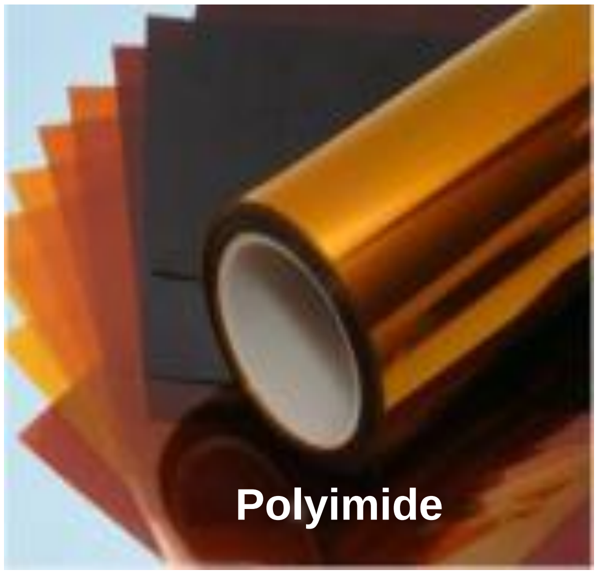
Laser induced graphene (LIG) and applications in water treatment

James M. Tour

Rice University

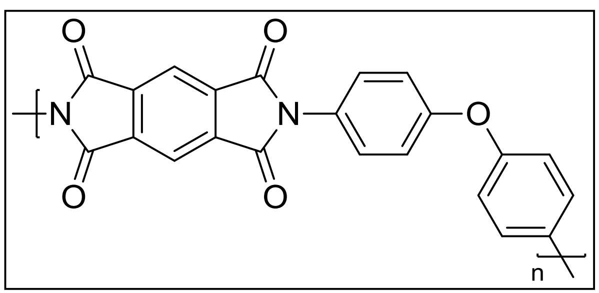
www.jmtour.com

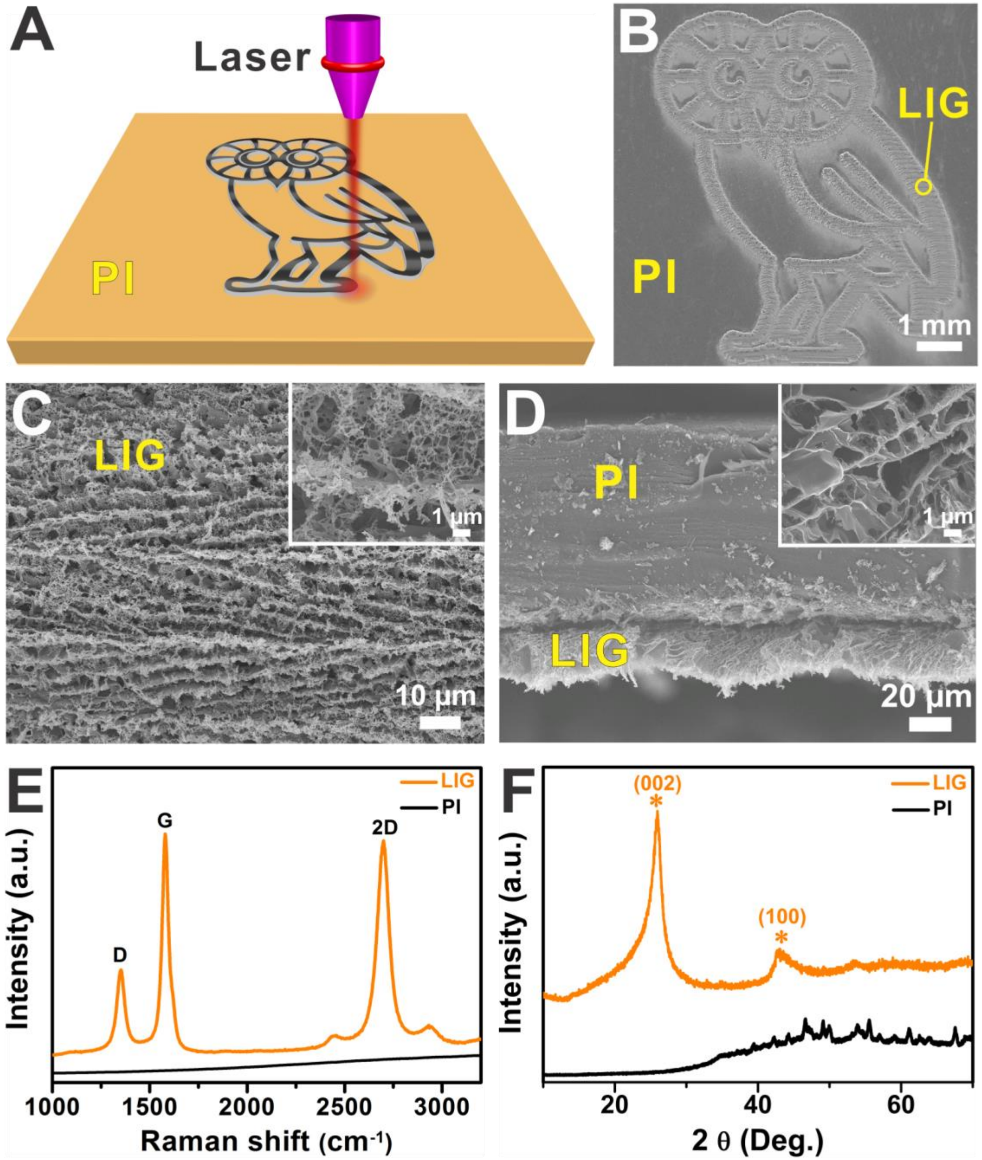
LIG 3D foams from commercial polyimide sheets



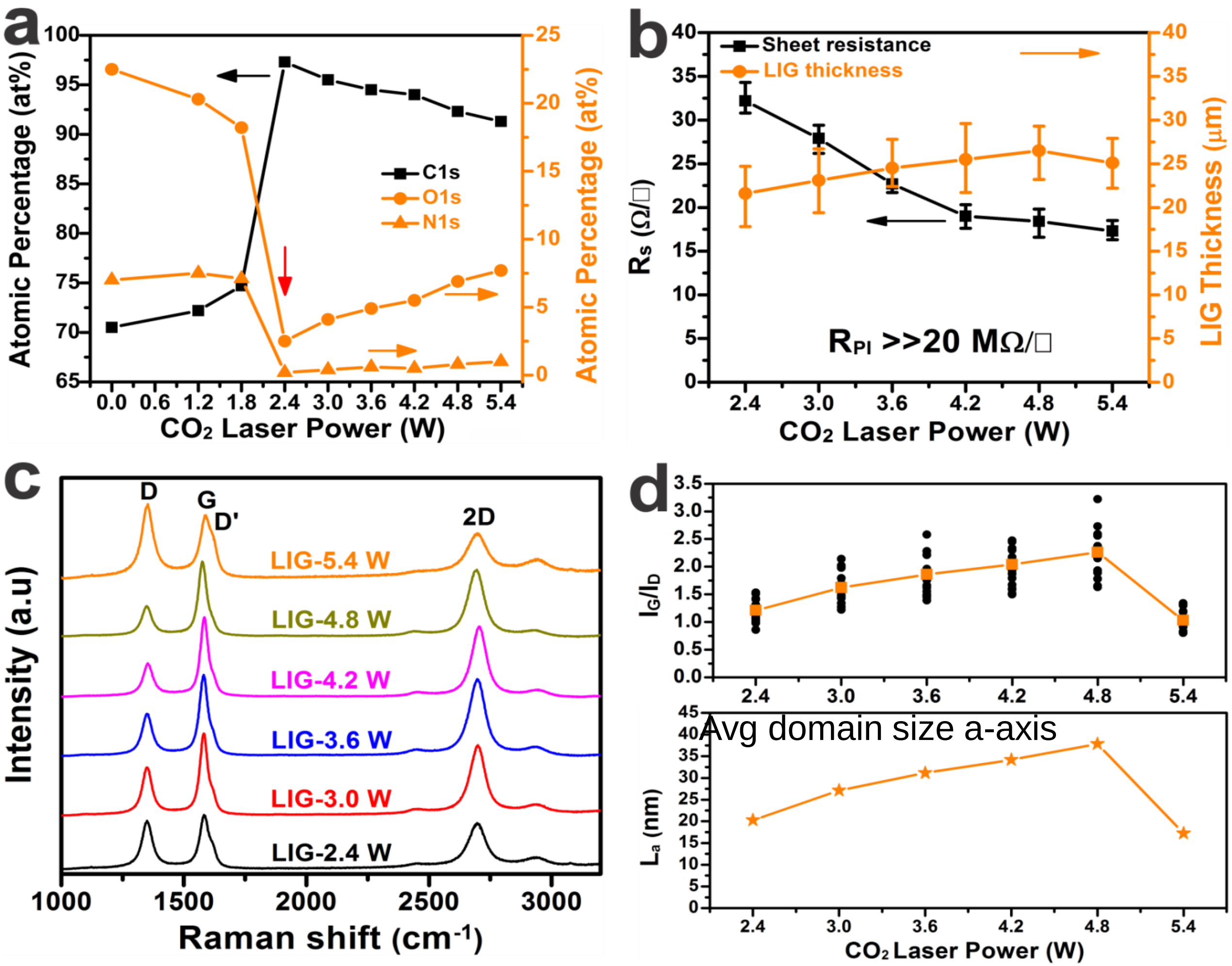
Ambient conditions

Laser-writing tool




A
Laser
PI
B
LIG
PI
1 mm
C
LIG
1 μm
10 μm
D
PI
1 μm
LIG
20 μm
E
LIG
PI
G
2D
D
Intensity (a.u.)
1000
1500
2000
2500
3000
Raman shift (cm-1)
F
(002)
LIG
PI
(100)
Intensity (a.u.)
20
40
60
2 θ (Deg.)

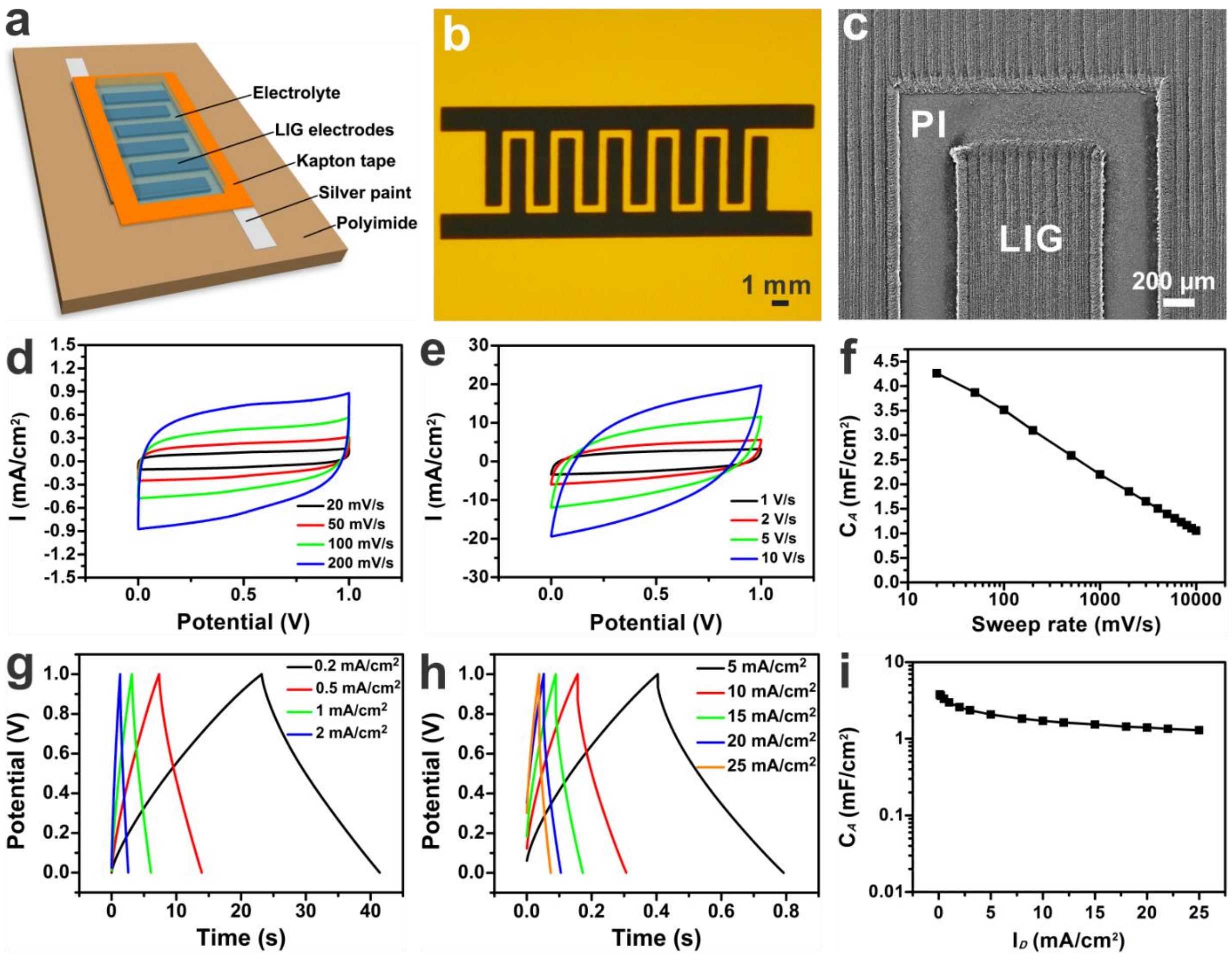
Quality Control of LIG with Different Laser Powers



Results:

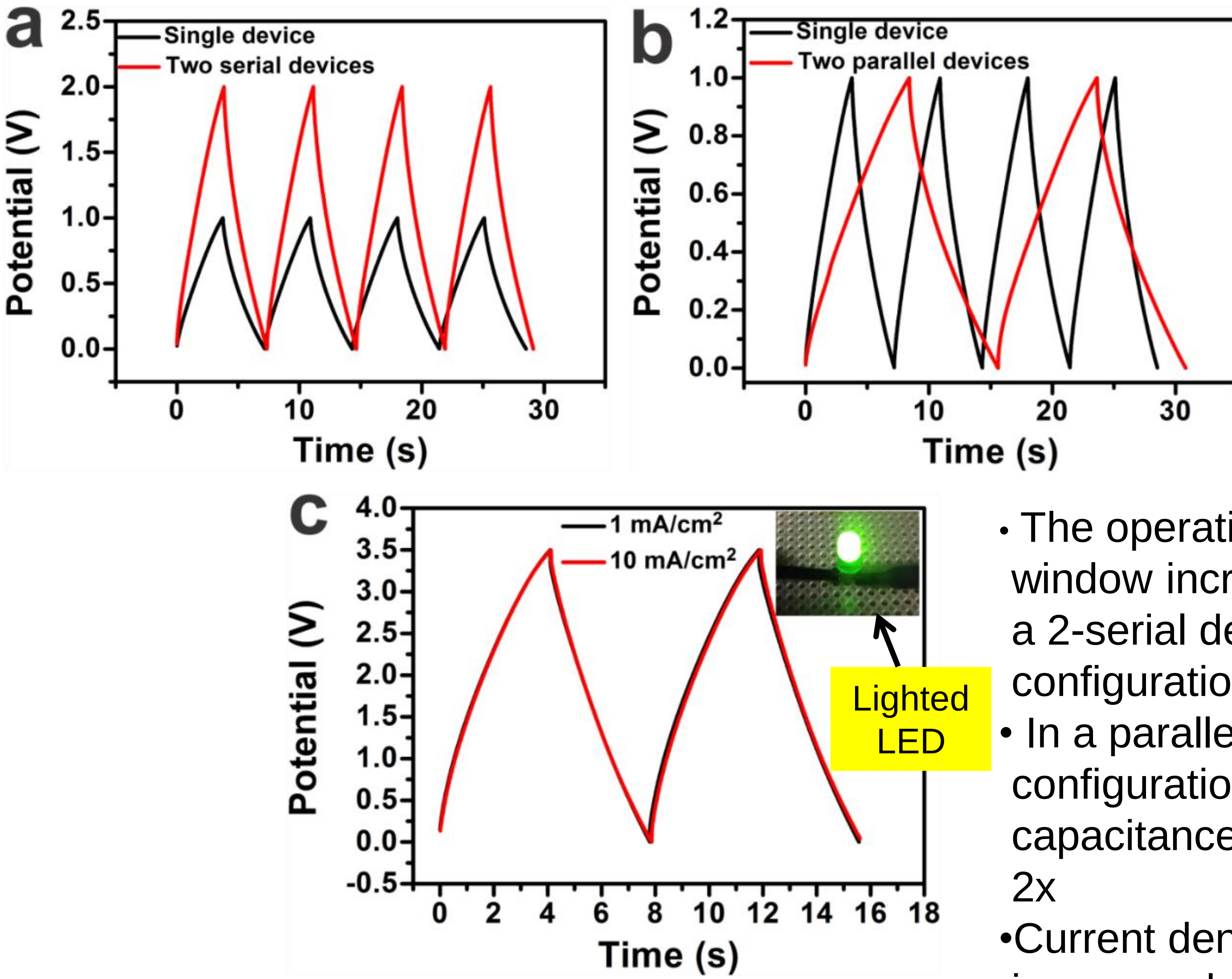
- Threshold laser power: **2.4** W
- GO: $R_{GO} \cong$ **1** MΩ/□; rGO: $R_{rGO} >$ **100** Ω/□)
- crystalline size along a-axis: from 20 nm to 40 nm
- Domain sizes calculated from Raman and X-ray

Electrochemical Performance of LIG Microsupercapacitors



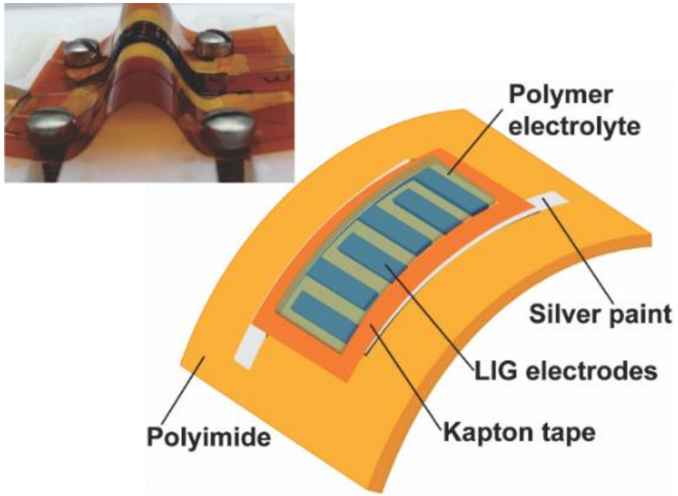
- Over **4** mF/cm^2 at a scan rate of 50 mV/s, higher than laser-scribe GO based microsupercapacitors (~**2.4** mF/cm^2 ; Nat. Commun. **2013**, 4, 1475.)
- Maintains good capacitive behaviors at $I_{discharge}$ of **15** mA/cm^2.

