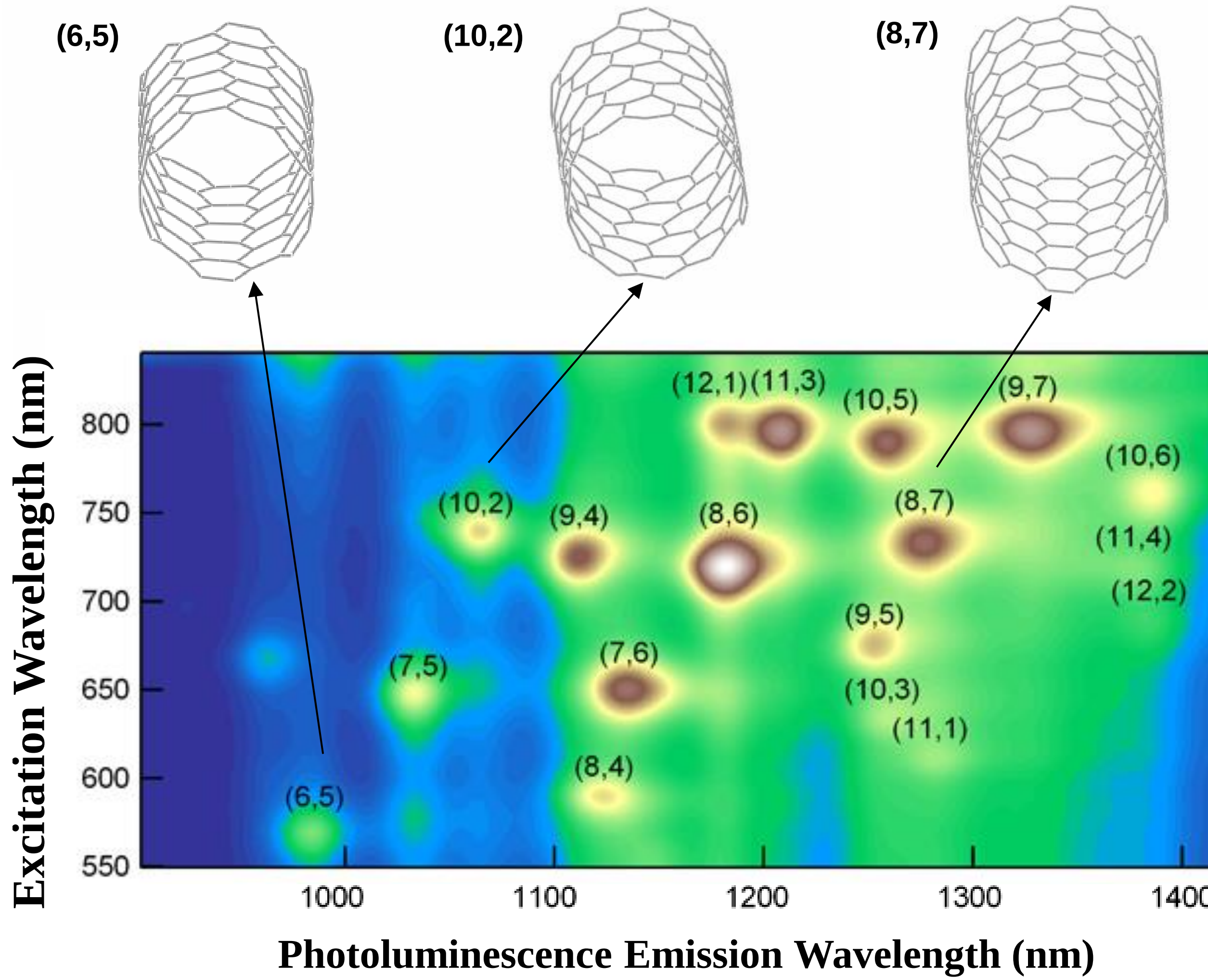


- Length 50- 200nm.
- Soluble in buffers and serum.
- Antibodies or peptides can be attached.

Carbon Nanotubes Fluorescence in NIR-II



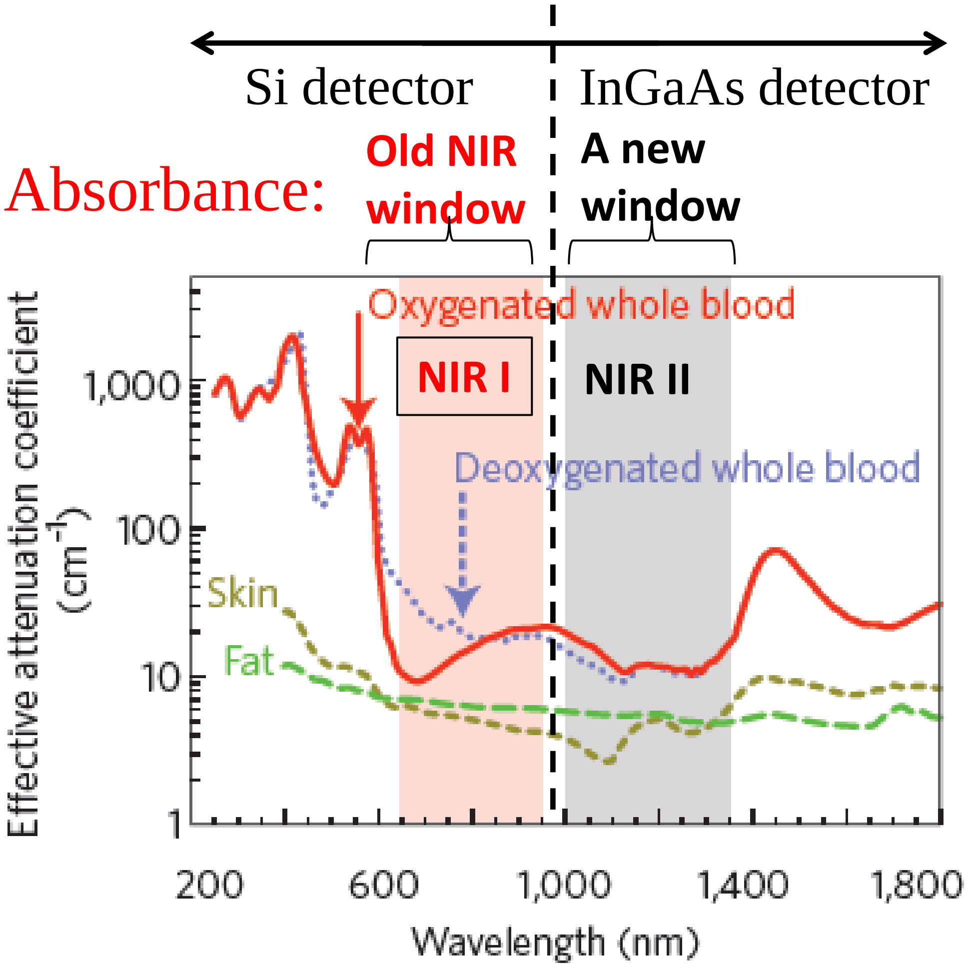
Weisman & Smalley @Rice



- Excited resonantly through E_{ii} transitions in 500-900nm range.
- Fluoresce in **1-1.4 μm range (NIR II)**; large Stoke's shift.

Developing Optical Imaging in The Second NIR Window (NIR-II, 1-1.4 μm)

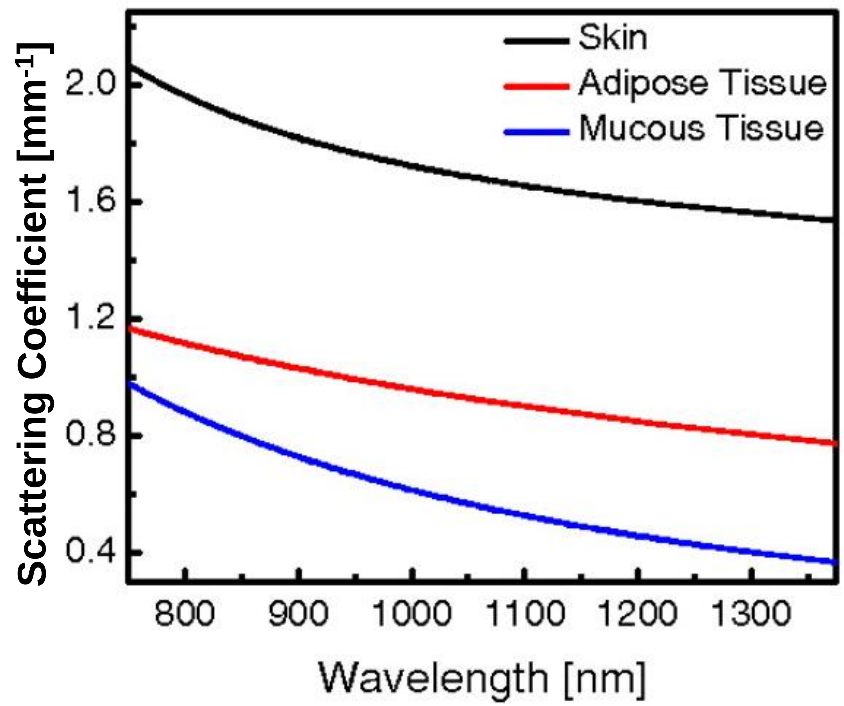
Absorbance:



Smith, Andrew. M., Mancini, Michael. C. Nie, Shuming. ***Nat Nano*** 2009, 4, 710.

Reduced tissue scattering in NIR-II

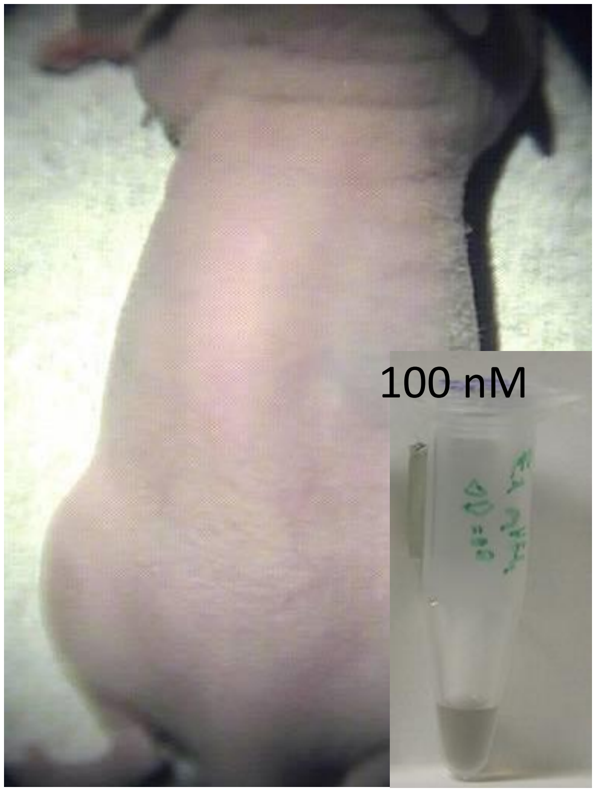
Scattering $\propto \lambda^{-\alpha}$:

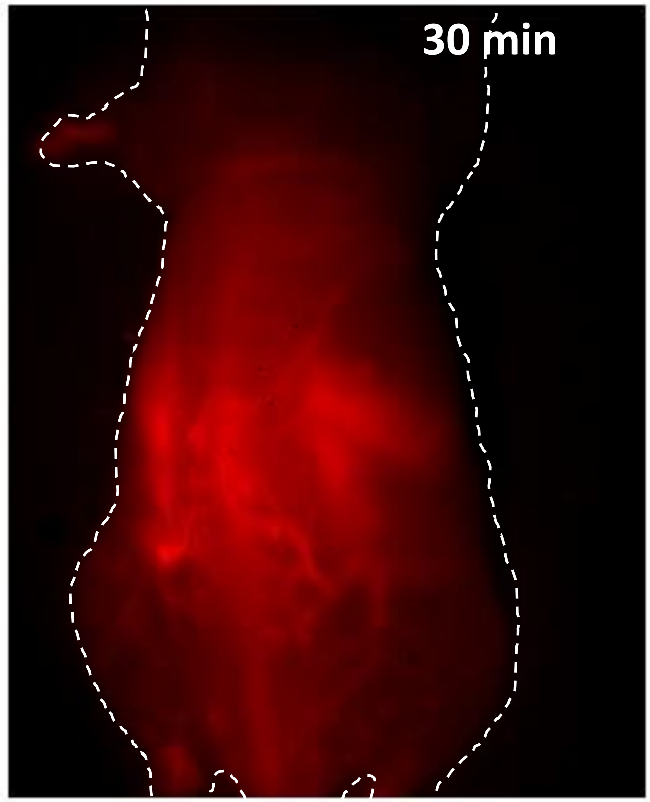


Kevin Welsher, Sarah P. Sherlock, and Hongjie Dai. ***PNAS.*** 108, 8943-8948, 2011.

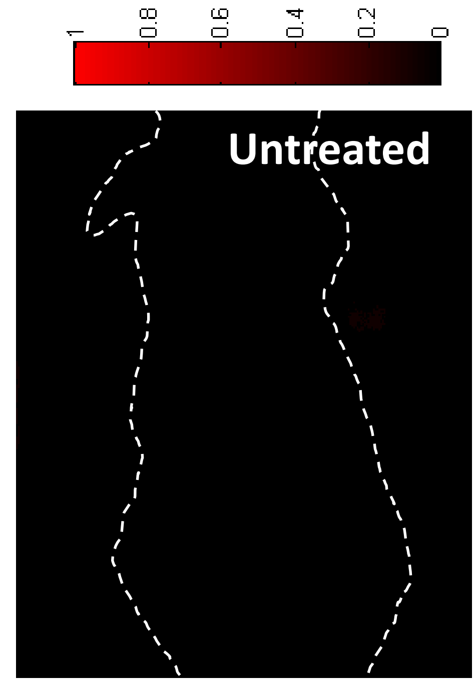
NIR II Imaging of Mice

With intravenously injected SWCNTs:





NIR-II signal
1000 nm – 1400 nm

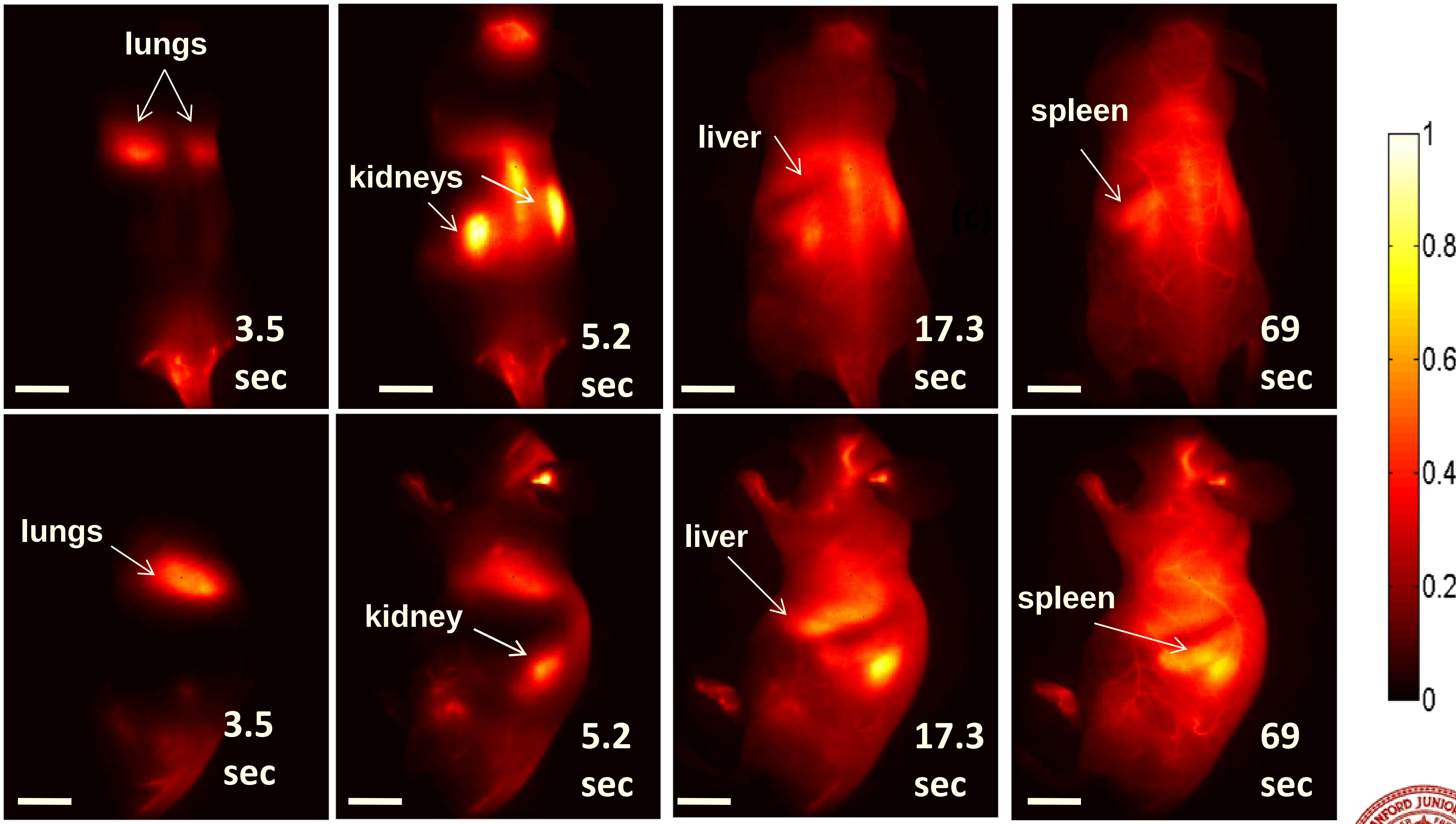


Little or no autofluorescence

Welsher, K. et al. ***Nature Nanotechnology***; 2009

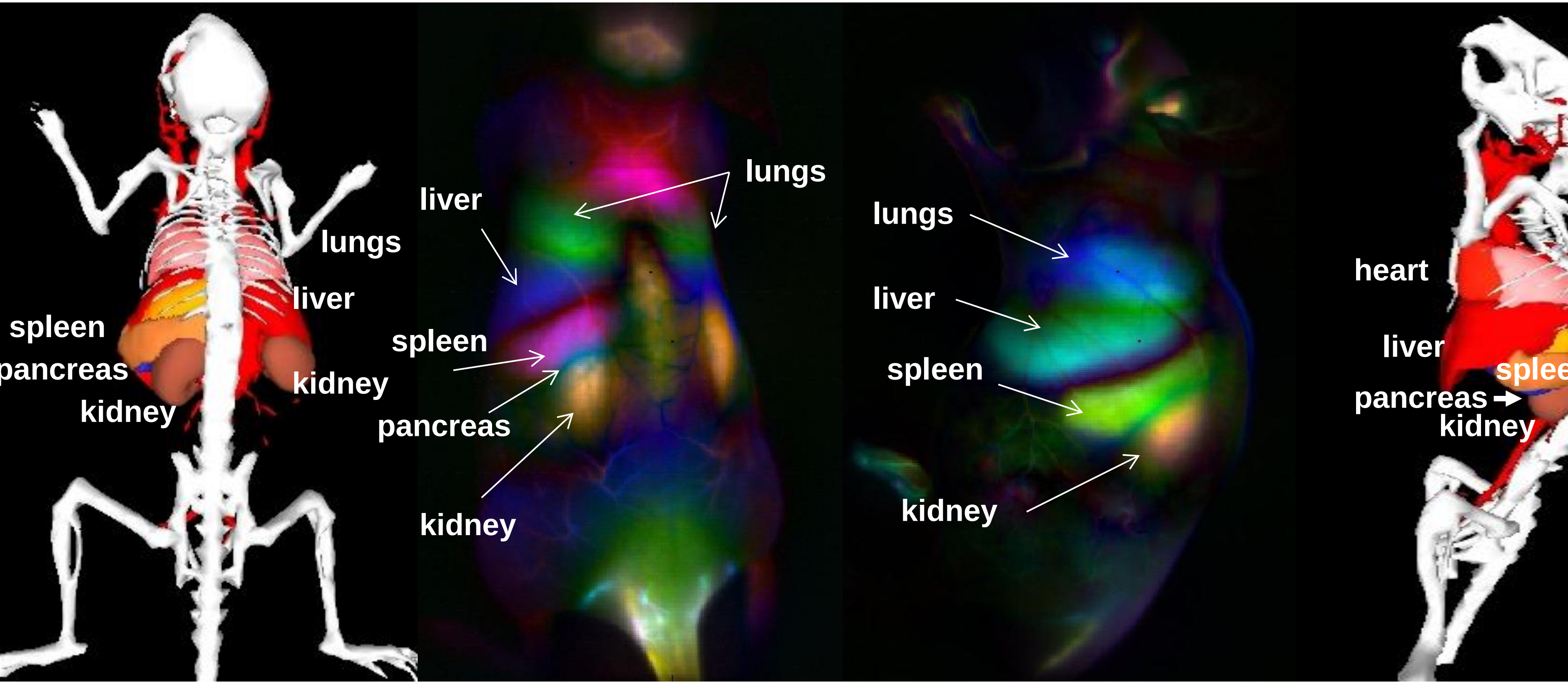
Deep-Tissue NIR II Video Rate Imaging

(Image into the body of a mouse optically)



Welsher, K.*, Sherlock, S.* Dai, H. **Proc. Nat. Acad. Sci.** 2011.

Anatomical Mapping by Principle Component Analysis (PCA) of NIR II Video Imaging

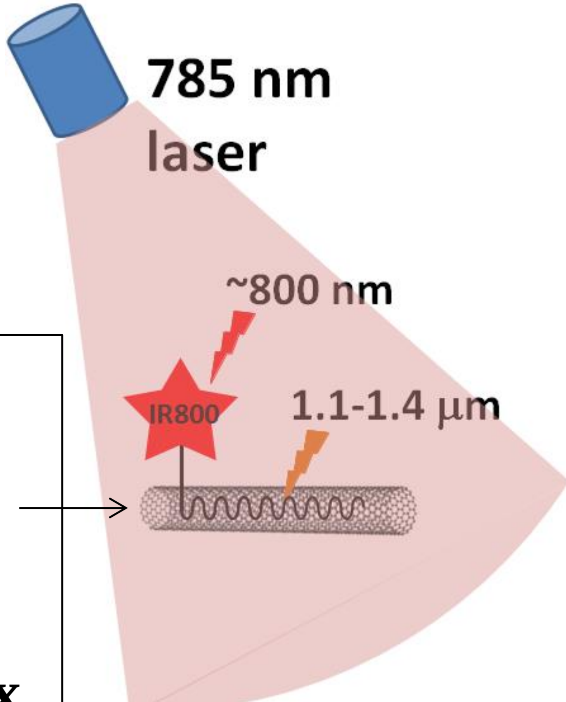


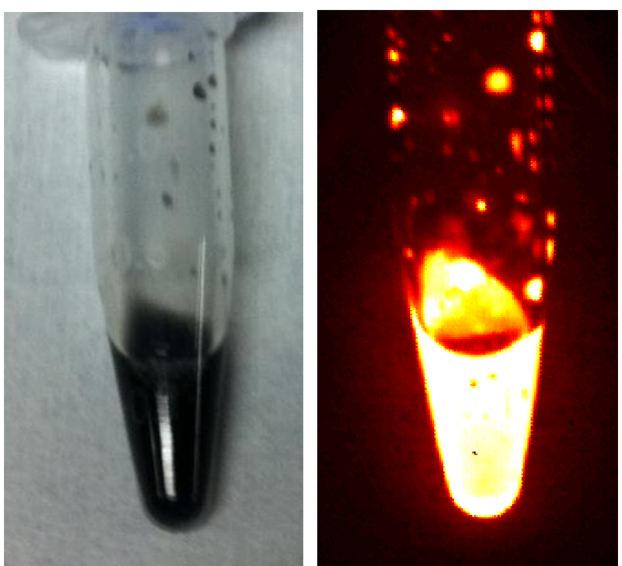
- PCA groups pixels with similar time variance in signal

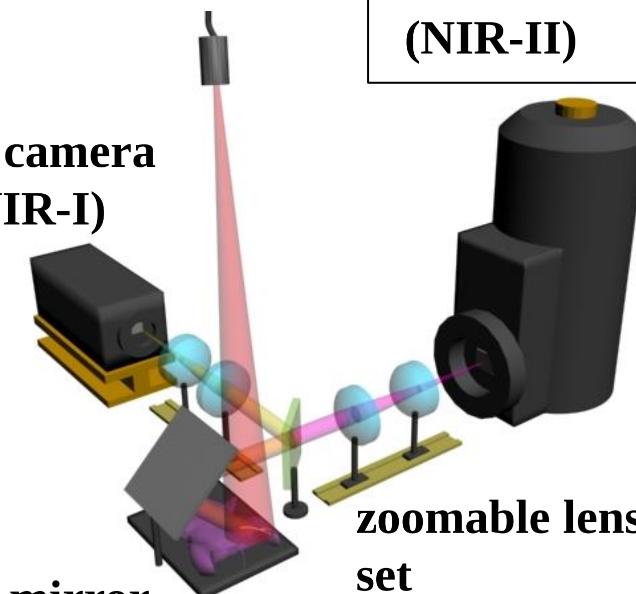
Welsher, K.*, Sherlock, S.* Dai, H. **Proc. Nat. Acad. Sci.** 2011.

Simultaneous Imaging in NIR-I &NIR II

SWNT
+
IRDye-800
complex

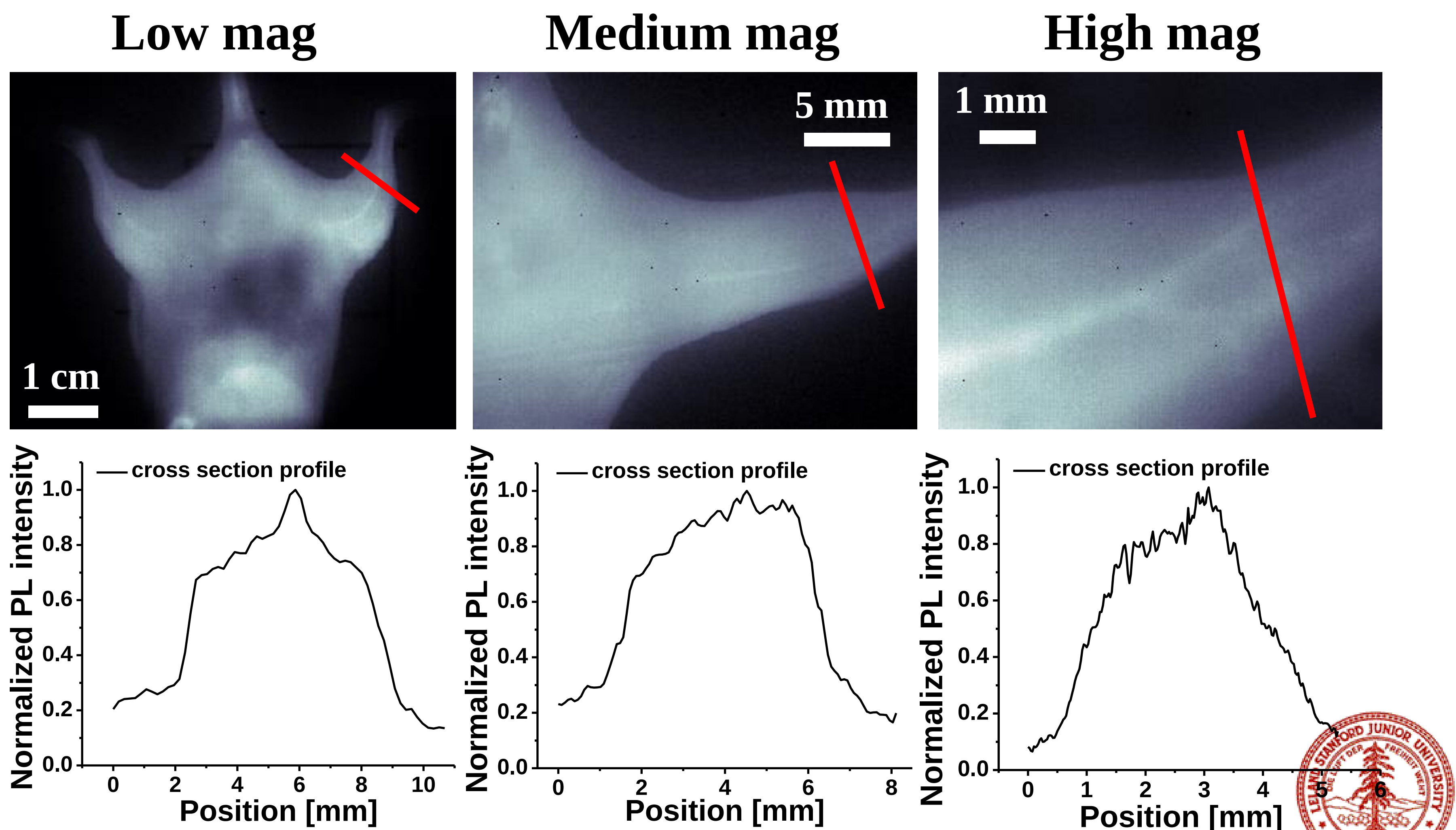






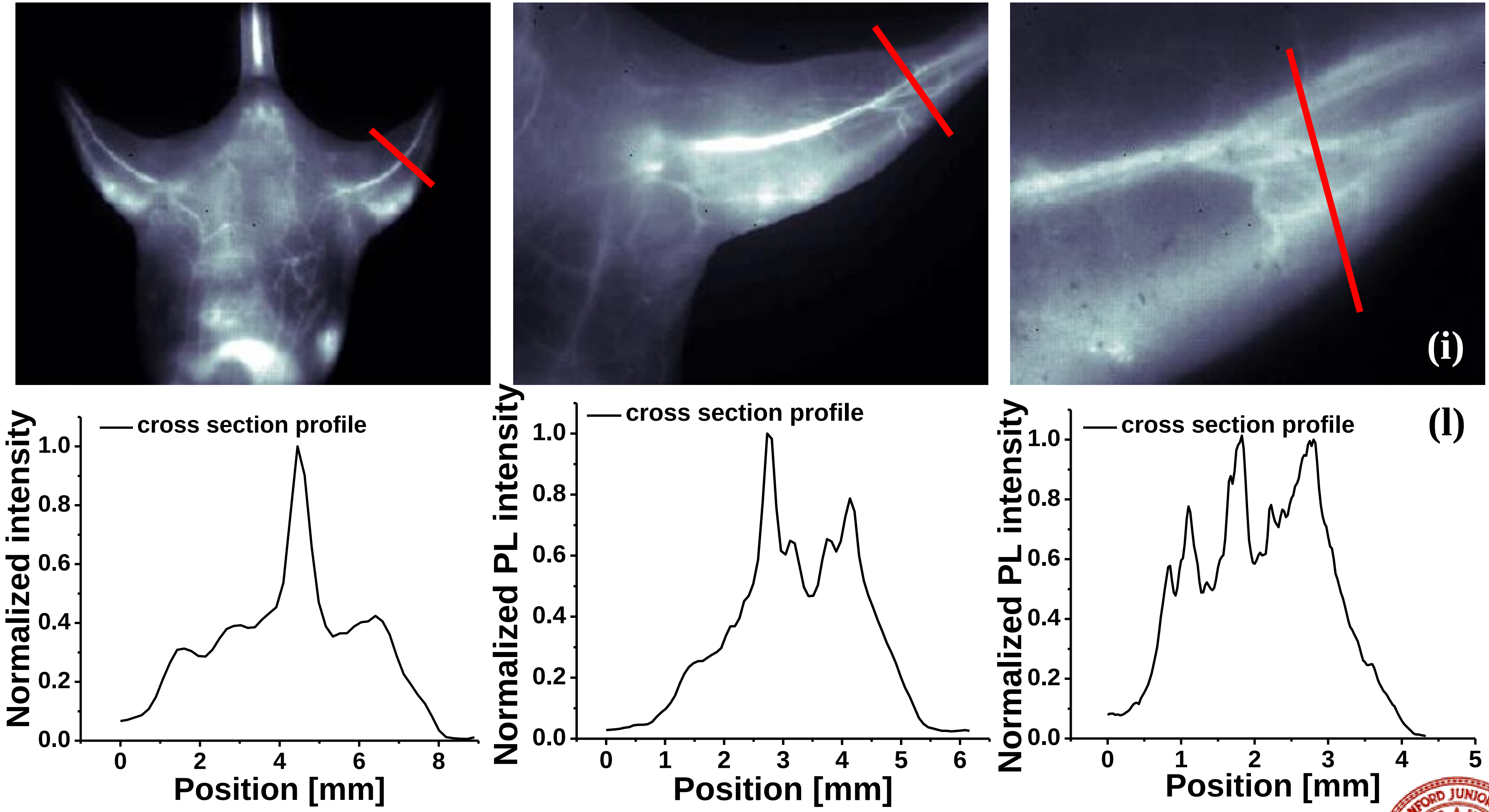
NIR-I Peripheral Vessel Imaging

Imaging in NIR-I by detecting IRDye800 fluorescence:



