

Tailoring Carbon Nanomaterials for Emerging Applications

presented by

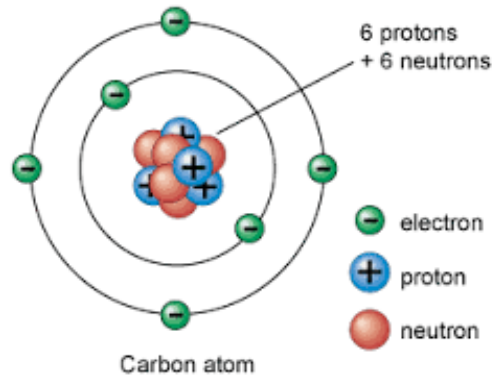
Yuan Chen

Associate Professor

School of Chemical and Biomedical Engineering

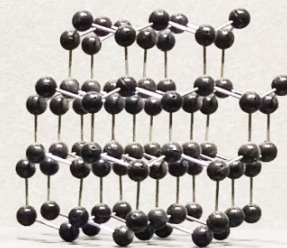
23 June 2015 @ 東京大学

Carbon Materials



◆ The **diamond and graphite** below are both pure carbon, but they have different atomic structures. Diamond's atoms are tightly linked, giving it superior hardness. Graphite's atoms are arranged in layers that easily slide across one another, making it soft and greasy.

sp^3 -bonded



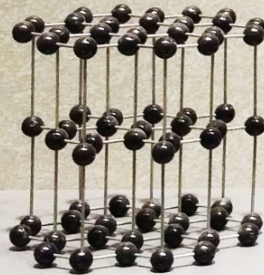
Diamond Atomic Structure
C

Diamond
With kimberlite
C
Kimberley, Cape Province,
South Africa

Courtesy of Beavers Miniature Models

R3

sp^2 -bonded



Graphite Atomic Structure
C

Graphite
C
Canada

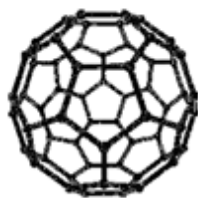
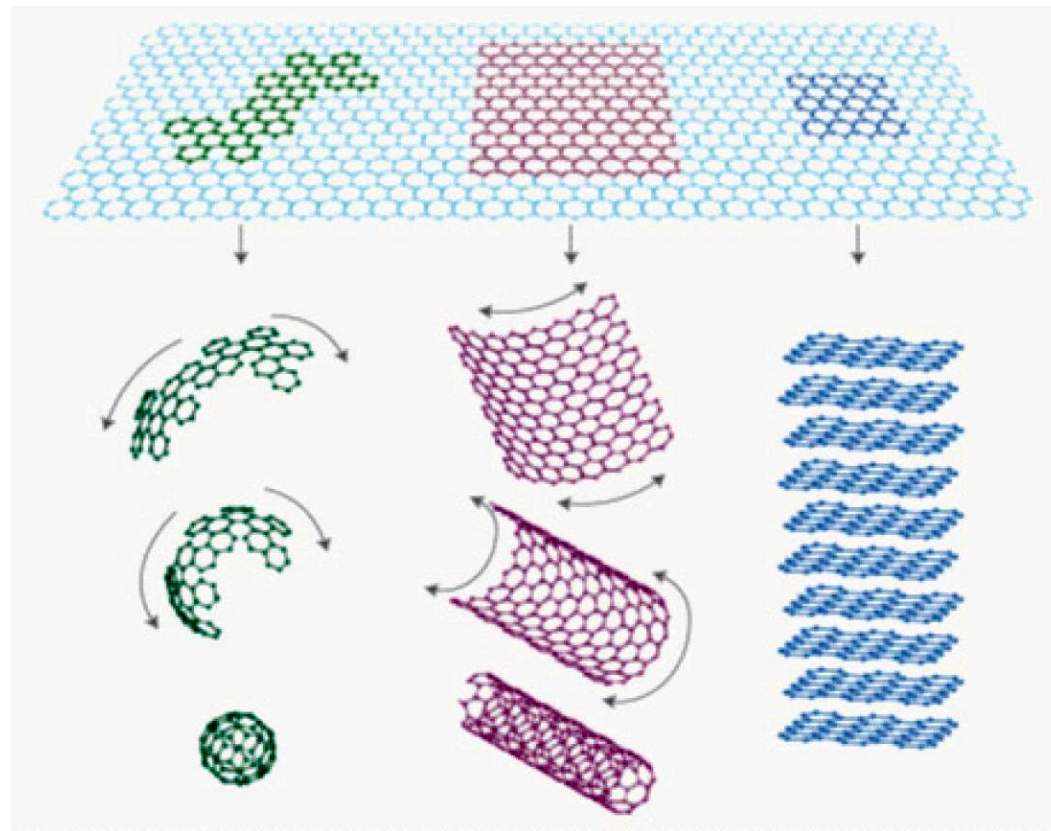
Courtesy of Beavers Miniature Models

American Institute of Mining Engineers 48201



Crater of Diamonds State Park, by A.C. Harabon, courtesy of Arkansas Department of Parks and Tourism

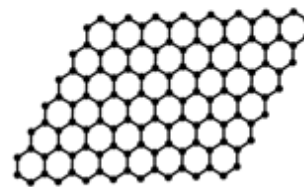
Carbon Nanomaterials



Fullerene



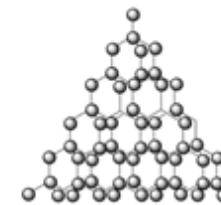
Carbon nanotubes
(CNTs)



Graphene



Carbon dots
(Cdots)



Nano-diamonds
(NDs)

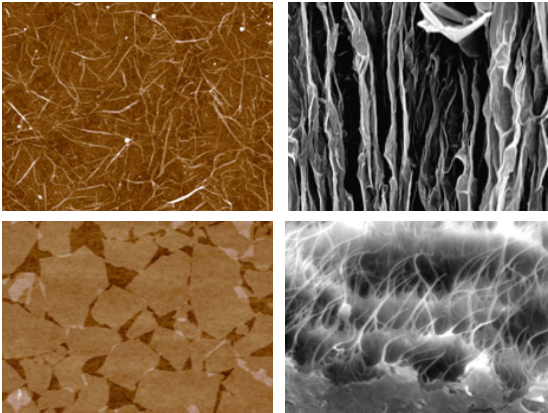
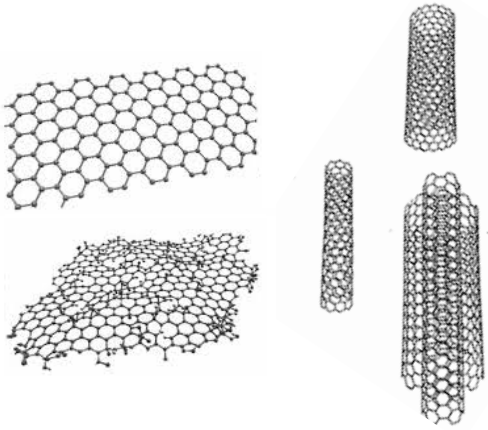
My Research Scope

Fundamental understandings

Nanoscale structures

Macroscale architectures

Performance evaluations



- *Macroelectronics*
- *Supercapacitors*
- *Smart textiles*
- *Electrocatalysts*
- *Membranes*
- *Antibacterial coatings*

Synthesis methods

Assembly techniques

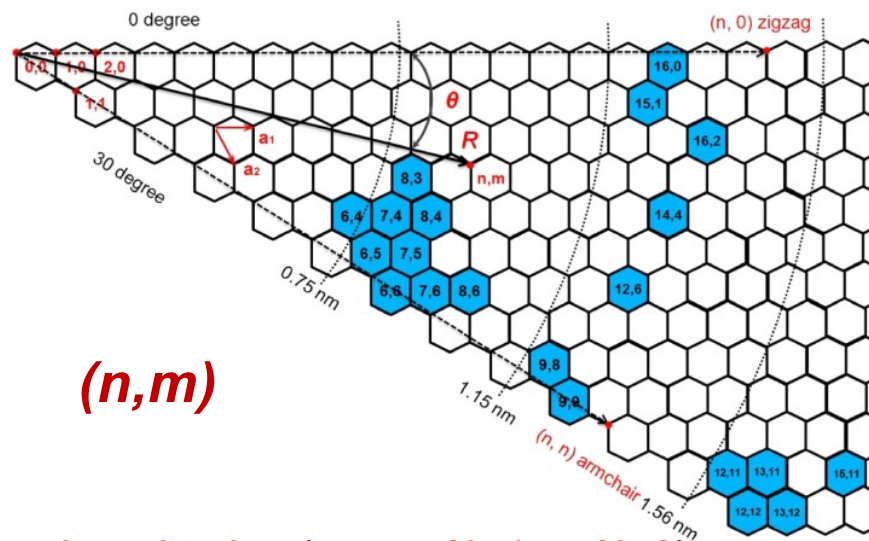
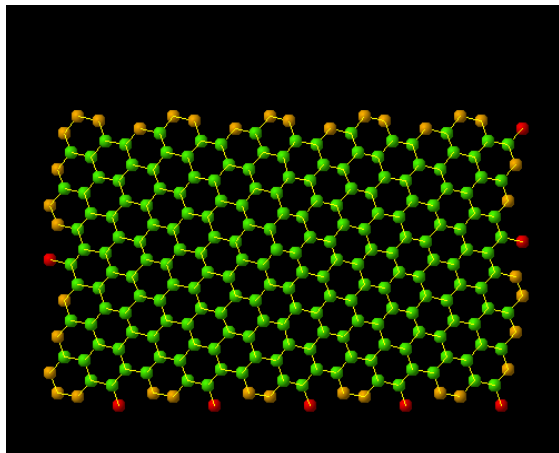
Application design

Chemical process design and development

Three Case Studies

- **Chirality selective synthesis of single-walled carbon nanotubes (SWCNTs)**
- Assembly of carbon nanotube/graphene hybrid carbon fibers for fiber supercapacitors
- Antibacterial activity of carbon nanotubes and graphene

Chirality of SWCNTs



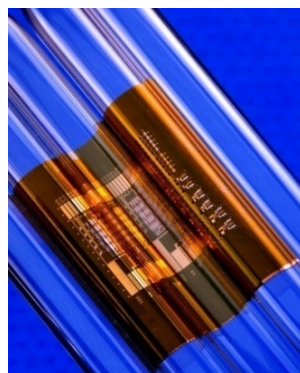
(n,m)

Metallic ($n-m = 3j$)

Semiconducting ($n-m = 3j+1$ or $3j+2$)



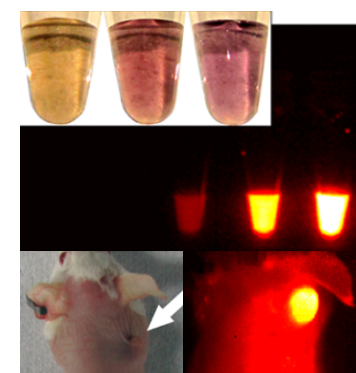
Conductive films



Electronic transistors

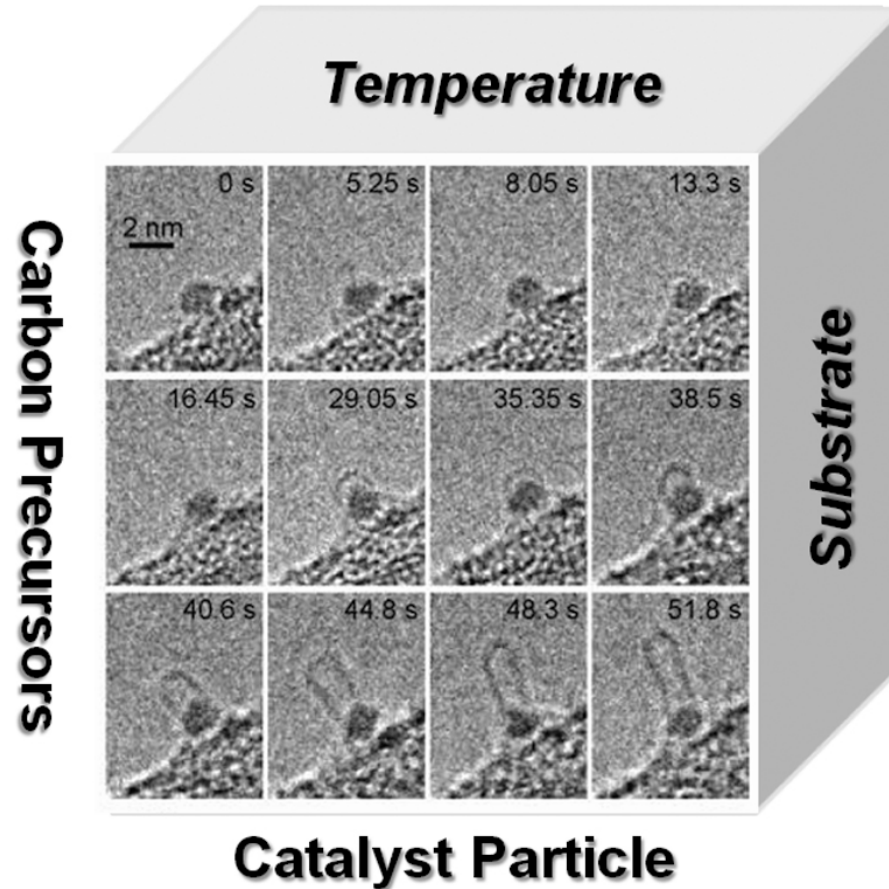


Photovoltaics



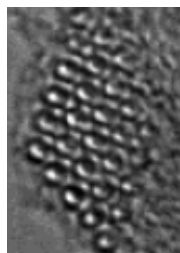
Bioimaging/phototherapy

Catalysts in Chemical Vapor Deposition of SWCNT Synthesis

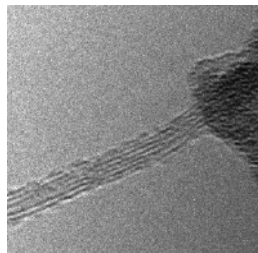


Efforts on Chirality Selective Synthesis

Co-MCM-41 (JPCB, 107, 11048; 108, 503)
Ni-MCM-41 (Nanotechnology, 16, S476)