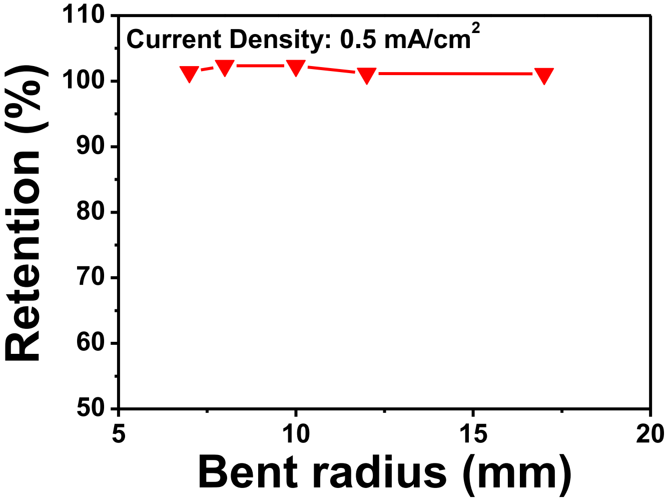
Serial and Parallel LIG Microsupercapacitors

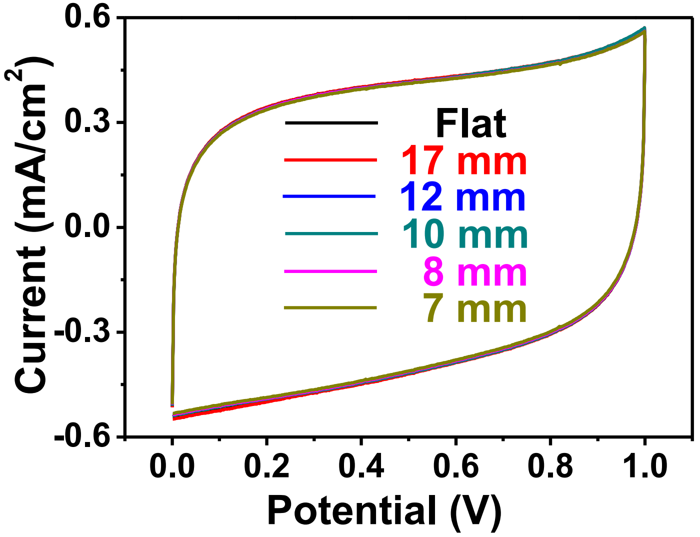


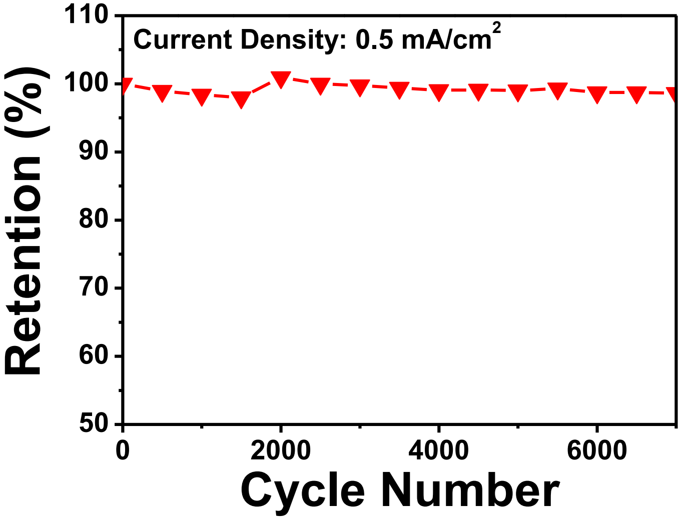
- The operation potential window increases 2x in a 2-serial device configuration
- In a parallel configuration the capacitance increases 2x
- Current densities increases by 10x with 10 paralleled single devices

