

Electrochemical Engineering and Direct Ink Writing 3D Printing: Cost-Effective Production of 2D Nanomaterials and their Bespoke Assemblies

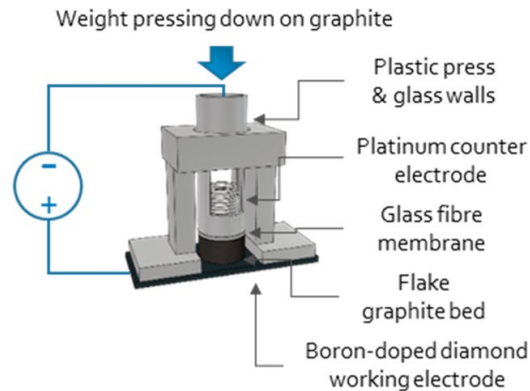
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Associate Professor & ARC Future Fellow
School of Environment and Science
Queensland Micro- and Nanotechnology Centre
Griffith University
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Electrochemical Engineering of Nanomaterials

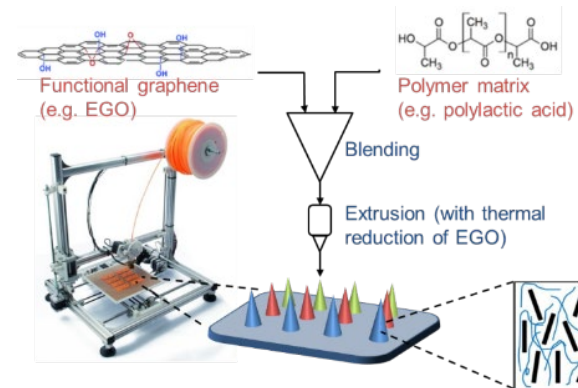


Additive Manufacturing of Devices

DE140101662 - Non-Oxidative and Scalable Electrochemical Production of Functional Graphene and its Nano hybrids

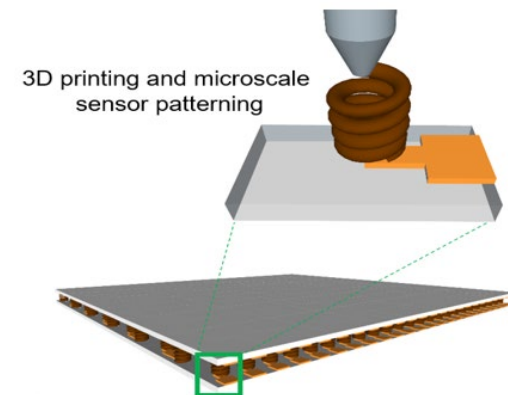


DP170104157 - Tailoring Nanocomposites with Controllable Structural-Property Relationship



DP190100120 - Towards High-Performance Wearable Devices: Materials and Microfabrication

FT200100015 - Advancing Green Electrochemical Engineering of Functional 2D Nanomaterials

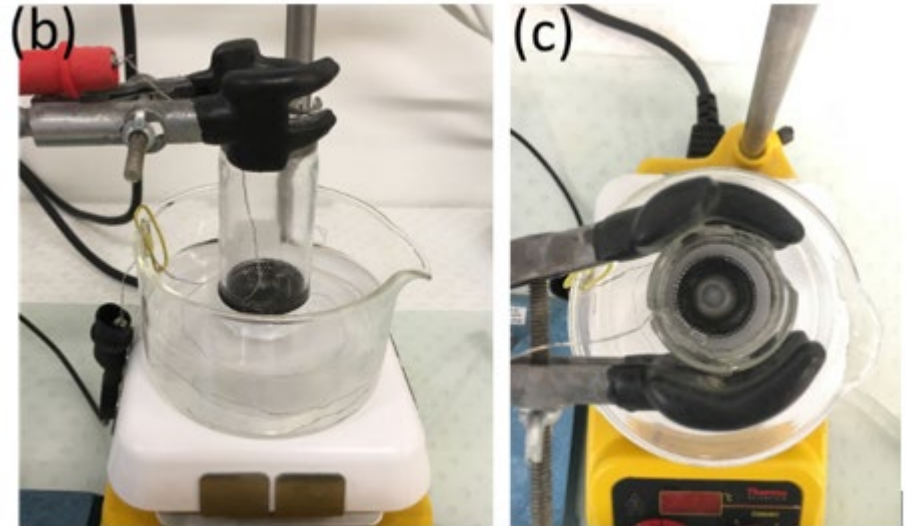
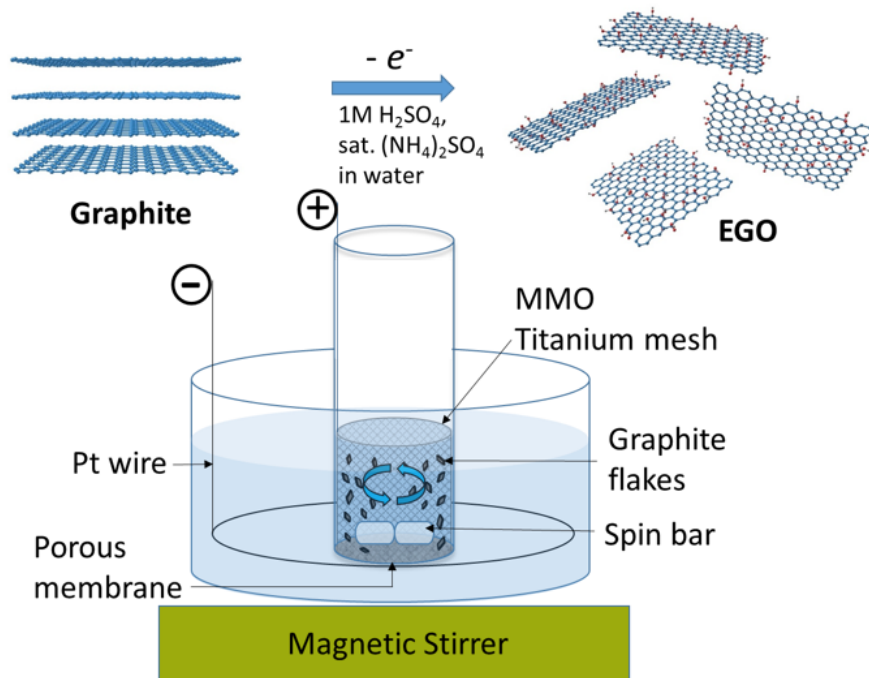


DP240100892 - Empowering Wearable Smart Devices with 3D Printed Energy Storage

Scalable Mechanically-Assisted EGO

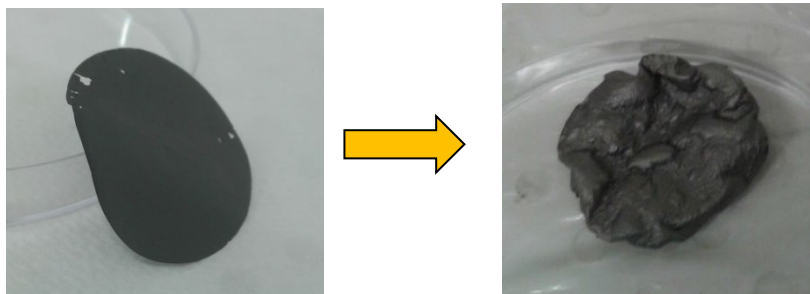
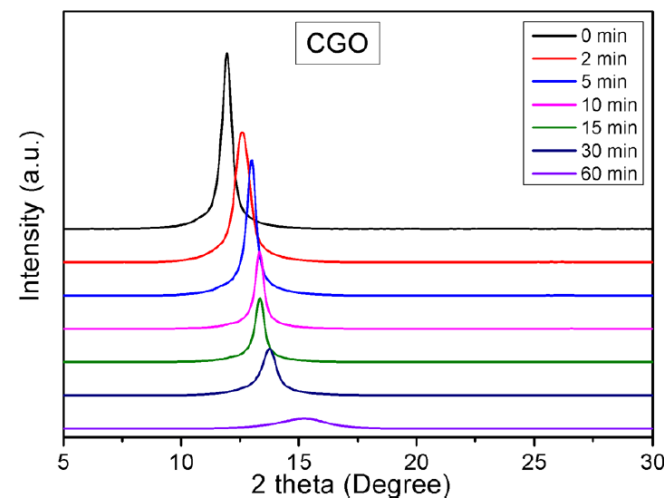
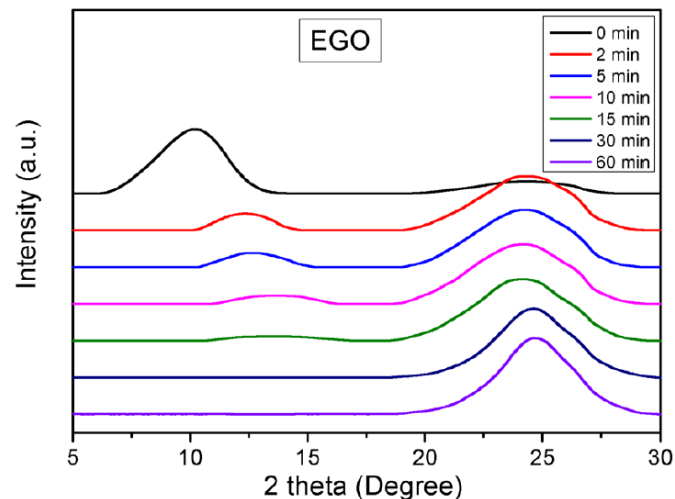
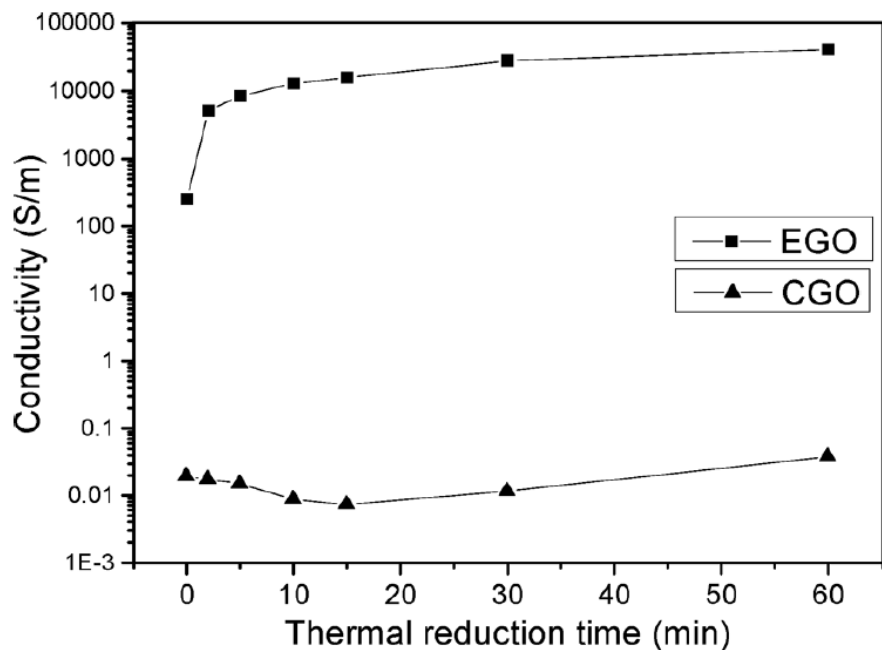
Y. L. Zhong, D. Li & G. P. Simon [Graphene Oxide and Method of Production Thereof](#). Patent Application No. PCT/CN2015/097227 (filed on December 14, 2015).

Y. Pei, Z. Tian, S. E. Lowe, ... D. Li & Y. L. Zhong [Mechanically-Assisted Electrochemical Production of Graphene Oxide](#). *Chem. Mater.* **28**, 8429-8438 (2016).



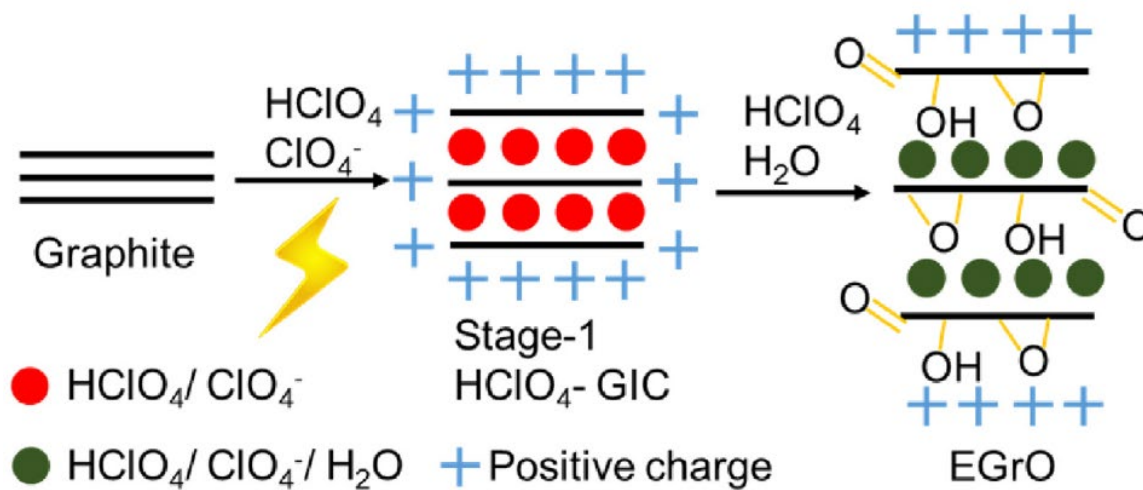
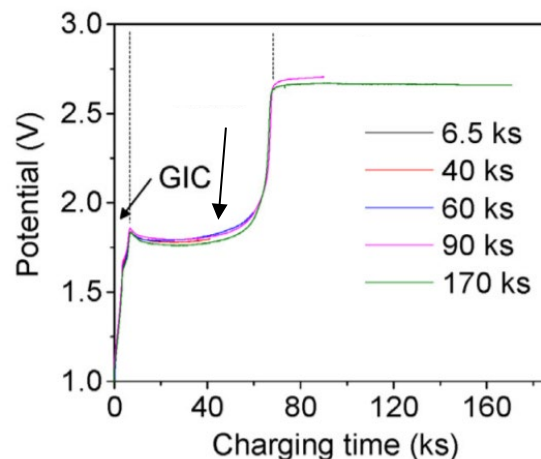
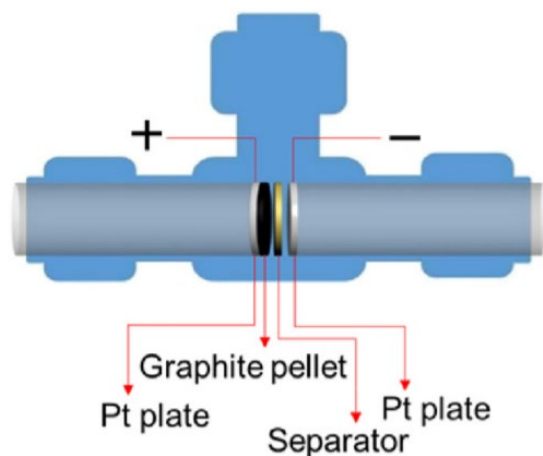
Low temperature conversion: 200 °C in air

Y. Pei, Z. Tian, S. E. Lowe,... D. Li & Y. L. Zhong [Mechanically-Assisted Electrochemical Production of Graphene Oxide](#). *Chem. Mater.* **28**, 8429-8438 (2016).



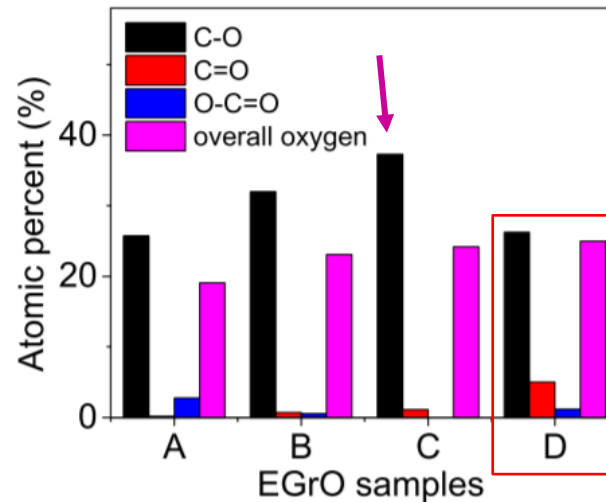
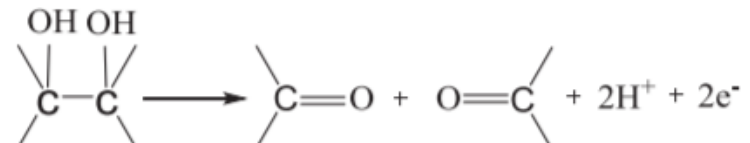
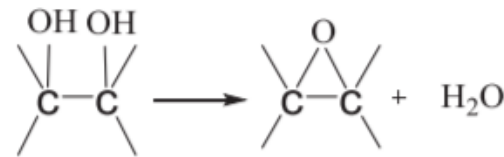
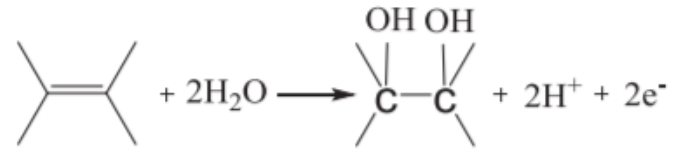
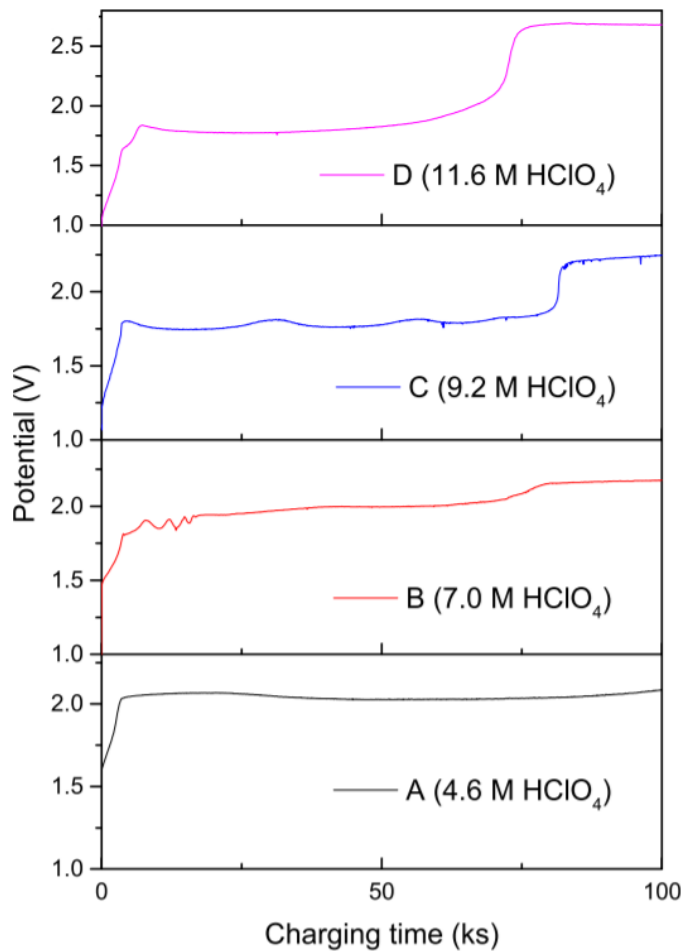
Mechanistic Study in T-cell

Z. Tian, P. Yu, S. E. Lowe, ... Y. L. Zhong & D. Li [Facile Electrochemical Approach for the Production of Graphite Oxide with Tunable Chemistry](#). *Carbon*, **112**, 185-191 (2017).



