Utilizing Engineered Carbon Surfaces – Fundamentals and Applications

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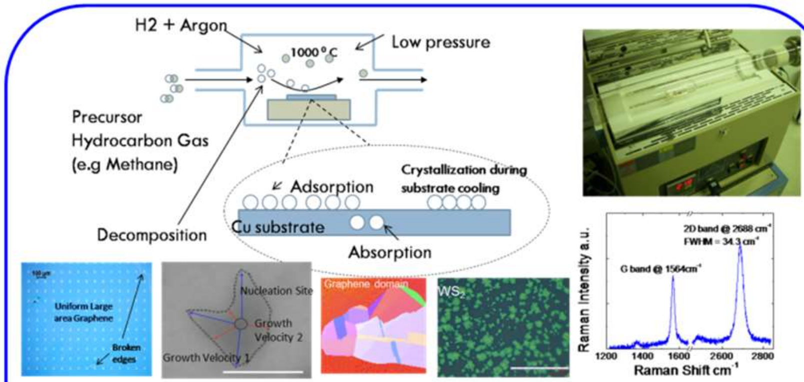
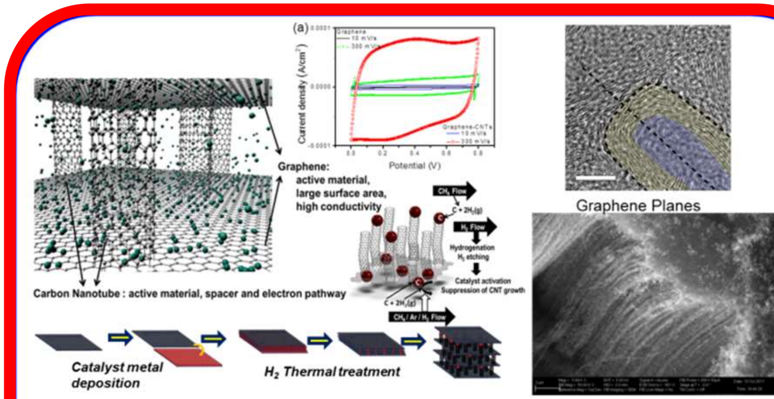
Stevens Institute of Technology

MSE Colloquium, Columbia University, November 14th, 2014

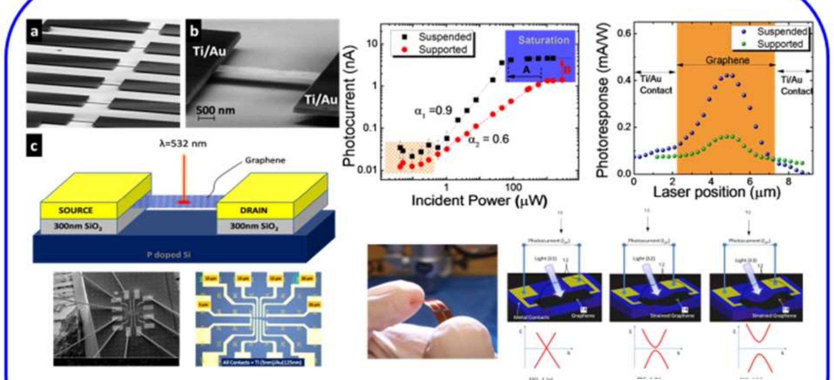
EH Yang Group Research



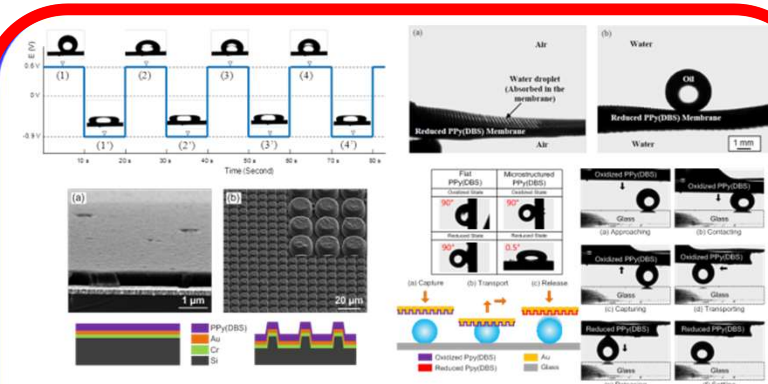
Graphene, CNT and WS_2 growths using chemical vapor deposition



Seamless Growth of CNTs on Graphene



Light-harvesting at Nanoscale



Smart Microfluidics (Tunable Wetting on Smart Polymer)

Outline of Presentation

I. Tunable Polymer Surface-based Microfluidics

II. Growth of CNTs on Graphene

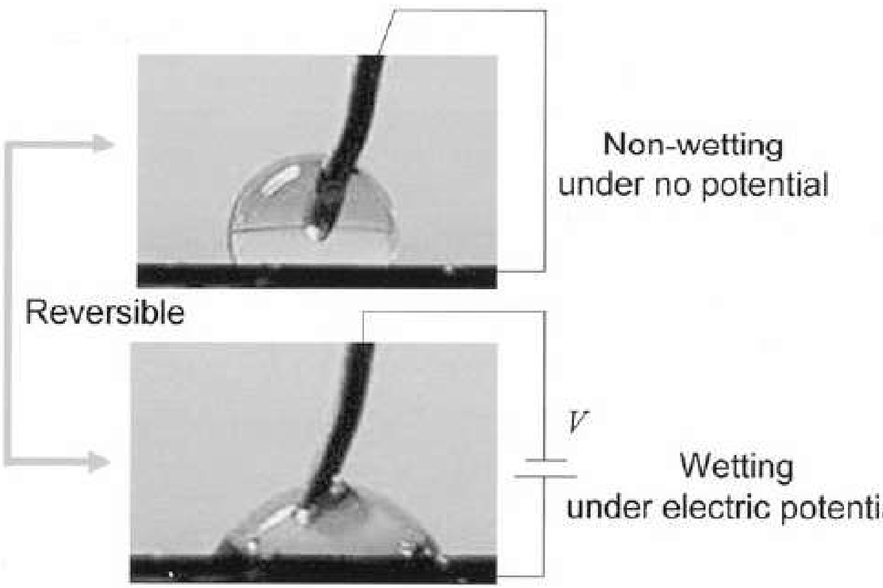
Wetting

- Wetting: The ability of a liquid to maintain contact with a solid surface.
- The wettability is determined by a force balance between adhesive and cohesive forces.

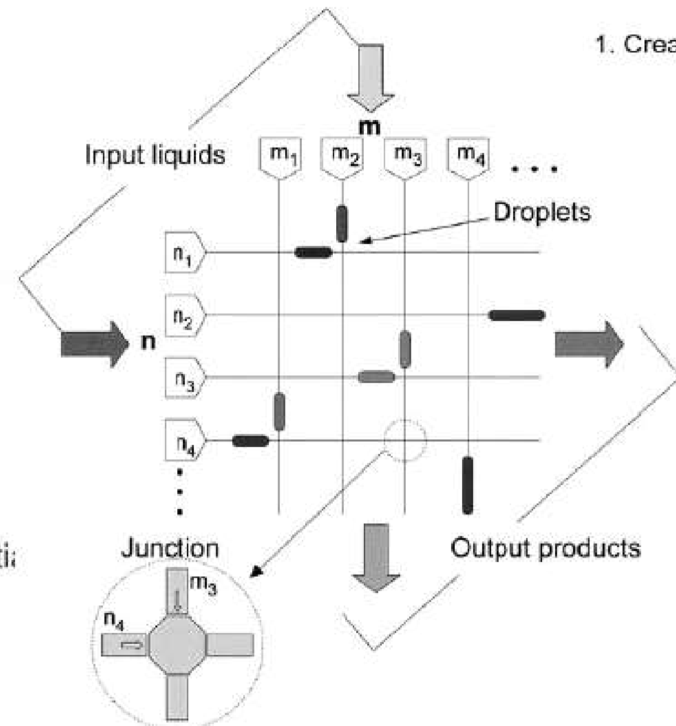
- At the interface between a liquid and a gas, forces develop in the liquid surface that causes the surface to behave as if a “membrane” were stretched over it.

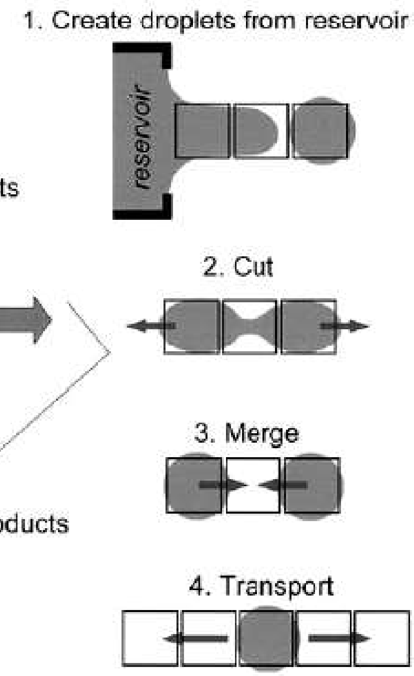
Water beads on a fabric that has been made non-wetting by chemical treatment.

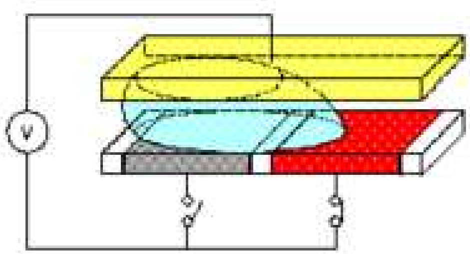
Electrowetting on Dielectric



Cho 2003 J MEMS







In electrowetting on dielectric (EWOD), an externally added electrostatic charge modifies the surface tension at the fluid-surface interface.

Jebrail 2010 Curr Opin Chem Biol

Electrowetting on Dielectric

http://microfluidics.ee.duke.edu/

Advanced Liquid Logic, Inc.

Advanced Liquid Logic
powered by Digital Microfluidics

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Home › Newborn Screening

Newborn Screening

Advanced Liquid Logic has developed the LSD-100, an automated newborn screening system capable of rapidly and simultaneously performing 5 assays on 40 dried blood spot extracts along with 4 controls & 4 calibrators.

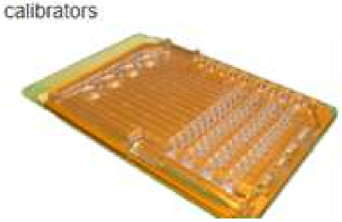
Components of the LSD-100 Newborn Screening System

The Newborn Screening Analyzer

- A small form-factor (8"x13"x20") bench-top instrument
- Houses electronics, thermal components and optical detection systems
- Up to four instruments controlled from one PC, providing scalability

Digital microfluidic cartridge

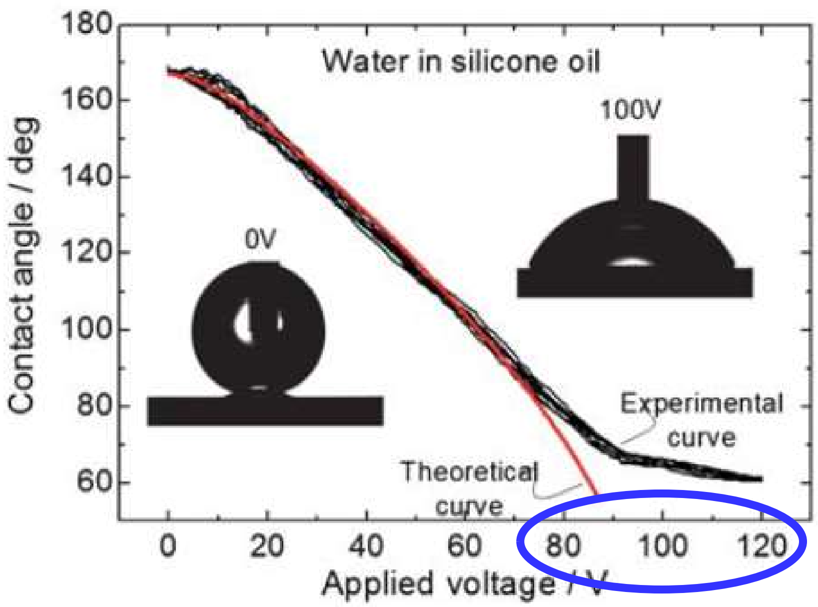
- Capable of rapidly and simultaneously performing 5 assays on 40 dried blood spot extracts along with 4 controls & 4 calibrators
- Minimal hands on time for reagent loading
- Disposable under standard biohazard procedures
- Reagents for each assay type are formulated at Advanced Liquid Logic under controlled manufacturing practices.

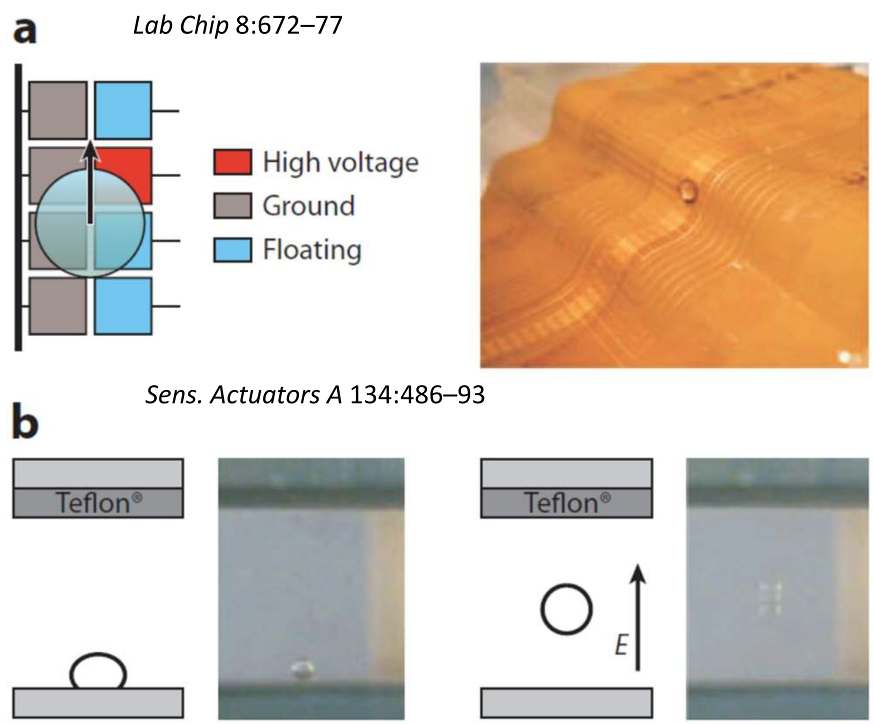


- Quantitative analysis of DNA (qPCR) and RNA (RT-qPCR)
- Protein analysis using both enzymatic and immunoassay techniques
- DNA sequencing using a sequencing-by-synthesis method
- Sample preparation from many different sample matrices (blood, swabs, saliva, etc.)
- Preparation of fragment libraries for next generation sequencing

http://www.liquid-logic.com/lsd-100

Electrostatic Charging



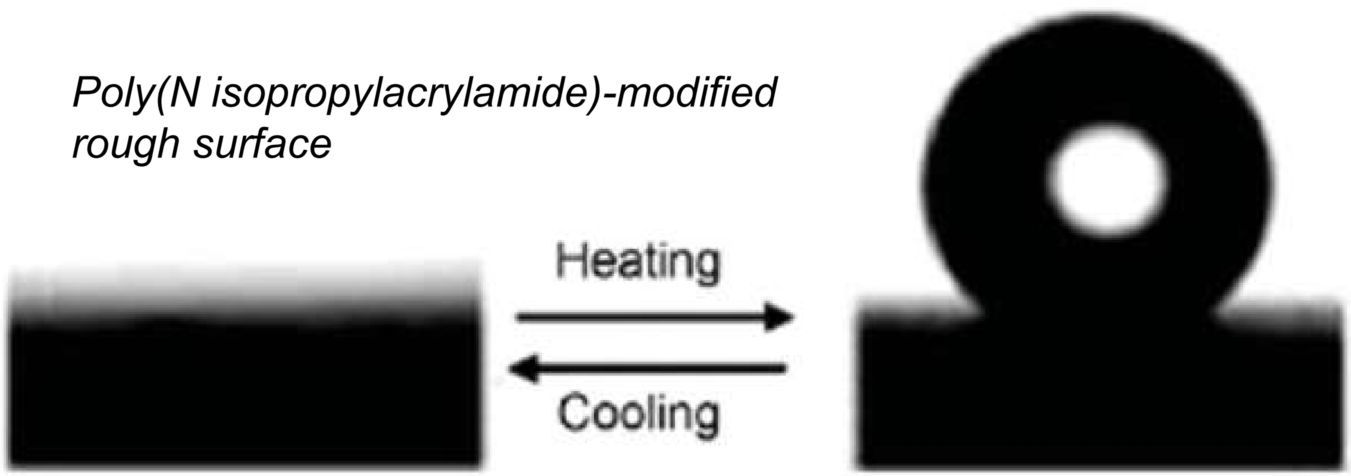


Water droplet displacement between plates of a plate condenser that were placed 10 mm apart (***with a voltage increase from 0 to 1,600 V***) in a digital microfluidic system.

Wetting on Smart Polymer

- Smart polymer (stimuli-responsive polymer) changes its property when triggered by an environmental stimulus—temperature, humidity, pH, light, electrical or magnetic field.

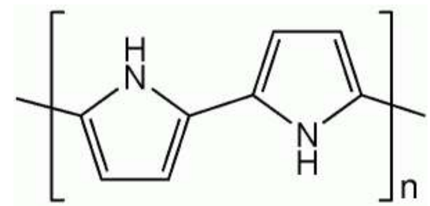
Poly(N isopropylacrylamide)-modified rough surface



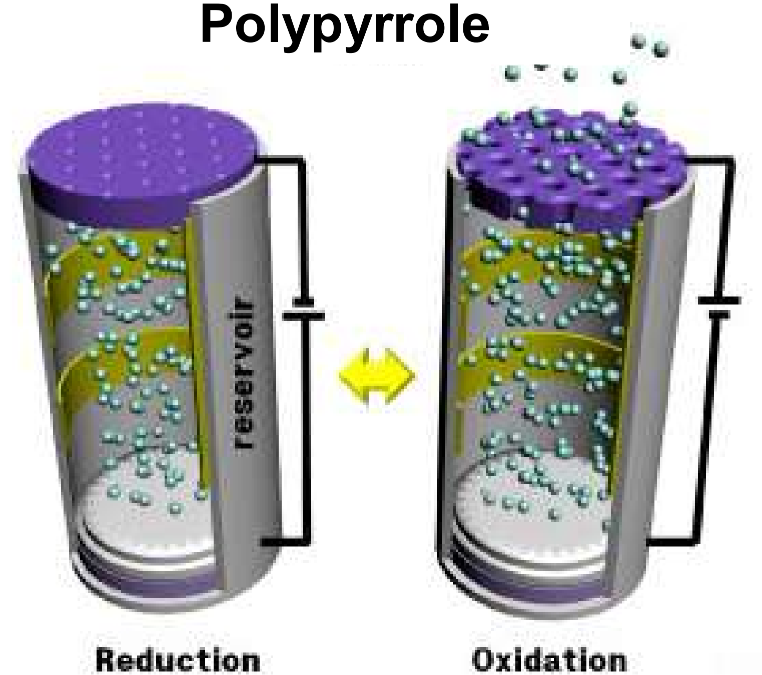
Angew. Chem., Int.Ed., 2004, 43, 357

Polypyrrole (PPy)

- Conjugated polymers have alternating single- and double-bonds between carbon atoms on the polymer backbone.
- Chemical/electrochemical oxidation or reduction facilitates reversible doping.
- Low actuation voltage (<1V).
- High conductivity : ~220 S/cm.
- Changes in volume and roughness



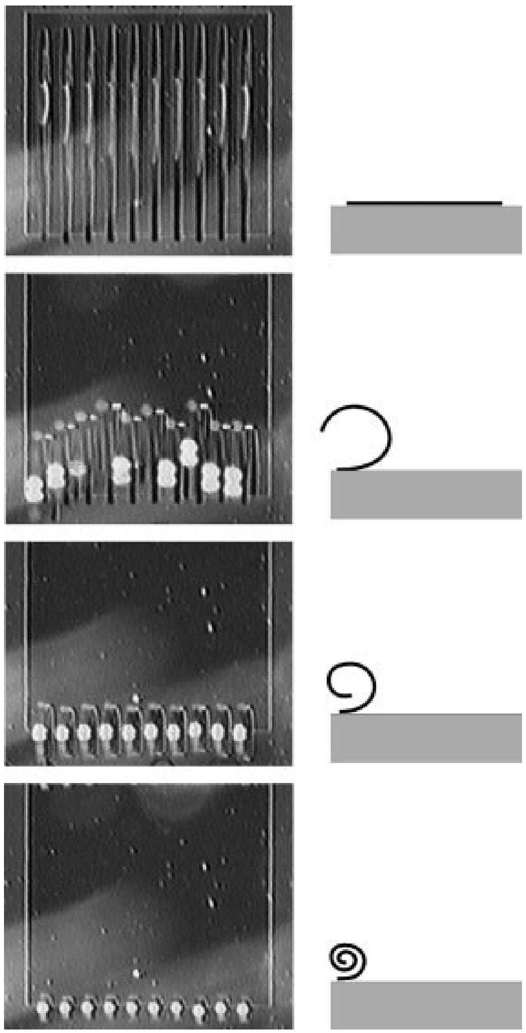
Polypyrrole

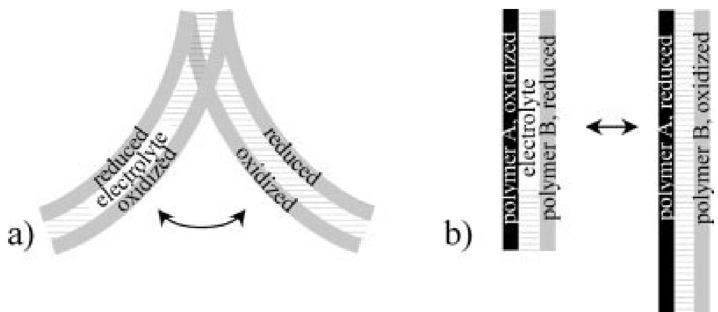


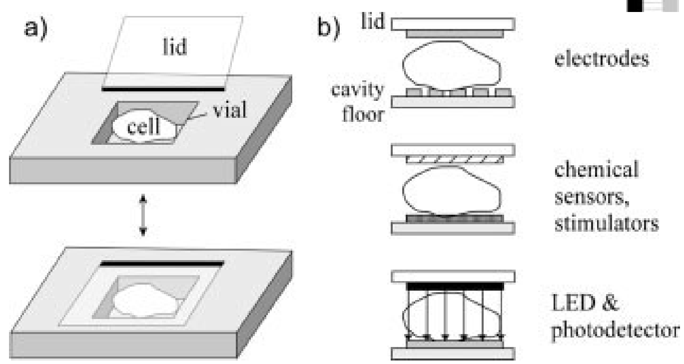
Electrically responsive nanoporous membrane

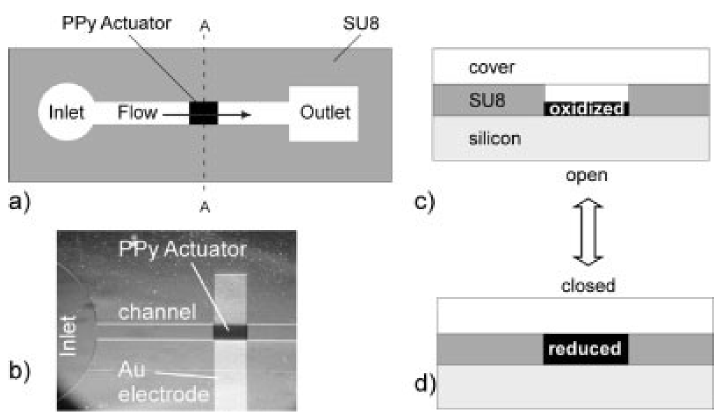
Nano Lett., 2011, 11 (3), pp 1284–1288

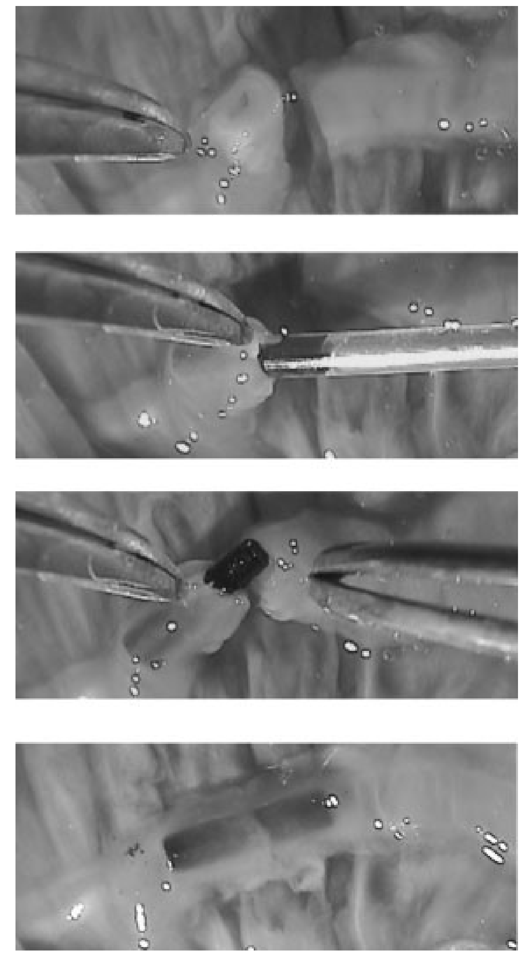
PPy Actuators





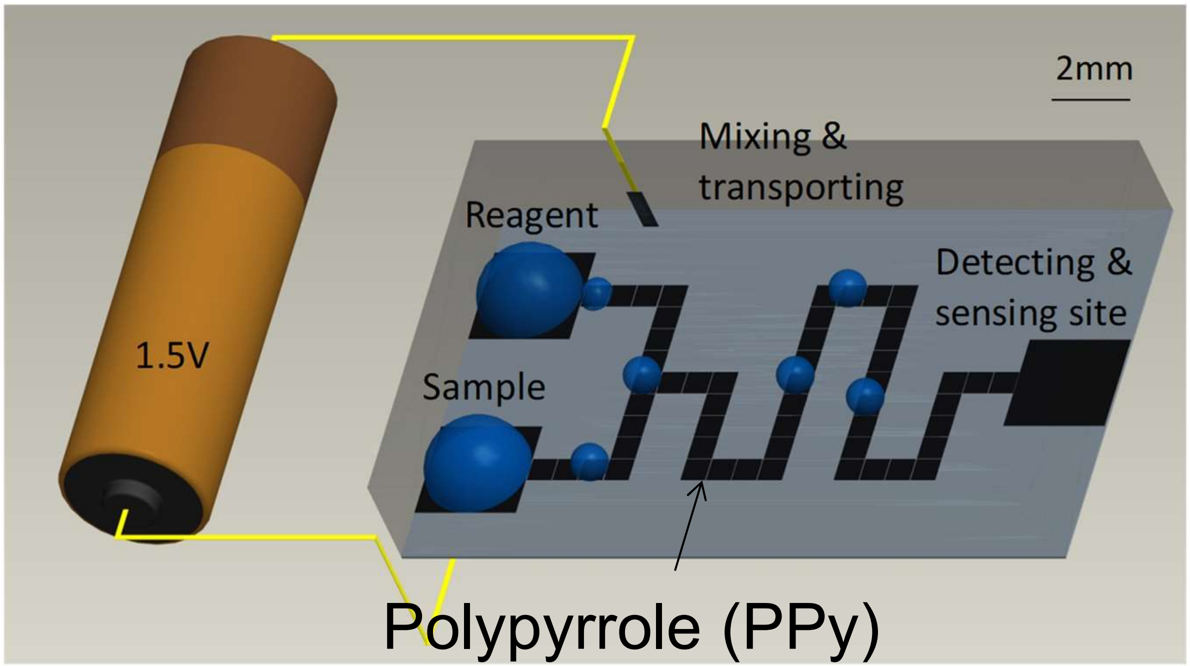


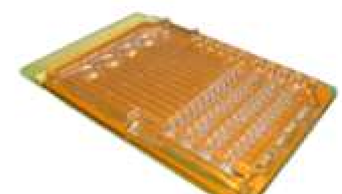




Smela Group, UMD

Droplet Manipulation at Low Voltages (<1.5V)

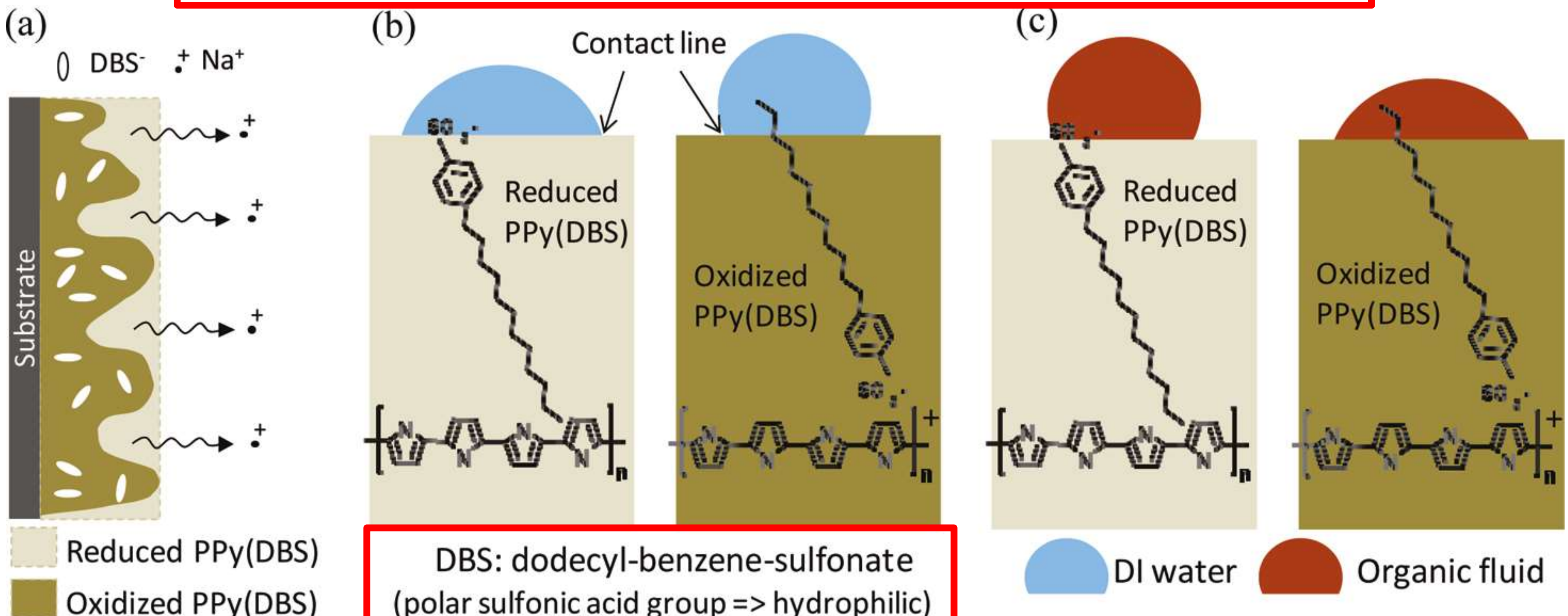




- Low-cost, hand-held device (directly powered by a AAA battery) containing complex liquid handling assays.
- Elucidate the ion-surfactant-liquid interactions at the conjugated polymer surface and the wetting properties.