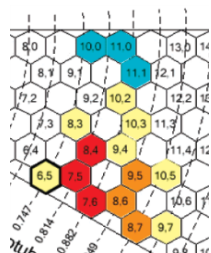


2003

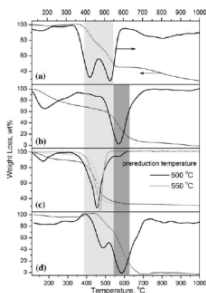


2005

Carbon feeds/P Supports (JMS, 44, 3285; Nano, 4, 99)
 (JACS, 129, 9014; Carbon, 45, 2217; JPCC, 111, 14612)

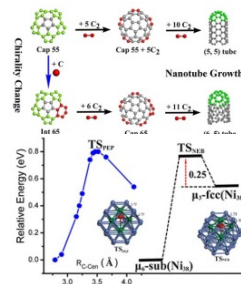


2007



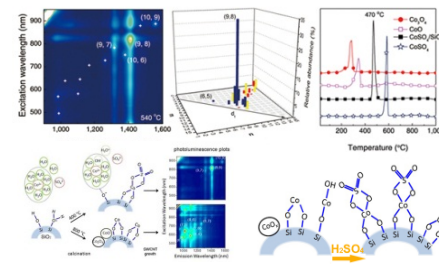
2009

Carbon dimer (ACS Nano, 4, 939; TCA, 128, 17)

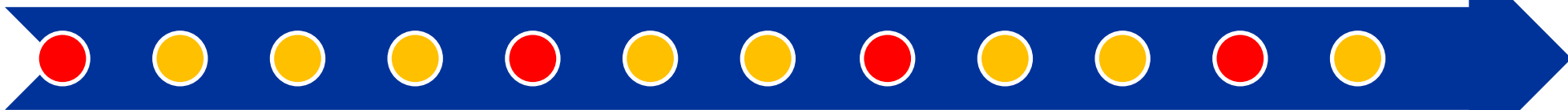


2011

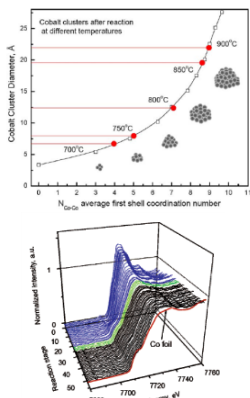
CoSO₄/SiO₂ (ACS Nano, 7, 614; JOC, 300, 91; CC, 49, 2031)



2013



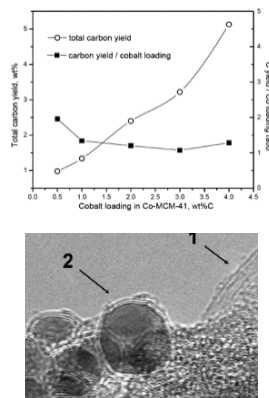
2004



T/P effects

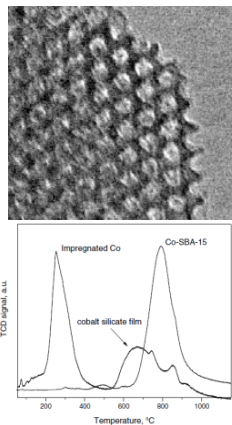
(JOC, 225, 453; 226, 351; JPCB, 108, 15565)

2006



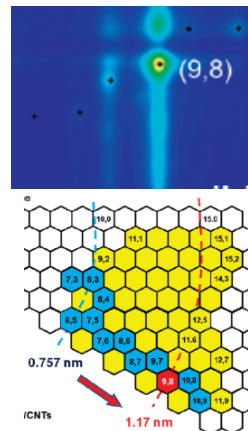
Metal loading (Carbon, 44, 67)

2008



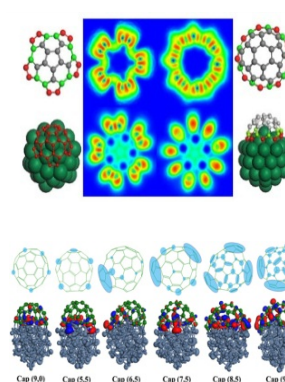
Co-SBA-15 (MMM, 110, 347)

2010



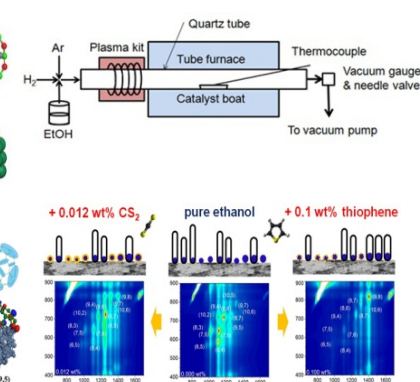
Co-TUD-1 (JACS, 132, 16747)

2012



Reactive sites (JPCL, 2, 1009; JPCC, 116, 11709)

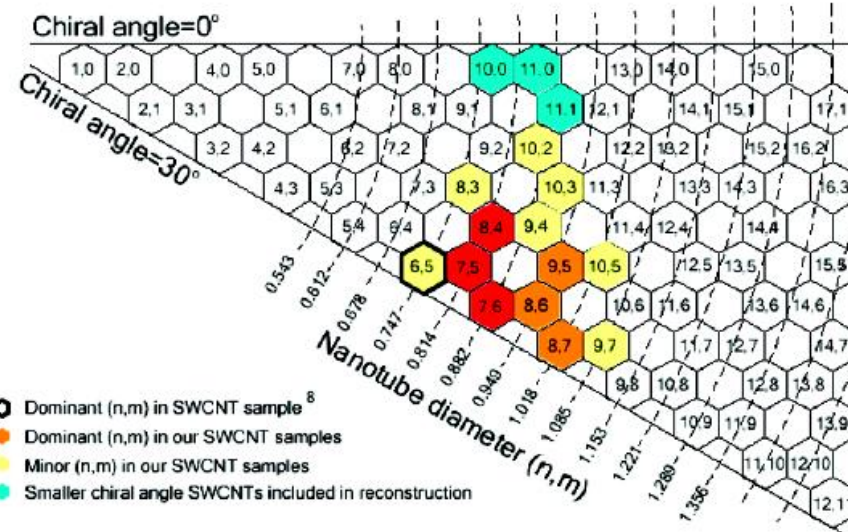
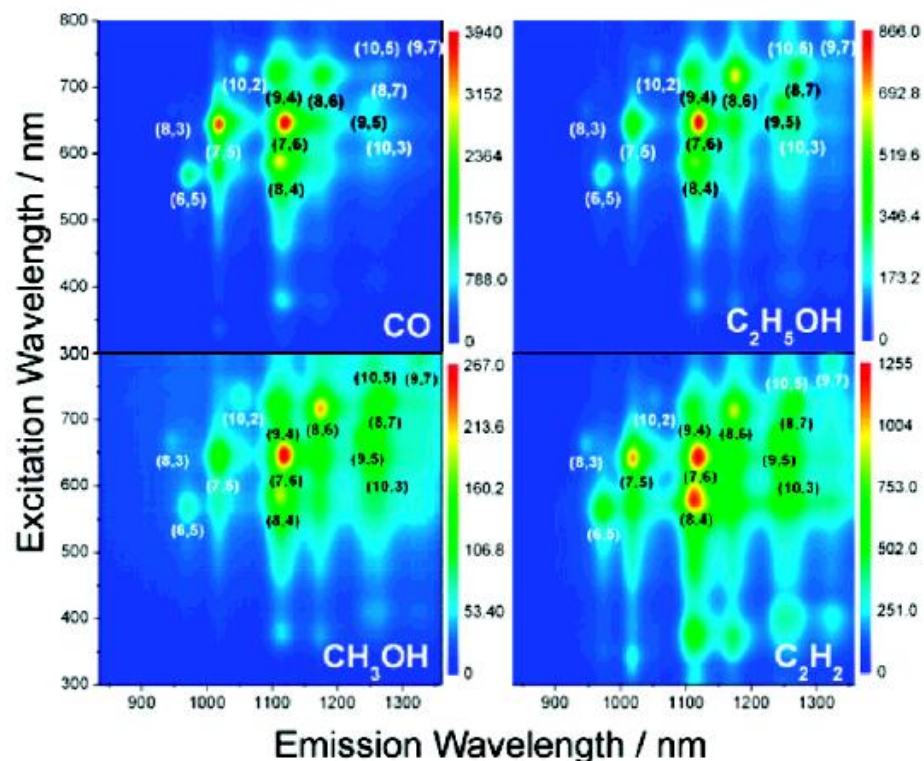
2014



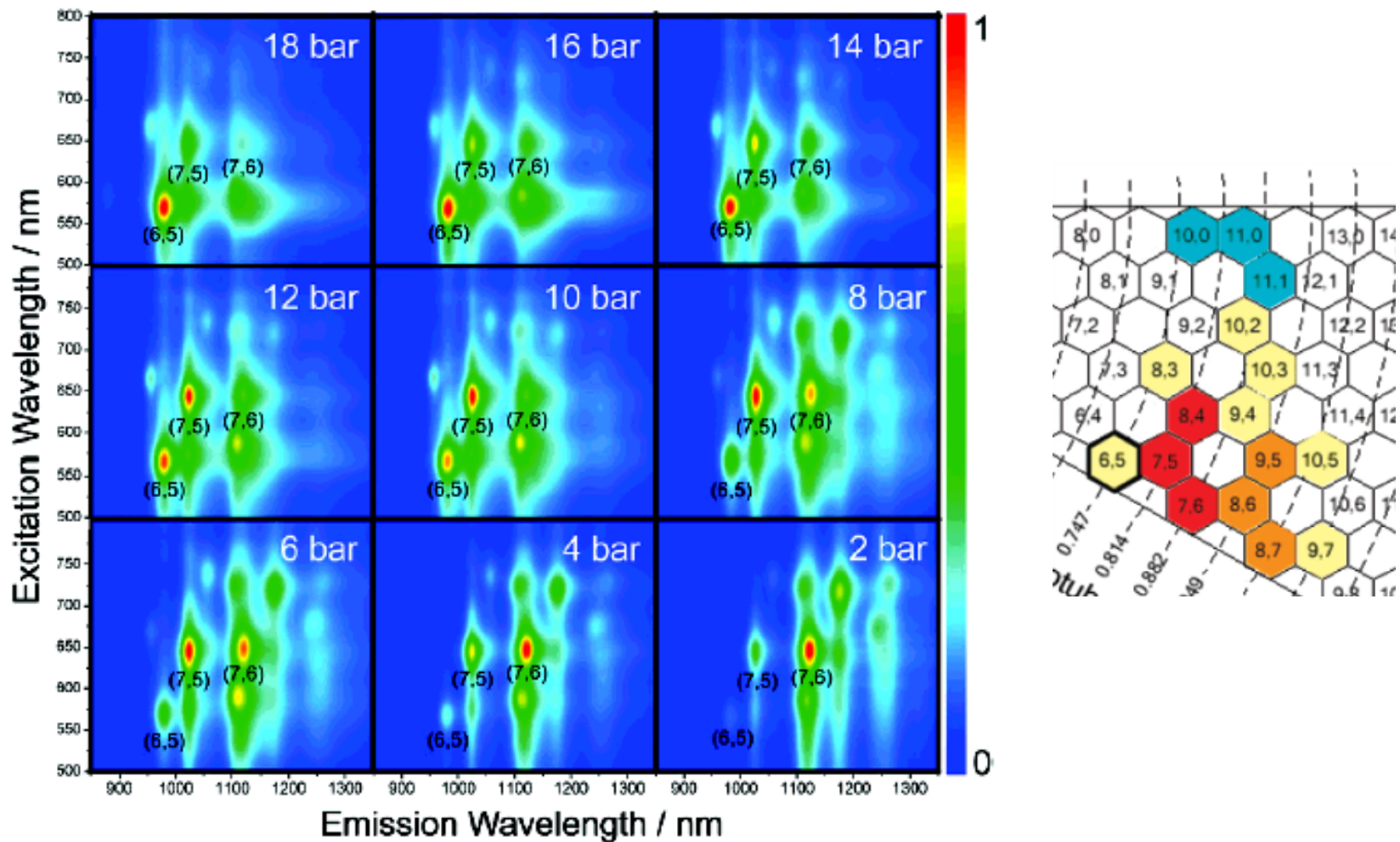
Plasma/S (Carbon, 66, 134; JMCA, 3, 3310)

Effect of Carbon Precursors

- Similar chirality distribution can be obtained using different carbon precursors
- Predominantly in the same high chiral angle region

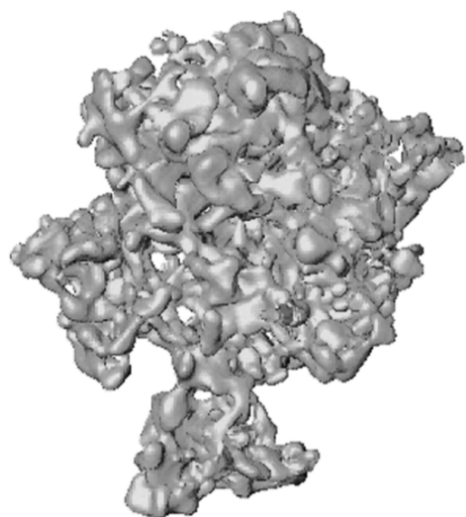


Pressure Induced Chirality Selectivity Changes

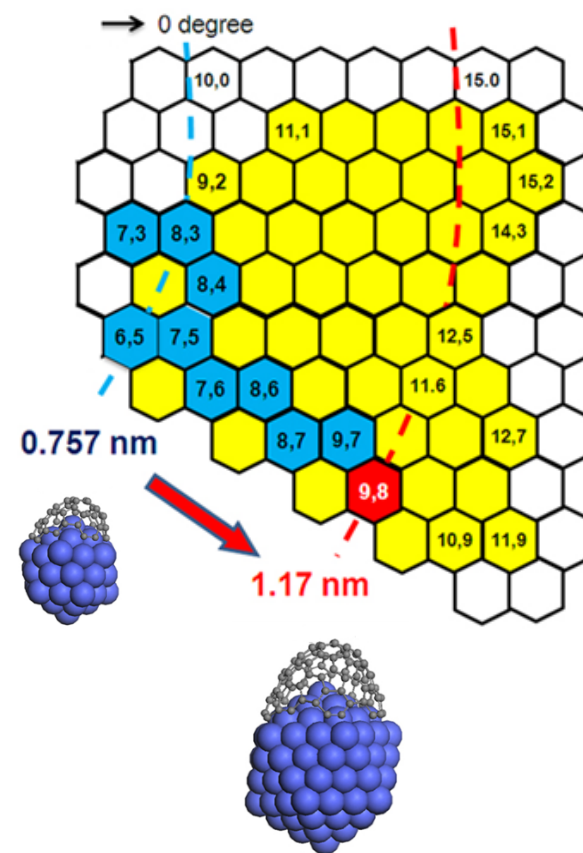
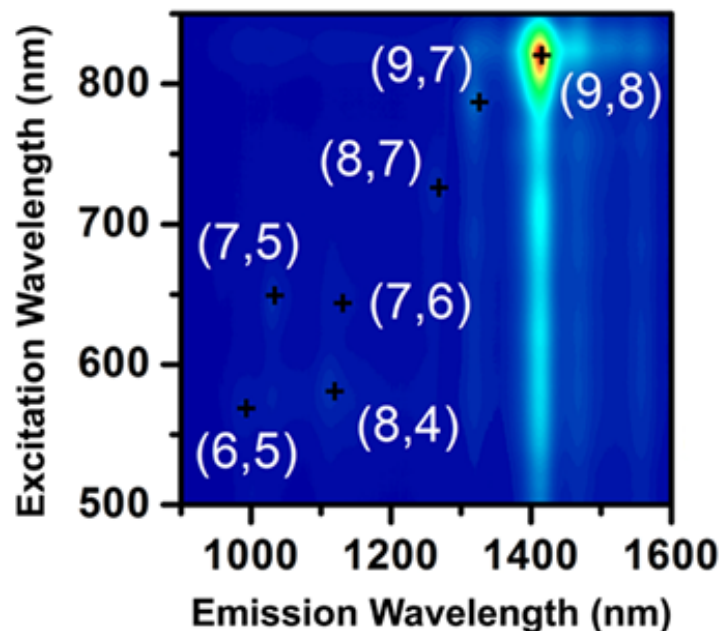