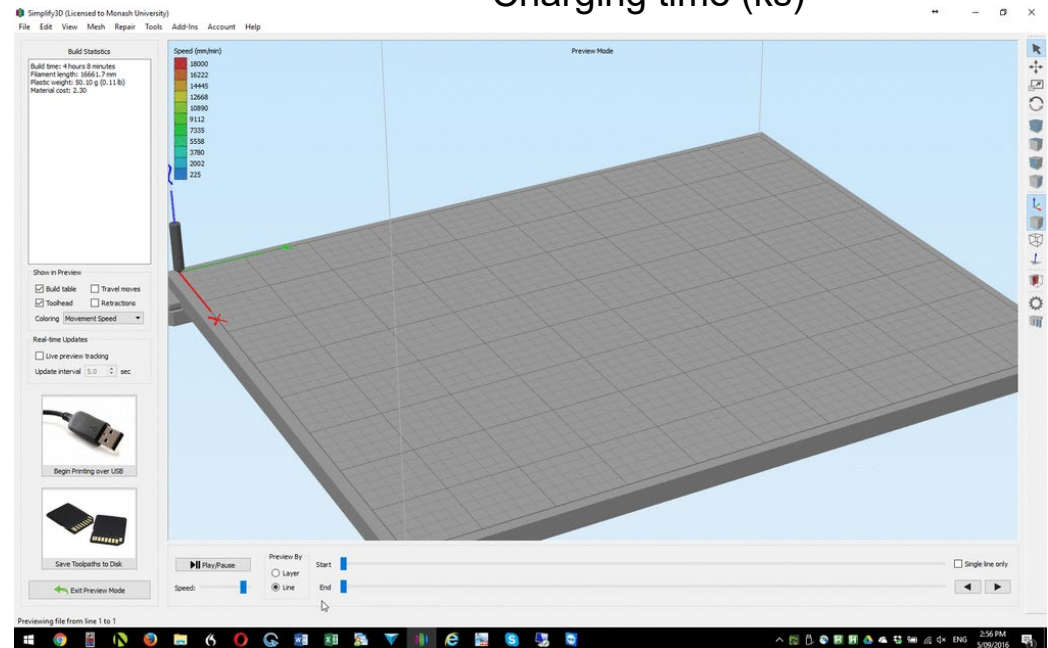
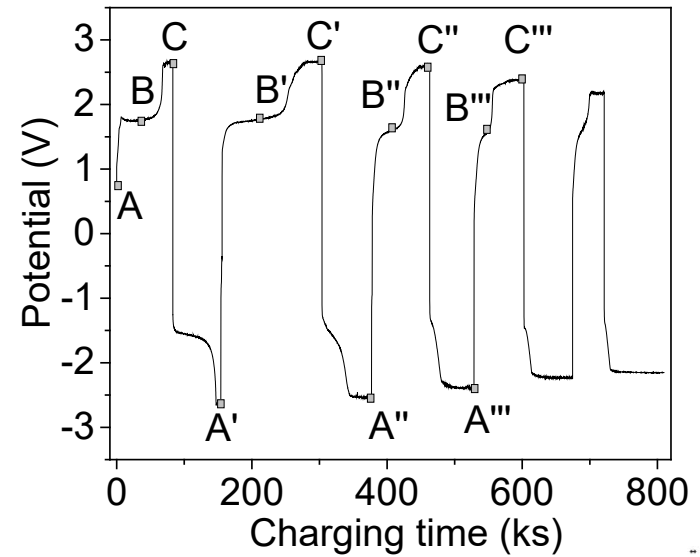
Effect of Electrolyte Concentration

Z. Tian, P. Yu, S. E. Lowe, ... Y. L. Zhong & D. Li [Facile Electrochemical Approach for the Production of Graphite Oxide with Tunable Chemistry](#). *Carbon*, **112**, 185-191 (2017).

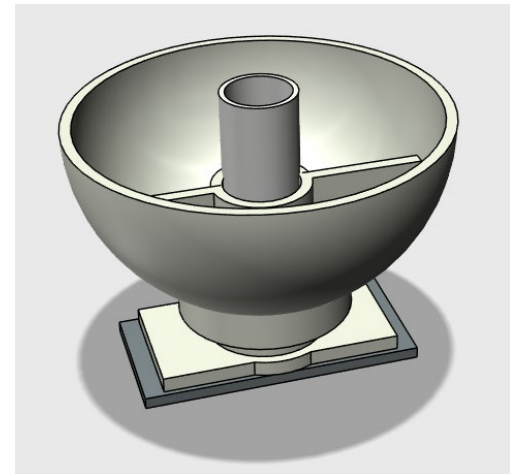
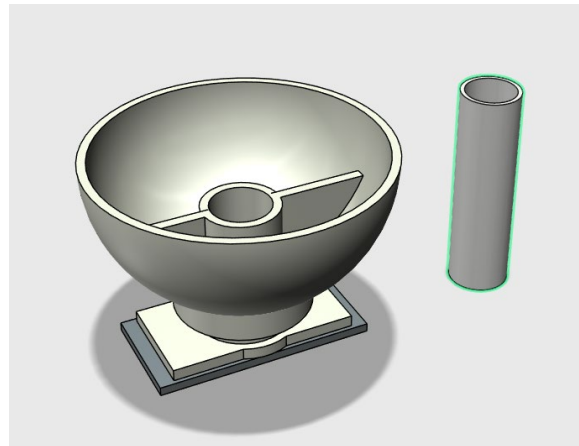
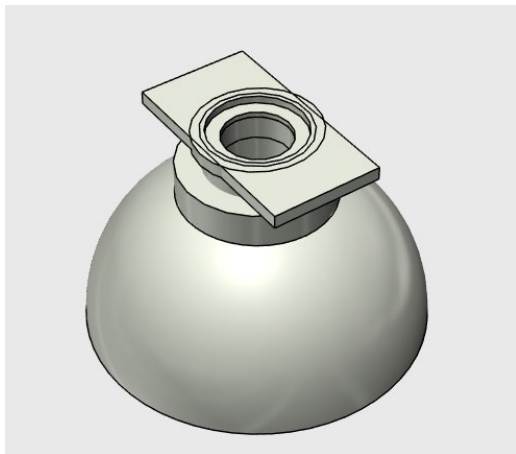
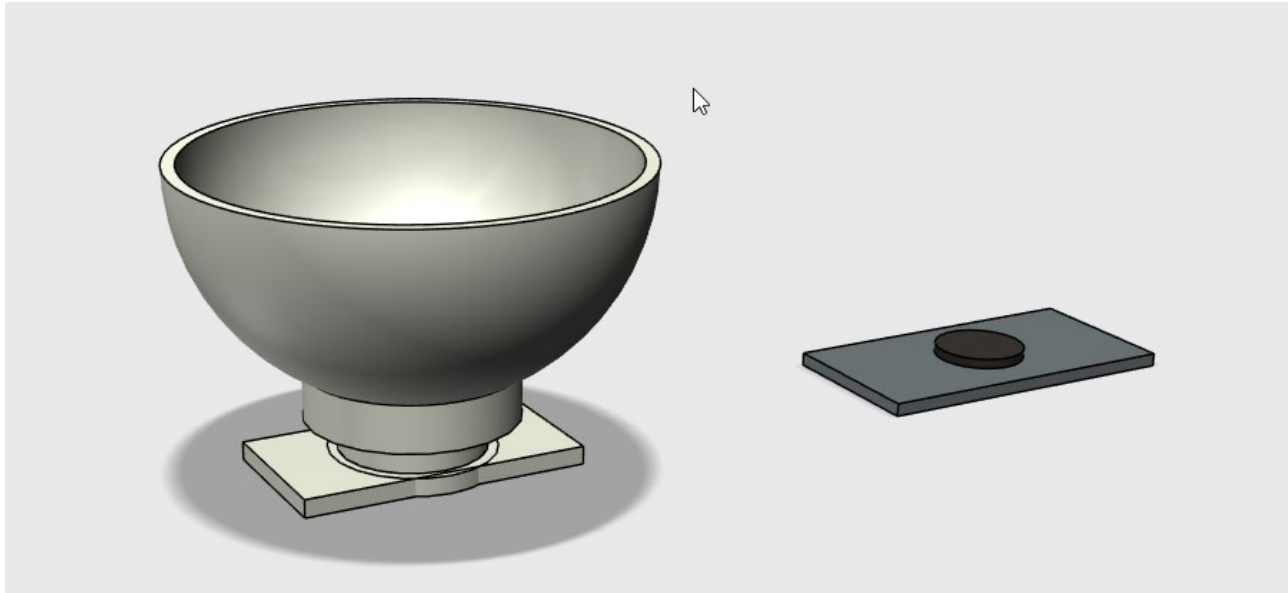


Other Parameters

- Type of electrolytes
- Additives
- Charging current/voltage
- Electrochemical reaction-wares design



3D-Printed Packed-Bed Electrochemical Reactor



3D-Printed Packed-Bed Electrochemical Reactor

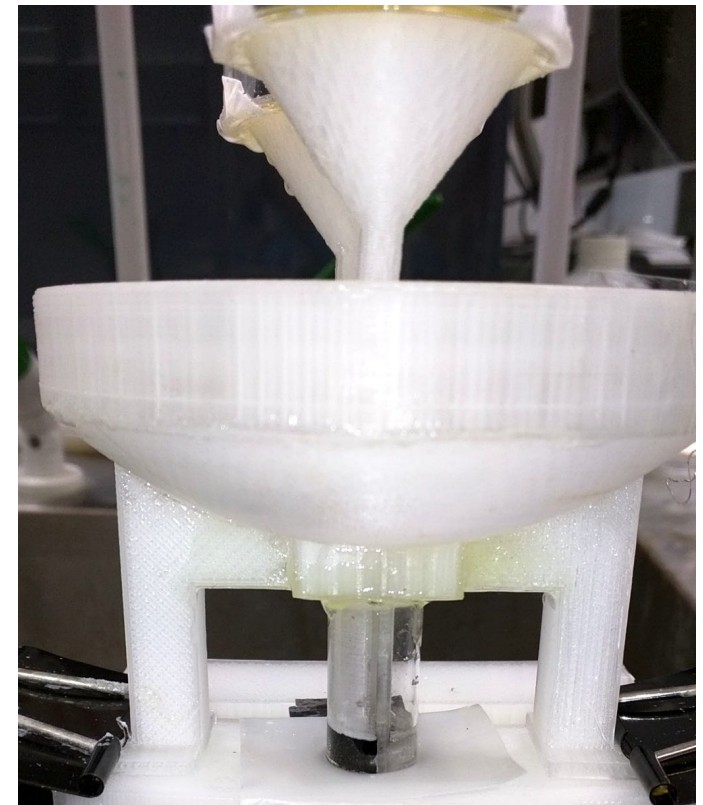
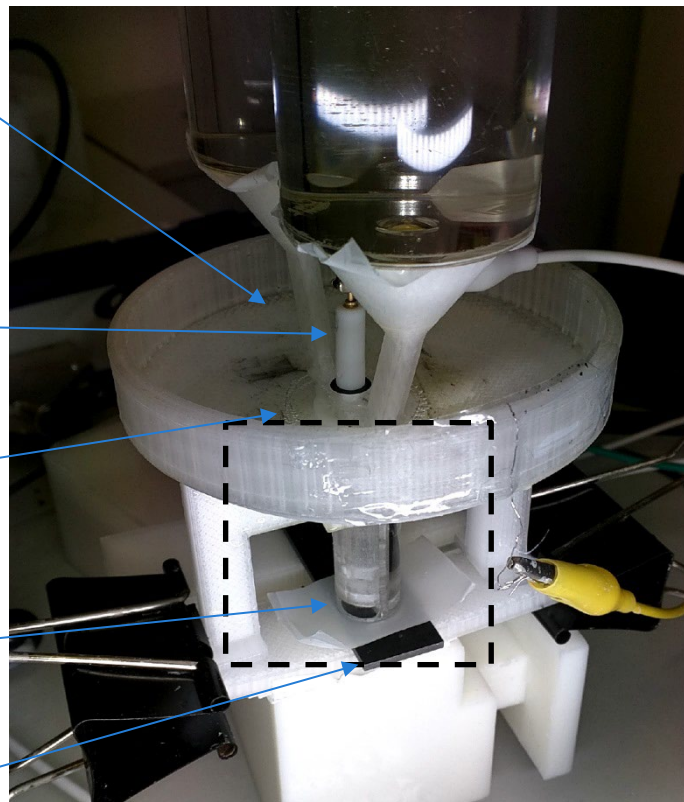
Saturated ammonium sulphate with 1 M sulphuric acid

Ag/AgCl Reference Electrode

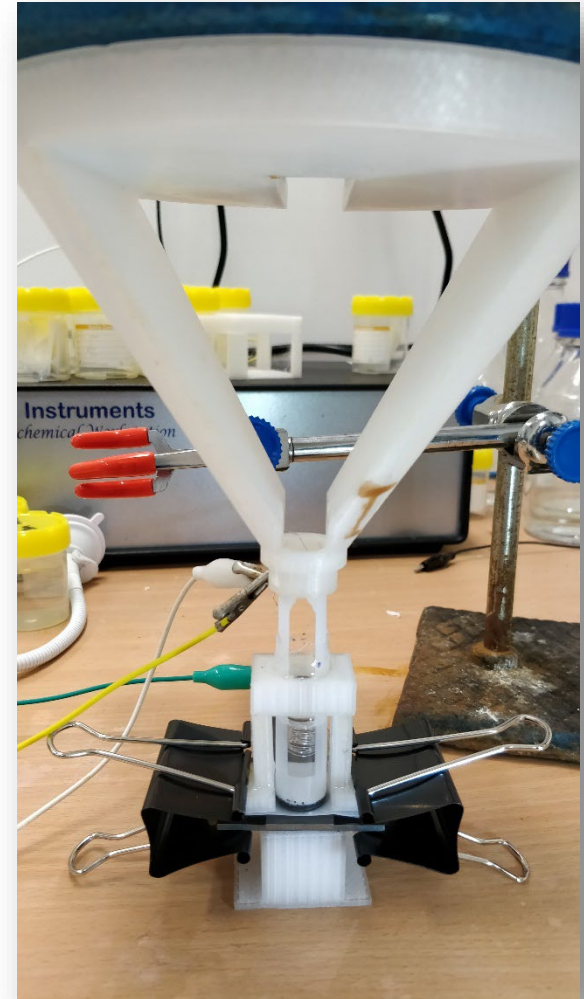
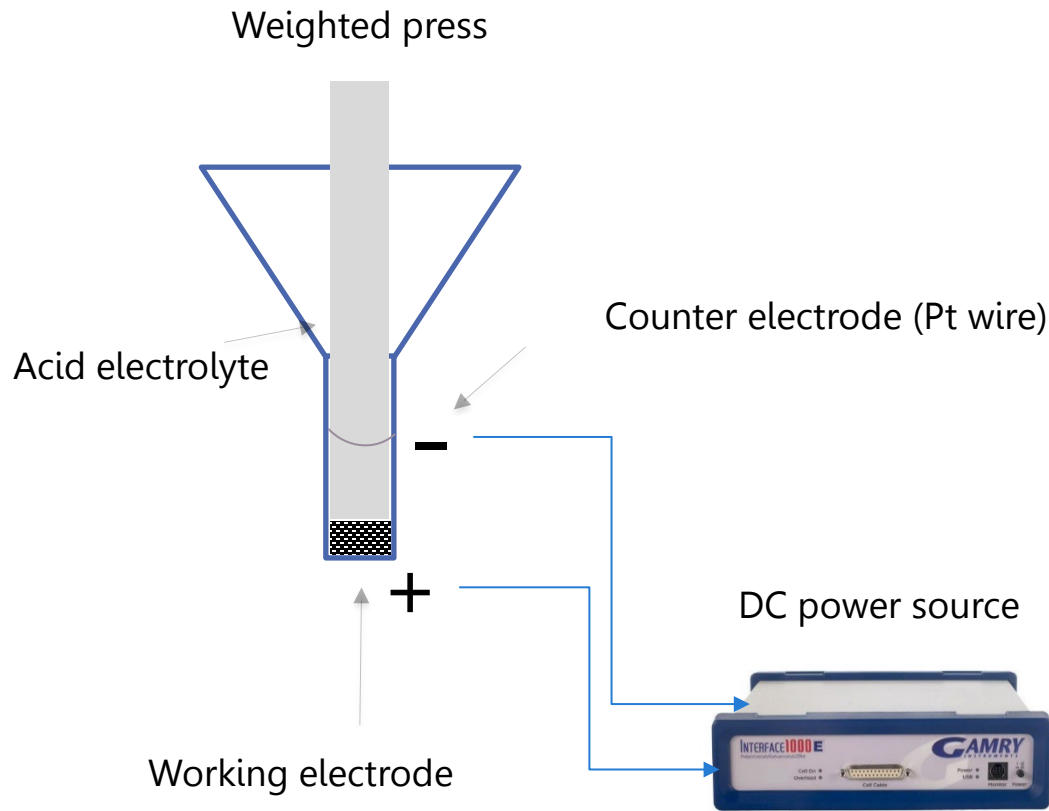
Pt counter electrode

25 mg flake graphite packed bed

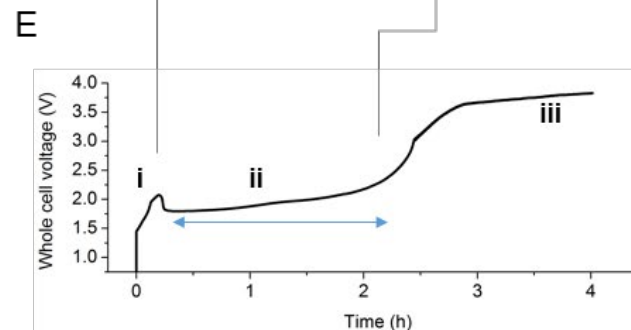
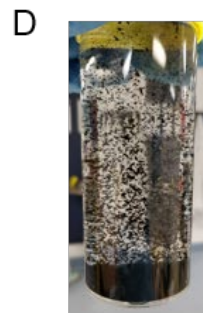
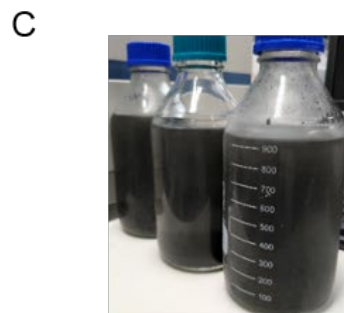
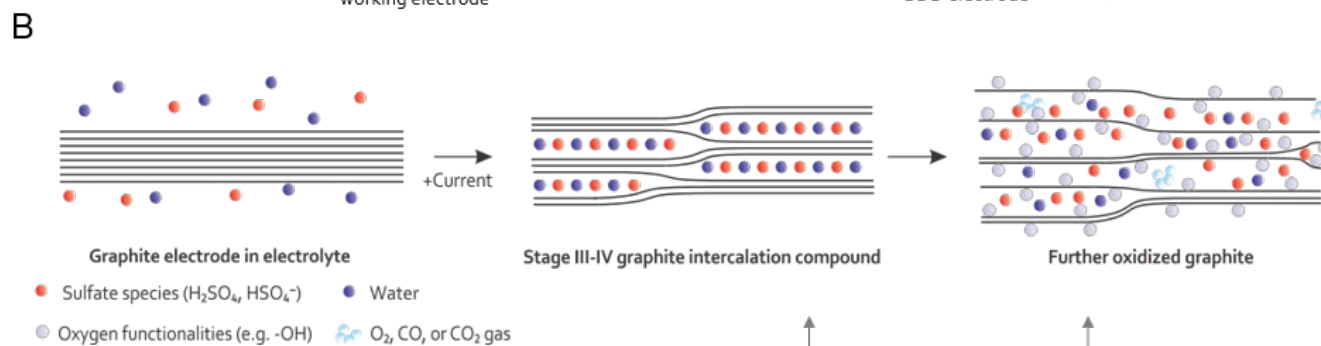
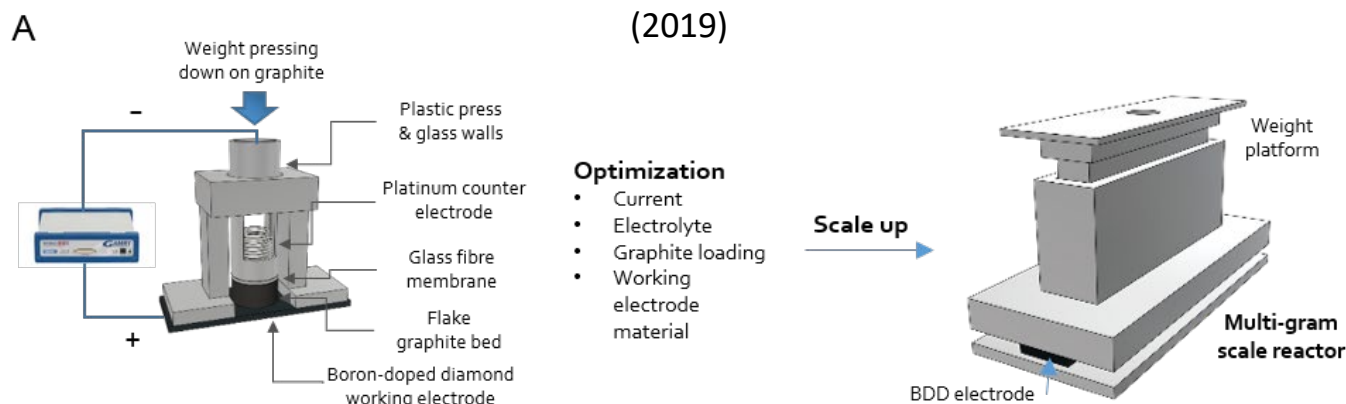
Working electrode substrate