DBS doped PPy (PPy(DBS))

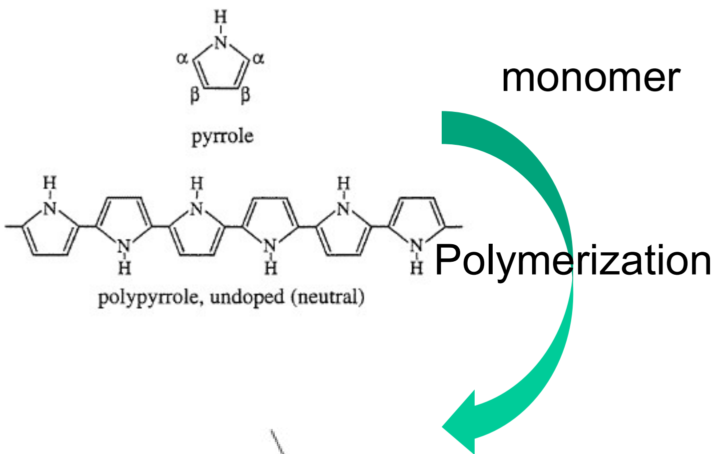
$$PPy^{+}(DBS)^{-} + Na^{+} + e^{-} \underset{\text{Oxidization}}{\overset{\text{Reduction}}{\rightleftharpoons}} PPy(DBS)^{-}Na^{+}$$

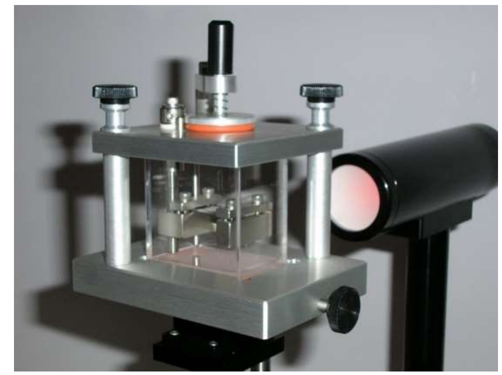


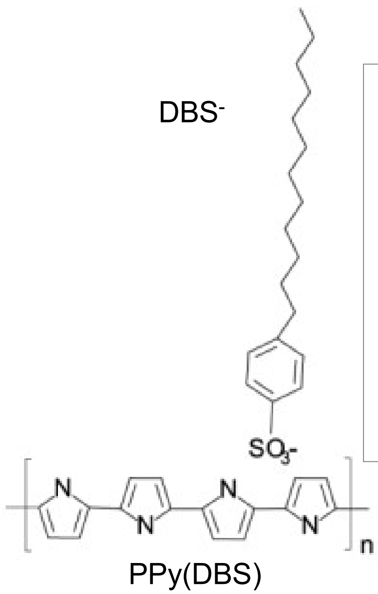
DBS: dodecyl-benzene-sulfonate
(polar sulfonic acid group => hydrophilic)

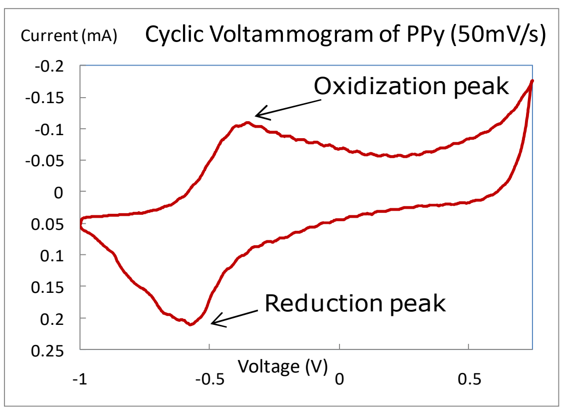
The reduced PPy has higher surface tension than the oxidized PPy.

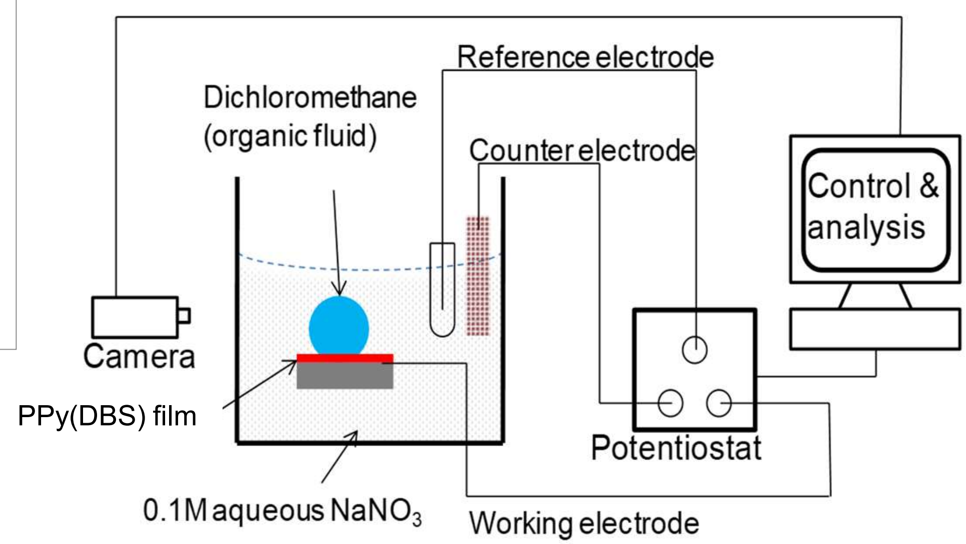
Electropolymerization and Test Setup



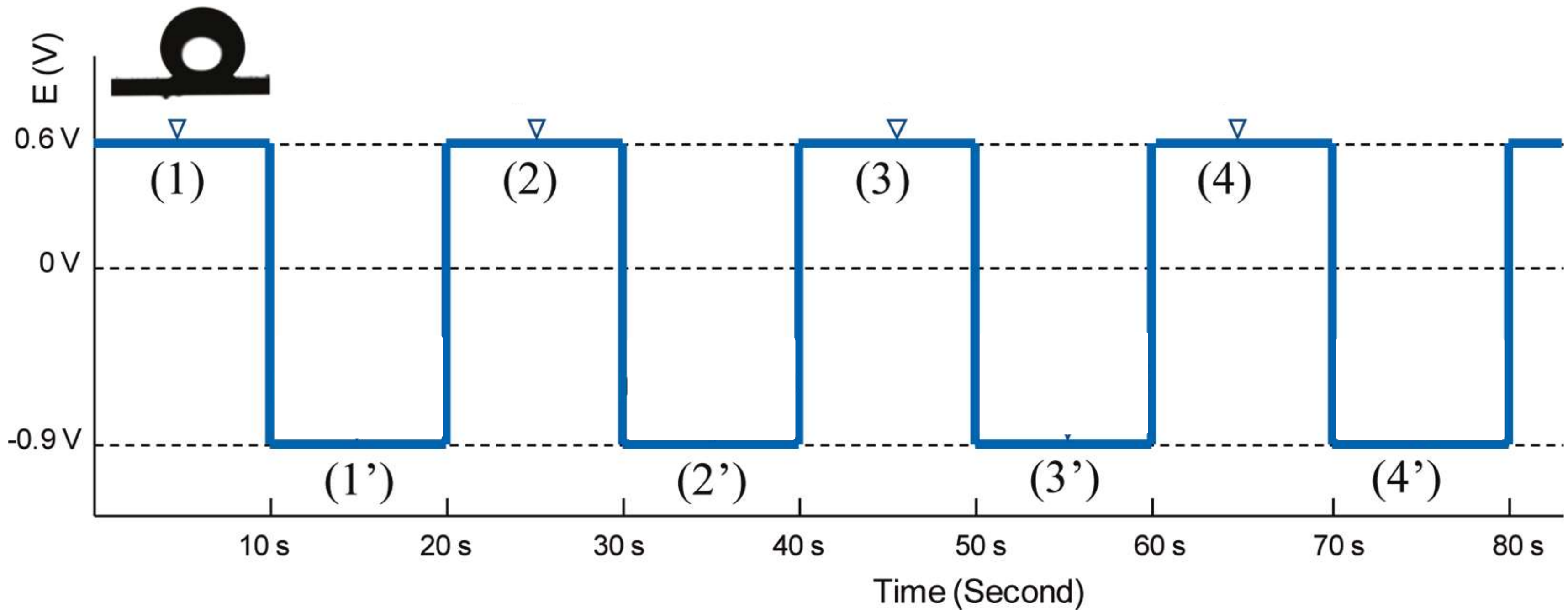


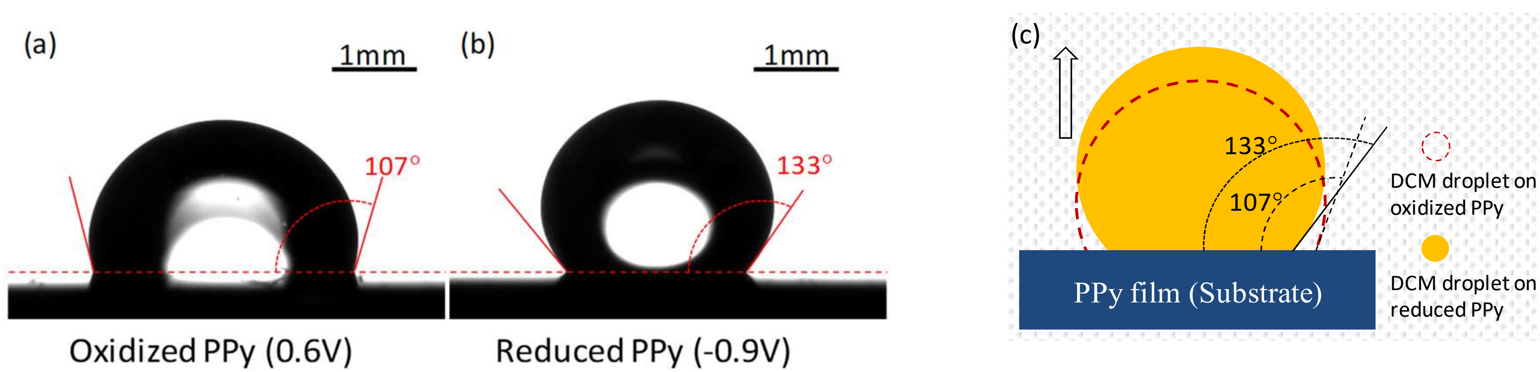




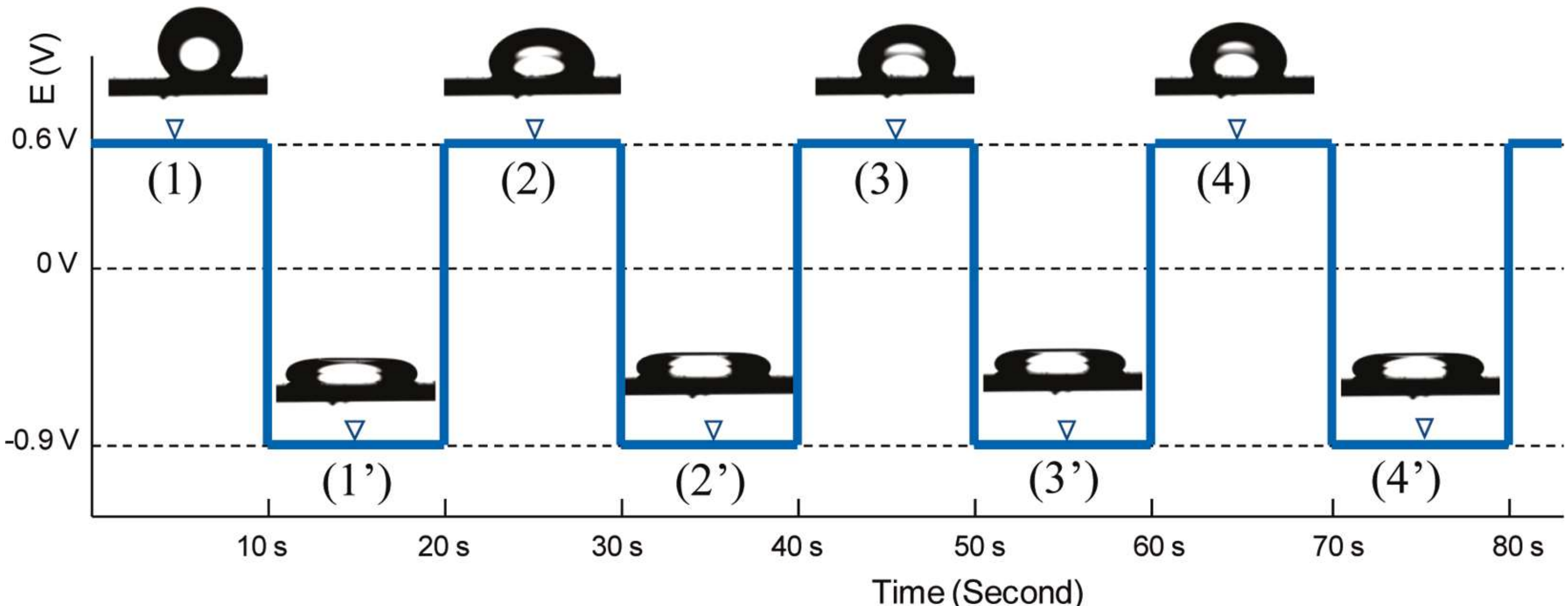


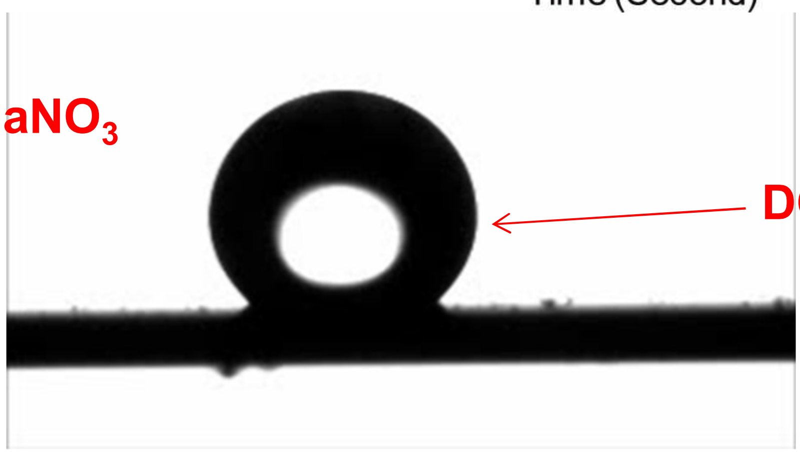
Manipulating a Liquid Droplet





Dynamic Behavior

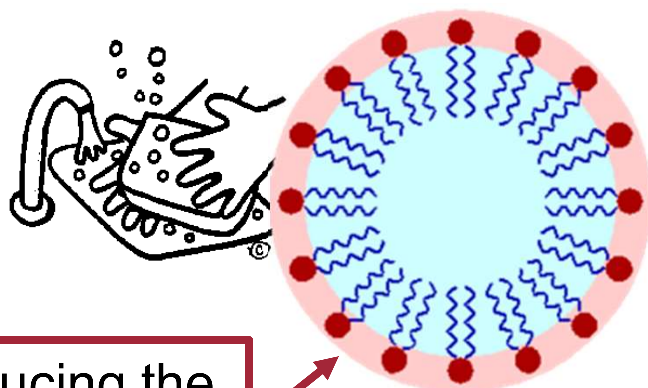




Langmuir, 27(7), 4249-4256 (2011).

Possible Explanation

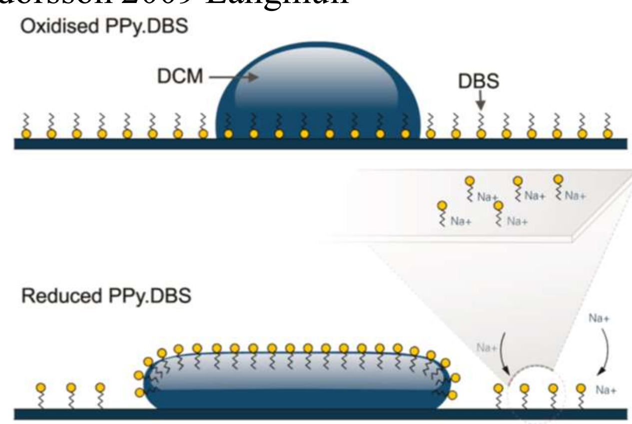
Surfactant DBS^-



Reducing the interfacial tension

- DBS^- molecules are immobile in PPy
  - Matencio 1995 Synth. Met.
  - Smela 1999 J. Micromech. Microeng.
  - Bay 2001 J. Phys. Chem. B
  - Matencio 1994 J. Braz. Chem. Soc.

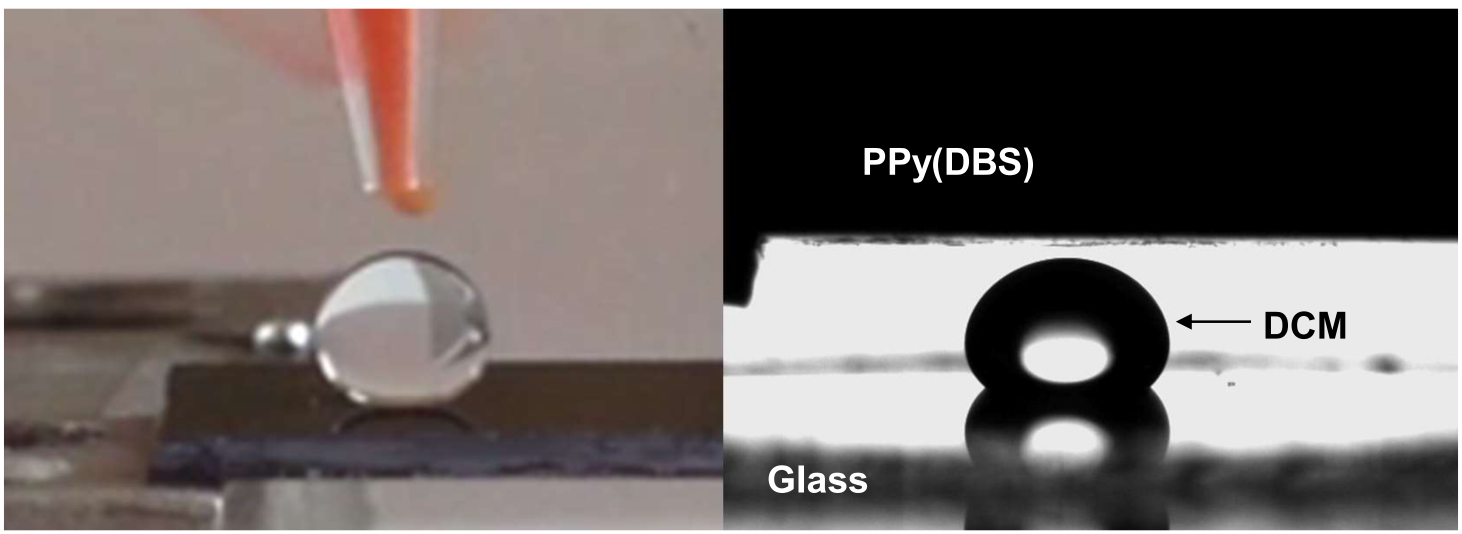
- DBS- molecules are released from PPy
  - Halldorsson 2009 Langmuir



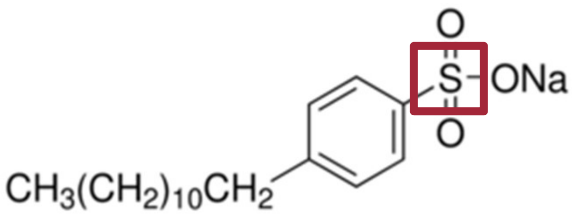
DBS Molecules and Droplet Flattening

Direct application of DBS^- molecules

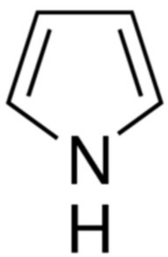
Non contact flattening, proving that DBS^- molecules are released from PPy surfaces