Co-TUD-1 Catalyst

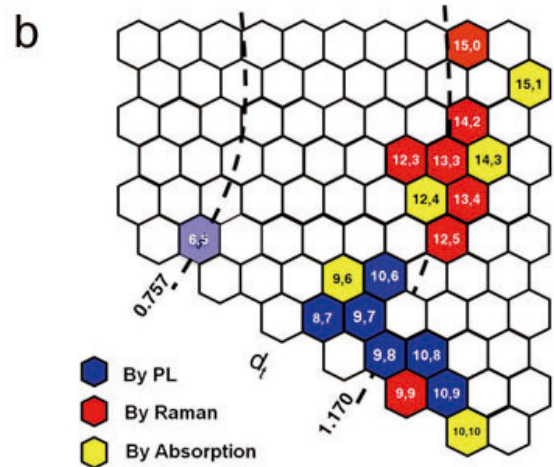
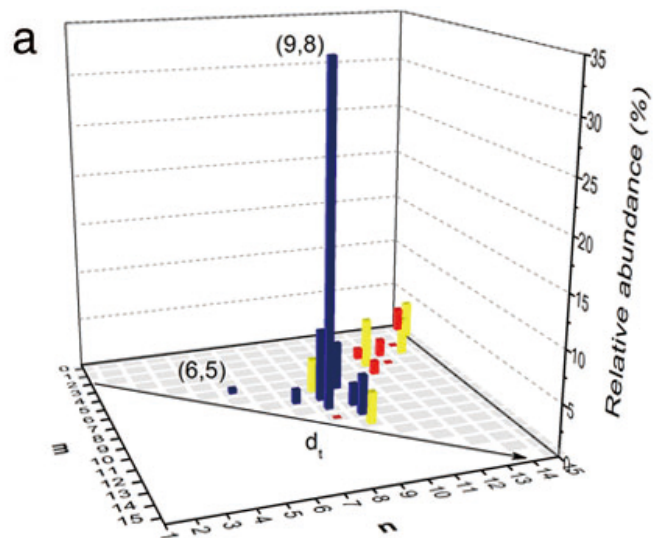
- SWCNTs with narrow (n,m) distribution at about 1.2 nm



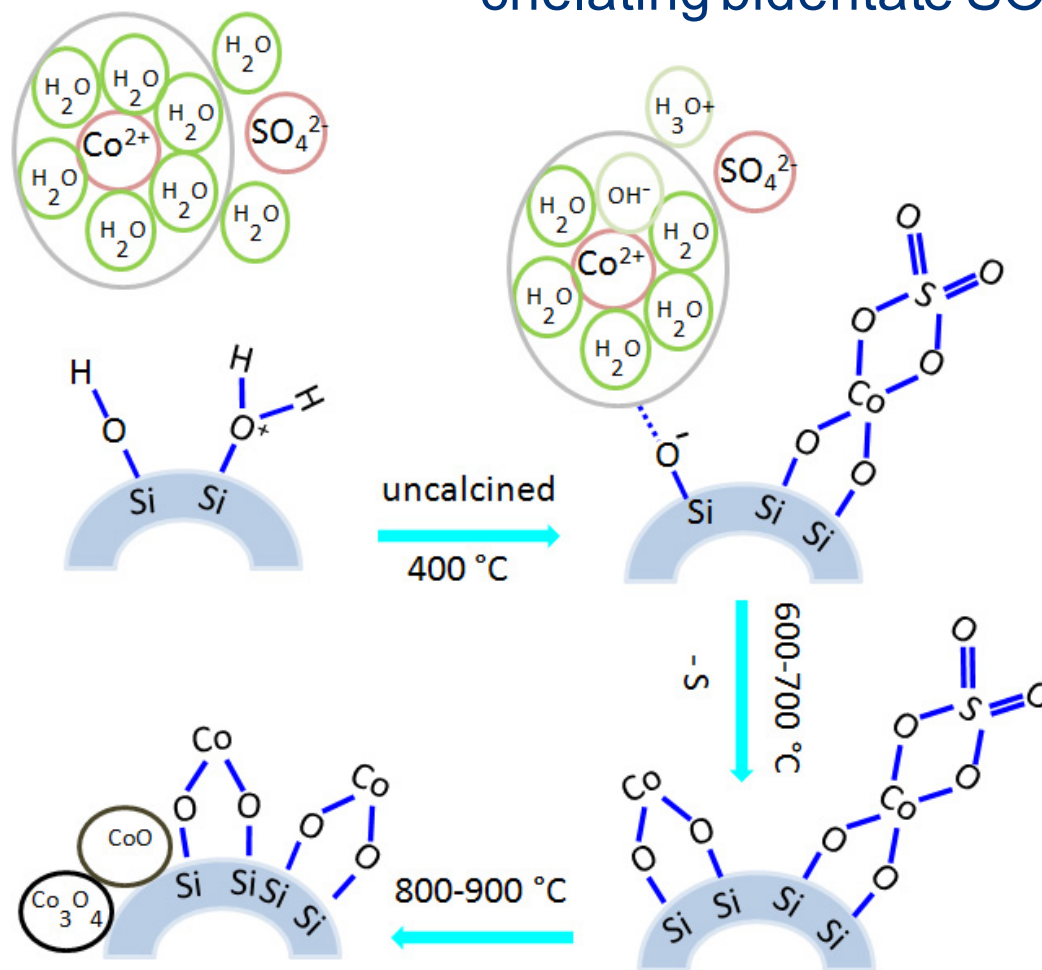
3D amorphous structure with random and interconnecting pores



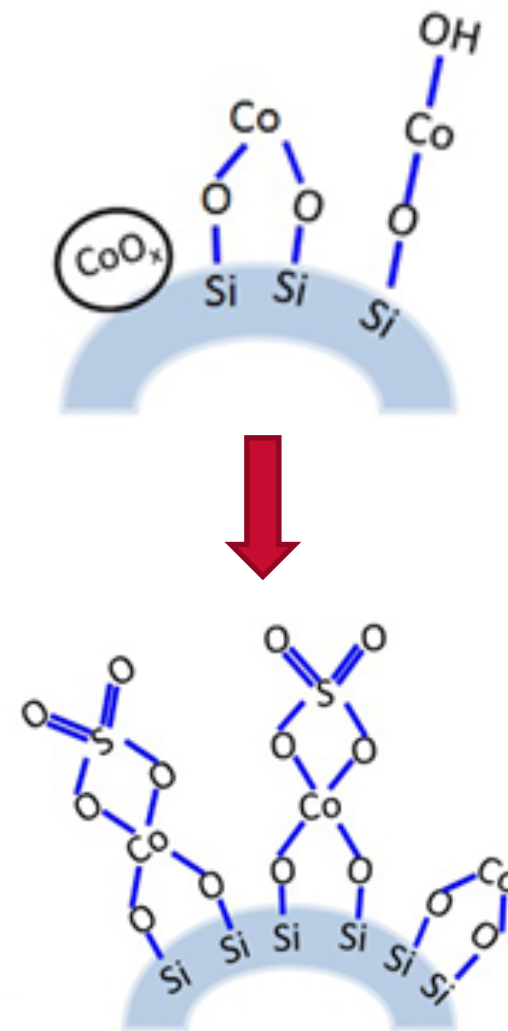
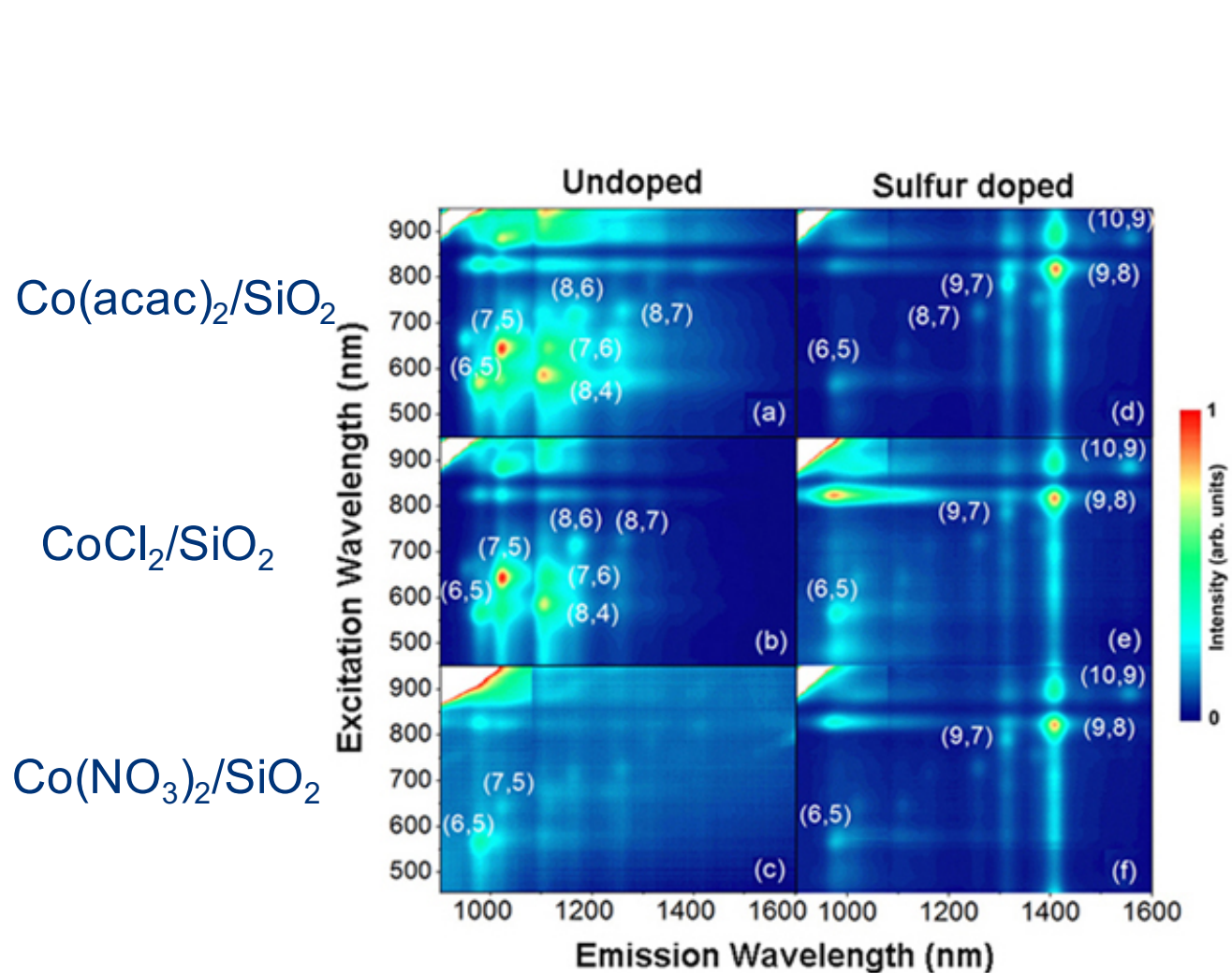
CoSO₄/SiO₂ Catalyst



Oxolation reaction
chelating bidentate SO₄²⁻



Sulfur Induced Chirality Selectivity



Catalysts for Chirality Selective Synthesis of SWCNTs

CARBON 81 (2015) 1–19



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Review

Catalysts for chirality selective synthesis of single-walled carbon nanotubes



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ABSTRACT

The chiral structures of single-walled carbon nanotubes (SWCNTs) can greatly affect their electronic, optical, thermal, mechanical and magnetic properties. As such, it has been a long-standing goal to selectively synthesize single chirality SWCNTs for potential applications ranging from electronics to medicine. Catalytic chemical vapor deposition is the prevalent method for chirality selective synthesis of SWCNTs. In this method, the catalyst plays a critical role in the chirality selection. This review summarizes the current state-of-the-art catalyst development for chirality selective synthesis of SWCNTs, and discusses the general principles in current state-of-the-art catalyst designs. Metal catalysts, which account for the majority of catalysts used so far, are first reviewed. They are divided into supported catalysts on porous and flat substrates and unsupported catalysts. The discussion is focused on catalyst preparation methods, which determine the performance of catalysts. Next, non-metal catalysts are examined. New approaches of using carbon seeds for SWCNT “cloning” are also summarized. Lastly, nanocarbon segments obtained from organic synthesis for SWCNT growth are discussed.