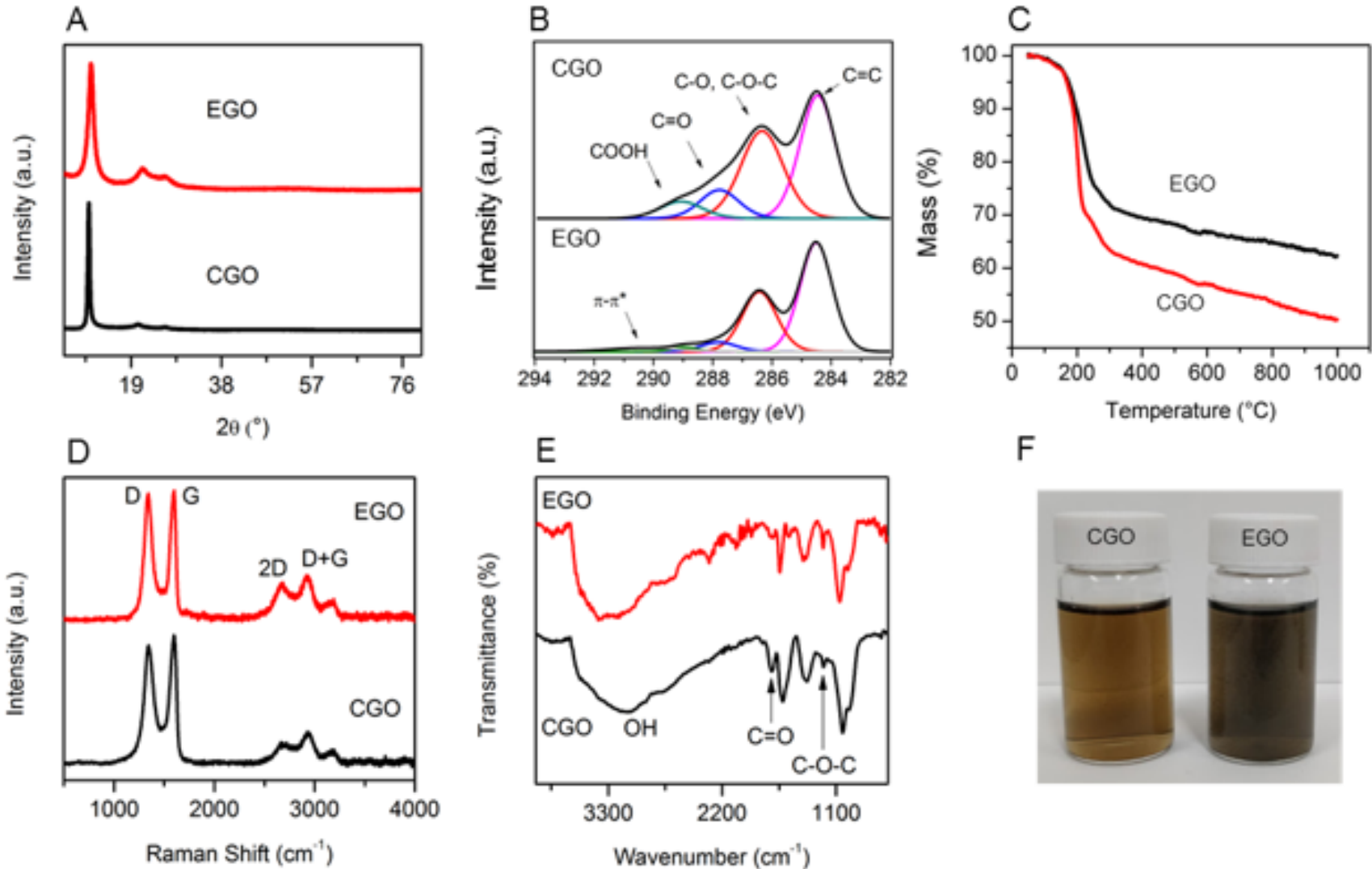
3D-Printed Packed-Bed Electrochemical Reactor



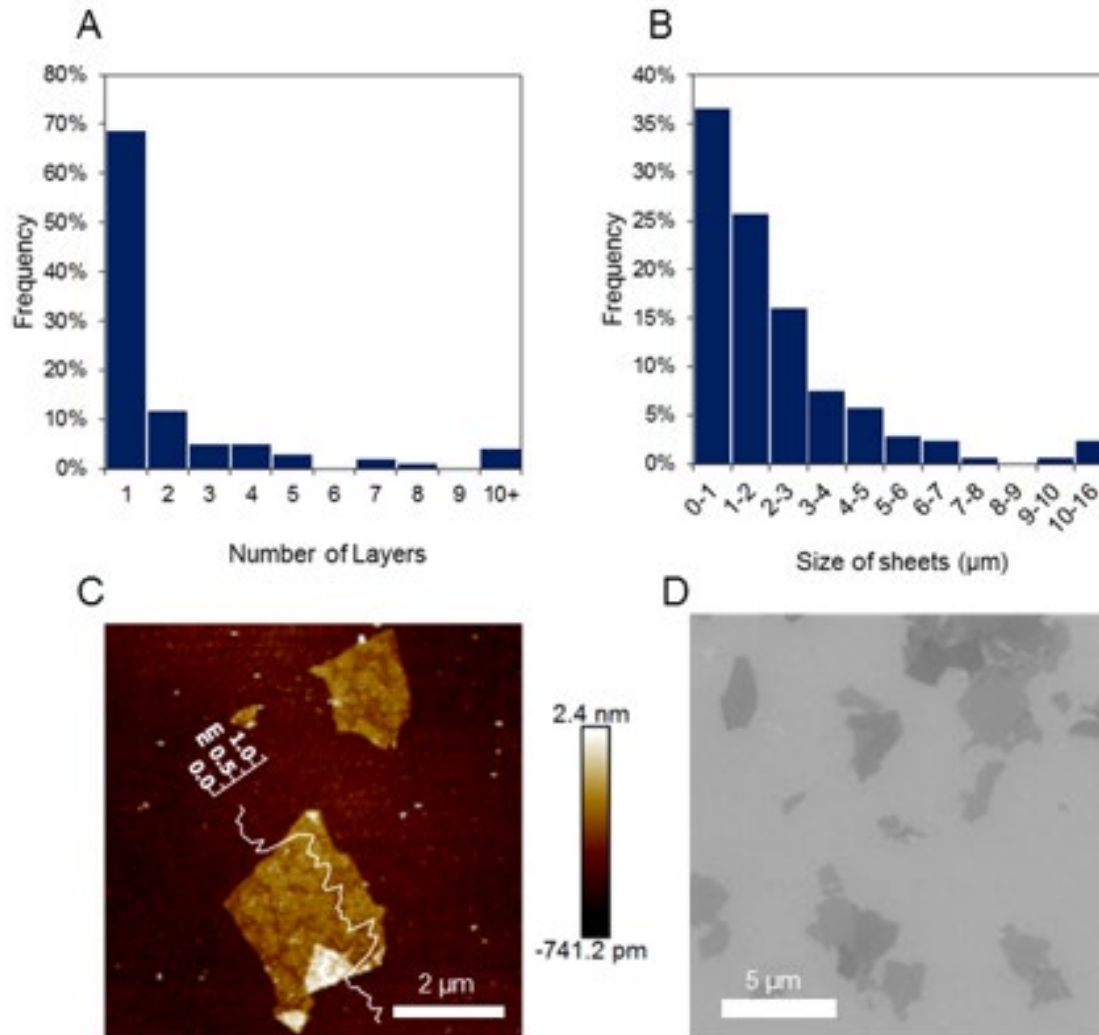
Sean E. Lowe,... Y. L. Zhong **Scalable Production of Graphene Oxide via a 3D Printed Packed-Bed Electrochemical Reactor with Boron-doped Diamond Electrode** *ACS Appl. Nano Mater.* **2**, 867–878



3D-Printed Packed-Bed Electrochemical Reactor



3D-Printed Packed-Bed Electrochemical Reactor



Scaling up with rapid prototyping (FDM)

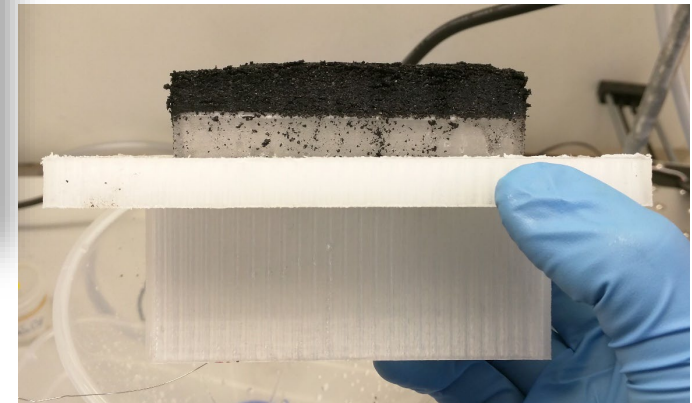
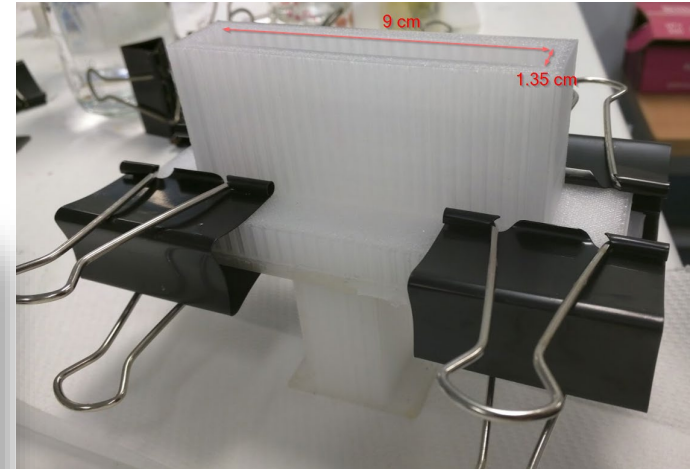
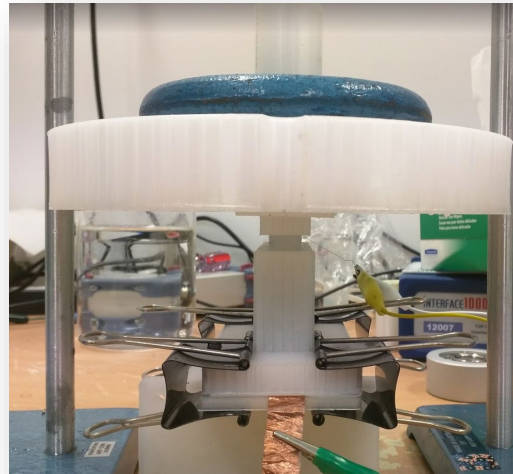
3D printed polypropylene reactor

Base area increased 8.5x

(1.43 cm² → 12.15 cm² footprint)

New starting graphite:

$$0.5 \text{ g} * 8.5 = 4.25 \text{ g}$$



Scaling up

3D printed polypropylene reactor

Base area increased 8.5x

(1.43 cm² → 12.15 cm² footprint)

New starting graphite:

$$0.5 \text{ g} * 8.5 = 4.25 \text{ g}$$

Next reactor size:

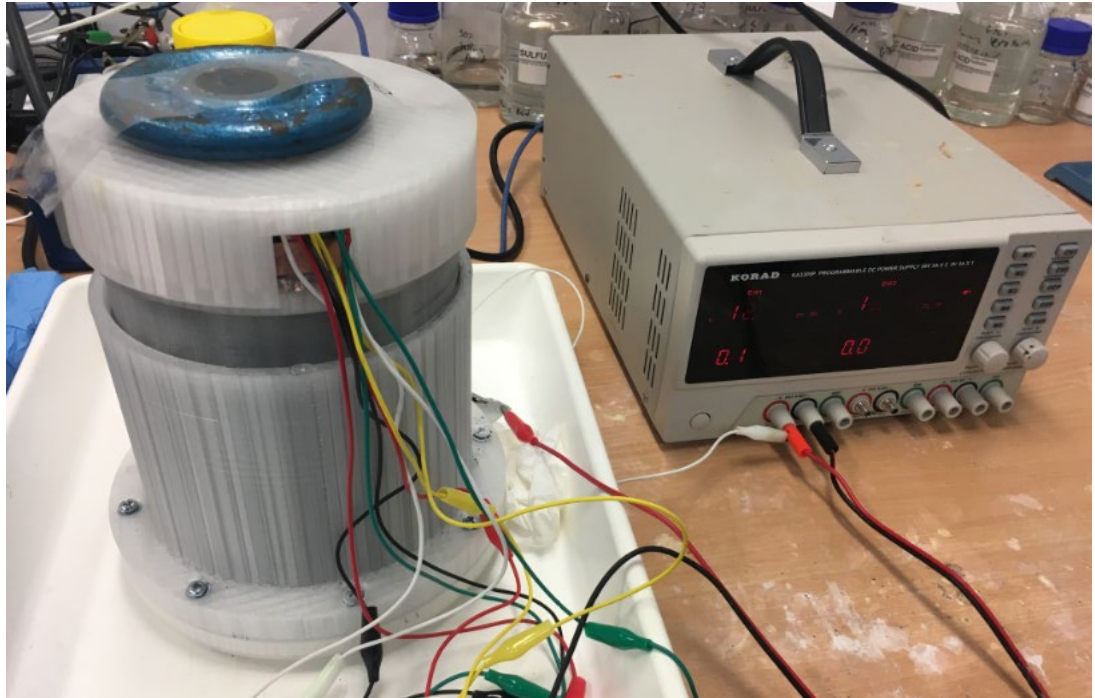
Base area 15 cm diameter →

$$176.74 \text{ cm}^2 \rightarrow 61.8 \text{ g}$$

Industrial scale size:

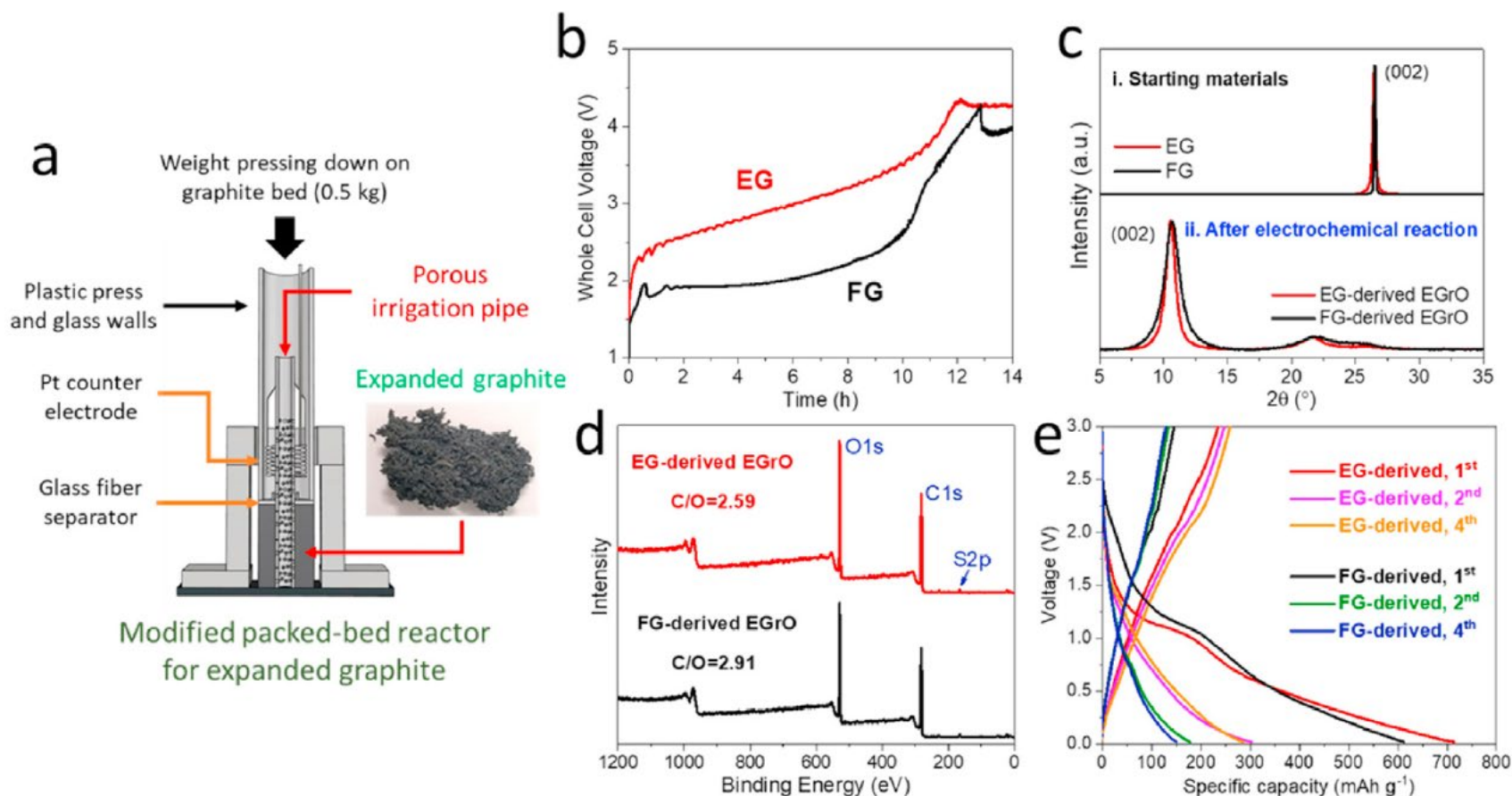
Base area 1 m diameter → 7855

$$\text{cm}^2 \rightarrow 2.75 \text{ kg}$$



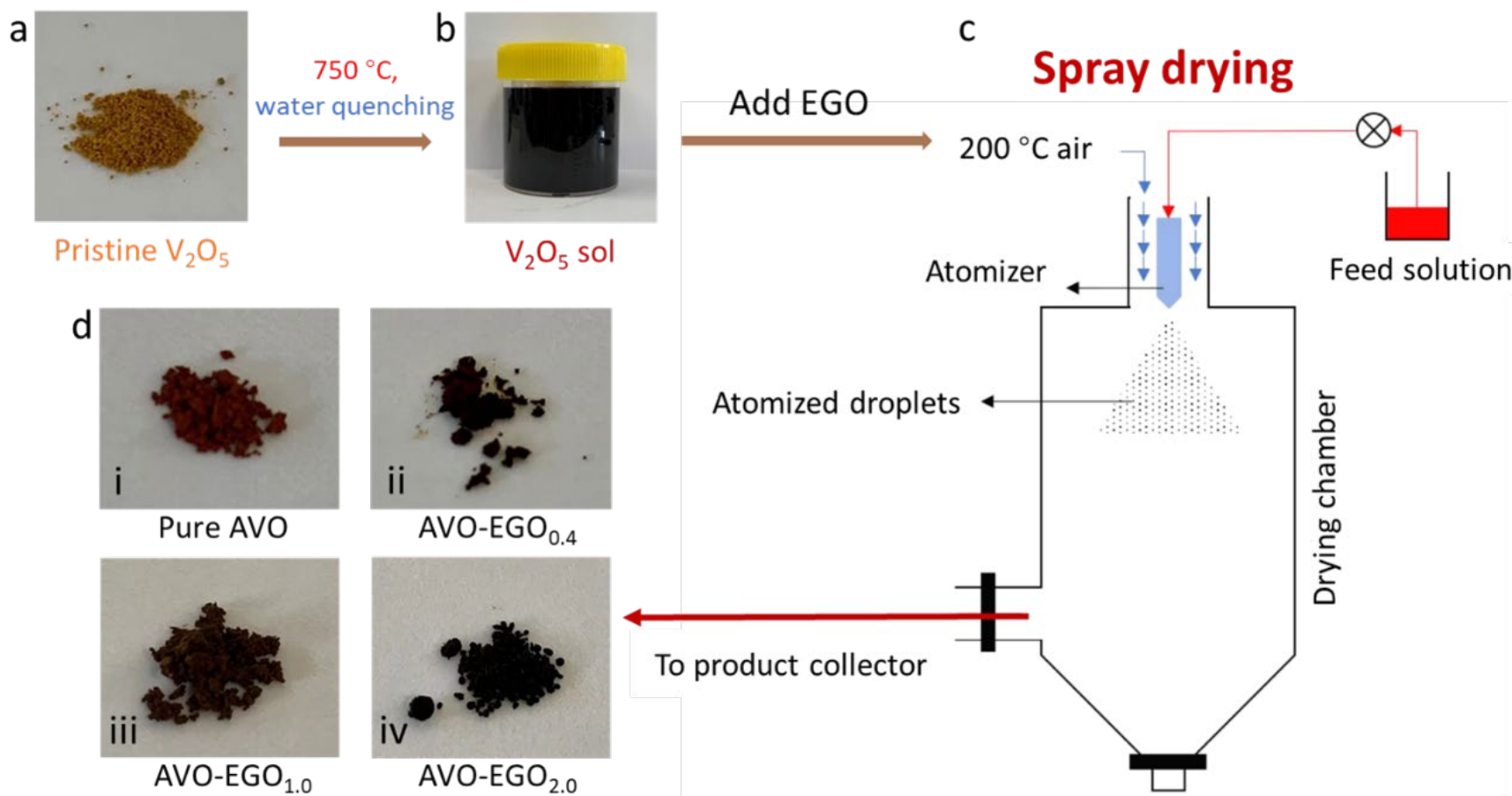
Application: Energy Storage

Yubai Zhang, Jiadong Qin... Y. L. Zhong [Enhanced electrochemical production and facile modification of graphite oxide for cost-effective sodium ion battery anodes](#) *Carbon* **177**, 71-78 (2021)