Flexibility test of LIG-MSC

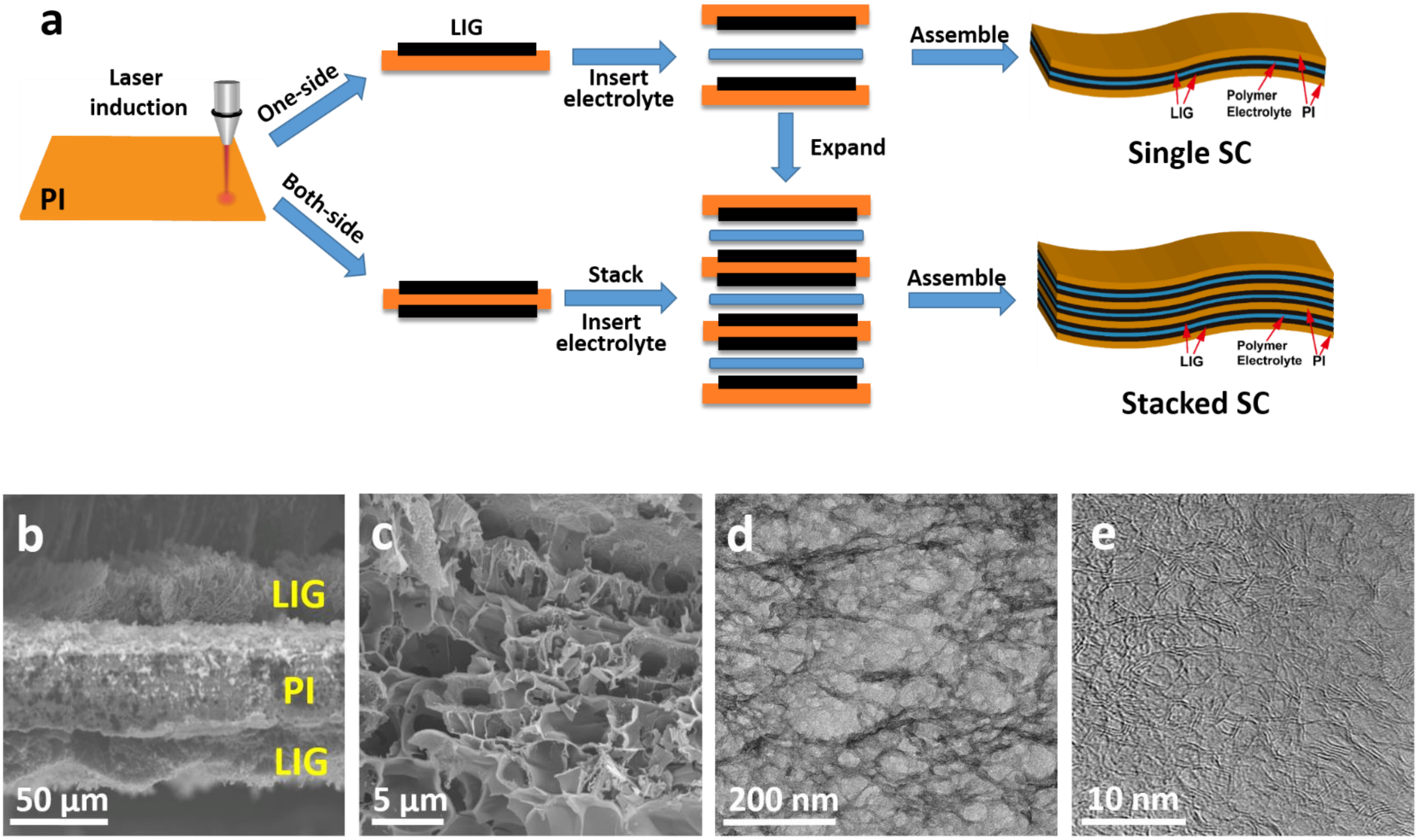




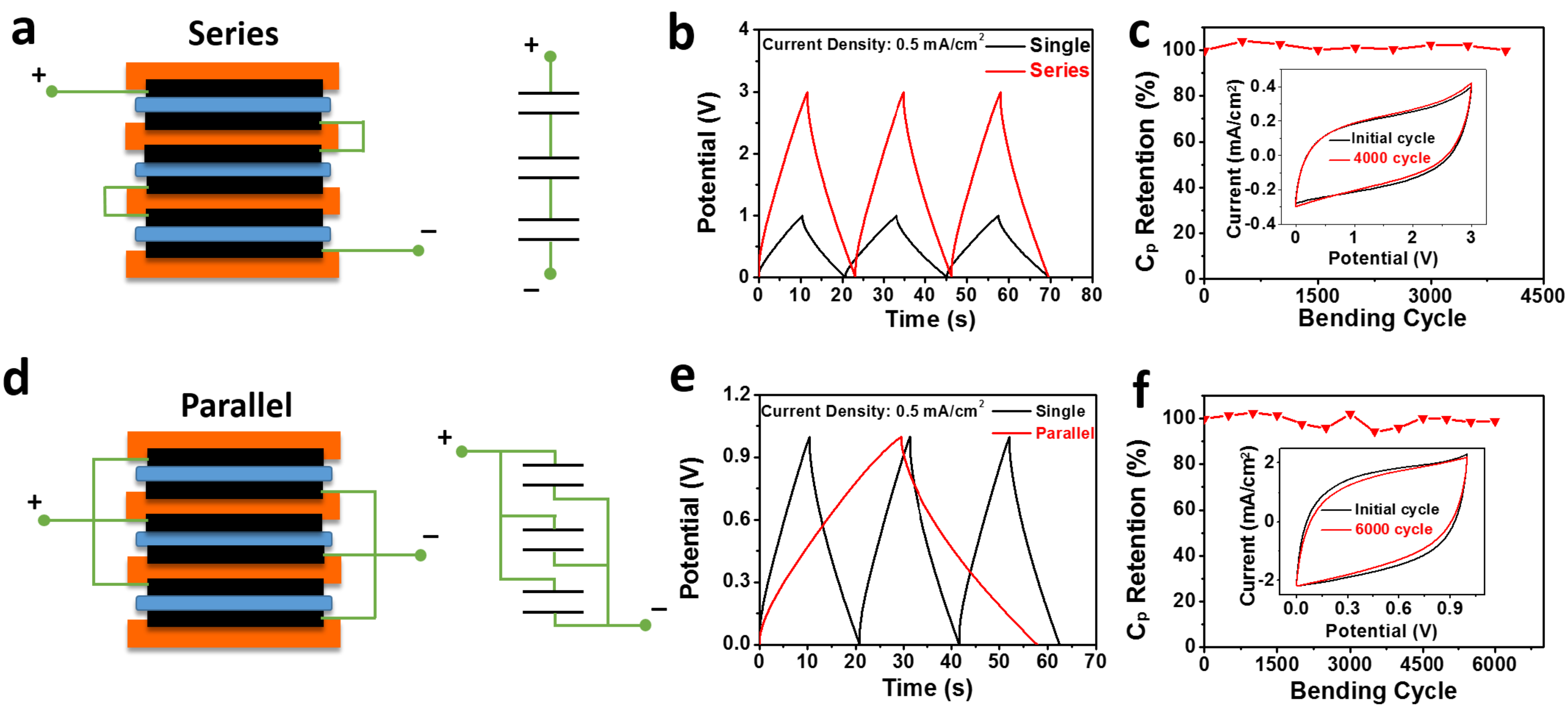




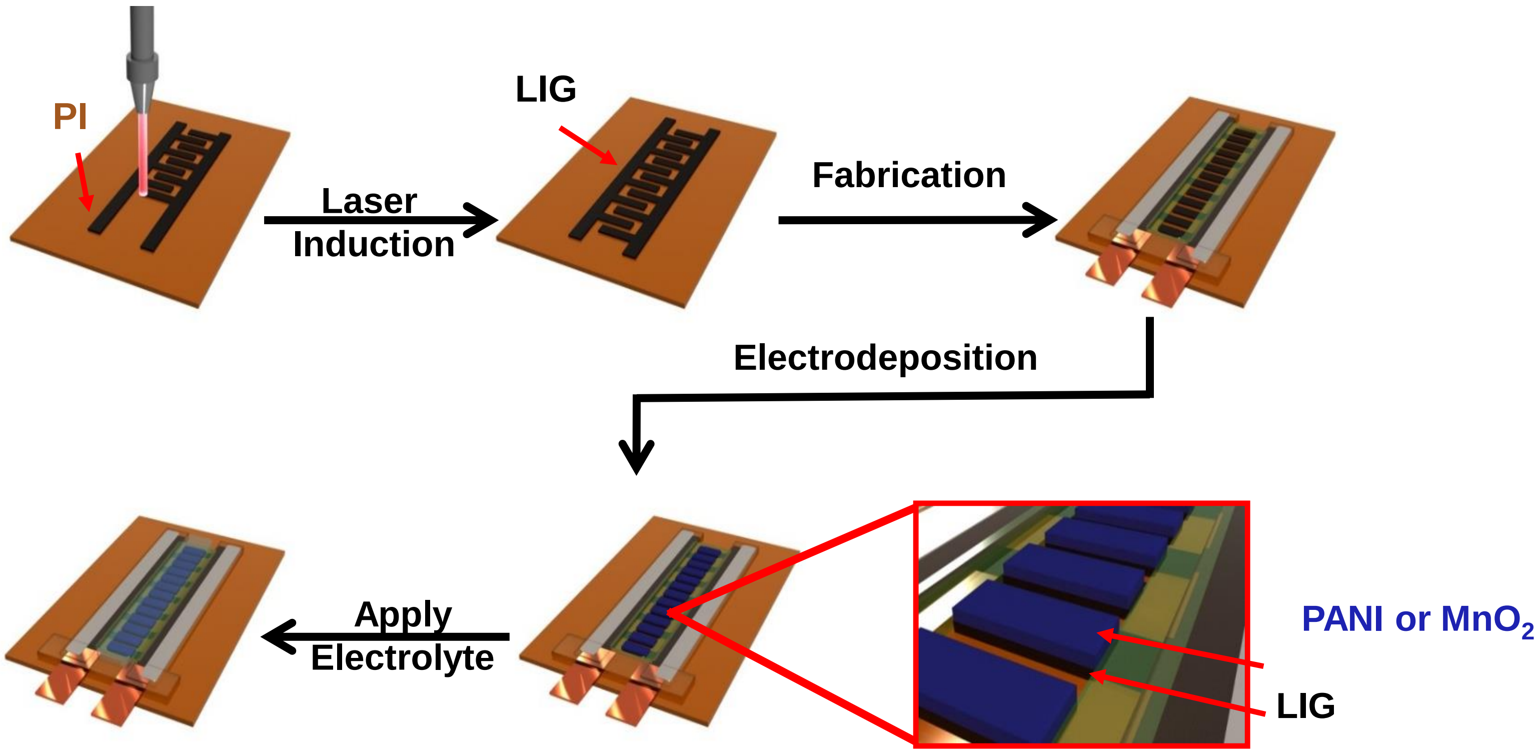
Vertical stacking



Vertically stacked SC



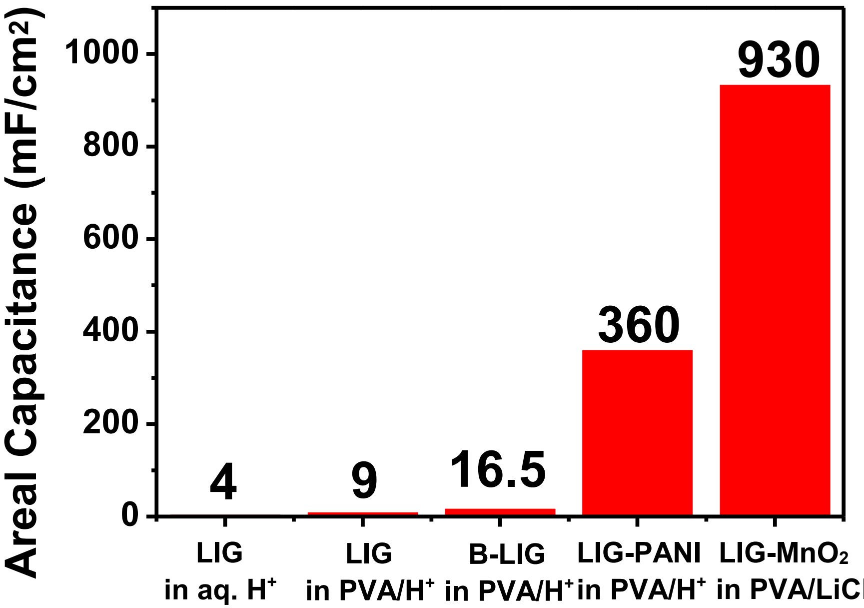
Electrodeposition of PANI or MnO_2

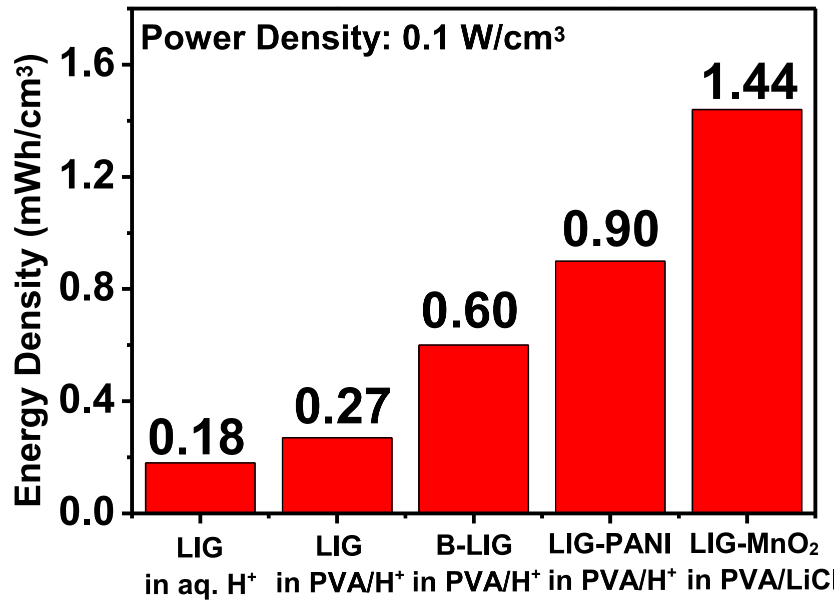


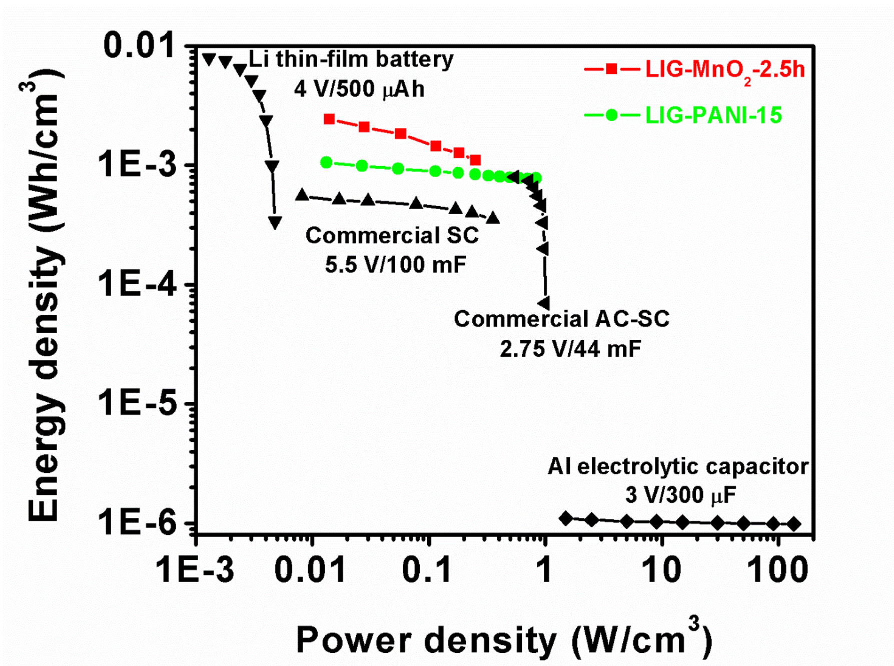
Two-step synthesis:

1. Laser induction for LIG
2. Electrochemical deposition for PANI or MnO_2
   - PANI: CV sweep (-0.2 V ~ 0.95 V, 50 mV/s)
   - MnO_2: Constant current (1 mA/cm^2)

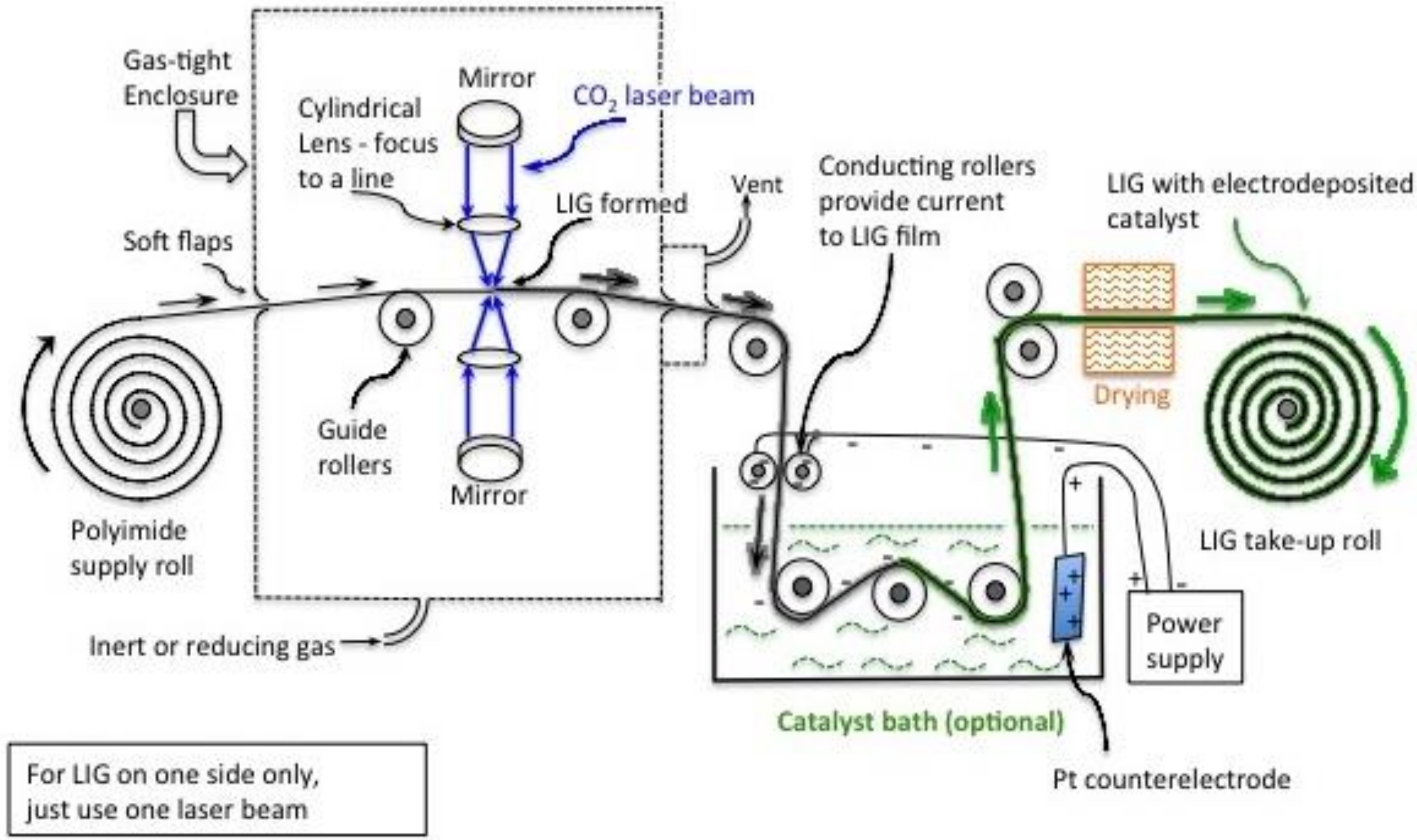
Milestones


Areal Capacitance (mF/cm²)
0
200
400
600
800
1000
4
9
16.5
360
930
LIG in aq. H+
LIG in PVA/H+
B-LIG in PVA/H+
LIG-PANI in PVA/H+
LIG-MnO2 in PVA/LiCl

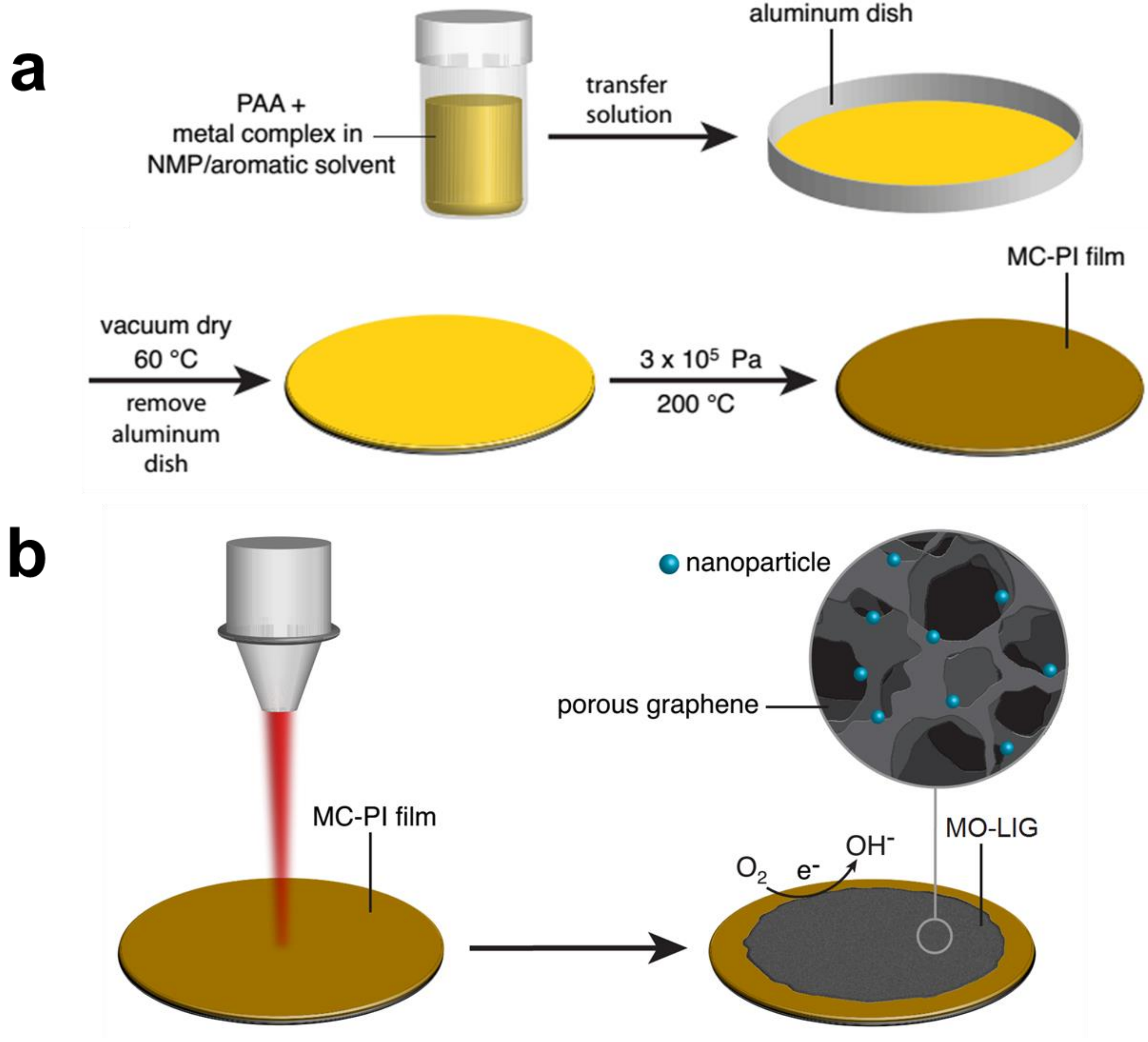

Power Density: 0.1 W/cm3
Energy Density (mWh/cm3)
0.0
0.4
0.8
1.2
1.6
0.18
0.27
0.60
0.90
1.44
LIG in aq. H+
LIG in PVA/H+
B-LIG in PVA/H+
LIG-PANI in PVA/H+
LIG-MnO2 in PVA/LiCl


Energy density (Wh/cm3)
Power density (W/cm3)
0.01
1E-3
1E-4
1E-5
1E-6
1E-3
0.01
0.1
1
10
100
Li thin-film battery
4 V/500 µAh
LIG-MnO2-2.5h
LIG-PANI-15
Commercial SC
5.5 V/100 mF
Commercial AC-SC
2.75 V/44 mF
Al electrolytic capacitor
3 V/300 µF