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Activity

Selectivity

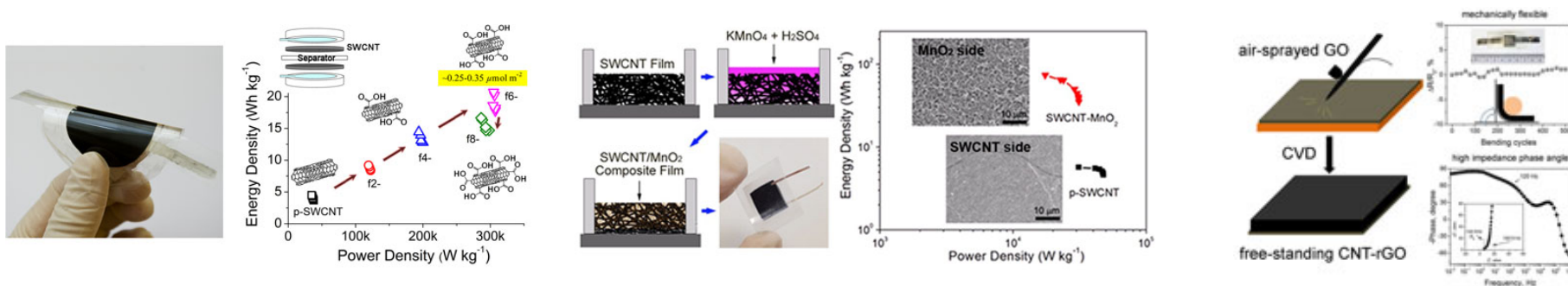
Stability

Cost

Three Case Studies

- Chirality selective synthesis of single-walled carbon nanotubes (SWCNTs)
- **Assembly of carbon nanotube/graphene hybrid carbon fibers for fiber supercapacitors**
- Antibacterial activity of carbon nanotubes and graphene

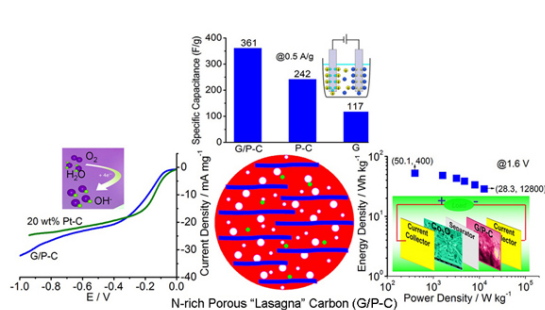
Carbon Based Electrodes/Electro-Catalysts



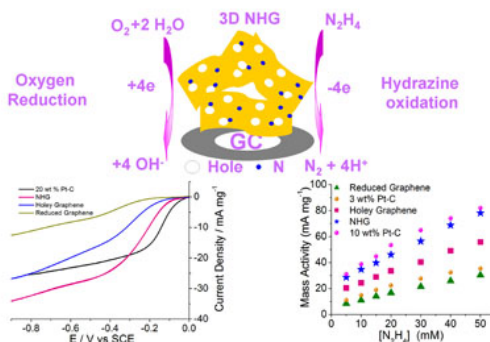
Energy & Environmental Science, 2011, 4, 4220

Electrochimia Acta, 2012, 78, 122-132

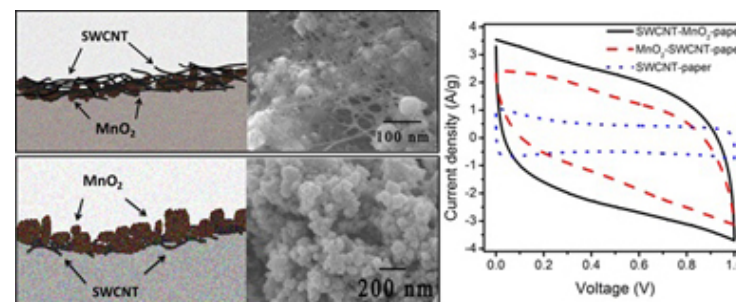
Journal of Solid State Chemistry, 2015, 224, 45



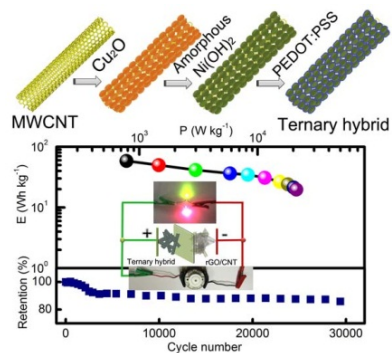
Journal of Materials Chemistry A, 2013, 1, 11061



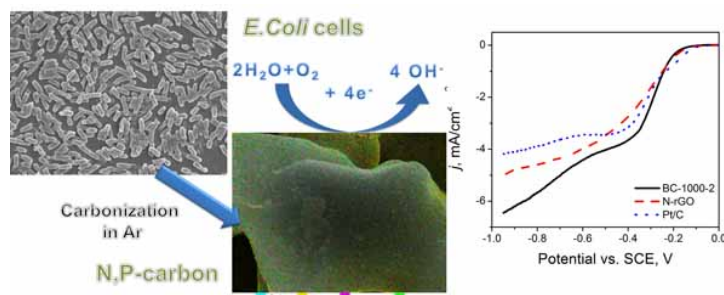
Nanoscale, 2013, 5, 3457



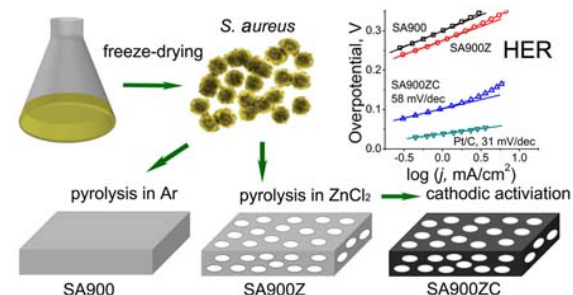
Nanoscale, 2013, 5, 11108



Advanced Functional Materials, 2015, 25, 1063



Catalysis Today, 2015, 249 228-235



Journal of Materials Chemistry A, 2015, 3, 7210-7214

Emergence of Fiber Supercapacitors



Chem Soc Rev

TUTORIAL REVIEW

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Cite this: DOI: 10.1039/c4cs00286e

Emergence of fiber supercapacitors

Dingshan Yu,^a Qihui Qian,^a Li Wei,^a Wenchao Jiang,^a Kunli Goh,^a Jun Wei,^b Jie Zhang^c and Yuan Chen^{*a}

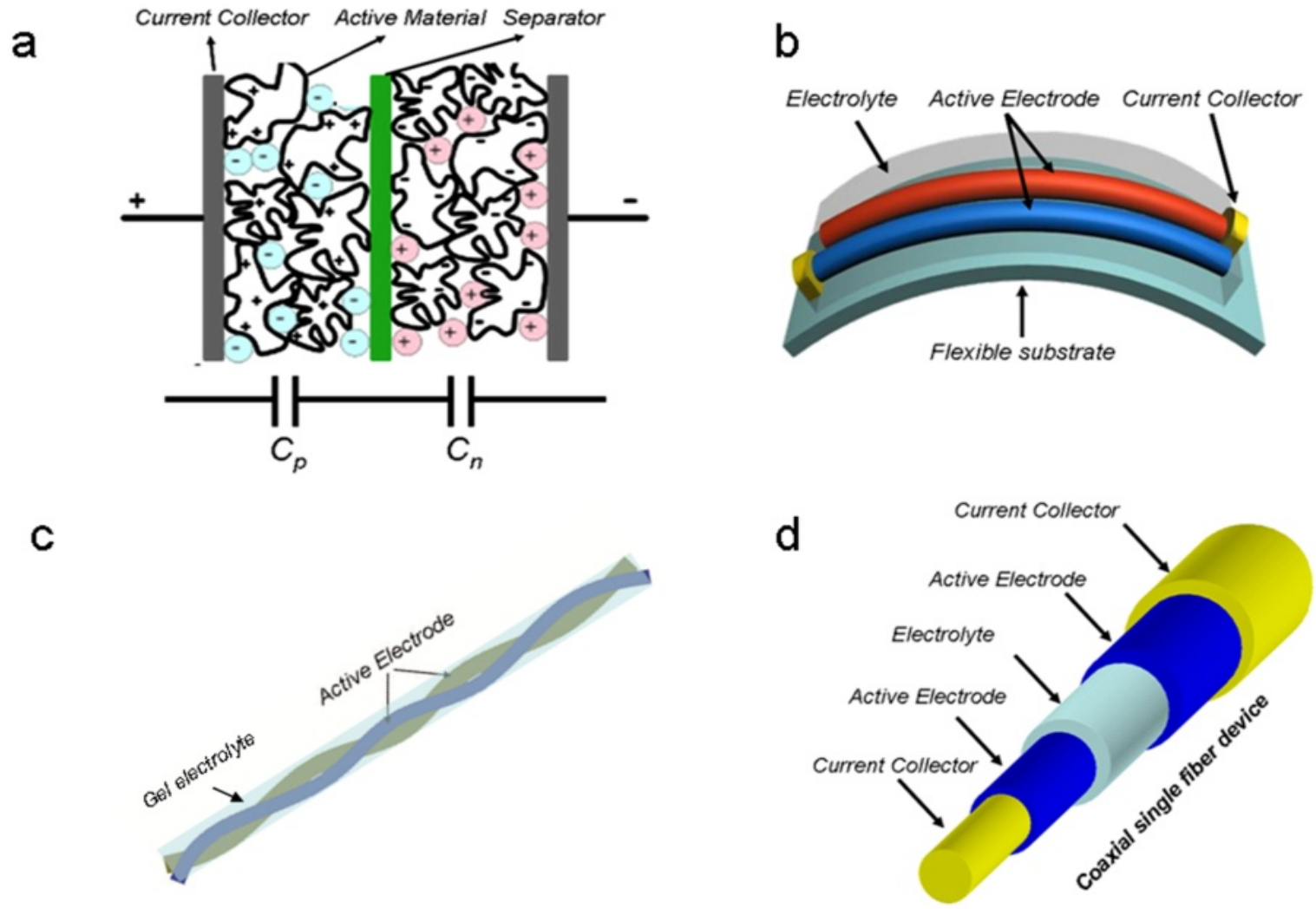
Supercapacitors (SCs) are energy storage devices which have high power density and long cycle life. Conventional SCs have two-dimensional planar structures. As a new family of SCs, fiber SCs utilize one-dimensional cylindrically shaped fibers as electrodes. They have attracted significant interest since 2011 and have shown great application potential either as micro-scale devices to complement or even replace micro-batteries in miniaturized electronics and microelectromechanical systems or as macro-scale devices for wearable electronics or smart textiles. This tutorial review provides an essential introduction to this new field. We first introduce the basics of performance evaluation for fiber SCs as a foundation to understand different research approaches and the diverse performance metrics reported in the literature. Next, we summarize the current state-of-the-art progress in structure design and electrode fabrication of fiber SCs. This is followed by a discussion on the integration of multiple fiber SCs and the combination with other energy harvesting or storage devices. Last, we present our perspectives on the future development of fiber SCs and highlight key technical challenges with the hope of stimulating further research progress.

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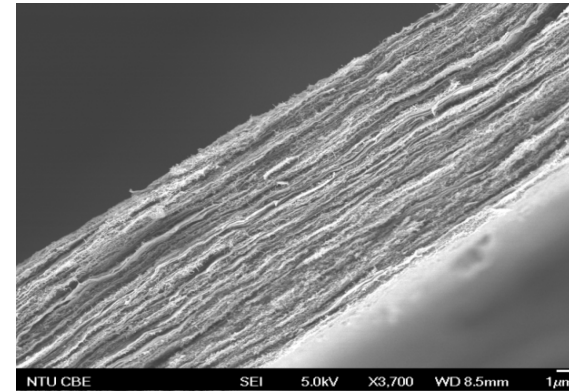
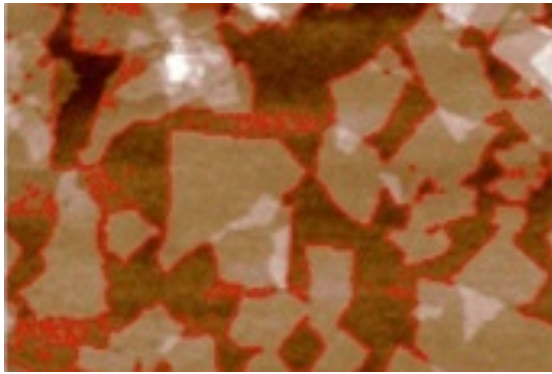
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Emergence of Fiber Supercapacitors