NIR-II Peripheral Vessel Imaging

Imaging in NIR-II by detecting SWNT fluorescence:

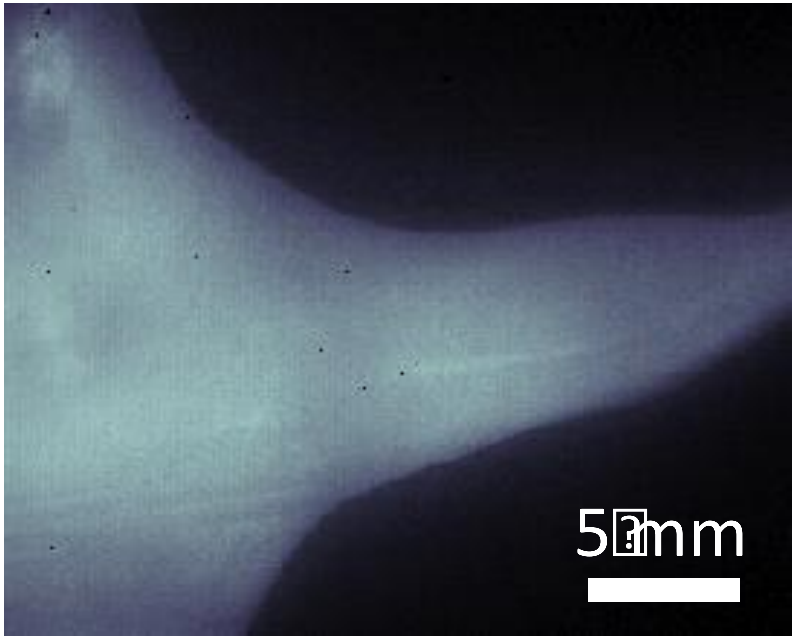


G. Hong, J. Lee, J. Cooke, H. Dai, **Nature Medicine**, 2012

NIR-II Imaging: Reduced Scattering

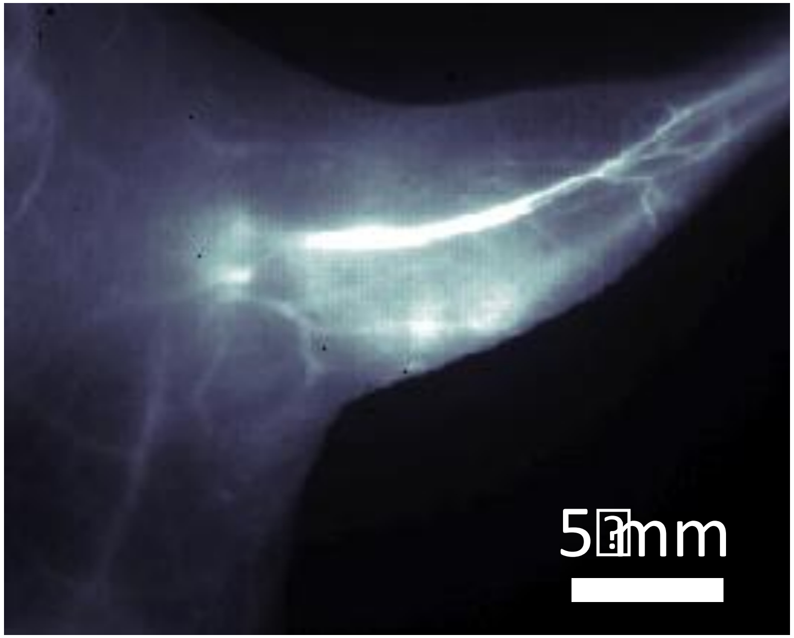
NIR-I

750-900 nm



NIR-II

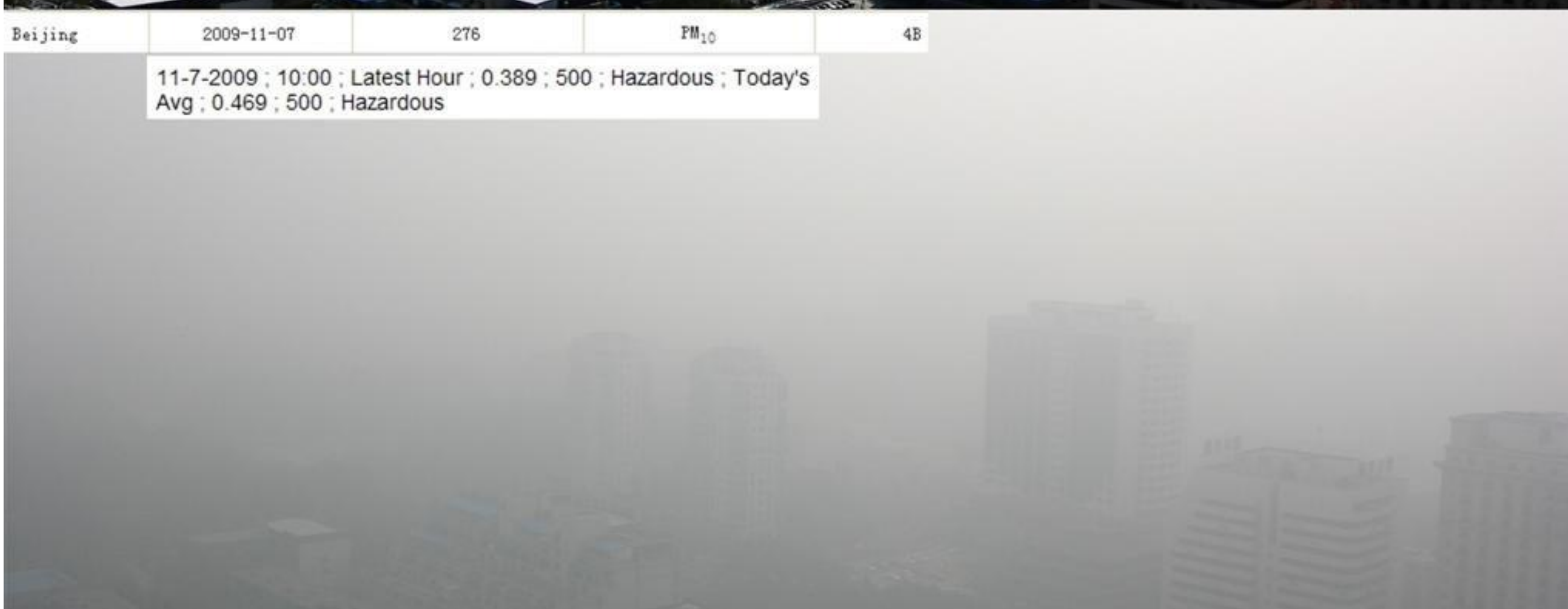
1000-1400 nm



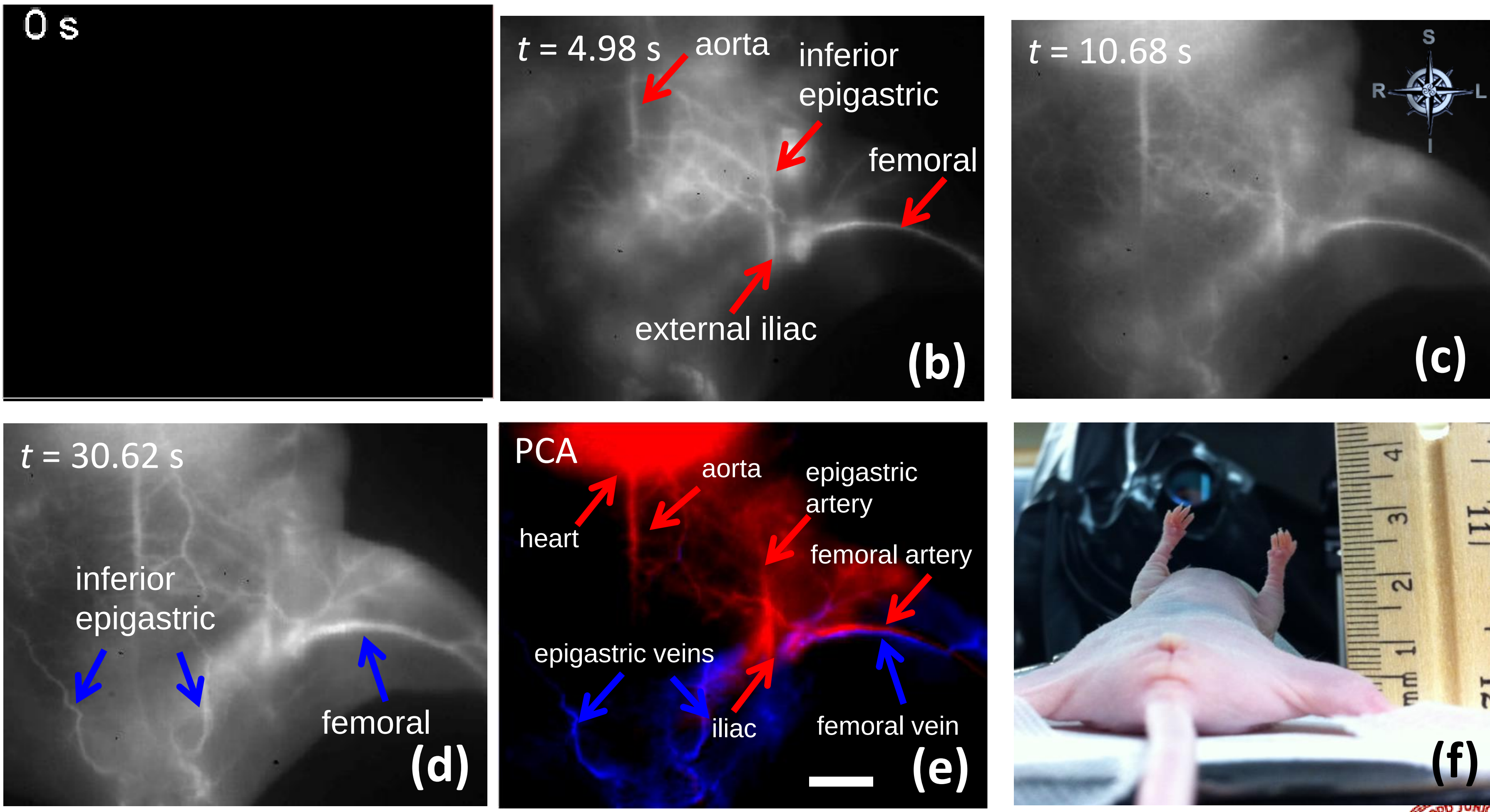
❖ Previous imaging modality: micro-CT, MRI

G. Hong, J. Lee, J. Cooke, H. Dai, **Nature Medicine**, 2012

Clear vs. Smoggy Day in Beijing

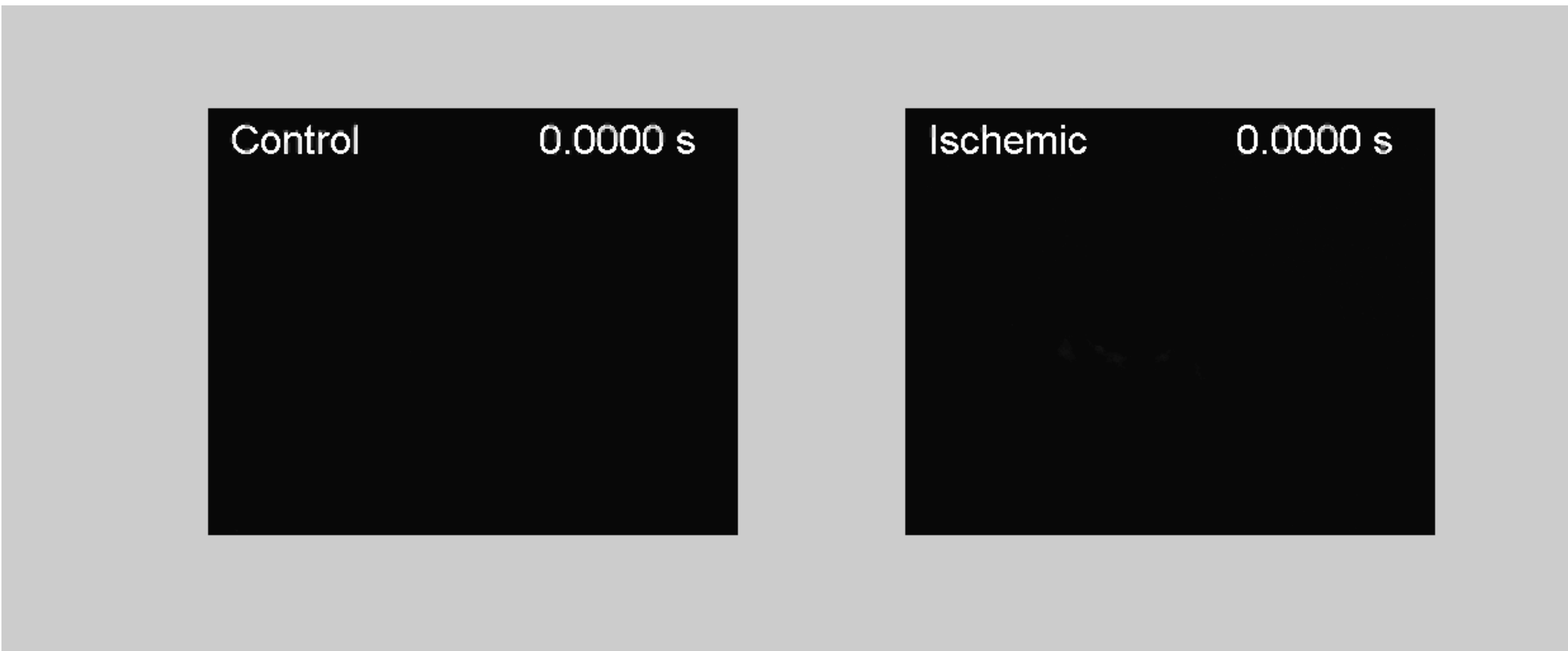


Sub-cm Deep Vessel Imaging & Differentiation



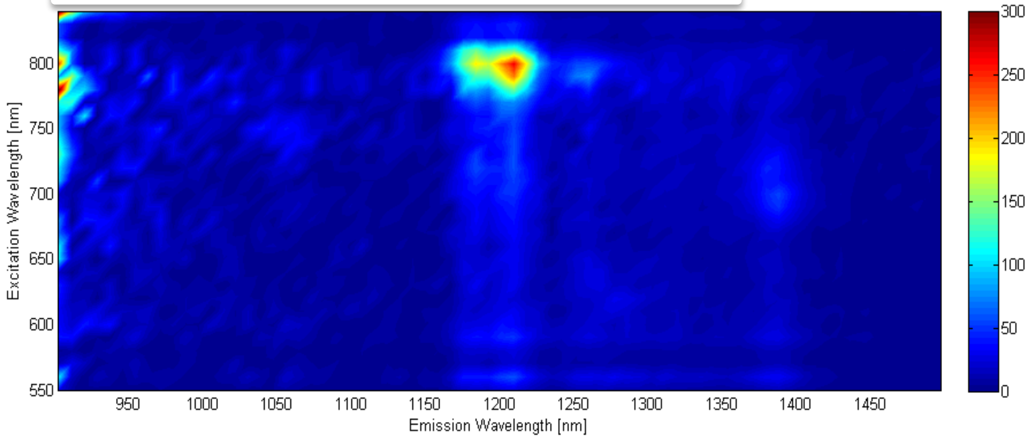
G. Hong, J. Lee, J. Cooke, H. Dai, **Nature Medicine**, 2012

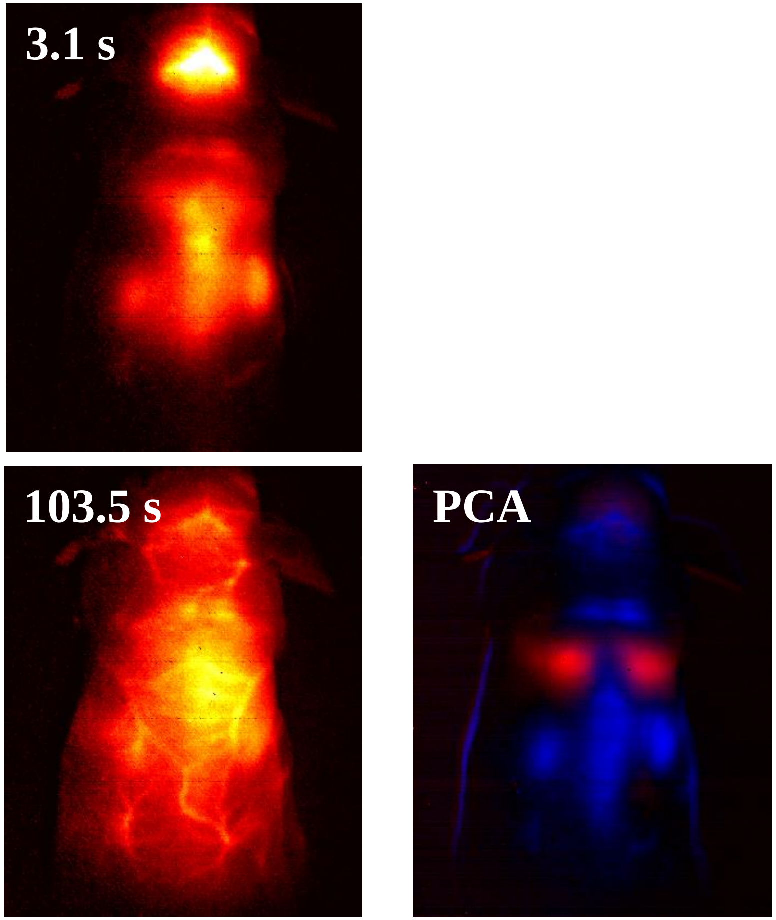
Video Rate Imaging of
Blood Flow in Healthy vs. Ischemic Hindlimb



Chirality Separated SWNT for NIR-II Imaging

(12,1)-enriched SWNTs



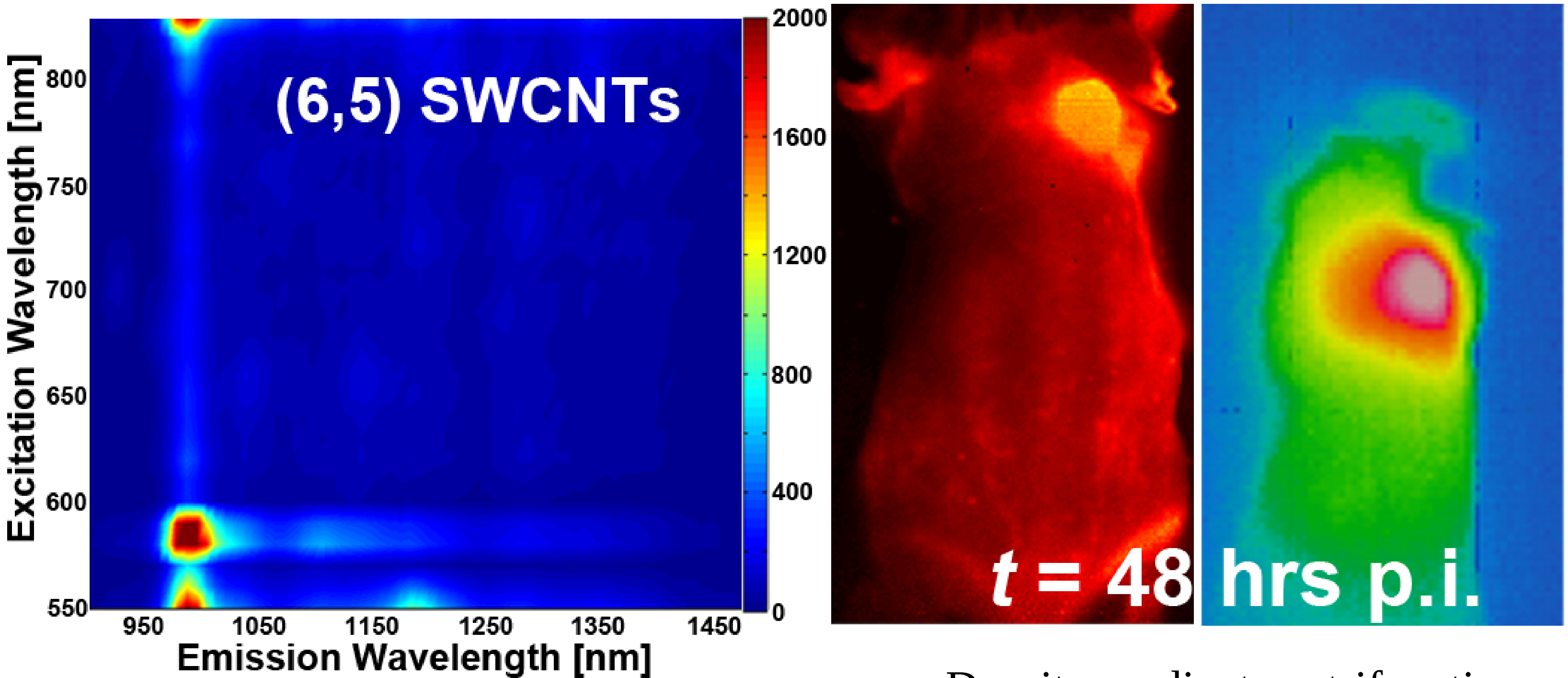


S. Diao, H. Dai, et al., **J. Am. Chem. Soc.** 2012

Gel filtration separation method:

F. Hennrich, M Kappes and coworkers @ Karlsruhe Institute of Technology

Chirality Separated SWNT for Tumor Photothermal Therapy

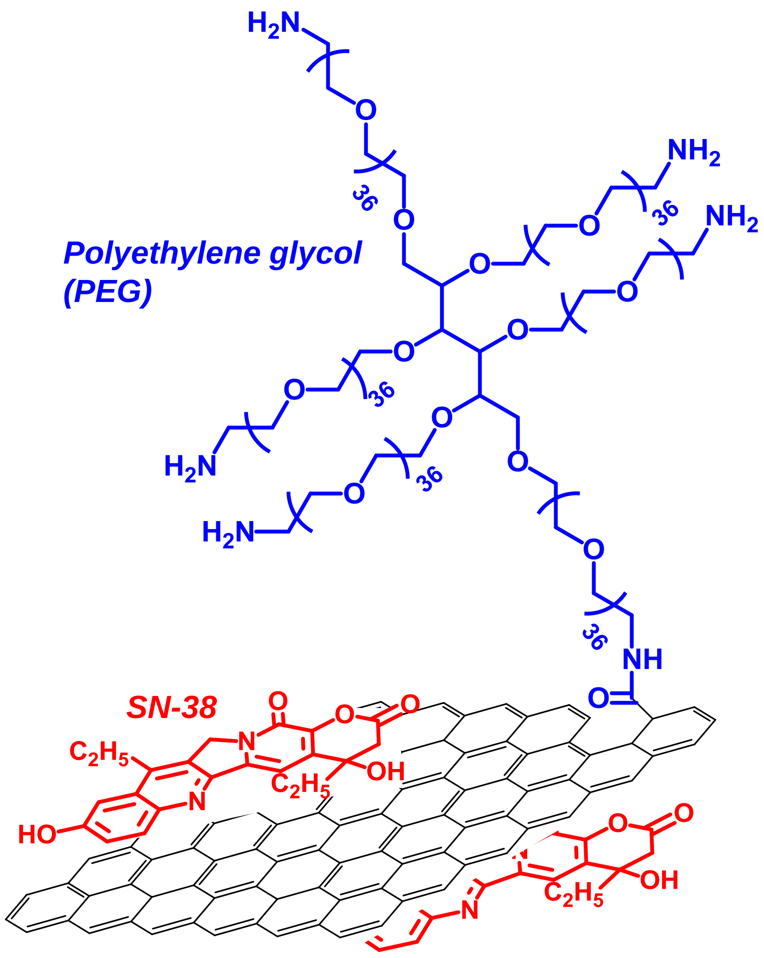


Density gradient centrifugation method: M. Hersam, Northwestern.