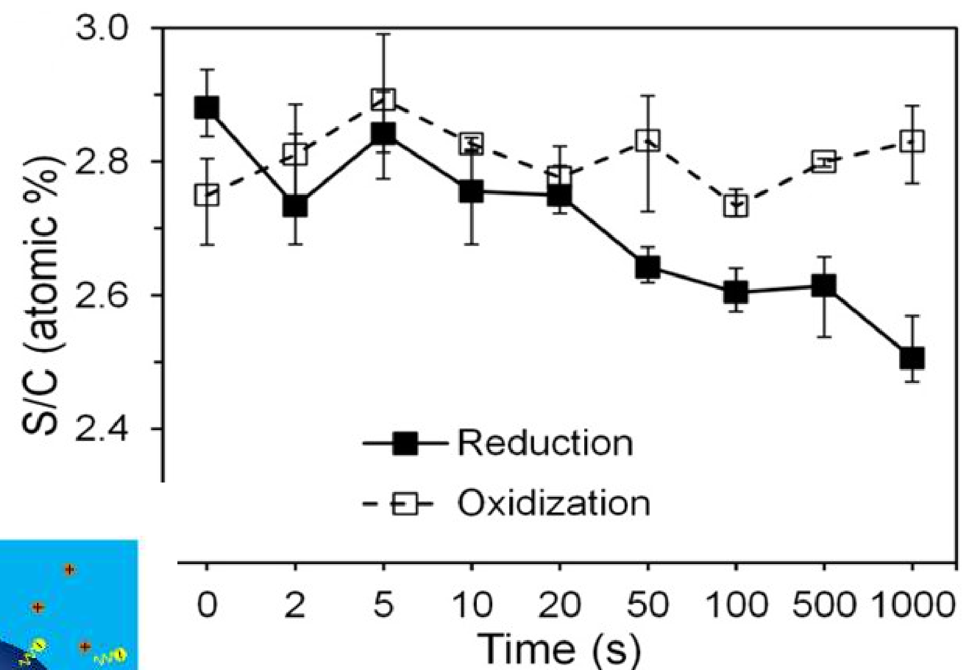
Release of DBS⁻ Molecules

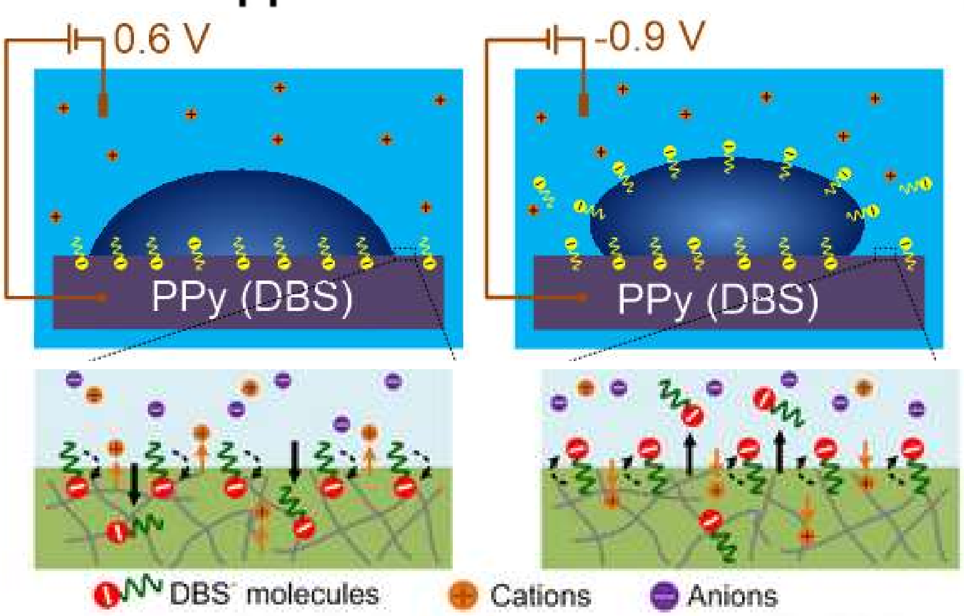


DBS⁻



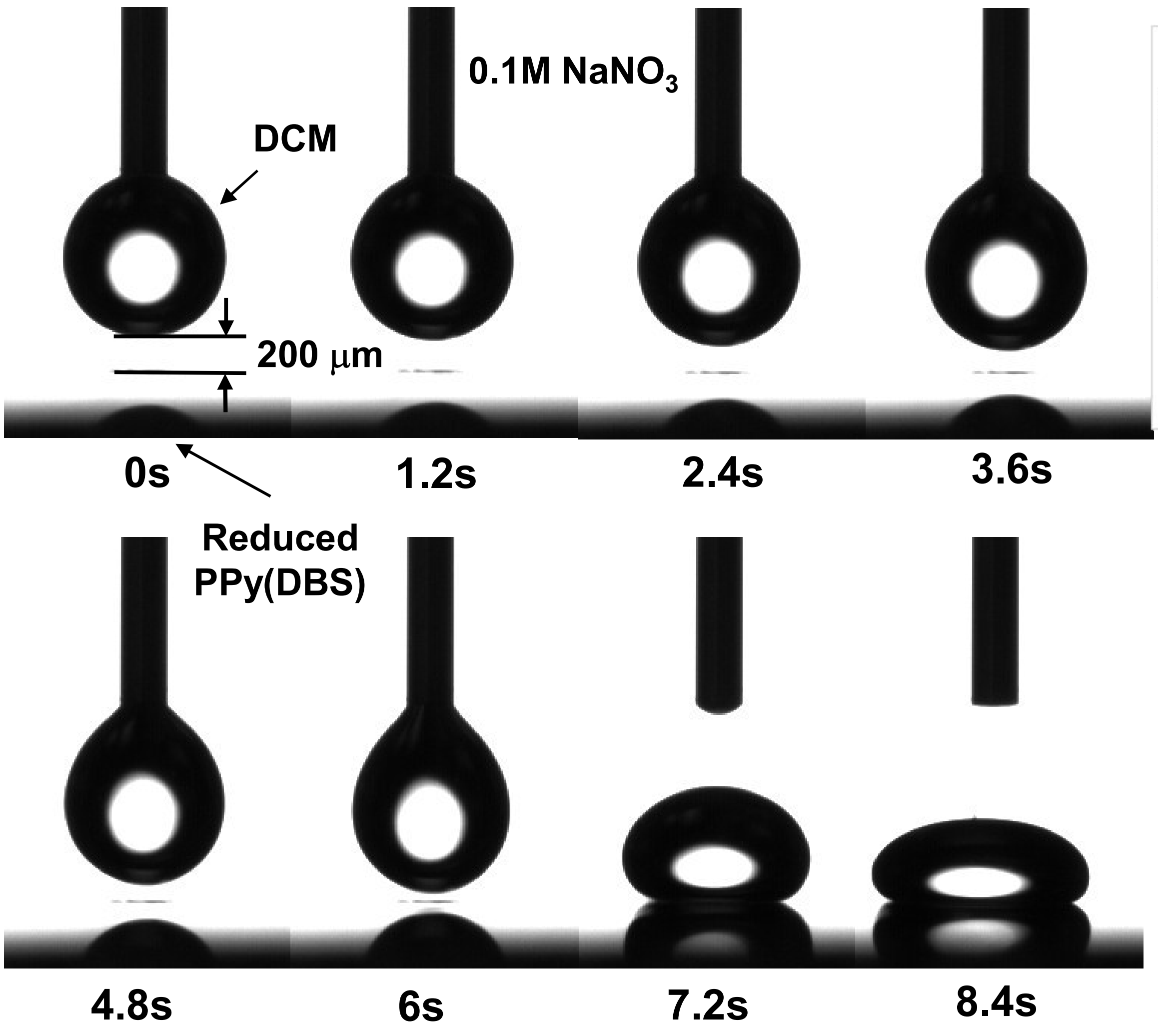
Pyrrole

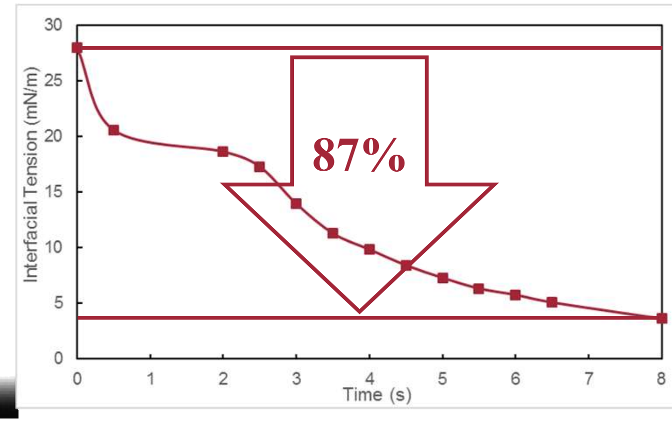




Loss of element S from PPy(DBS) during redox

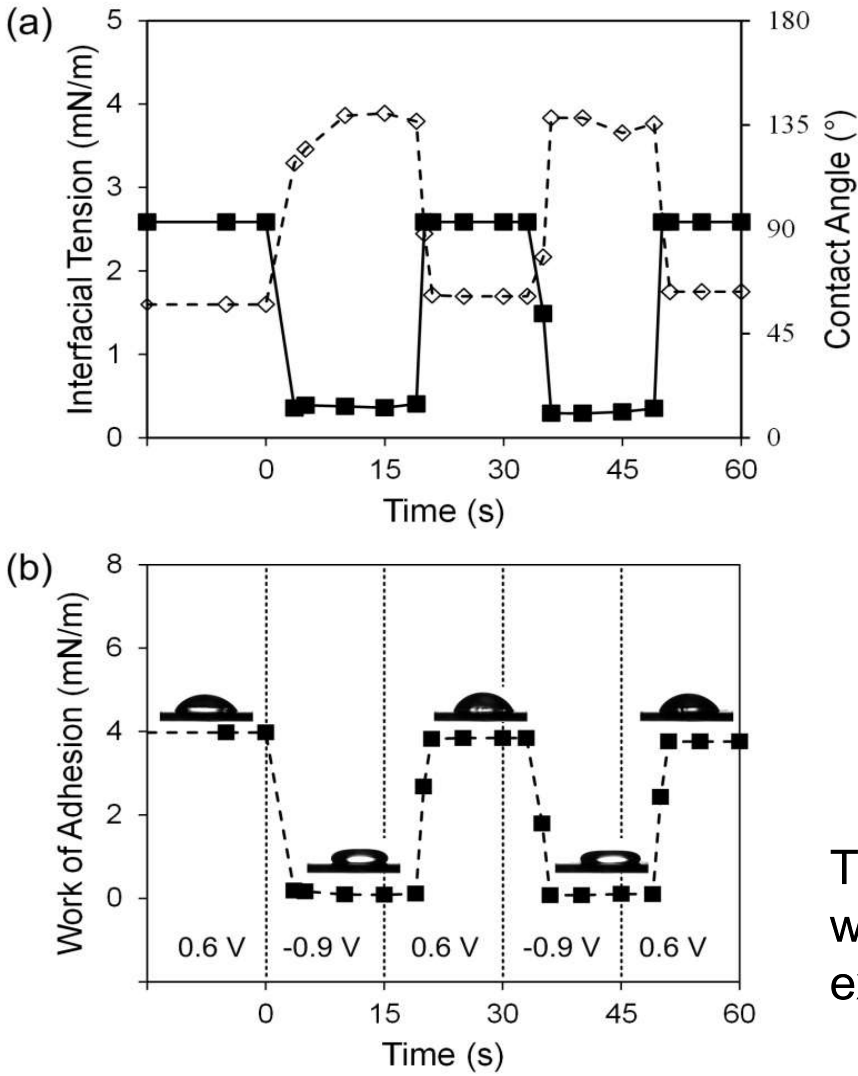
Interfacial Tension





Since the pendant droplet undergoes a balance in forces between interfacial tension and gravity, the shape change and falling of the droplet indicates a decrease in interfacial tension .

Reversible Change of Interfacial Tension



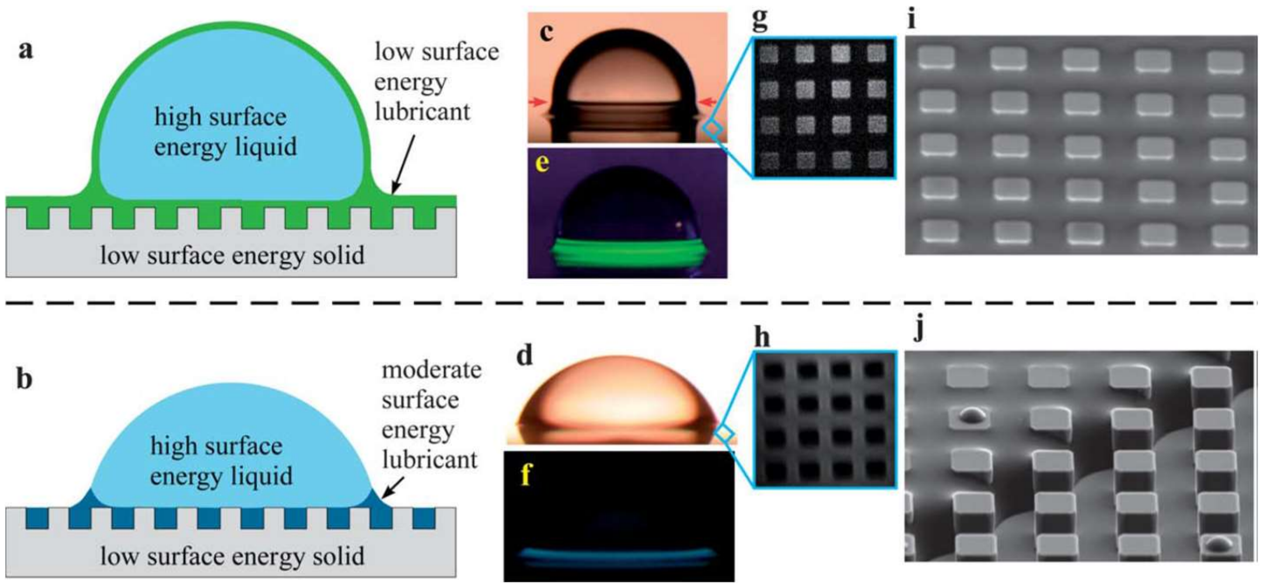
- Young-Dupré equation
- $W_a = \gamma\,(1 + cos\theta)$
  - W_a is the work of adhesion of the liquid to the solid
  - γ is the interfacial tension
  - θ is contact angle

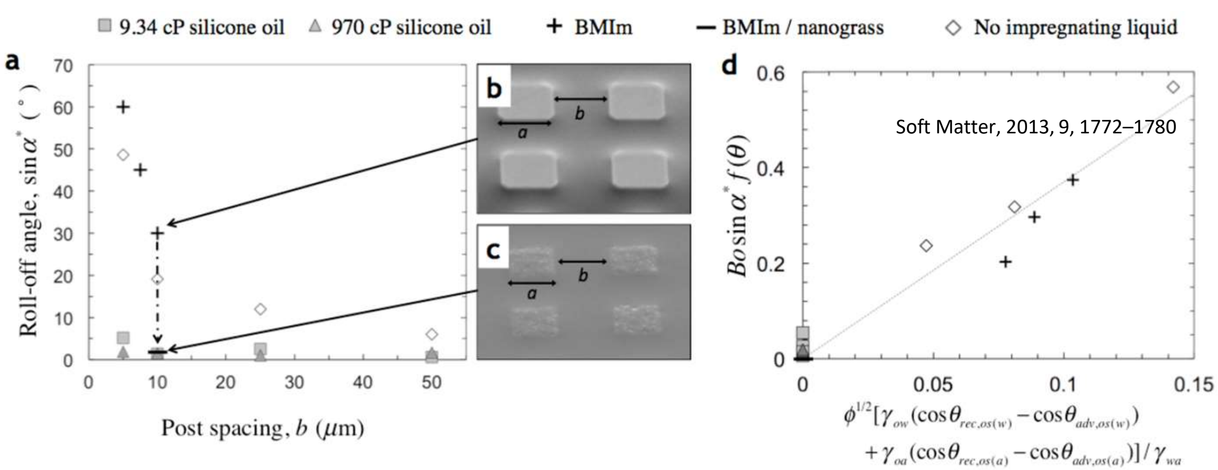
- γ becomes smaller
- θ becomes bigger (>90°), hence $cos\theta$ becomes smaller
- Much smaller adhesion

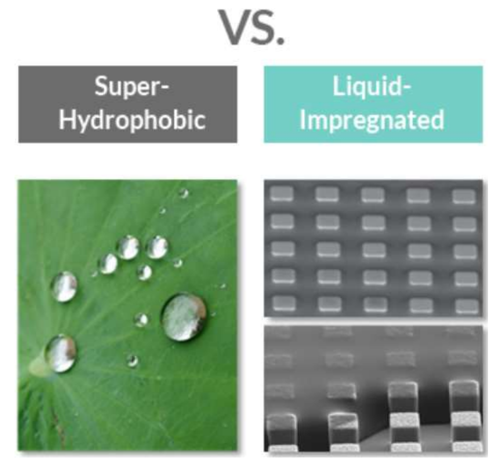
The decrease of interfacial tension associated with the increase of contact angle results in an extremely low adhesion.

Submitted

Lubricant-Impregnated Surface (MIT)

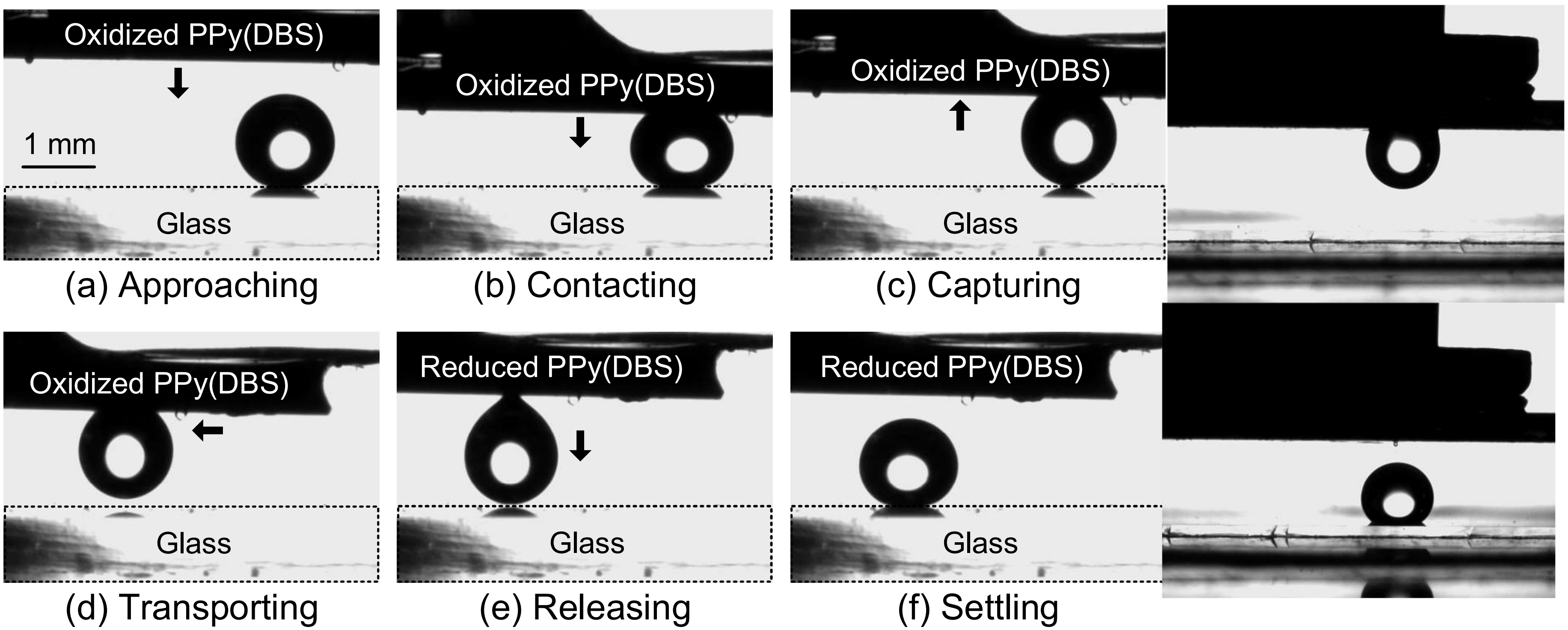






http://liquiglide.com/tech/

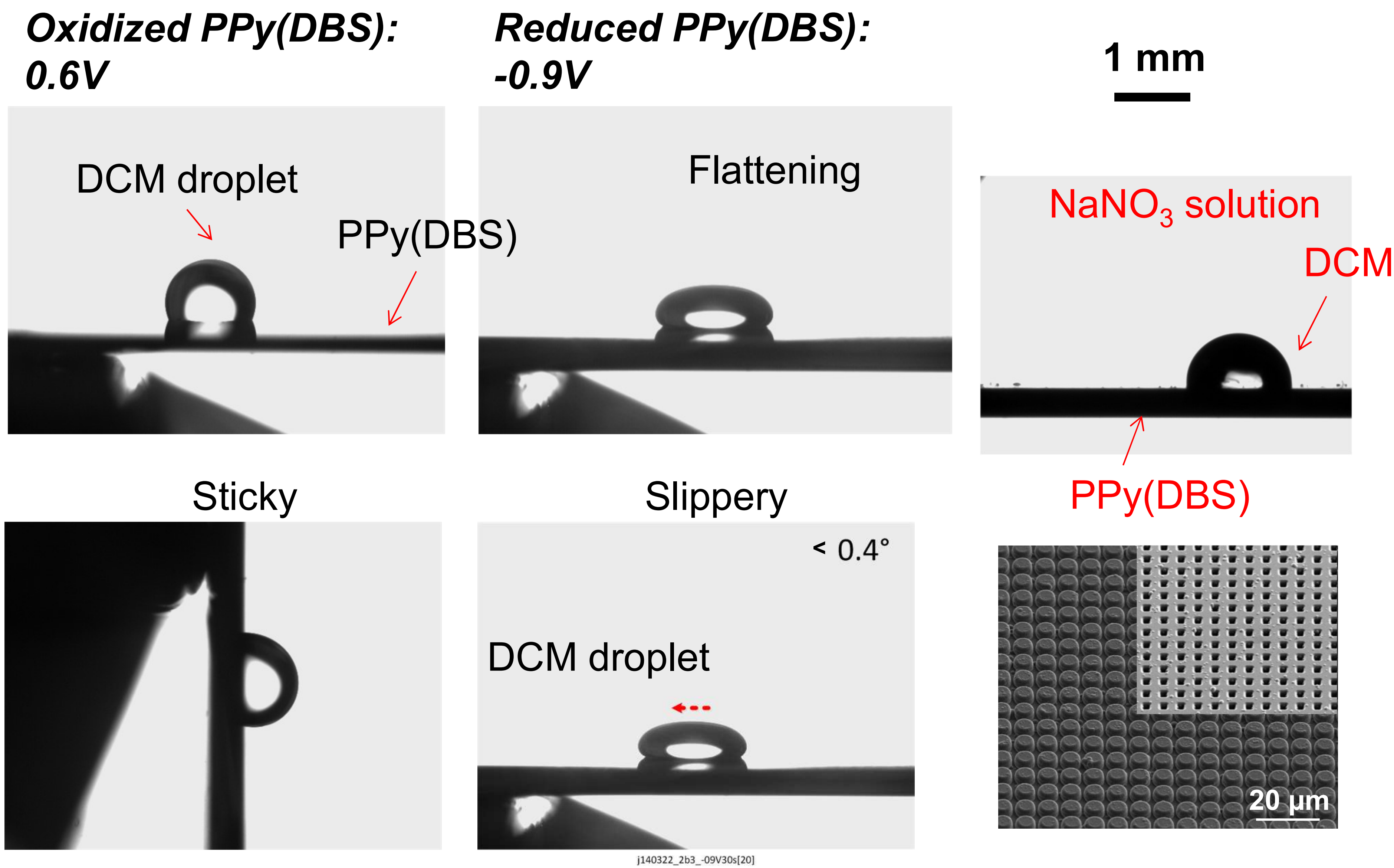
Switching of Adhesive Properties



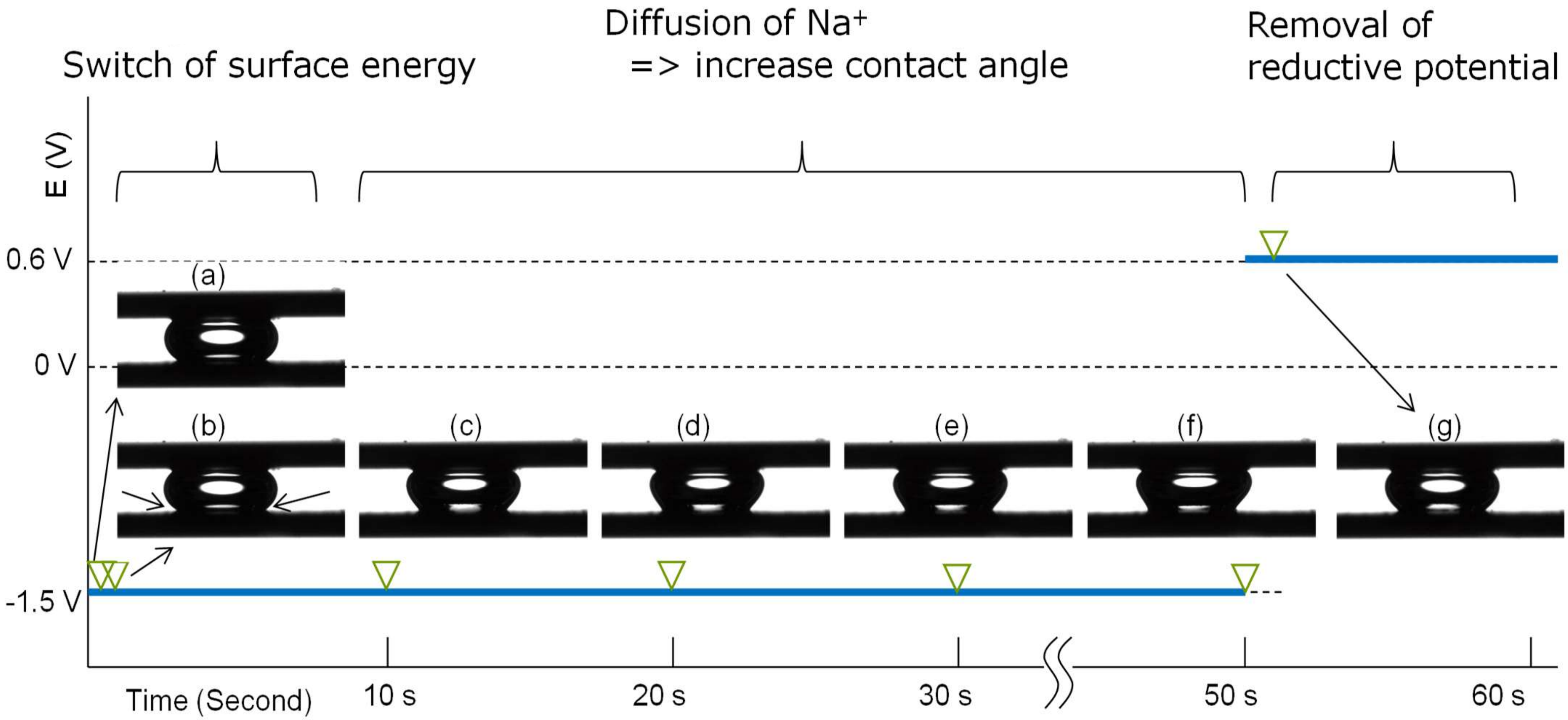
- Capturing the droplet by oxidization (no need to apply any potential)
- Releasing the droplet by reducing the PPy.

Hilton Head Workshop, Hilton Head Island, SC, 2014

On-Demand Switching: Sticky to/from Slippery



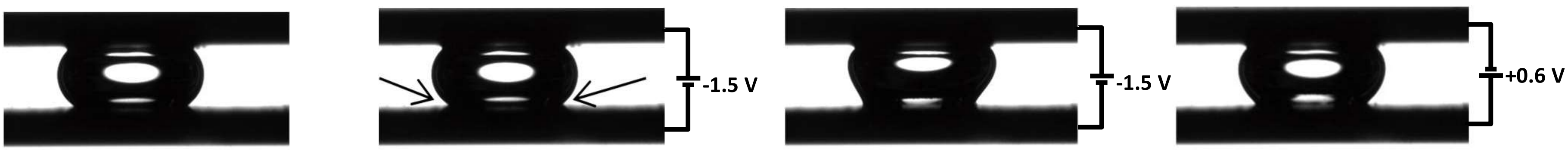
Lateral Diffusion of Cations

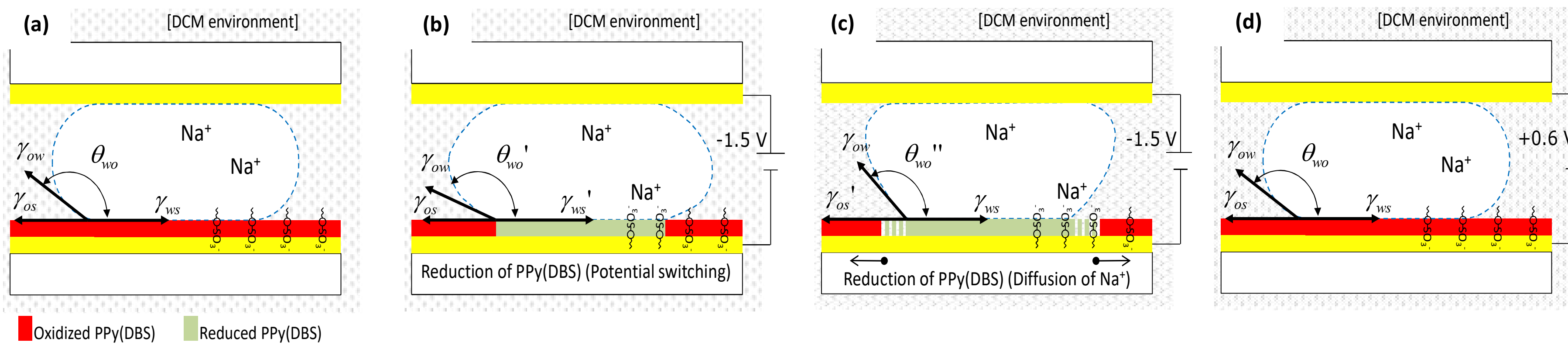


Lab Chip, 13, 302 (2013)

Lateral Diffusion of Cations

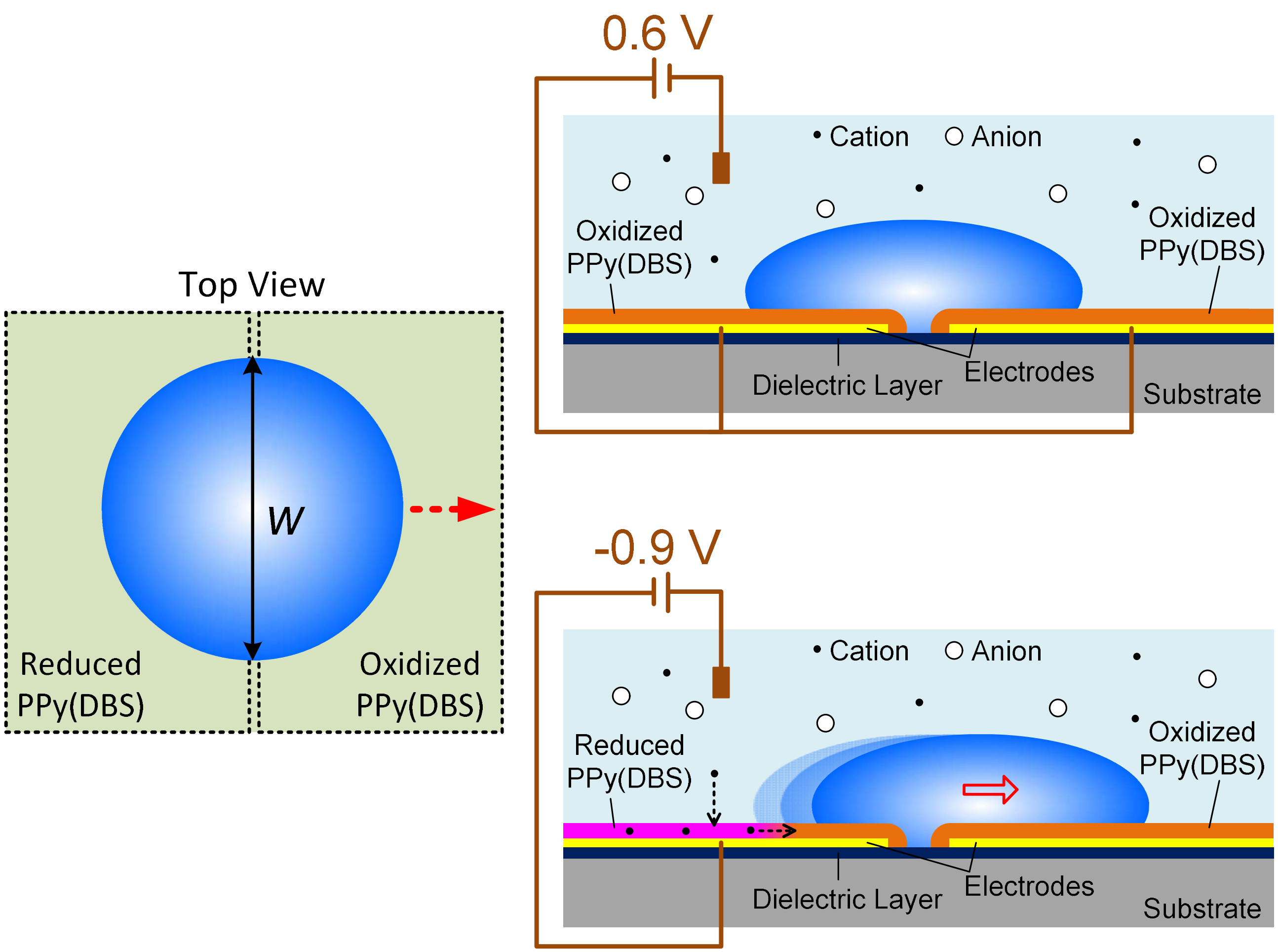
$$PPy^{+}(DBS)^{-} + Na^{+} + e^{-} \underset{\text{Oxidization}}{\overset{\text{Reduction}}{\rightleftharpoons}} PPy(DBS)^{-}Na^{+}$$





The contact angle decreases when a reductive potential is applied for over 10 seconds, where the cations gradually diffuses out through the PPy(DBS) layer and the reduction is propagated laterally.