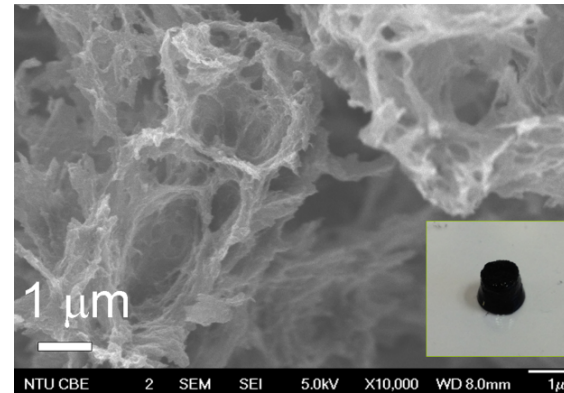


Synthesis of Carbon Composites

Graphene oxide sheets
Specific surface area: 2630 m²/g



Stacked GO films: 20-50 m²/g

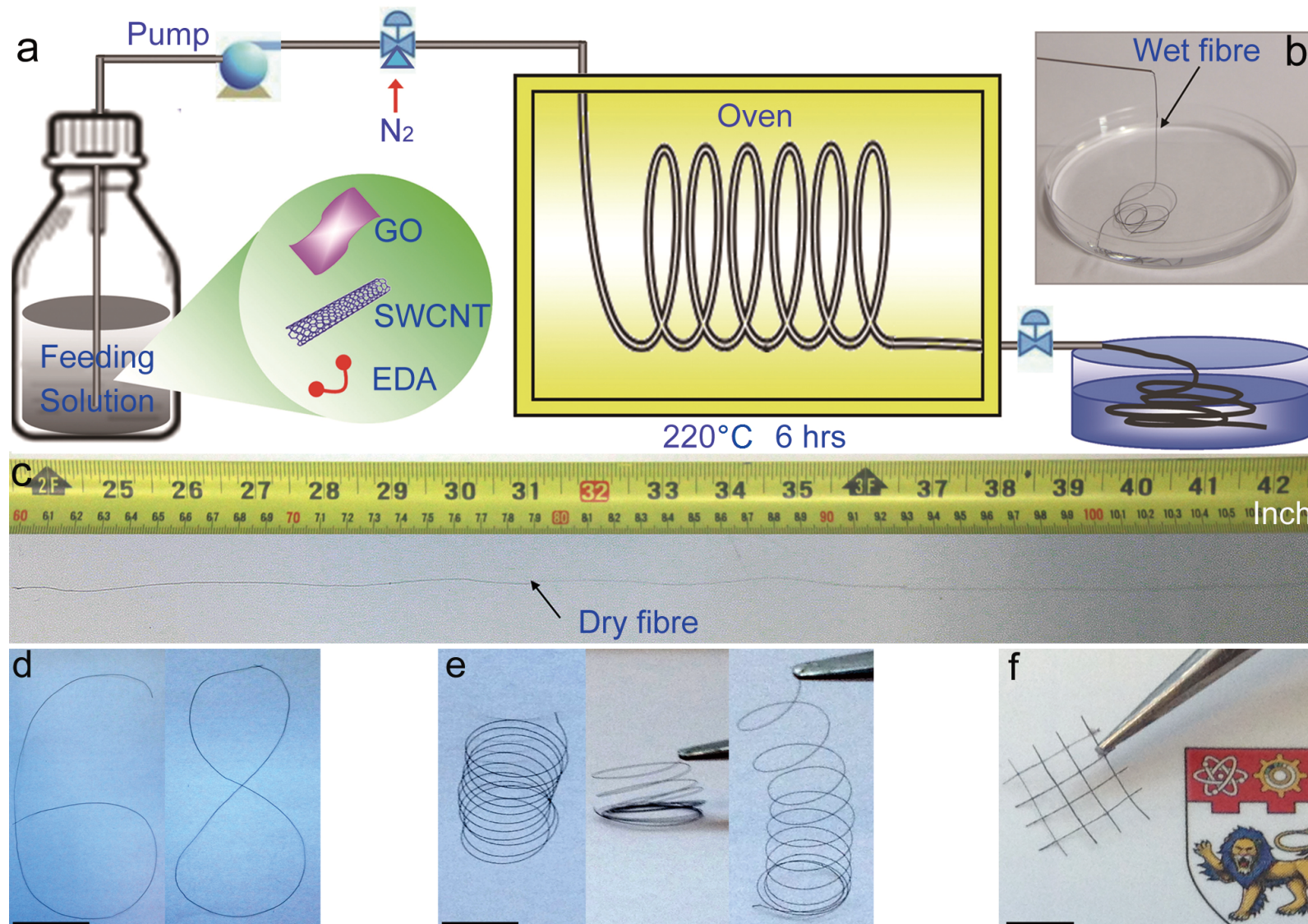


3D GO composites: 800 m²/g
Density: < 1 mg/cm³

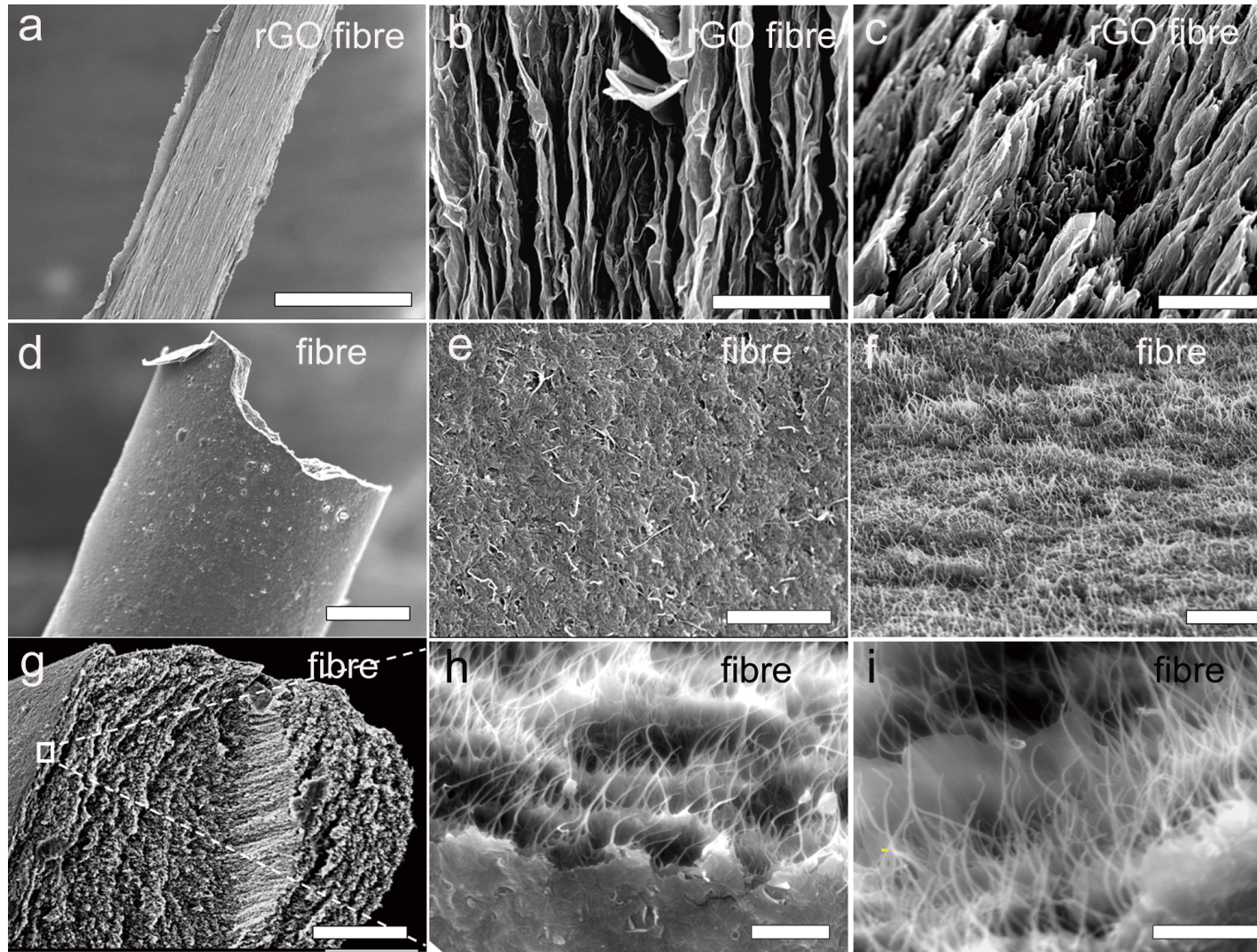
Hydrothermal
synthesis in
autoclaves



Synthesis of Carbon Hybrid Fibers

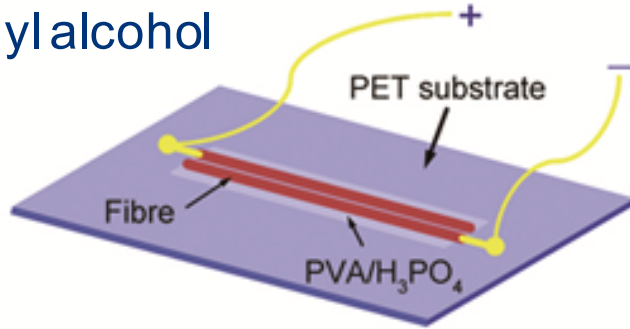


3D Composite Confined within 1D Fiber

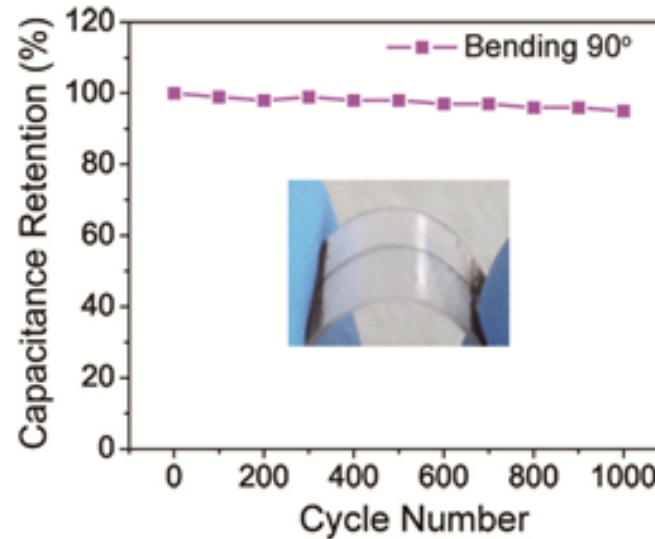
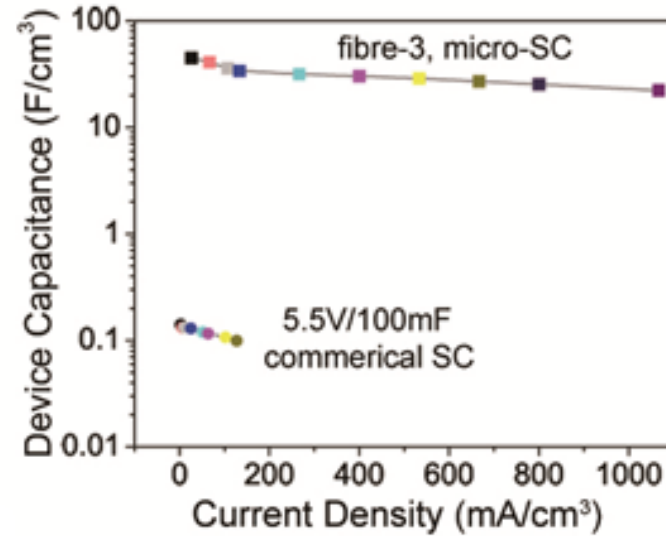
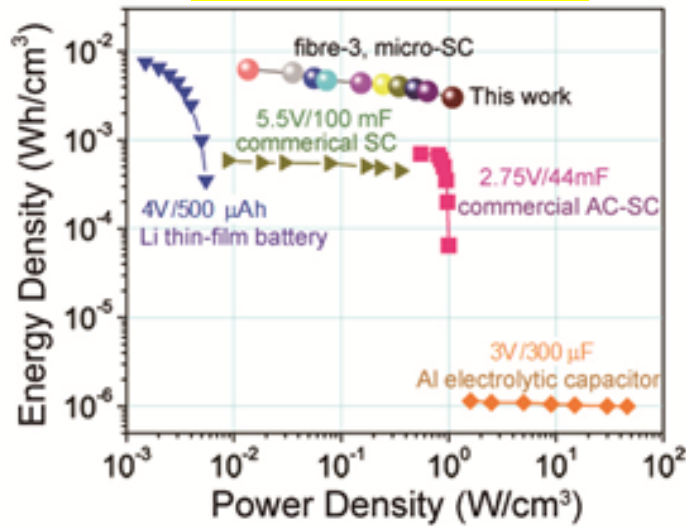