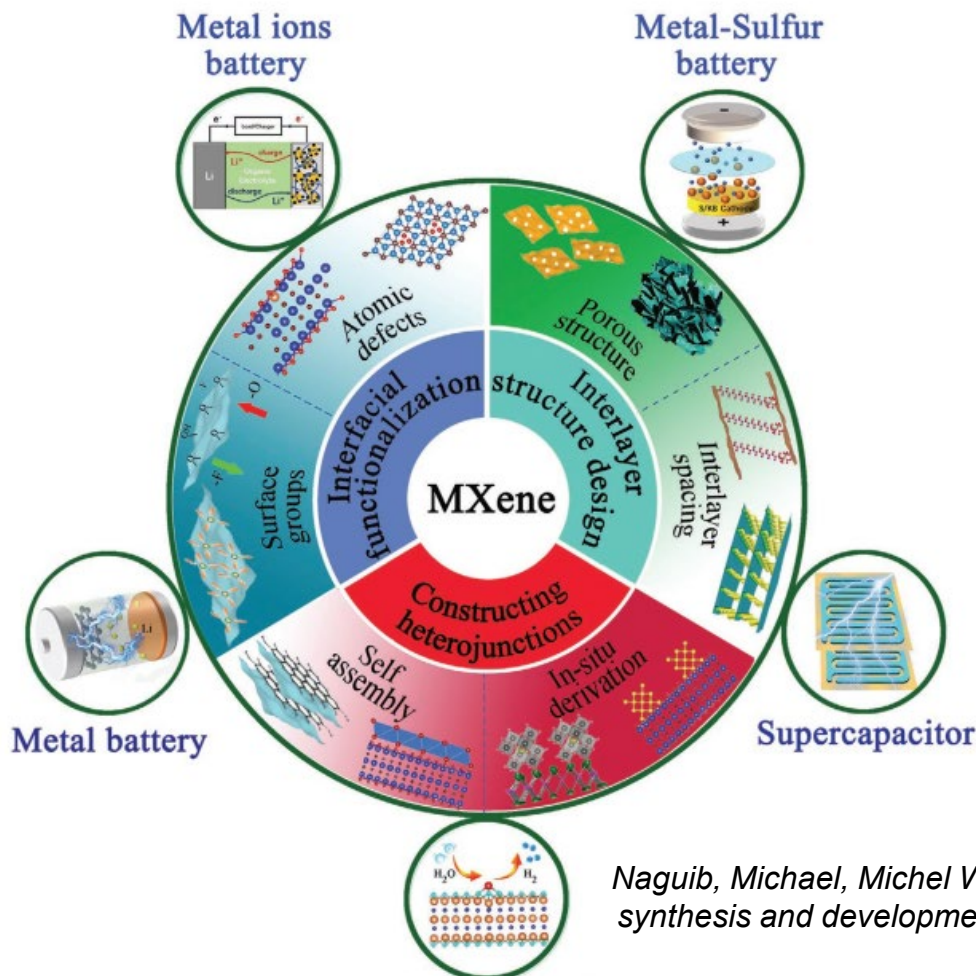


Yubai Zhang, Jiadong Qin... Y. L. Zhong Scalable Spray Drying Production of Amorphous V_2O_5 -EGO 2D Heterostructured Xerogels for High-Rate and High-Capacity Aqueous Zinc Ion Batteries

Small **18**, 2105761 (2022)



MXene-based nanomaterials and their applications in electrochemical energy storage



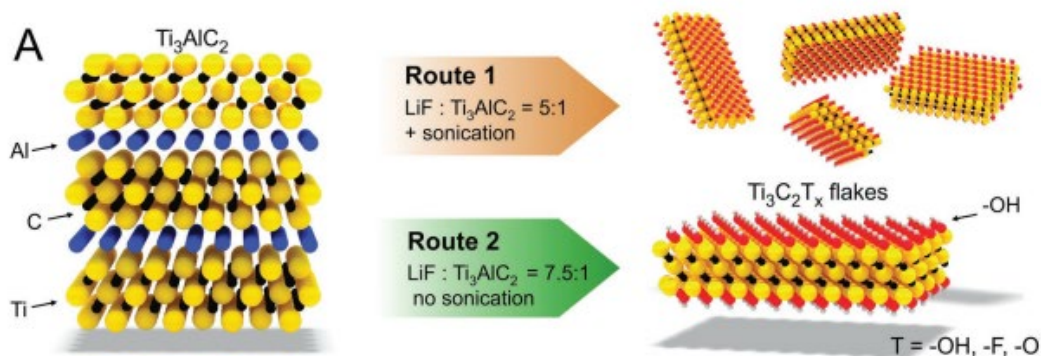
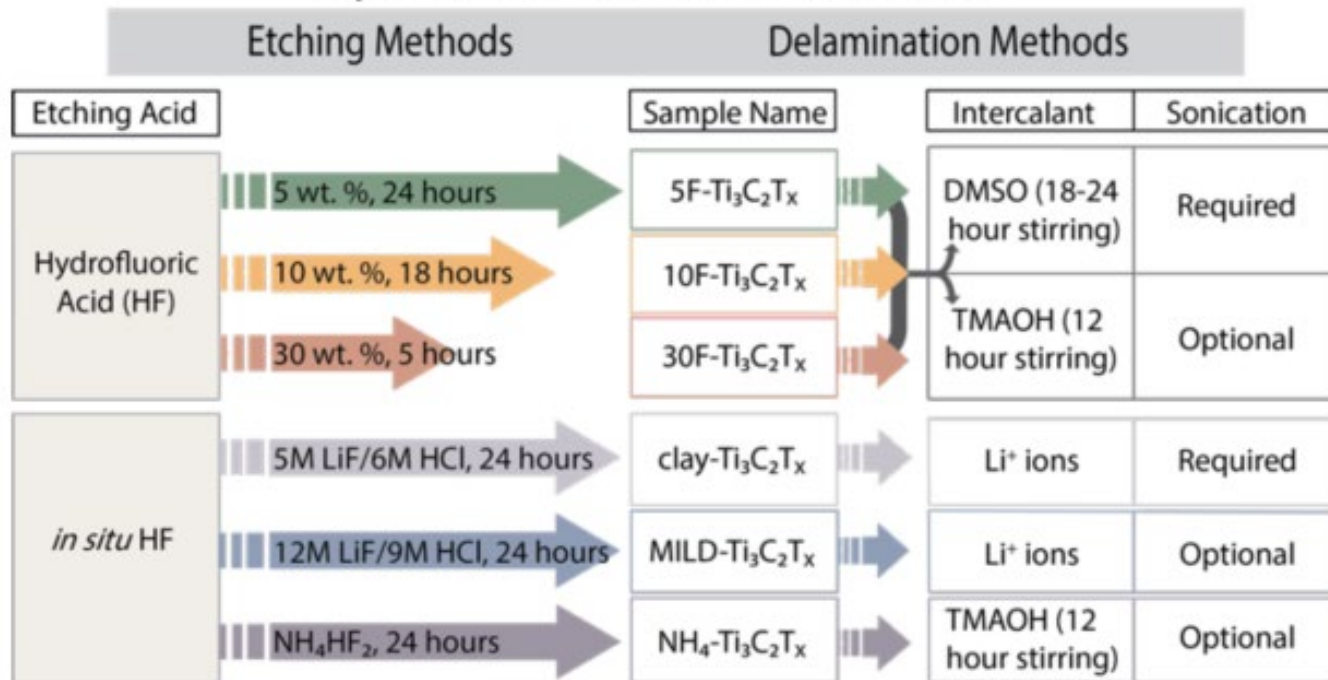
Merits of MXenes

- ❖ Excellent electrical conductivity
- ❖ Tunable layer structure
- ❖ Hydrophilic surface

Naguib, Michael, Michel W. Barsoum, and Yury Gogotsi. "Ten years of progress in the synthesis and development of MXenes." *Advanced Materials* 33.39 (2021): 2103393.

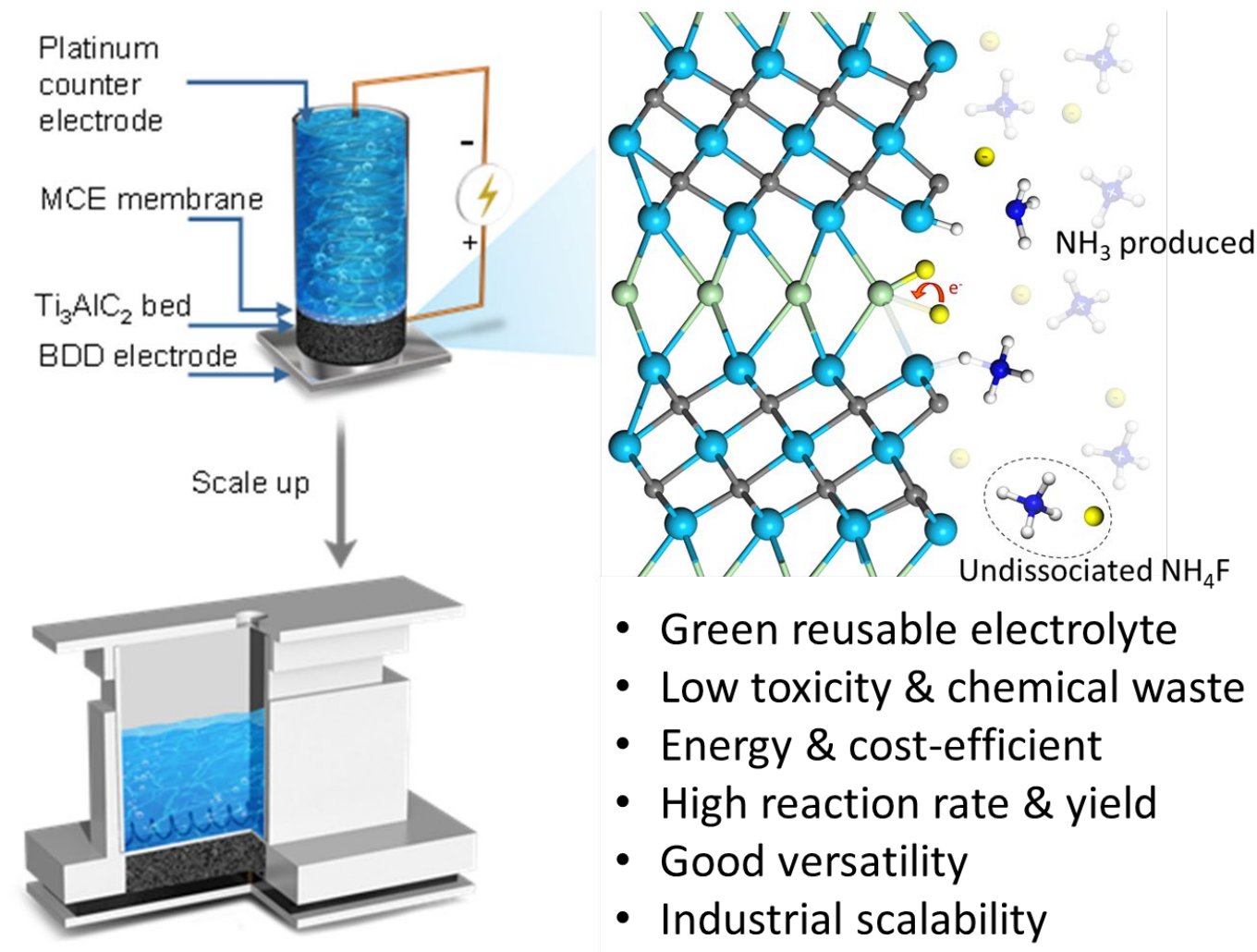
Electrocatalysis Hui, Xiaobin, et al. "Interface Chemistry on MXene-Based Materials for Enhanced Energy Storage and Conversion Performance." *Advanced Functional Materials* (2020): 2005190.

Synthesis of $Ti_3C_2T_x$ MXene

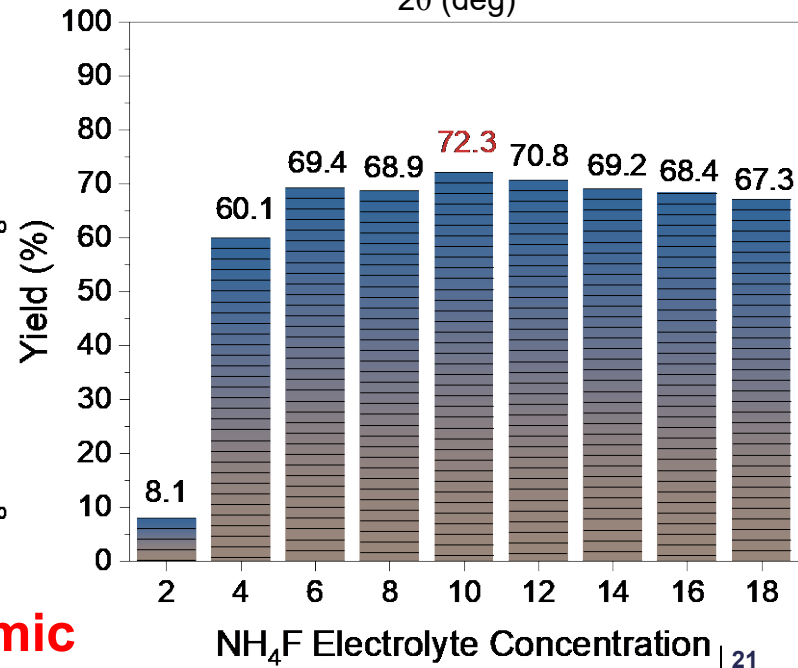
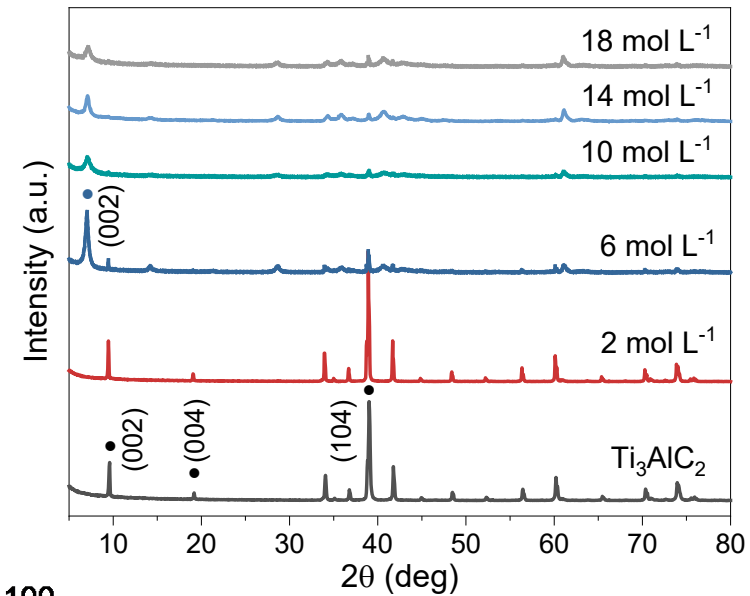
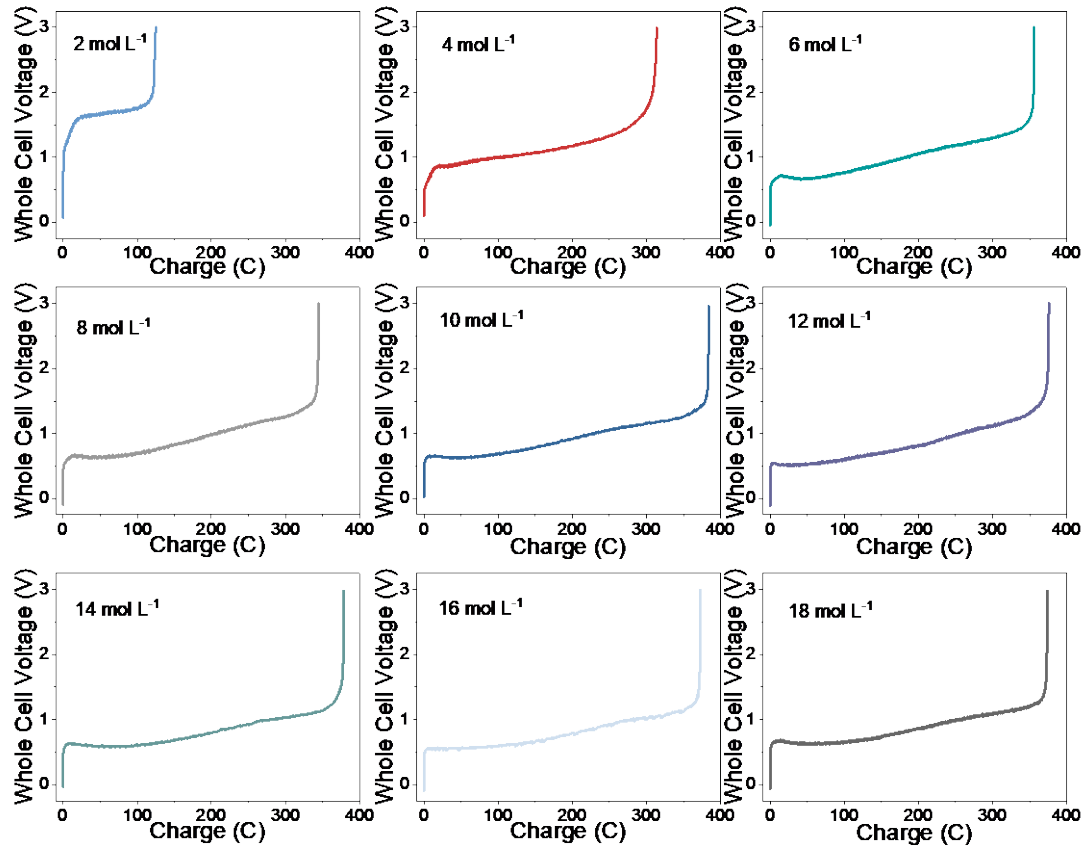


Alhabej, Mohamed, et al. "Guidelines for synthesis and processing of two-dimensional titanium carbide ($Ti_3C_2T_x$ MXene)." *Chemistry of Materials* 29.18 (2017): 7633-7644.