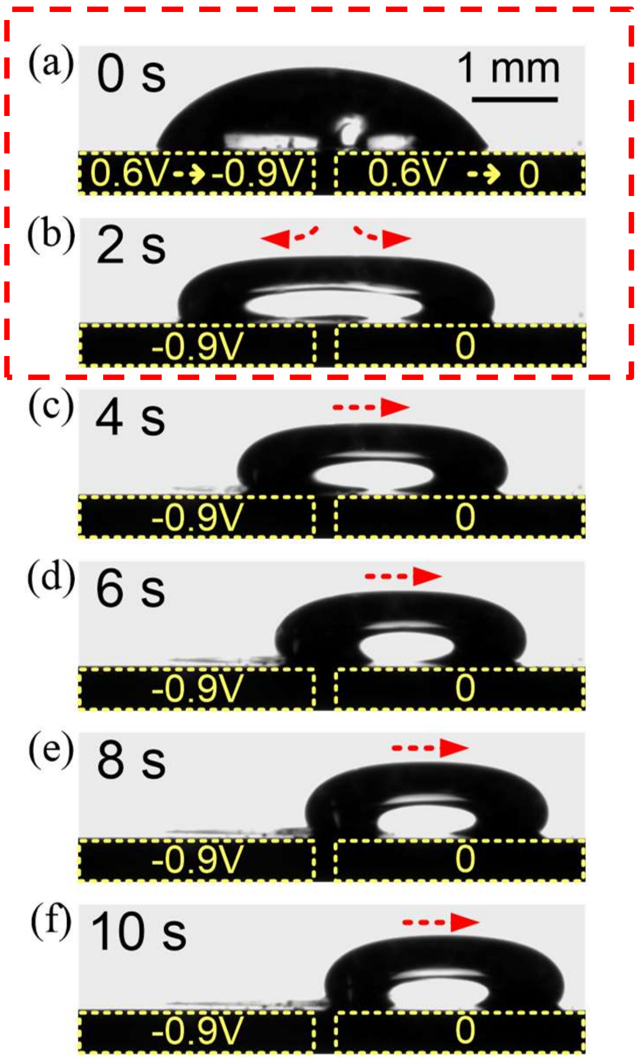
Droplet Transportation from One Electrode to Another

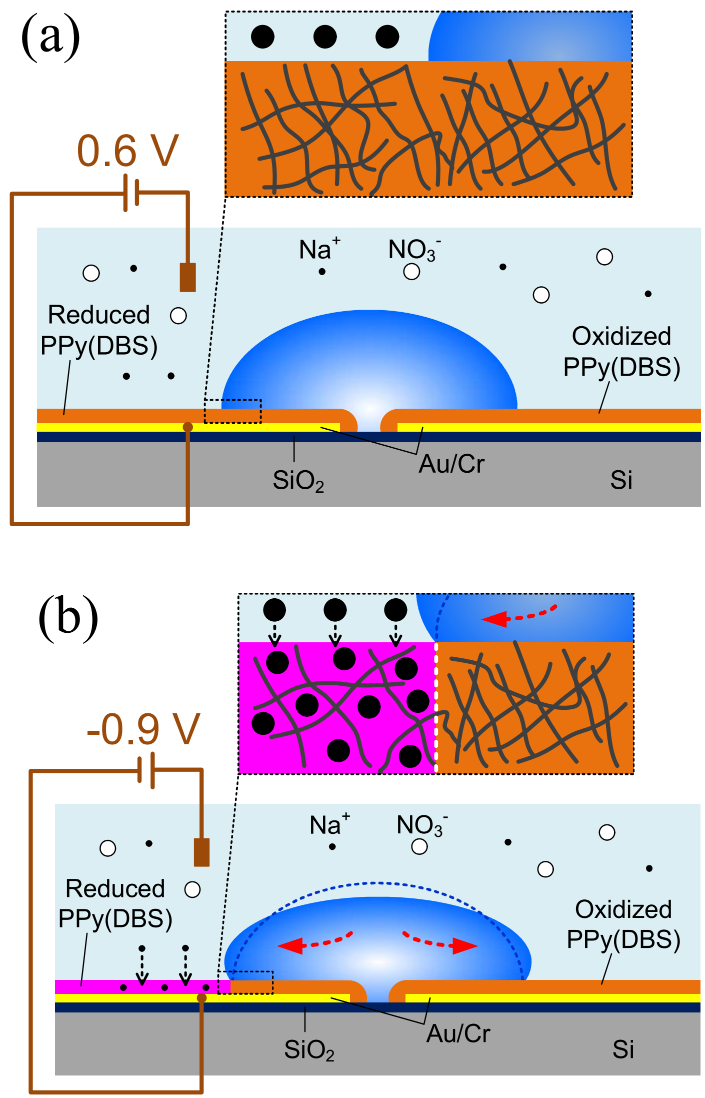


An organic droplet moves from the reduced electrode to the oxidized electrode due to a surface wettability gradient and lateral diffusion of cations.

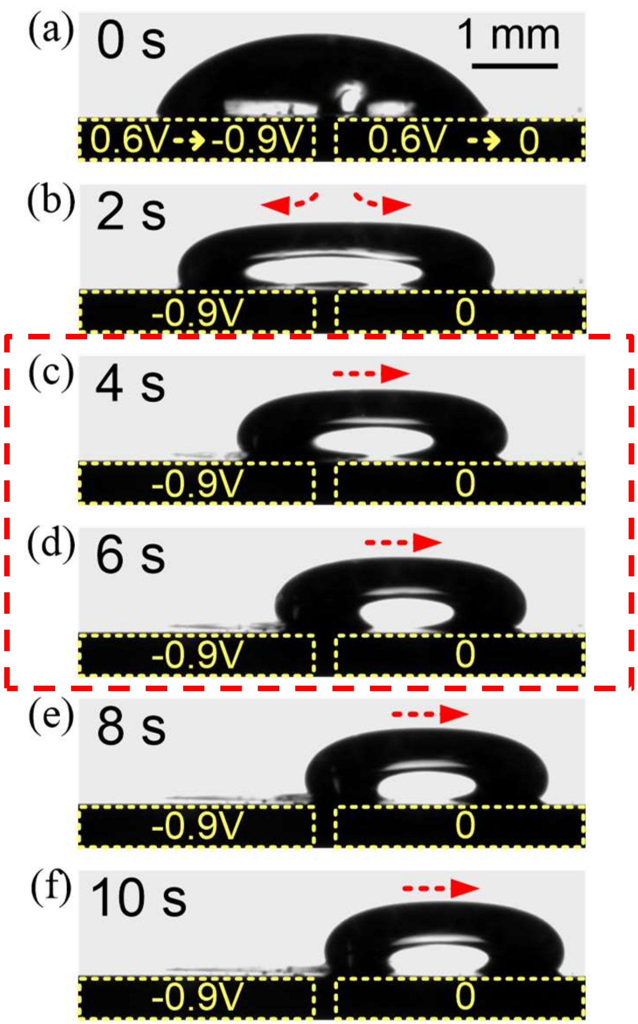
Transducers, Barcelona, **Spain 2014**

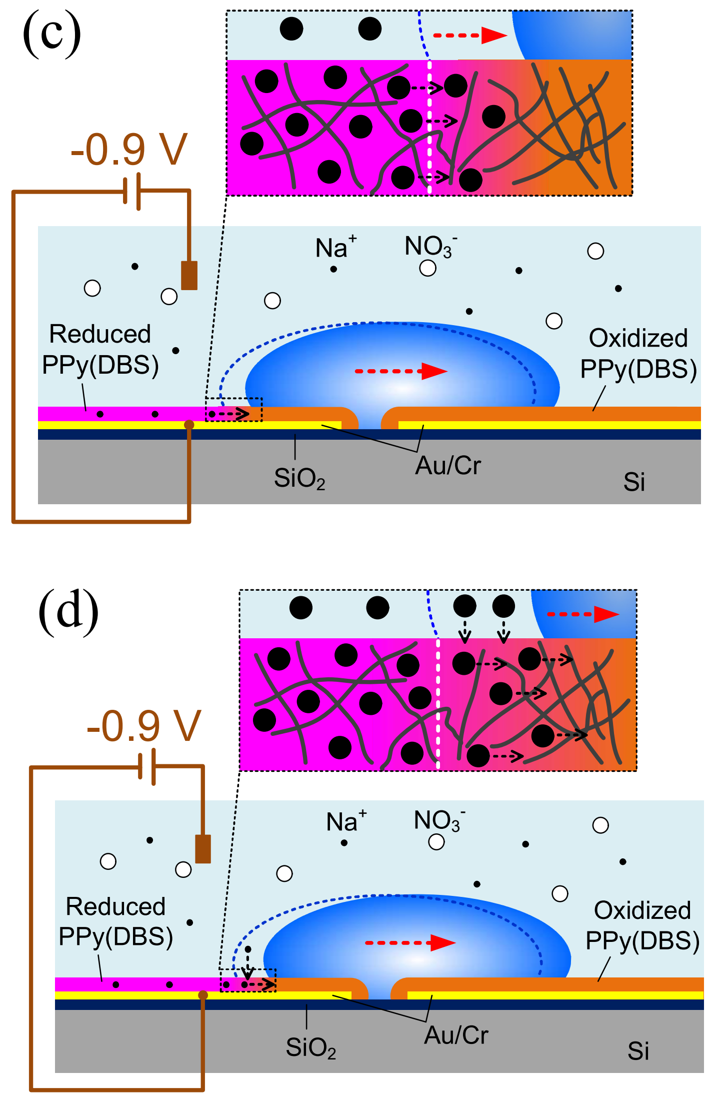
Droplet on Tunable Electrodes (1)



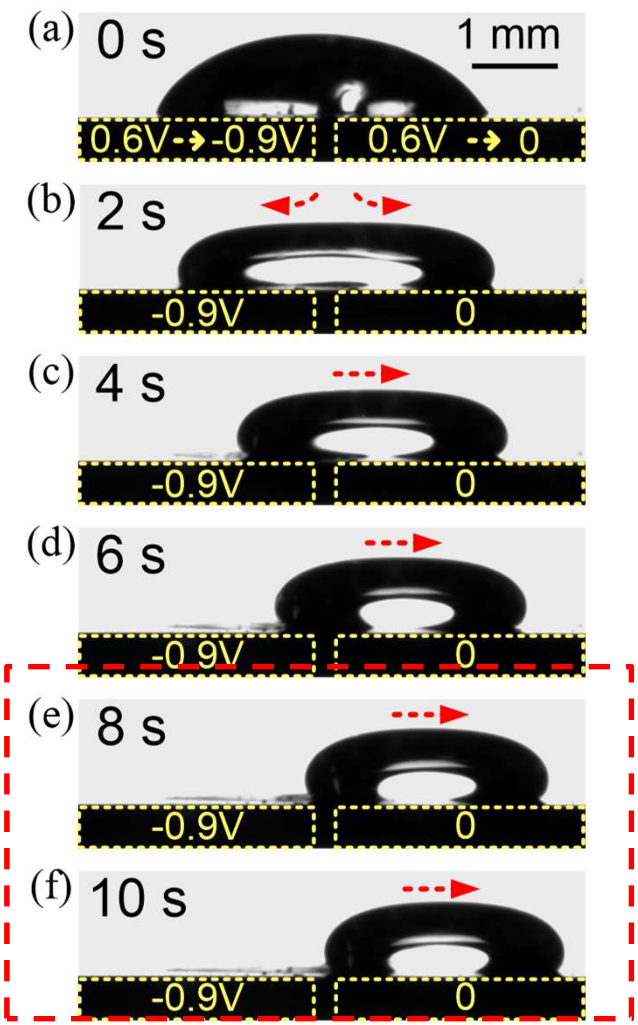


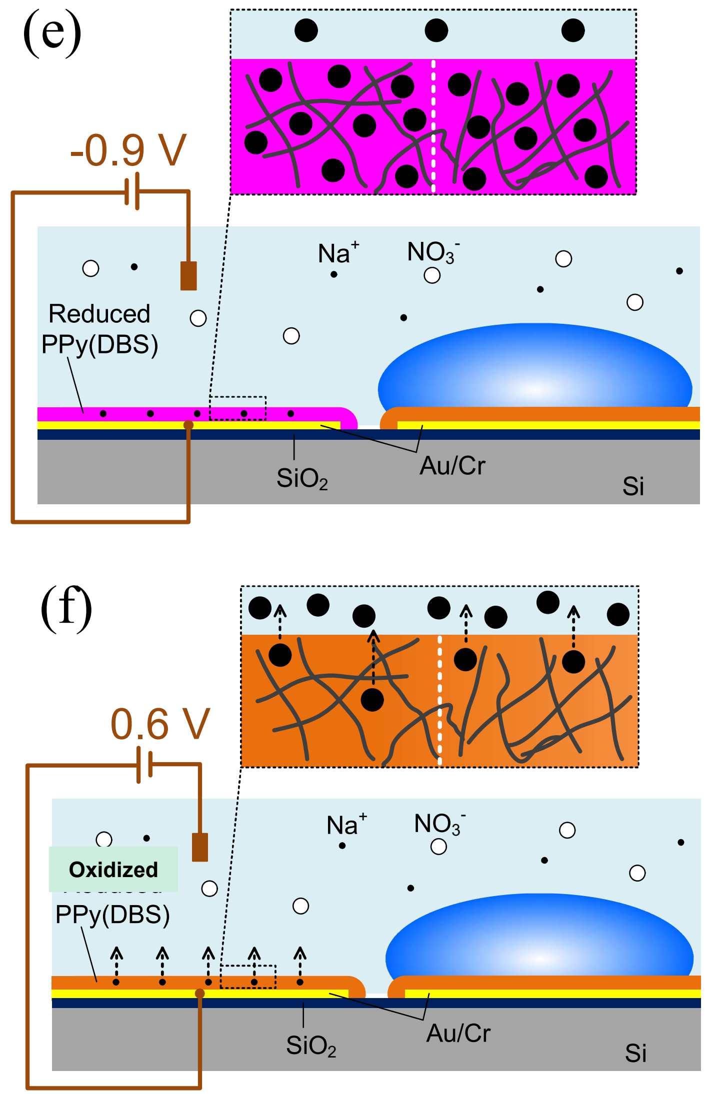
Droplet on Tunable Electrodes (2)



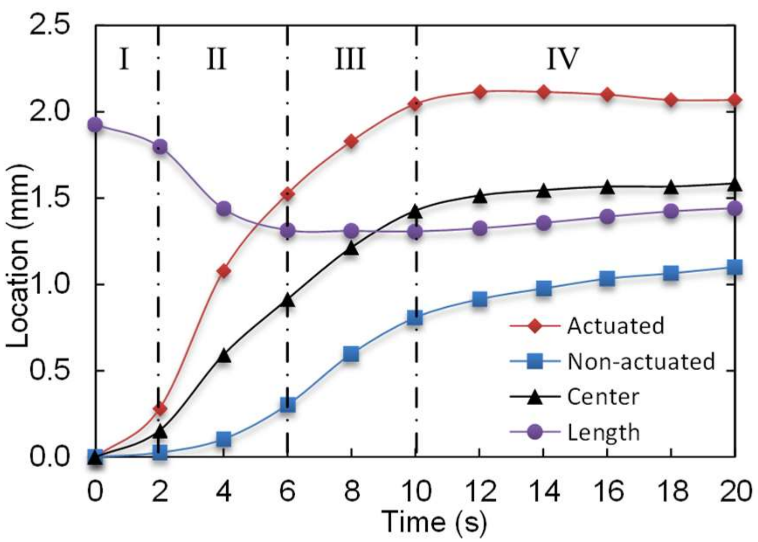


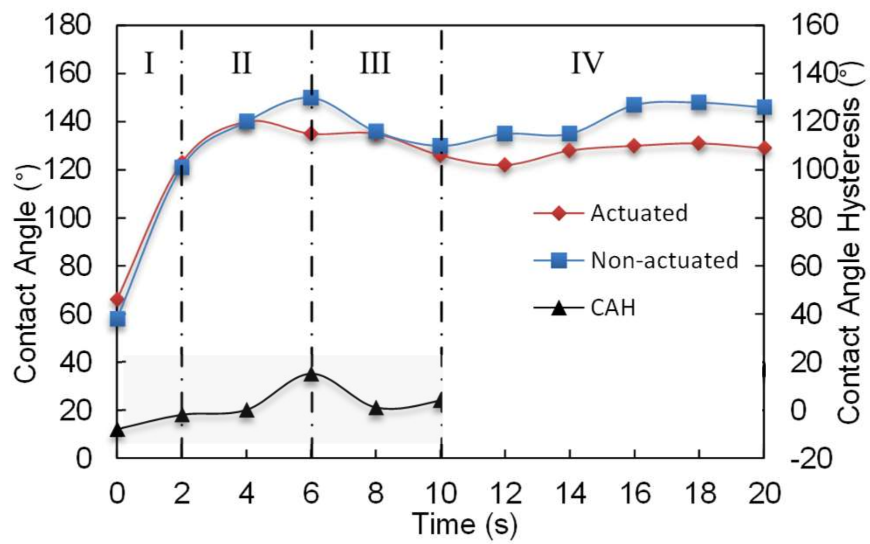
Droplet on Tunable Electrodes (3)



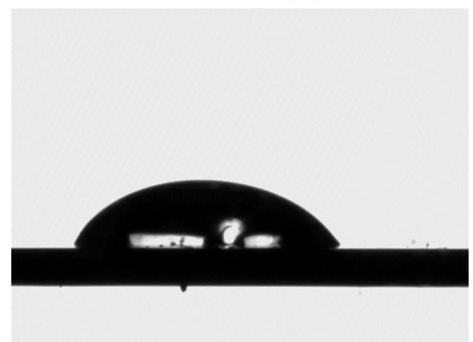


Transportation Dynamics



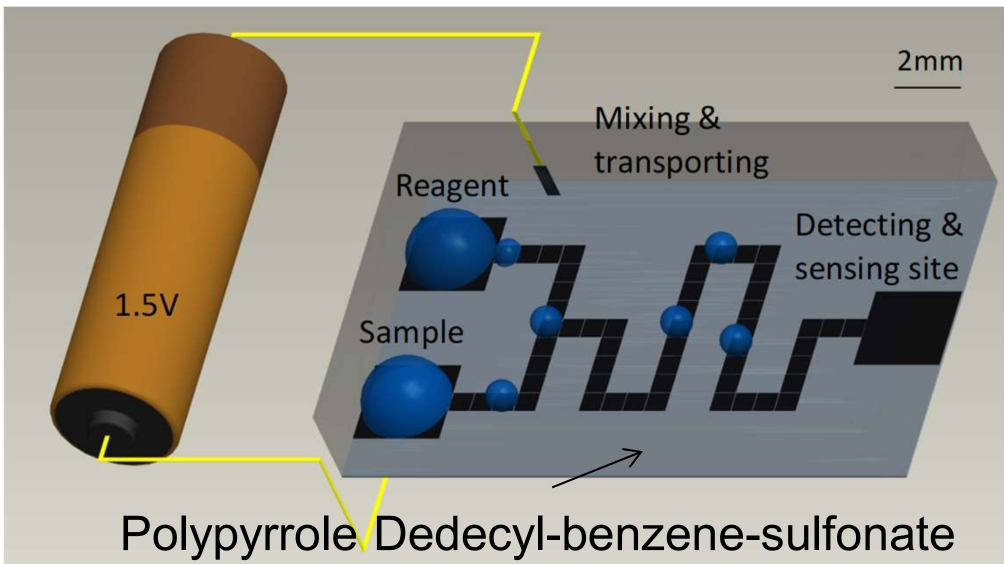


I: Initial droplet flattening
II : Transportation
III: Deceleration
IV: Stabilization

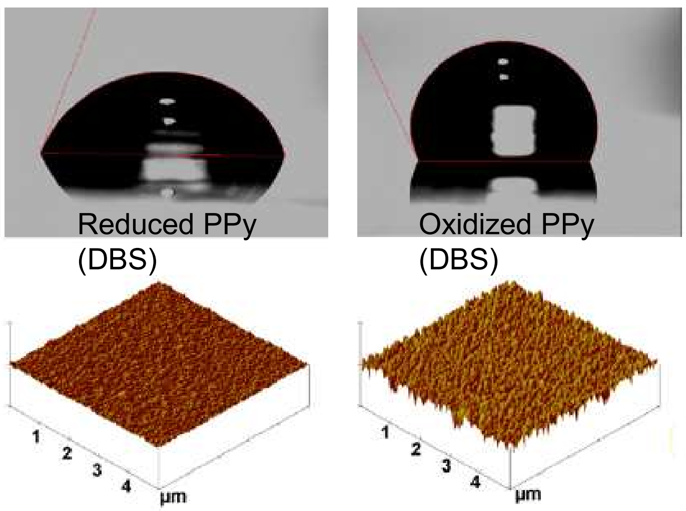


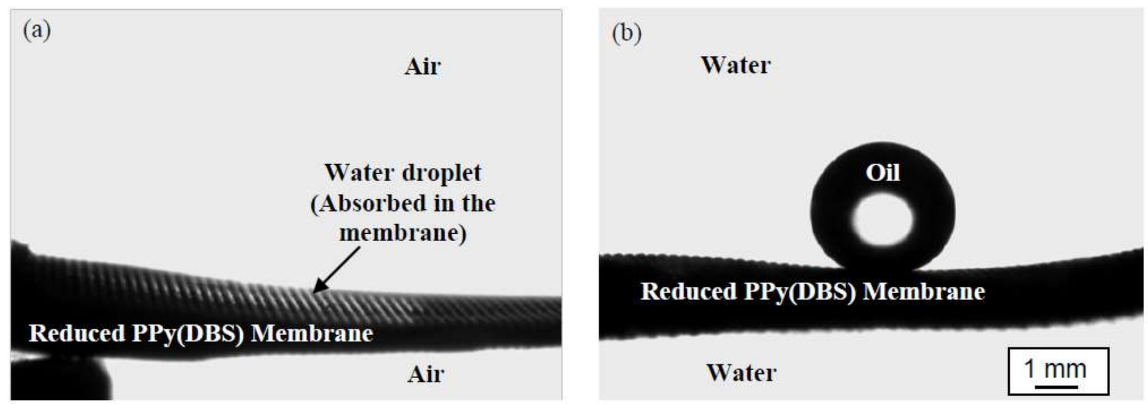
- PPy(DBS) electrodes exhibit extremely low friction during the movement of a droplet evident by a small contact angle hysteresis.