All-Solid-State Flexible Fiber Capacitors

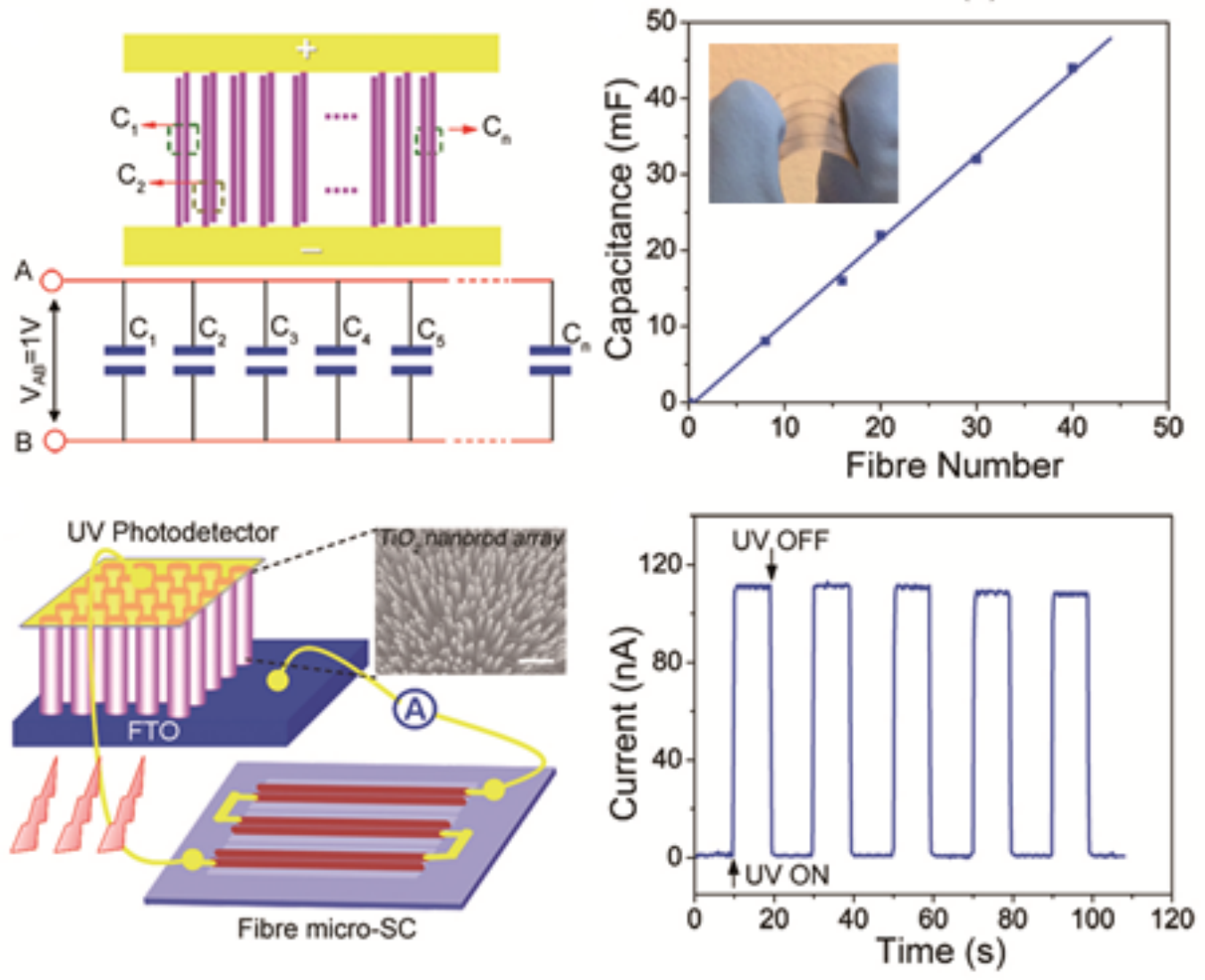
polyvinyl alcohol



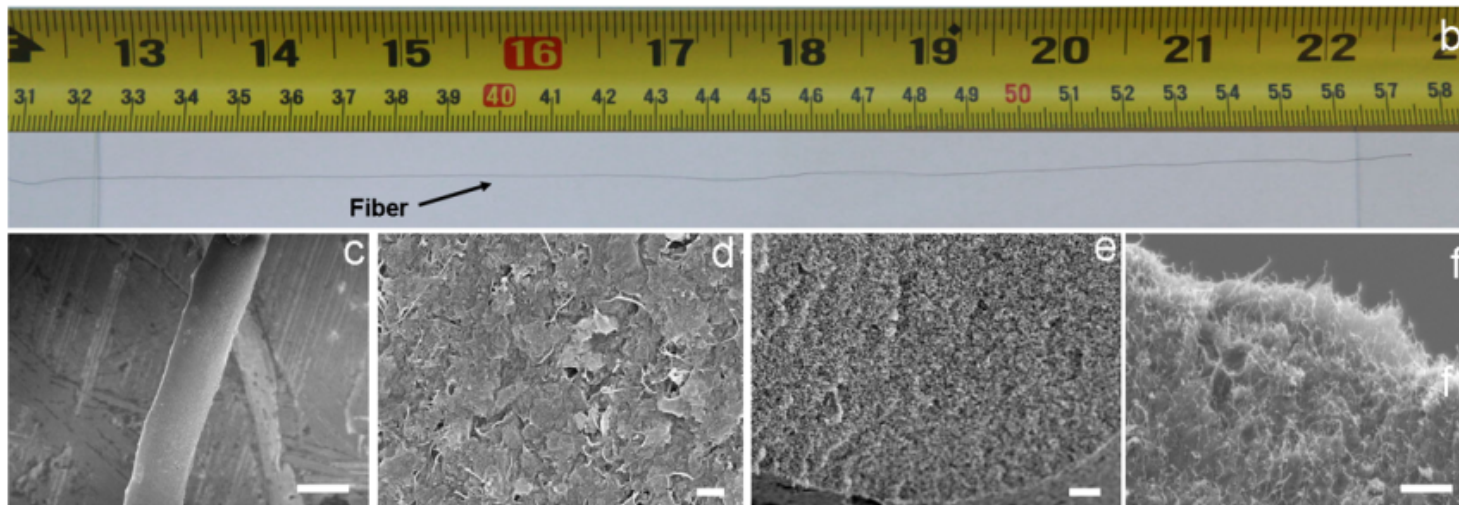
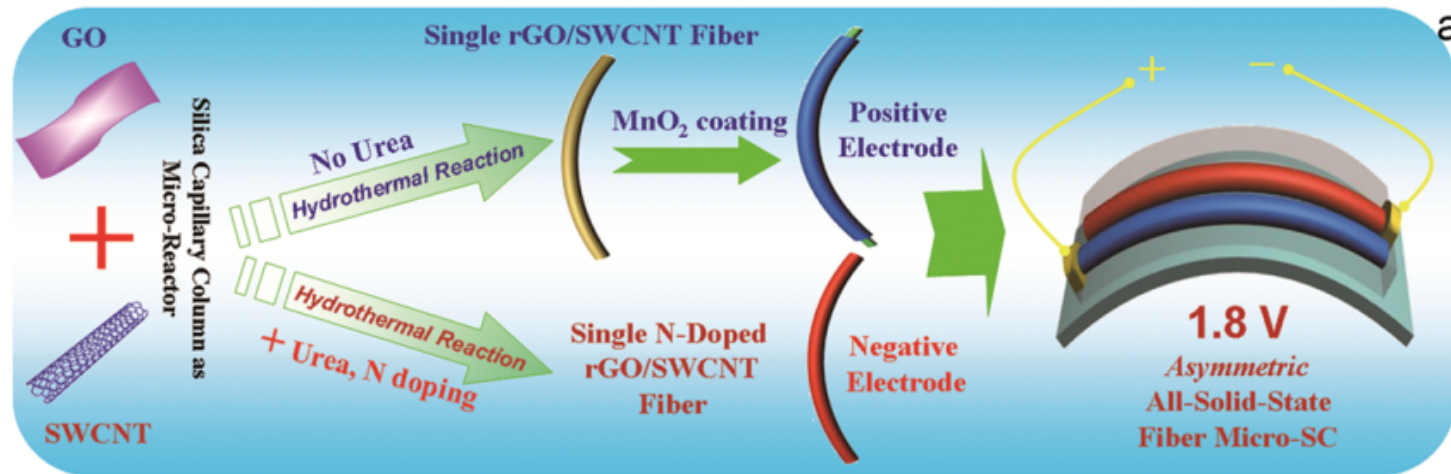
6.3 mWh/cm³



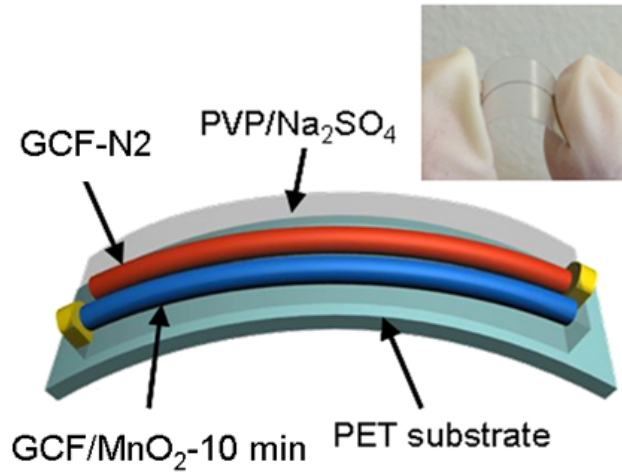
Integration in a Self-Powered Nanosystem



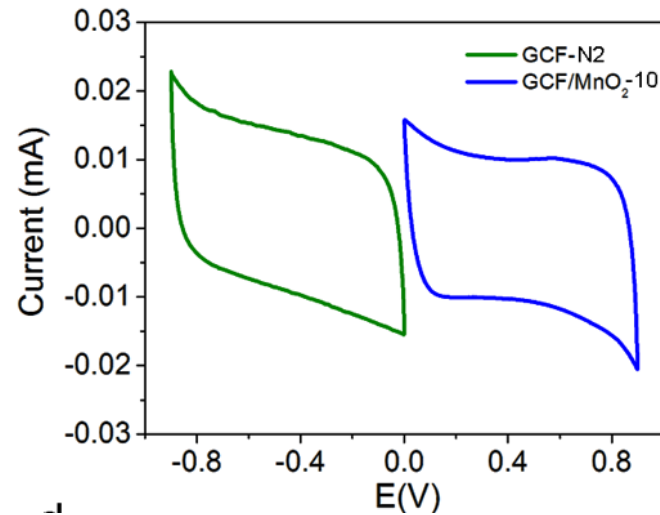
Controlled Functionalization of Carbon Hybrid Fibers



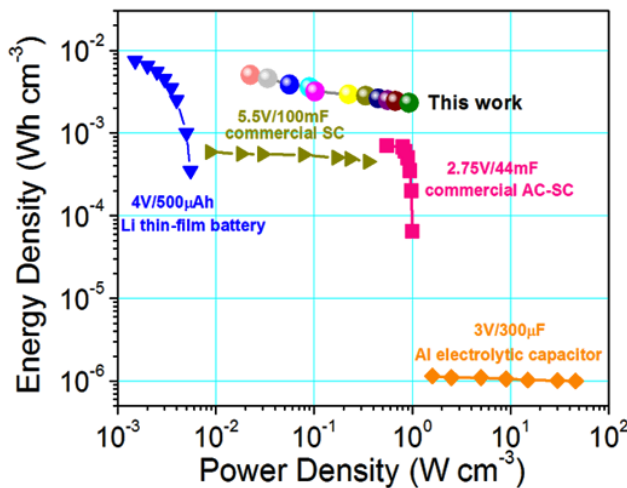
Asymmetric Solid-State Micro-Supercapacitors