- Ultra-low dosage: ~ 4 µg of (6,5) SWCNTs per mouse (0.254 mg/kg)
- Dual imaging & photothermal therapy

A. Antaris, et. al., **ACS Nano,** 2013

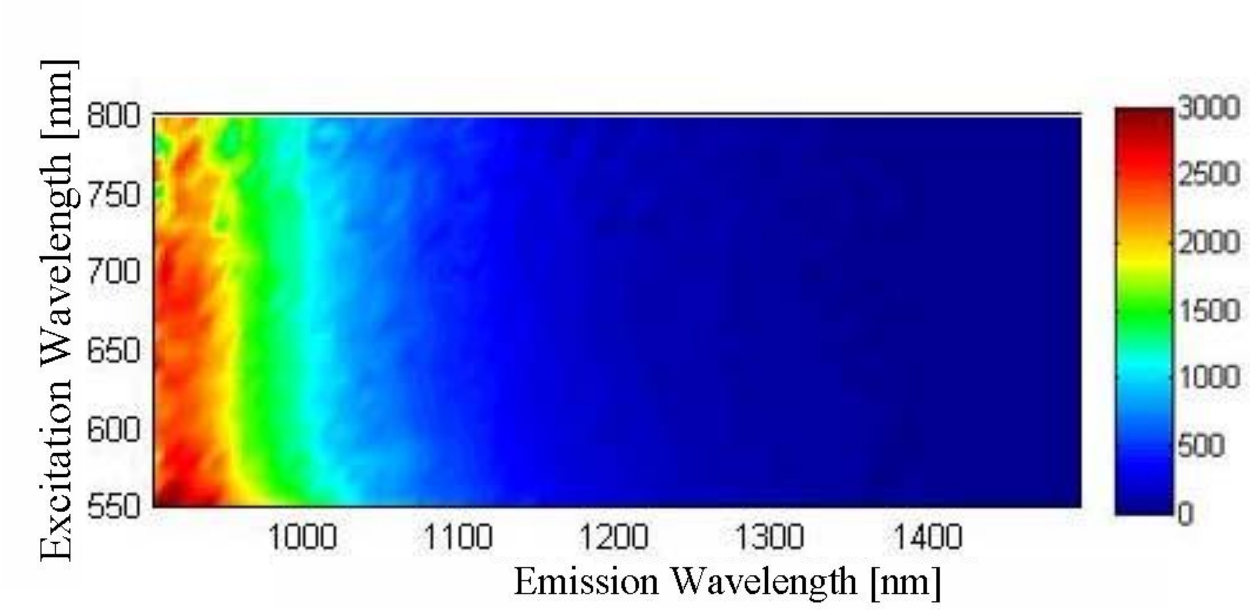
Graphene for Biology and Medicine



- π-stacking of SN38 cancer drug graphene oxide for drug delivery.
- SN38: a potent, insoluble cancer drug

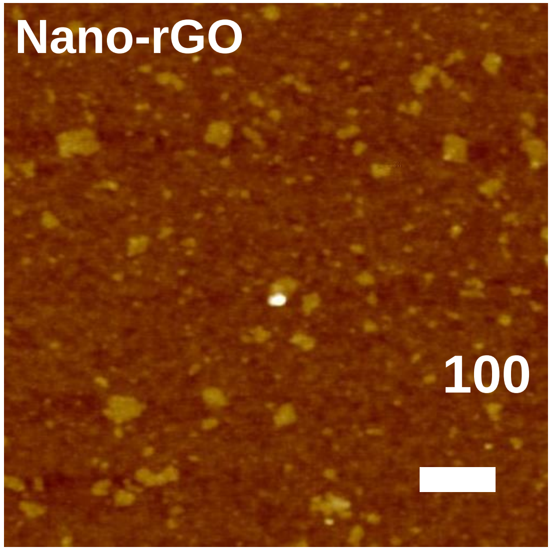
Z. Liu, H. Dai et al., **J. Am. Chem. Soc.** 2008

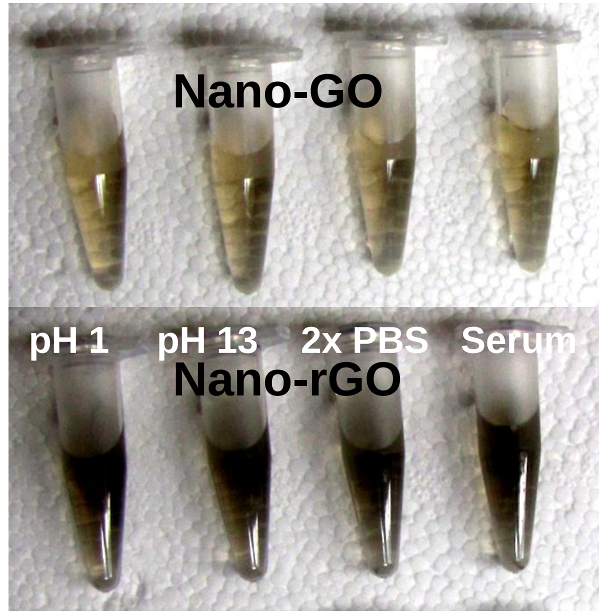
Graphene Oxide Are Fluorescent in NIR-I & NIR-II

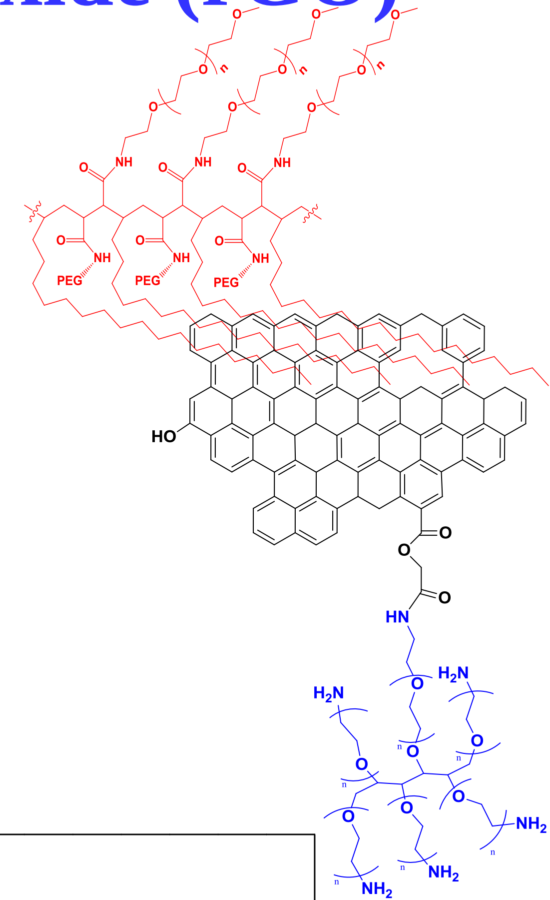


X. Sun, H. Dai, et. al. **Nano Res**, 1, 203-212 , 2008.

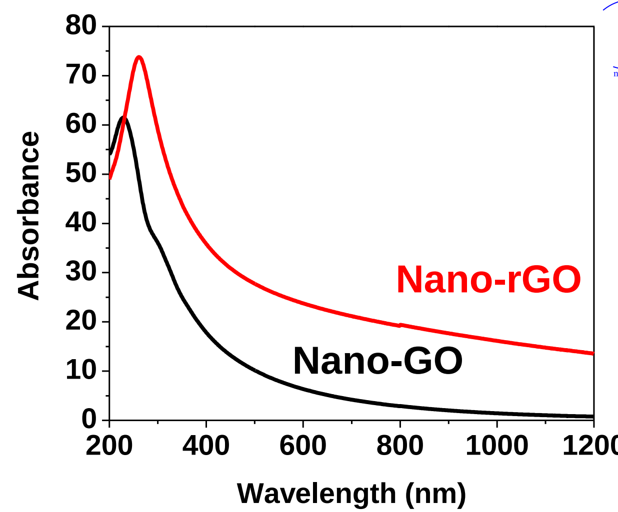
Nano-Sized Reduced Graphene Oxide (rGO)





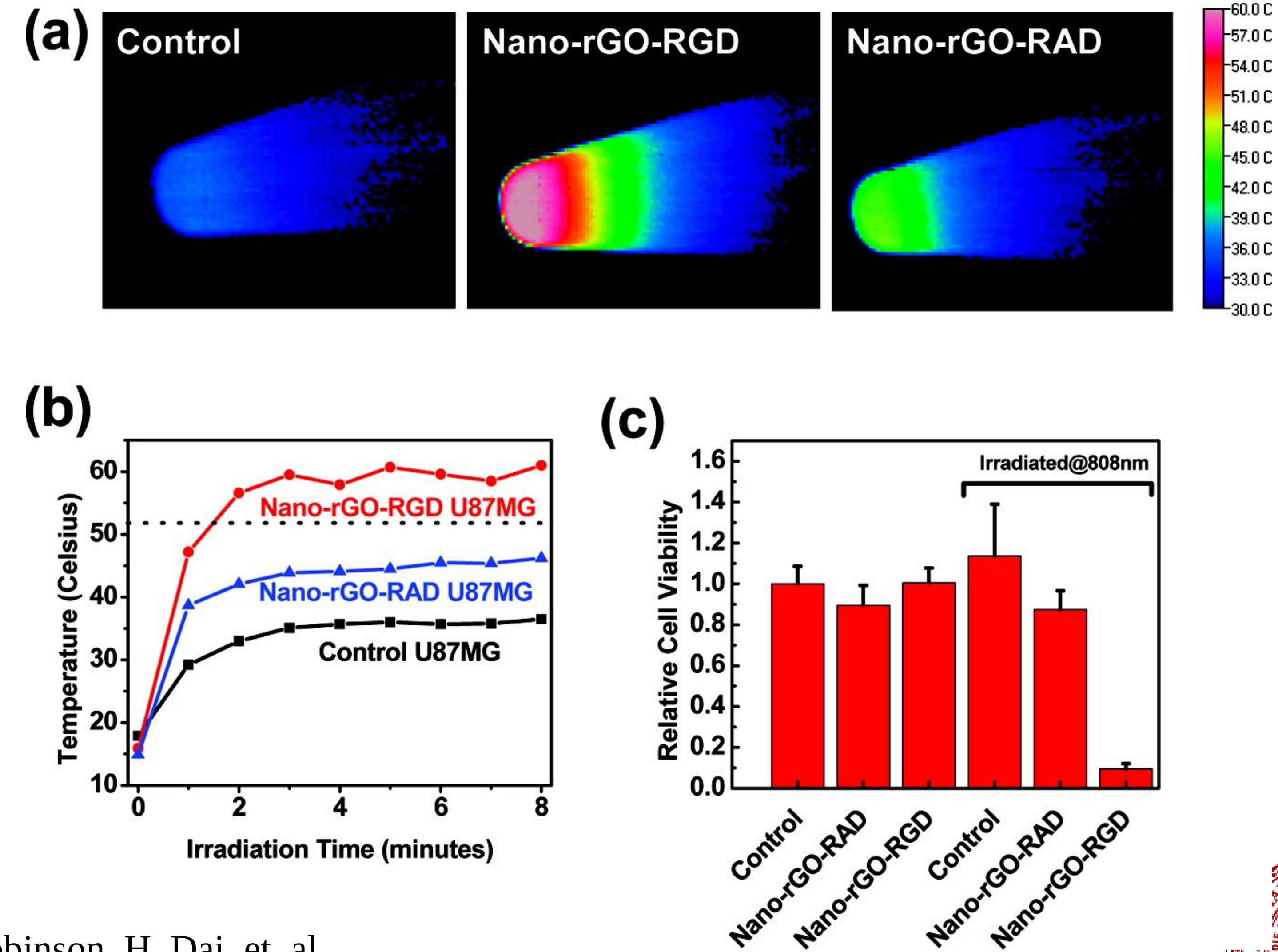


- ➢ Non-covalent functionalized nano-rGO
- ➢ Biocompatible
- ➢ High optical absorbance in NIR
- ➢ Useful for photothermal therapy



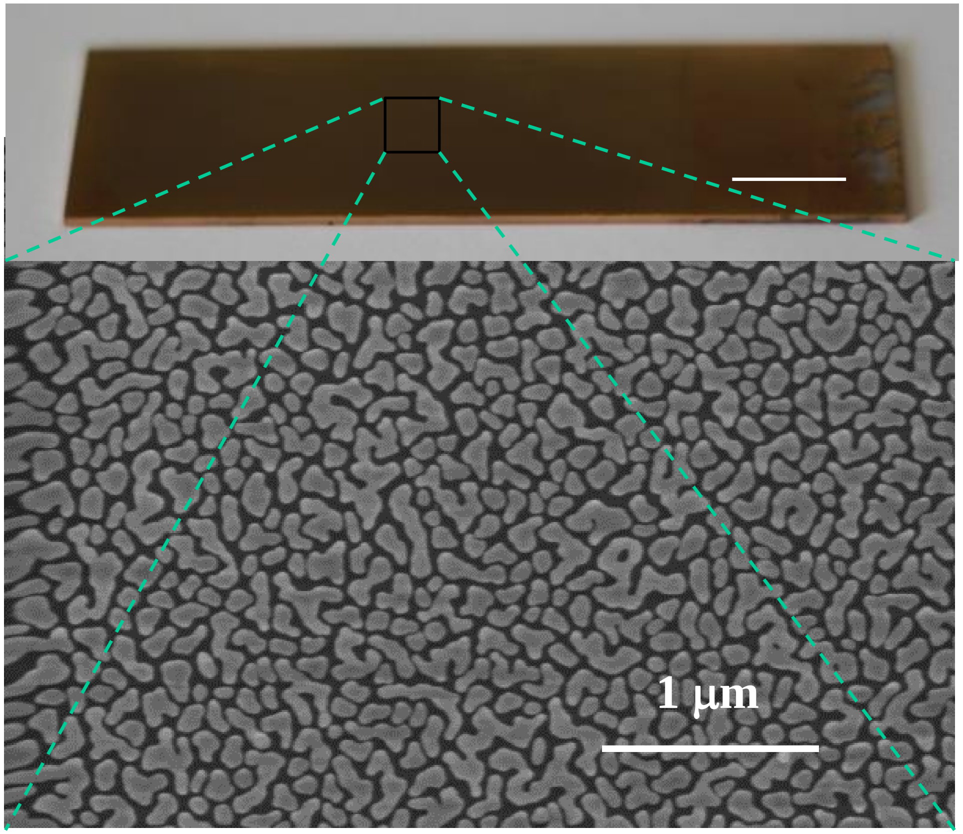
Joshua T. Robinson, H. Dai, et. al.
J. Am. Chem. Soc. 133, 6825-6831, 2011.

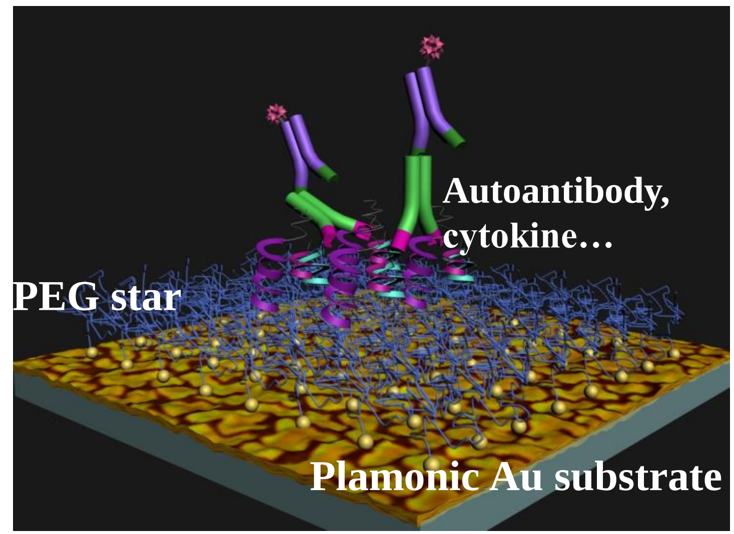
Photothermal Ablation of Cancer Cells With RGD Peptide/Nano-rGO Complex



Joshua T. Robinson, H. Dai, et. al.
J. Am. Chem. Soc. 133, 6825-6831, 2011.

A Nanostructured Gold Platform for Biological Assays (ELISA, Microarrays…)

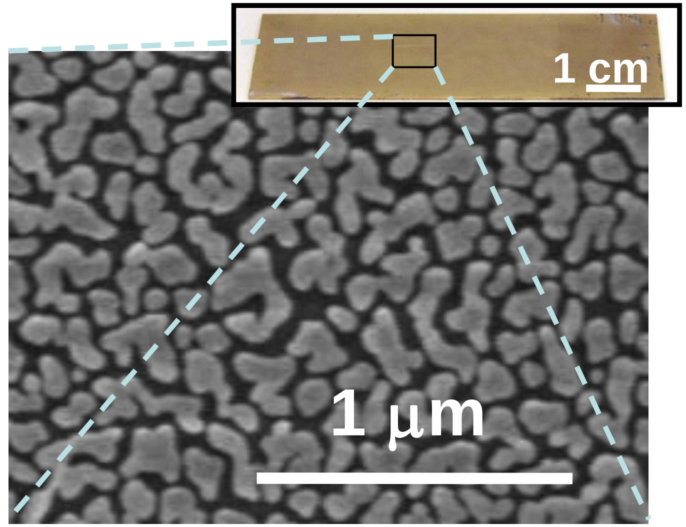


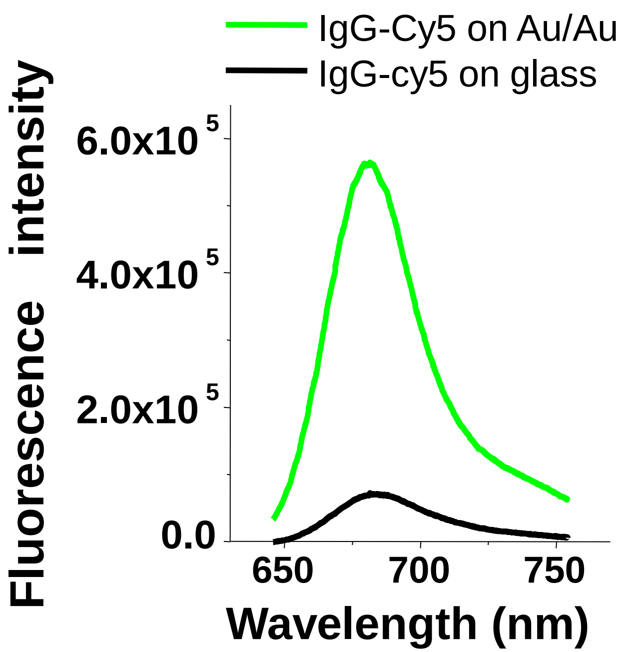


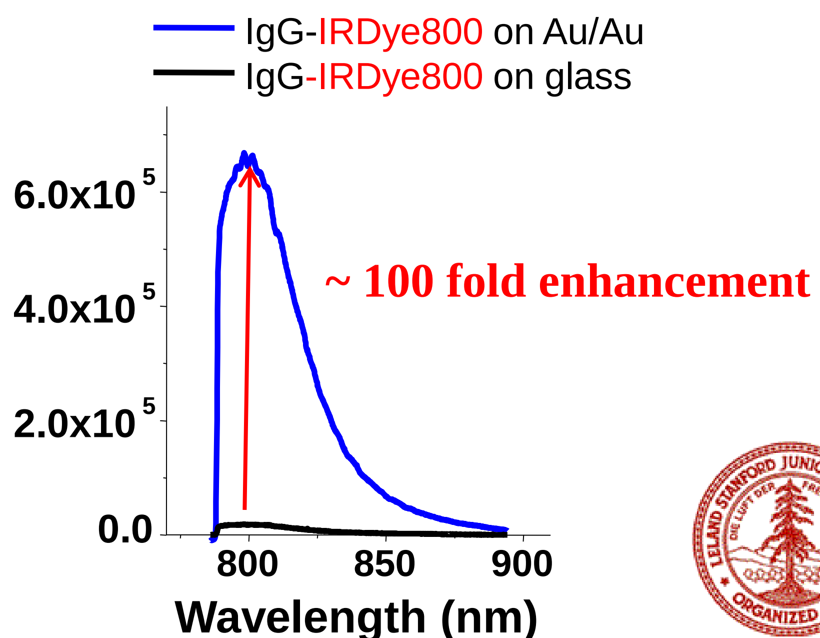
- Many nano-gaps
- Gold film surface plasmon resonance in NIR range

S. Tabakman et al., ***Nature Comm.*** 2011

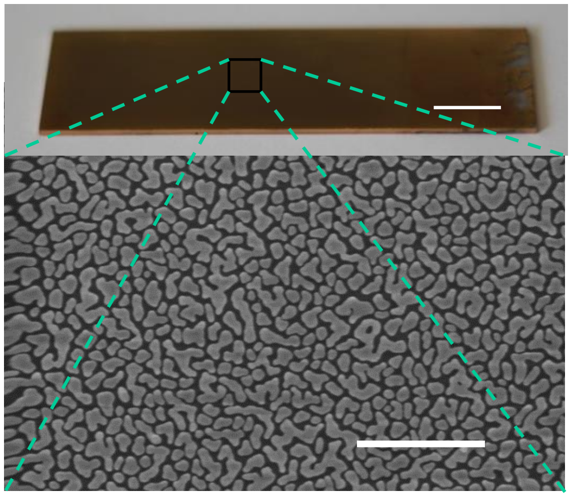
Fluorescence Enhancement of NIR Dyes

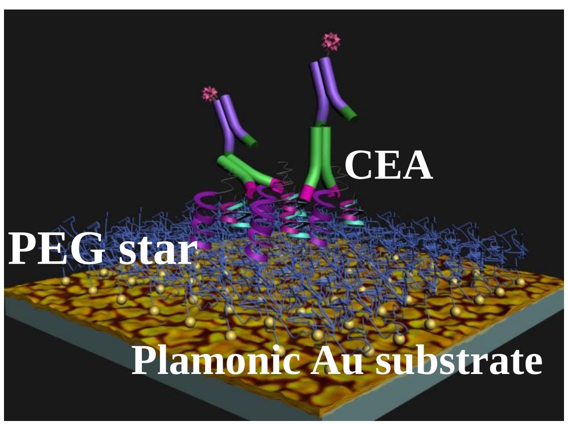






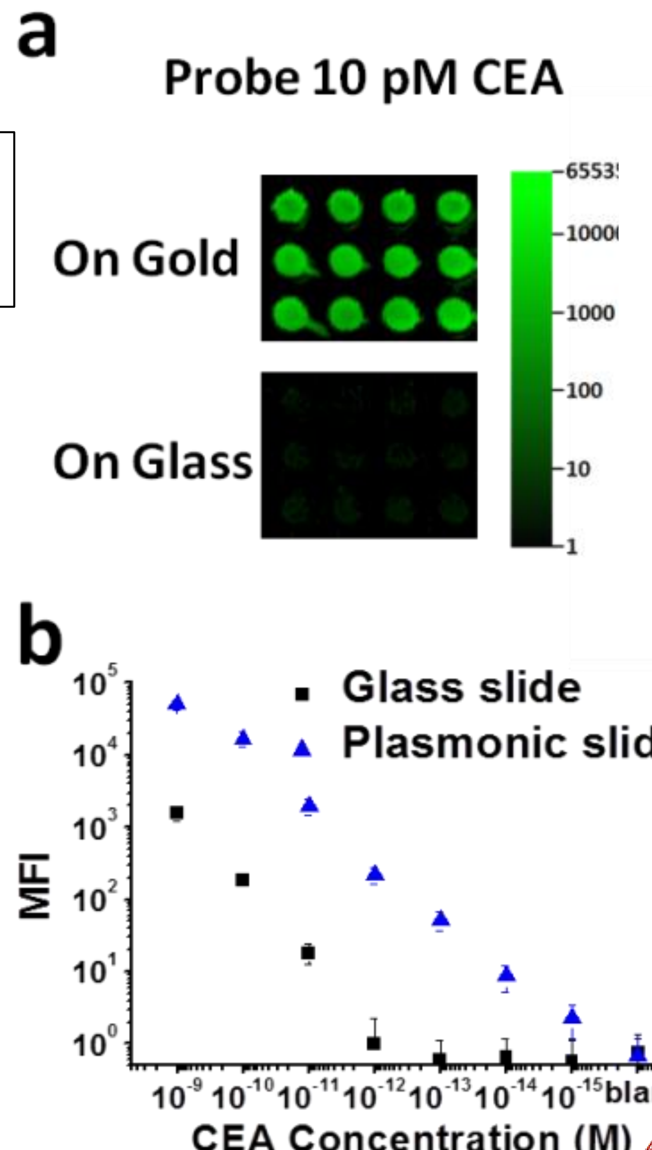
Cancer Biomarker Detection on Au Platform Towards Early Cancer Diagnosis





- **fM sensitivity**
- **6 logs**

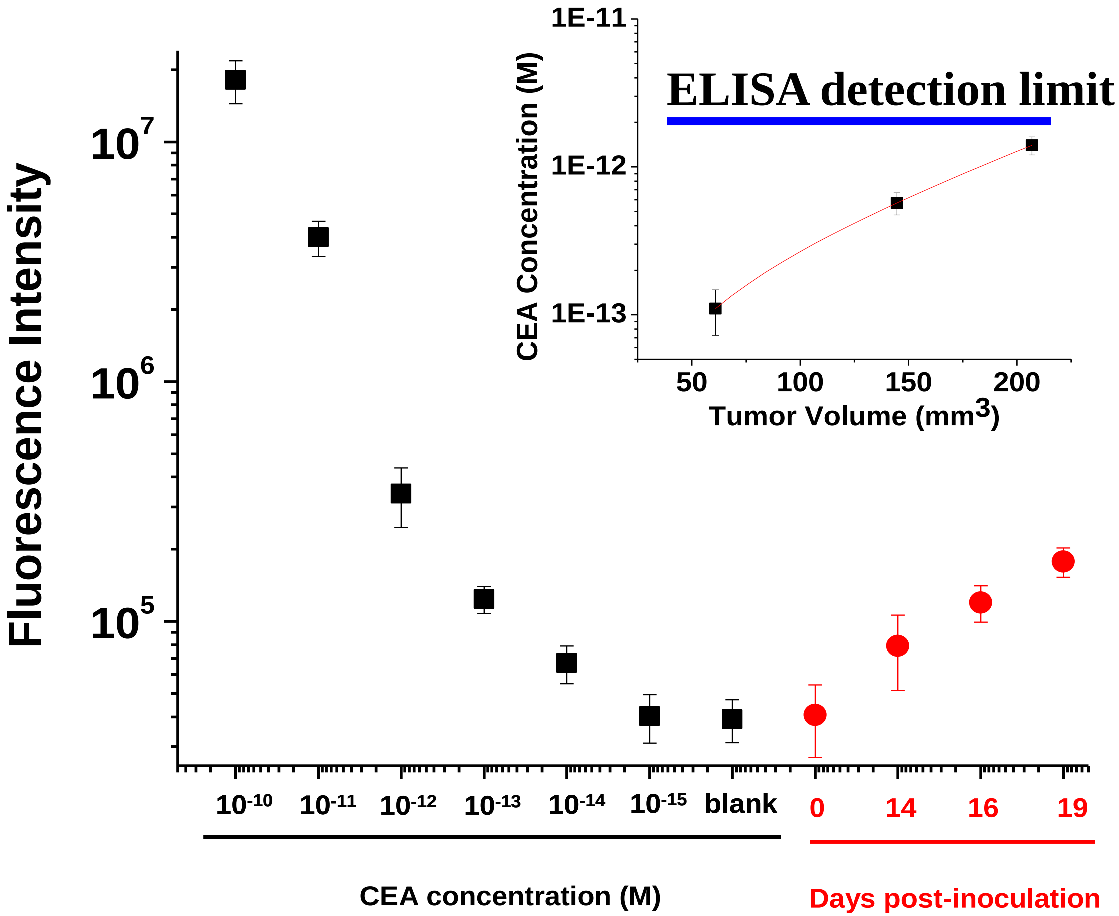
- **Branched PEG-star blocking: minimal non-specific binding**
- **Plasmonics: boosts specific signal**

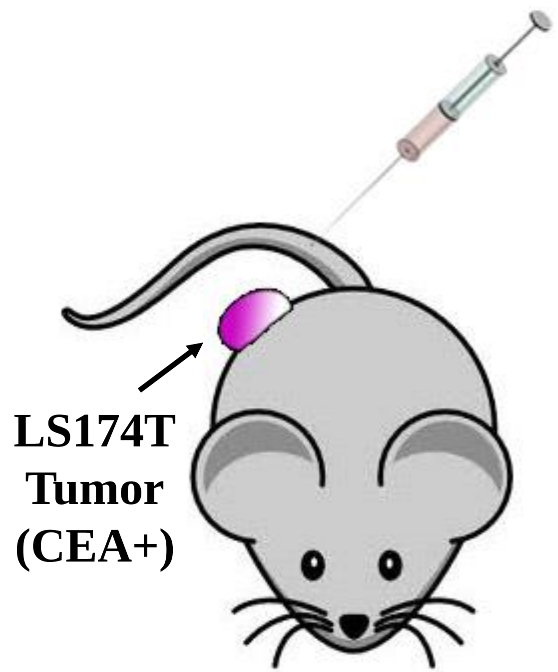


S. Tabakman et al., ***Nature Comm.*** 2011

Cancer Biomarker Detection from Tumor-Bearing Animals

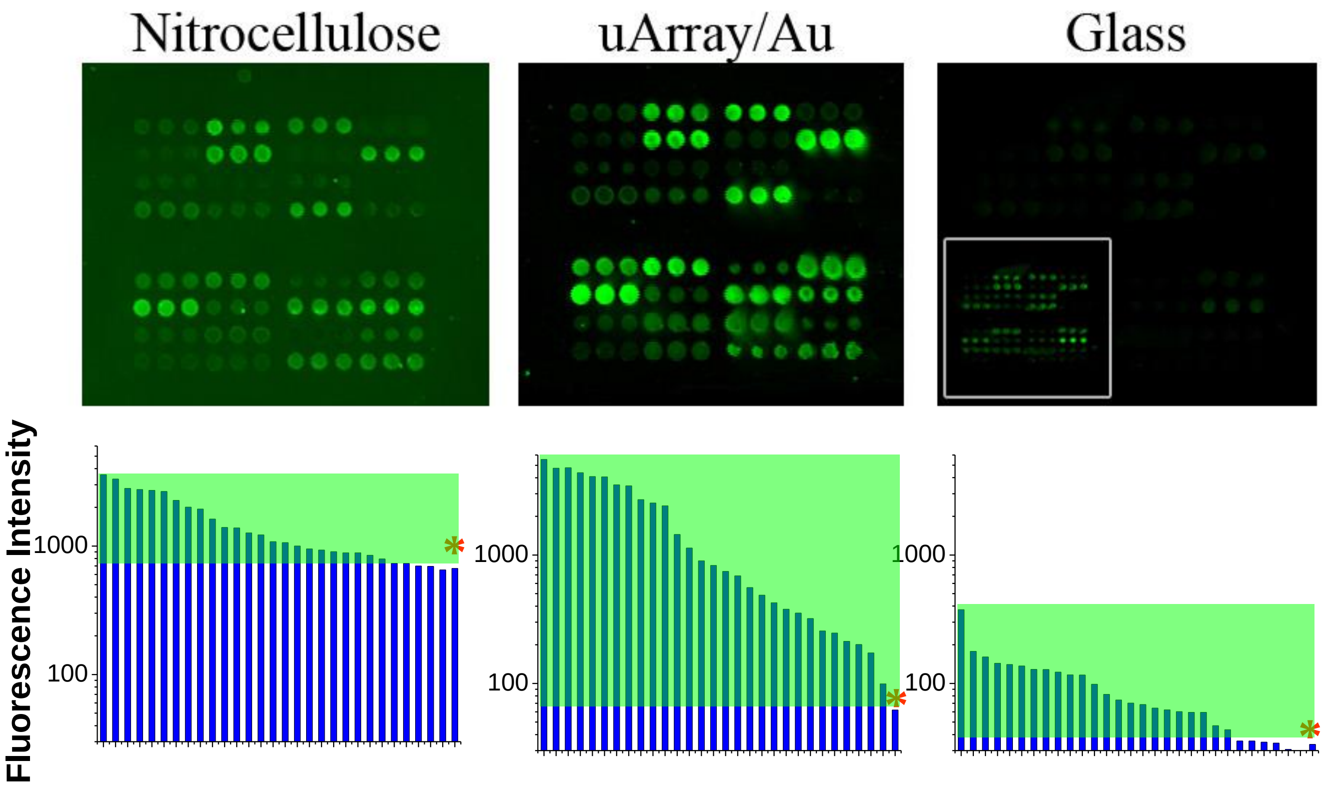
- **CEA in the serum of LS174T xenograft mouse models measured on plasmonic Au/Au films**