Future Applications

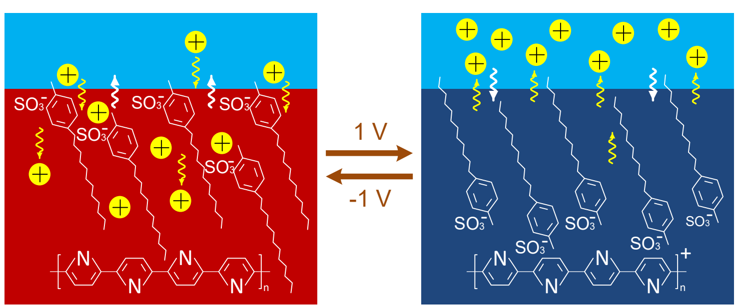


Future Applications



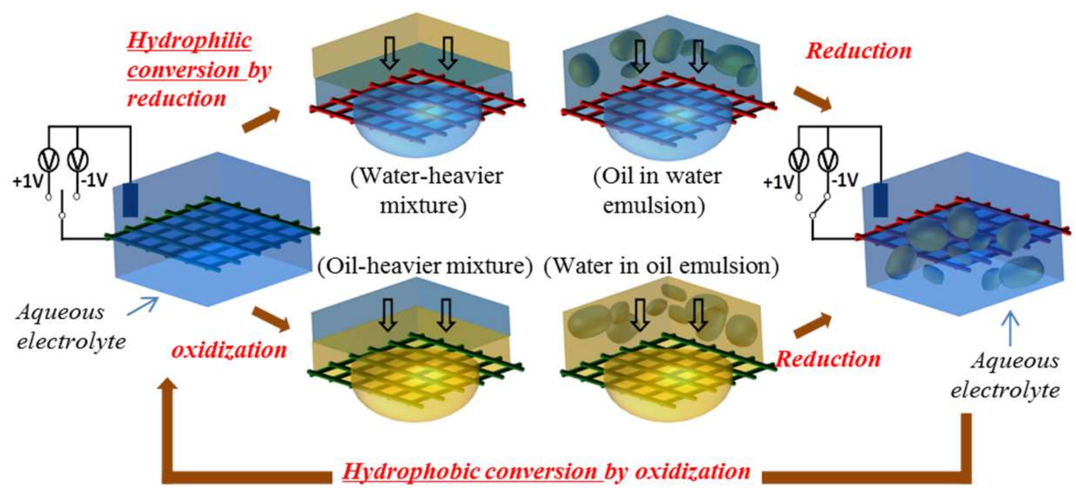


Teh 2009 Sensors and Actuators A



Reduction for cations absorption

Oxidization for cations desorption



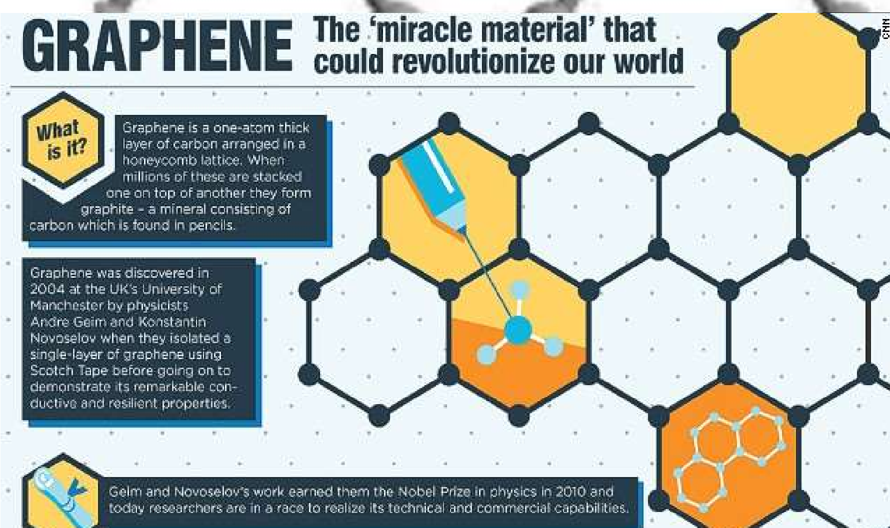
Outline of Presentation

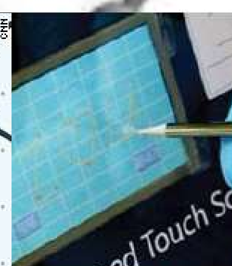
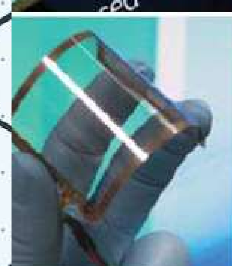
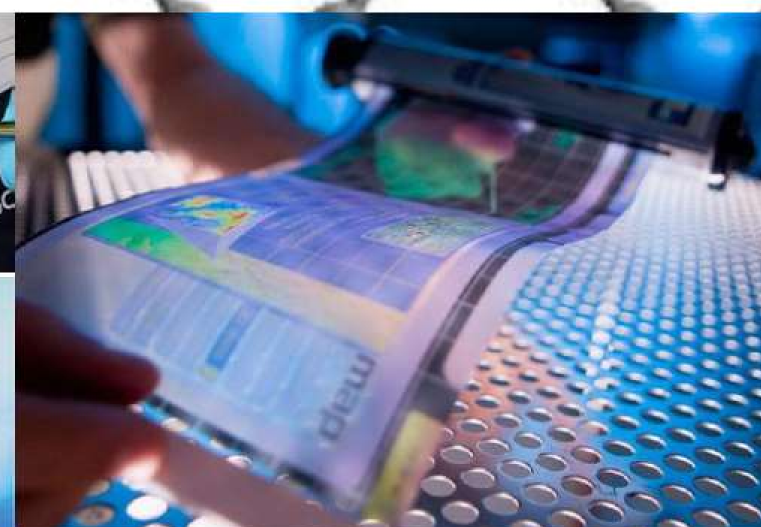
I. Tunable Polymer Surface-based Microfluidics

II. Growth of CNTs on Graphene

Graphene

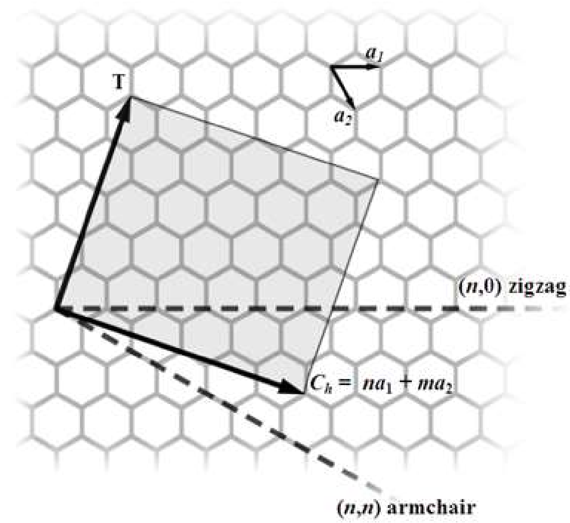
- Graphene is composed of carbon atoms arranged in tightly bound hexagons just one atom thick.
- In 2004, Geim and Novoselov demonstrated that single layers could be isolated, resulting in the award of the Nobel Prize for Physics in 2010.
- It is a good thermal and electric conductor.
- Experiments have shown it to be incredibly strong.

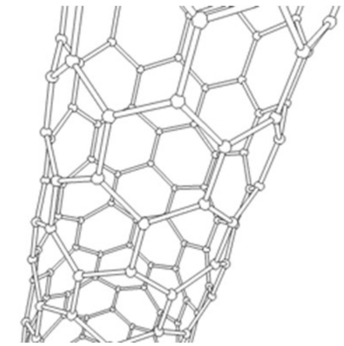


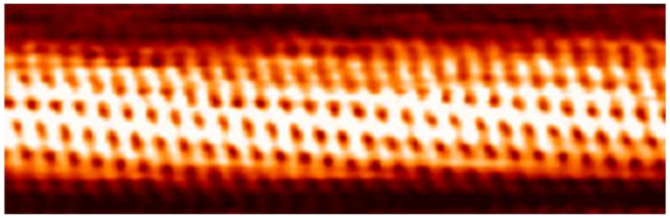




Carbon Nanotubes

- Carbon nanotubes are sheets of graphene rolled into cylinders.
- The diameter of the tubes are typically of nanometer dimensions, while the lengths are typically micrometers.
- This huge aspect ratio leads to unusual electrical transport.
- Some tubes behaving as metals and others as semiconductors.
- The band structure of graphite was first calculated by Wallace in 1947, but it was not until 1991 that multi-walled nanotubes were discovered.





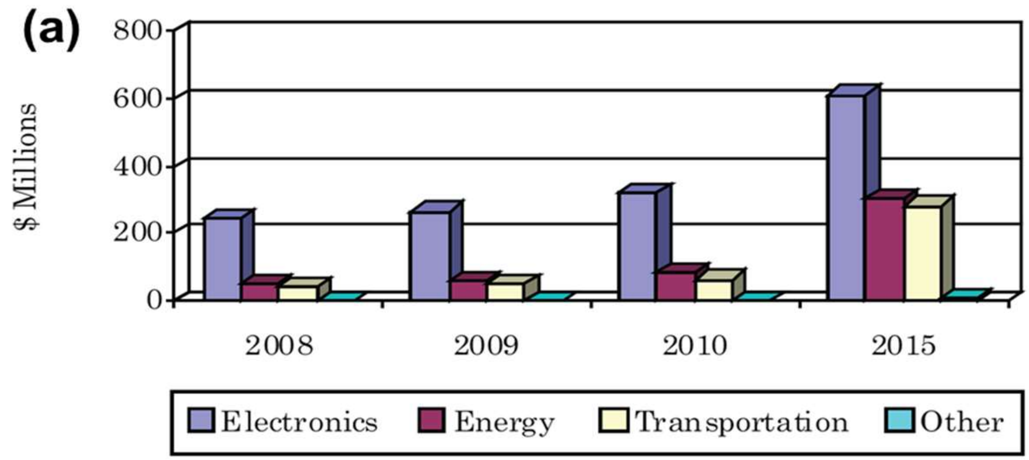


Material Properties

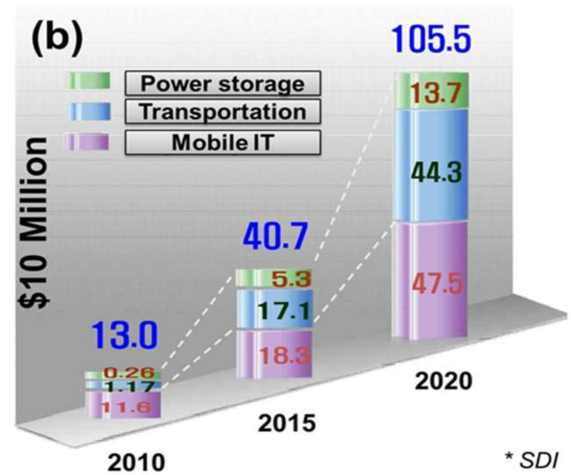
Property	Graphene	CNT	Compare to..
Elastic Modulus	1060 GPa	~1000-5000 GPa	1220 GPa (Diamond)
Intrinsic Fracture Strength	130 GPa	13-53 GPa	6.8 GPa (UH-MW-Polyethylene)
Charge Mobility	2,000-200,000 $cm^2/V\text{-}s$	100,000 $cm^2/V\text{-}s$	8,500 $cm^2/V\text{-}s$ (GaAs) or 1,000 $cm^2/V\text{-}s$ (Si)
Resistivity	10^{-2}-10^{-8} Ω-cm	~10^{-2} Ω-cm	1.59 x 10^{-8} Ω-cm (Ag)
Thermal Conductivity	5000 W/m-K	>3000 W/m-K (MWNT)	400 W/m-k (Cu)
SSA	2630 m^2/g	50-1315 m^2/g	XX
Permeability	Impermeable	N/A	XX
Transmission	97.7%	N/A	85-92% (ITO)

Utilizing the Surface Area

BCC Research's new report, "Graphene: Technologies, Applications, and Markets"



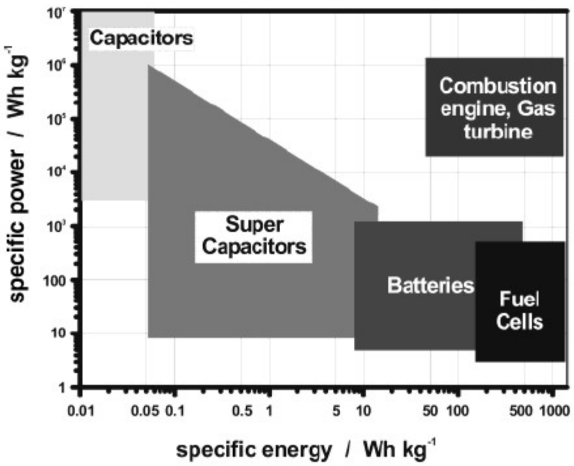
* BCC Research



* SDI

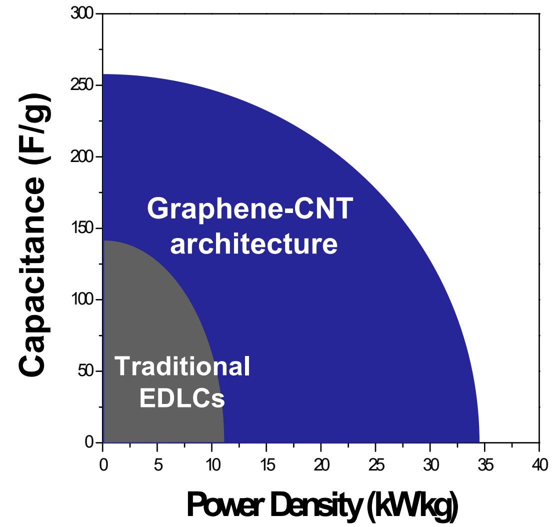
- **Graphene-based supercapacitors**: 67.2% 5-year CAGR, from $26 million in 2015 to $340 million in 2020.
- **Structured materials**: 39.1% 5-yr CAGR, from $17.5 million in 2015 to $91 million in 2020.
- **Graphene in displays**: This segment will reach $43.8 million in 2020.
- **Graphene-based photovoltaics (PV):** 36.1% 5-yr CAGR, from $7.5 million in 2015 to $35 million in 2020.

Supercapacitor



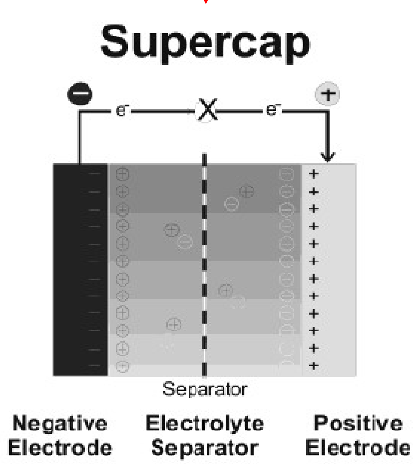
Supercapacitor:

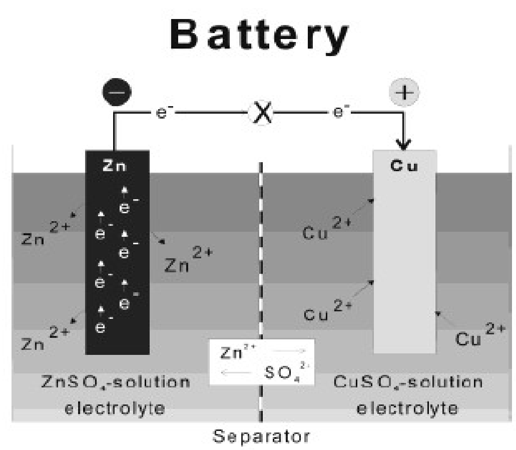
- An electrochemical capacitor with
  - *High power density (~14 kW/kg)*
  - *Long cycle life*
  - *Fast charge storage*
- Ideal for energy storage that undergoes frequent charge and discharge cycles at high current.

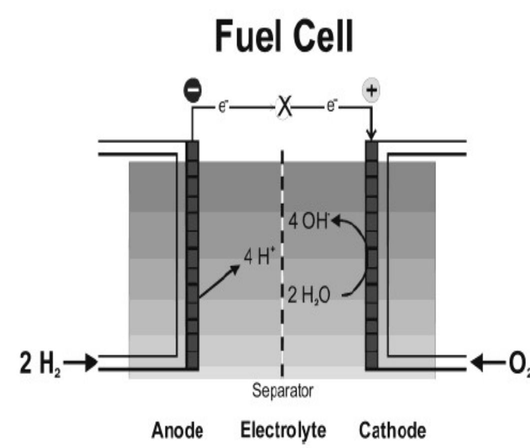


Energy Storage

Energy Conversion

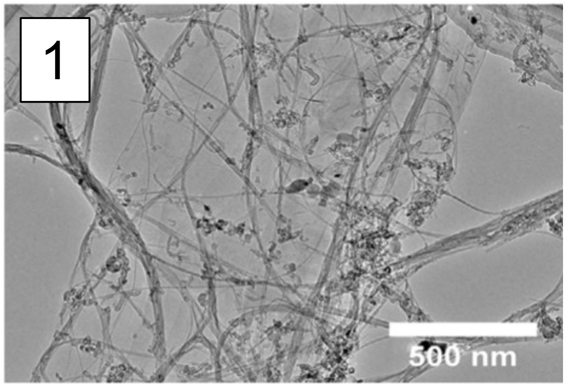




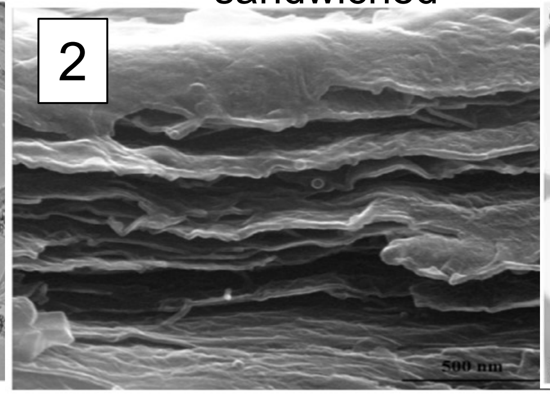


Graphene-CNT Composites/Structures

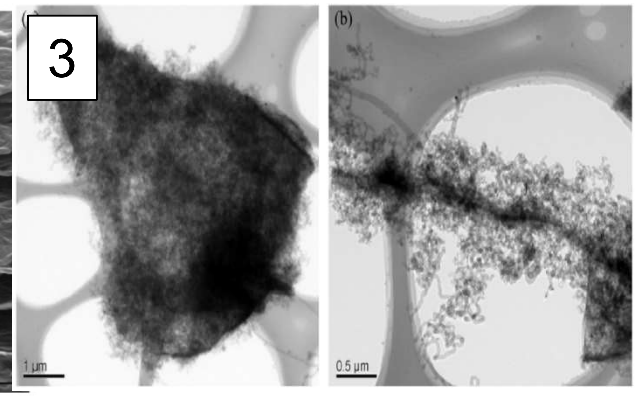
“Spider web” like CNT/G



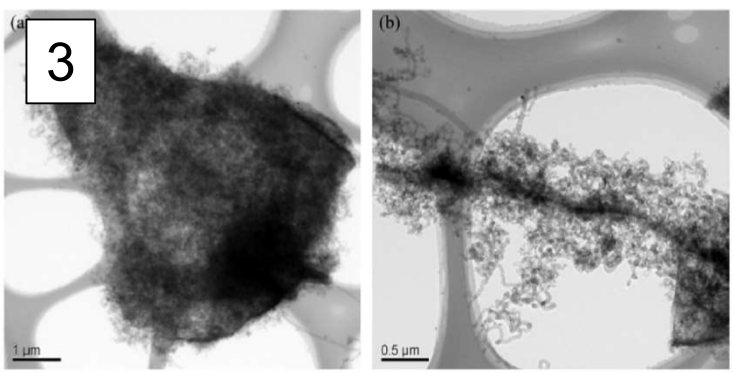
Highly porous, with SWCNTs sandwiched



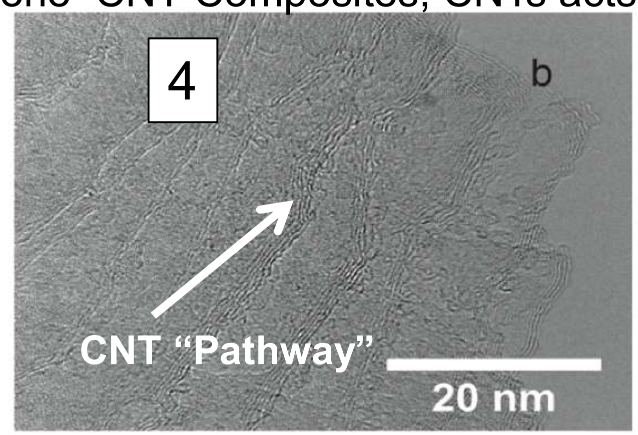
Graphene-CNT Hybrids



Reticular Branch Structures



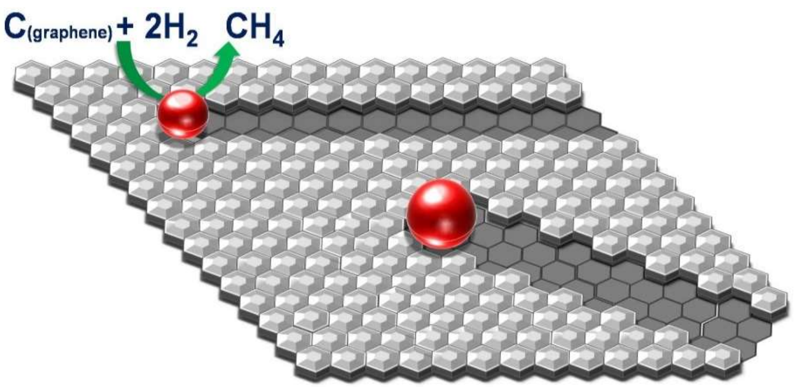
Graphene–CNT Composites, CNTs acts as “Pathway”

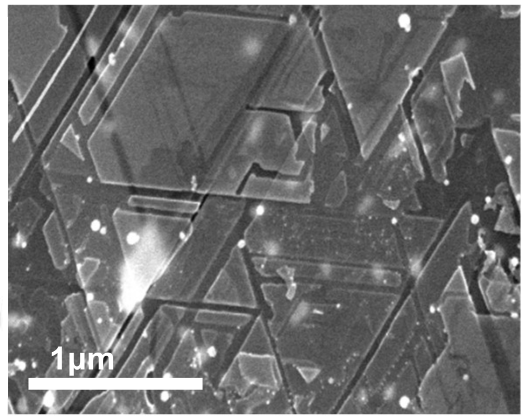


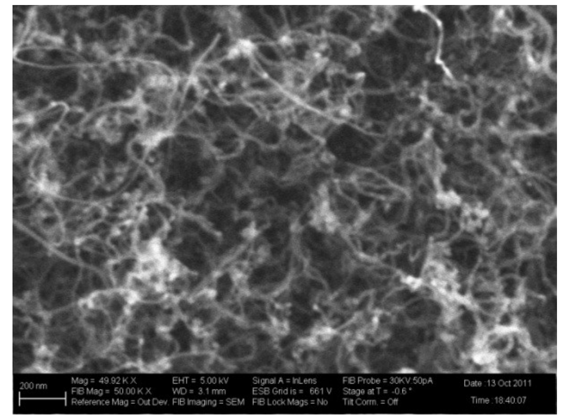
1. Cheng et al, Joural of Power Sources 2013;
2. Wimalasiri et al, Carbon 2013;
3. Kong et al, Carbon 2014;
4. Zhao et al, Materials Chemistry and Physics 2013;
5. Cheng et al, Sci. Technol. Adv. Mater. 2014

Self-aggregation issue

Graphene Etching vs. CNT Growth

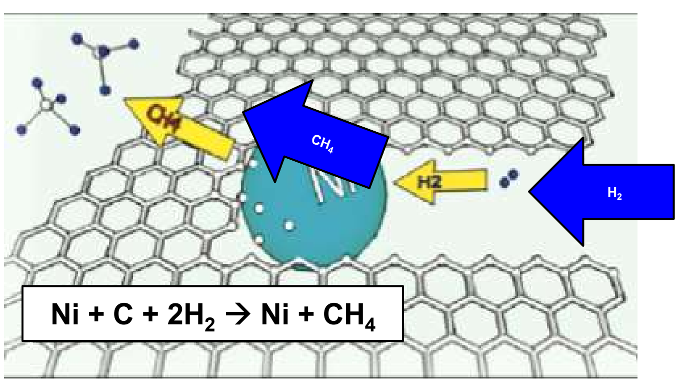






Graphene Week 2010, College Park, MA, USA 2010

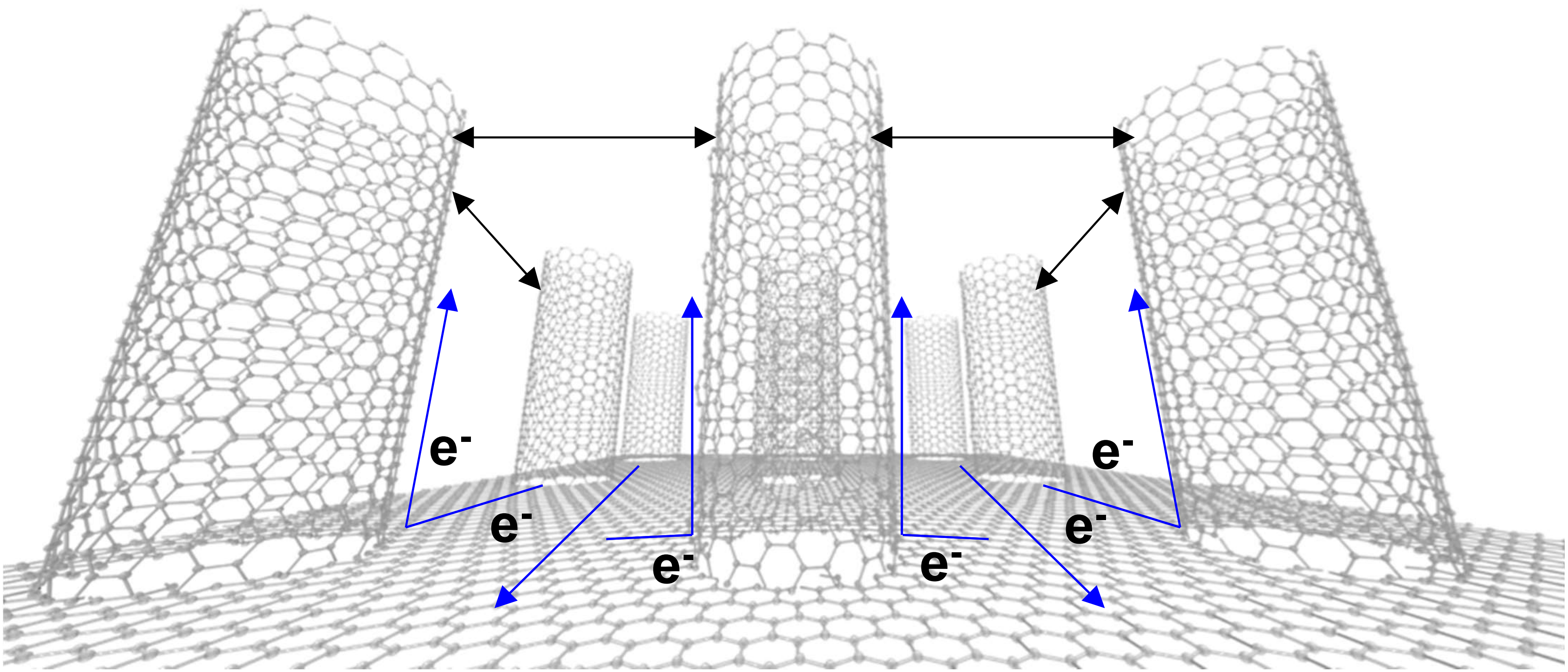
Hydrogenation Reaction



The reaction equilibrium between the source hydrocarbon decomposition and carbon saturation into and precipitation from the catalyst nanoparticles shifts toward either CNT growth or graphene etching.