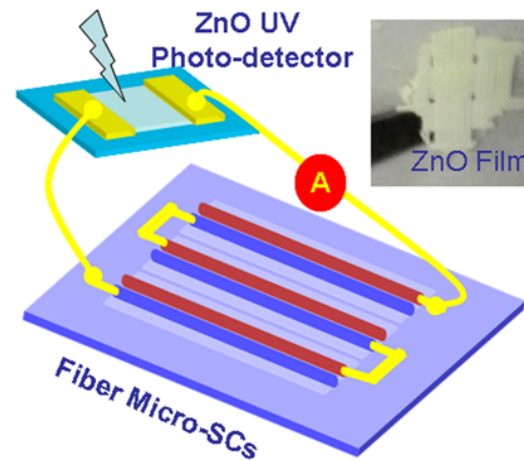
Neutral Electrolyte



Wider voltage window: 1.8 V



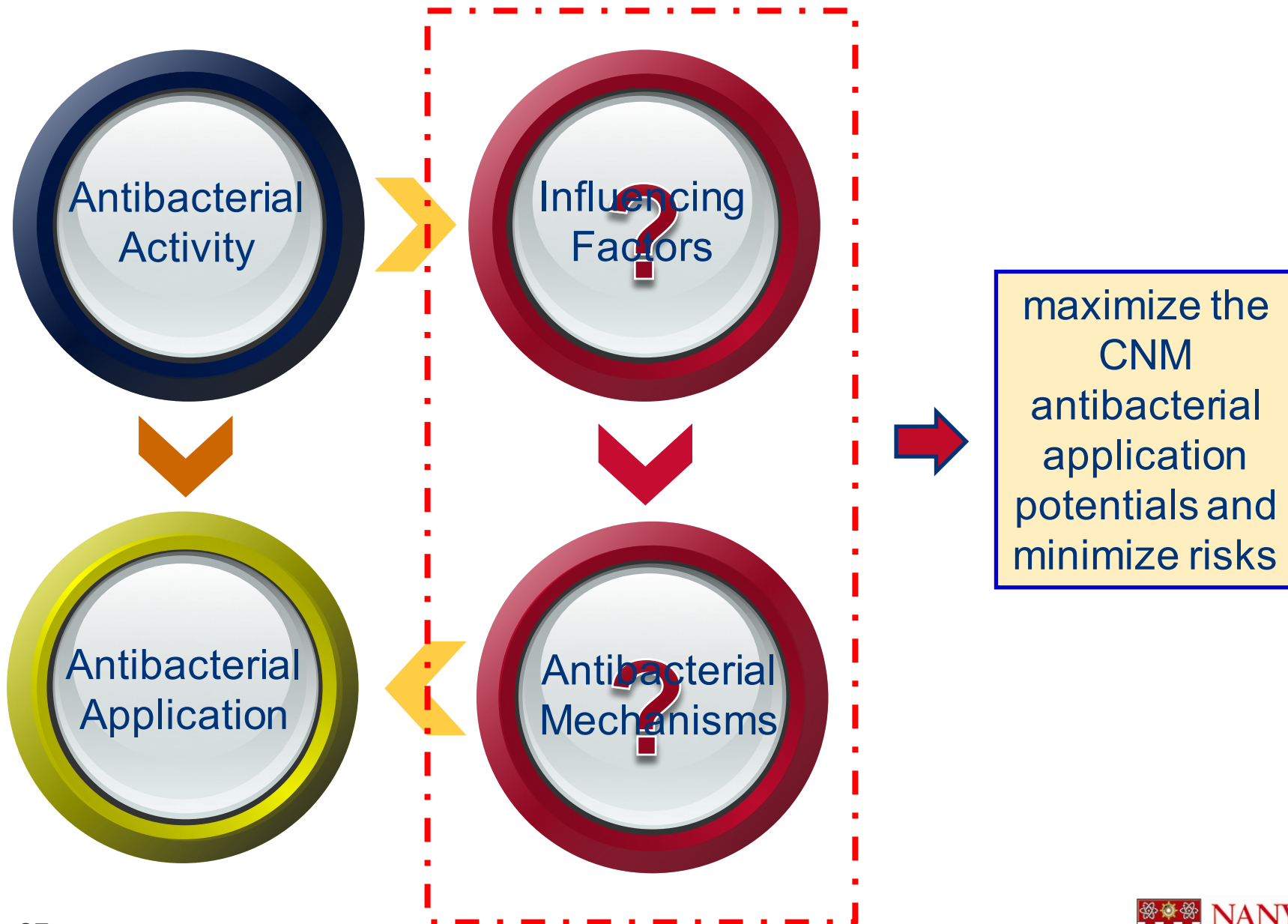
High energy/power density



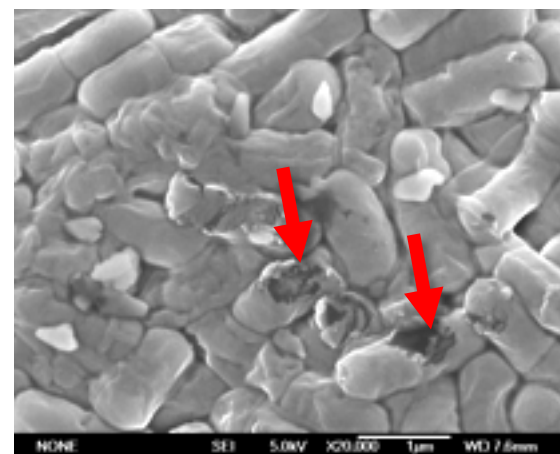
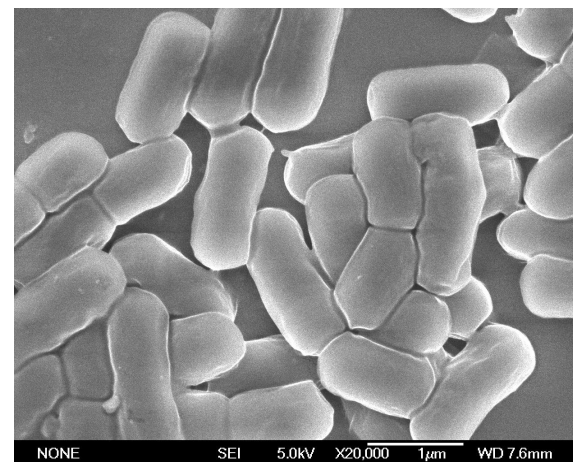
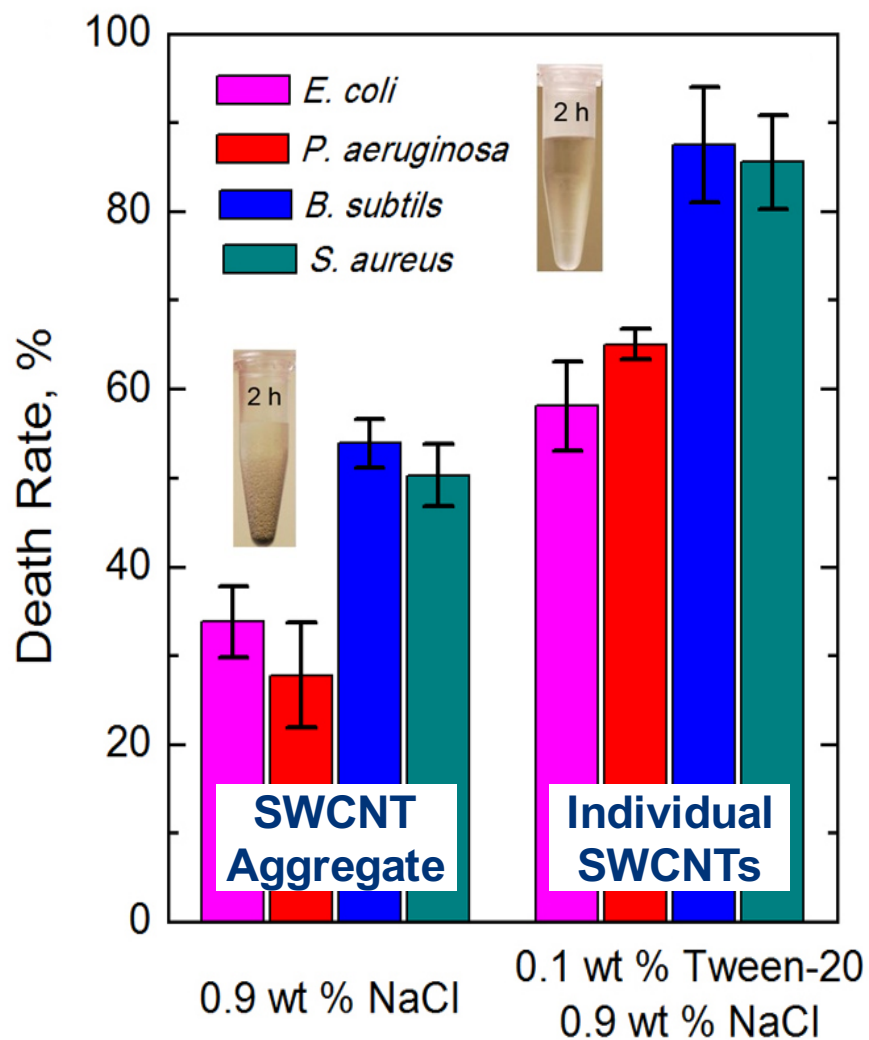
Integratable in nanosystem

Three Case Studies

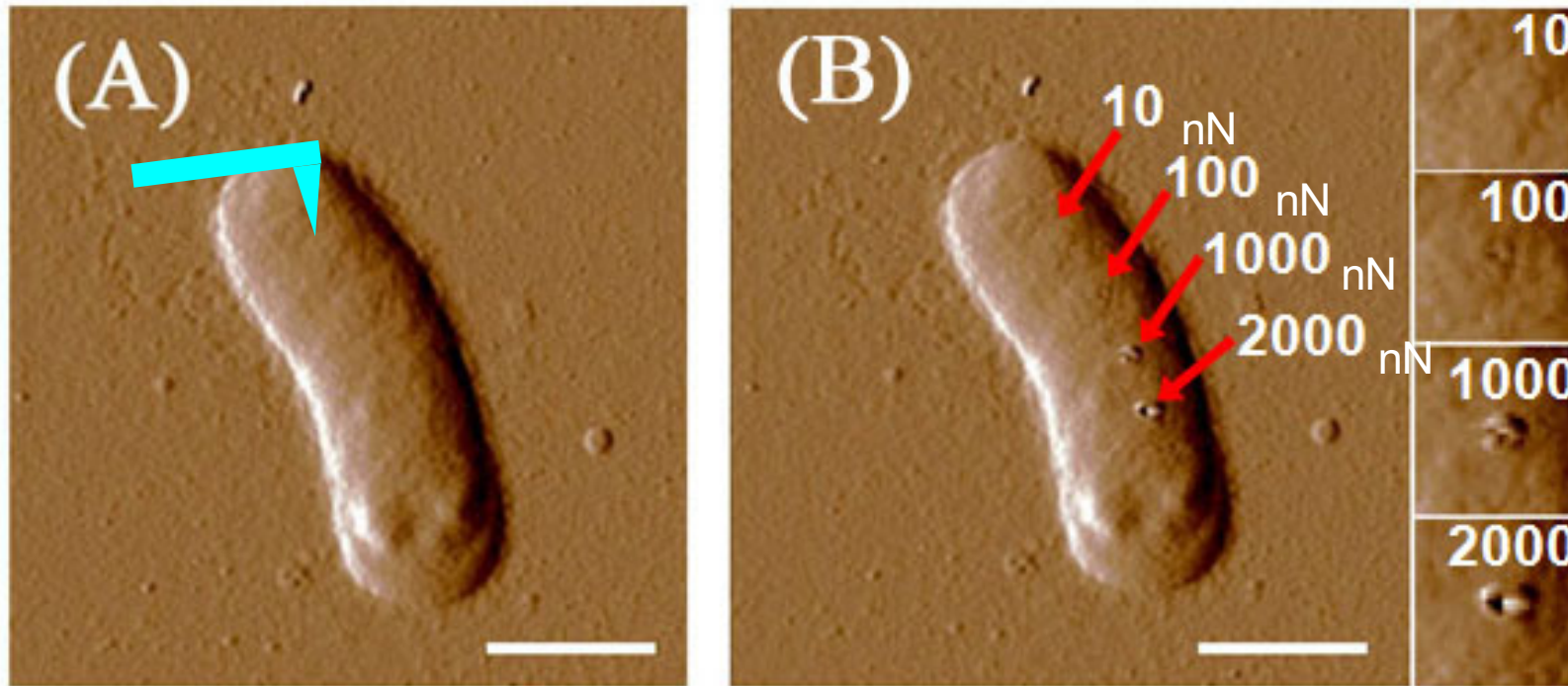
- Chirality selective synthesis of single-walled carbon nanotubes (SWCNTs)
- Assembly of carbon nanotube/graphene hybrid carbon fibers for fiber supercapacitors
- **Antibacterial activity of carbon nanotubes and graphene**



Dispersed SWCNTs Kill More Bacteria



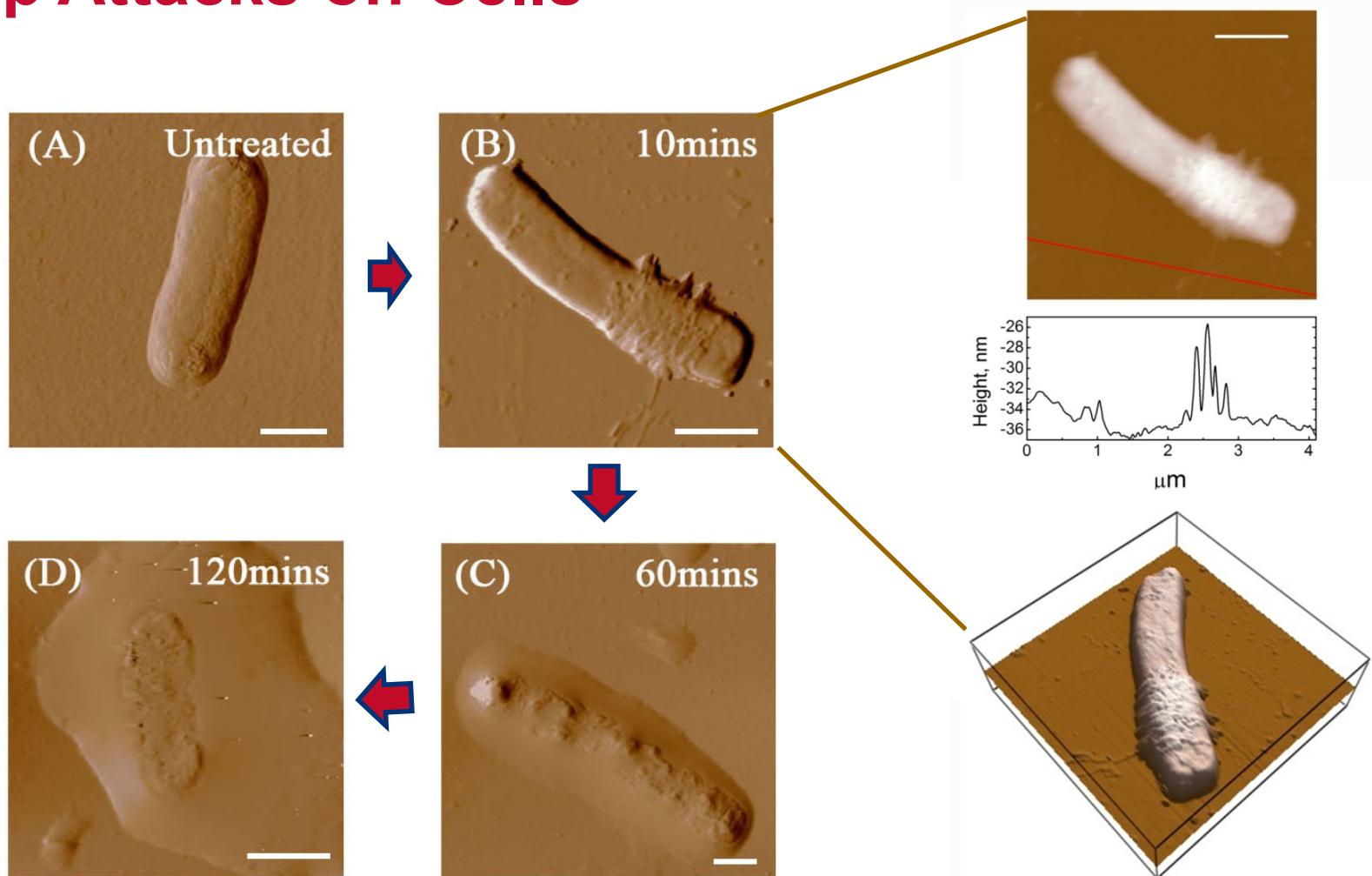
Atomic Force Microscopic Study of Cells



AFM amplitude images of (A) E. coli and (B) E. coli after piercing by a 2 nm AFM tip for 200 times at different locations.

SWCNTs dispersed in solution cannot induce large forces (> 10 nN)

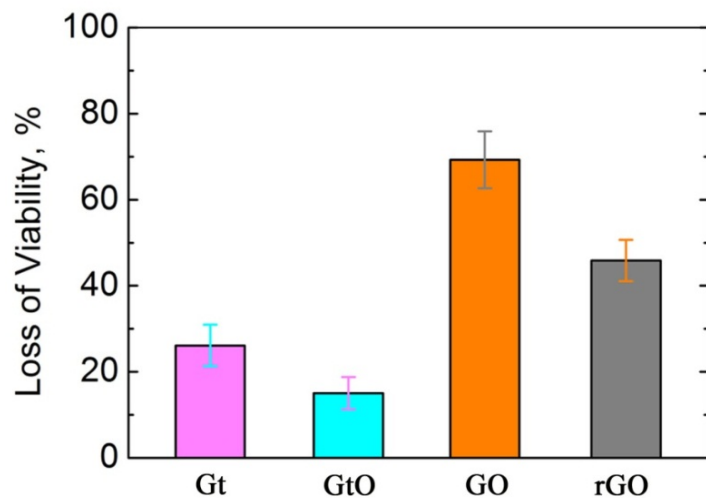
Group Attacks on Cells



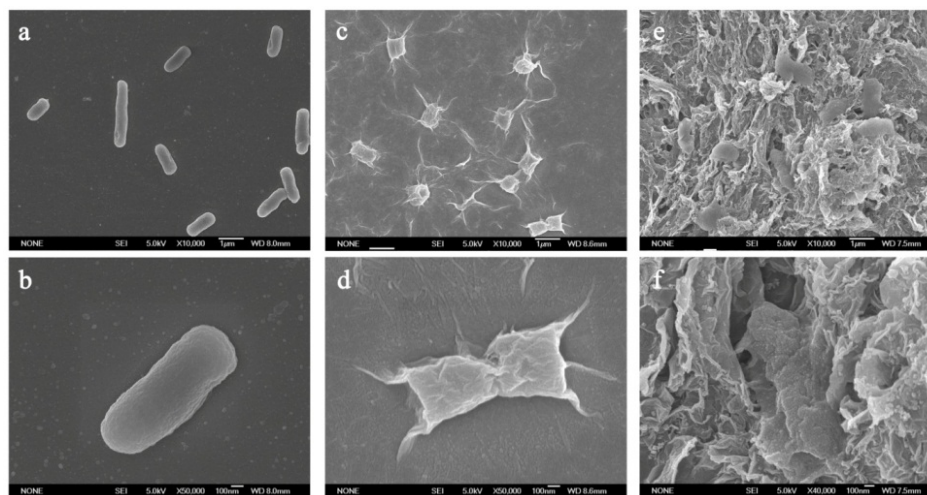
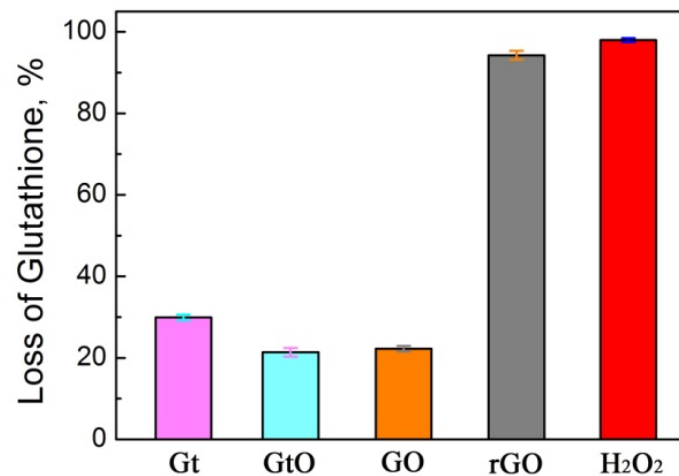
The antibacterial activity of SWCNTs is the accumulation effect of large amount of nanotubes through interactions between SWCNT networks and bacterial cells.