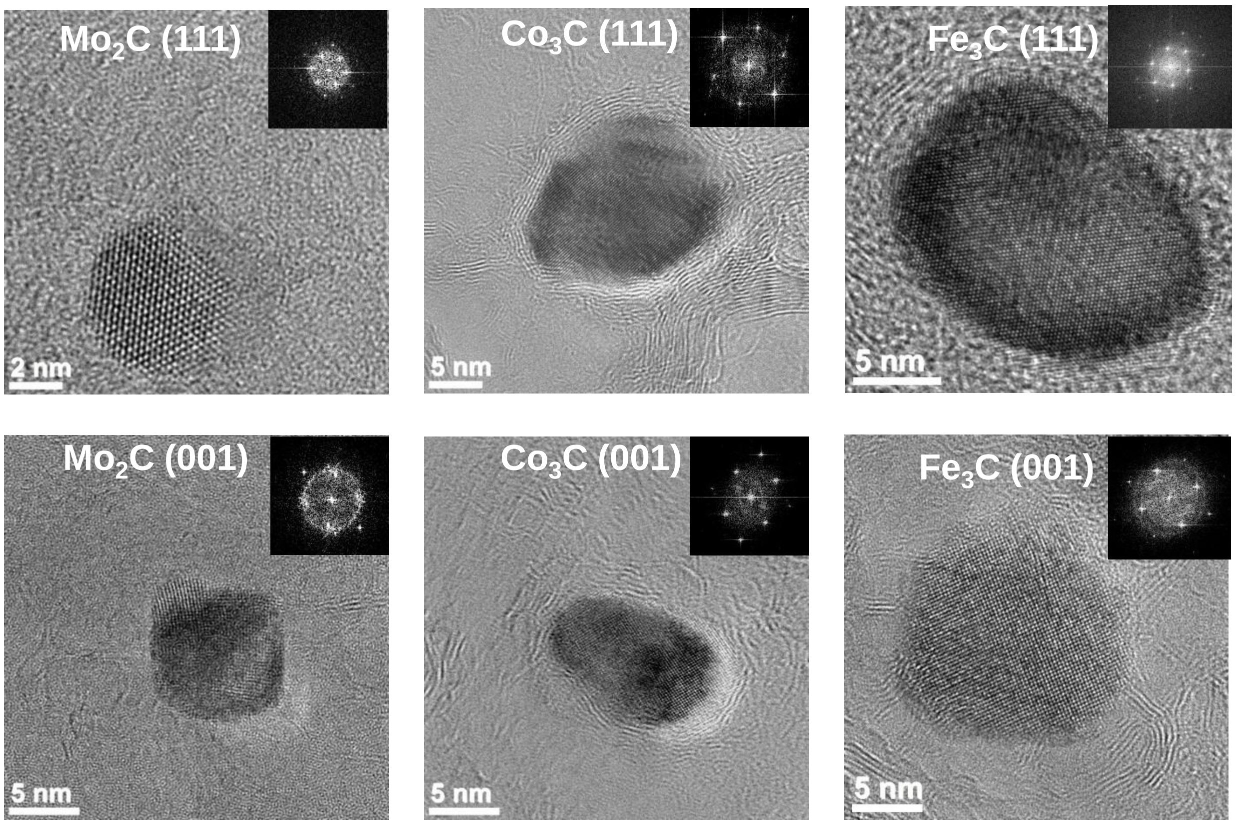
Future Designs for Roll-to-Roll Scaling



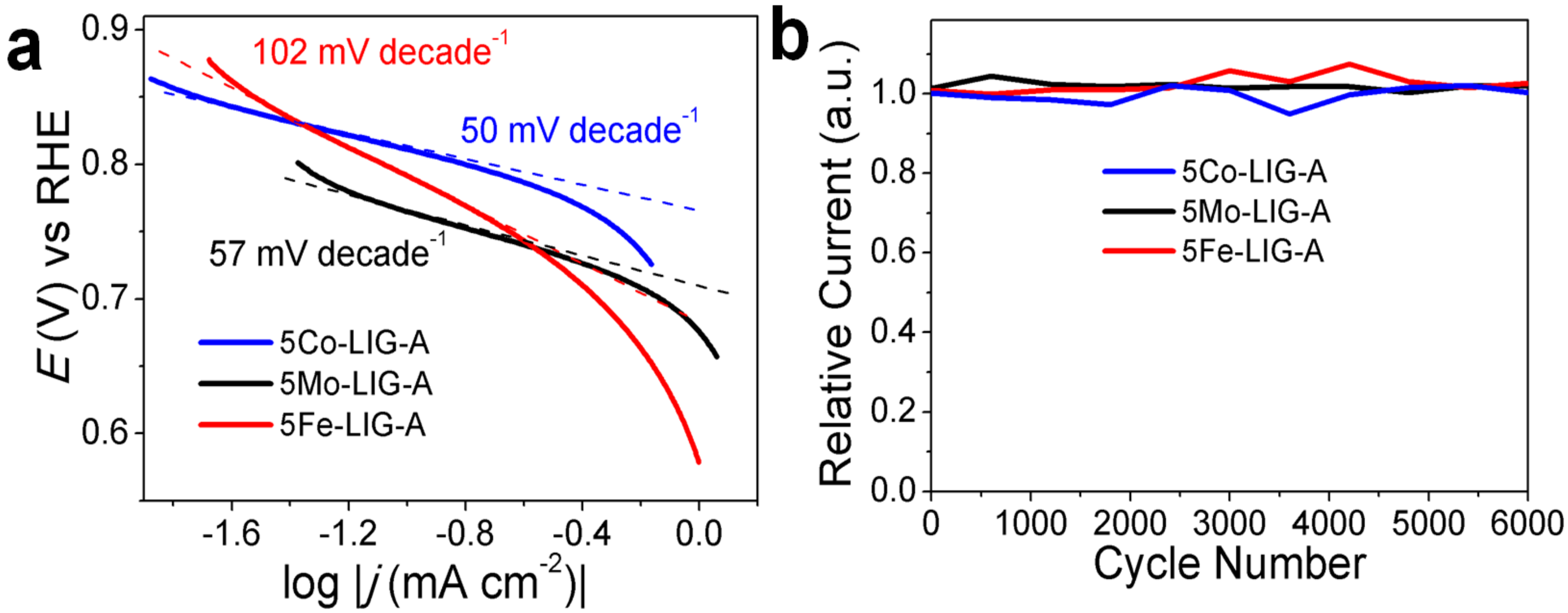
Metal Carbide LIG for Electrocatalysts



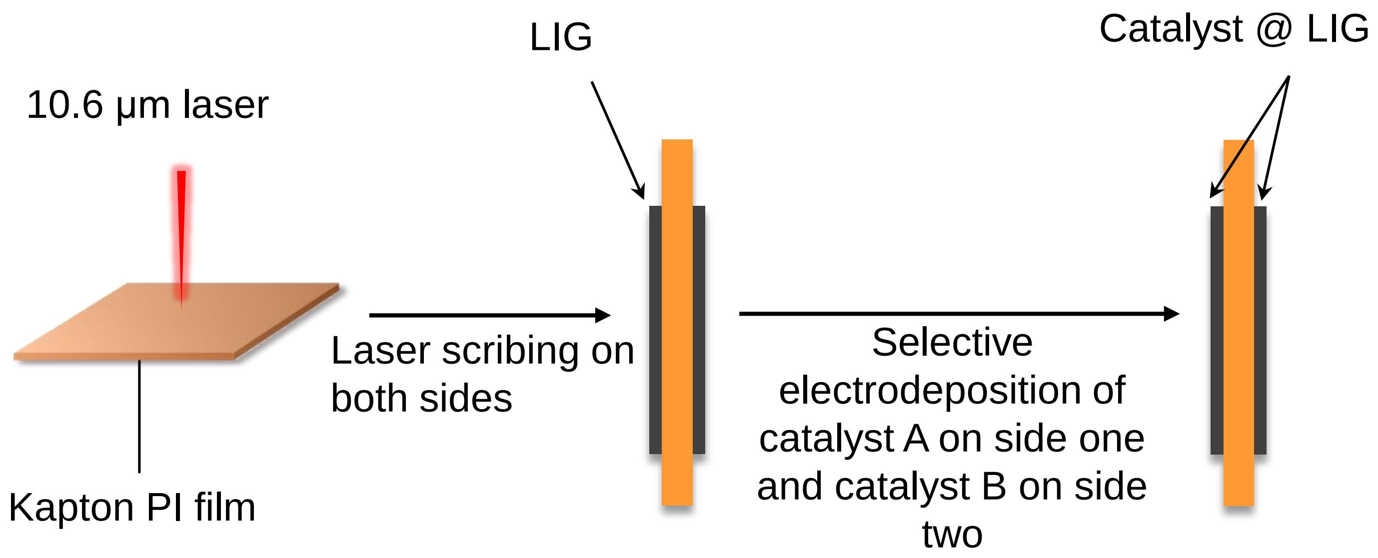
MC_x nanoparticles



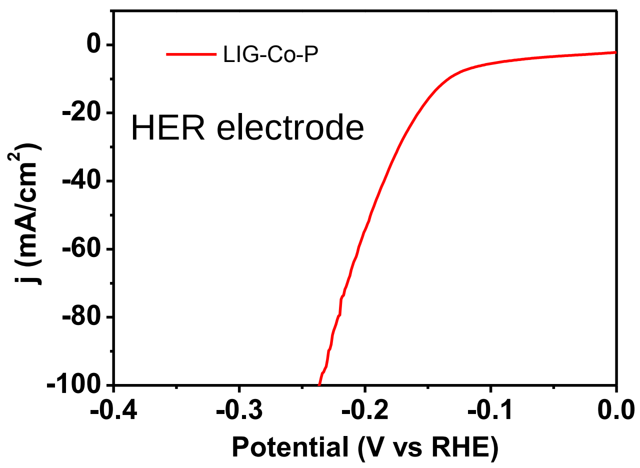
ORR performance

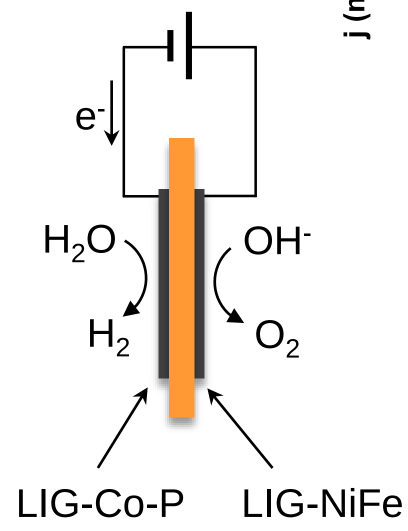


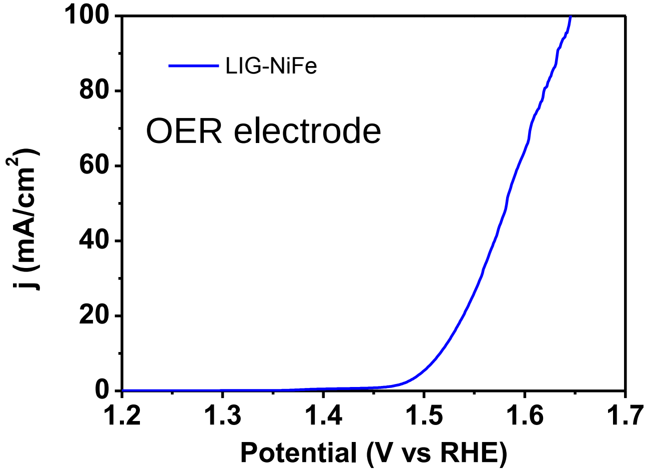
LIG-Based Water Electrolyzer



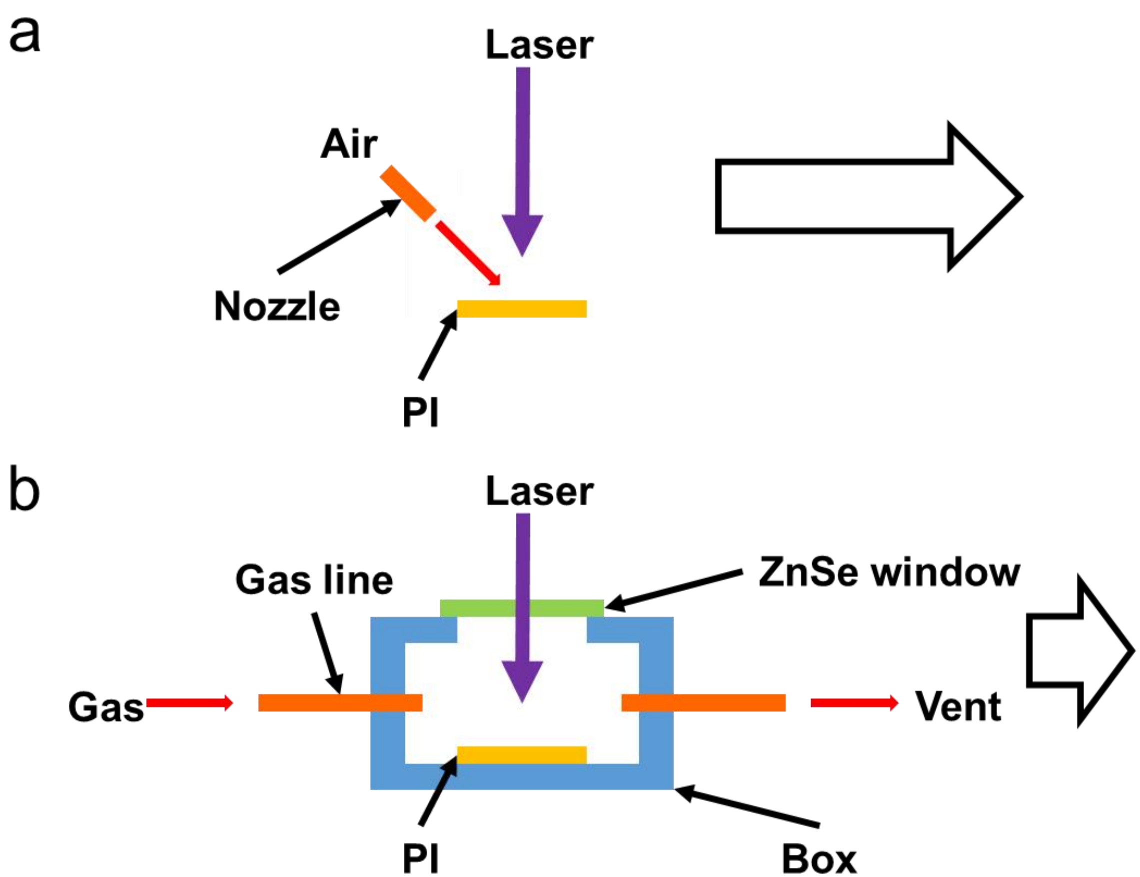
LIG-Based Water Electrolyzer





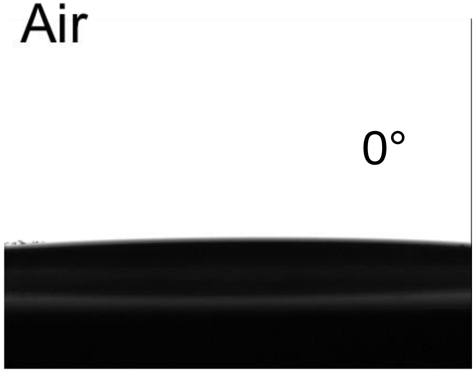


Fabrication of LIG under controlled gas atmosphere



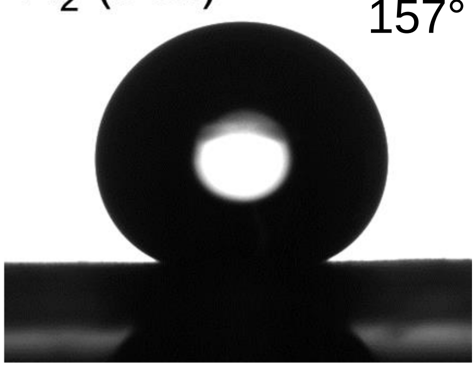
Goniometry

Air



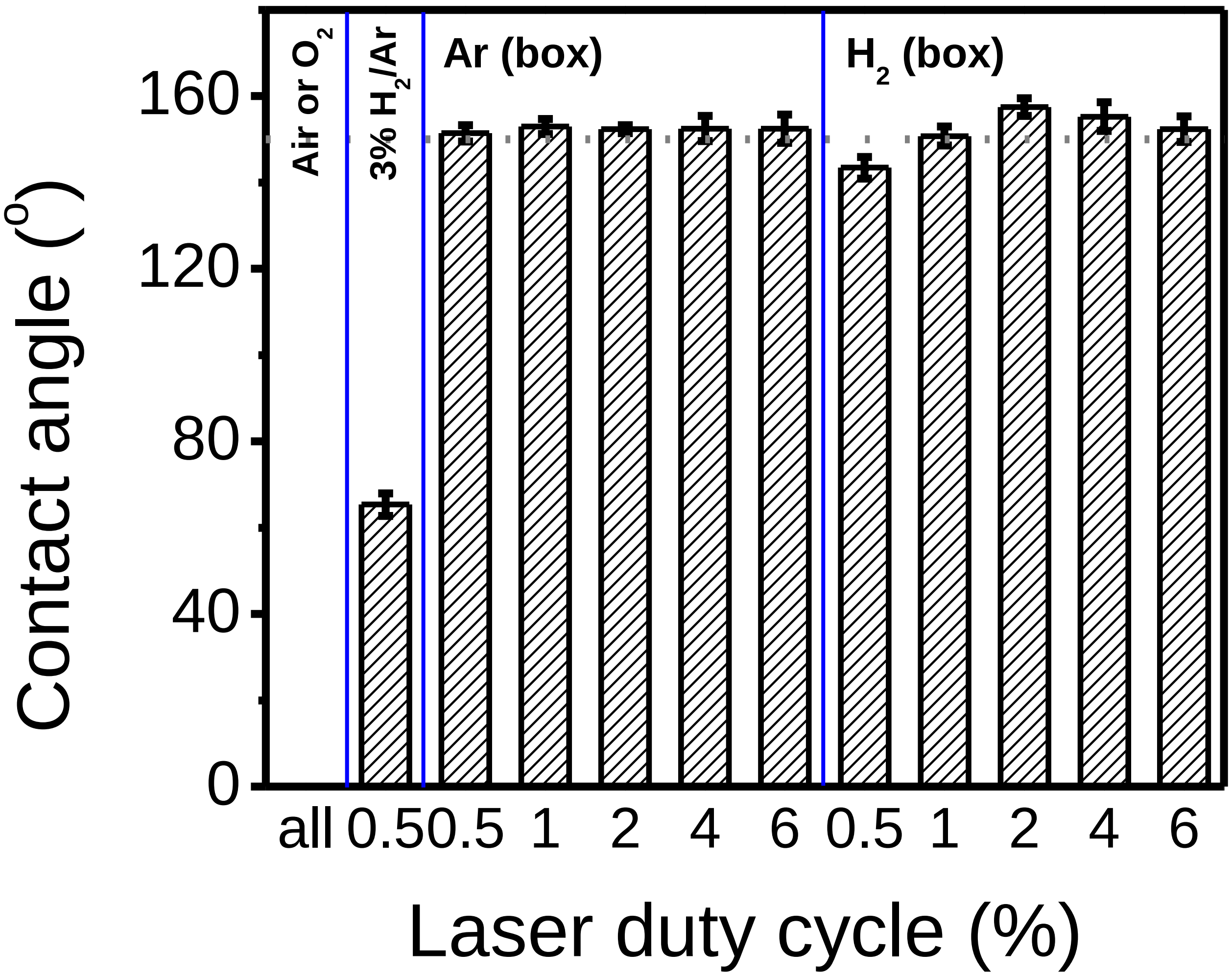
superhydrophilic

H_2 (box)