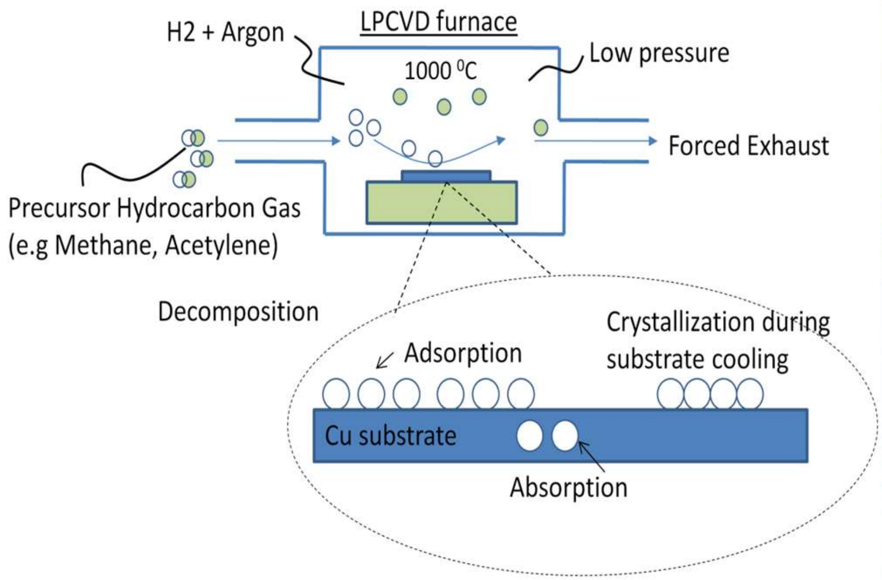
Campos et al, Nano Letters 2009

Seamless Graphene-CNT Architectures



- Continuous Structure
- Charge carrier paths well aligned
- No aggregation
- High surface area-volume ratio

CVD Graphene Growth



Cu Substrate

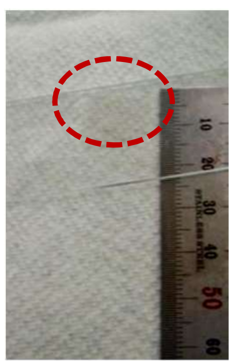
⇩

$Ar+H_2+CH_4$ flow

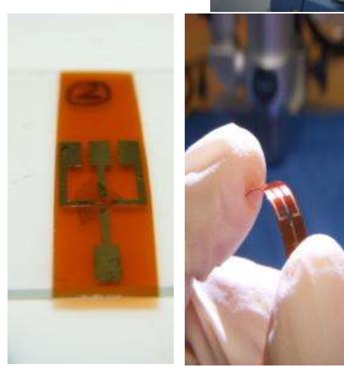
⇩

Computerized precise heating and cooling cycles

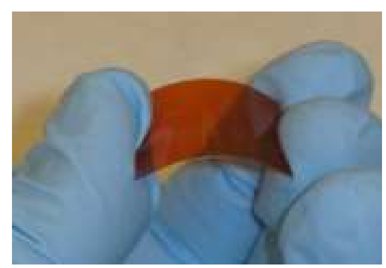
Graphene on water



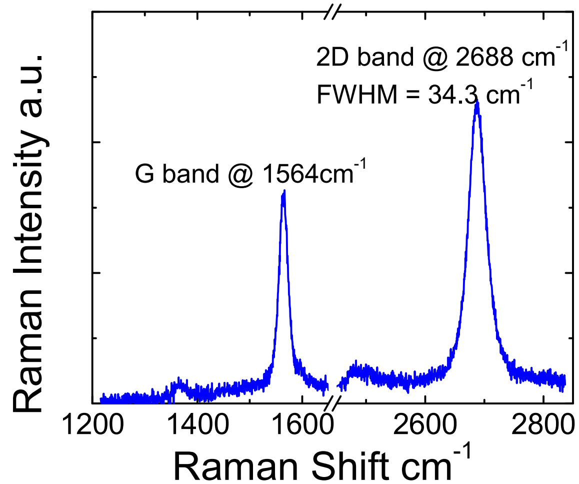
Transferred graphene on glass

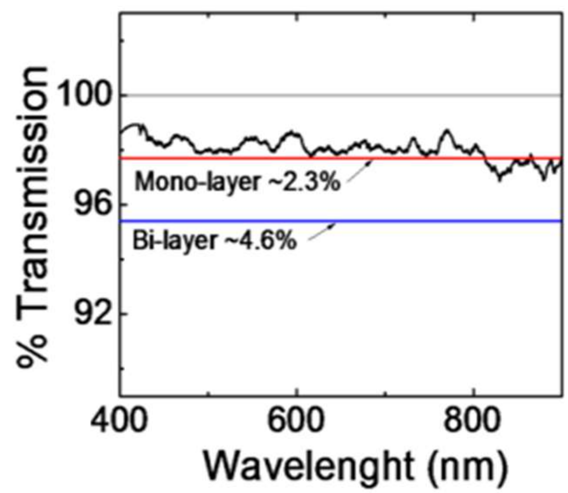


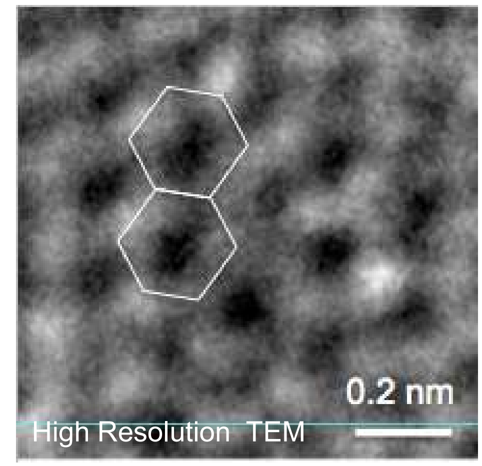
Transferred graphene on flexible substrate



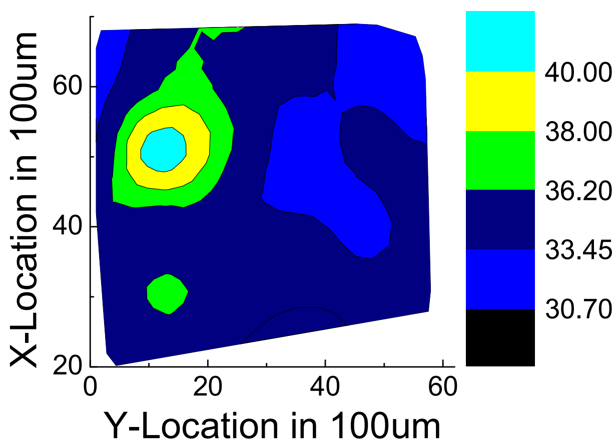
CVD Graphene Growth

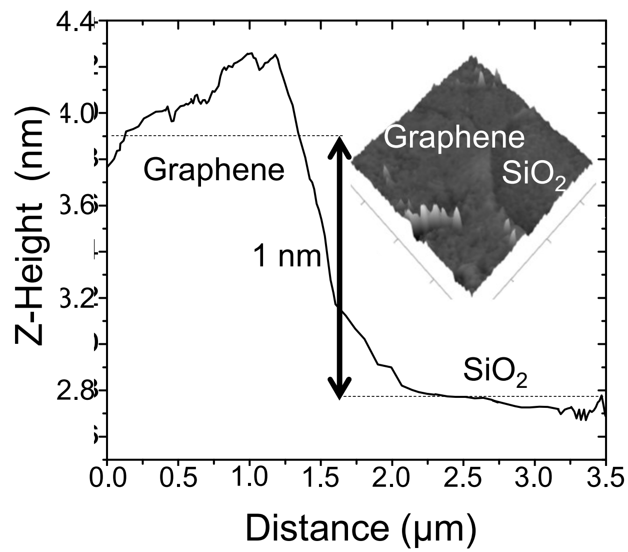


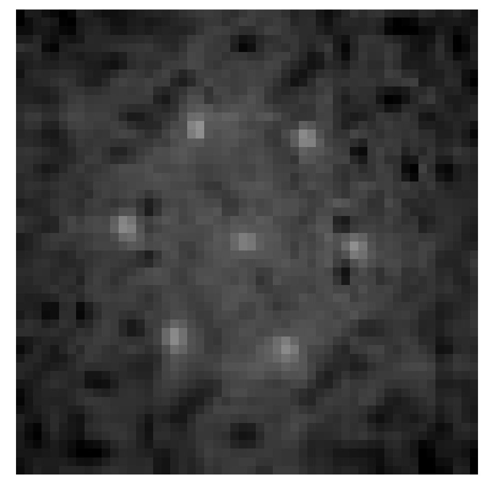




2D Intensity mapping



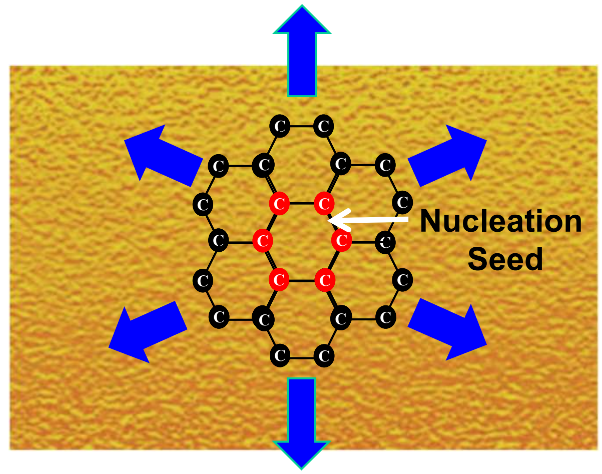




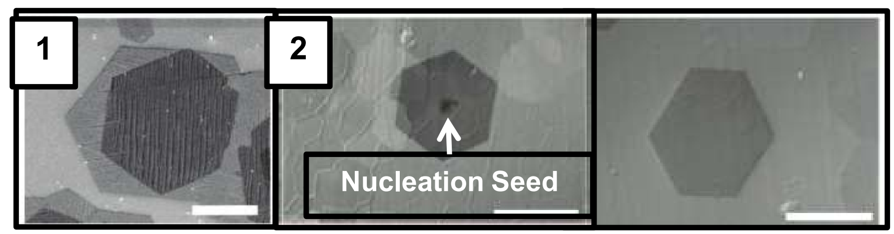
Fast Fourier Transform, showing six-fold symmetry, a signature of monolayer graphene

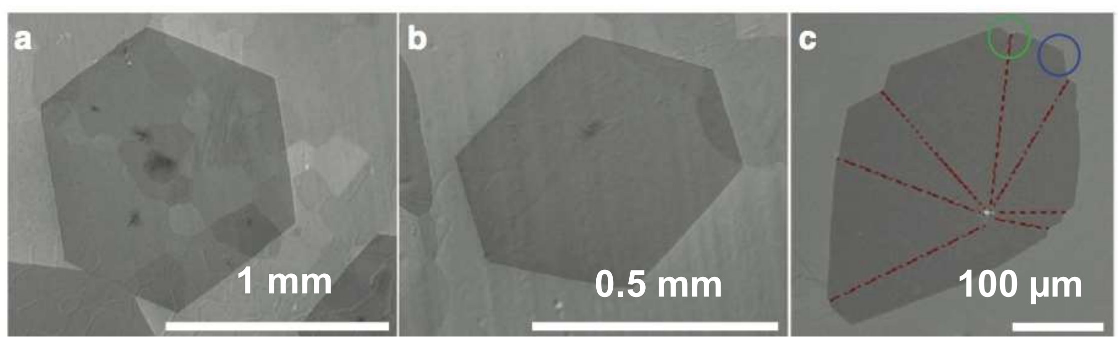
Domain Study

- CVD graphene → Polycrystalline
- Electronic and mechanical properties affected by presence of grain boundaries.
- Key challenge → control of domain
  - Shape
  - Orientation
  - Size
- Cu/graphene interface influences domain growth mode



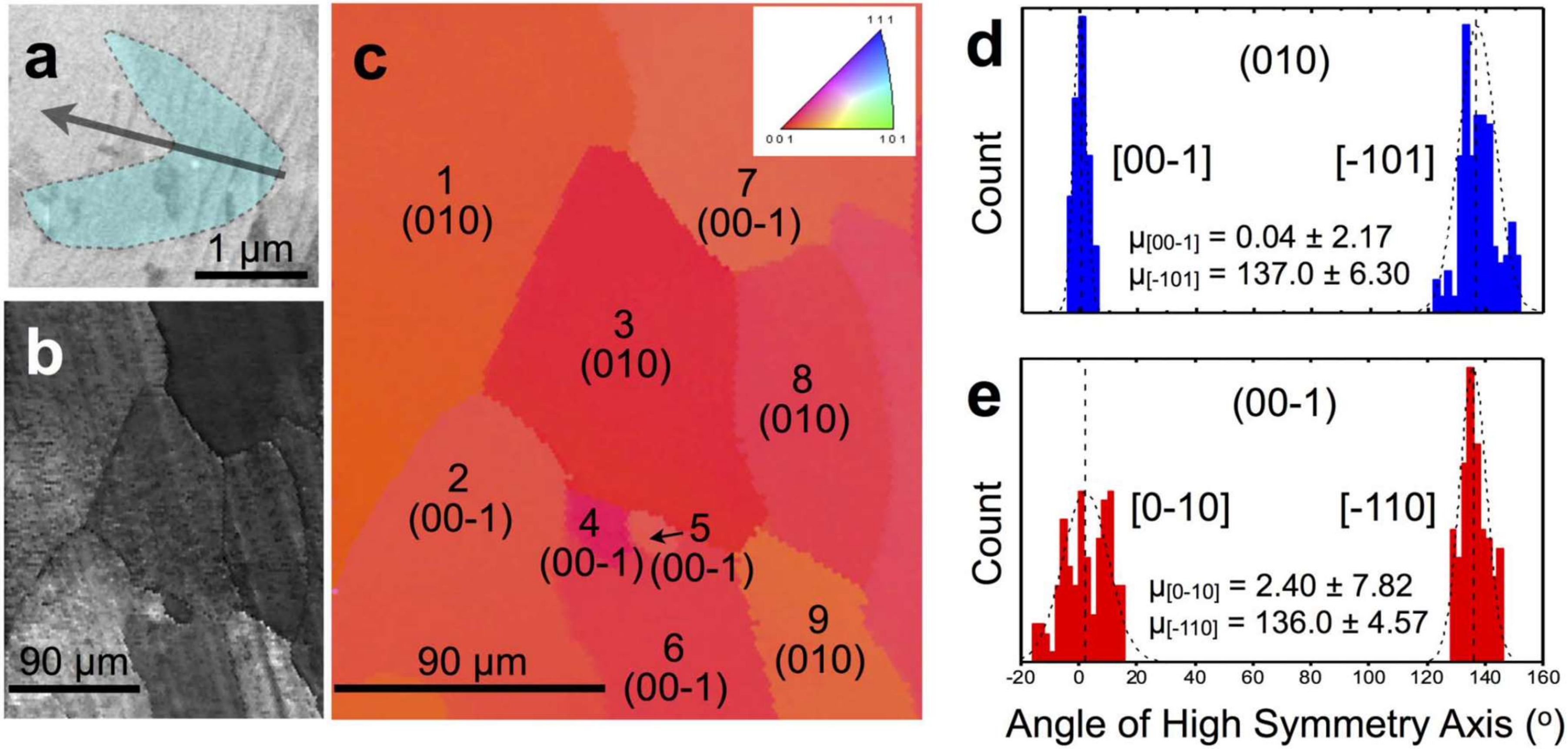
1 Vlassiouk et al, ACS Nano 2011
2 Gao et al, Nature Comm 2012





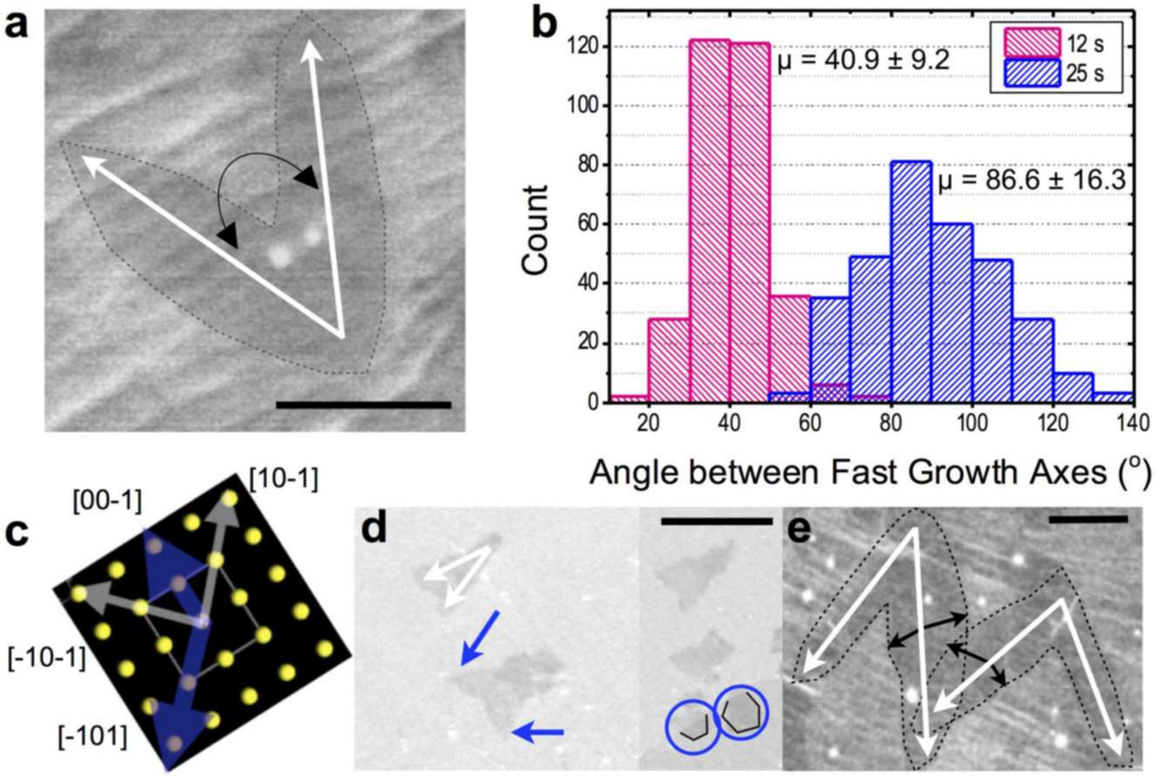
Gao et al, Nature Comm 2012

Cu Grain Effect on Graphene Domain Shape



Growth of 2-lobed symmetrical curvilinear graphene domains specifically on Cu{100} surface orientations ➔ directly influenced by surface energy anisotropy stemming from electron density correlations between the Cu lattice directions (4-fold symmetry) and the graphene fast growth axes (6-fold symmetry).

2-lobed Symmetrical Curvilinear Graphene Domains



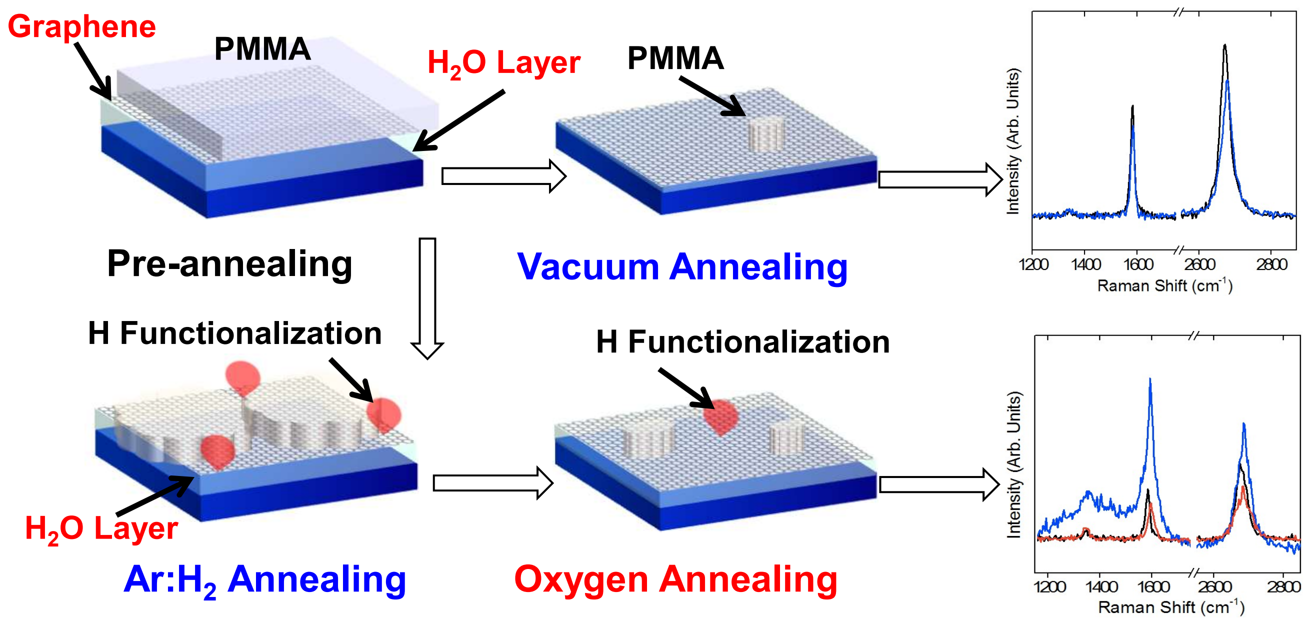
$$v(\theta) = (1+r) + (1-r)\cos(\theta)$$

- v: growth velocity
- θ: angle between the edge normal and slow growth direction
- r: ratio of the velocities in the slow and the fast directions and is *the anisotropy factor for the 4-fold symmetric Cu(100) surface*.

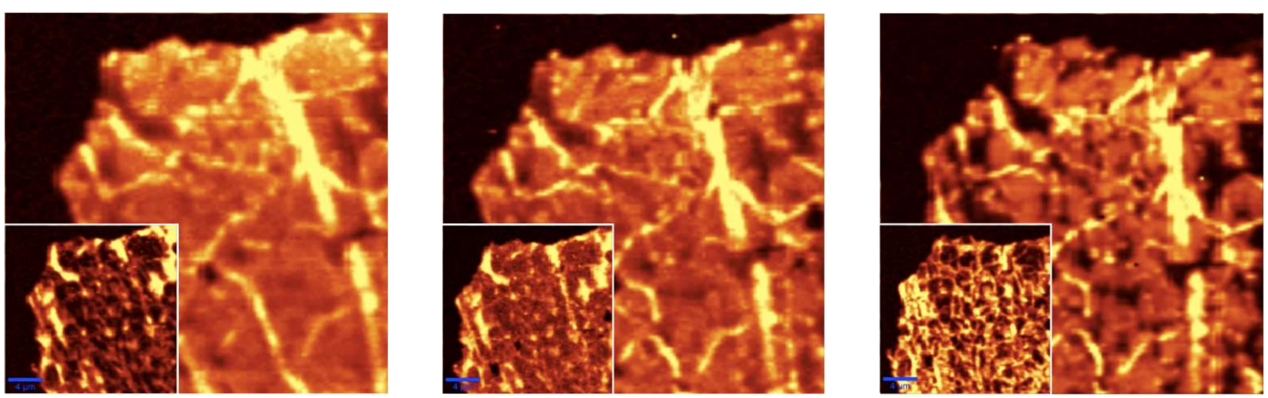
The observed shape of a curvilinear lobe fits well to the function describing the angular dependence of the fast growth velocity to surface anisotropy. The distinctive shape of the graphene lobes on Cu{100} emerges from a growth velocity, dependent on surface anisotropy.

Scientific Reports, (3) 2571 (2013)

Graphene - Annealing Effect



- Impact of polymer removal by annealing on the doping, strain, and morphology of graphene.
- Annealing-based processes create morphological changes and directly influence doping and strain

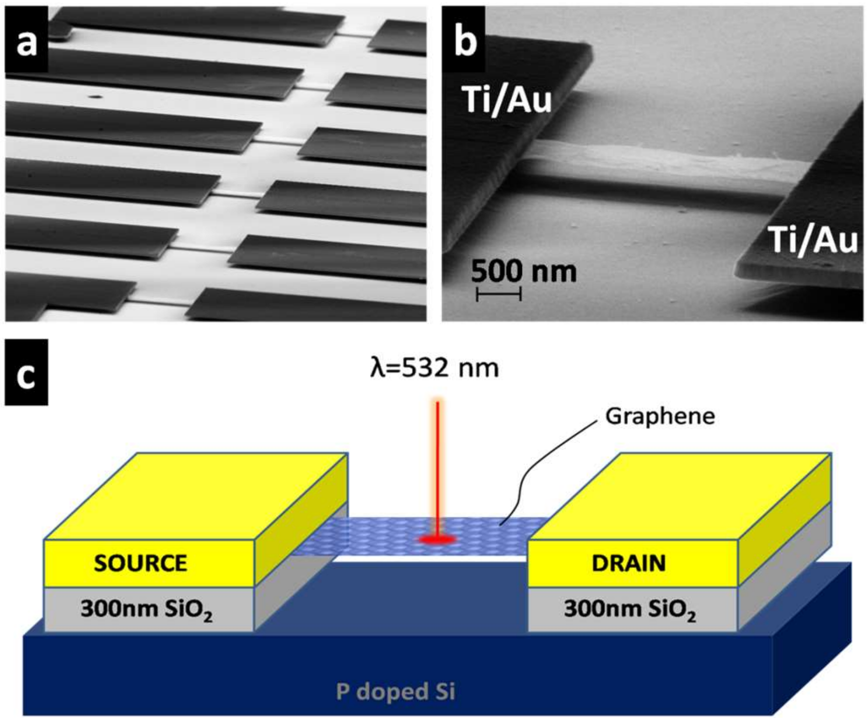


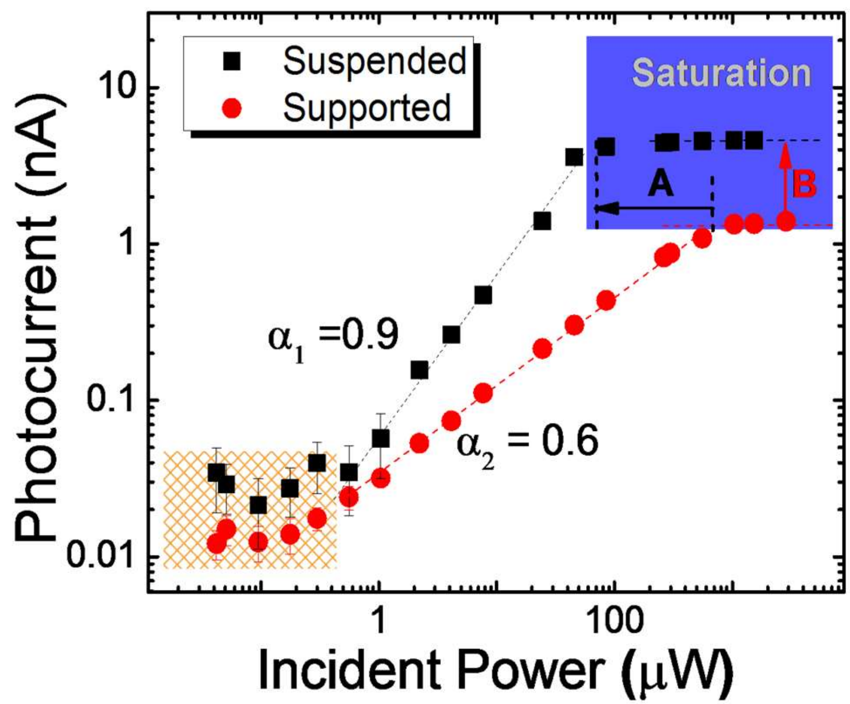
Pre-Annealing | $Ar:H_2$ annealing | Oxygen annealing

Carbon, (64), 35, (2013)

Graphene Micro Ribbons for Photodetectors

Photoelectric (PE) effect ➔ $I_{PE} \propto P_{opt}$ Thermoelectric (PE) effect ➔ $I_{TE} \propto (P_{opt})^{2/3}$



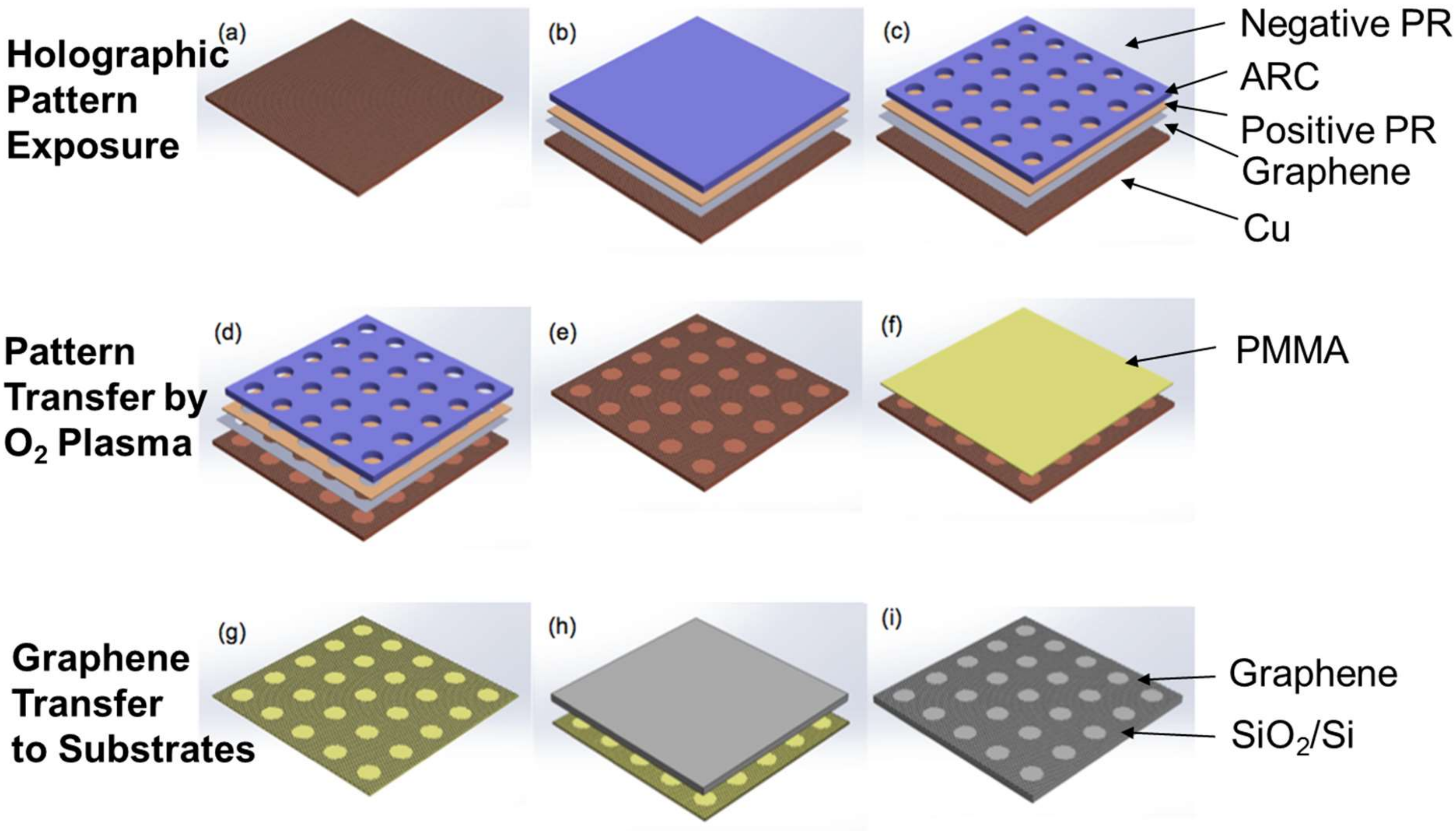


- *The fully-suspended CVD graphene is dominated by the faster photoelectric effect.*