Zimo Huang, ... Y. L. Zhong [A Green and Scalable Electrochemical Route for Cost-Effective Mass Production of MXenes for Supercapacitor Electrodes](#) *Carbon Energy* (2023) DOI: 10.1002/cey2.295

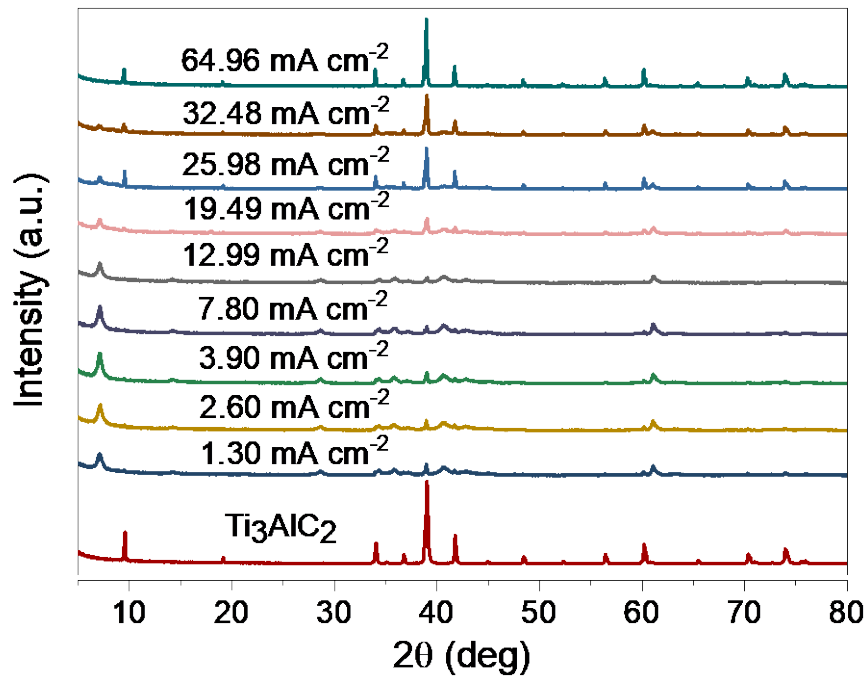
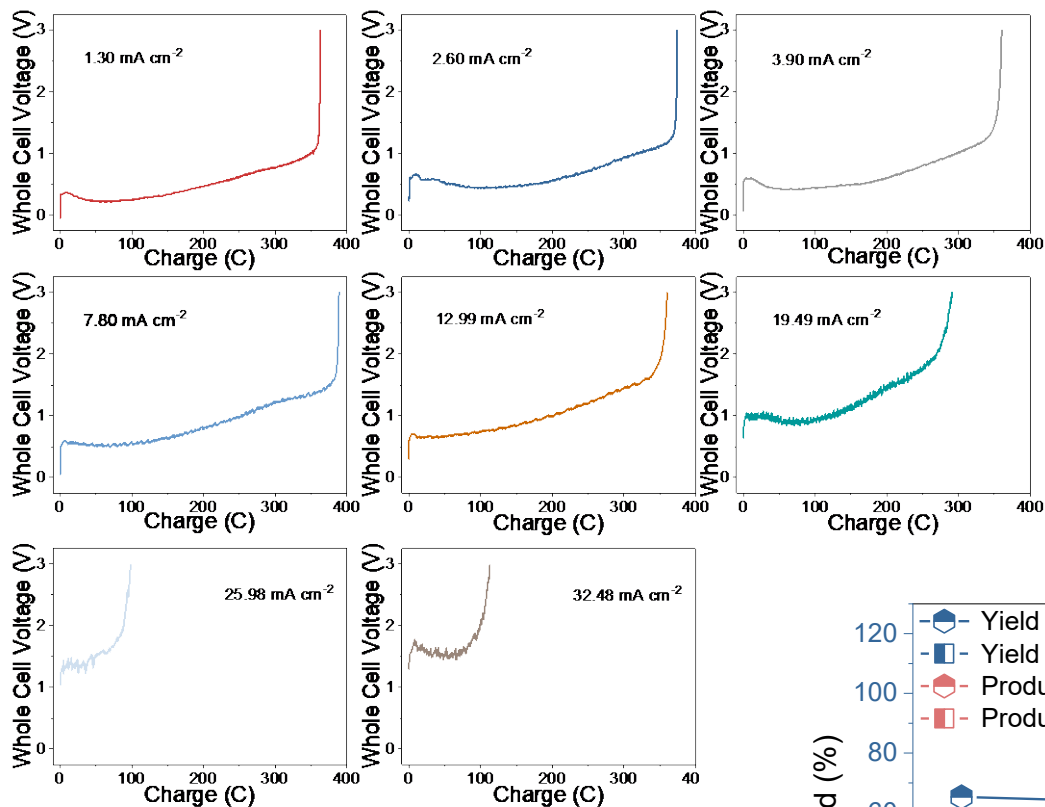


Optimization of key parameters in the electrochemical reaction (NH_4F electrolyte concentrations)

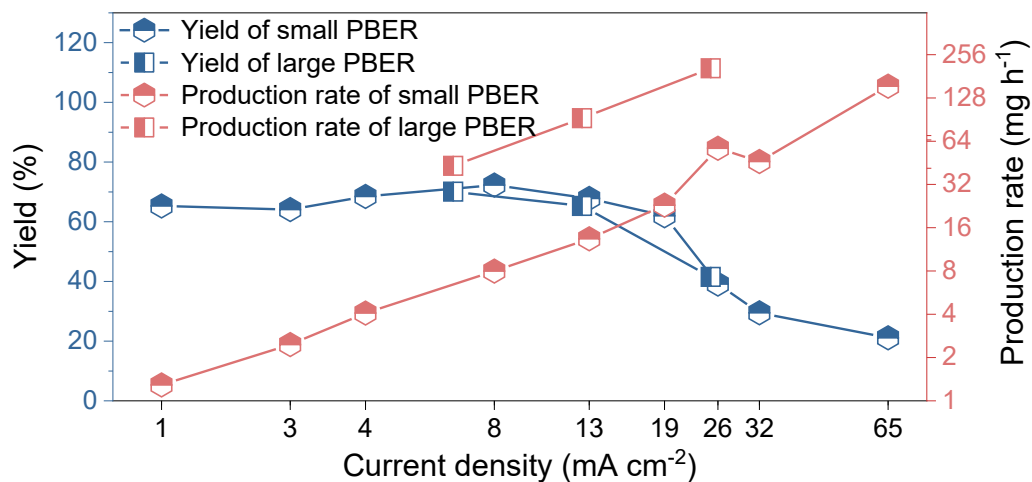


Thermodynamic

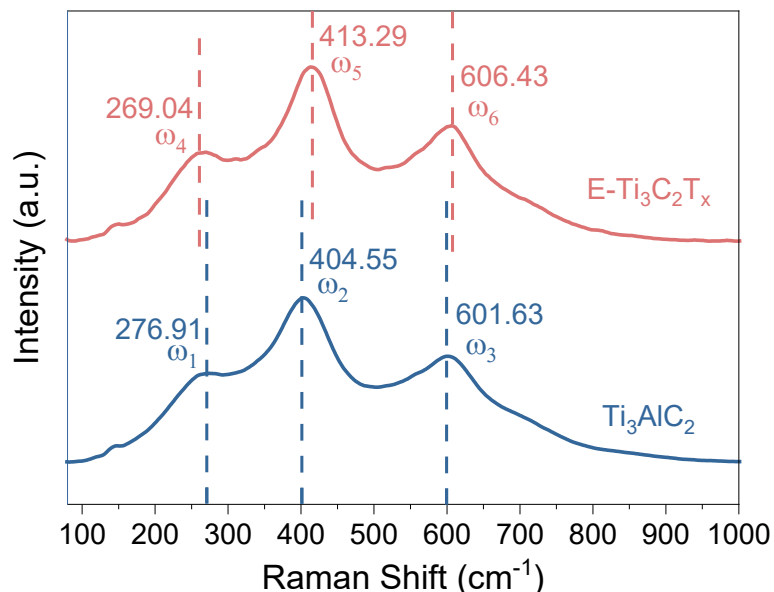
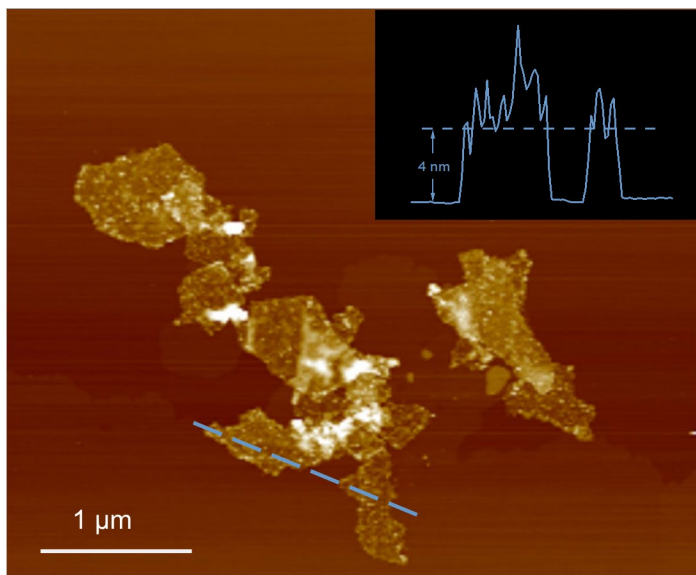
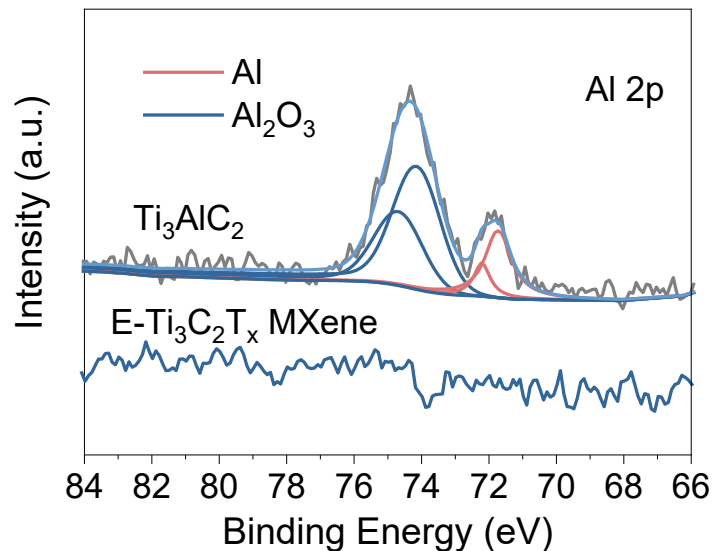
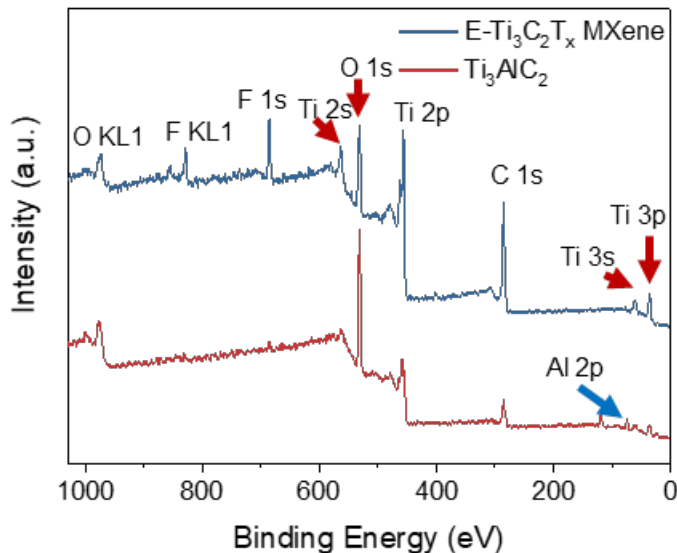
Optimization of key parameters in the electrochemical reaction (current density)



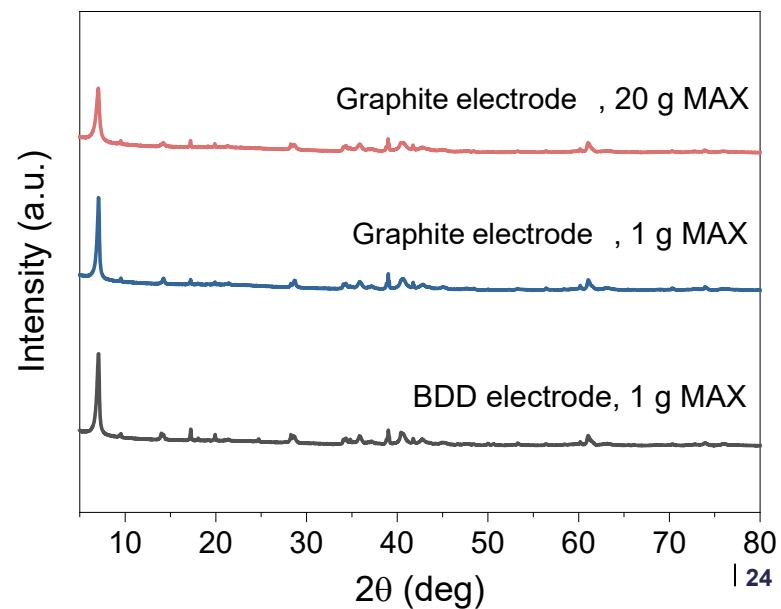
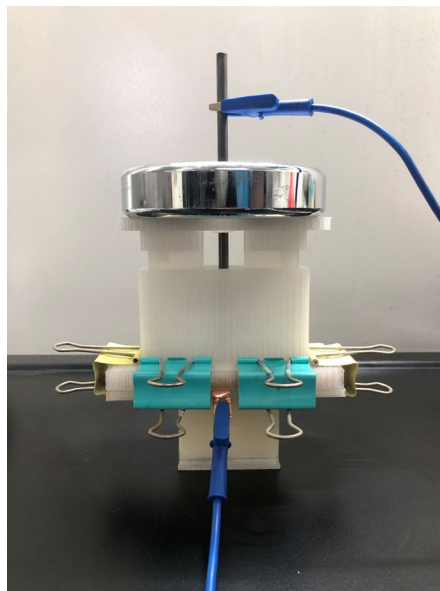
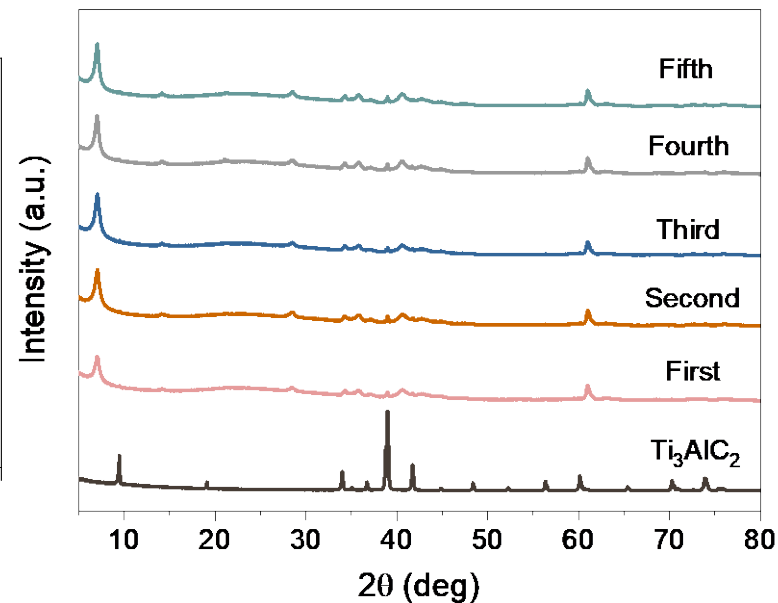
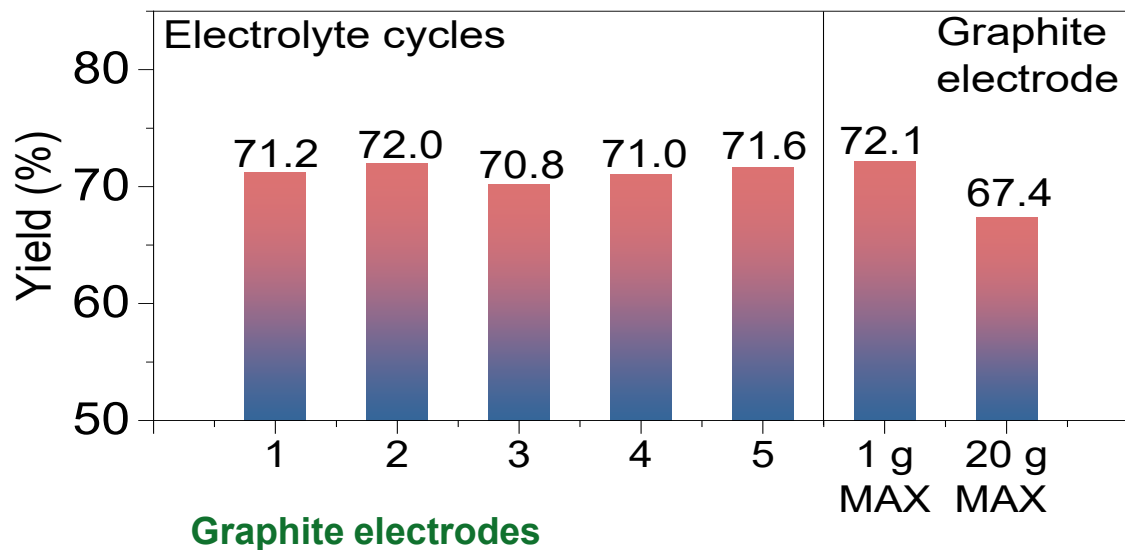
Kinetics



Characterization of $Ti_3C_2T_x$ eMXene



Cost-effectiveness of PBER

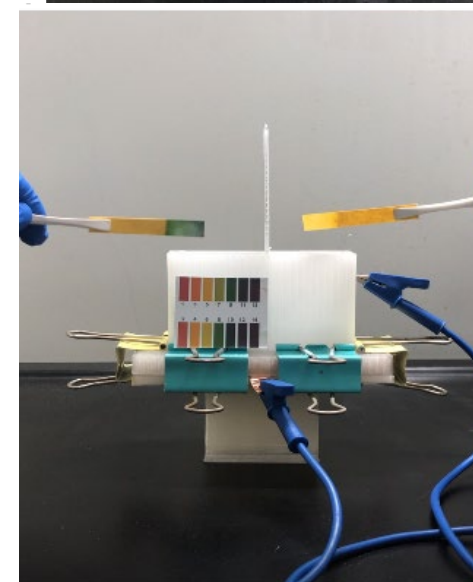
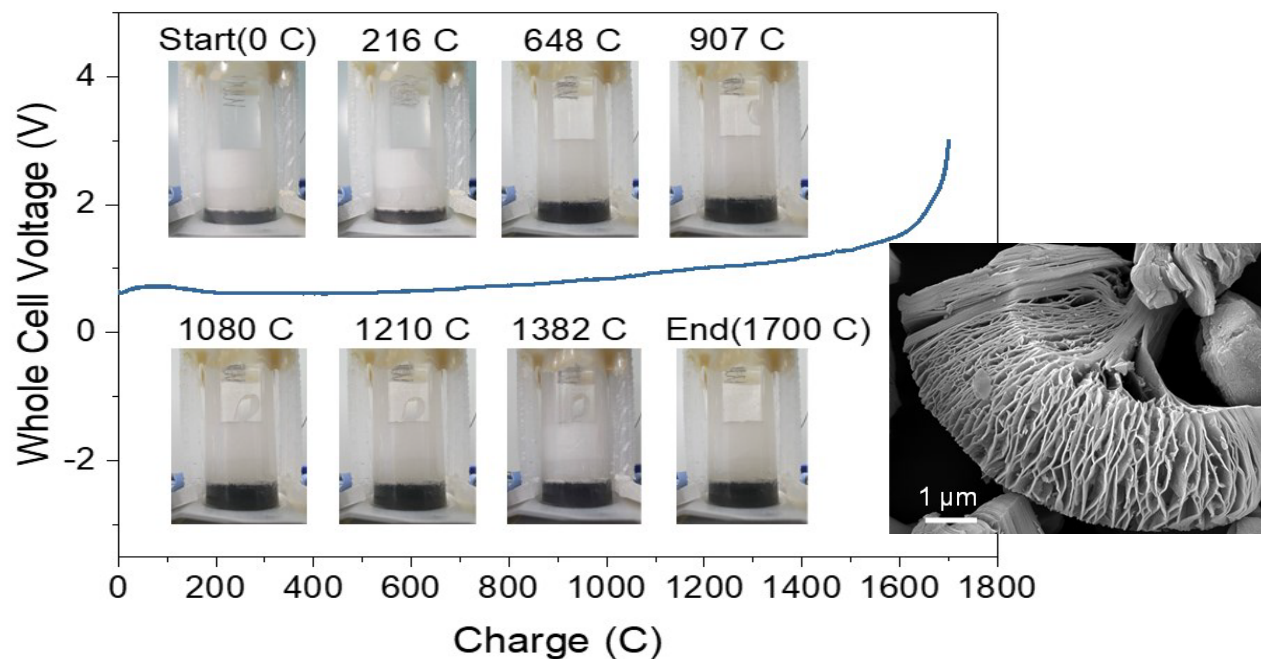
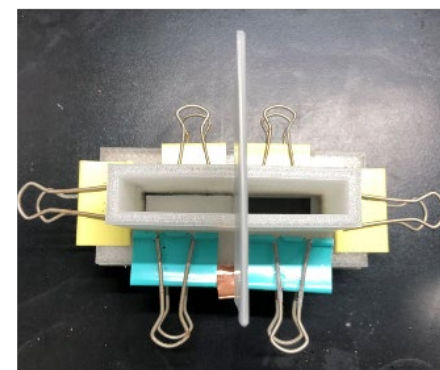
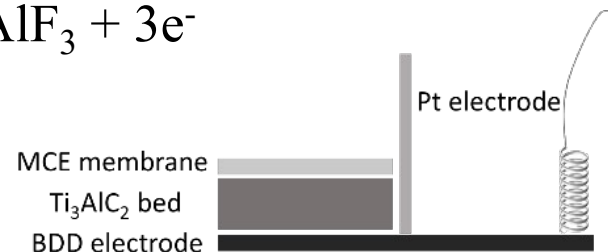
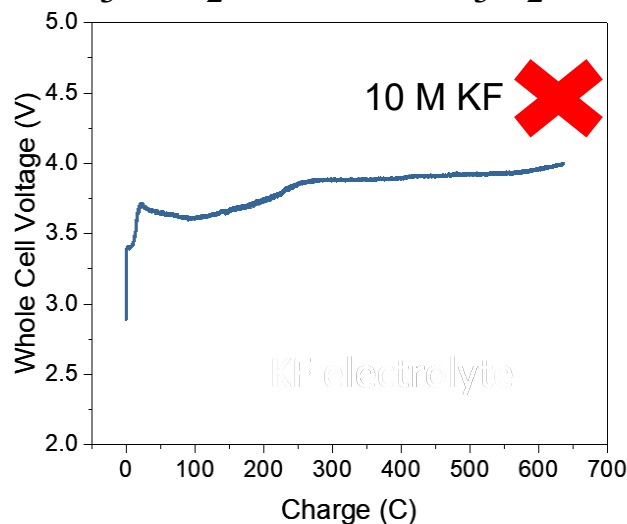