S. Tabakman, *Nature Comm.* 2011

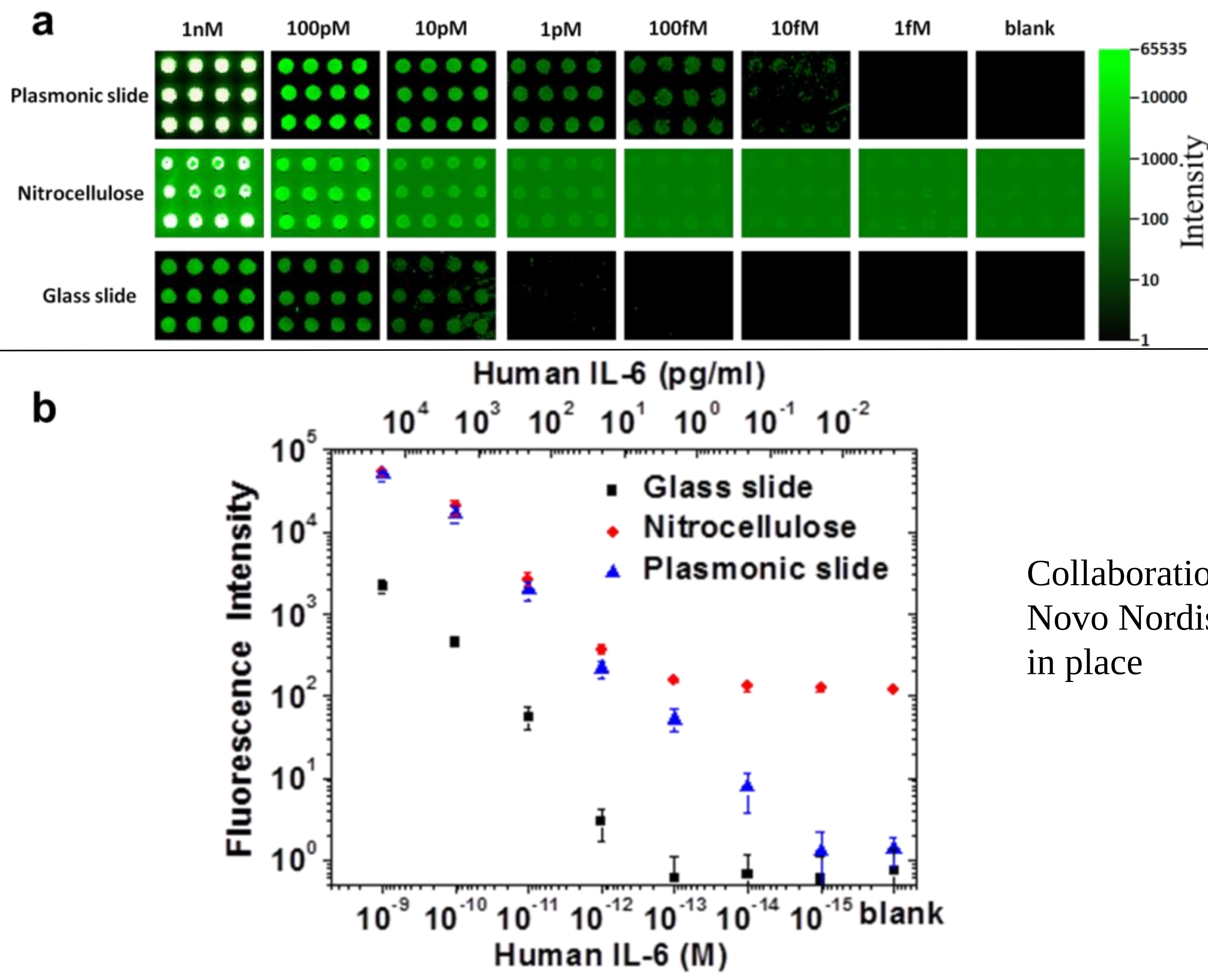
Multiplexed Autoantibody Detection on Gold



With Dr. P.J. Utz,
Stanford Medical School

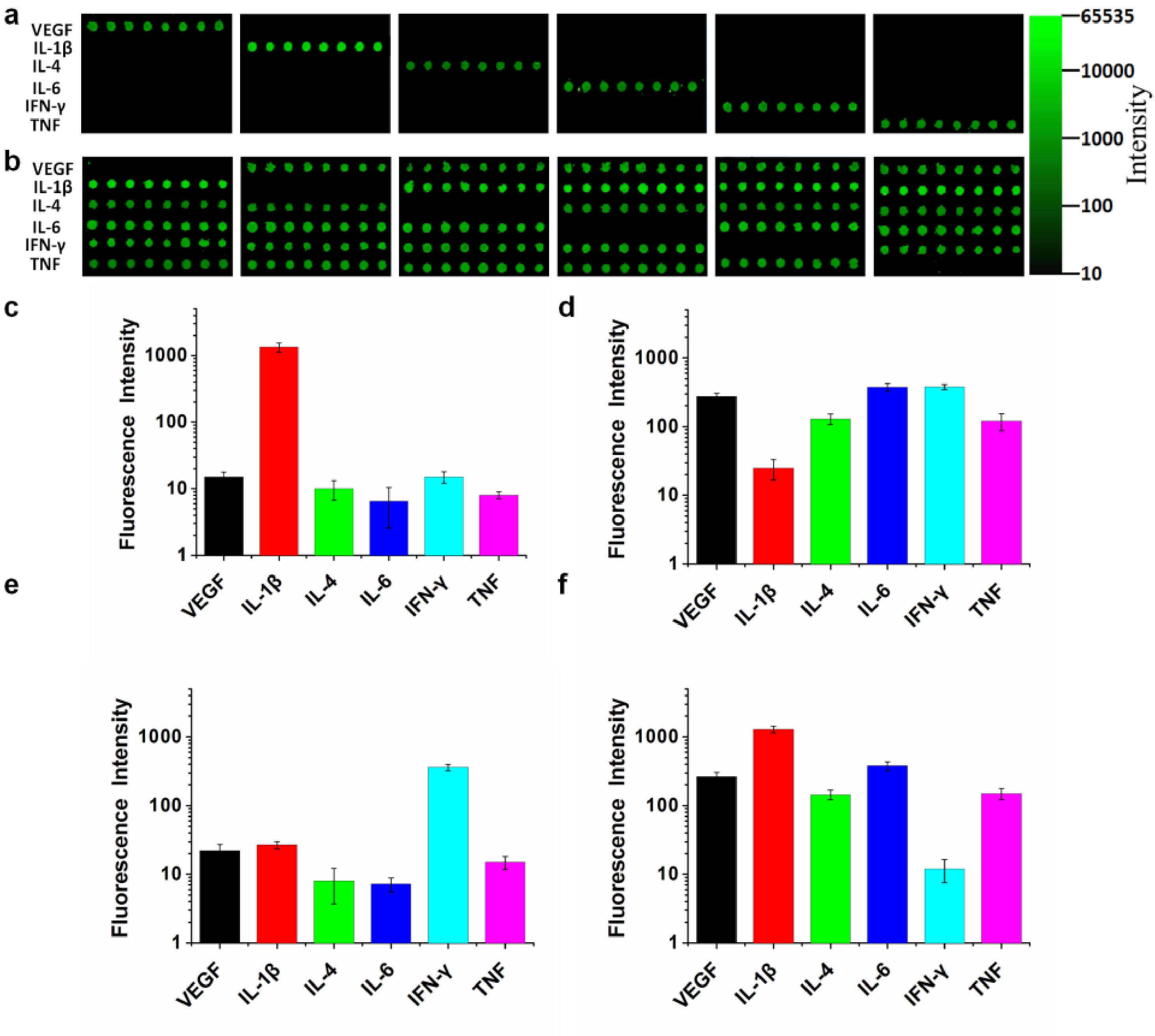
- Much broader dynamic range on gold.
- Lower detection limit down to fM
- <u>Highly sensitive antigen microarrays</u>

Human Cytokine (IL-6) Detection on Gold

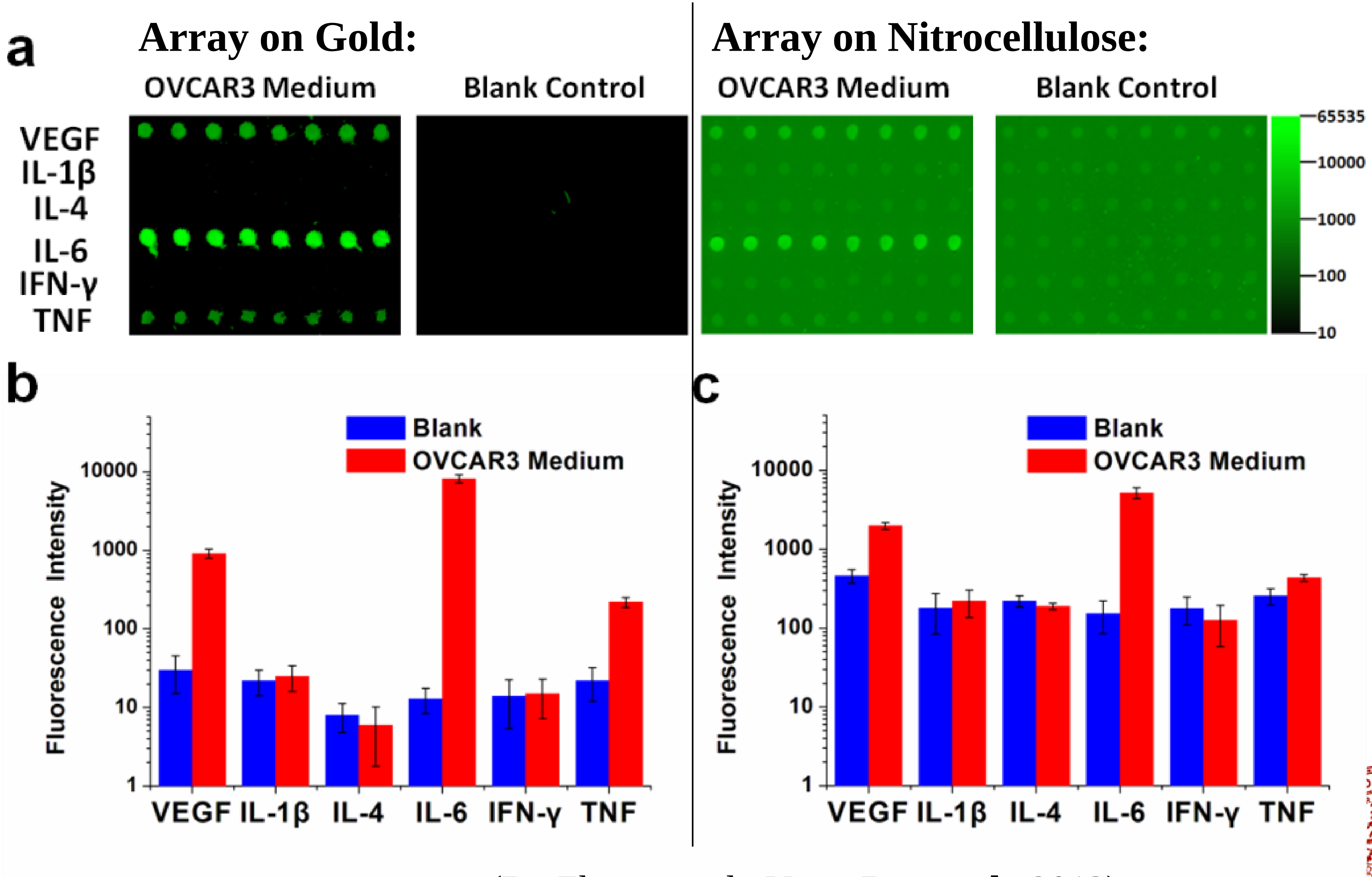


Collaboration with
Novo Nordisk
in place

Selective Cytokine Detection on Gold



Multiplexed Detection of Cytokines Secreted by Cancer Cells



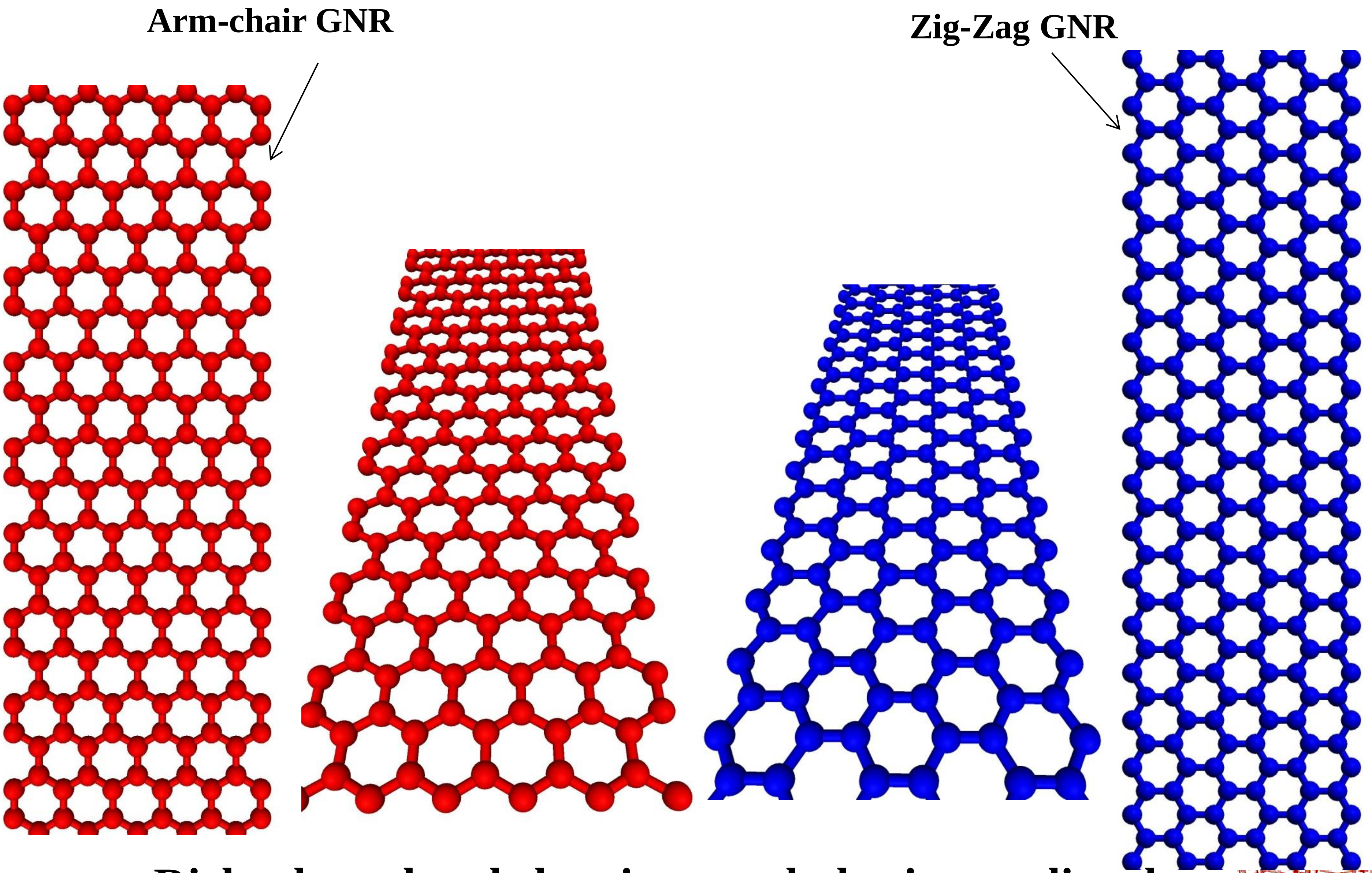
(Bo Zhang, et al., **Nano Research**, 2013)

A New Platform for Biological Detection

- A plasmonic Au platform for ELISA & microarray detection.
- Sensitivity: down to ~ 1 fM (0.01 pg/ml) level.

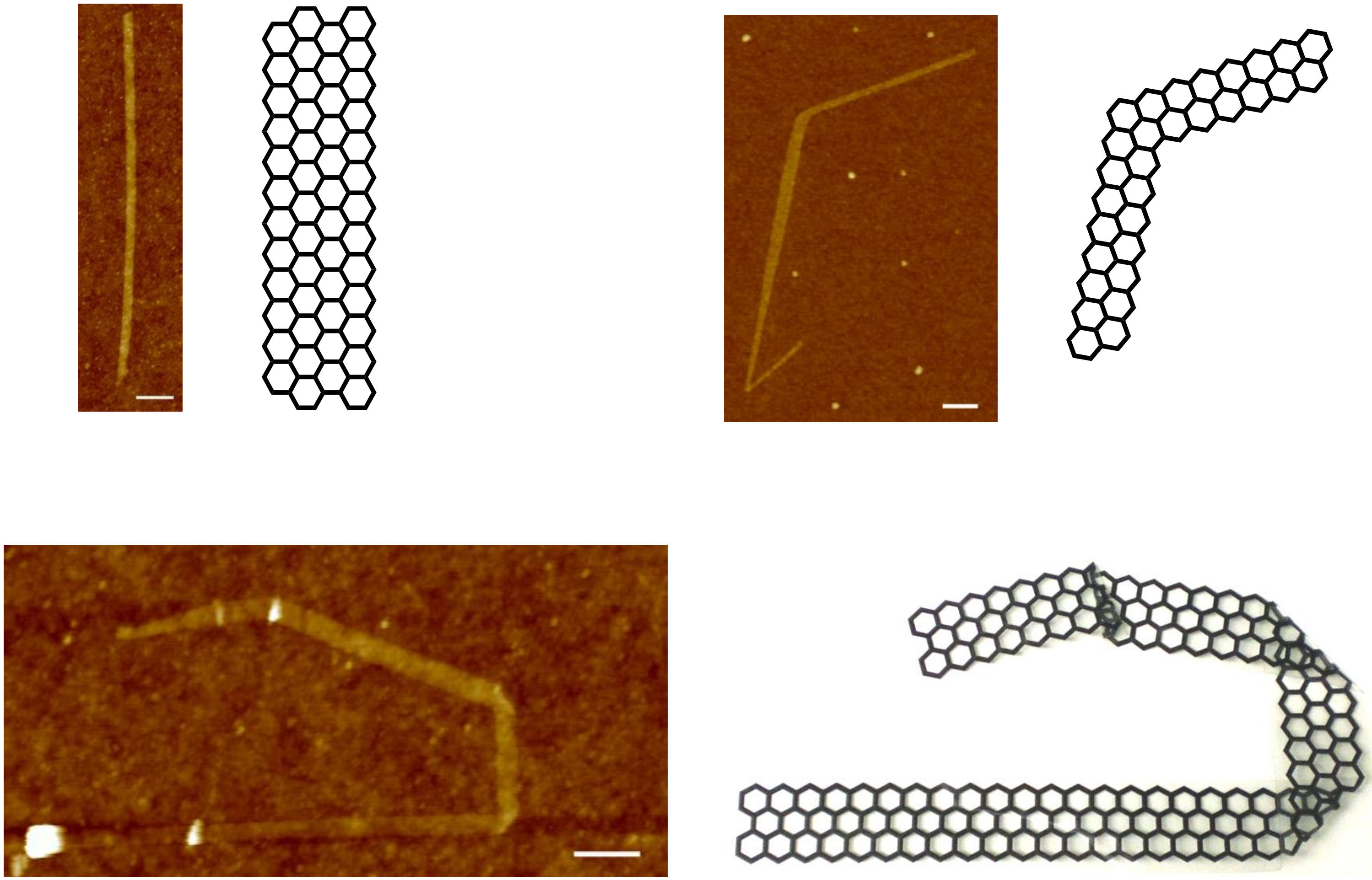
- Dynamic range spans > 6 orders of magnitude.
- Single assay or multiplexed.
- Uses small volume of serum/blood or other samples.
- Simple & low cost
- Compatible with existing instrumentation.
- Protein arrays, cytokine arrays, antigen arrays, peptide, carbohydrate, DNA, RNA…
- For genomics, proteomics research and diagnostics.

Graphene Nanoribbons (GNR)



Rich edge related chemistry and physics predicted

Chemical Synthesis of Graphene Nanoribbons



(Xiaolin Li, Xinran Wang, et al., **Science,** 2008**)**

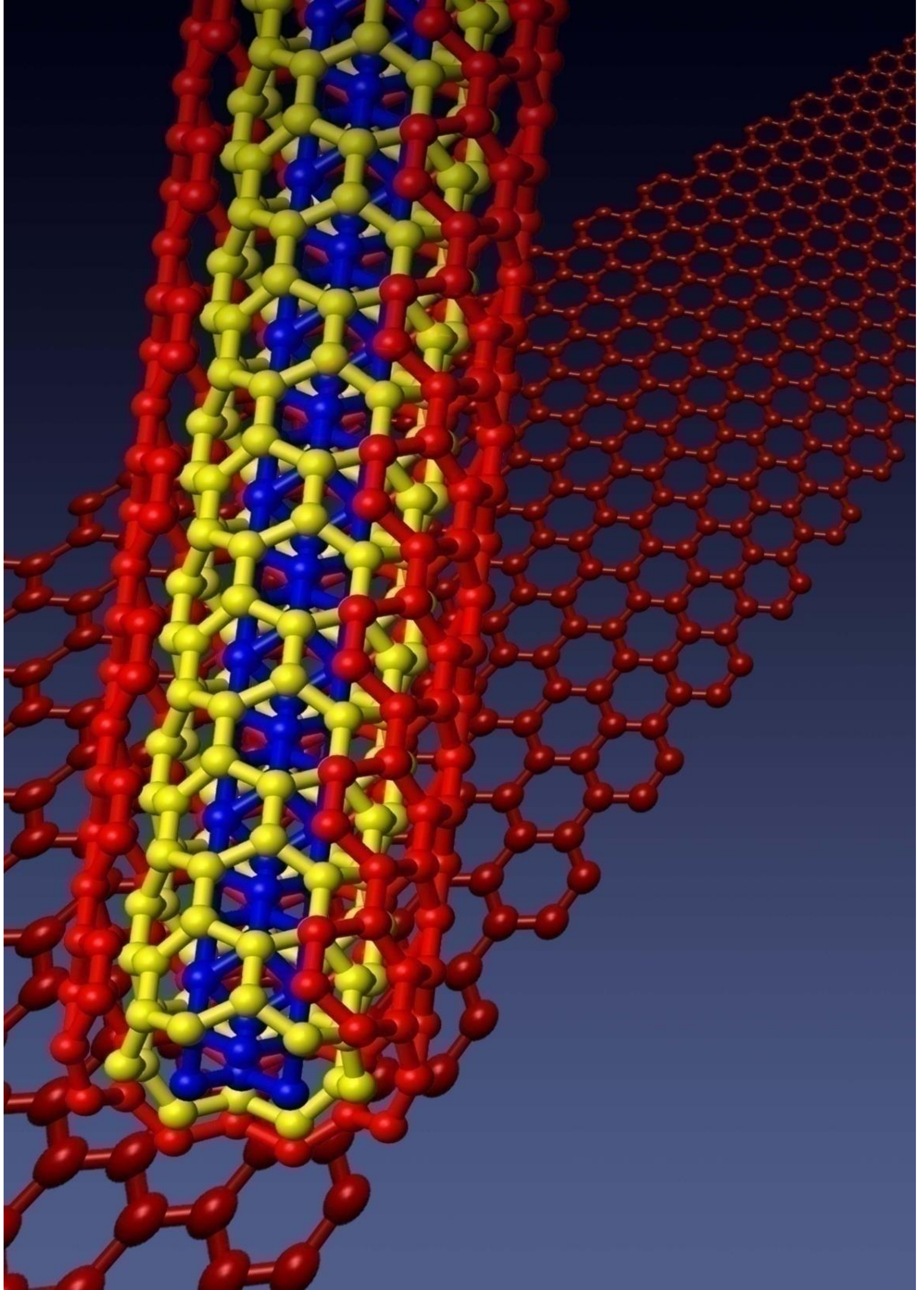
Unzip Nanotubes

For

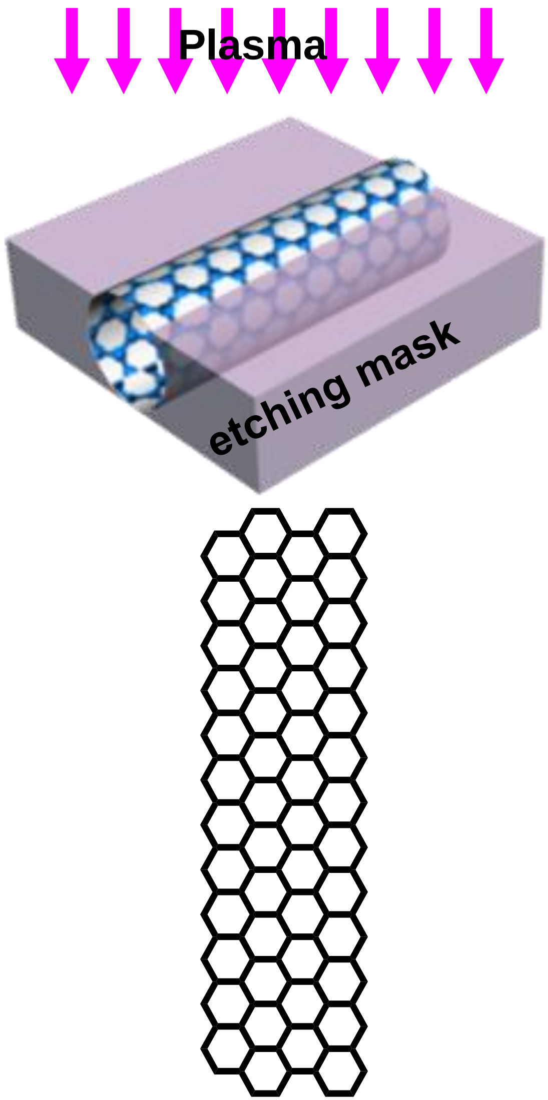
Graphene Nanoribbons

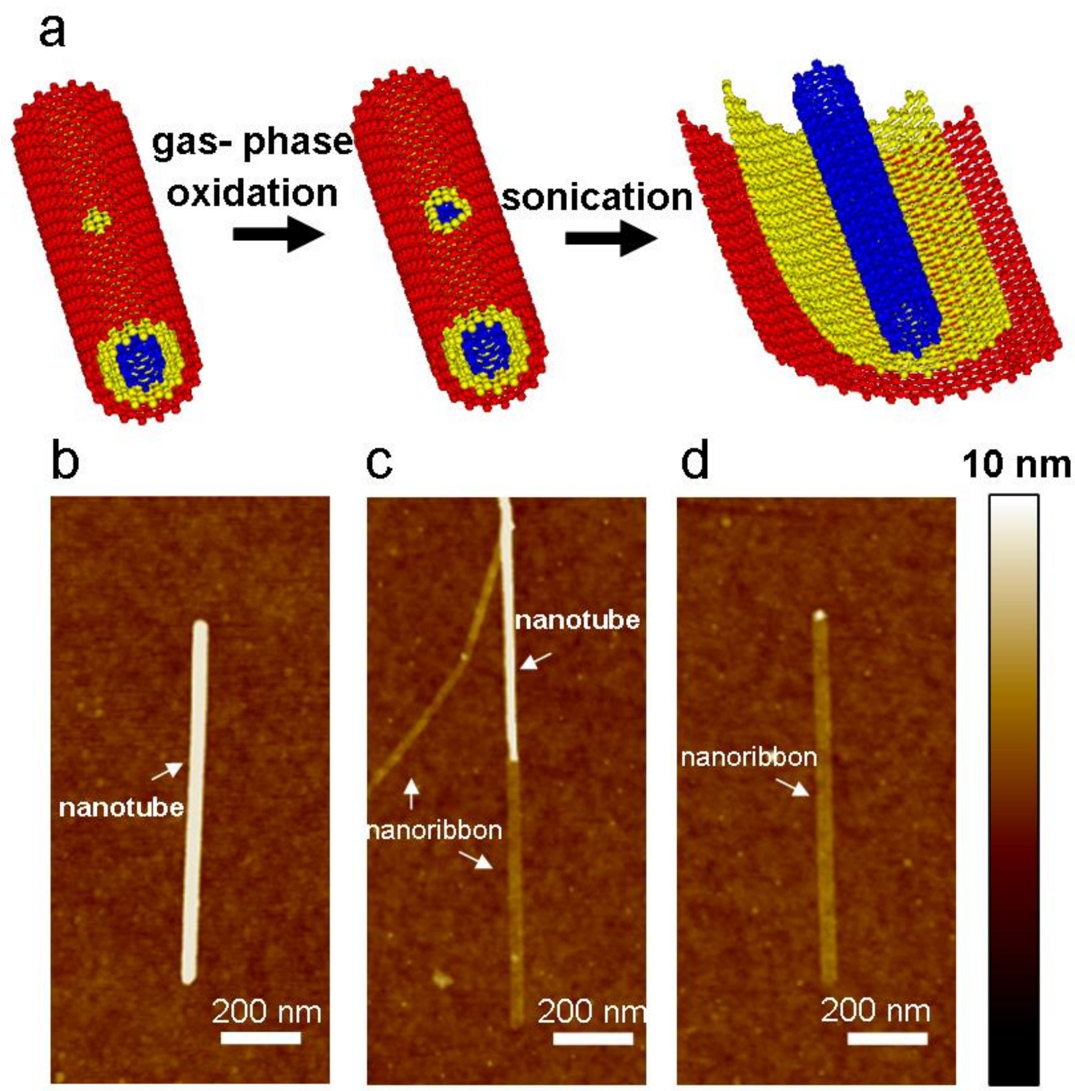
(L. Jiao, et. al., **Nature**, 2009;