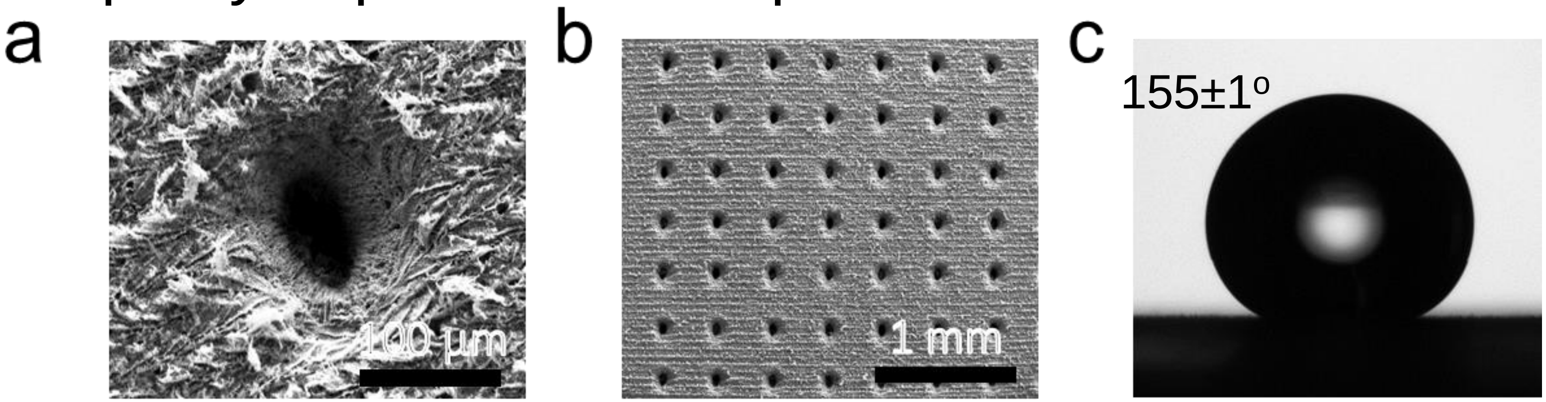
superhydrophobic

Contact angles



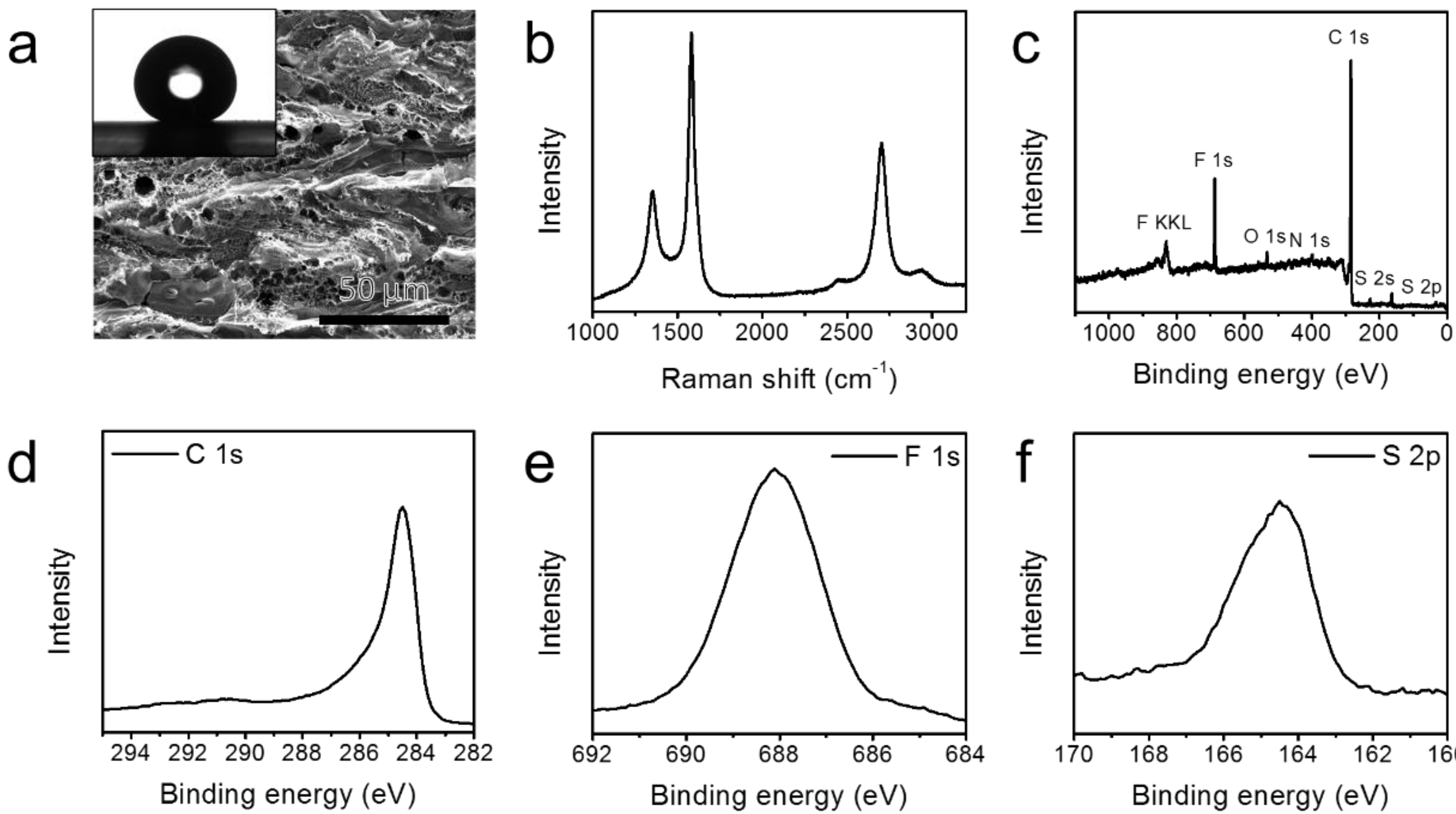
Filter for oil/water separation

- Superhydrophobic LIG on porous PI

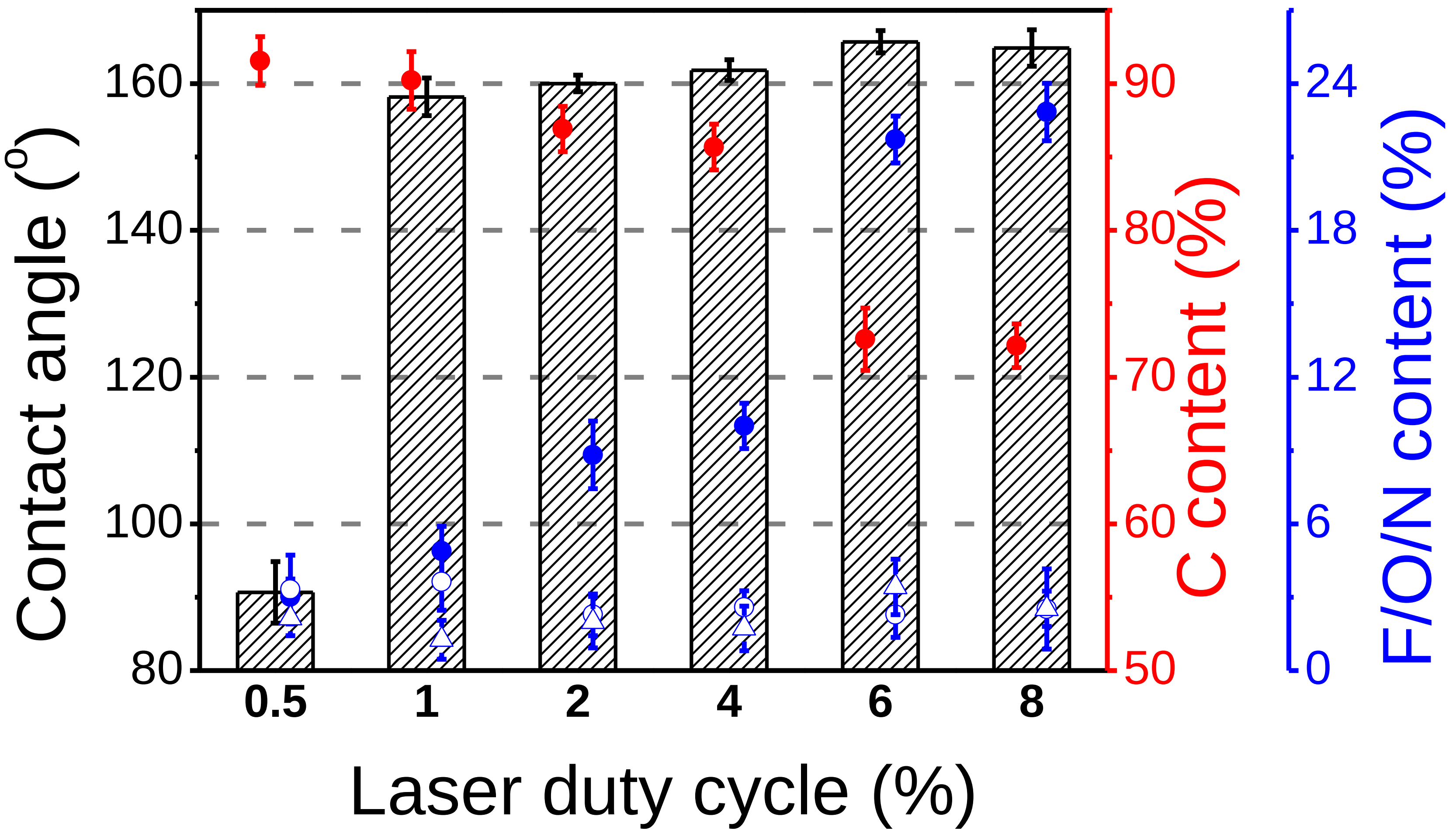


- $H_2O/CHCl_3$ separation (oil-blue in $CHCl_3$)

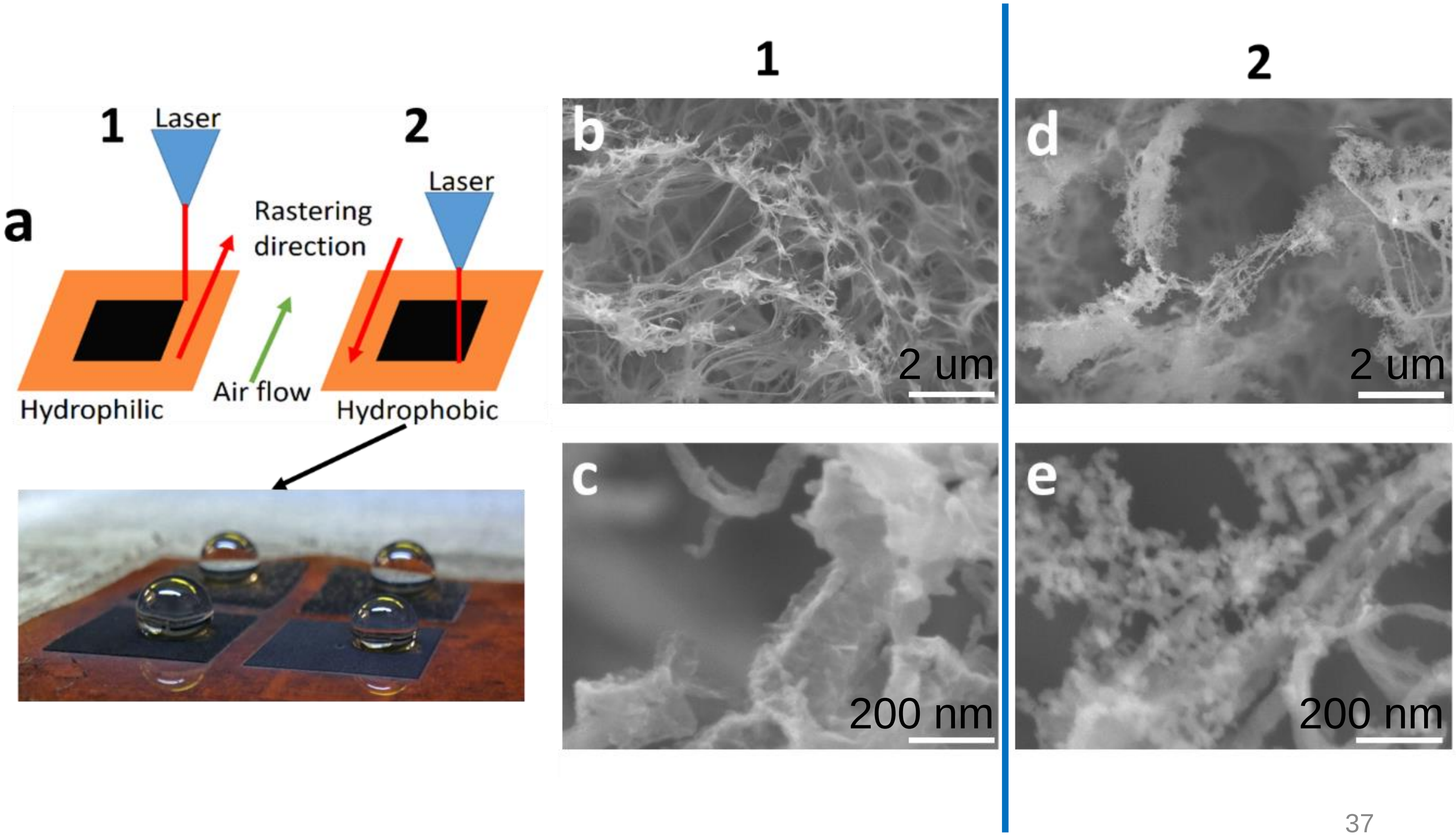
F-doped LIG with SF_6 gas



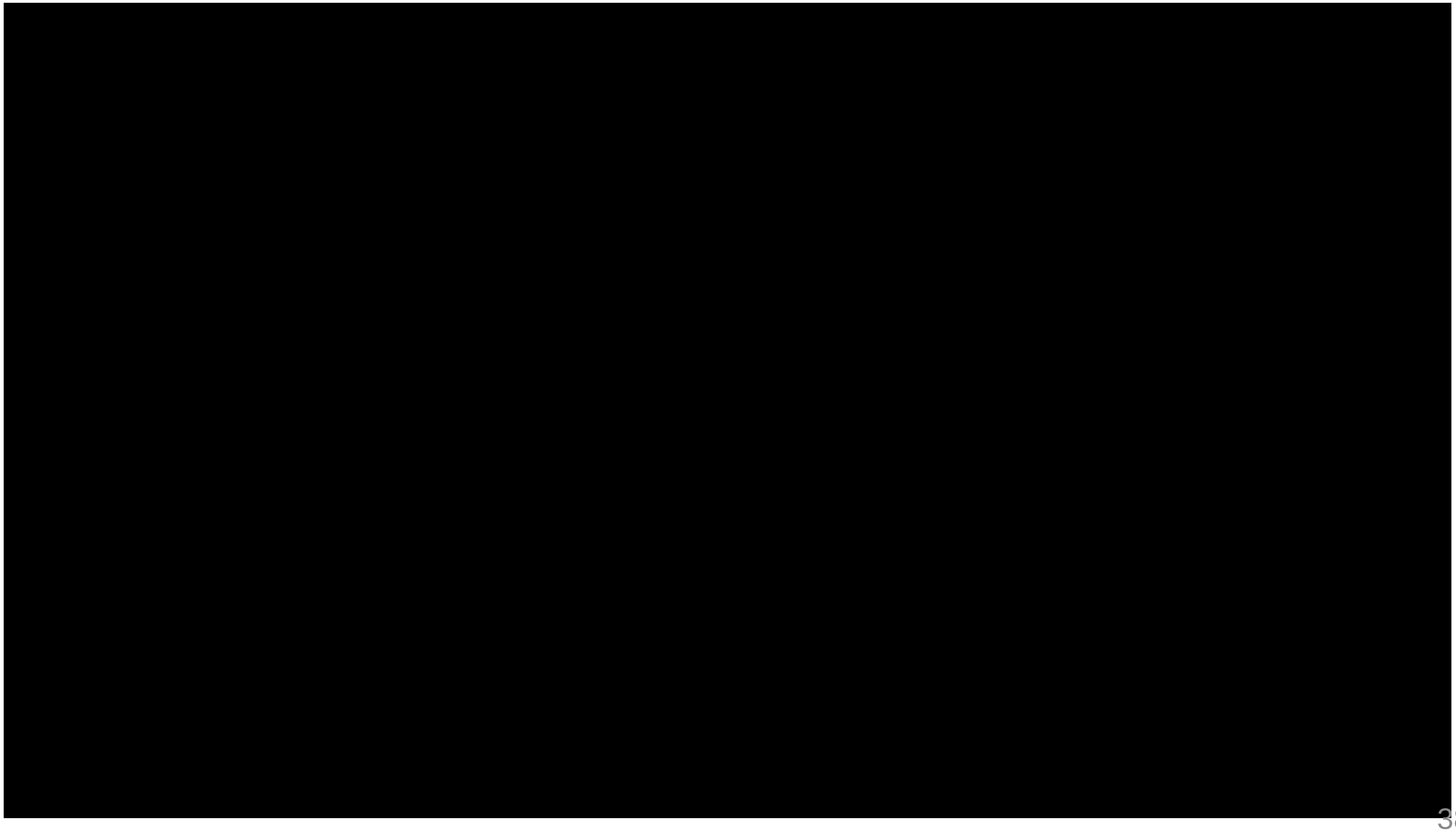
Controlling the F content



Another way to prepare hydrophobic vs hydrophilic films



Hydrophobic vs. Hydrophilic LIG



Antibiofouling properties of LIG

In collaboration with

Prof. Christopher J. Arnusch

Dr. Franklin Sargunaraj

Ben-Gurion University of the Negev

Goal and approach

- To investigate the antimicrobial and antibiofilm properties of various LIG samples under different gas atmospheres
- Antibiofilm activity: biofilm growth in flow cell, and confocal laser scanning microscopy (CLSM) analysis (*Pseudomonas aeruginosa, Sphingomonas wittichii*)
- Antimicrobial activity: “bacterial contact killing assay” (*Pseudomonas aeruginosa*)

Passive antibiofilm activity – method

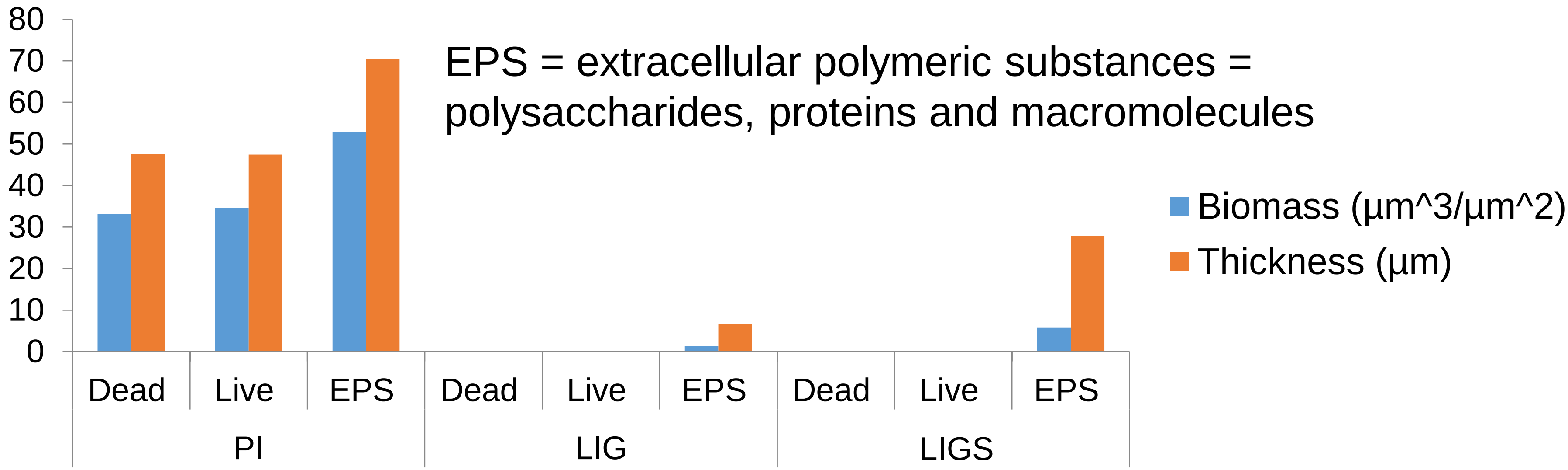
- Flow cell
  - *Pseudomonas aeruginosa* with **nutrients** as flow cell medium
  - *Sphingomonas wittichii* with **waste water** as medium

PI film and LIG samples attached to glass slide and placed in flow cell

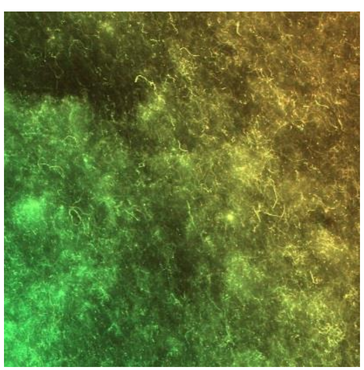
Passive antibiofilm activity - results

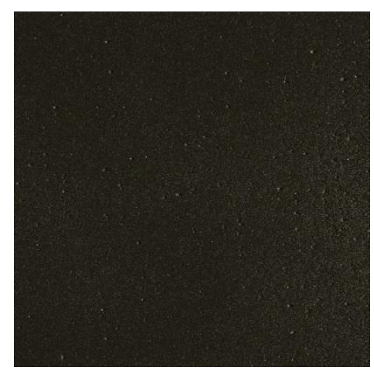
- *Pseudomonas aeruginosa* with nutrients