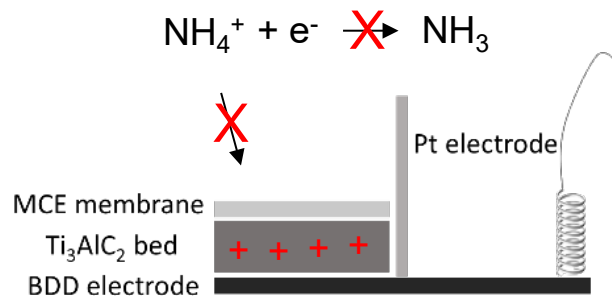
Reaction Mechanism



Observations:

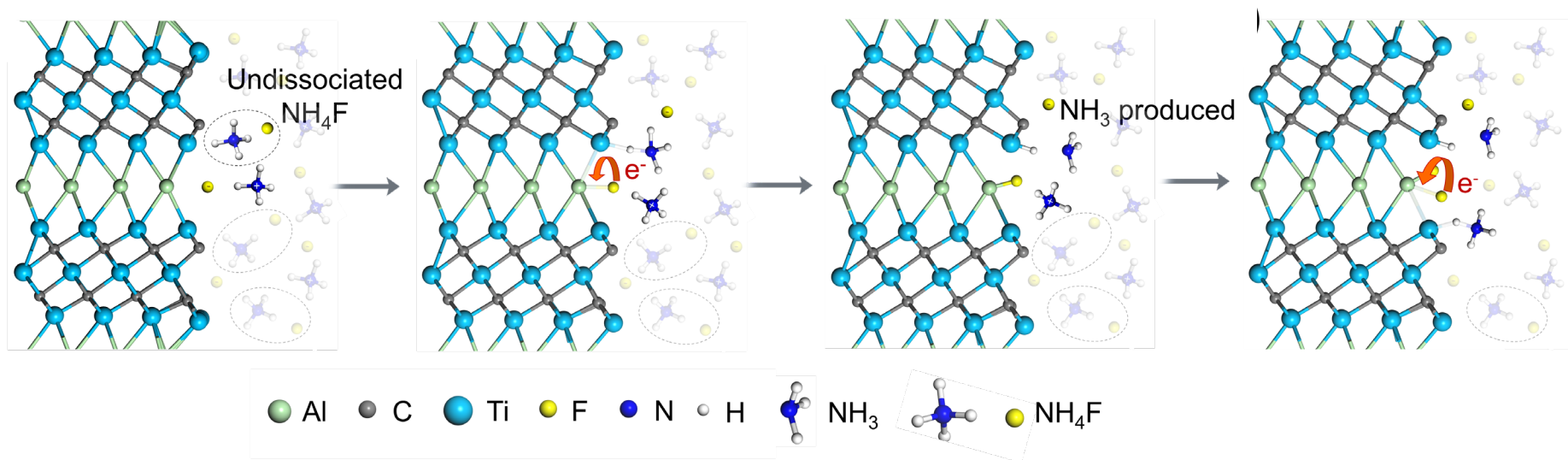
1. Electrolyte cation
2. Expanded MAX
3. Gas evolution



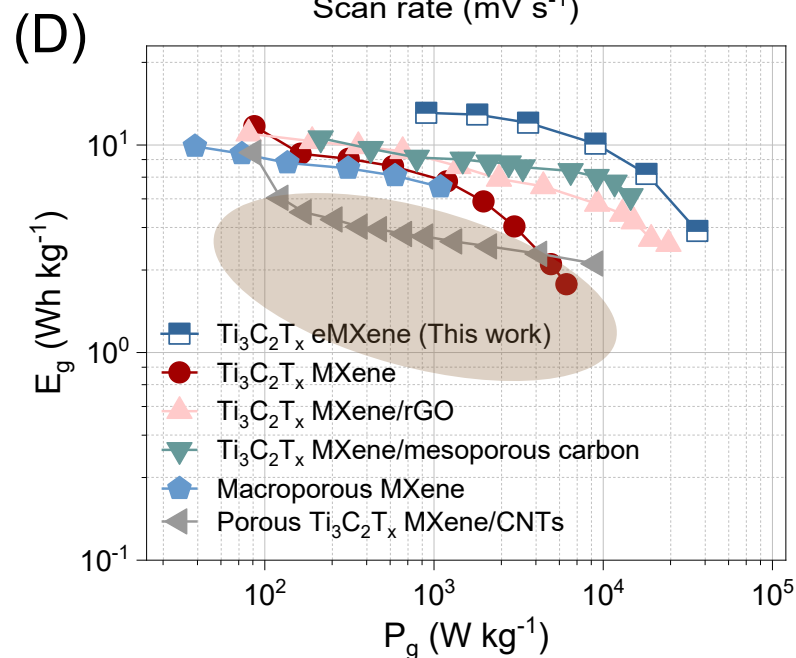
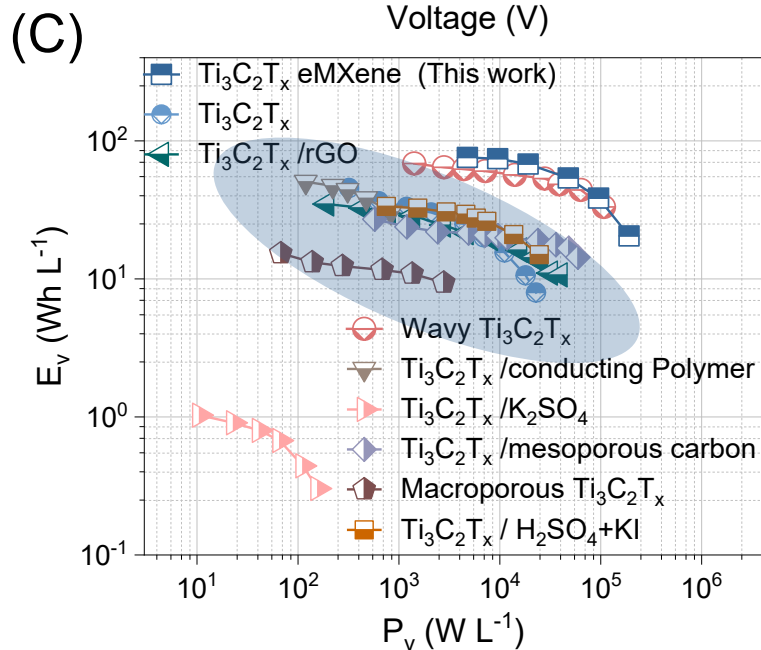
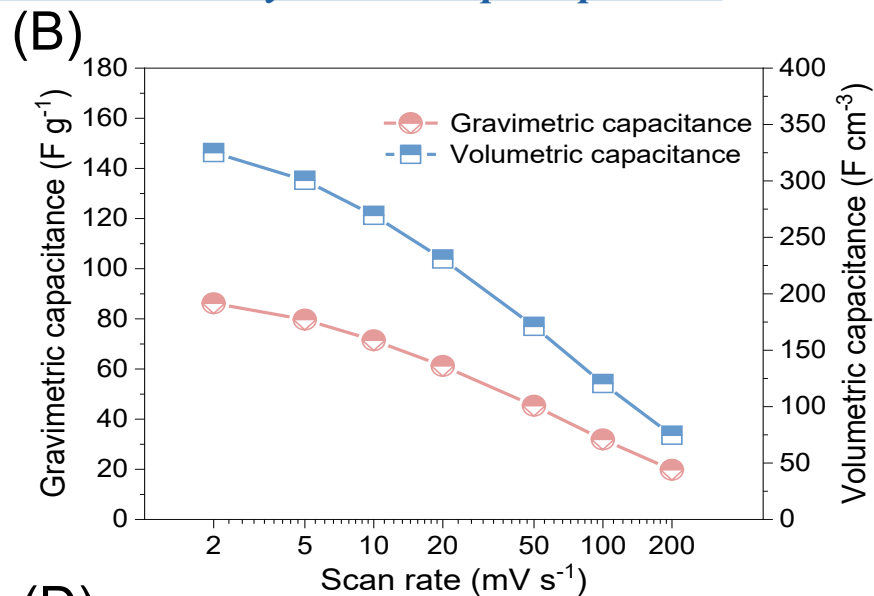
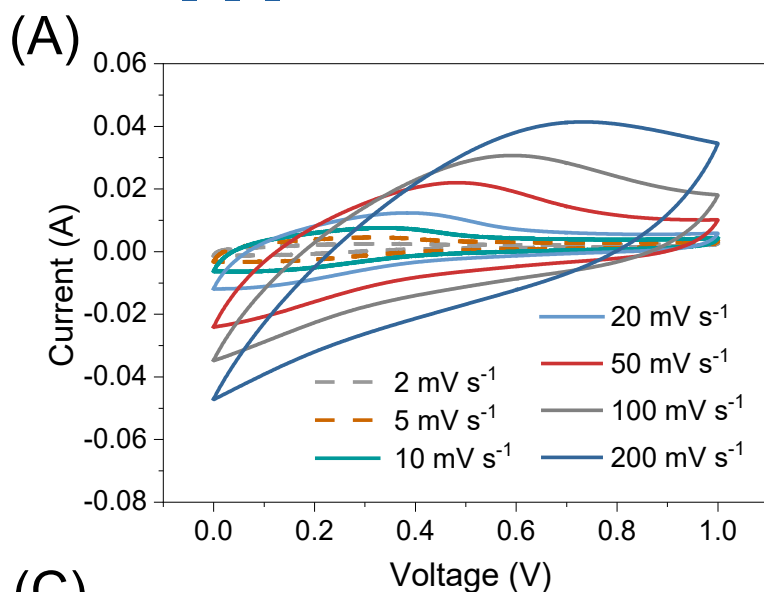


$K_{\text{sp}}(\text{NH}_4\text{F}) = 44$: 10M NH_4F contains 1.6M undissociated NH_4F
 2M NH_4F contains 0.08M undissociated NH_4F

$K_{\text{sp}}(\text{KF}) = 11606$: 10M KF contains 0.0086M undissociated KF

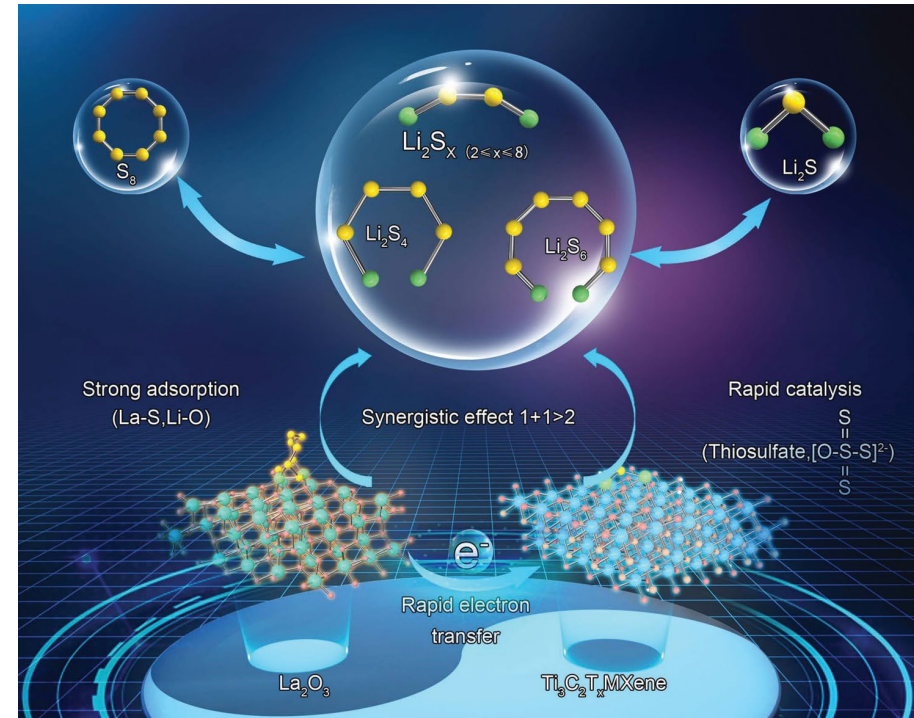
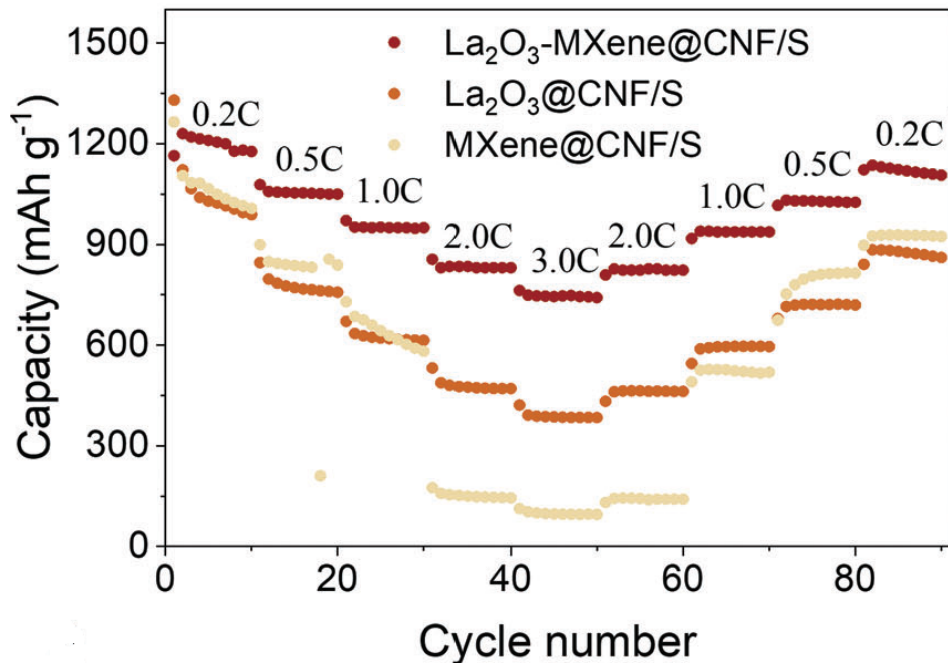
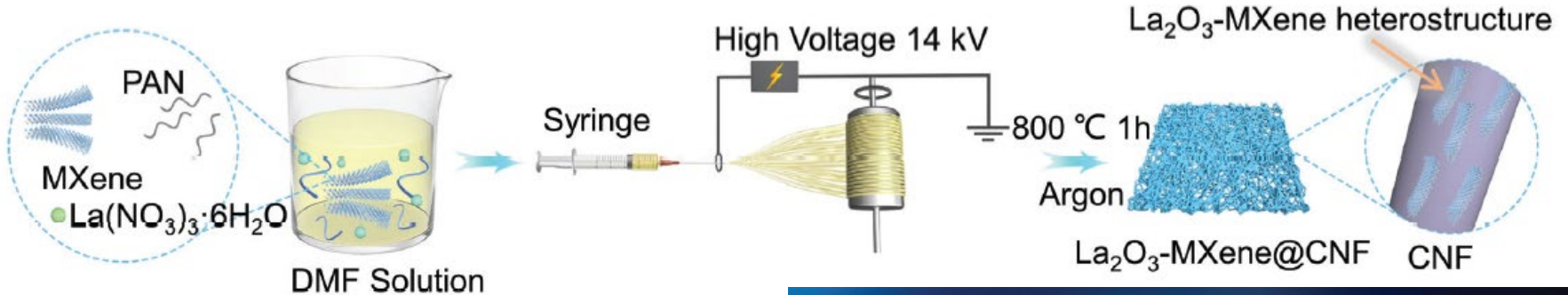


The $Ti_3C_2T_x$ free-standing membrane in two-electrode symmetric supercapacitors



Application: Energy Storage

Zimo Huang, ... Shanqing Zhang, Y. L. Zhong [Efficient Synergism of Chemisorption and Wackenroder Reaction via Heterostructured \$\text{La}_2\text{O}_3\text{-Ti}_3\text{C}_2\text{T}_x\$ -Embedded Carbon Nanofiber for High-Energy Lithium-Sulfur Pouch Cells](#) *Adv. Funct. Mater.* (2023) DOI: 10.1002/adfm.202303422

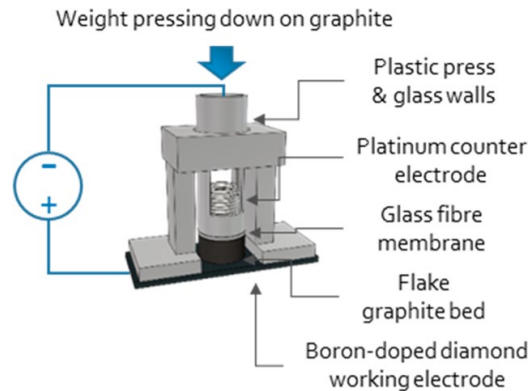


Electrochemical Engineering of Nanomaterials

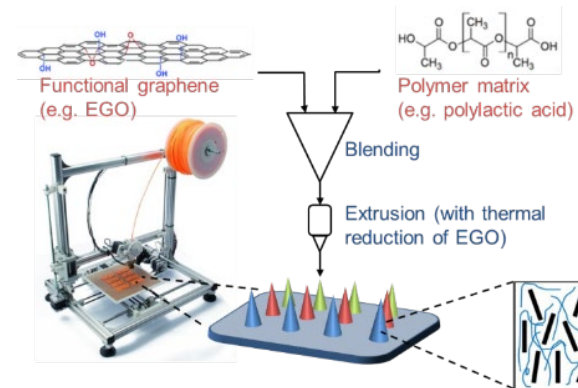


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DE140101662 - Non-Oxidative and Scalable Electrochemical Production of Functional Graphene and its Nano hybrids

