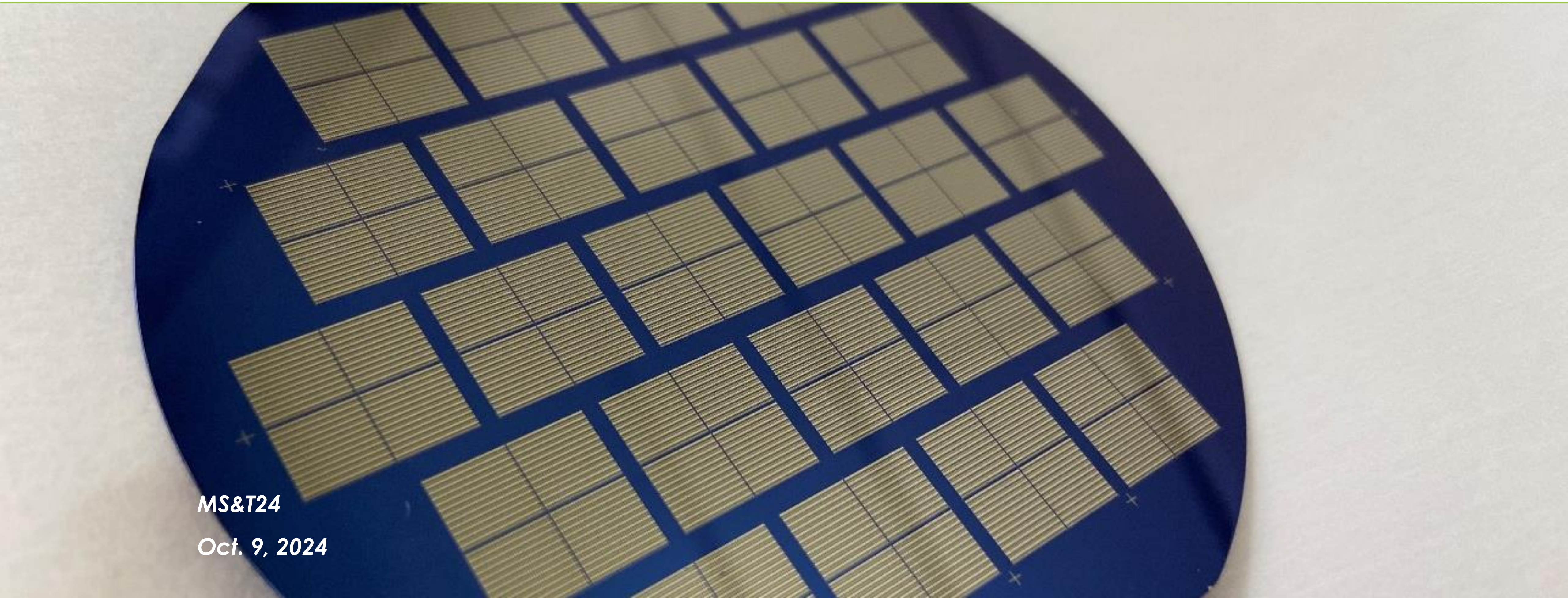
2D Amorphous Carbon Dielectric Prepared from Solution Precursor for Nanoelectronics

Viet Hung Pham
Research Engineer, NETL Support Contractor



MS&T24

Oct. 9, 2024

Disclaimer

Authors and Contact Information

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Outline

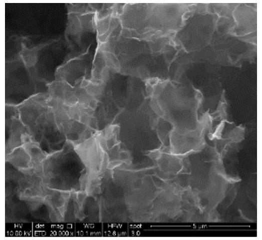
- Introduction
- Synthesis, Characterization, and Optimization of Solution Precursors and 2D Amorphous Carbon
- 2D Amorphous Carbon Dielectrics for Next Generation Microelectronic Devices
- Summary
- Acknowledgments