Antibacterial Activity of Graphene Based Materials

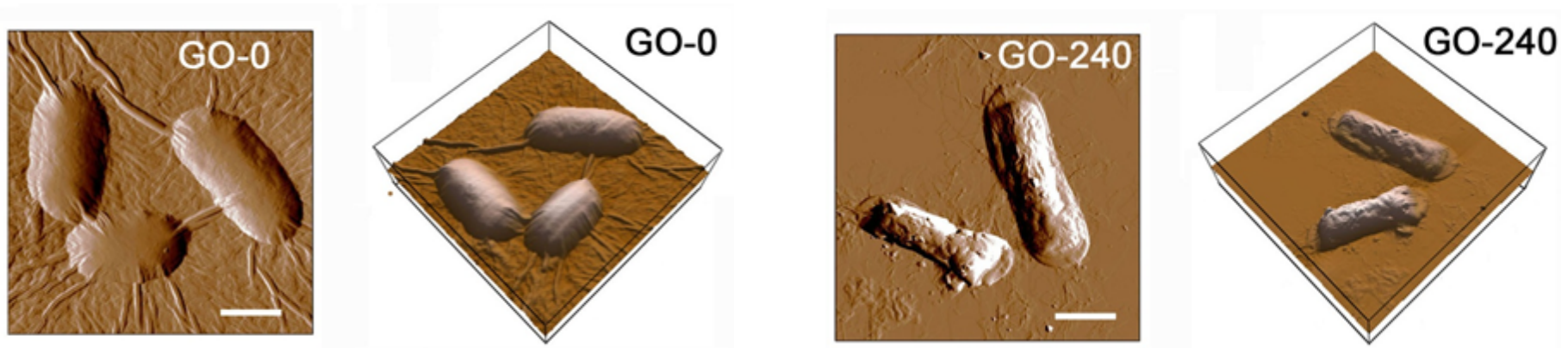
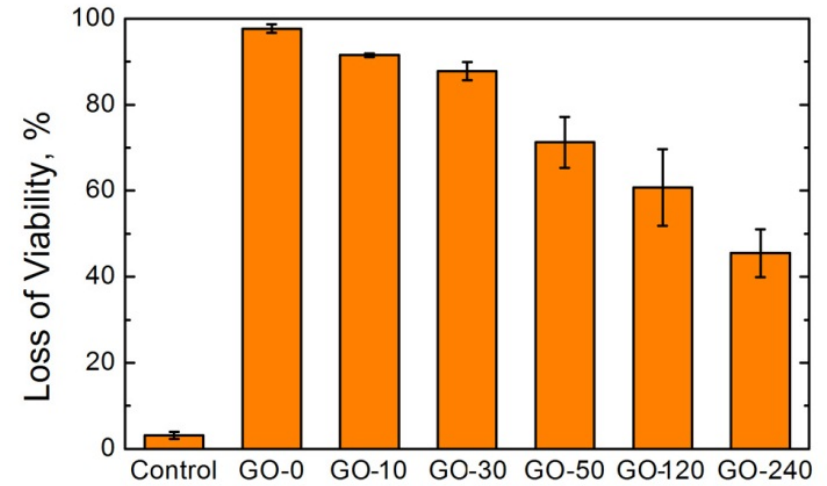
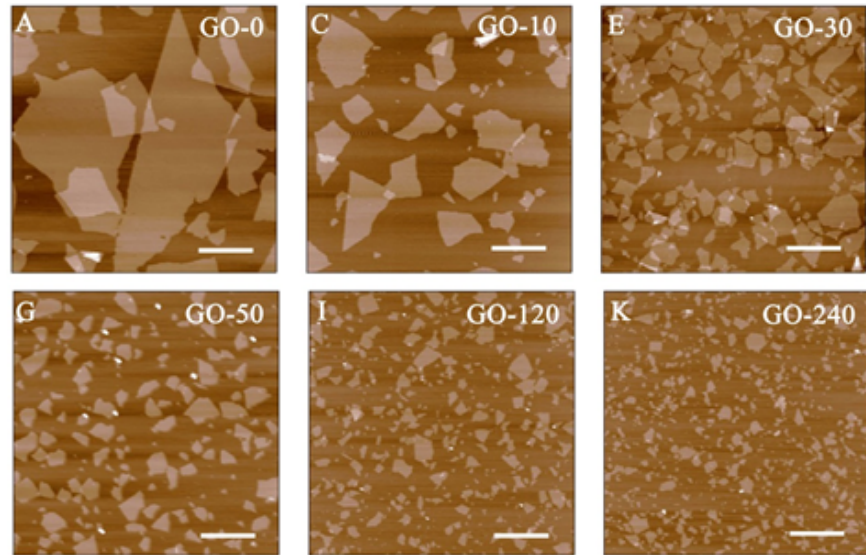
Antibacterial activity
GO > rGO > Gt > GtO



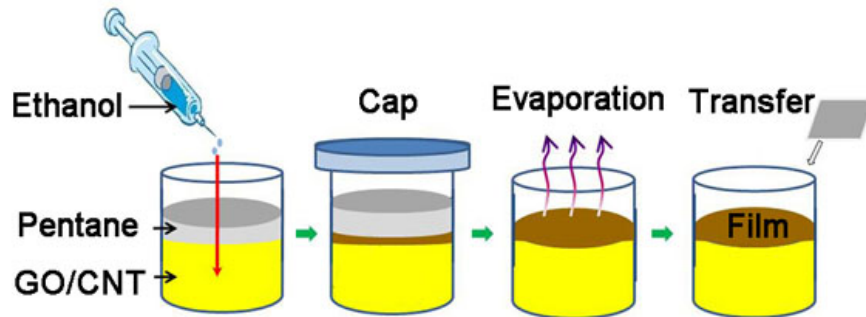
Oxidative stress
rGO > Gt > GO ≈ GtO



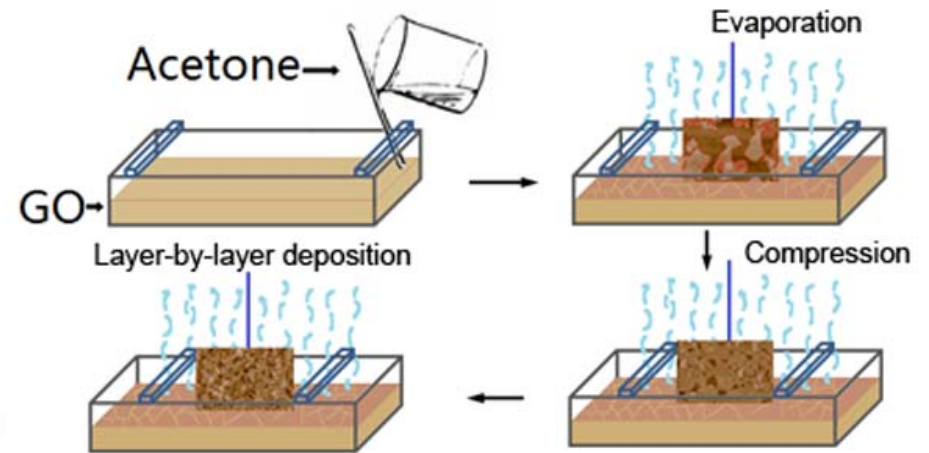
Size Effect on Antibacterial Activity of GO



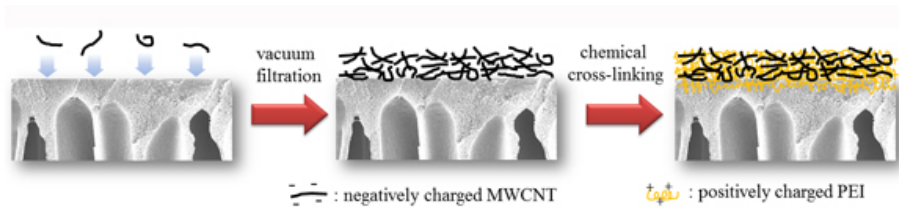
Exploring Potential Antibacterial Applications



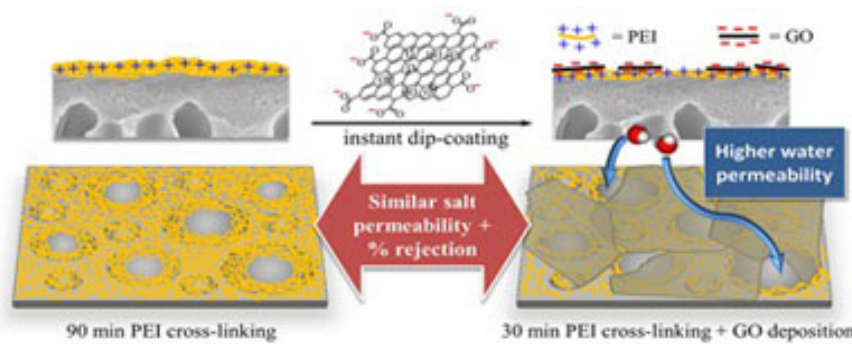
Langmuir, 2011, 27, 9174



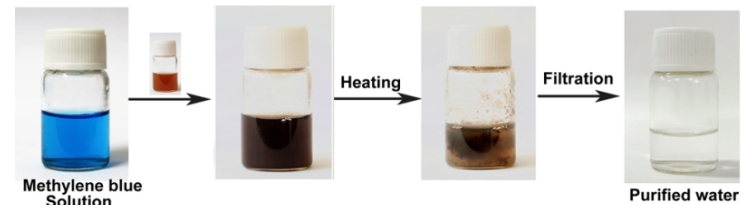
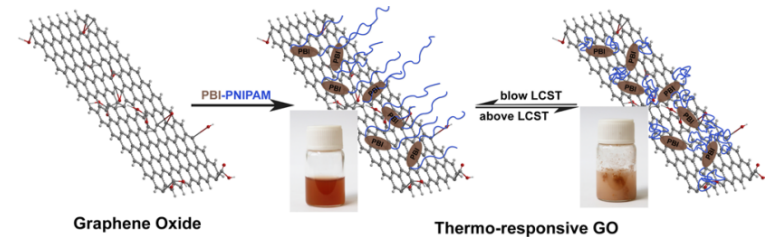
Chemistry - An Asian Journal, 2013, 8, 437



Journal of Membrane Science, 2013, 446, 244



Journal of Membrane Science, 2015, 474, 244



Journal of Colloid and Interface Science, 2014, 430, 121

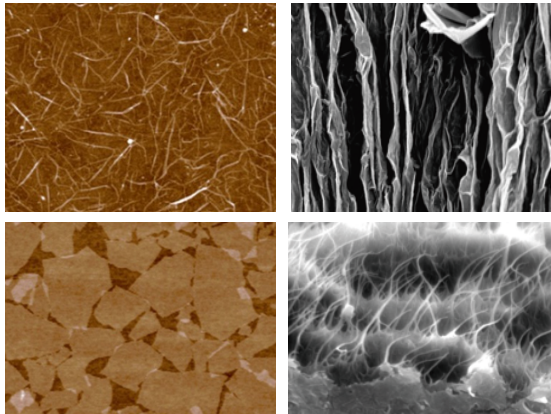
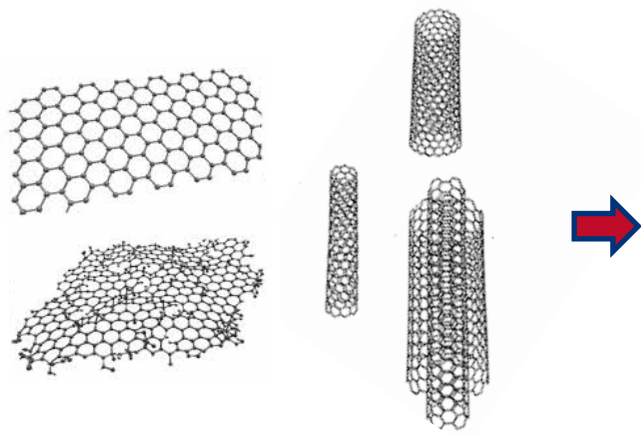
My Research Scope

Fundamental understandings

Nanoscale structures

Macroscale architectures

Performance evaluations



- *Macroelectronics*
- *Supercapacitors*
- *Smart textiles*
- *Electrocatalysts*
- *Membranes*
- *Antibacterial coatings*

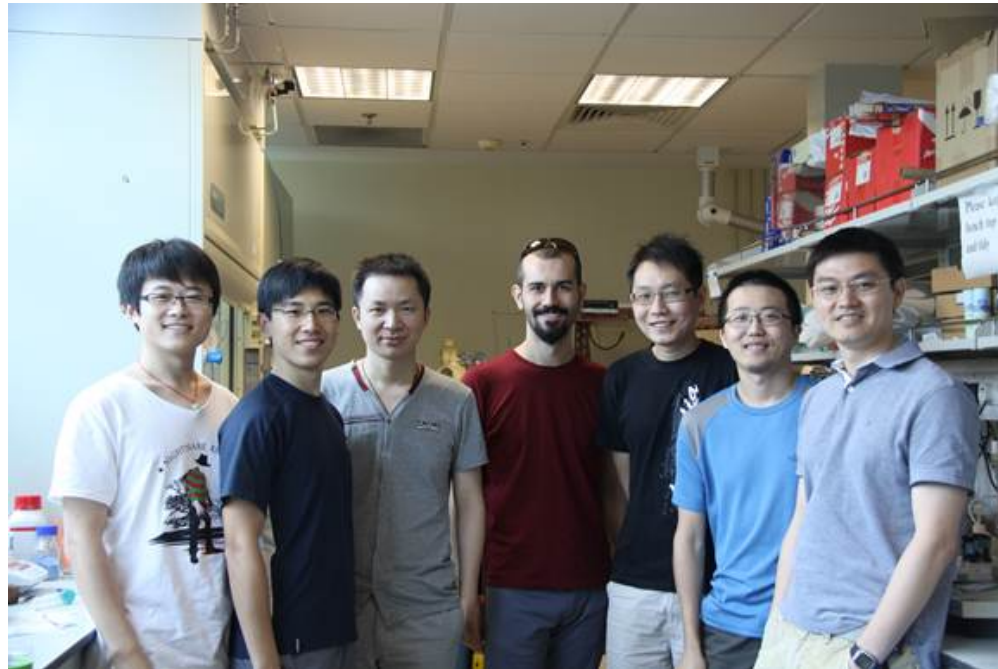
Synthesis methods

Assembly techniques

Application design

Chemical process design and development

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