J. Tour group, **Nature**, 2009)



Nanoribbons Synthesis by Physical and Chemical Means

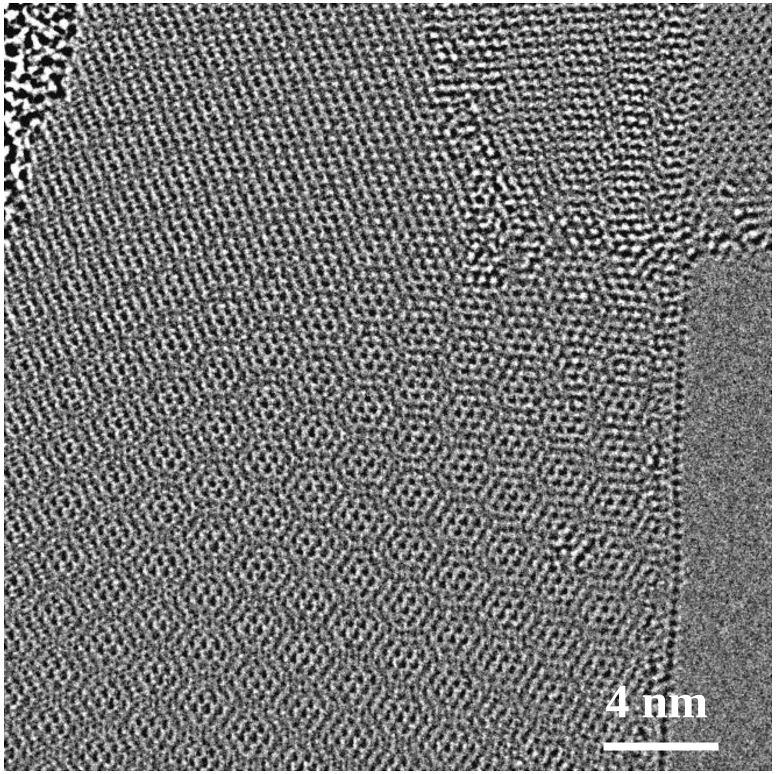


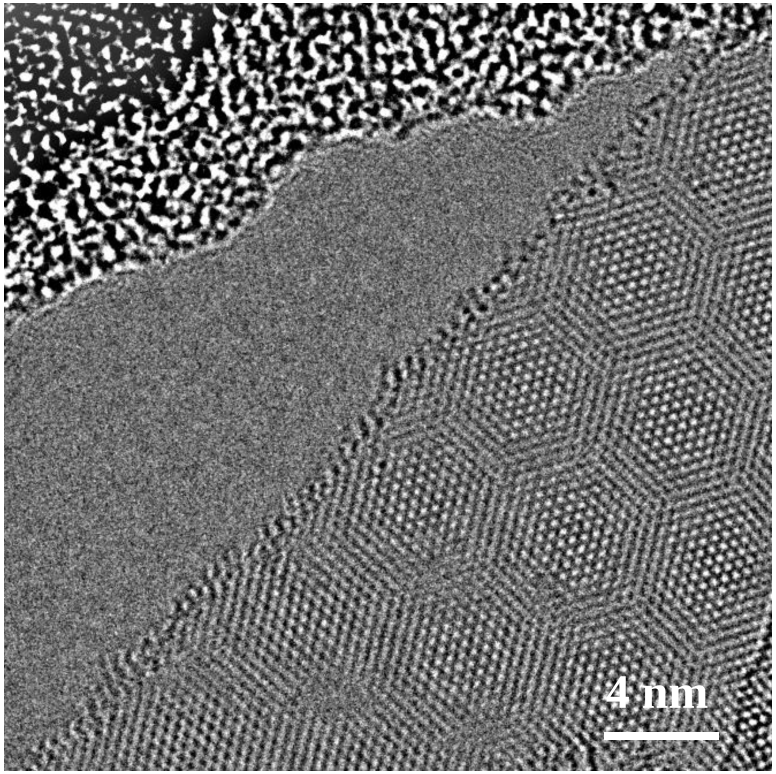


L. Jiao, et. al., **Nature**, 2009;

L. Jiao, et. al., **Nature Nano**, 2010;

High Quality Nanoribbons with Smooth Edges



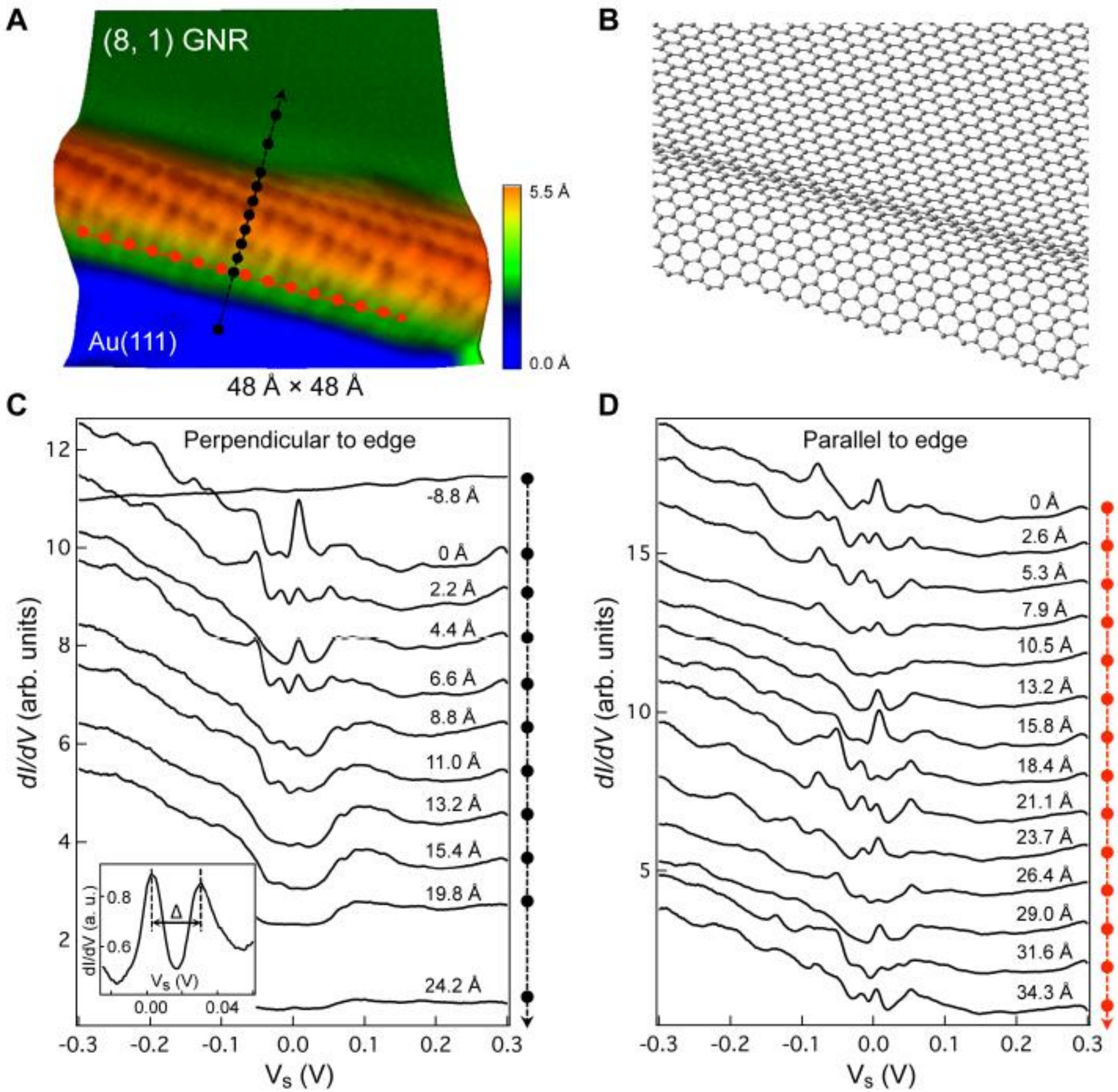


- Moire pattern between layers

- Smooth edges, little roughness.

L. Xie (with K. Suenaga group) et al., **JACS**, 2011

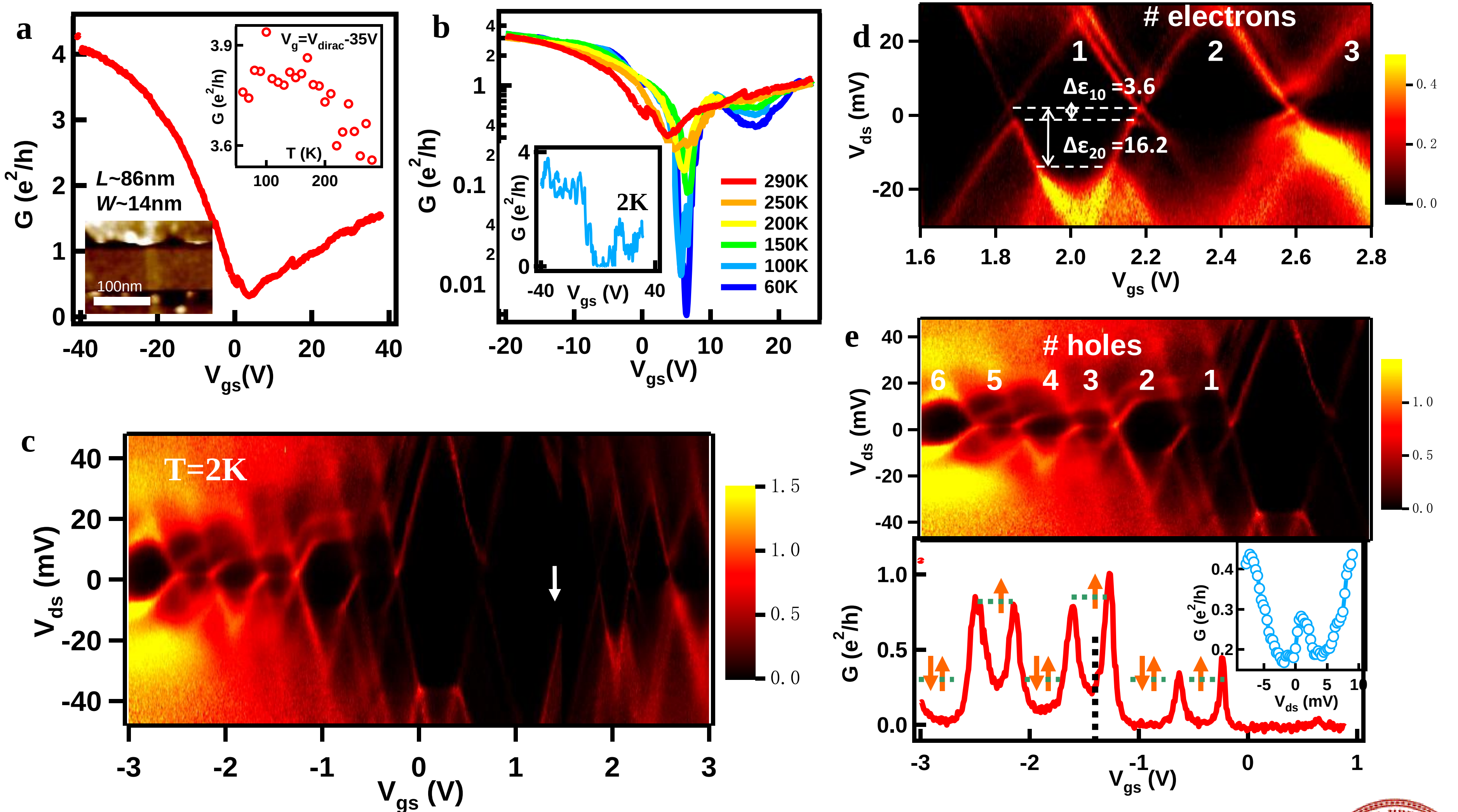
STM of Graphene Nanoribbons (GNR)



- Highly Smooth edges
- Observation of magnetic edge states at nanoribbon edges

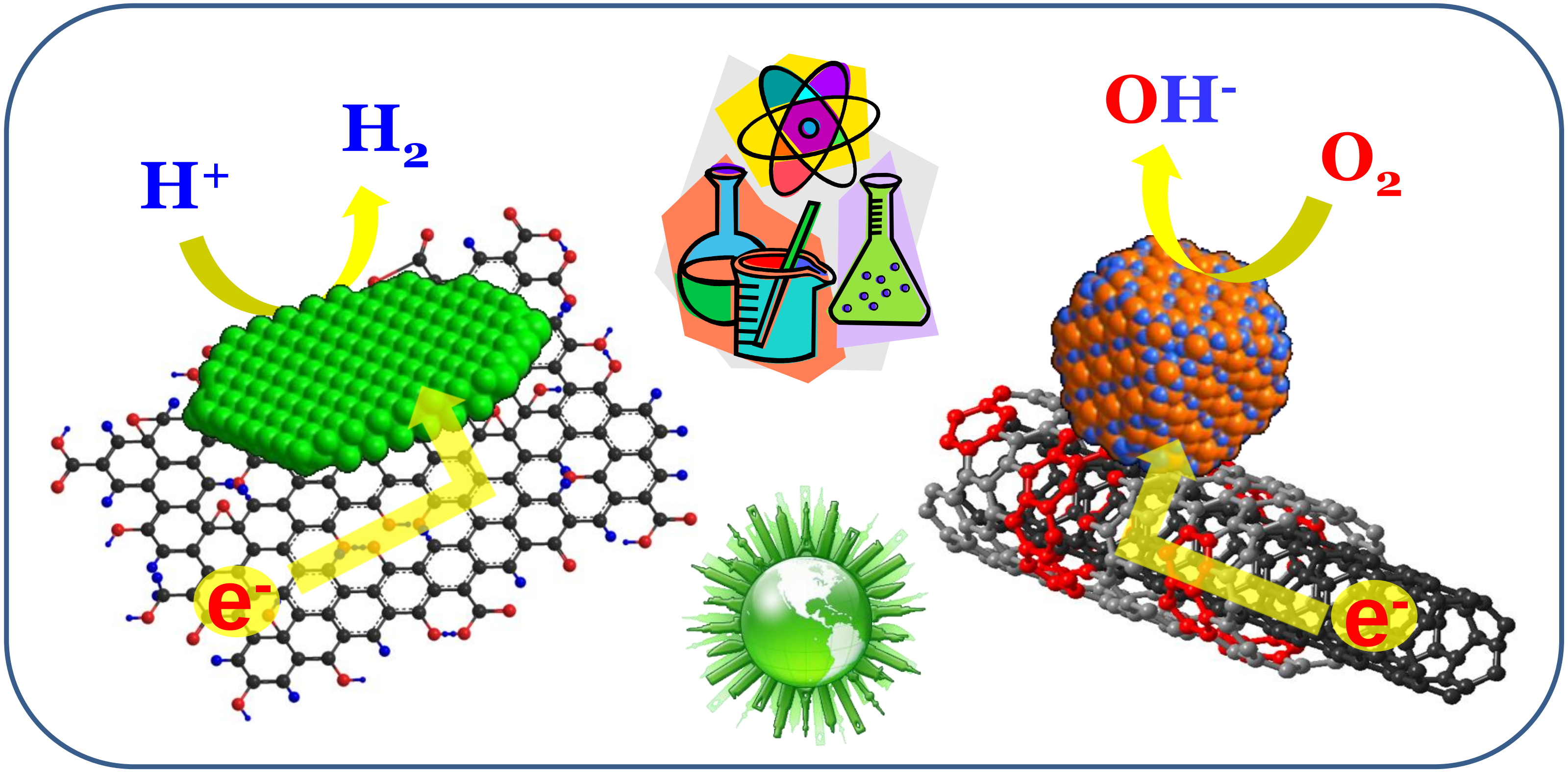
Crommie, Dai, Louie groups, **Nature Physics**, 2011

Quantum Transport of High Quality Nanoribbons at 1.5 K



(Xinran Wang et al., **Nature Nano**, 2011)

Growth of Inorganic-NanoCarbon Hybrid for Energy Storage and Electrocatalysis



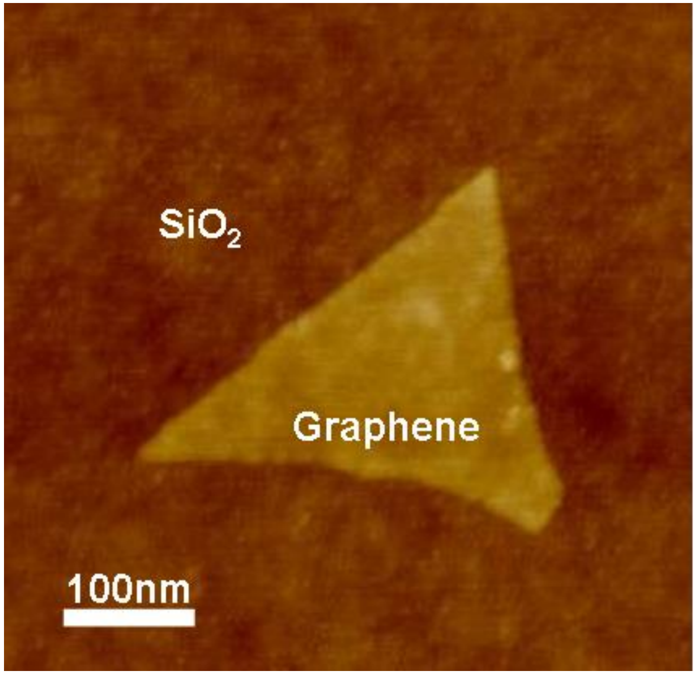
- High activity and rate capability.
- Durable.
- Low cost; non-precious metal based

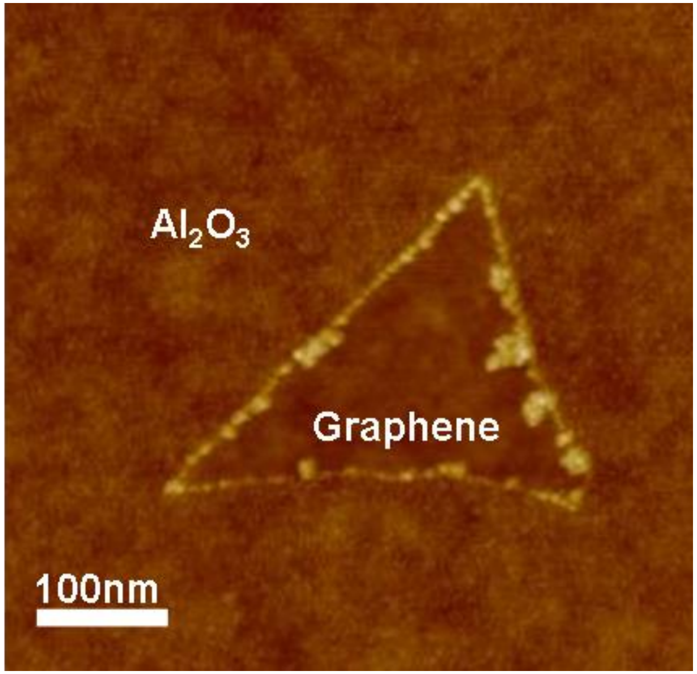
(H. Wang et. al., **Chem. Rev.,** 2013)

(Y. Liang et. al., **JACS (perspective),** 2013)

ALD Growth of Metal Oxide on Graphene

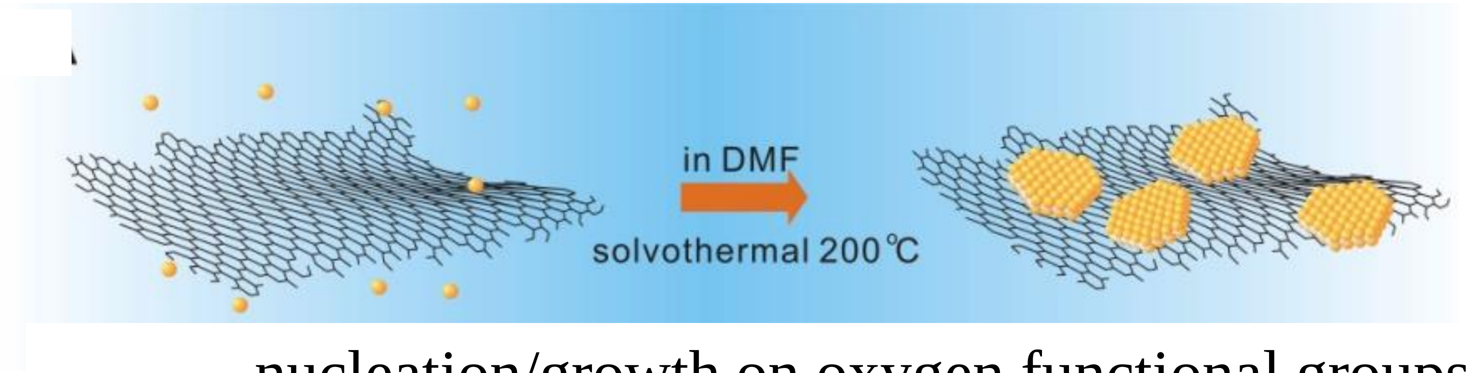
(X. Wang, H. Dai, et al. **JACS**, 2008)



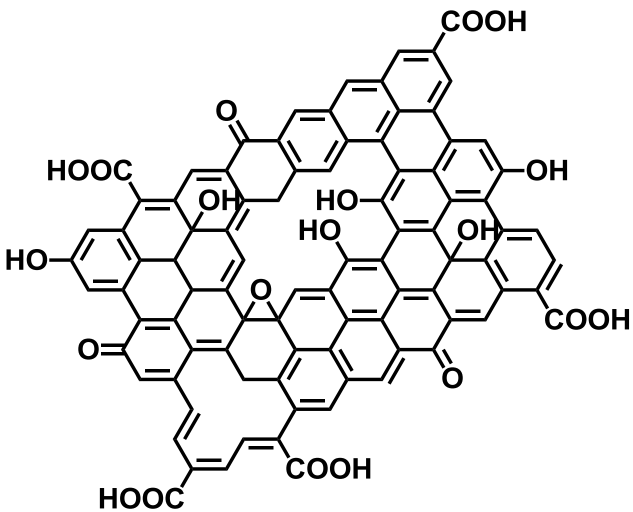


- ALD nucleation requires surface functional groups.
- Graphene edges and defect sites are more reactive.

Nucleation and Growth of Inorganic Materials on Oxidized Nano-Carbon

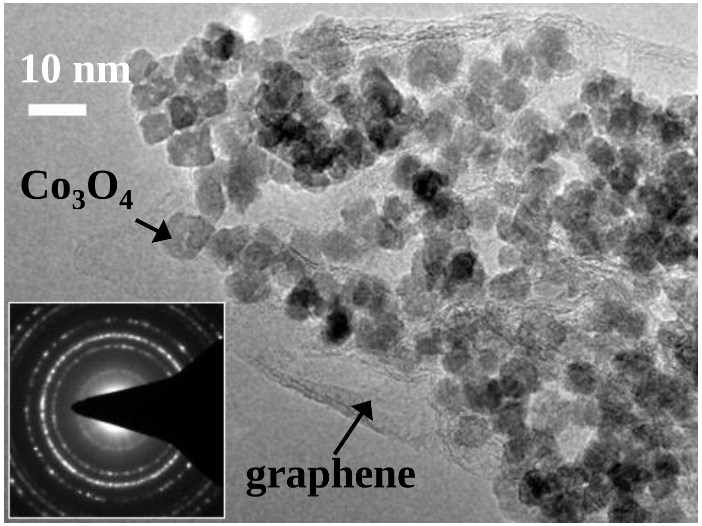


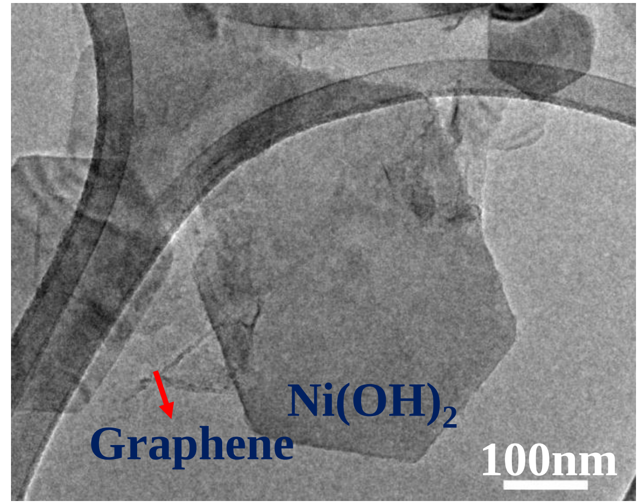
nucleation/growth on oxygen functional groups on nano-carbon

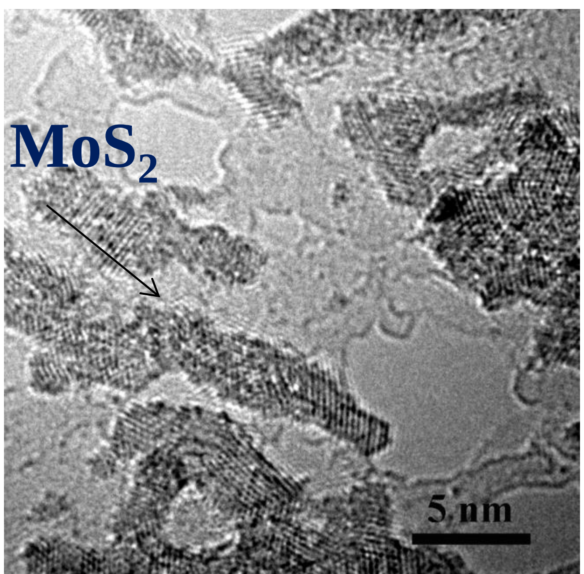


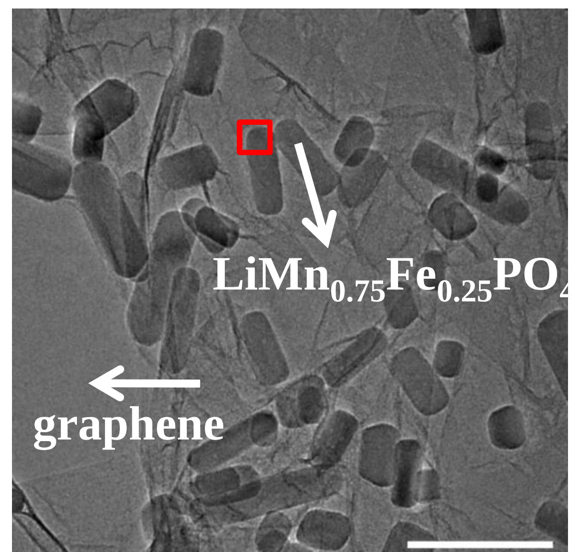
‘Strongly coupled hybrid’ of inorganic/nano-carbon (SC-hybrid)

Strongly Coupled-Hybrid of Oxides, Hydroxides Phosphate, Sulfides… and Graphene





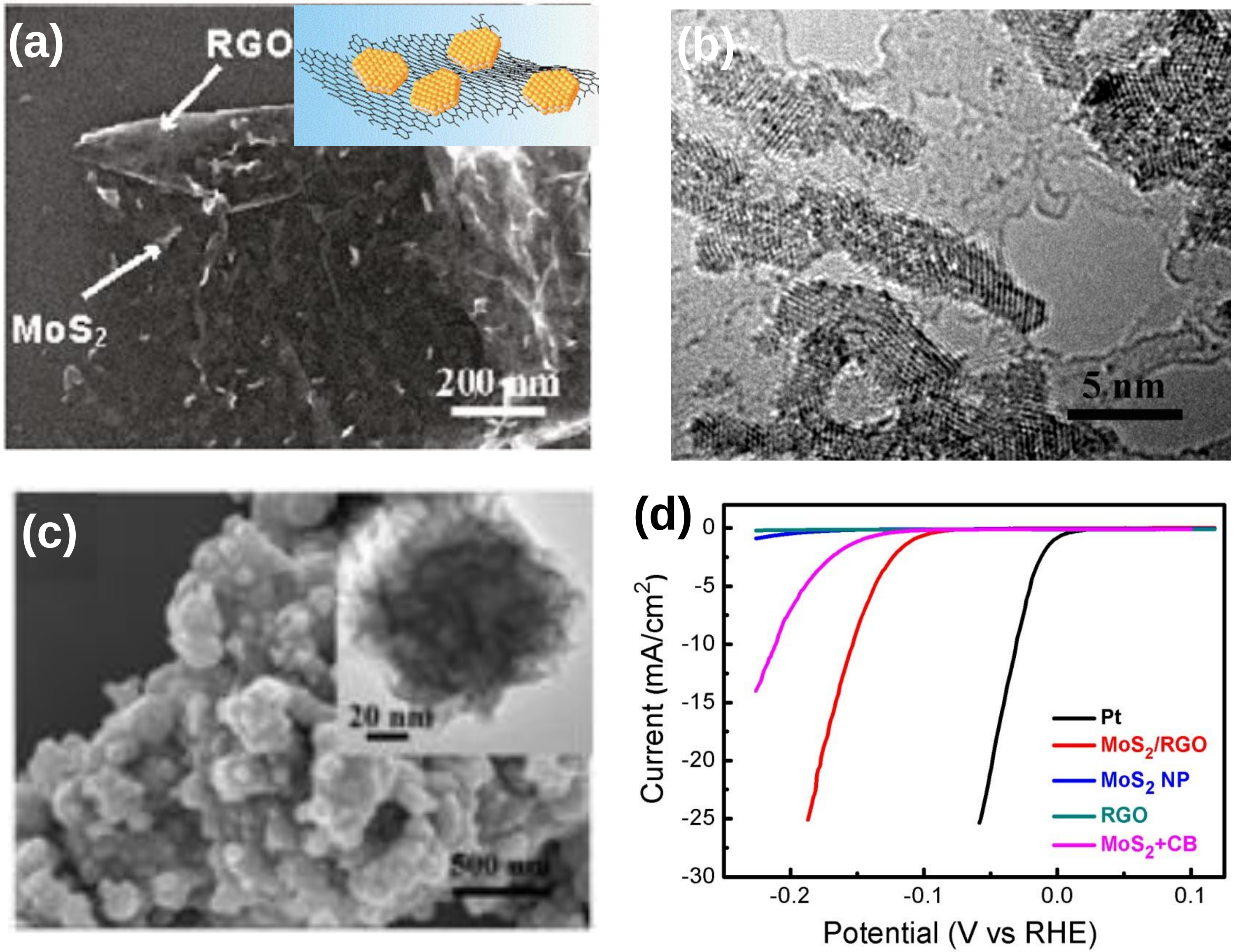




Nanoparticle Growth Morphology
(MoS_2:/graphene: an advanced hydrogen evolution catalyst)