High Value Carbon Materials & Enabling Technologies

NATIONAL ENERGY TECHNOLOGY LABORATORY

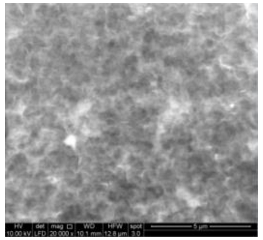
Carbon Materials of Diverse Structures & Properties from Domestic Feedstocks

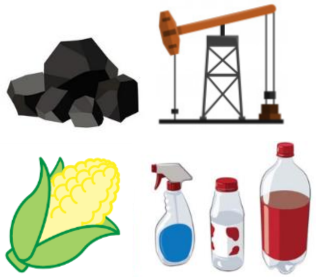
3D Few-Layer Graphene



Graphite

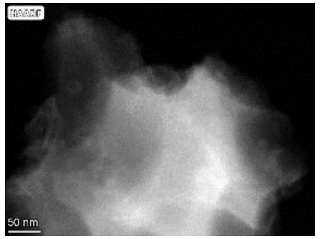
Graphene Oxide





Coal & Mining Waste, Petroleum, Biomass, Plastic Waste

Graphene Nanoflakes

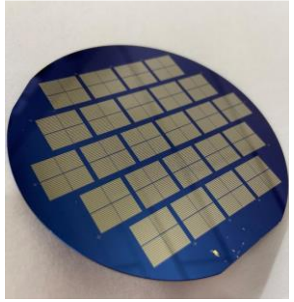


Porous Carbons

Carbon Quantum Dots

Energy Storage

Carbon Electronics



Construction Materials

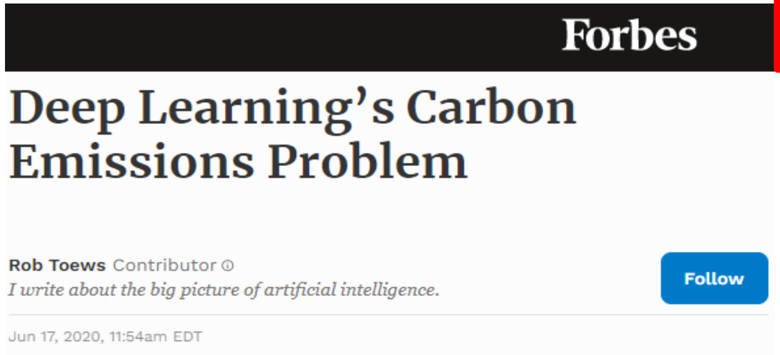
UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN

OAK RIDGE National Laboratory

Energy Consumption & CO_2 Emissions of Modern Computing

NATIONAL ENERGY TECHNOLOGY LABORATORY

Efficient Microelectronic Devices Needed to Reduce Energy Consumption & Emissions



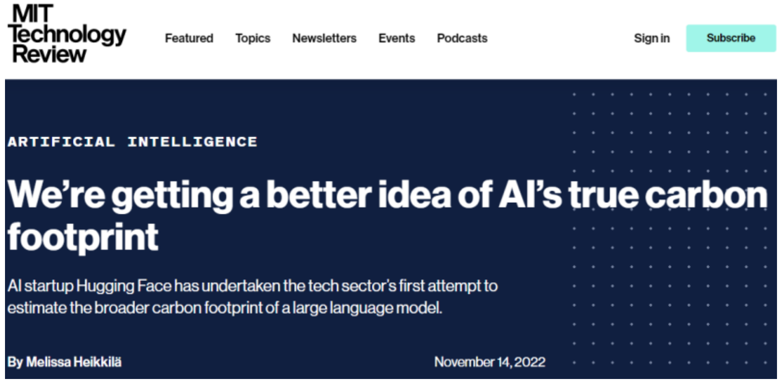
Forbes

Deep Learning's Carbon Emissions Problem

Rob Toews Contributor

I write about the big picture of artificial intelligence.