EPS = extracellular polymeric substances = polysaccharides, proteins and macromolecules



CLSM Images

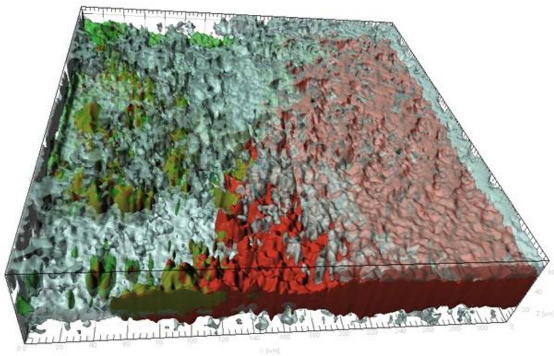




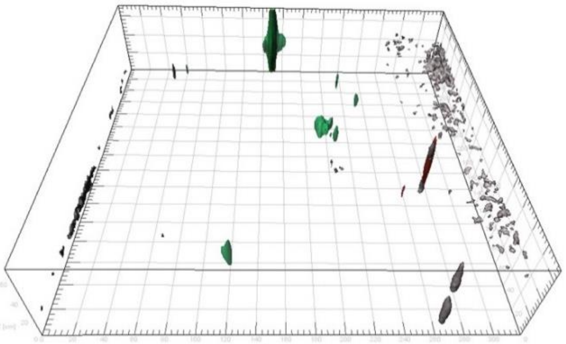
No bacteria observed on LIG or LIGS

IMARIS images of *P. aeruginosa*

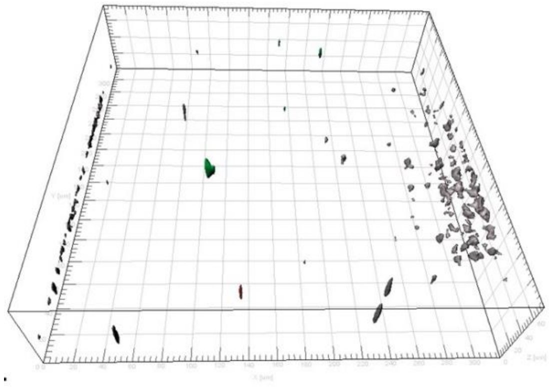
PI



LIG



LIGS



Red: dead bacteria
Green: live bacteria
Grey: EPS

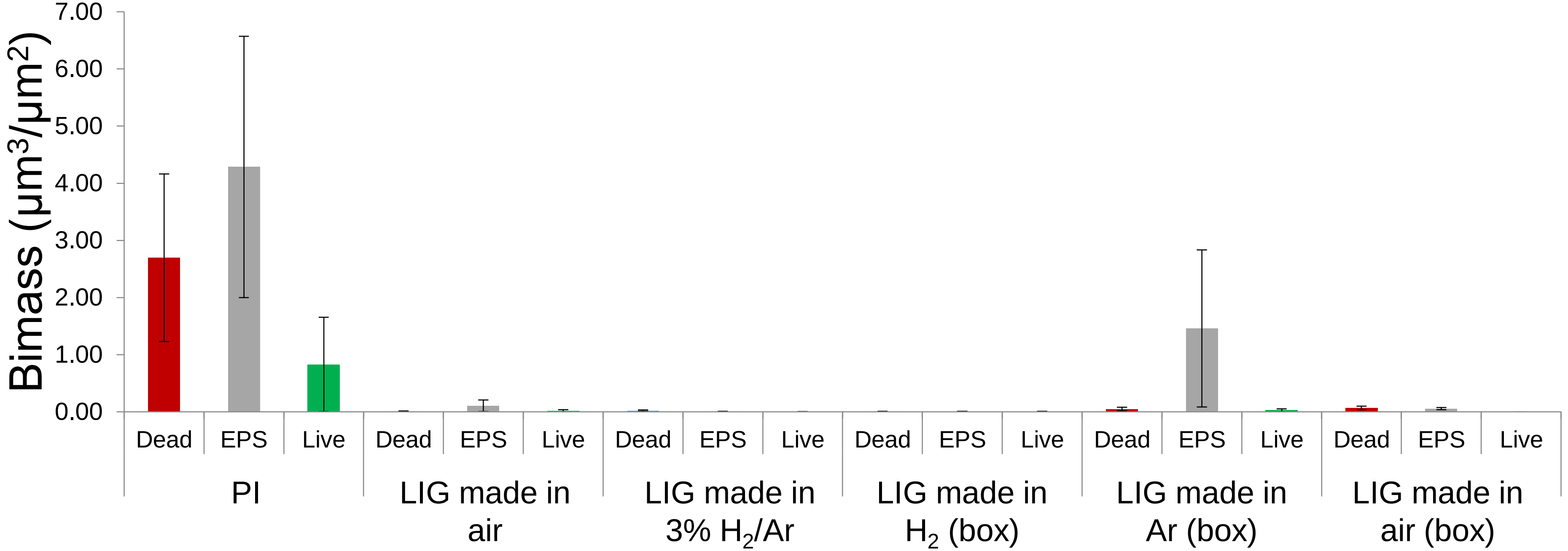
Passive antibiofilm activity - results

- *S. wittichii* with waste water

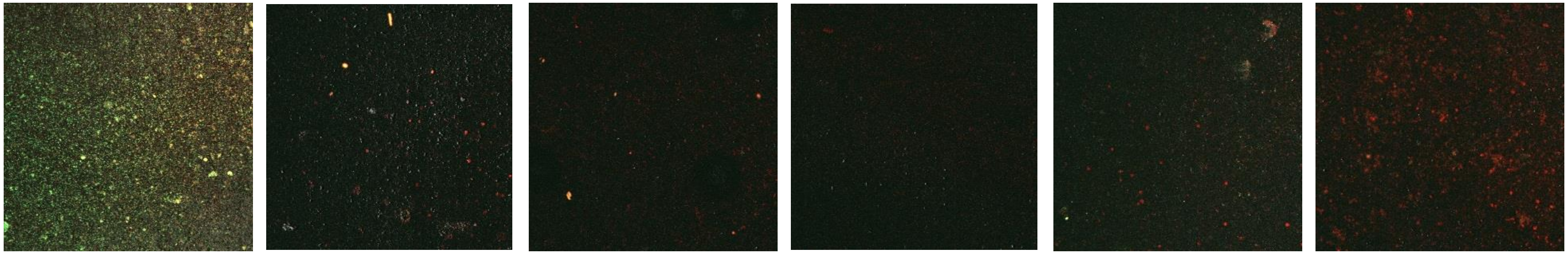
The LIG samples showed almost no biofouling, but for LIG made in Ar there are EPS

Passive antibiofilm activity - results

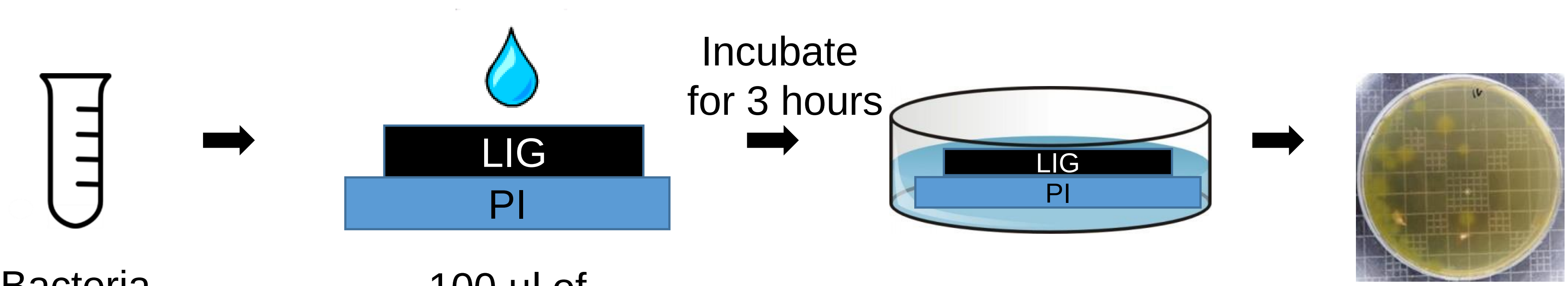
- *S. wittichii* with waste water



CLSM Images



Passive antimicrobial activity - method



Bacteria in PBS

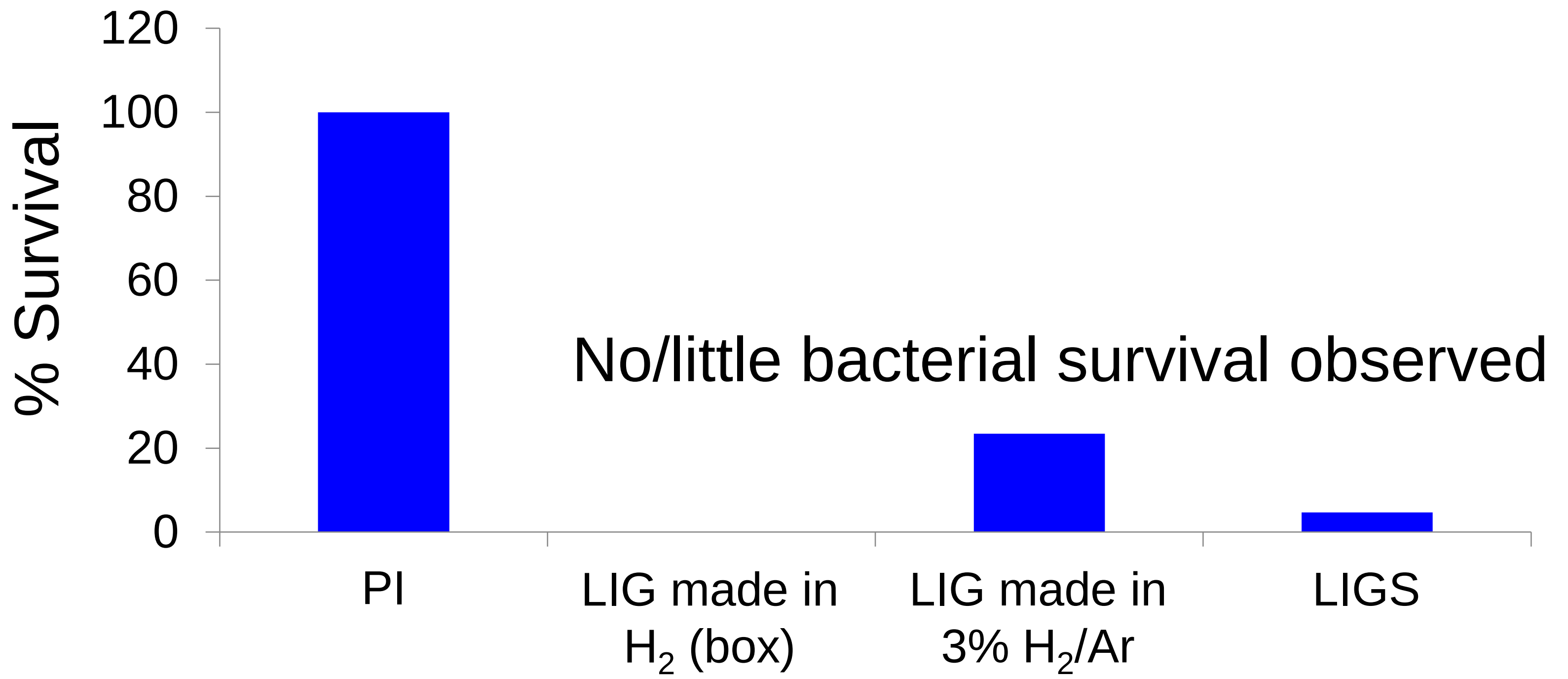
100 µl of bacteria was placed on LIG or polyimide

Washed in 4 ml PBS

Bacterial colonies counted

- LIGs made under different gas atmospheres were used in the test

Passive antimicrobial activity - results



*results for other LIG samples in progress

LIG spacers for active elimination of biofouling in water purification applications

In collaboration with

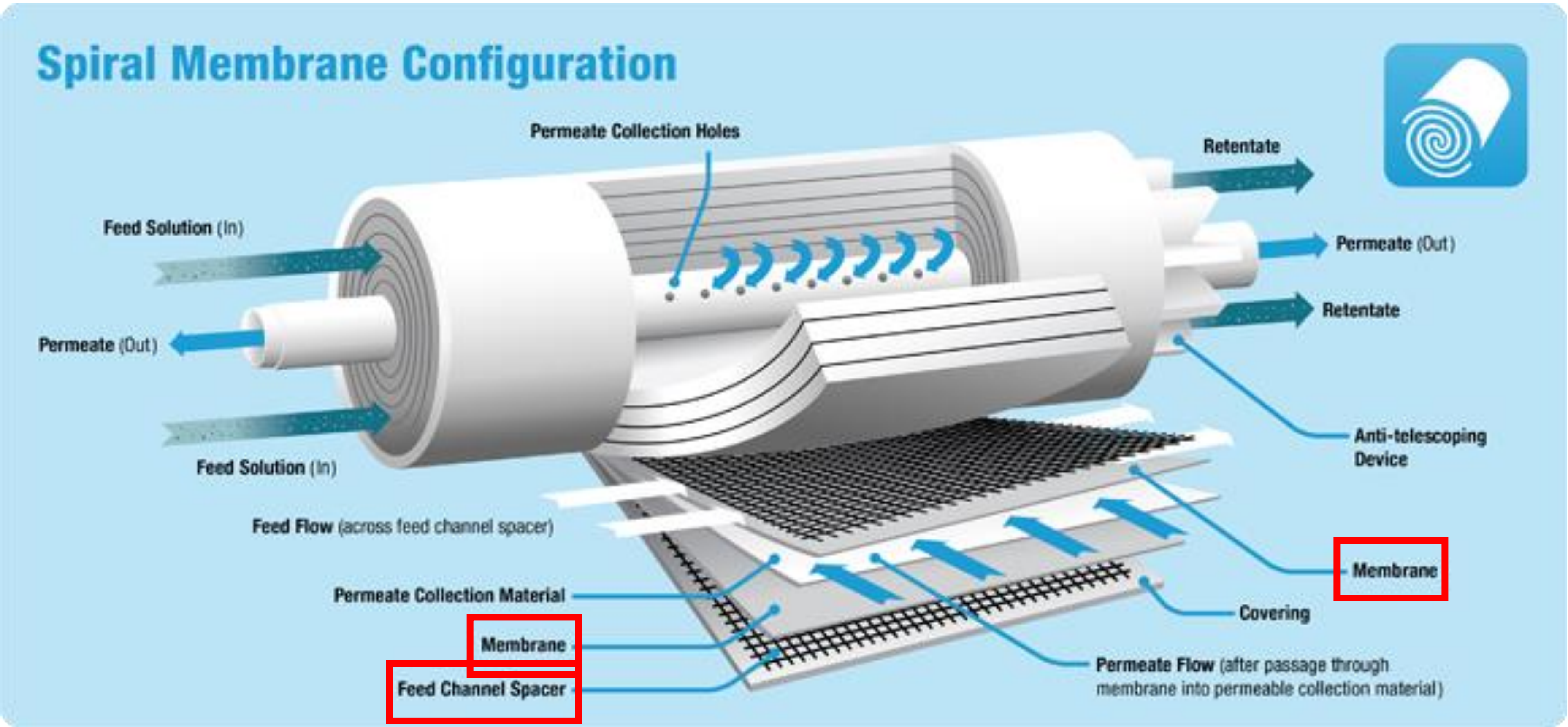
Prof. Christopher J. Arnusch

Dr. Swatantra P. Singh

Prof. Yoram Oren

Ben-Gurion University of the Negev

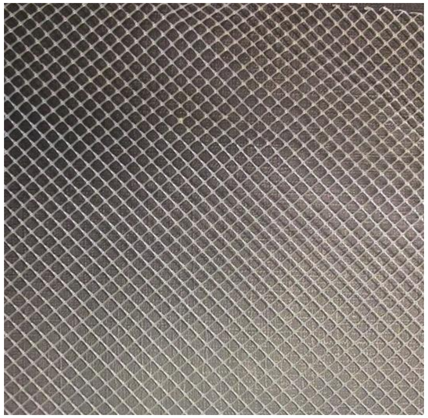
Spiral membrane for water treatment



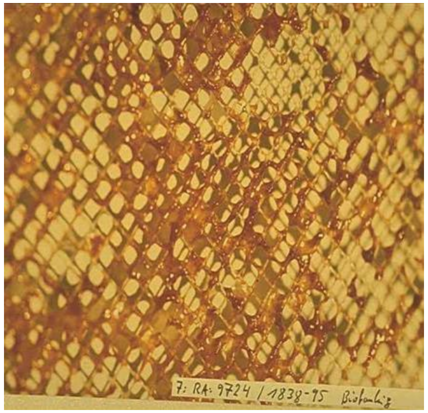
http://www.kochmembrane.com/Learning-Center/Configurations/What-are-Spiral-Membranes.aspx

Spacer: major culprit for fouling

- Membrane Fouling
  - Undesirable deposition of retained particles, colloids, macromolecules and salts on the polyamide film
- Biofouling
  - Biologically active organisms
  - Diminish the treatment efficiency
  - Biofouling is more complicated because microorganisms can grow, multiply and relocate on the membrane surface
  - **Most of the biofouling were seen at the spacers of spiral membranes**