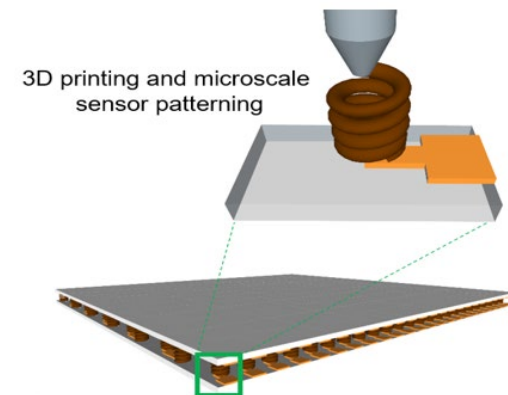
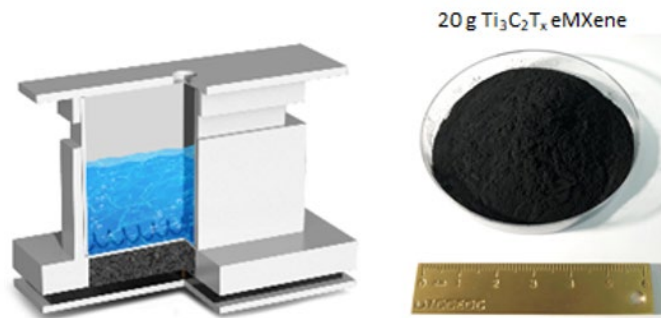


DP170104157 - Tailoring Nanocomposites with Controllable Structural-Property Relationship



DP190100120 - Towards High-Performance Wearable Devices: Materials and Microfabrication

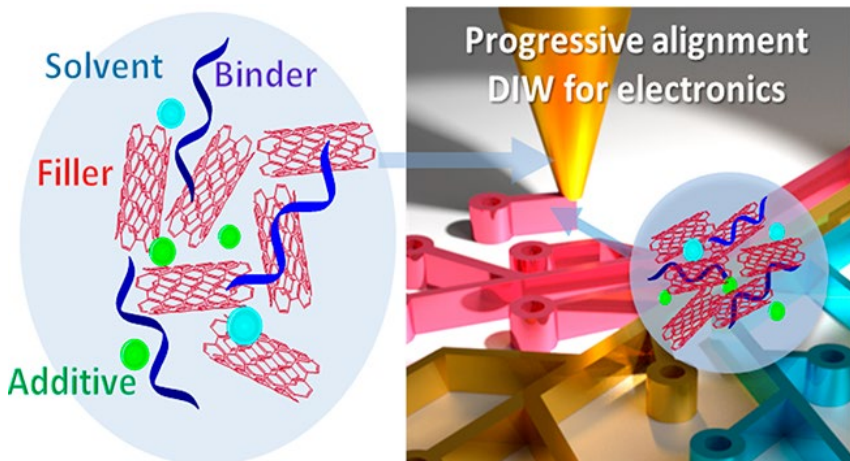
FT200100015 - Advancing Green Electrochemical Engineering of Functional 2D Nanomaterials



DP240100892 - Empowering Wearable Smart Devices with 3D Printed Energy Storage

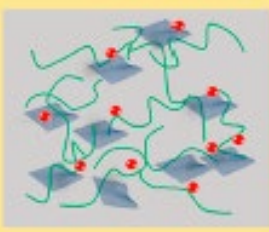
3D Direct Ink Writing

Y. Zhang, G. Shi,... Y. L. Zhong [Recent Progress of Direct Ink Writing of Electronic Components for Advanced Wearable Devices](#) *ACS Appl. Electron. Mater.* **1**, 1718-1734 (2019)




a Ink preparations

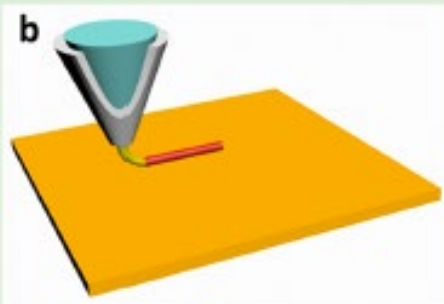
Ink Formulation



Ink Rheology



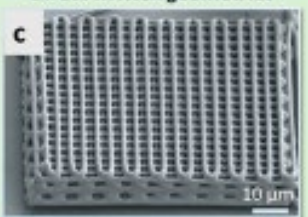
3D DIW



■ Low viscosity when extruded through the nozzle
■ Increased viscosity upon exiting the nozzle
■ High viscosity after deposition

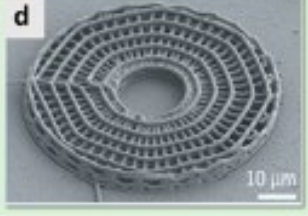
Direct written geometries

c



10 μm


d



10 μm

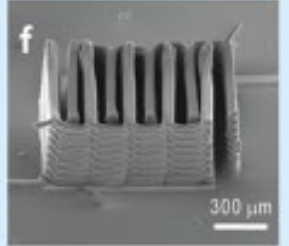
Wearable applications

e



Strain sensors

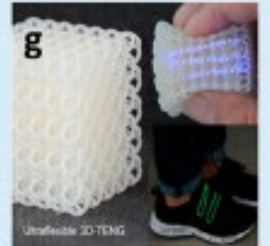
f



300 μm

Energy storage devices

g



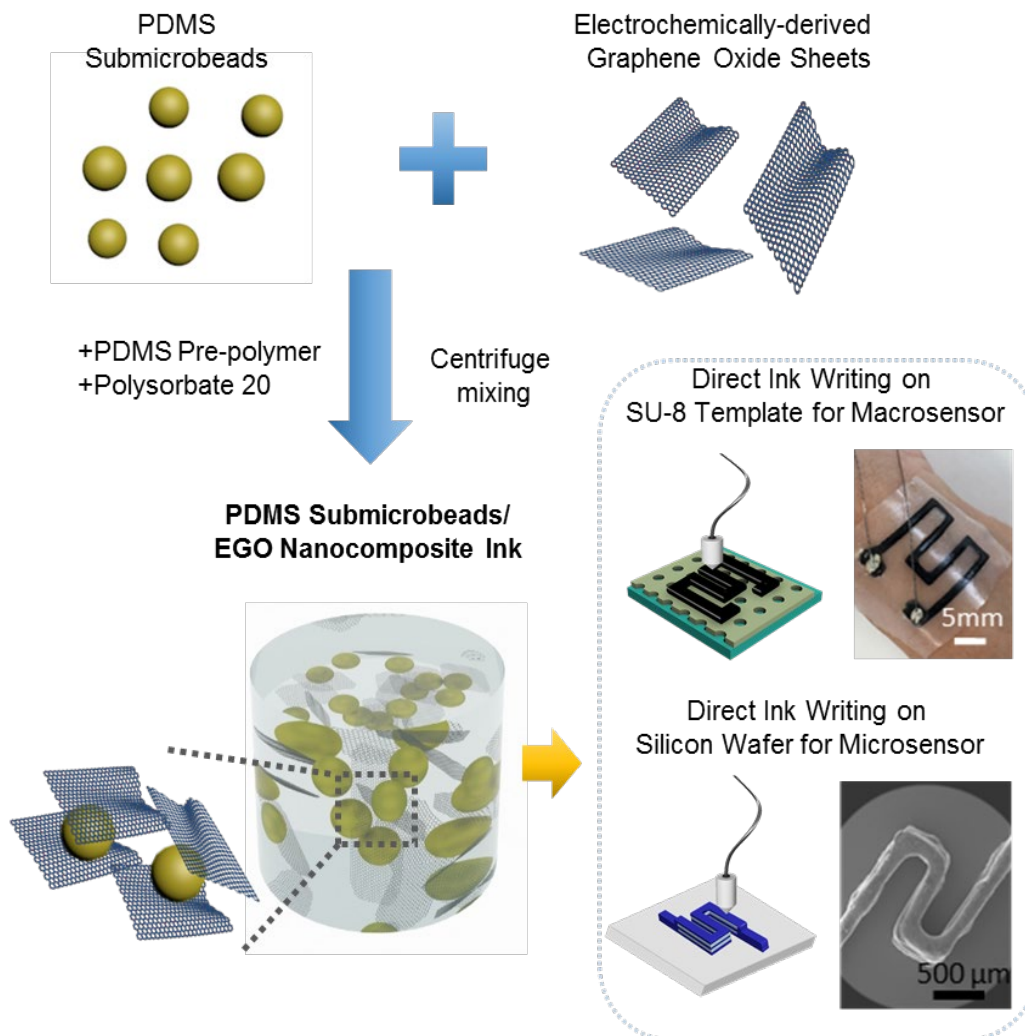
Ultraflexible 3D-TENG

Nanogenerators

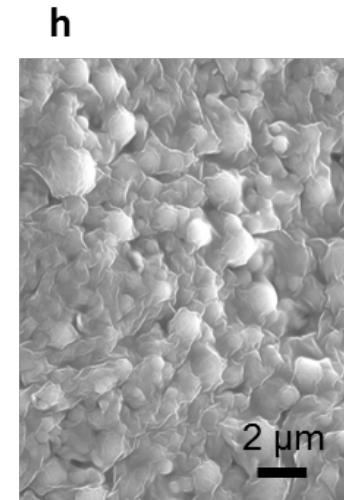
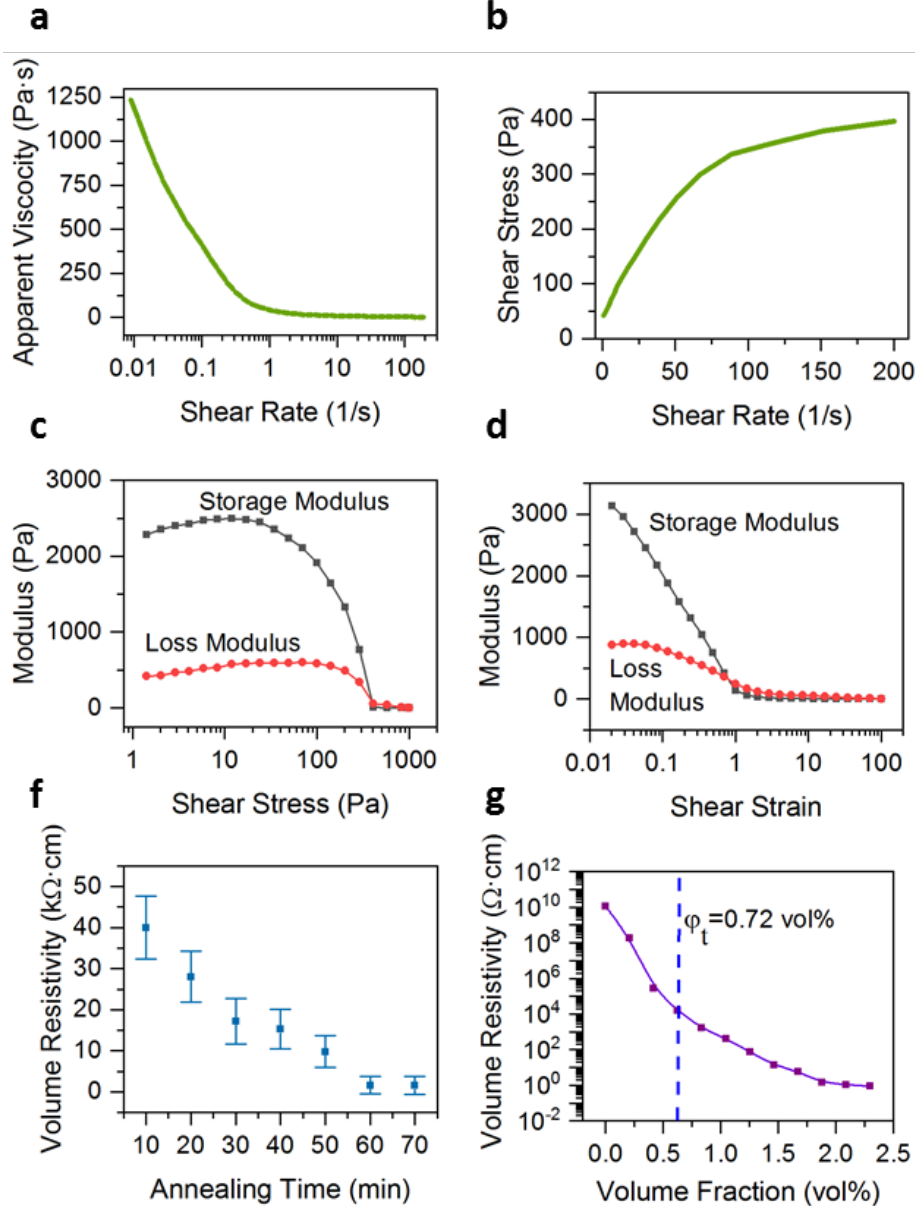
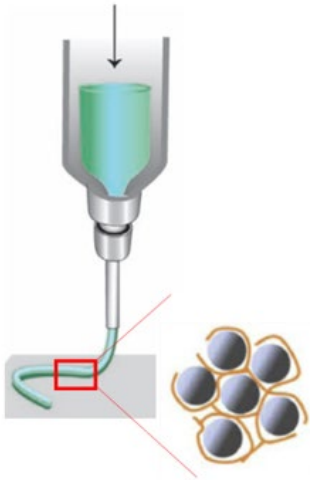
Application: Wearable Tactile Sensor

Ge Shi,... Y. L. Zhong [A Versatile PDMS Submicrobead/Graphene Oxide Nanocomposite Ink for the Direct Ink Writing of Wearable Micron-Scale Tactile Sensors](#) *Appl. Mater. Today* **16**, 482-492

(2019)

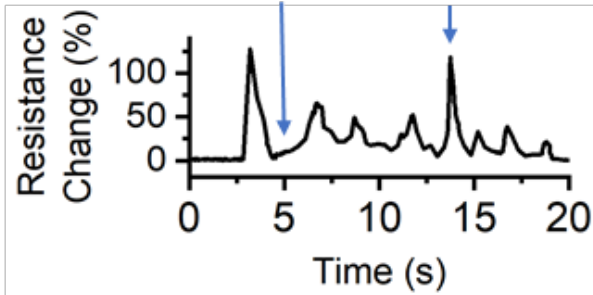


Application: Wearable Tactile Sensor

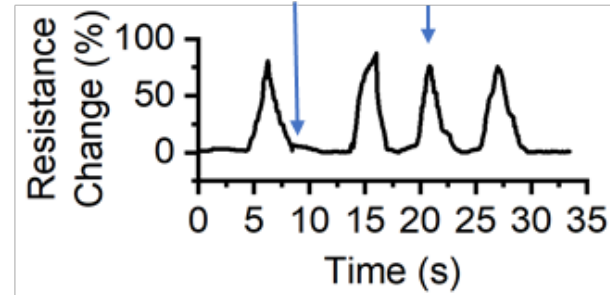
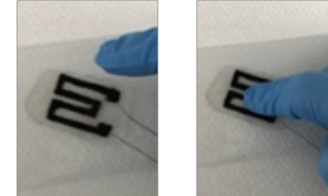


Application: Wearable Tactile Sensor

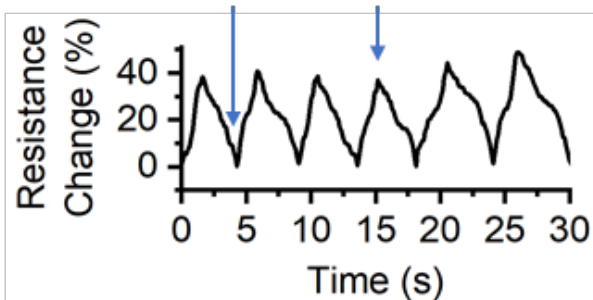
a Elbow Bend



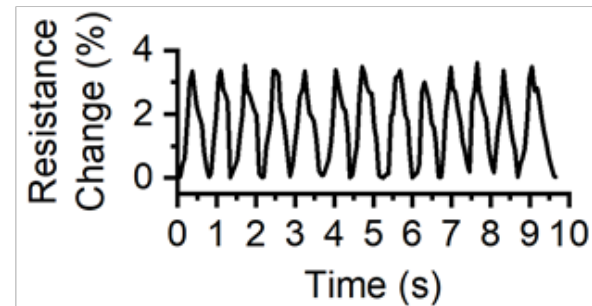
b Finger press



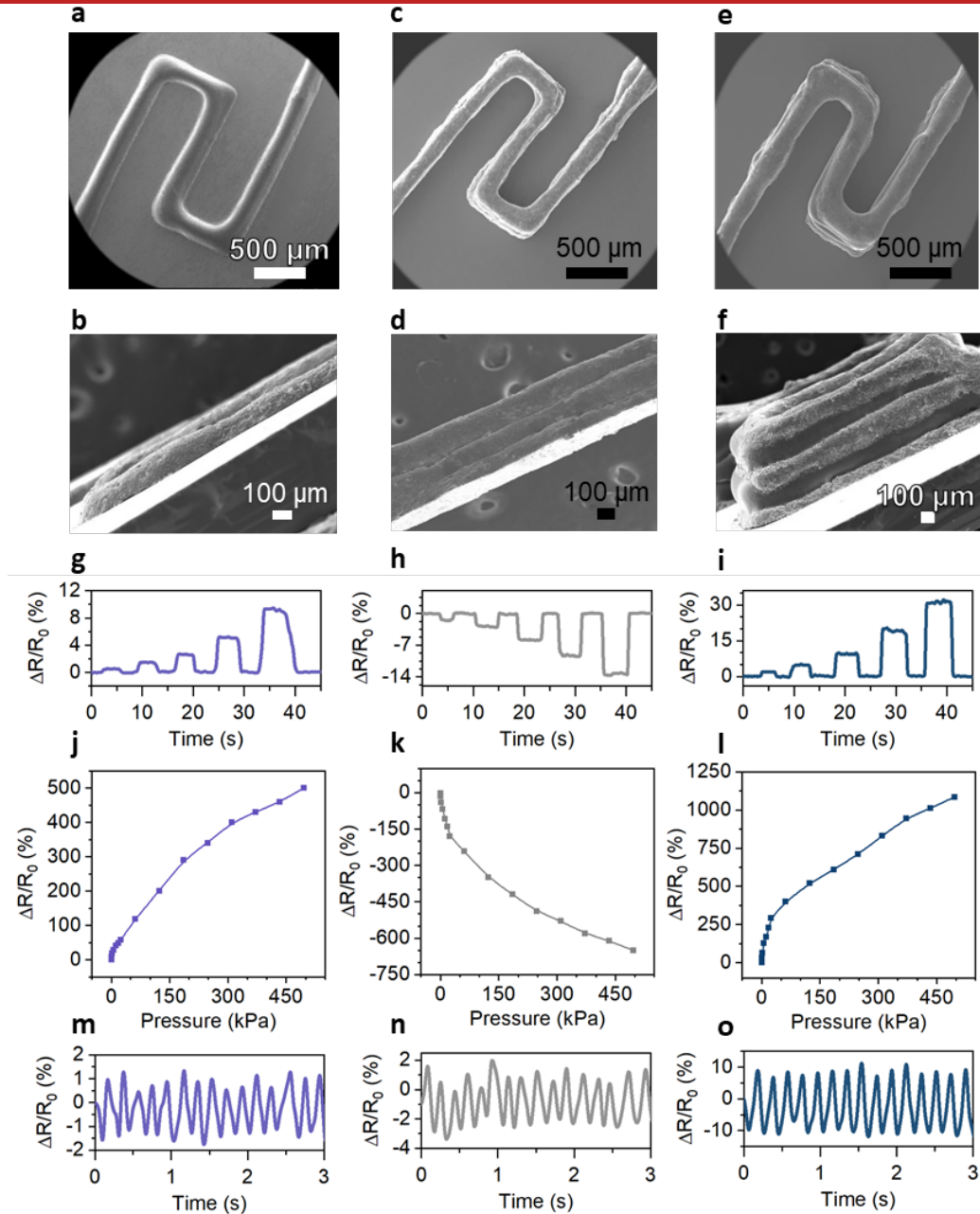
c Finger Bend



d Ulnar Pulse

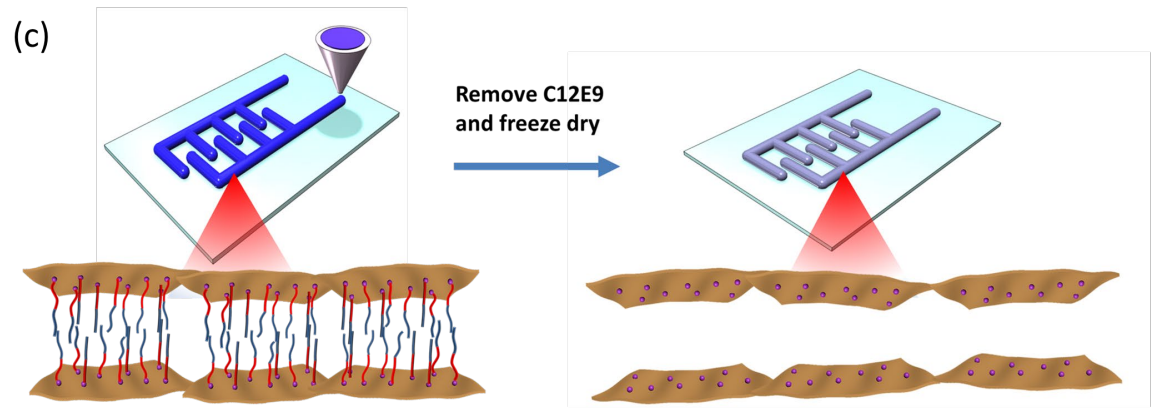
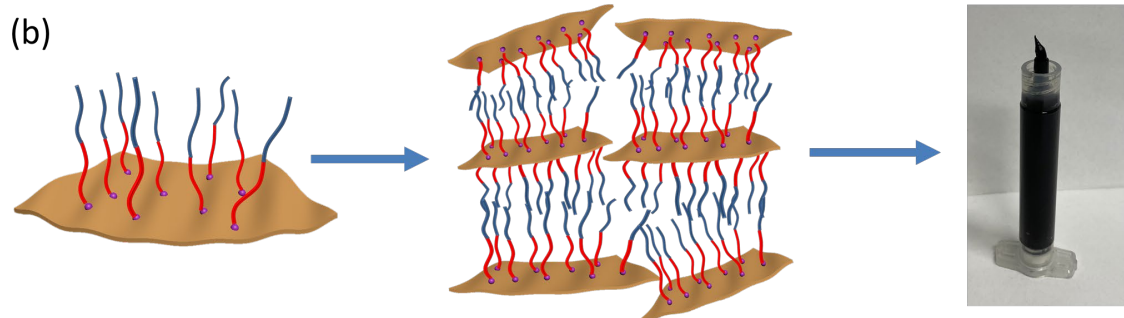
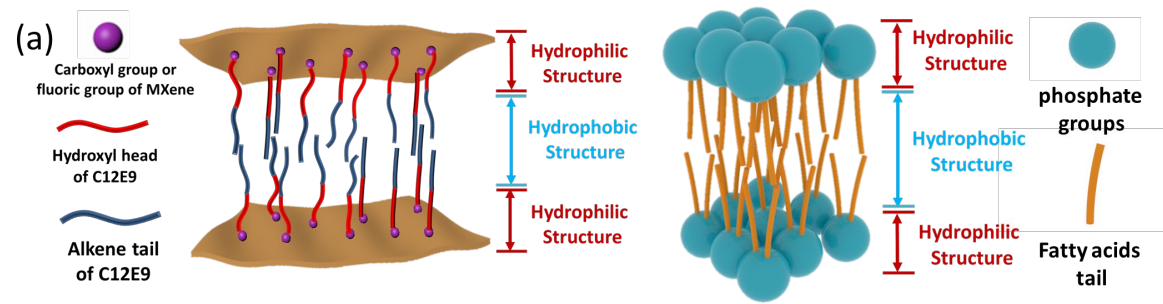