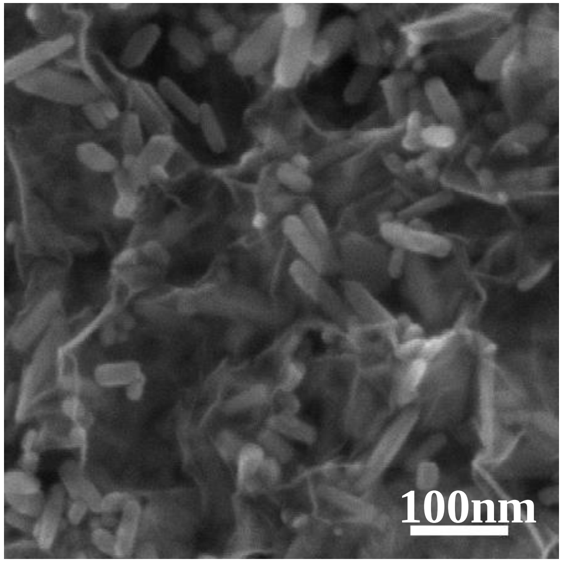
Growth on GO →

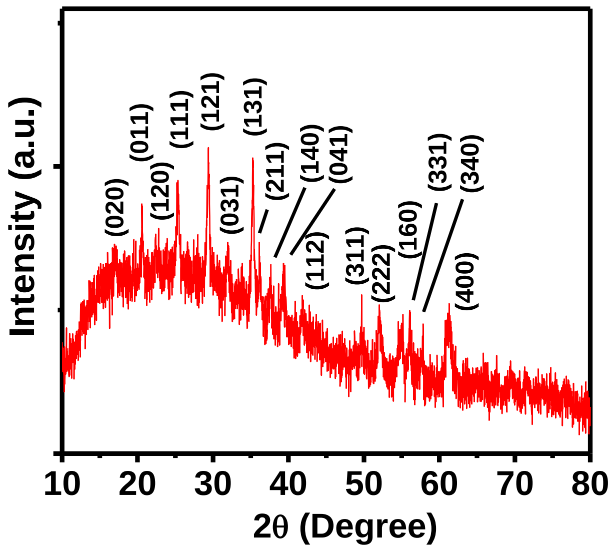
Free growth →

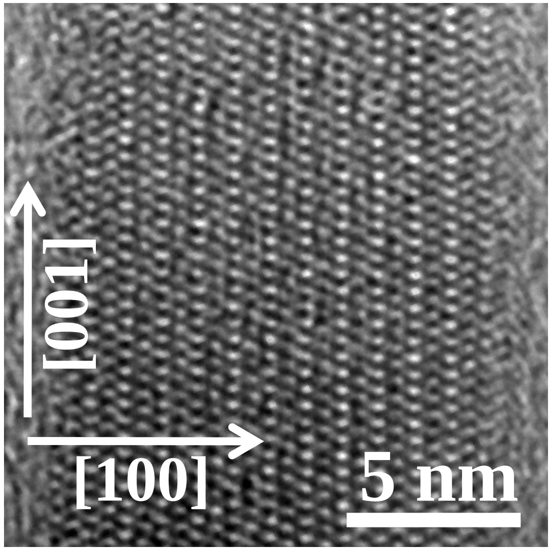


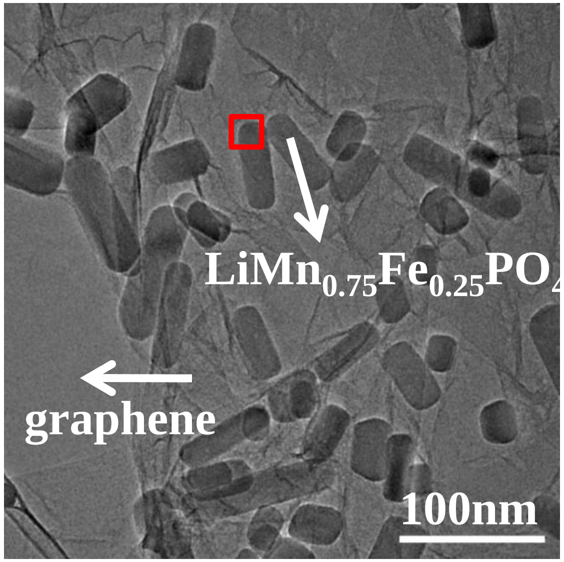
(Y. Li et al., **JACS**, 2011)

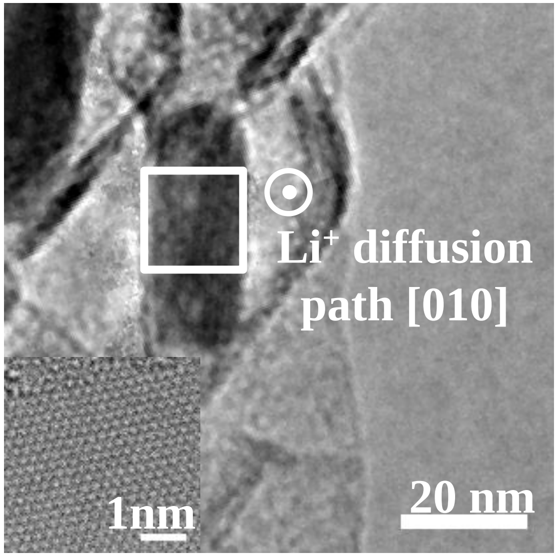
$LiMn_{0.75}Fe_{0.25}PO_4$ Grows into Nanorods on Graphene

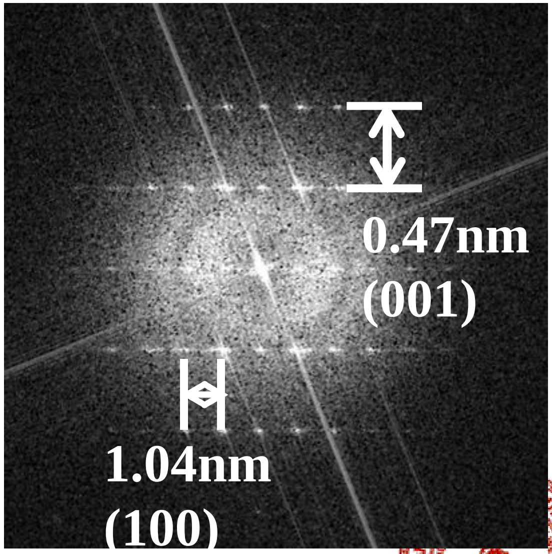






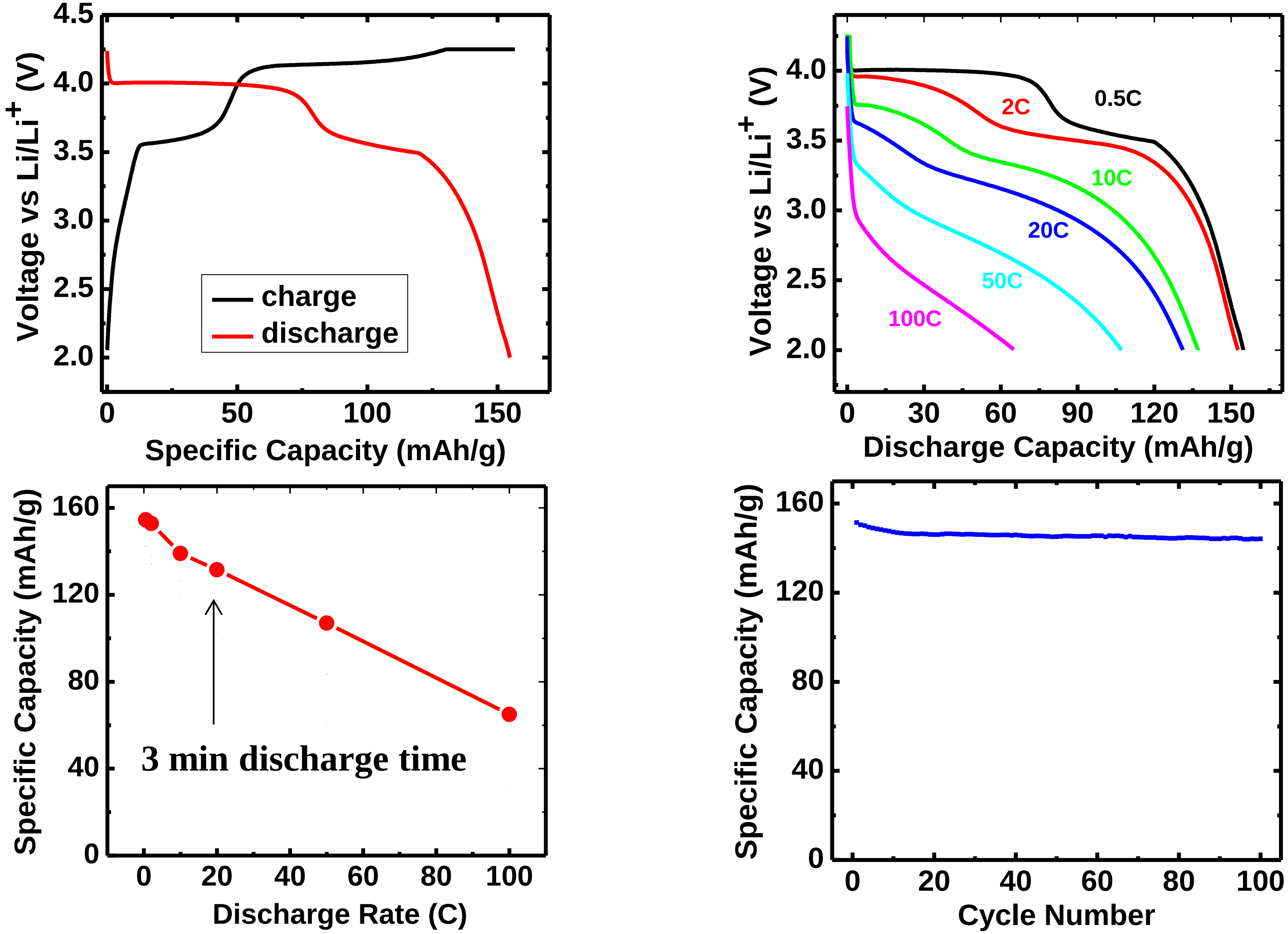




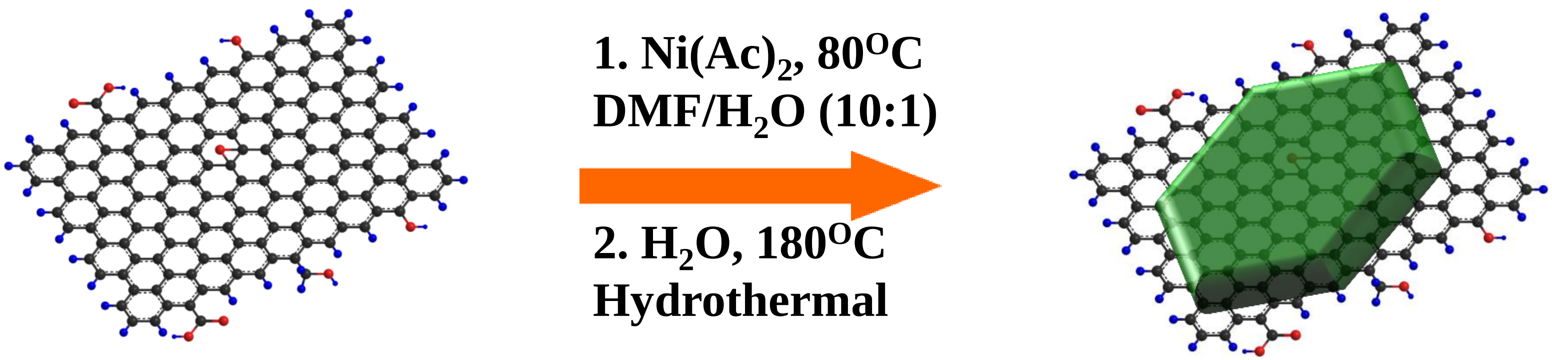


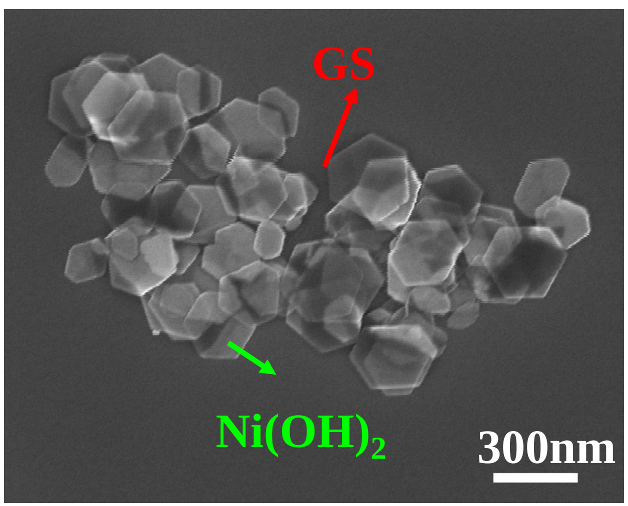
(H. Wang et al., with Yi Cui group, **Angew Chemie**, 2011)

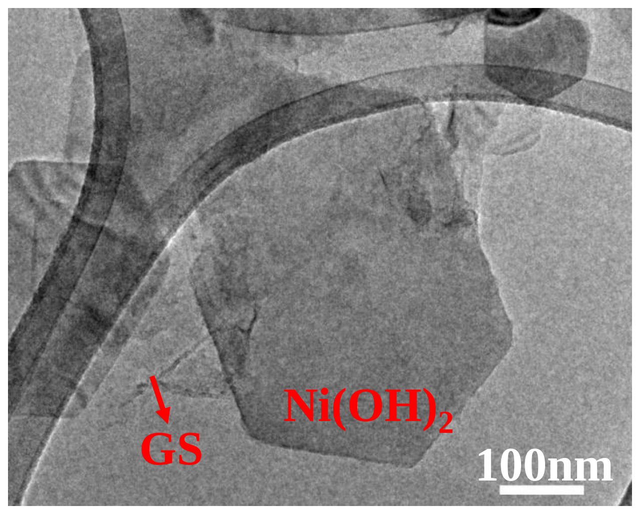
$LiMn_{0.75}Fe_{0.25}PO_4$ /GO as a Fast, High-Voltage, Stable Cathode Material for Li Ion Battery

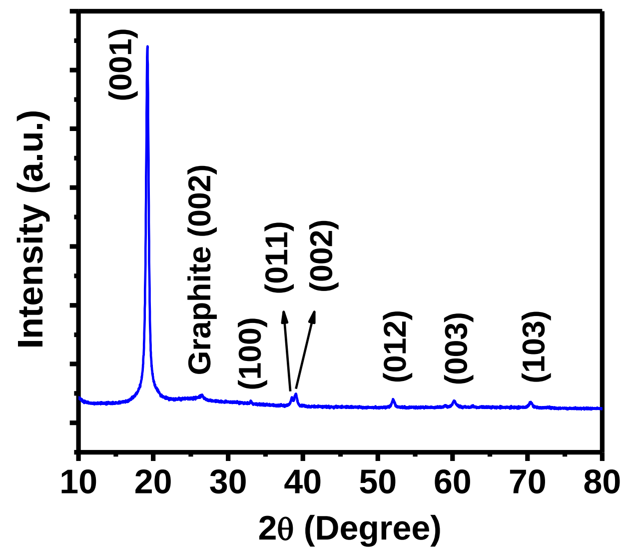


$Ni(OH)_2$ Nanoplates Grown on Graphene





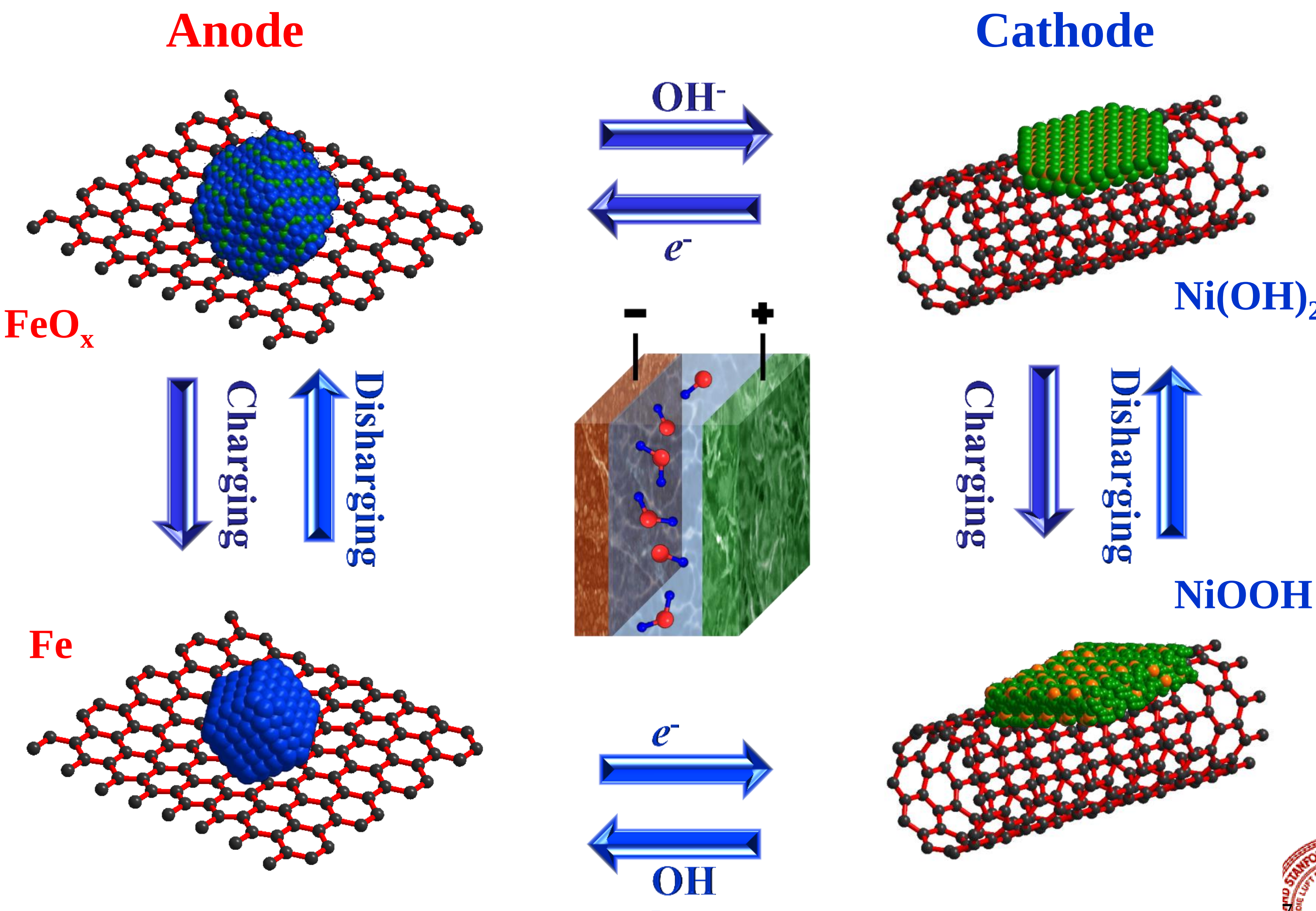




For ultra-fast Ni based alkaline batteries

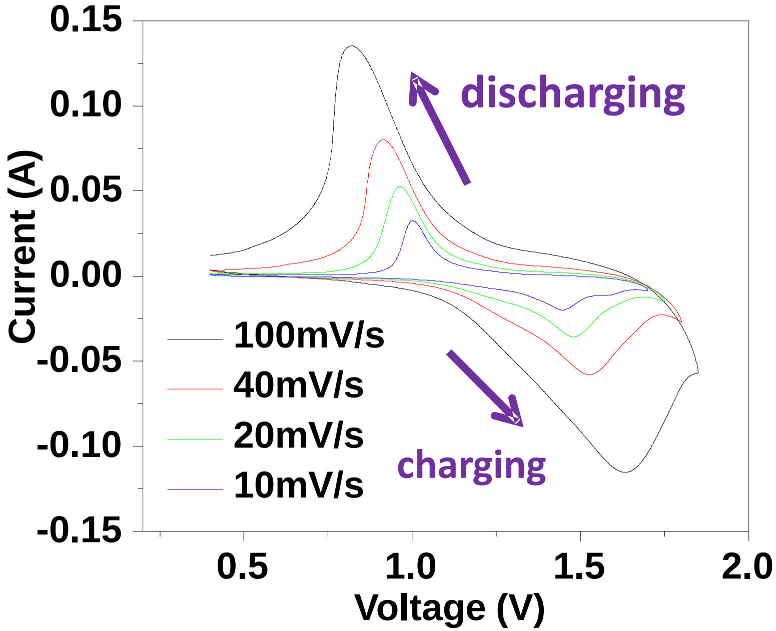
(Hailiang Wang et al., **J. Am. Chem. Soc.**, 2010)

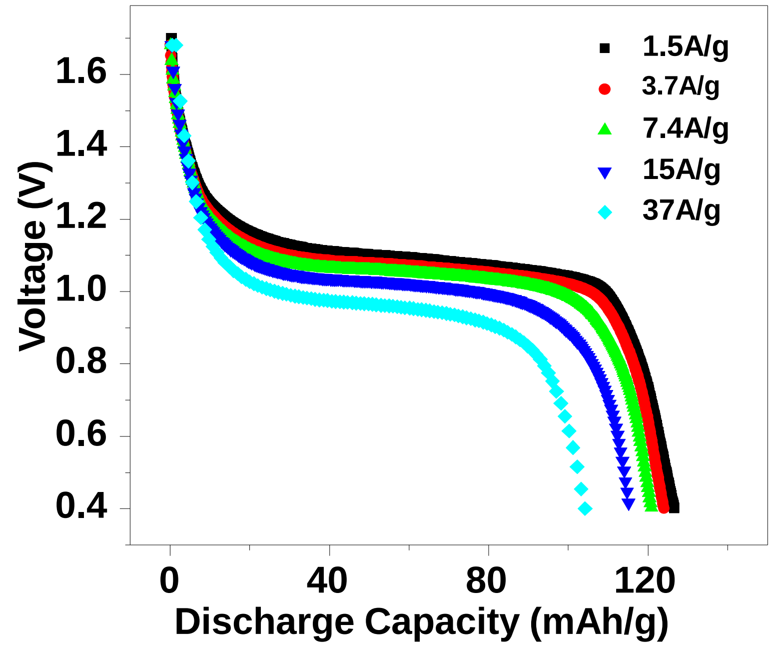
Ultrafast Ni-Fe Battery



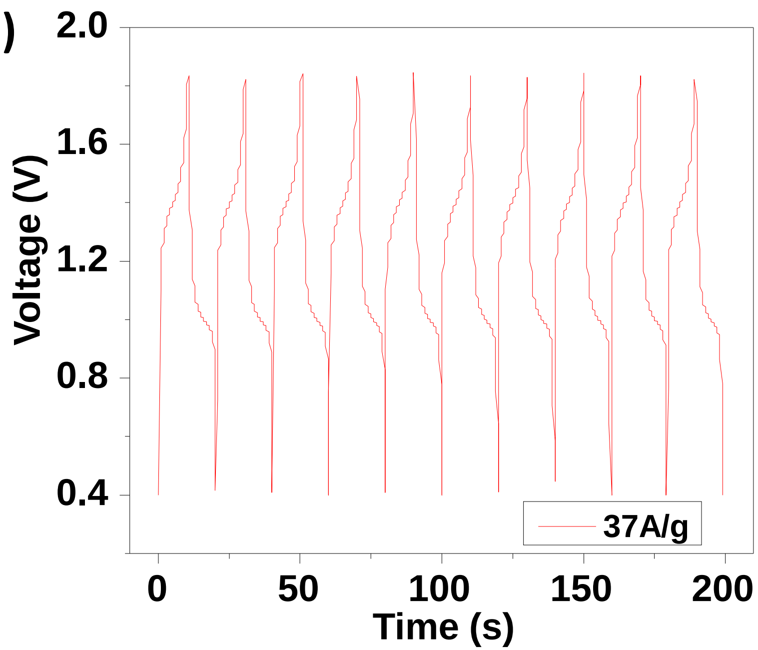
(H, Wang, et al., **Nature Comm.,** 2012)

Ultra-Fast Ni-Fe Battery





(e)



- ❖ Higher energy density than supercapacitors
- ❖ Safe (KOH in water as electrolyte).
- ❖ fast (2 min charge; 10 s discharge) like supercap

(H, Wang, et al.**, Nature Comm., 2012**)

Speeding Up Thomas Edison's Ni-Fe Battery

- ❖ Have been used for > a century.
- ❖ Good energy density; Safe (KOH as electrolyte).
- ❖ Slow (hours of charge-discharge).

Los Angeles Times

SCIENCE

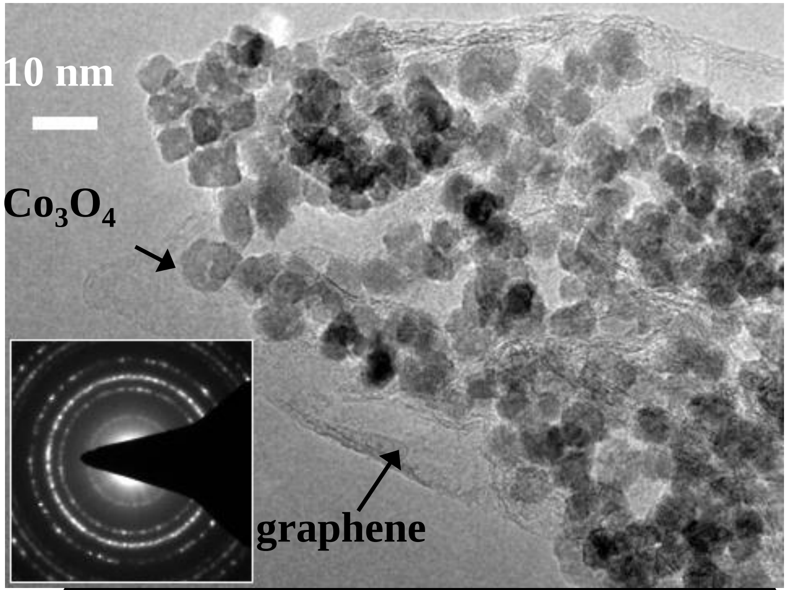
Stanford researchers update safer, cheaper Edison battery

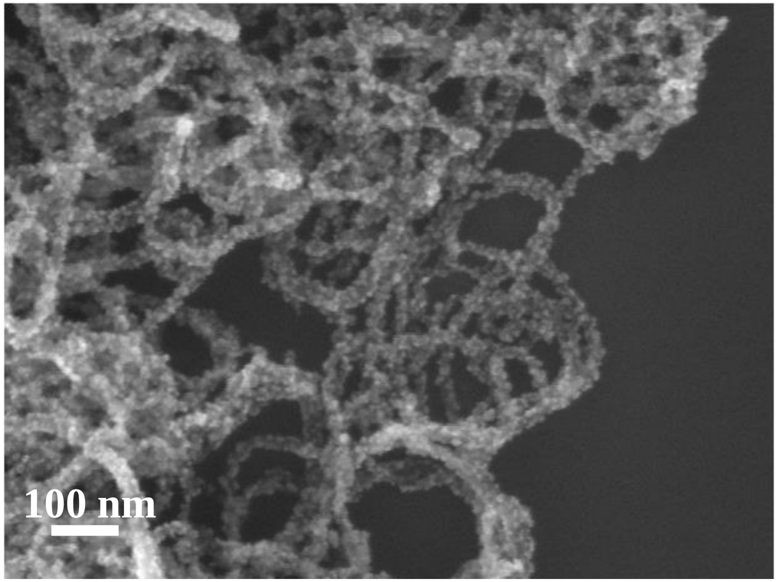
Recharge a car in minutes?