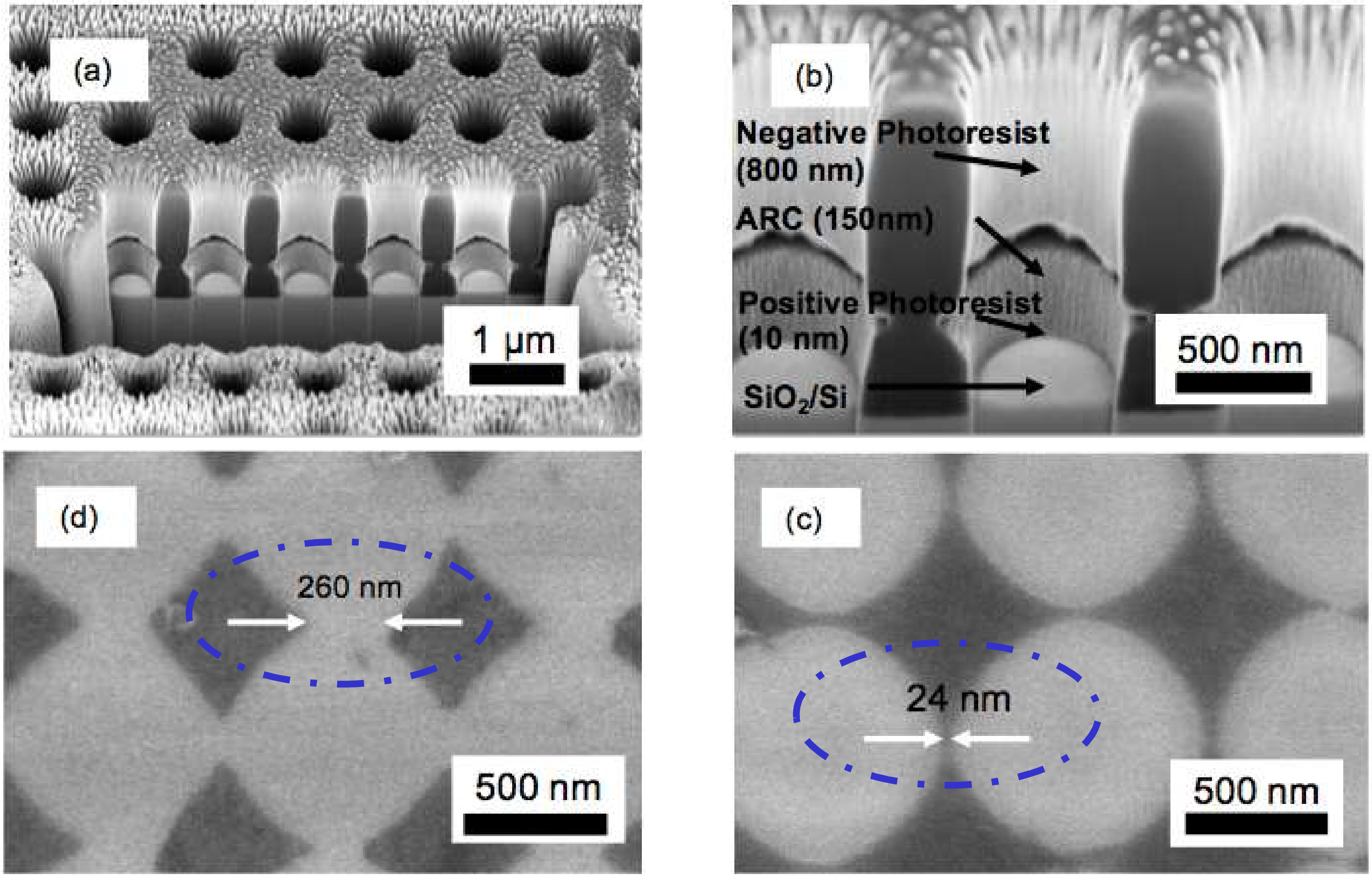
➔ *Promising towards fabrication of graphene photodetectors with high cut-off frequencies.*

Scientific Reports, (3), 2791 (2013)

Transfer of Large-area Nanopatterned Graphene

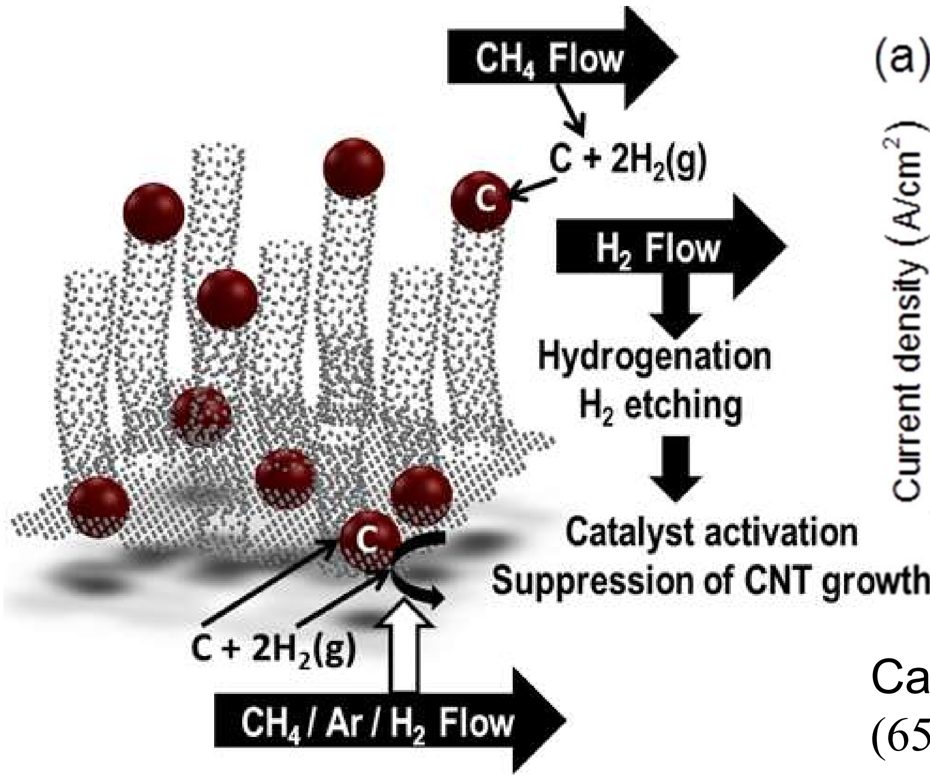


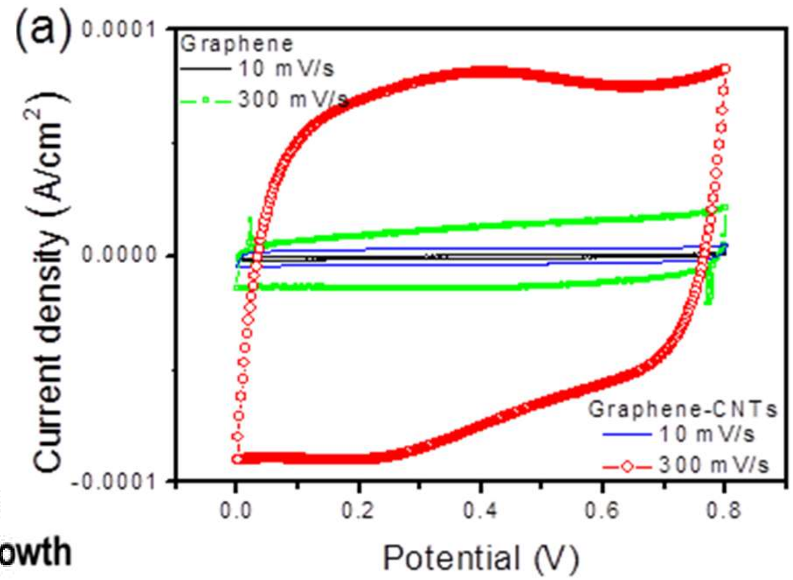
Wafer-Scale Nanopatterned Graphene



Journal of Vacuum Science and Technology B, 6(32), 2166-2746 (2014)

Growth of CNTs on Graphene





Capacitance of the graphene-CNT sample
(653.7 μF/cm^2 at 10 mV/s)

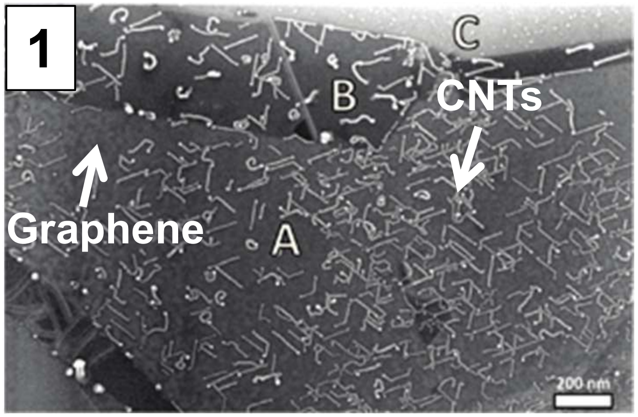
Two competing reactions. 1. carbon growth out of metal catalyst islands.
2. hydrogenation (the reaction of ambient H_2 with the carbon growth in the presence of catalyst to form methane gas), resulting in an etching of the graphene substrate.

Nanotechnology, 23, 015301 (2012)

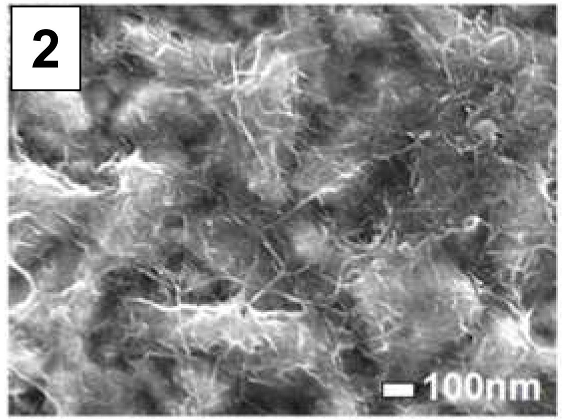
Graphene-CNT Composites/Structures

2-D

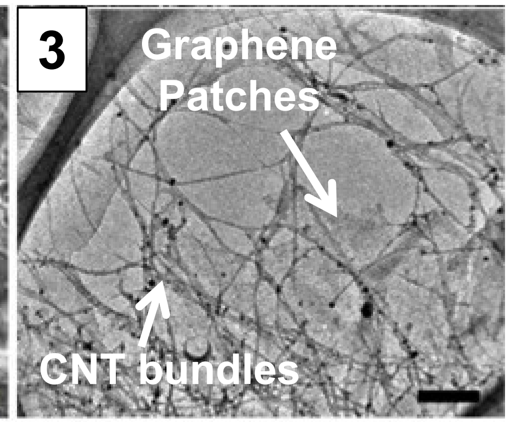
CNTs in-plane on few-layer graphene



Graphene-CNT composite

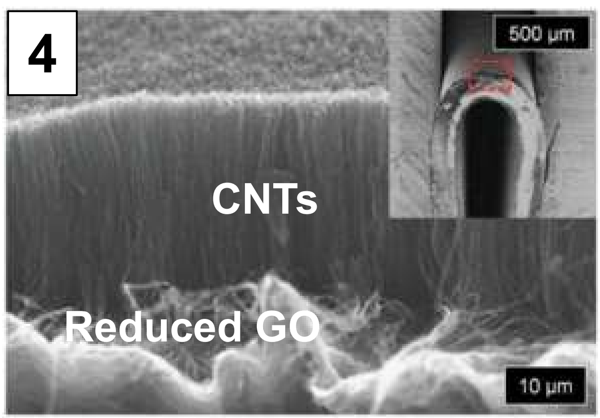


Graphene-CNT network

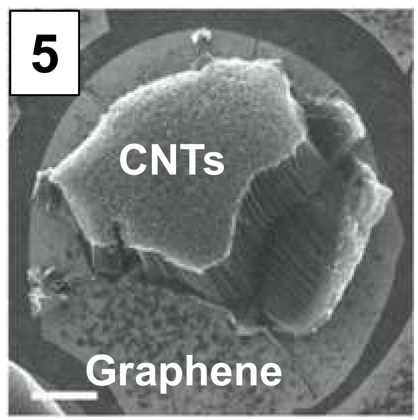


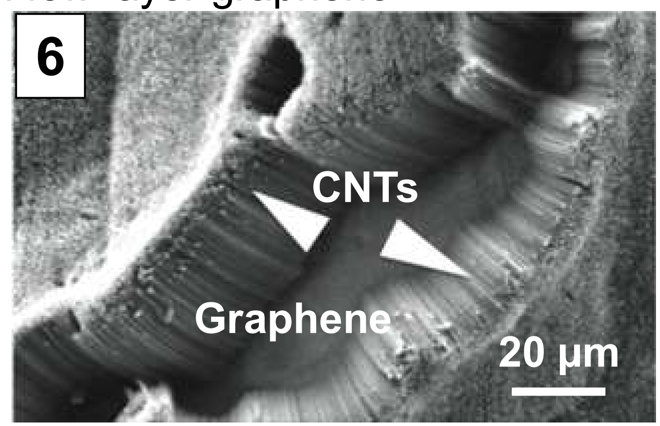
3-D

CNTs on reduced graphene oxide



CNTs on few-layer graphene

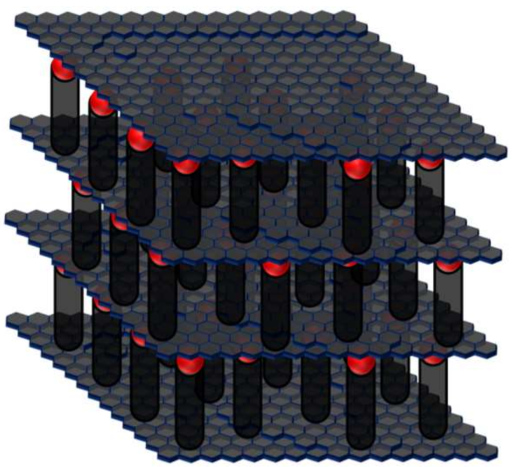


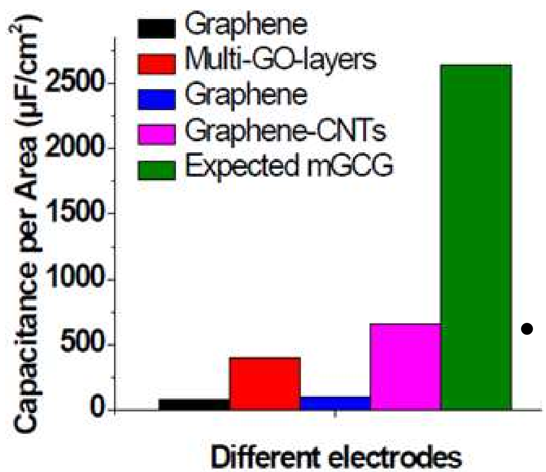


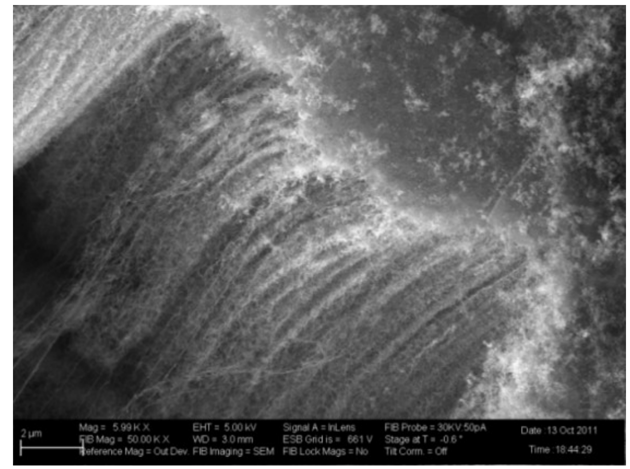
1 Hunley et al, ACS Nano 2011
2 Kim et al, J Mater Chem 2012
3 Li et al, J Phys Chem C 2010
4 Lee et al, Adv Mater, 2010
5 Zhu et al, Nature Comm, 2012
6 Paul et al, Small 2010
7. Wimalasiri et al, Carbon 2013;
8. Kong et al, Carbon 2014;
9. Cheng et al, Sci. Technol. Adv. Mater. 2014

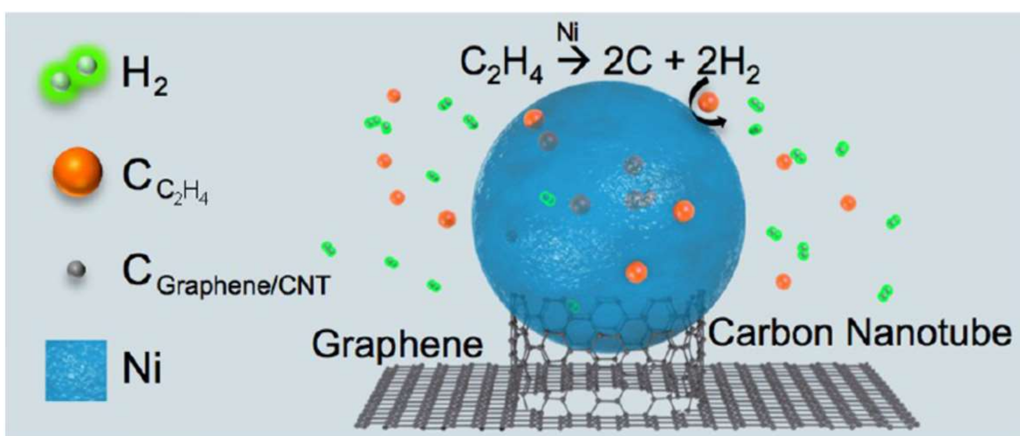
Reaction Equilibrium: Growth of CNTs on Graphene

Graphene-CNTs multi-stack nanostructures may achieve an extremely high *active* surface area with well aligned charge carrier paths.





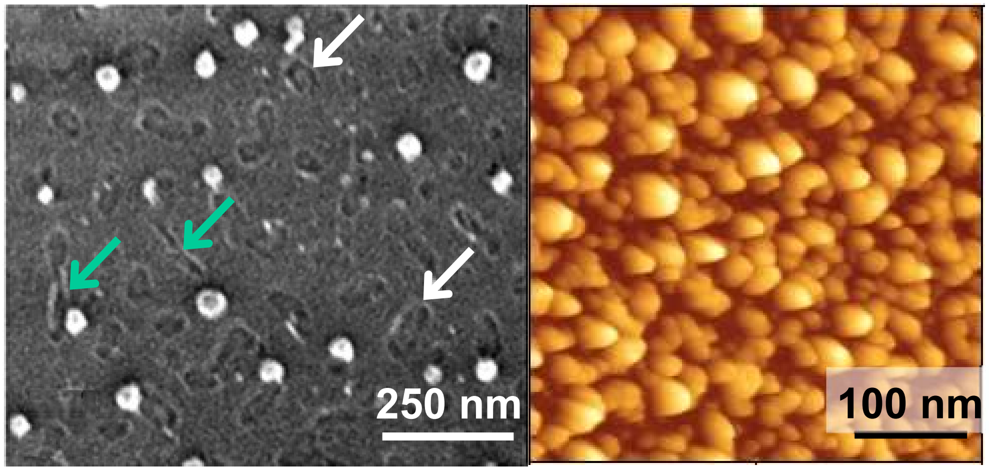


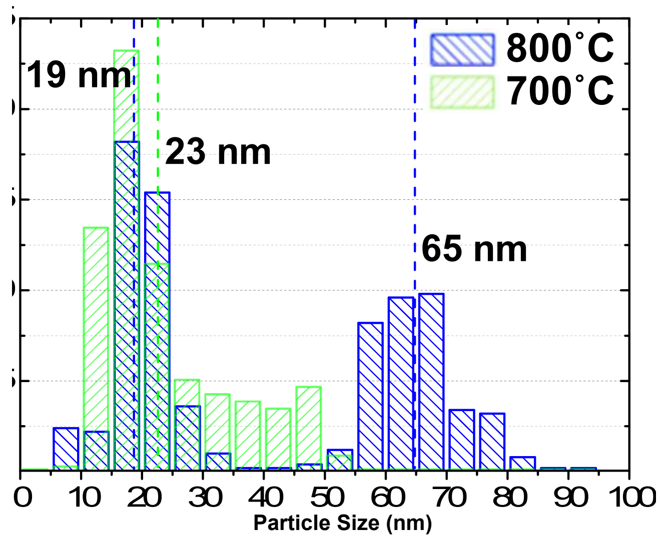


- The full utilization of a graphene-CNT construct requires maintaining the integrity of the graphene layer during the CNT growth step.
- Successful growth occurs when the reaction equilibrium is *shifted towards suppression* of hydrogenation reaction.

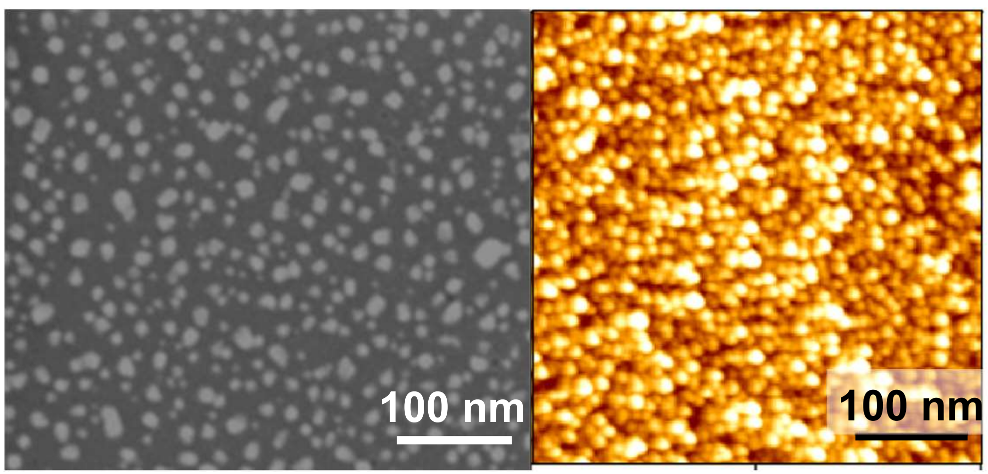
CNT Catalysts: Thermal Treatment

800˚C





700˚C



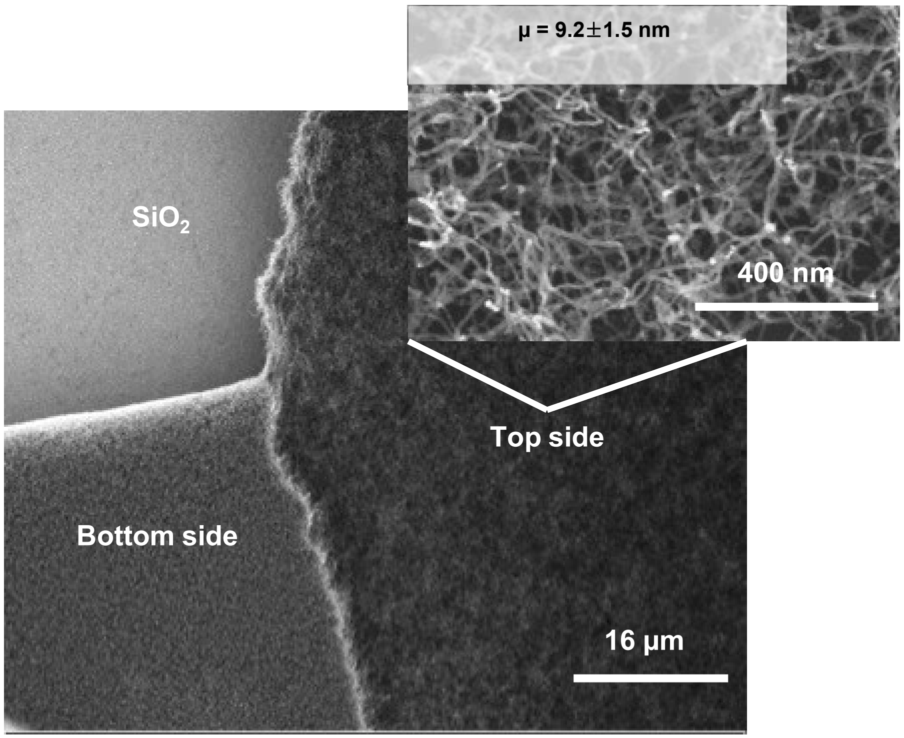
Ar/H_2 (400/50 sccm)

800˚C
Low density nanoparticles
Hydrogenation active

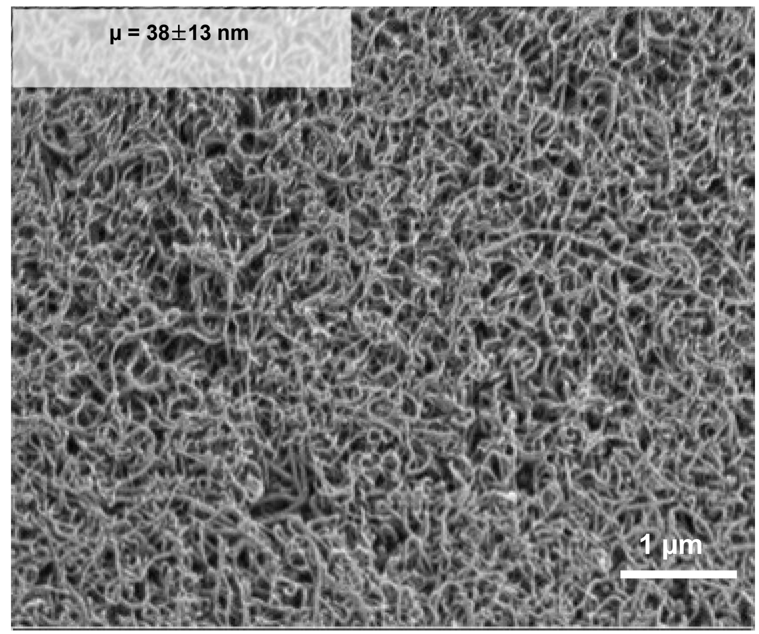
700˚C
High density nanoparticles
Hydrogenation suppressed