Multicomponent 3D DIW

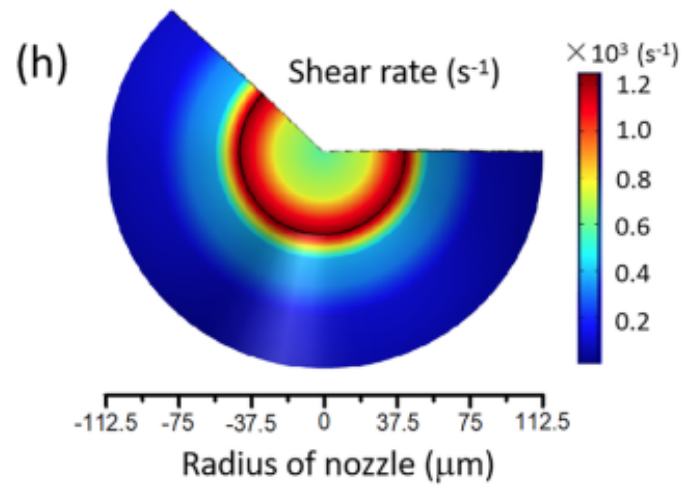
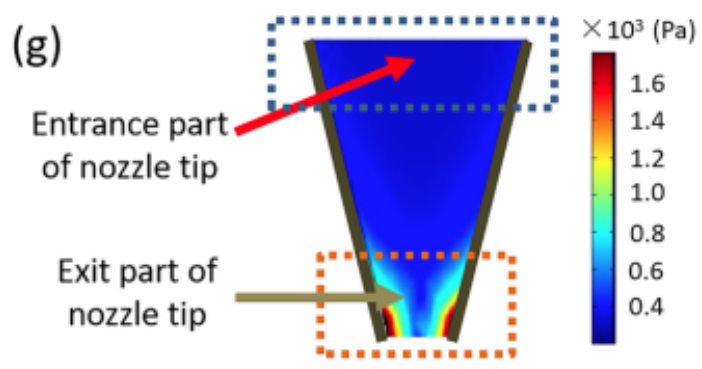
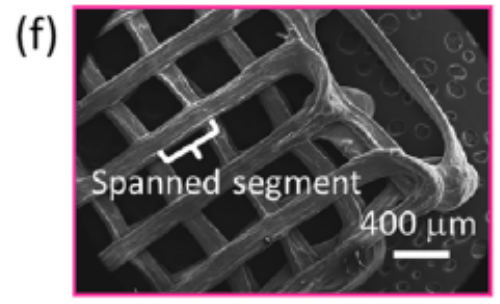
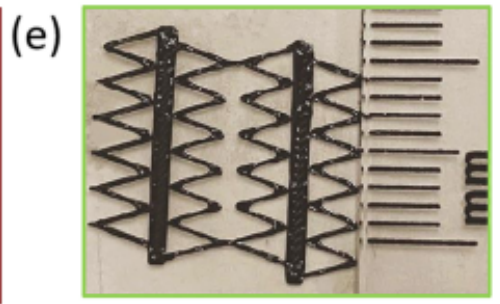
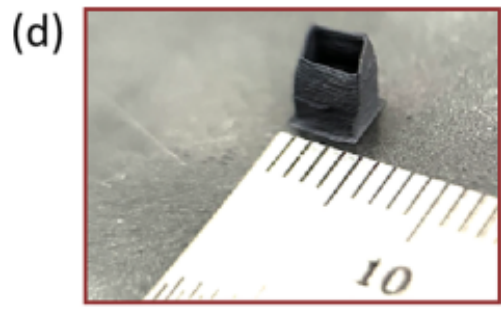
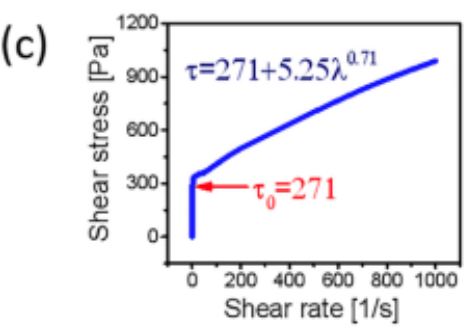
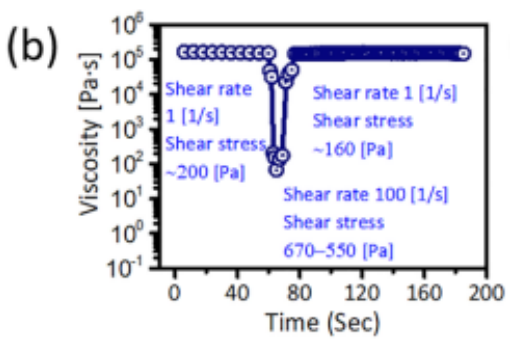
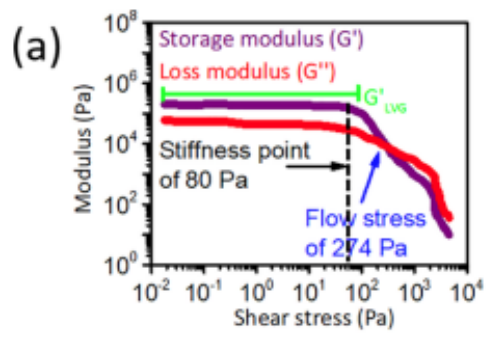


Application: Flexible Energy Storage

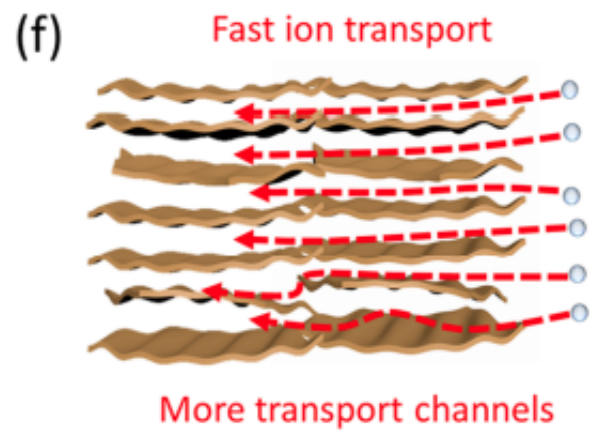
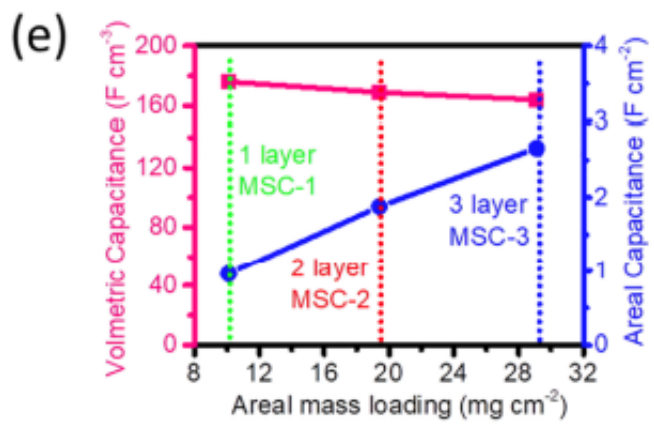
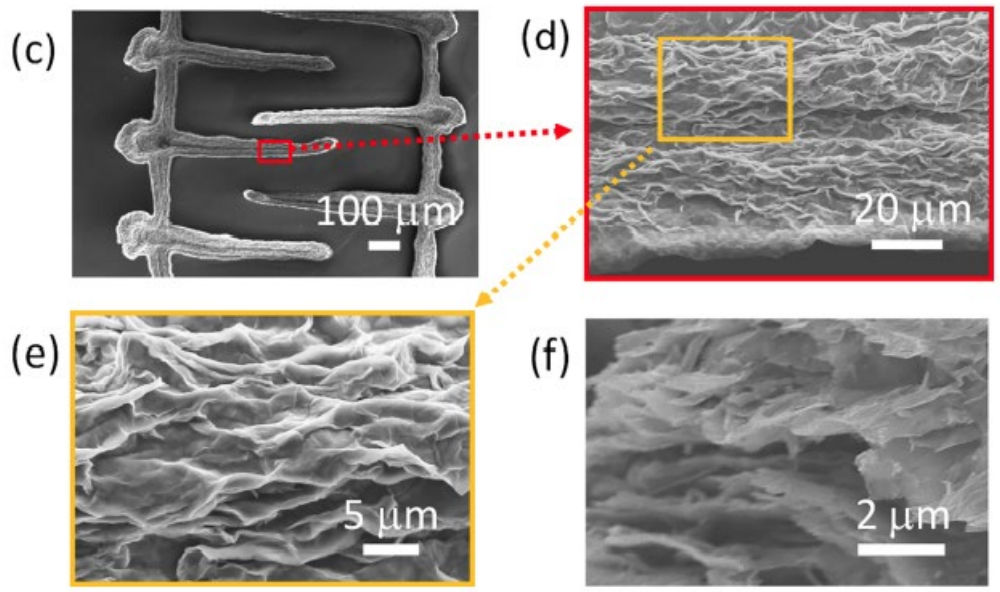
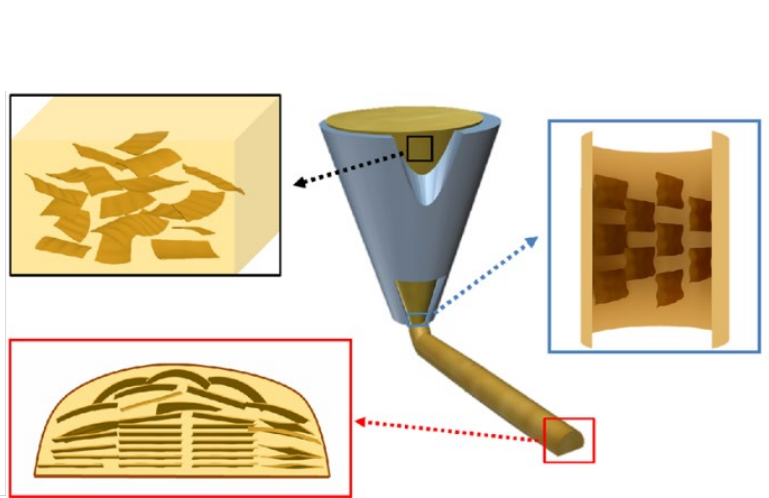
Ge Shi,... Y. L. Zhong [Cytomembrane-Inspired MXene Ink with Amphiphilic Surfactant for 3D Printed Microsupercapacitors](#) *ACS Nano* 16, 14723-14736 (2022)



Application: Flexible Energy Storage

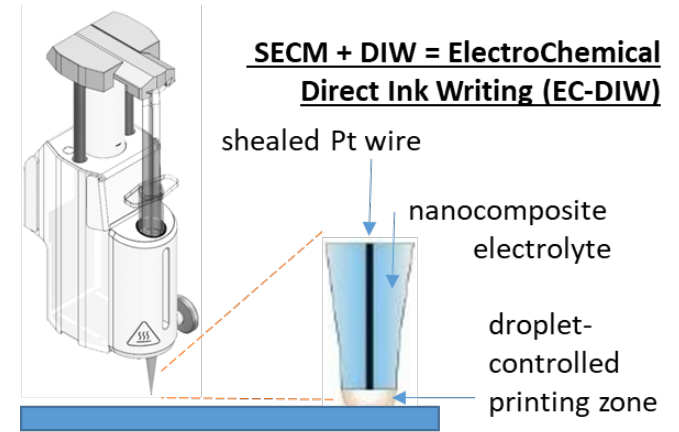
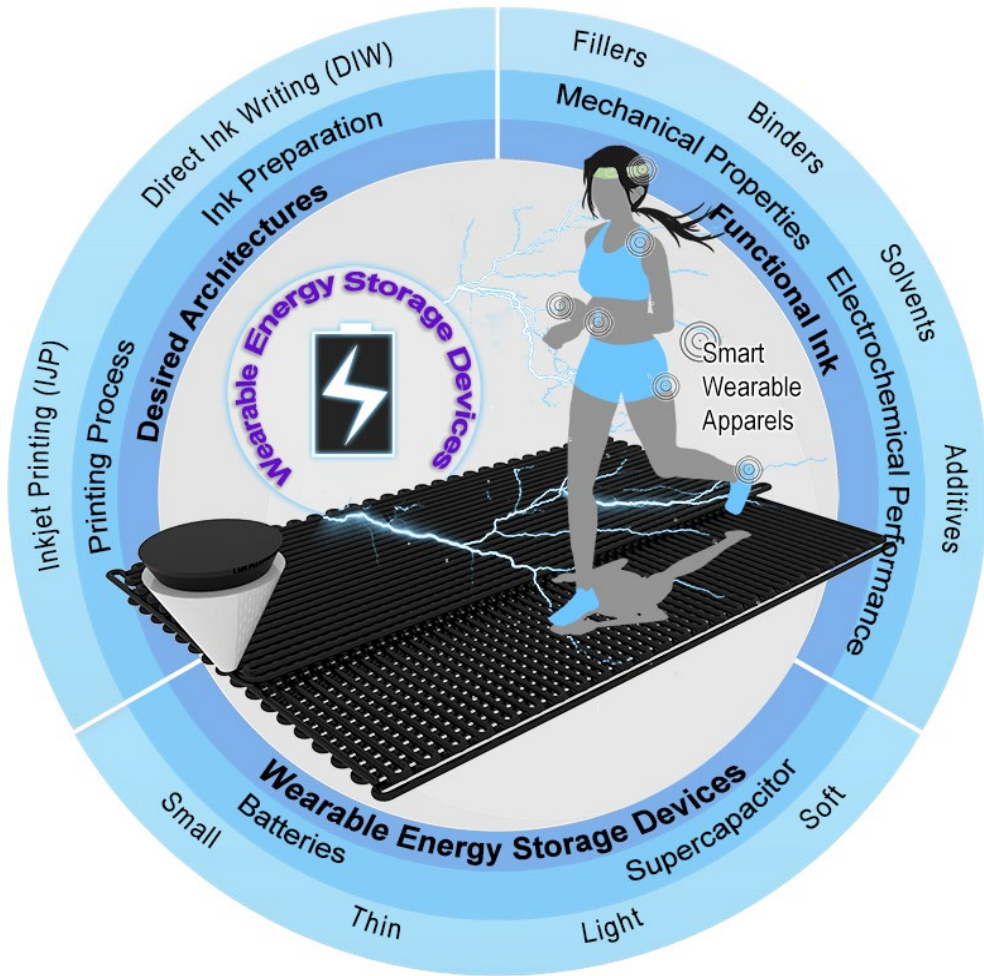


Application: Flexible Energy Storage



Application: Flexible Energy Storage

Yuxuan Zhu,... Y. L. Zhong [A Focus Review on 3D Printing of Wearable Energy Storage Devices](#)
Carbon Energy 4, 1242-1261 (2022)

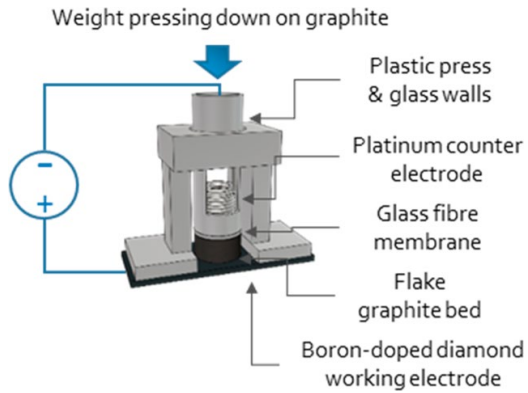


Electrochemical Engineering of Nanomaterials

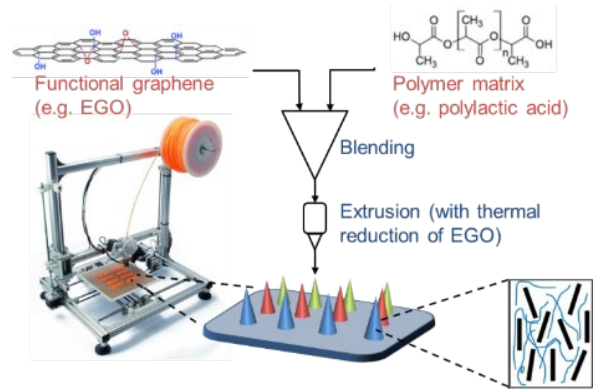


Additive Manufacturing of Devices

DE140101662 - Non-Oxidative and Scalable Electrochemical Production of Functional Graphene and its NanoHybrids



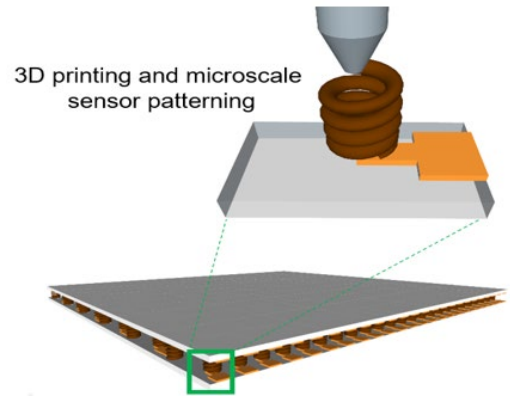
DP170104157 - Tailoring Nanocomposites with Controllable Structural-Property Relationship



FT200100015 - Advancing Green Electrochemical Engineering of Functional 2D Nanomaterials



DP190100120 - Towards High-Performance Wearable Devices: Materials and Microfabrication



??? - Electric Field-Enhanced Packed-Bed Electrochemical Reactors

DP240100892 - Empowering Wearable Smart Devices with 3D Printed Energy Storage