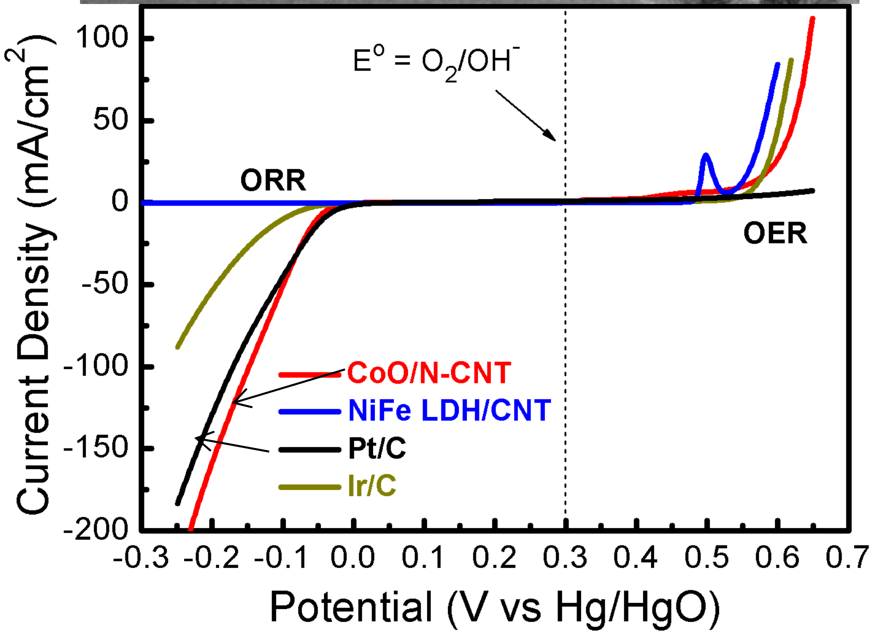
To demonstrate the reliability of the Edison nickel-iron battery, a battery-powered Bailey was entered in a 1,000-mile endurance run in 1910. (National Park Service / June 26, 2012)

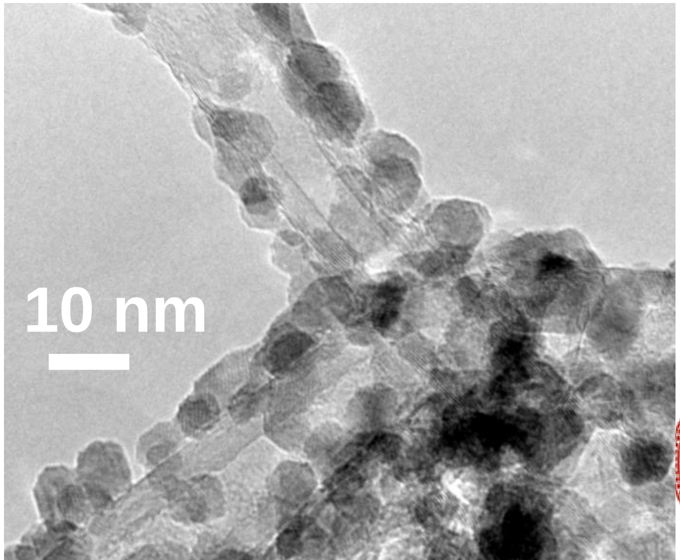
Co_3O_4/Graphene and Co_3O_4/Nanotube Electrocatalysts for Oxygen Reduction (ORR) and Evolution (OER)

(Y. Liang, Y. Li, H. Wang, et al., **Nature Materials**, 2011; **J. Am. Chem. Soc.** 2012)

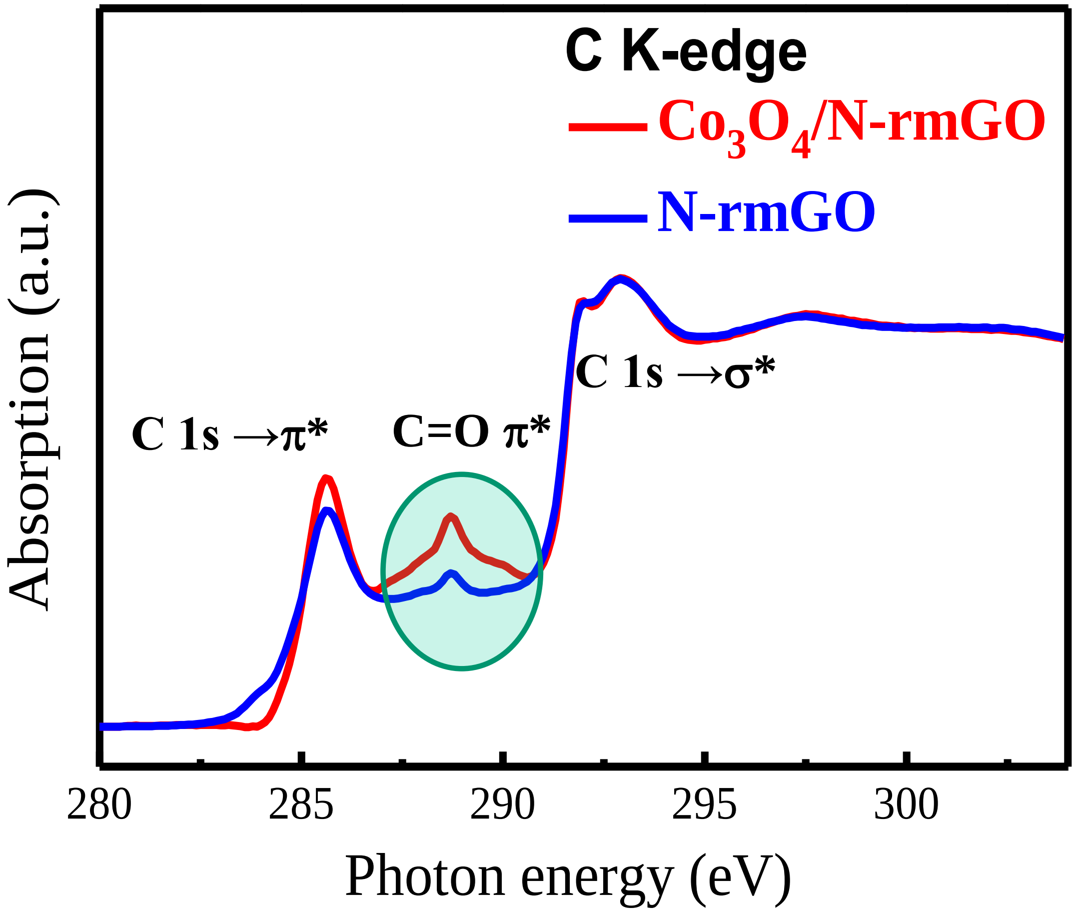






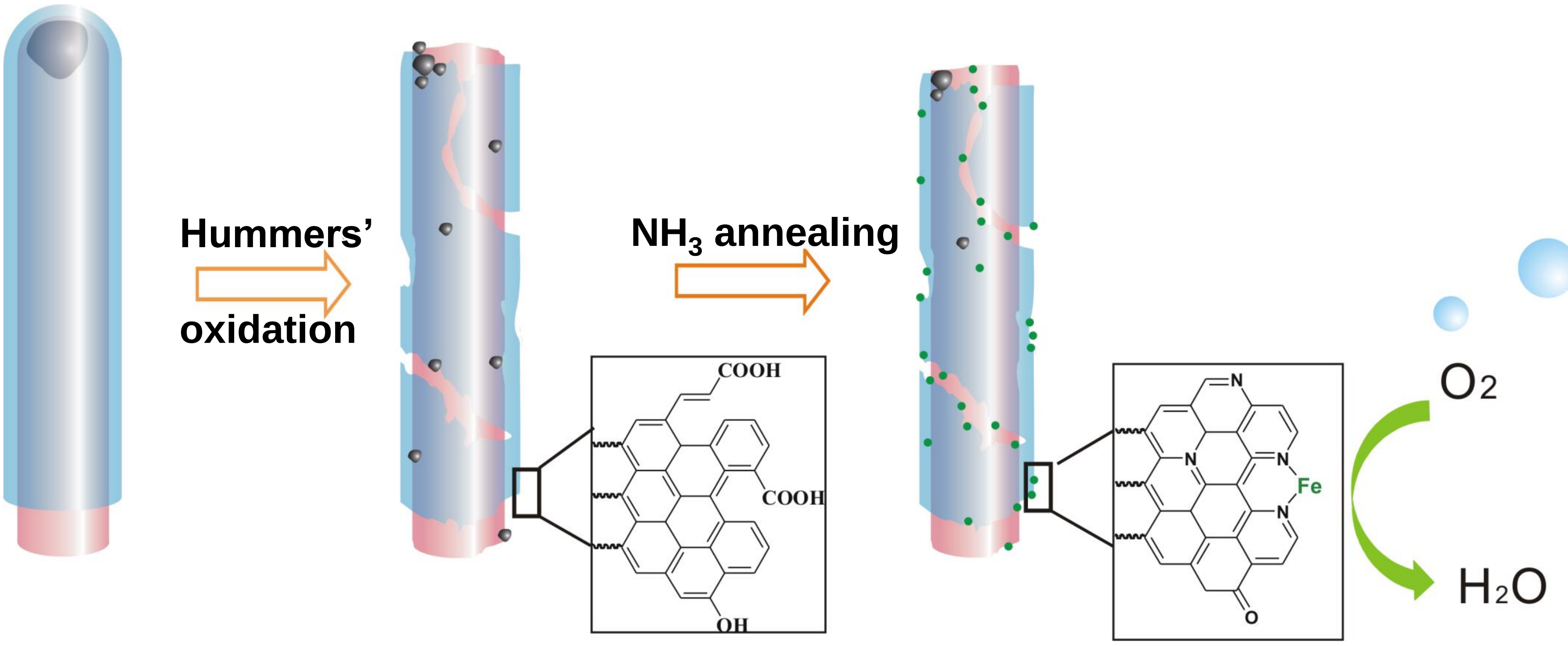


X-Ray Absorption Spectroscopy



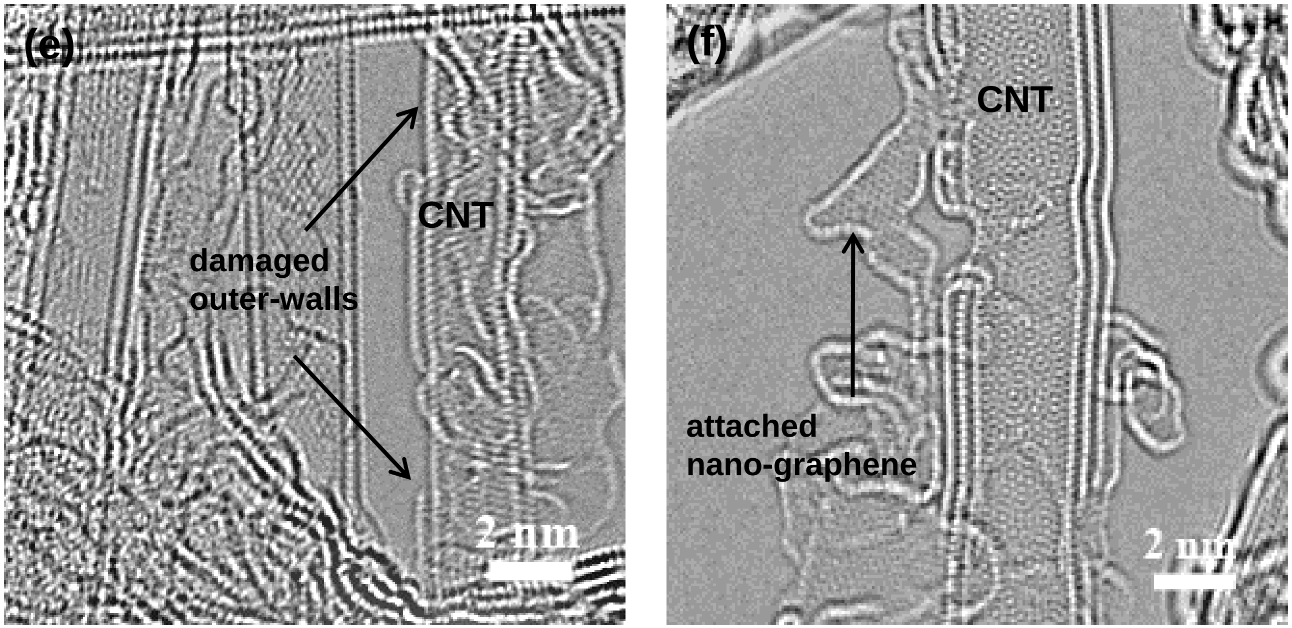
- Perturbed C-O groups in GO upon particle growth: evidence of Co-O-C-graphene bonding
- Strong coupling is responsible for high activity and stability of catalysts

Exfoliating Double (Triple) Walled Nanotubes for ORR Catalysts in Acids



Y. Li et al., **Nature Nano**, 2012

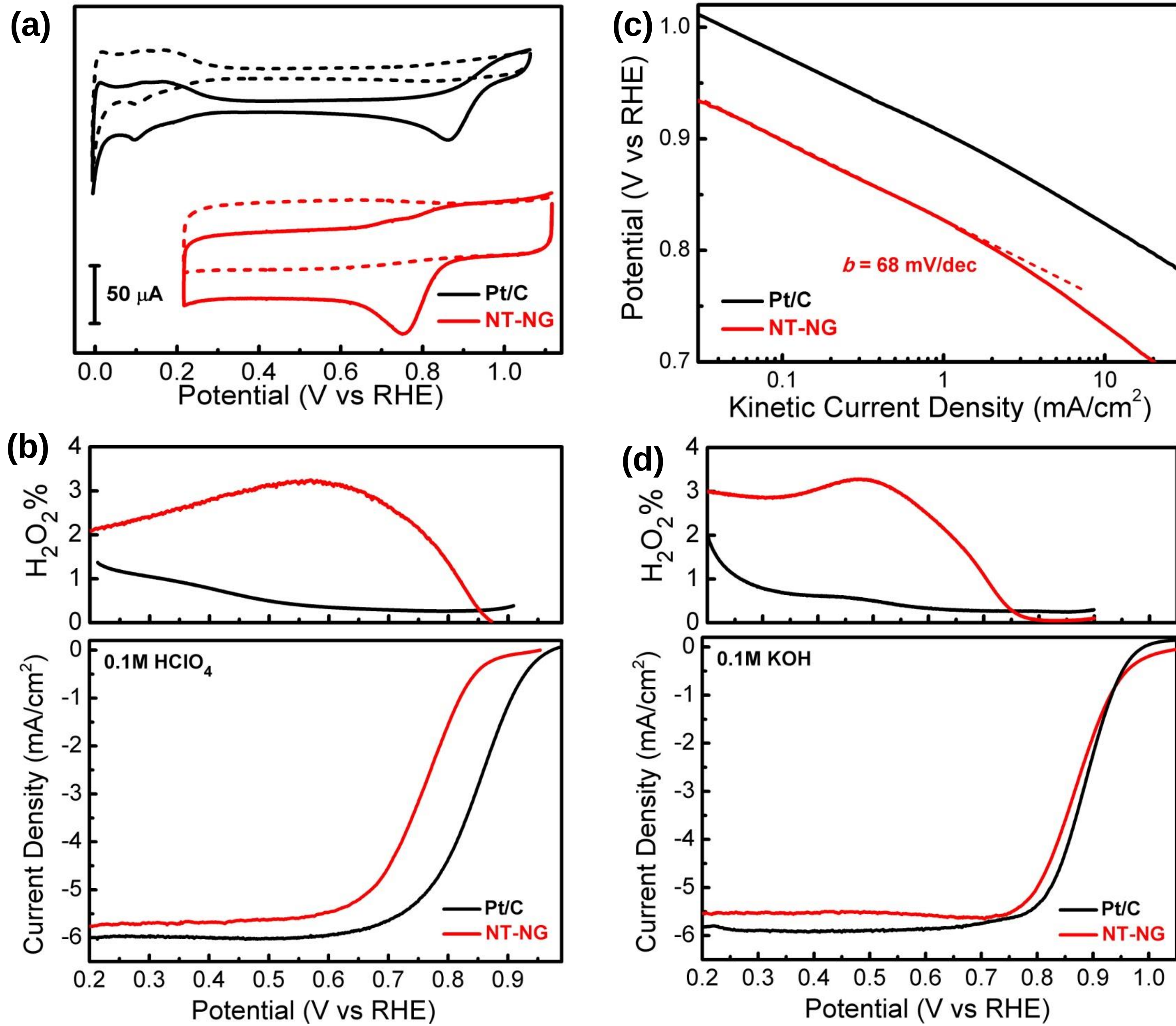
Nanotube-Nanographene Complexes Doped with Fe and N



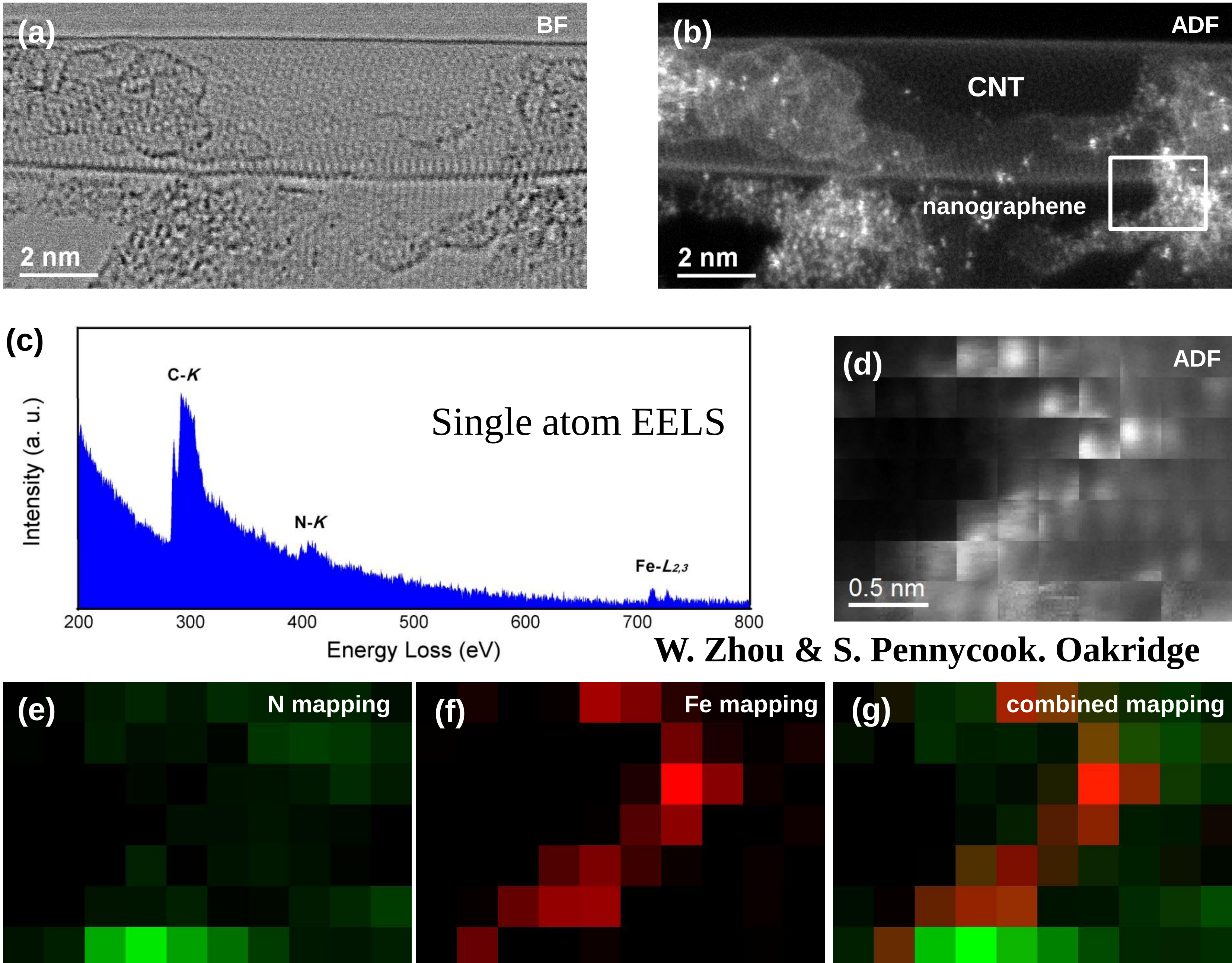
- Intact inner wall for charge transport
- Highly defective/functional outerwall for catalytic sites
- Fe impurities are from nanotube raw material

Y. Li et al., **Nature Nano**, 2012

An Active ORR Catalyst in Acid & Base

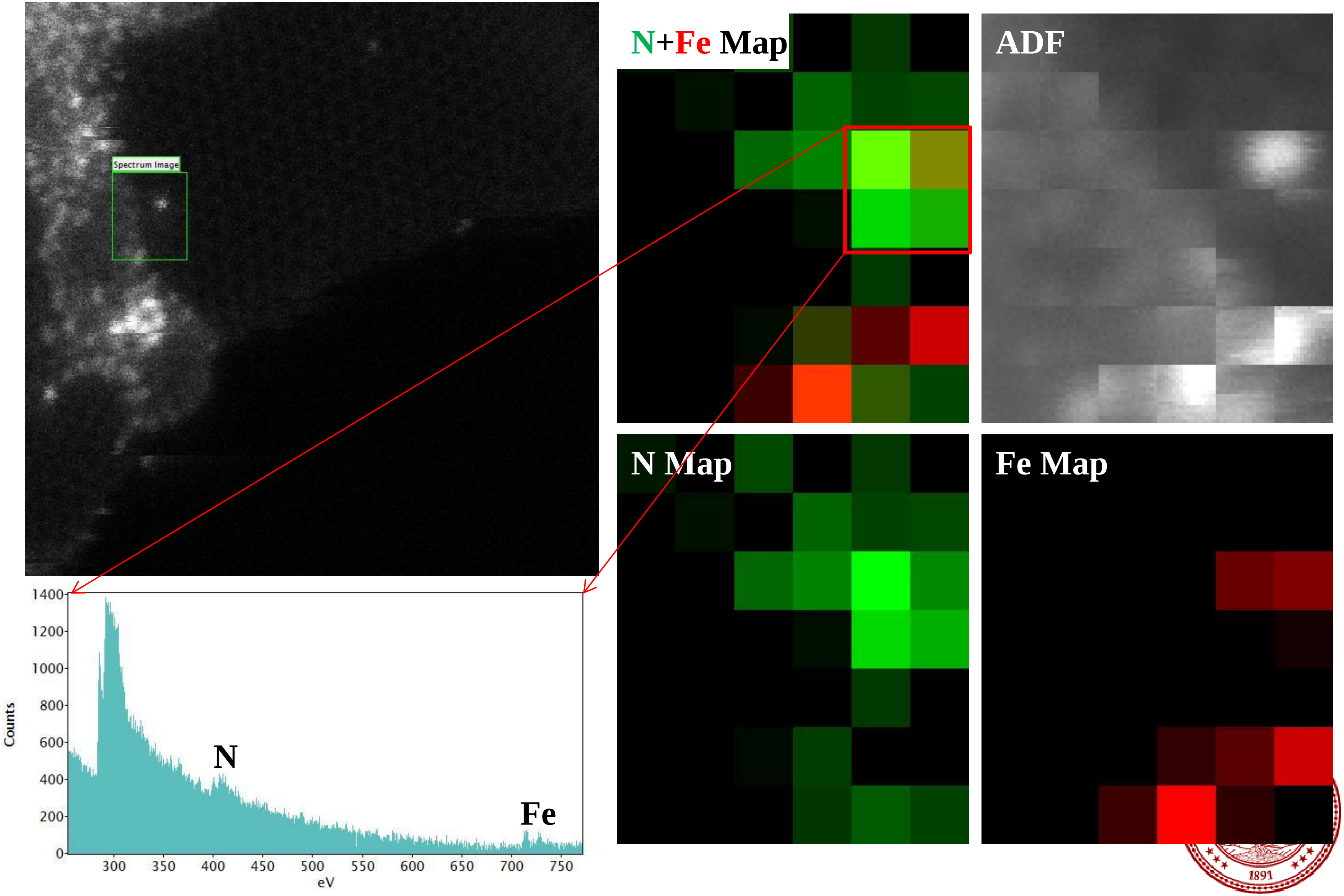


Atomic Scale Imaging and Chemical Mapping



W. Zhou & S. Pennycook. Oakridge

Single-Atom Imaging: Fe, N and C

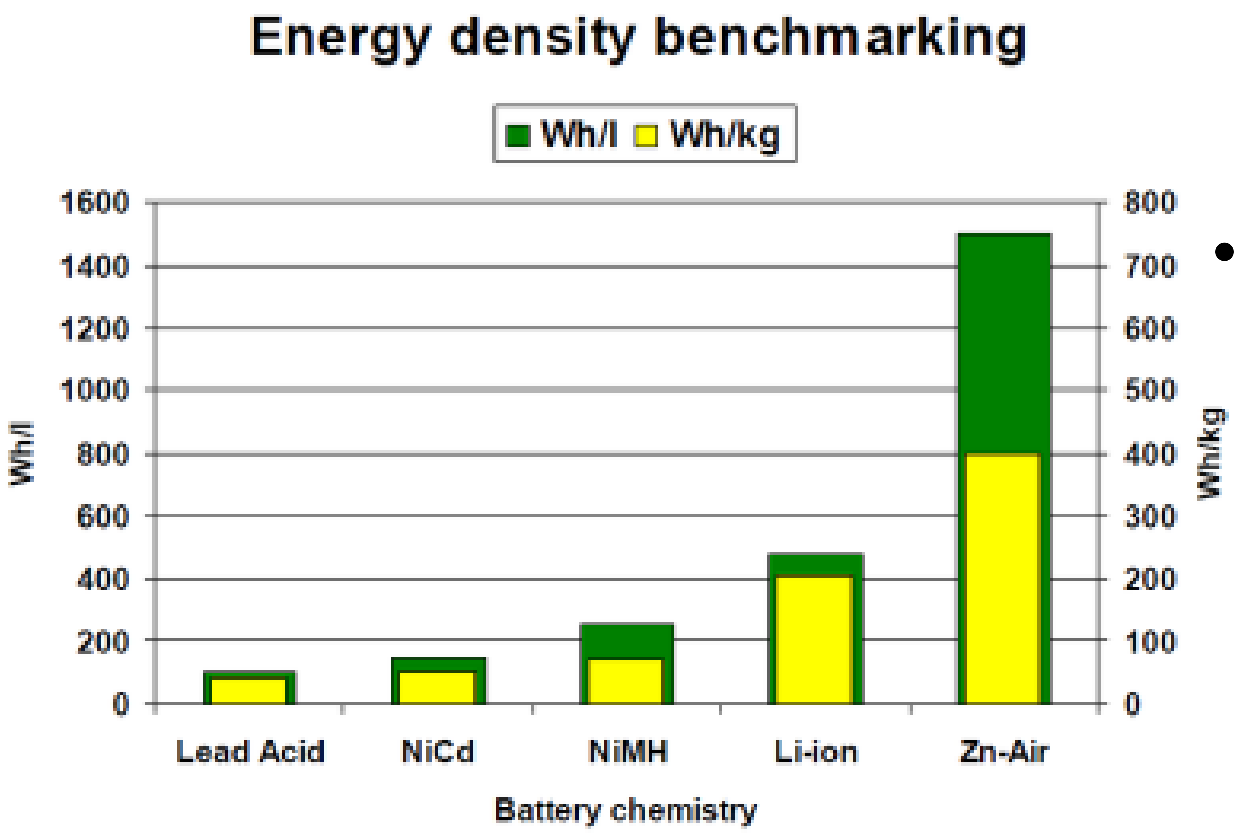


High Energy Rechargeable Zinc-Air Battery

$$Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$$

- Primary Zn-air battery has been commercialized
- Not rechargeable battery

Why Zinc-Air Battery?



- Much higher energy density than lithium ion batteries

Benefit of Rechargeable Zn Air Batteries

Why Zn air?

- Abundance of Zn on earth
- Safety and low-cost
- High energy density: 2 times of lithium ion battery.

Anode: $Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$

Cathode: $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ **(ORR/OER)**

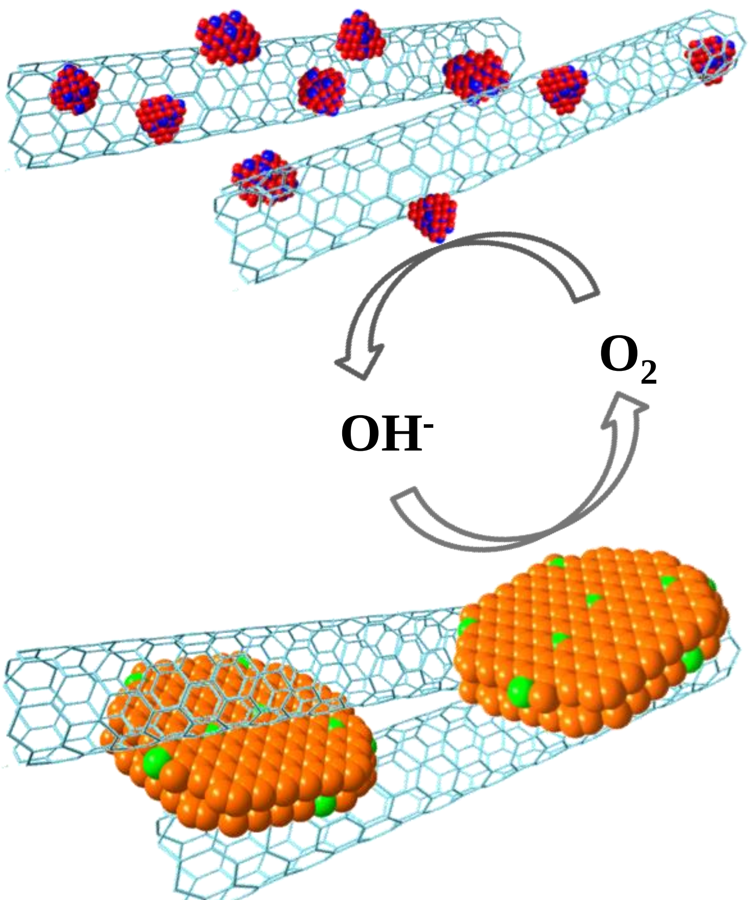
ORR: oxygen reduction reaction
OER: oxygen evolution reaction

One of the challenges for rechargeable Zn-air batteries:

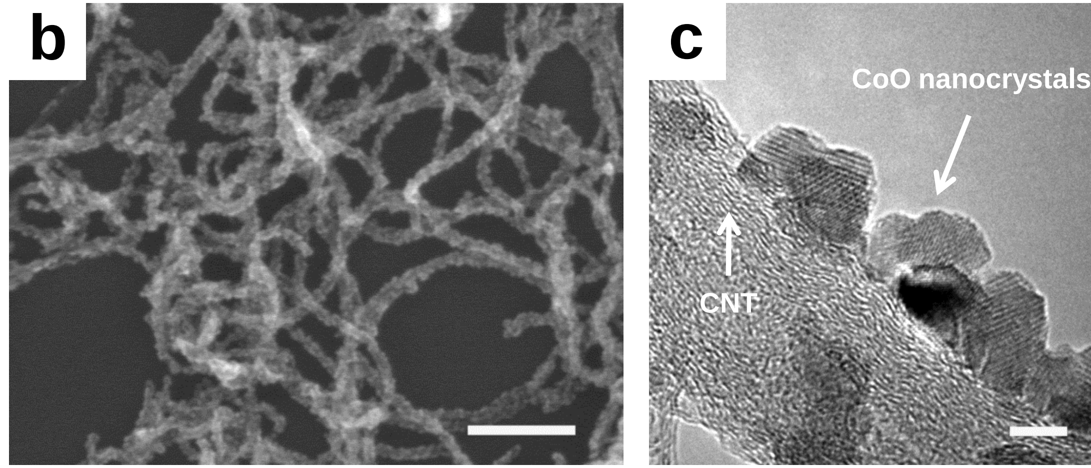
- Cathode side need more active and stable electrocatalysts for ORR & OER