Spacer of reverse osmosis (RO) membrane

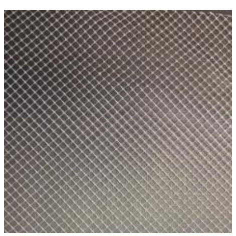


Biofouling within the spacer of RO membrane

http://www.aquatis.com.au/innovative-membrane-solutions/technology/

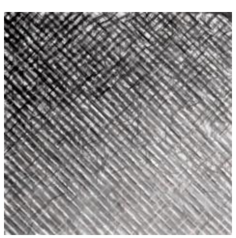
Solution: a spacer that is antimicrobial, and can generate active chlorine to actively eliminate biofouling

- LIG-based spacers
  - Antimicrobial properties
  - Generate low amounts of active chlorine species with applied voltage **at exactly where biofouling occurs**

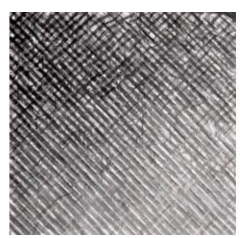


Present situation

Fouling



Proposed solution: LIG spacer



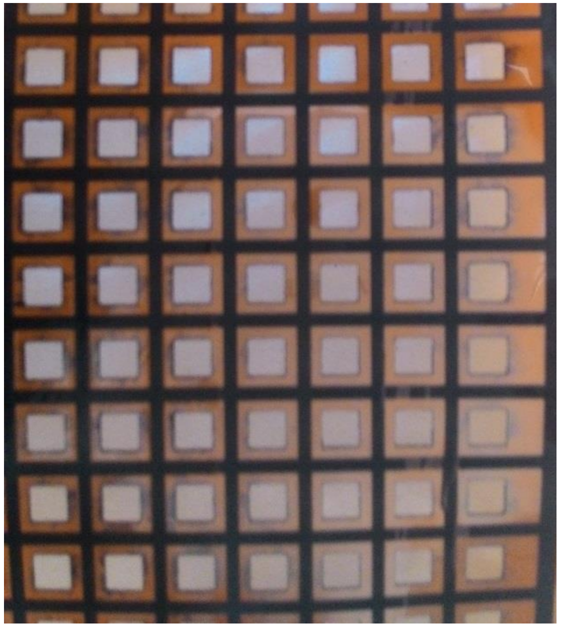
No Fouling

Antimicrobial/***active chlorine generation*** eliminates microbes

LIG-based spacers

- Reduce biofouling via
  - Killing the microbe directly upon contact
  - Generation of controlled amounts of chlorine by electrolysis of dissolved chloride ion

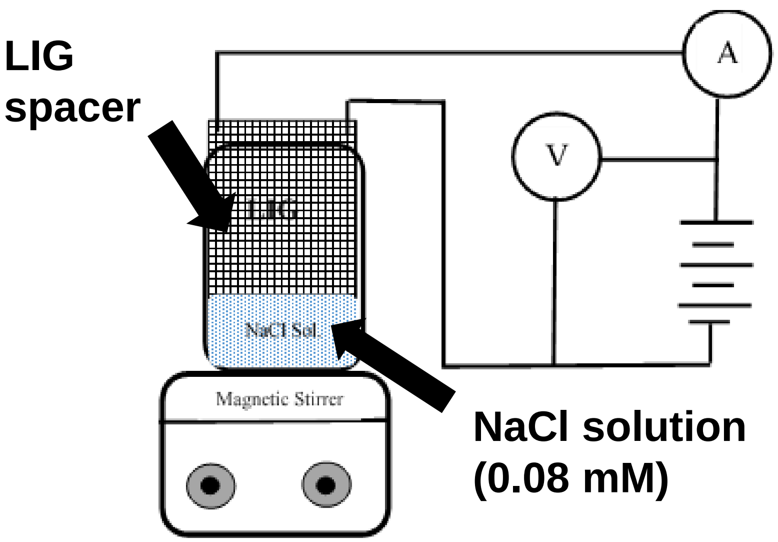
- Preliminary results
  - No microbial growth was observed on the LIG
  - Controlled amounts of active chlorine species could be generated with applied voltage in saline solutions
  - 2 log reduction in concentrated *Pseudomonas aeruginosa* solutions



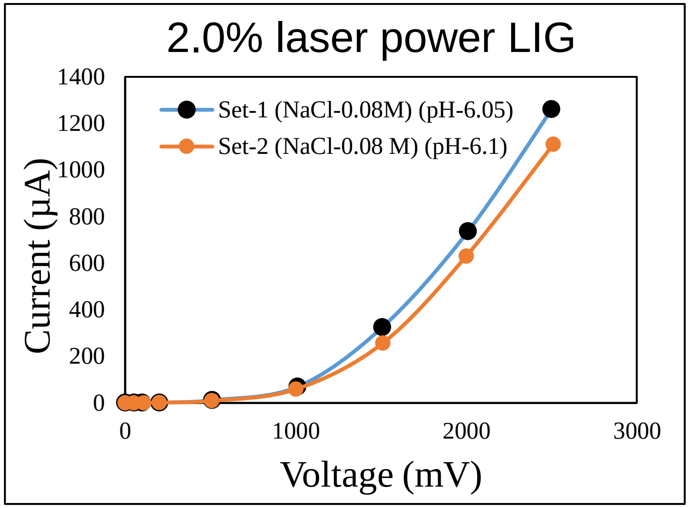
Spacer both side coated with LIG

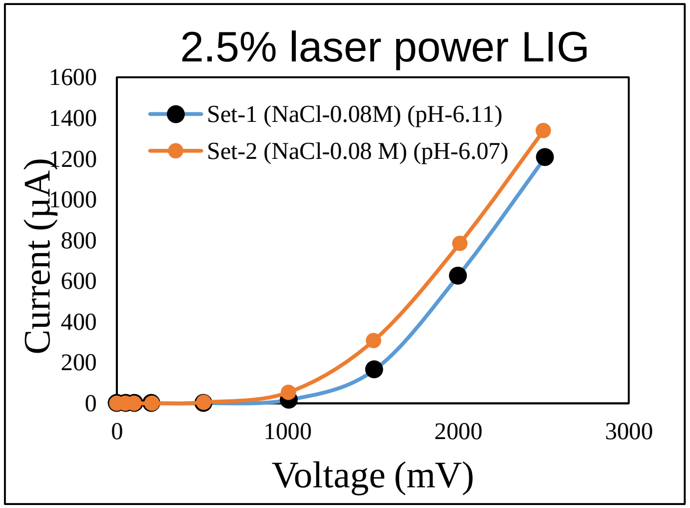
Preliminary results

- LIG on both sides of PI in a square pattern using 2% and 2.5% laser duty cycle
- I-V curves for both LIGs, negligible changes in different cycles



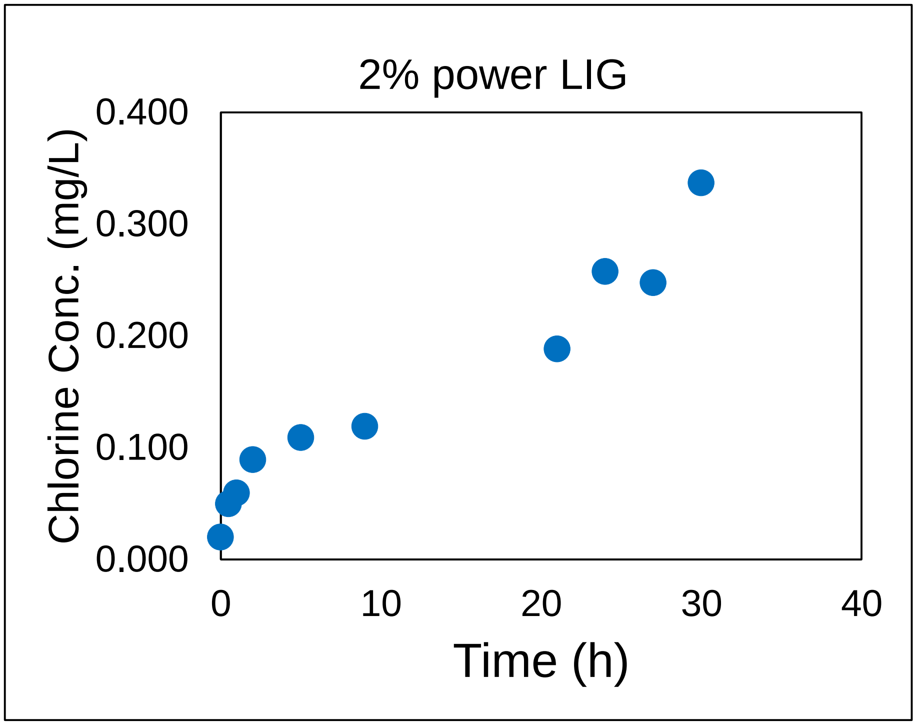
Setup for initial experiments

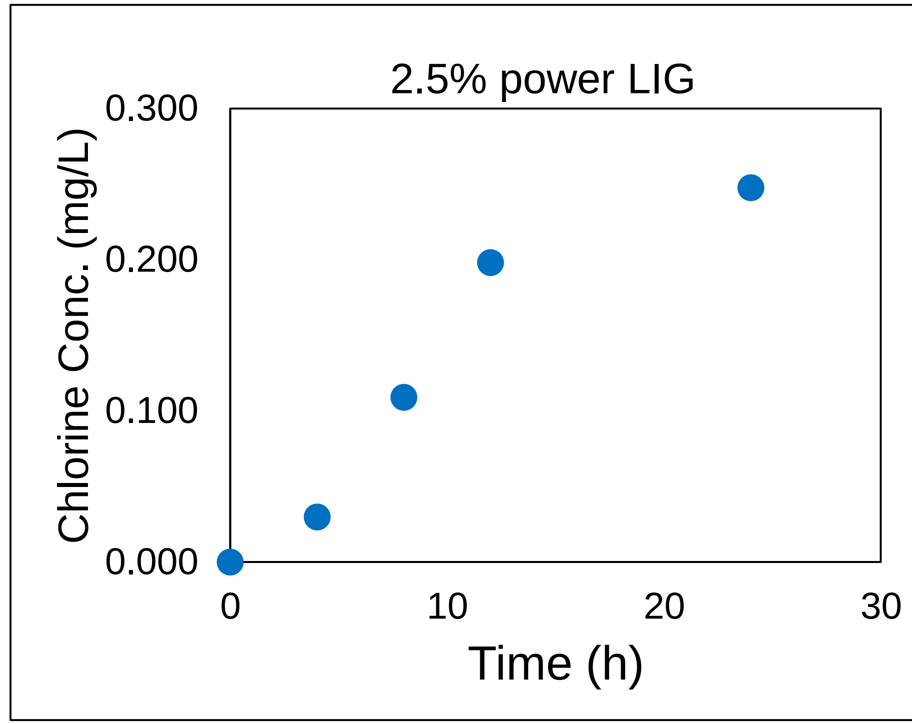




IV curves for 2.0% and 2.5% laser power LIG

Generation of active chlorine





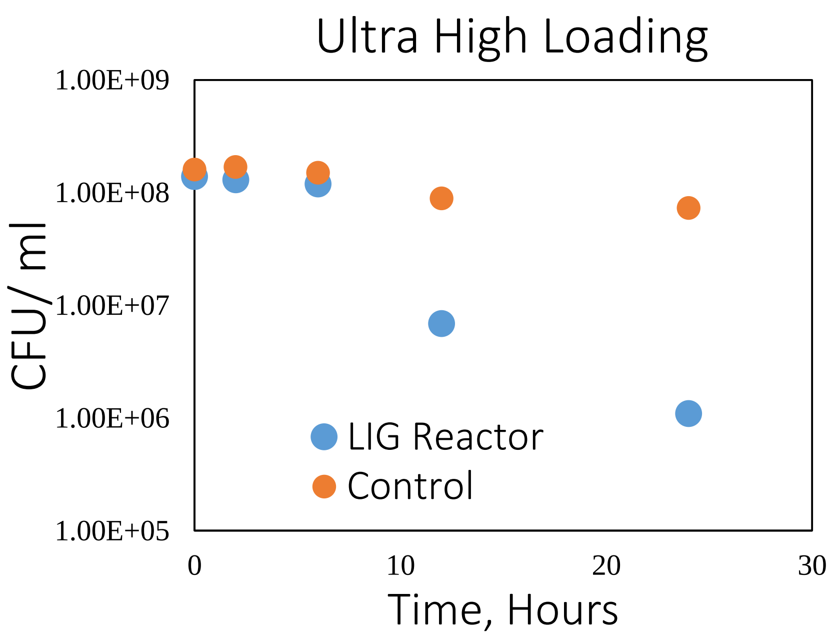
Bulk active chlorine species concentration with applied voltage of 1.5 V

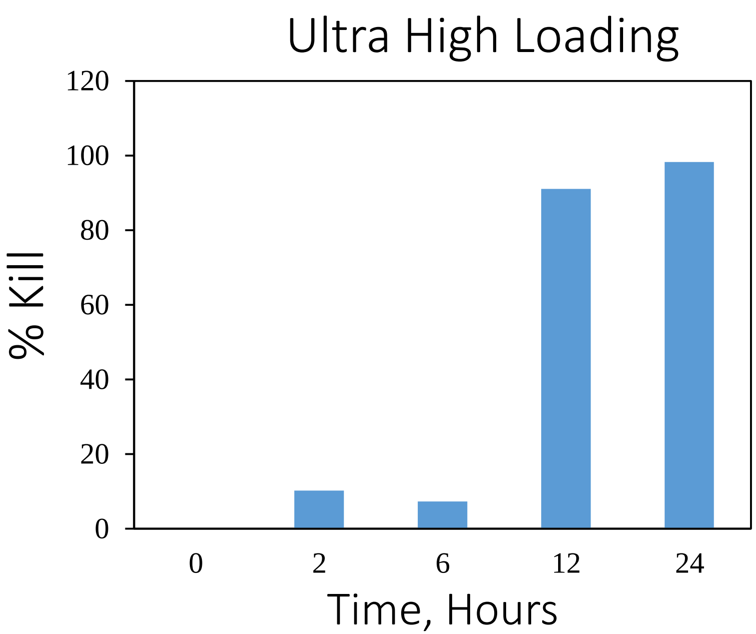
0.1 mg/L - 0.2 mg/L chlorine generally needed for antibacterial activity

Active antimicrobial test – high loading

- Ultra high bacterial loading
  - Two log reduction was seen
  - Active chlorine concentration was always below detection level (safe for polyamide RO membrane surfaces)

CFU = colony forming unit
Measure of viable bacteria or fungi

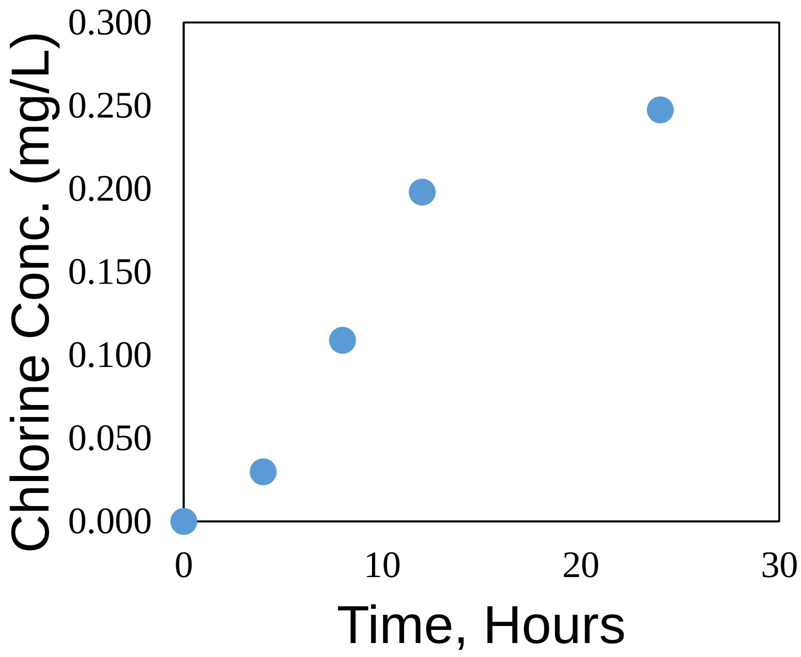




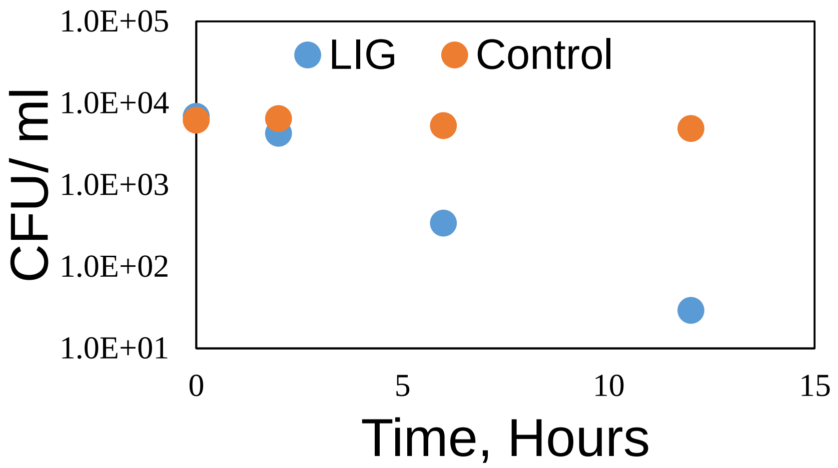
Bacterial population with 2.5% power LIG at 1.5V

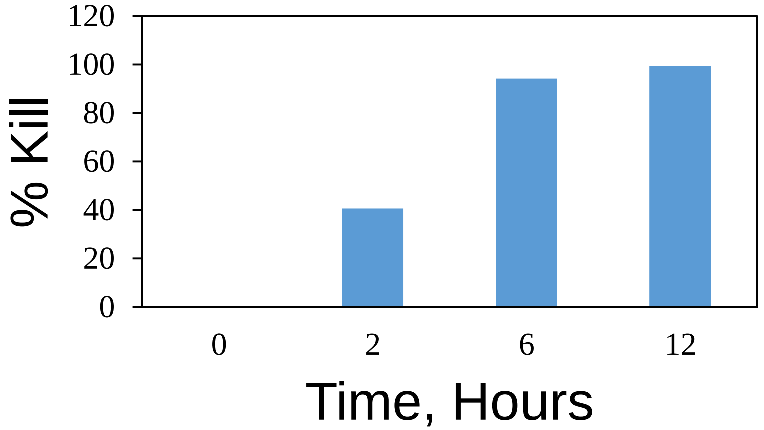
Active antimicrobial test – low loading

- Low bacterial loading
  - 99.99% bacterial removal
  - Chlorine was detected



Chlorine concentration with 2.5% power LIG at 1.5 V with low bacterial population





Bacterial population with 2.5% power LIG at 1.5 V

Potential concerns with active chlorine generation

- Concern: active chlorine has long been known to destroy certain types of polymer membranes, especially polyamide. Chlorine is absorbed/reacts into the polymer via an Orton rearrangement, pH-dependently chlorinating the nitrogen in the amide, and then aromatic rings (doi:10.4172/2155-9589.1000115)
- Answer: We can precisely control the dose, and have the active chlorine at exactly the spots where fouling occurs. Our preliminary tests show efficacy at ≤0.1 mg/L (0.1 ppm). In literature comparisons, membranes have been tested at 30 mg/L (300x higher) for 300 hours with only small effects in performance.
- Concern: Why do we need *in situ* generation of active chlorine species? Why not just add chlorine to the water before it goes into the module at the same concentration that the spacer could generate it.
- Answer: this has been tried but it is unsuccessful– chlorinating the water, and then adding sodium metabisulfite to neutralize the chlorine before it goes in the module. This destroys the bacteria in the feed water, but then all the products from the dead bacteria become a food source for the bacteria already in the module, leading to worse biofilm growth. Also, chlorinating water in the stages before the RO units may kill bacteria in the sand filters, which consume the nutrients for bacterial growth in the modules. (doi:10.1016/j.watres.2015.03.029) Moreover, the *passive* antibiofilm and antimicrobial effects of an LIG-coated spacer would be advantageous even by themselves.