Graphene Etching during CNT Growth: C_2H_4

Thermal Treatment: 800˚C
CNT Growth: 800˚C



Two stage growth
1. C_2H_4 and graphene → bottom side
2. C_2H_4 → top side

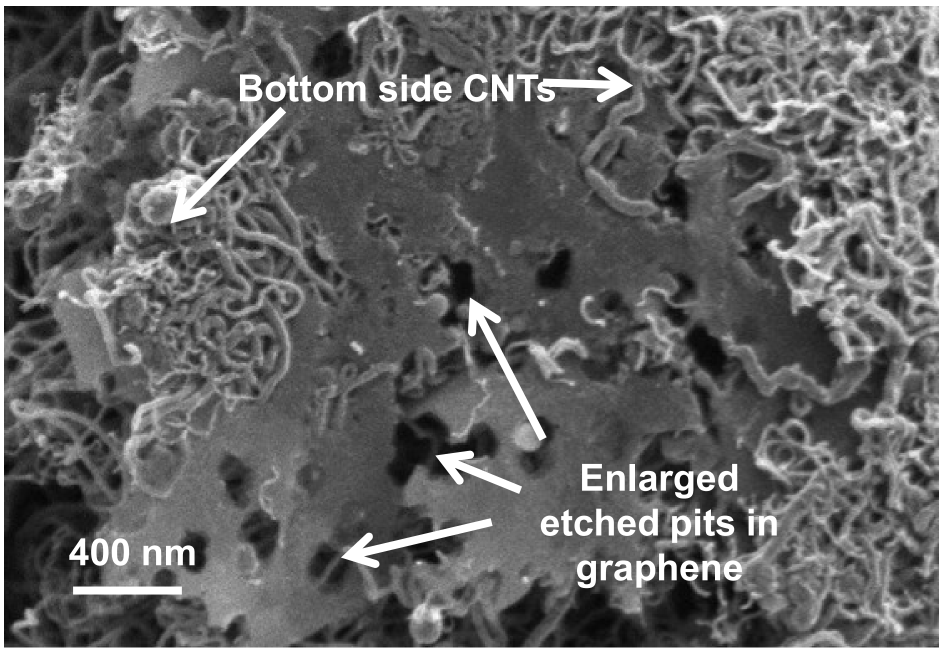


Bottom Side

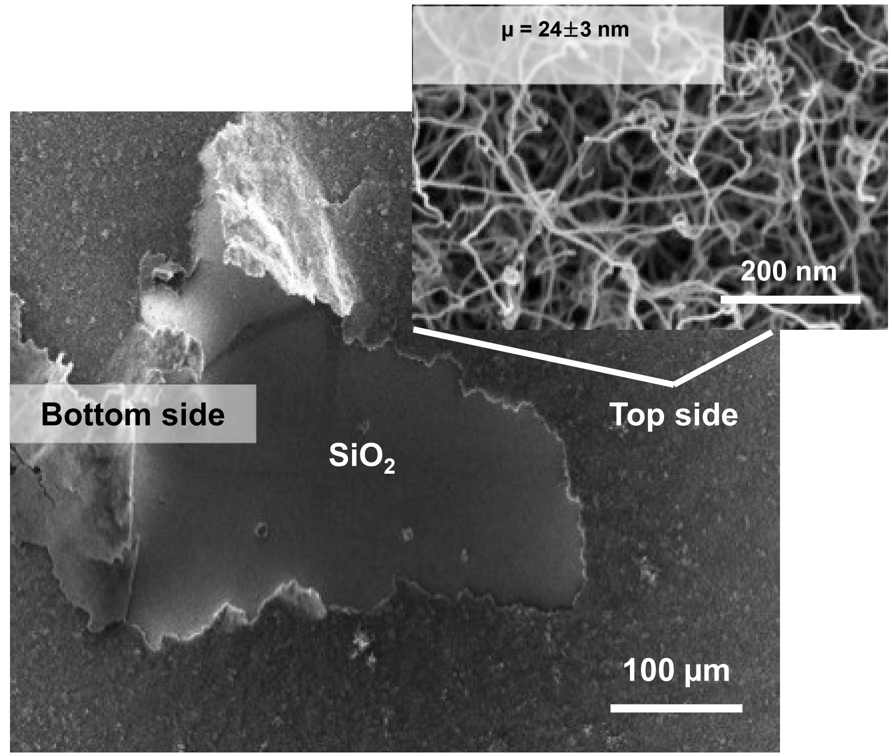
$Ar/H_2/C_2H_4$ = 400/50/50 sccm

Carbon Feedstock: C_2H_4

Thermal Treatment: 700˚C
CNT Growth: 800˚C

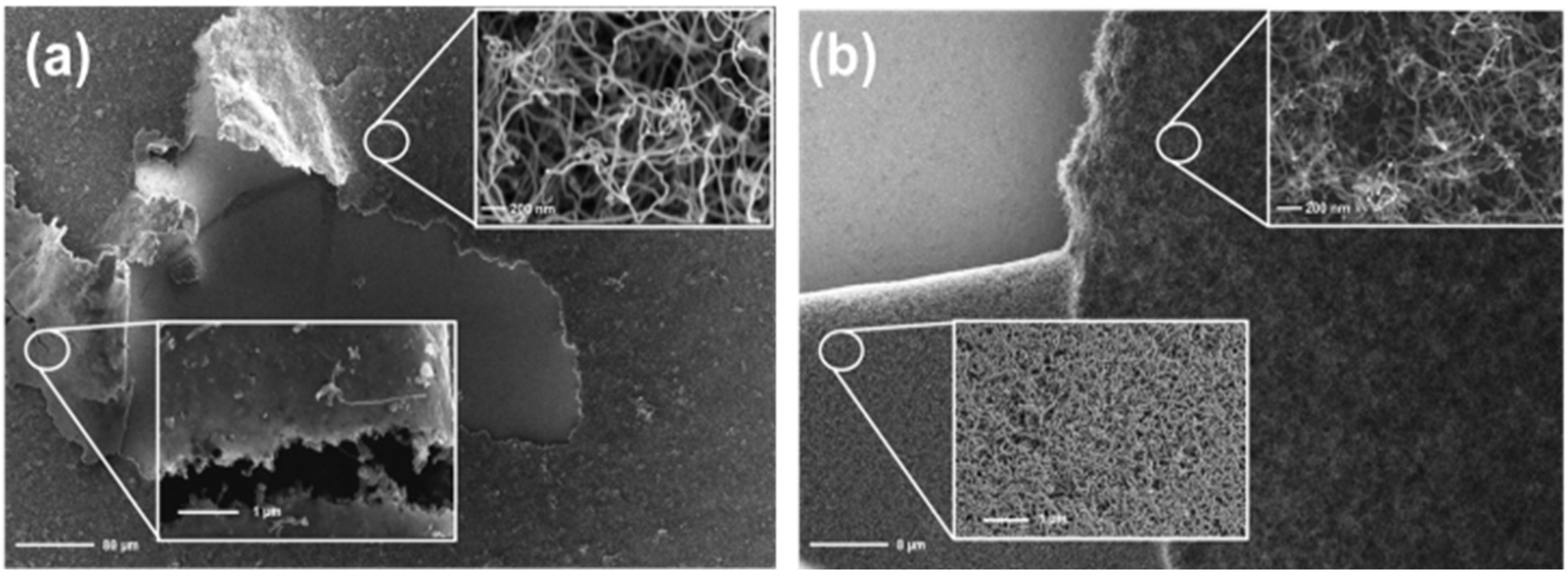


Thermal Treatment: 700˚C
CNT Growth: 700˚C



- Nanoparticles are non-mobile during growth step
- At high temperatures, H_2 from C_2H_4 contributes to hydrogenation: results in the primary growth of etched pits and lines.

Suppressed Graphene Etching During CNT Growth



(a) intact graphene substrate and (b) without graphene (etched away)

Using C_2H_4 gas as a hydrocarbon source under low temperature (700°C) and controlled gas ratio conditions ➔ Catalytic hydrogenation reaction suppressed to avoid etching of graphene during the CNT growth process.

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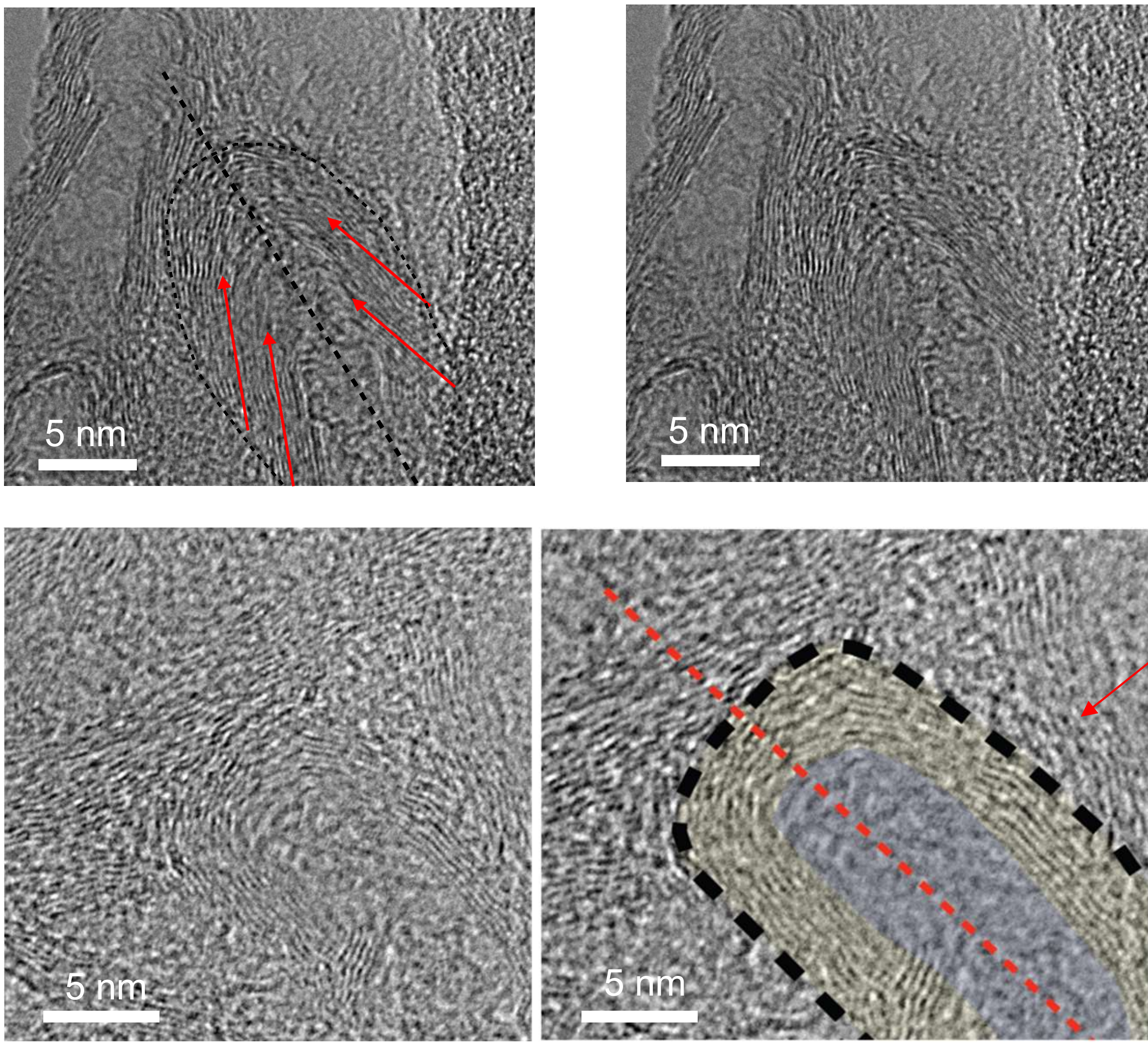
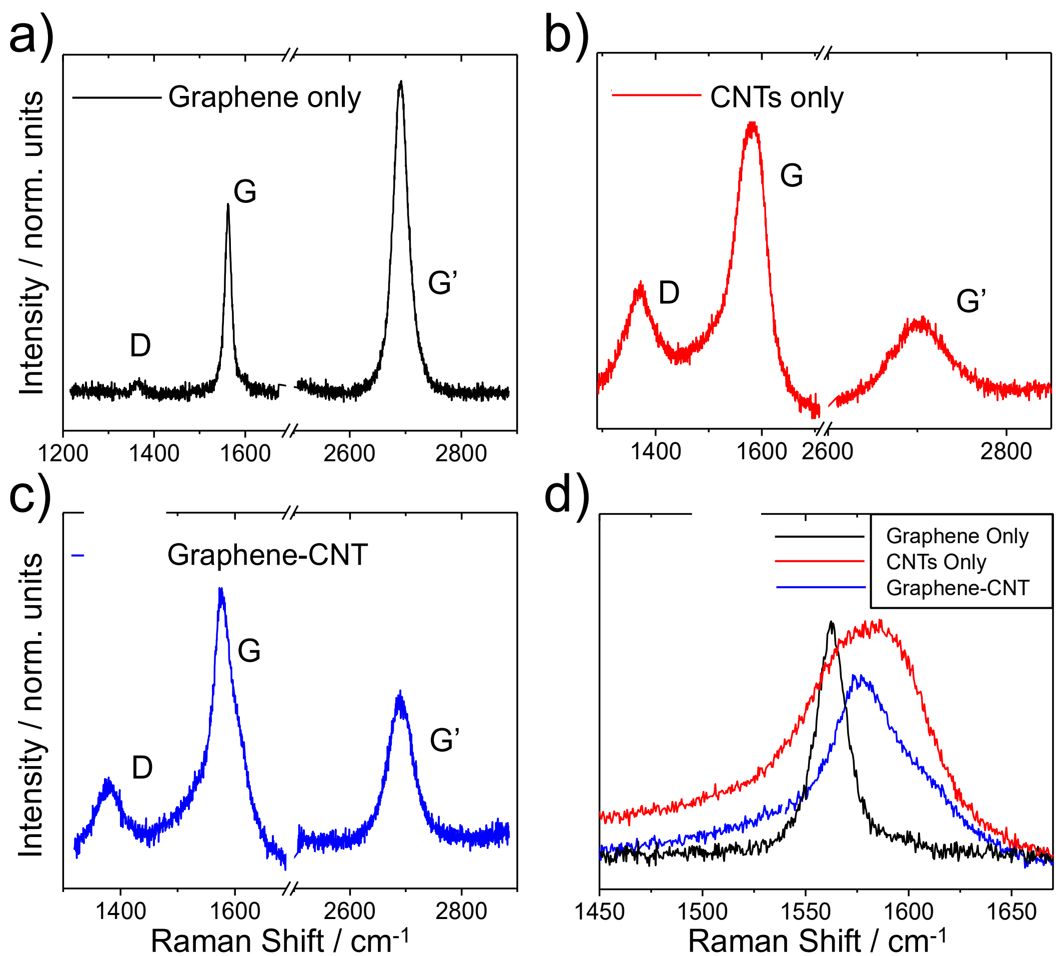
CNFs vs. CNTs



Our growth: The graphene planes within
the yellow region are parallel to the tube growth axis, verifying that CNTs have been grown.

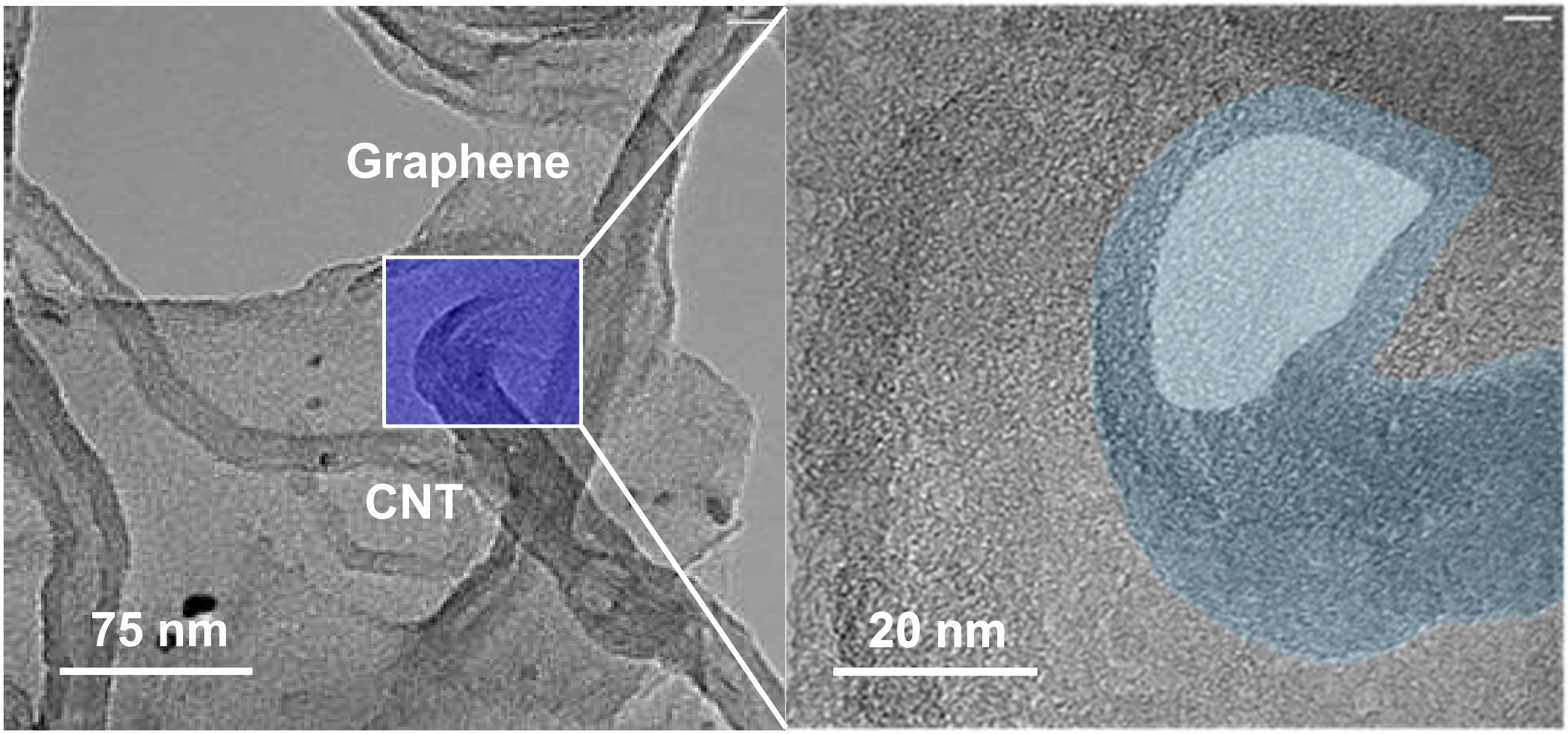
Raman Spectra of CNT/Graphene



Although the G band of graphene is sharp and symmetric, it is broad and asymmetric in the CNTs only and graphene-CNT sample because of a smeared splitting effect from the G^+ and G^- components.

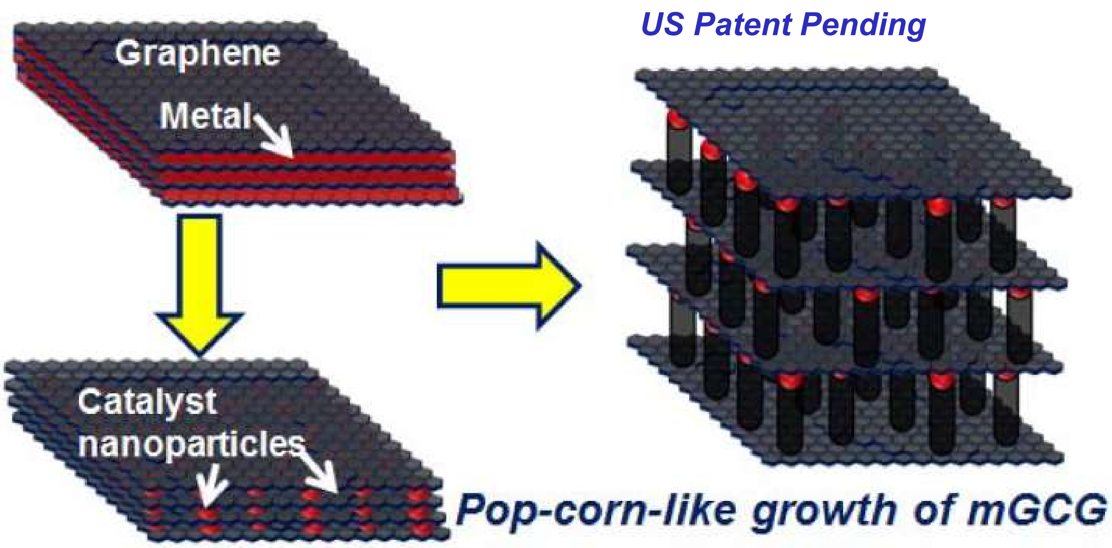
The G^- (~1570 cm^{-1}) component arises from vibrations along the circumferential direction of the CNTs, whereas the G^+ (~1610 cm^{-1}) component arises from vibrations along the tube growth axis.

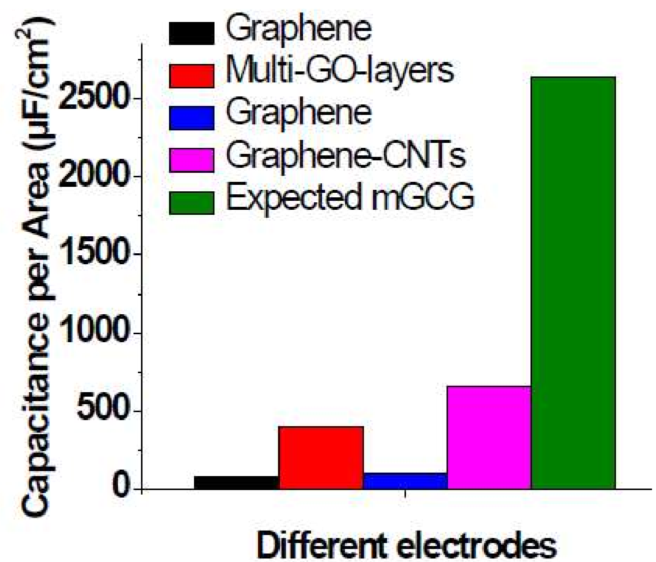
Seamless Growth of CNTs from Graphene

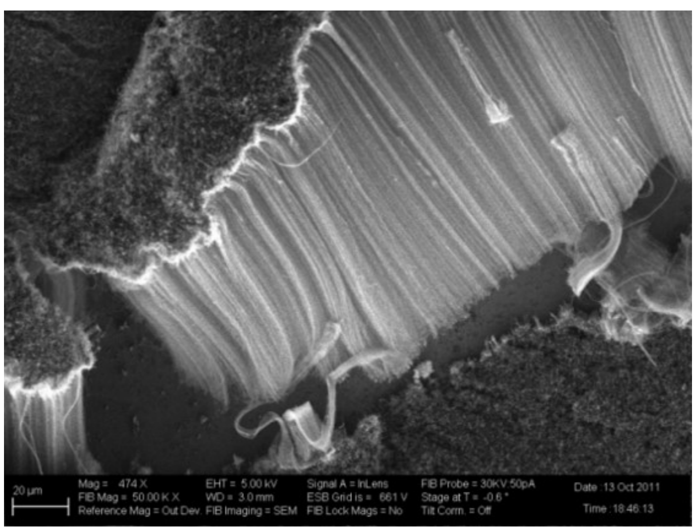


The blue color indicates the CNT walls extending from the graphene support, and the white color further highlights the root region.

Multi-stack Increases Surface Area







The seamless growth of CNTs from graphene with suppressed graphene etching permits multistack CNT-graphene architectures.

Conclusions

Tunable Wetting on Conjugated Polymer Surfaces

- We studied controlled switching of adhesive properties and their relationship with ion-surfactant-liquid interactions.
- The decrease of interfacial tension associated with the increase of contact angle yields an extremely low adhesive property.
- This tunable wetting technology is a pathfinder for next generation lab chip, oil separation, and antimicrobial engineering applications.

Growth of CNTs on Graphene

- The full utilization of a graphene-CNT construct requires maintaining the integrity of the graphene layer during the CNT growth.
- We studied optimized CNT growth process to exhibit graphene-CNT hybrids with continuous, undamaged structures.
- With further improvement in growth techniques, we pursue energy storage and sensing applications.

Acknowledgement

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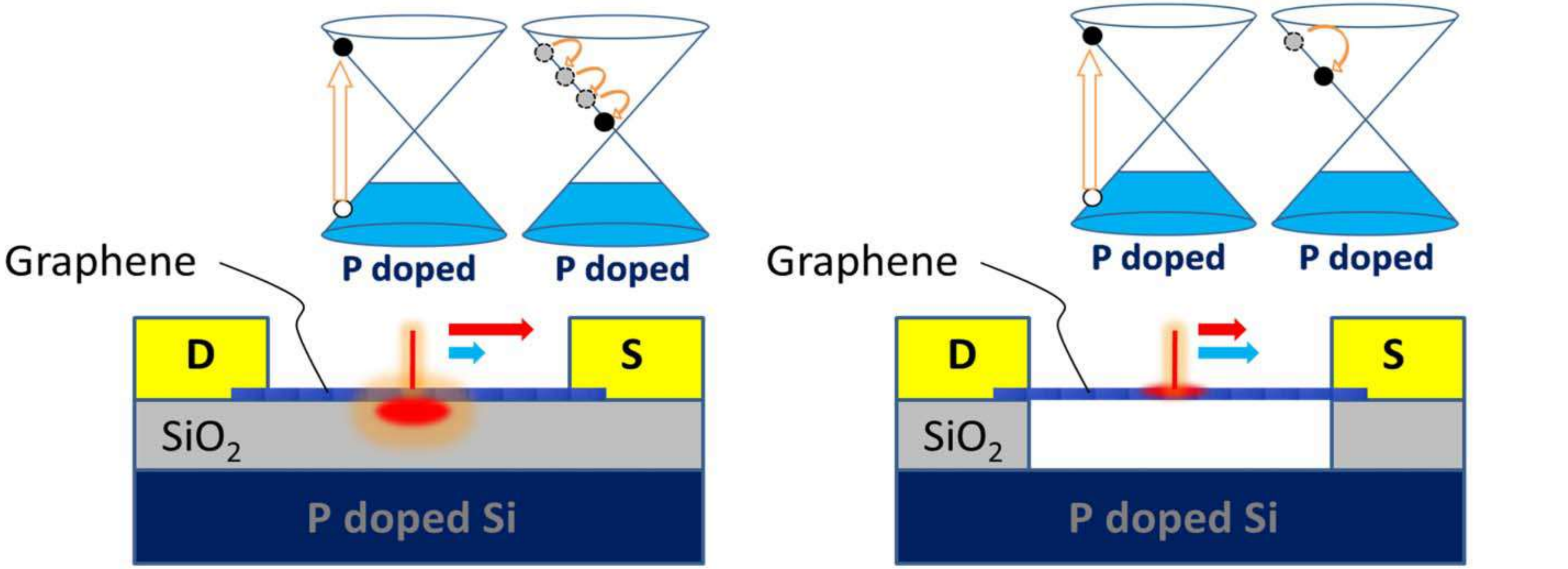
Nanofabrication J. Ding, X. Wang, G. Hader, S. Fu, A. Palumbo, R. Mcilraith

Graphene and 2D materials K. Kang, K. Godin (K. Kumar, V. Patil, Y. Kim)

Collaborators in microfluidics and CNT/Graphene:
Strauf, Choi, Fisher


Question?

Photocurrent Generation Process



- **Substrate-Supported**: Carriers relax due to substrate scattering effects and low mobility resulting in a limited contribution from the photoelectric effect.
- **Fully Suspended**: Carriers experience a slow-down in relaxation due to absence of substrate scattering and enhanced mobility/heat-conduction, resulting in a lager contribution of the photoelectric effect.