Electrocatalysts for Oxygen Electrodes

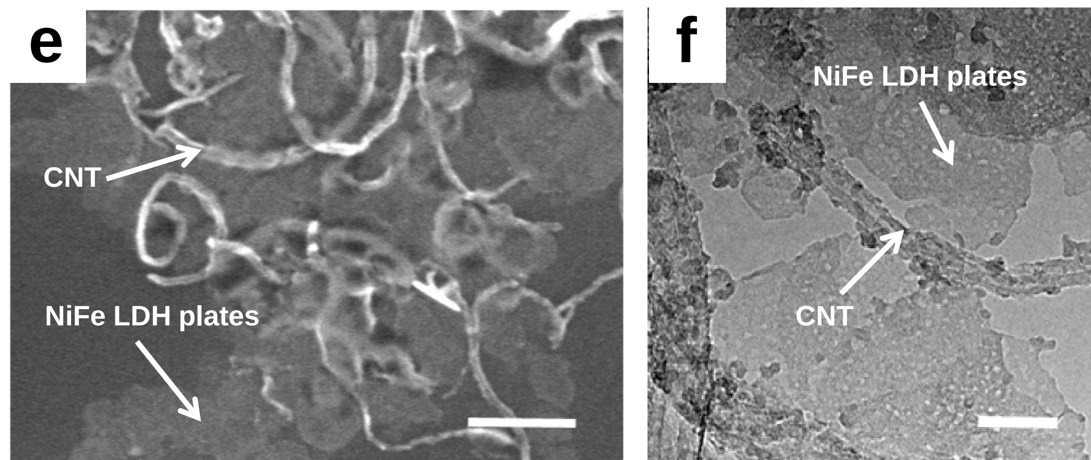
ORR: **CoO/N-CNT**



OER: **NiFe LDH/CNT**



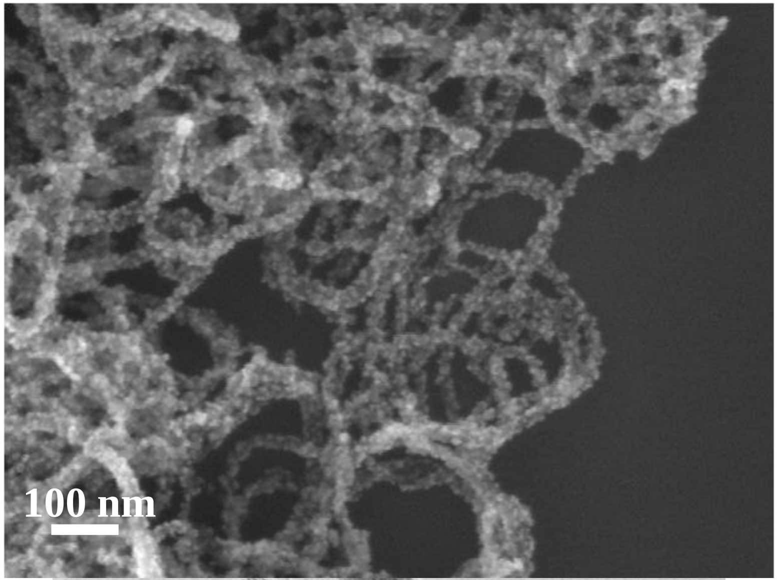
(Y. Liang, **Nature Mater.** 2011, **JACS**, 2012)

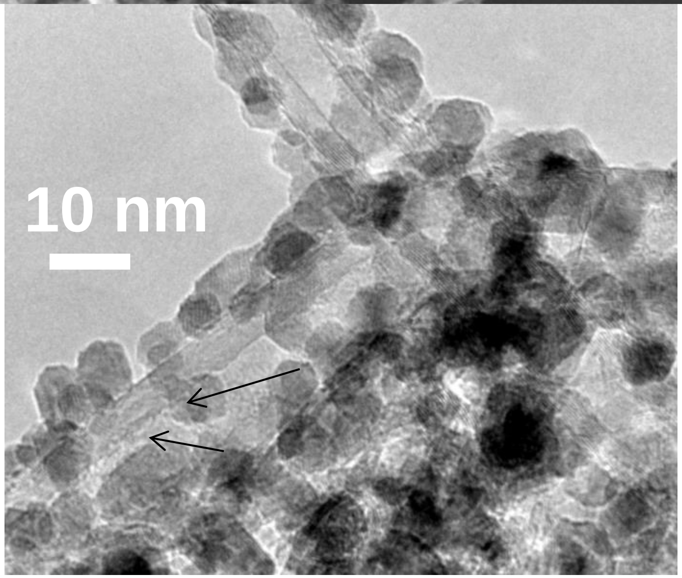


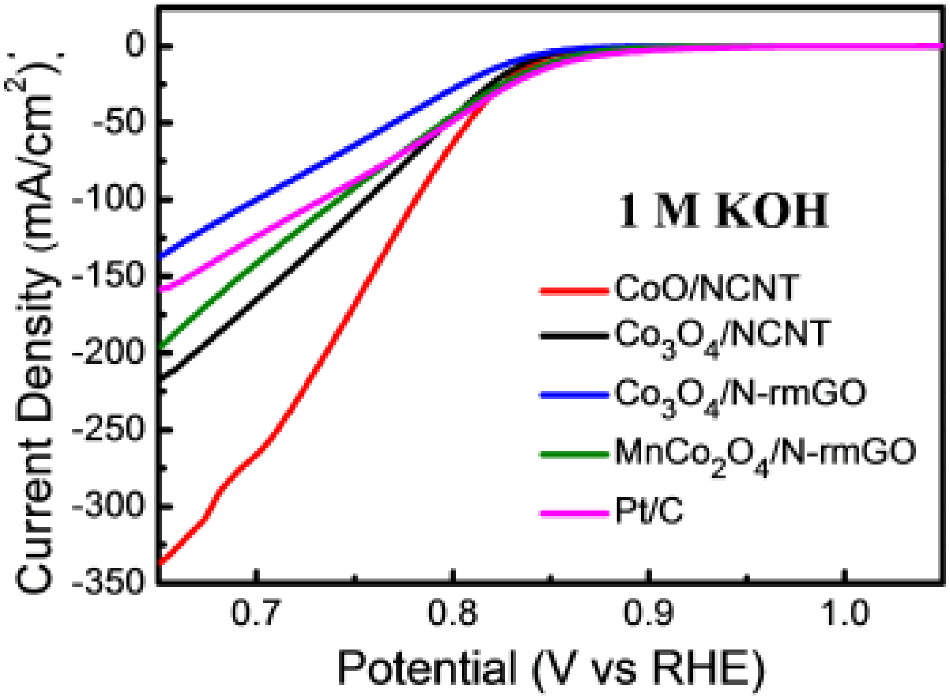
(M. Gong, **JACS**, 2013)

CoO/Oxidized-Nanotube Electrocatalyst for ORR

(Y. Liang, Y. Li, H. Wang, et al., **J. Am. Chem. Soc.** 2012)

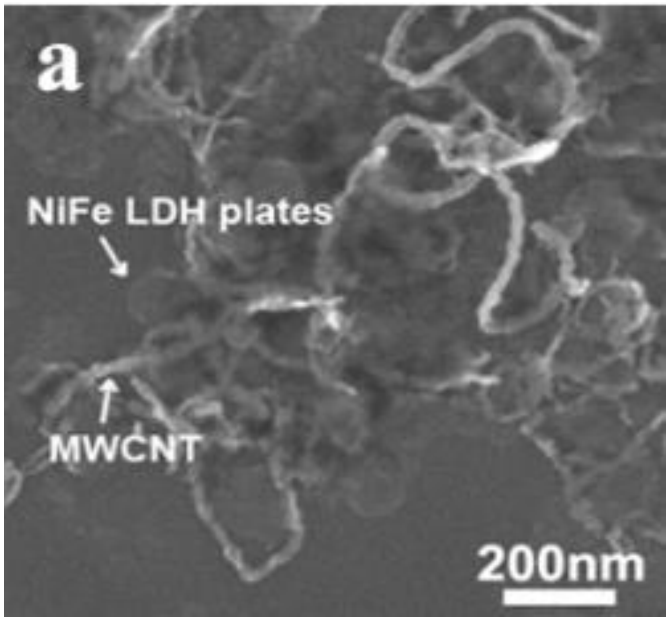


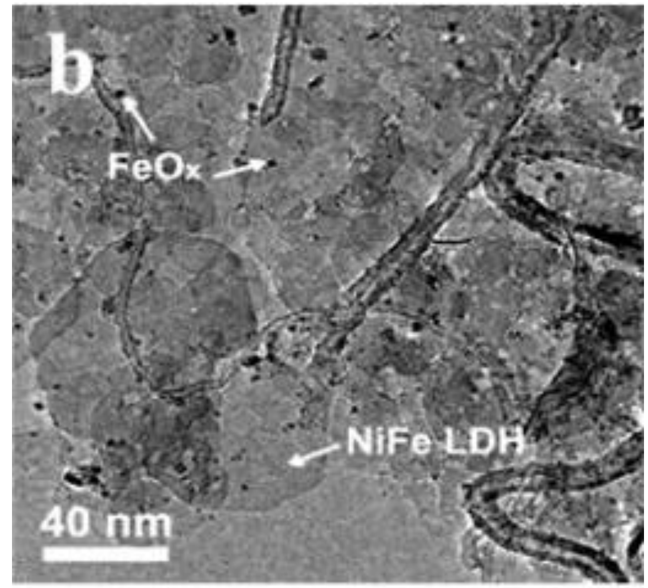




- Metal-oxide/Nanotube hybrid outperform metal-oxide/graphene
- Higher electrical conductivity of oxidized multi-walled nanotubes

A New OER Catalyst: Ultrathin Nanoplates of NiFe Layered Double Hydroxide/CNT Hybrid

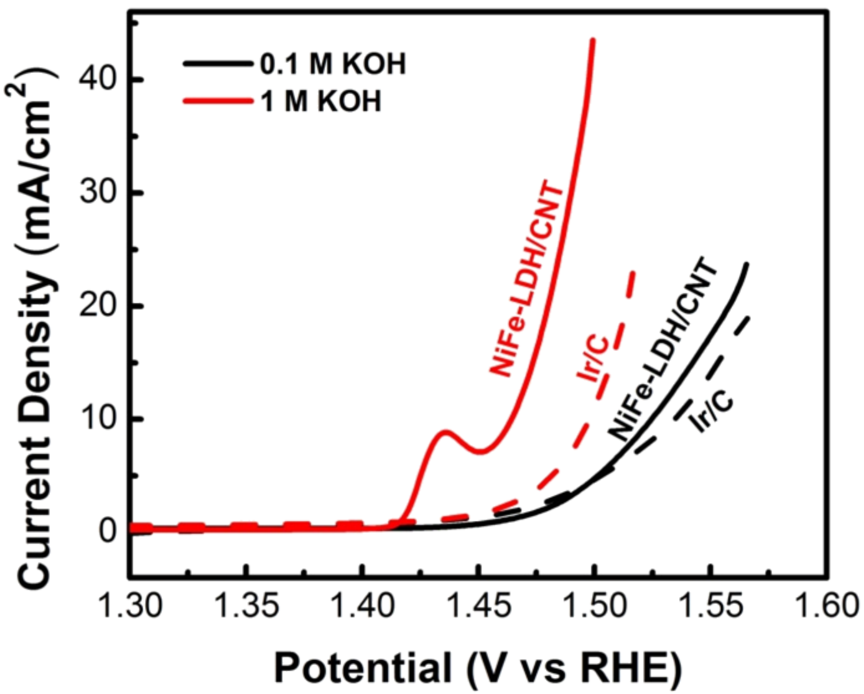


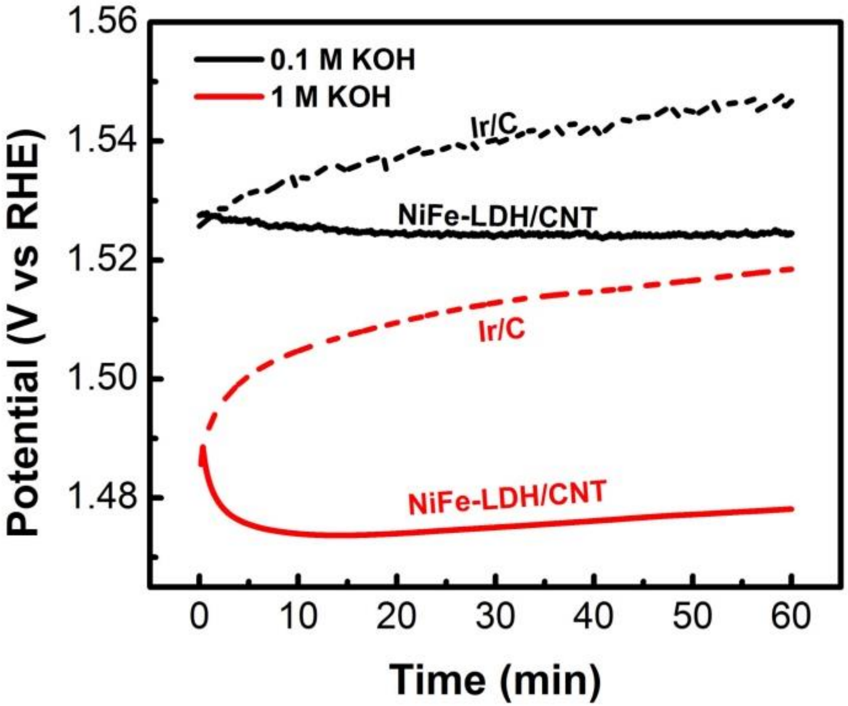


- One of the most active catalyst to evolve oxygen in alkaline solutions
- Cheap and stable

(M. Gong et al., **JACS**, 2013)

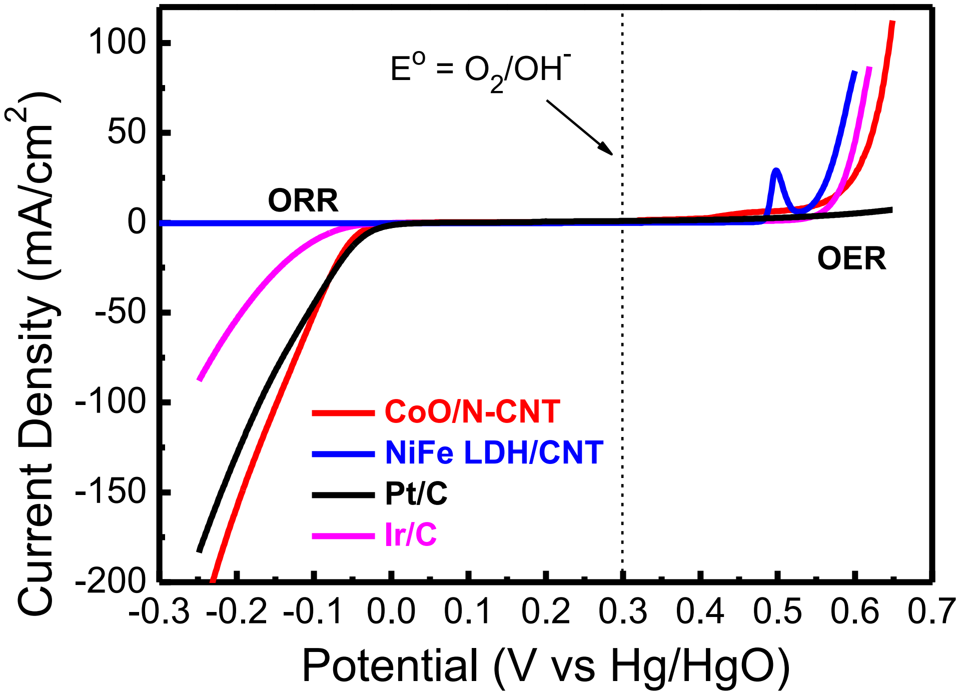
Higher Activity and Durable than Ir/C in Basic Solutions

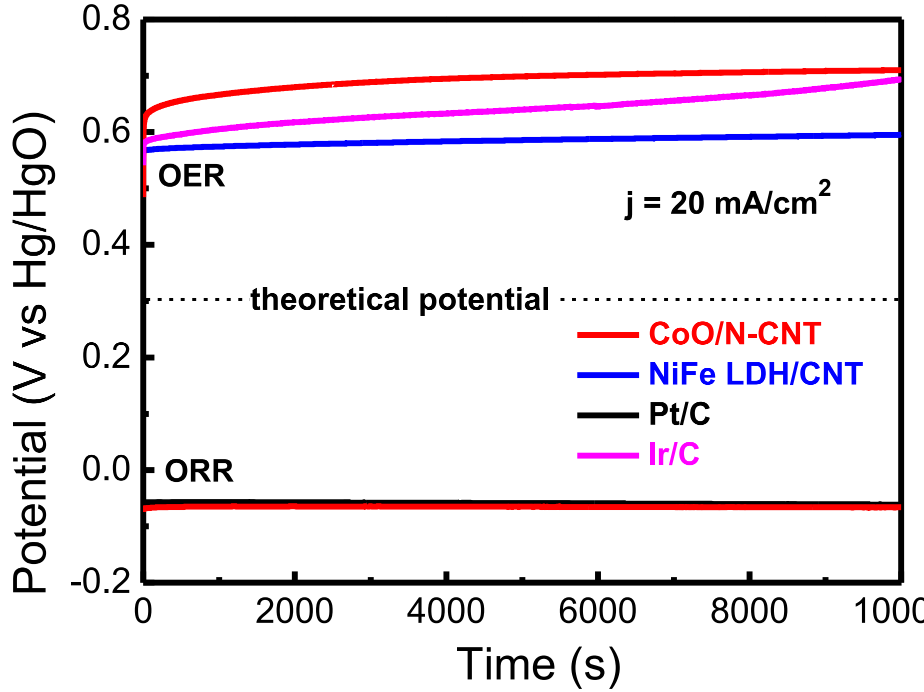




Electrocatalysts for Oxygen Electrodes

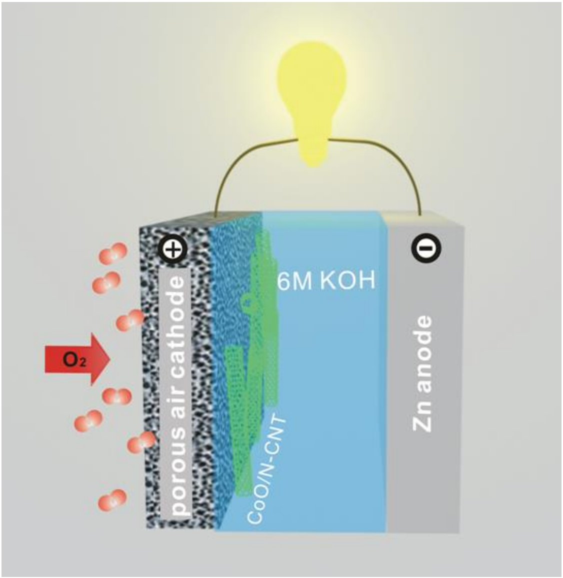
(Y. Li et al., **Nature Comm.**, in press)

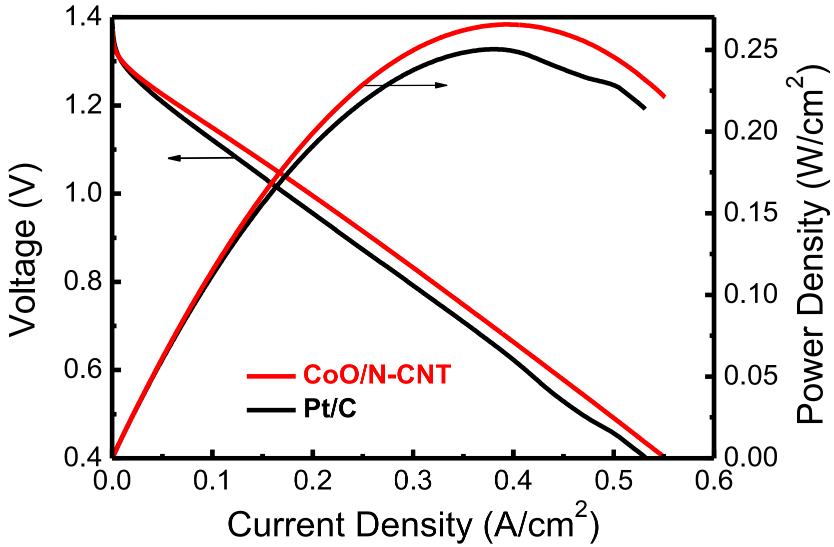


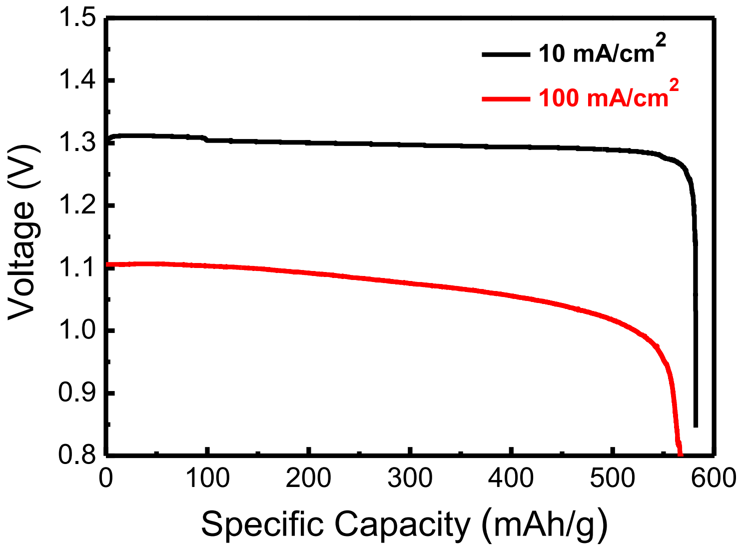


- Highly active in basic solutions, matching Pt or Ir.
- Stable over days tested.

Primary Zn-Air Battery



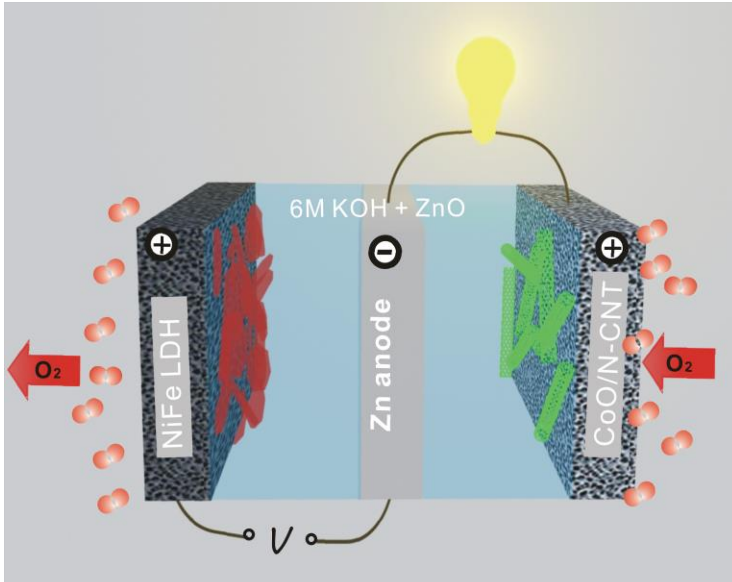


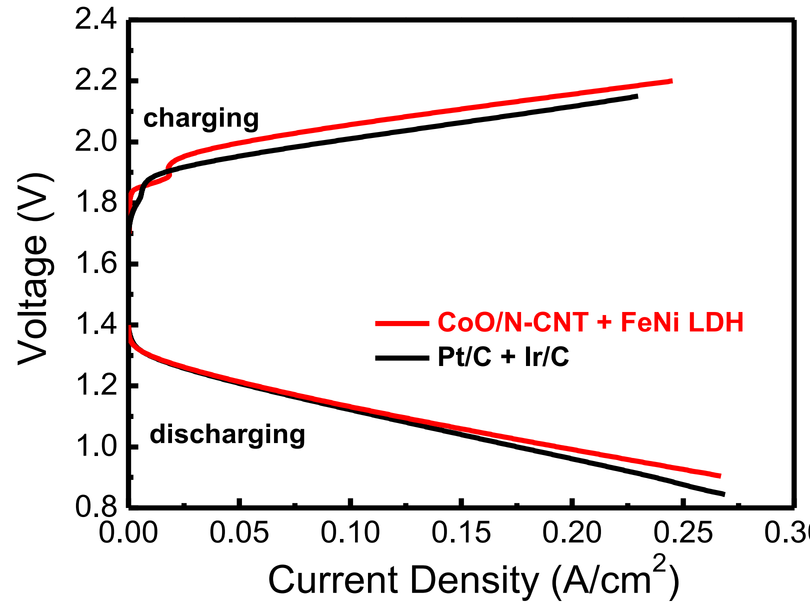


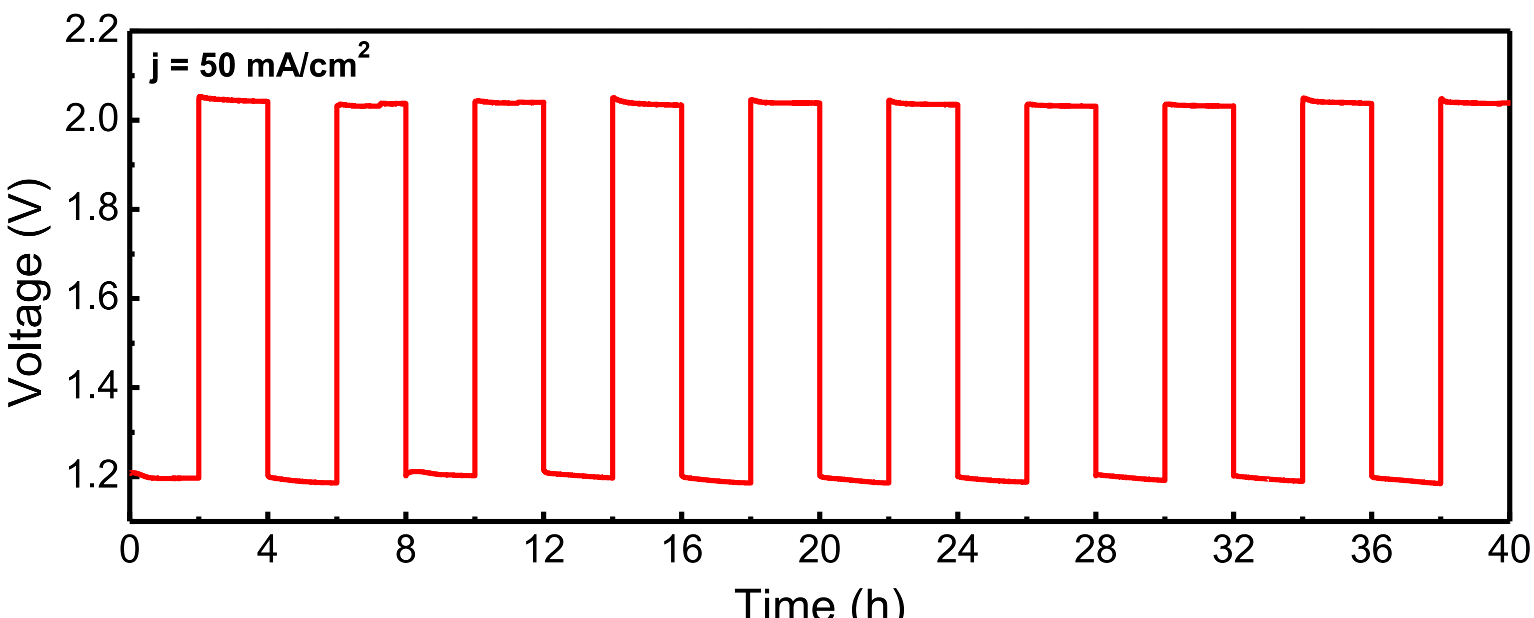
- High discharge peak power density ~265 mW/cm^2
- Current density ~200 mA/cm^2 at 1 V
- Energy density > 700 Wh/kg.

Y Li et al., **Nature Comm.**, 2013

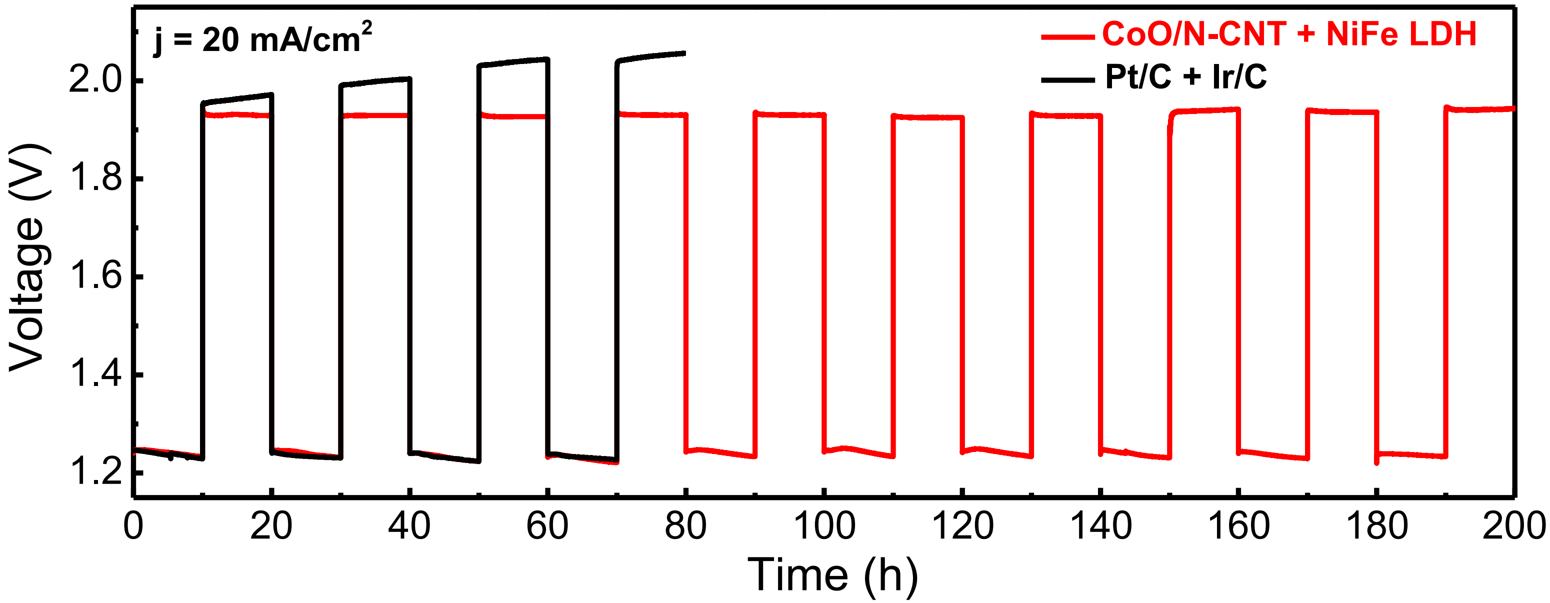
Rechargeable Zn-Air Battery in a Tri-Electrode Configuration







High Performance Rechargeable Zn-Air Battery



- Low charge-discharge voltage polarization of ~ 0.70 V at 20 mA/cm^2
- High reversibility and stability over long charge and discharge cycles (10 h discharge time)

Y Li et al., **Nature Comm.**, 2013

Summary

- CNTs and nano-graphene for biology and medicine.
- A new near-infrared II imaging is developed.
- High quality graphene nanoribbons for physics and devices.
- Novel Inorganic-carbon hybrid materials for fast energy storage/release & advanced electrocatalysis.
- Graphene allows atomic/chemical imaging of catalyst sites

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