LIG for capacitive deionization (CDI) devices

In collaboration with

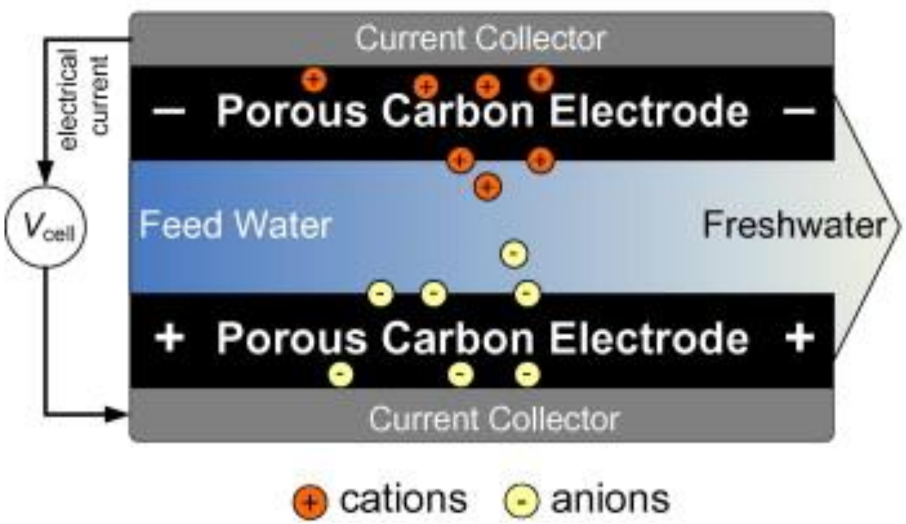
Jun Kim

Prof. Qilin Li

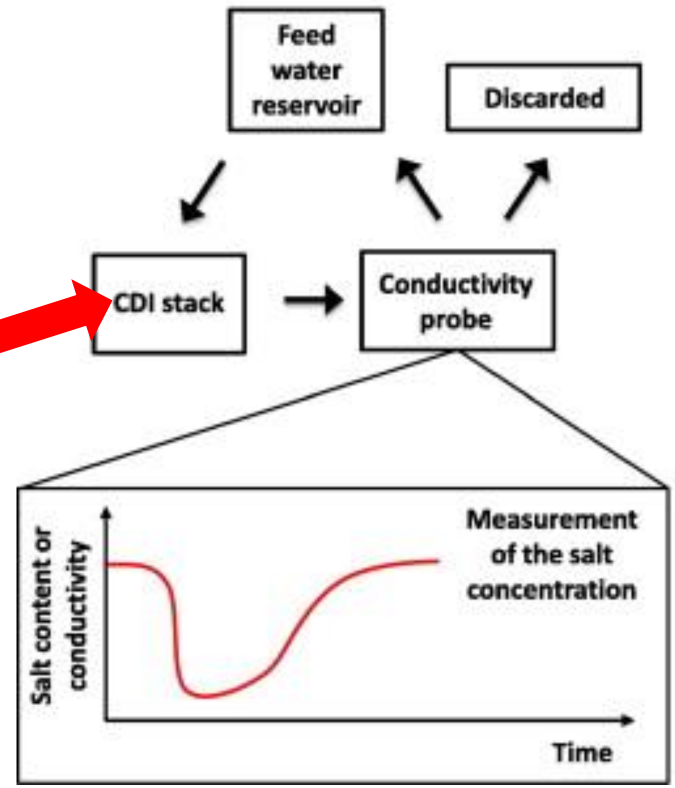
Rice University

CDI system

CDI electrodes



Experimental setup



Porada, S. *et al*, *Progress in Materials Science* **2013**, *58*, 1388.

Advantages in using LIG in CDI

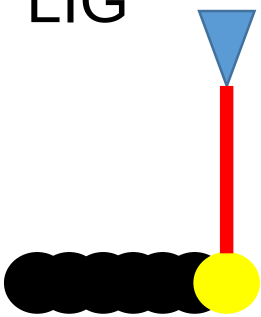
- Easy to prepare in a roll-to-roll process
- Porous structure
- Highly conductive
- Easy to fabricate into CDI device
- Antibiofouling
- Tunable hydrophilicity / morphology
- Other potential modifications
  - Heteroatom doping
  - Electrochemical deposition

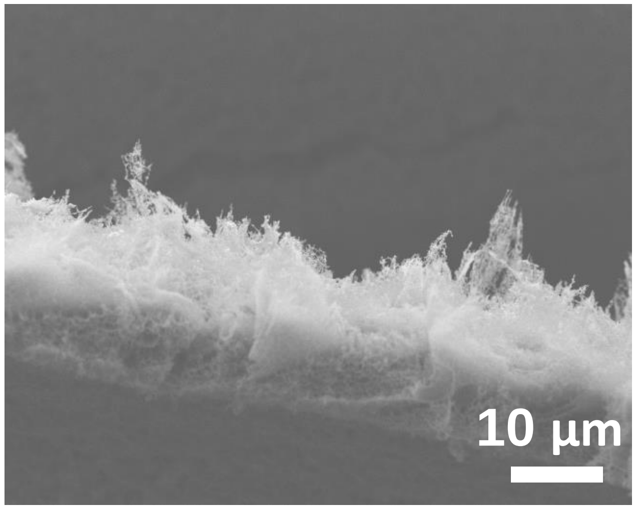
Initial results

- Note:
  - Preliminary data
  - Large dead volume (relative to sample weight)
  - Low signal/noise ratio
- LIG made under air
  - Sorbent density 0.375 mg/cm^2
  - Tested with salt conc. of 500 mg/L
  - Adsorption density 40~70 mg/g (literature values normally less than 20 mg/g)
- Insufficient LIG per unit area since LIG is only 20 μm thick
  - We will use laser-induce graphene scrolls (LIGS) since they can be grown to even to millimeters thick

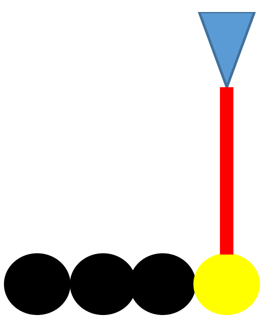
Laser-induced graphene (LIG) vs. laser-induced graphene scrolls (LIGS)

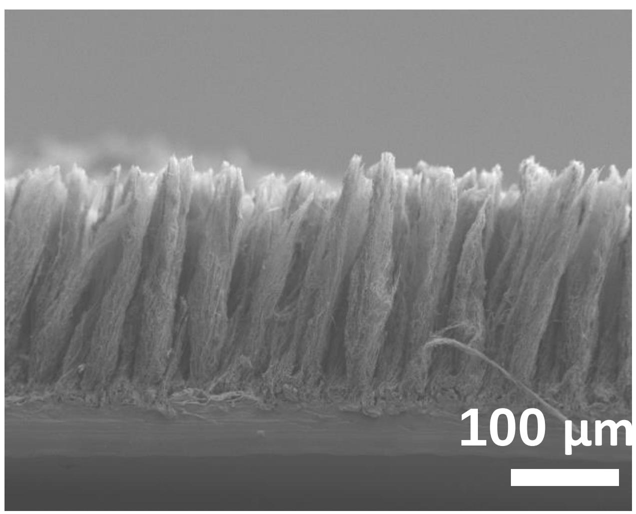
LIG

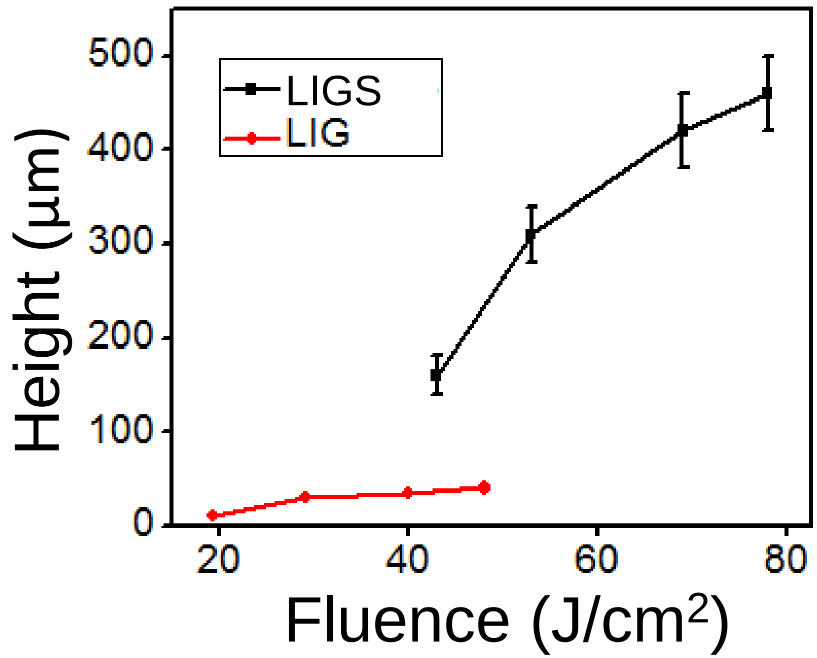




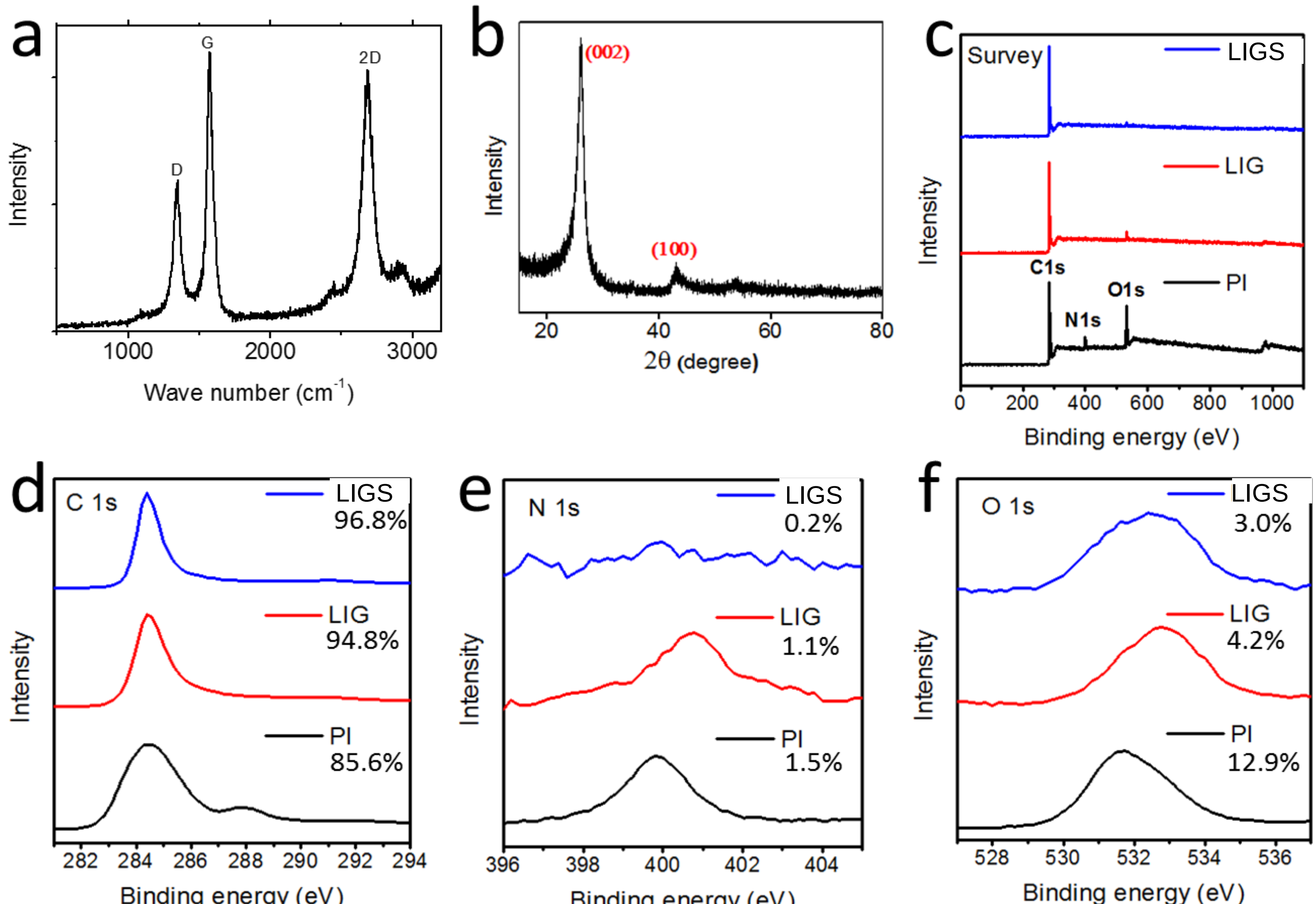
LIGS



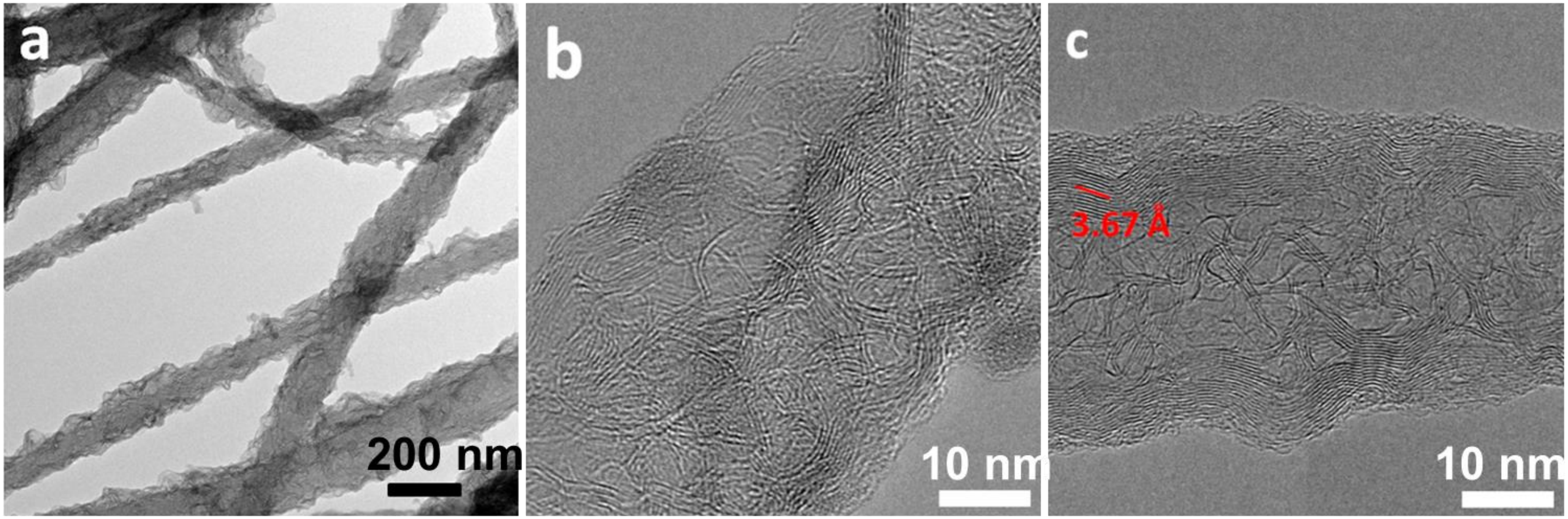




Spectroscopy characterization



TEM characterization of LIGS



Future work with CDI

- Increase the density of graphene per unit area by increasing their height using LIGS
- More CDI testing including adsorption/desorption cycles, stability and selectivity

Acknowledgements

- AFOSR and Vietnam Education Foundation Fellowship for the LIG and LIGS processes
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    - Yilun "Ethan" Li
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