Jun 17, 2020, 11:54am EDT



ARTIFICIAL INTELLIGENCE

We're getting a better idea of AI's true carbon footprint

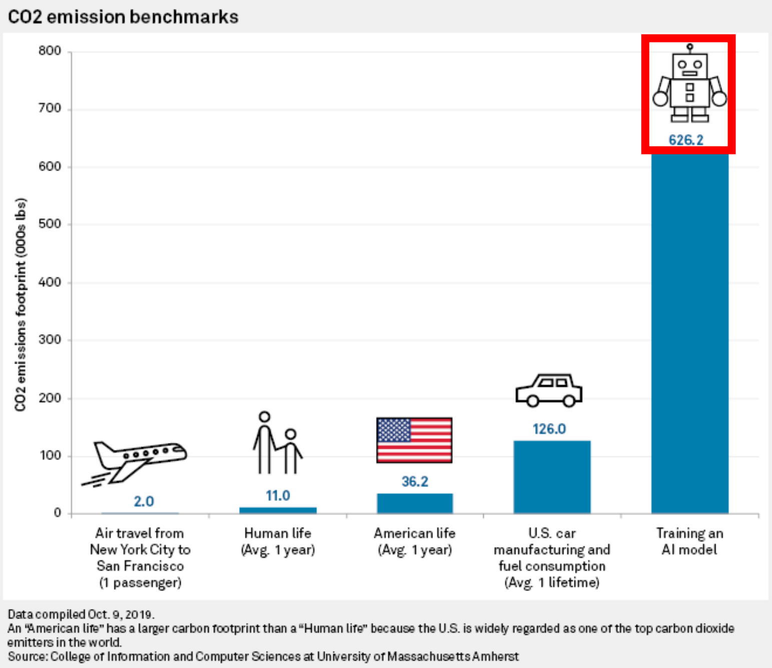
AI startup Hugging Face has undertaken the tech sector's first attempt to estimate the broader carbon footprint of a large language model.

By Melissa Heikkilä

November 14, 2022

WOW!

500 metric tons of CO_2 = 600 flights between London and New York

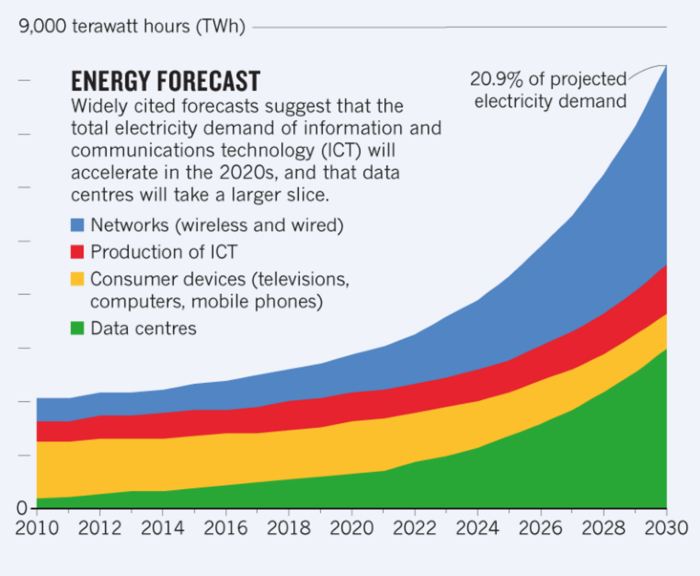


CO2 emission benchmarks

Data compiled Oct. 9, 2019.

An "American life" has a larger carbon footprint than a "Human life" because the U.S. is widely regarded as one of the top carbon dioxide emitters in the world.

Source: College of Information and Computer Sciences at University of Massachusetts Amherst



ENERGY FORECAST

Widely cited forecasts suggest that the total electricity demand of information and communications technology (ICT) will accelerate in the 2020s, and that data centres will take a larger slice.

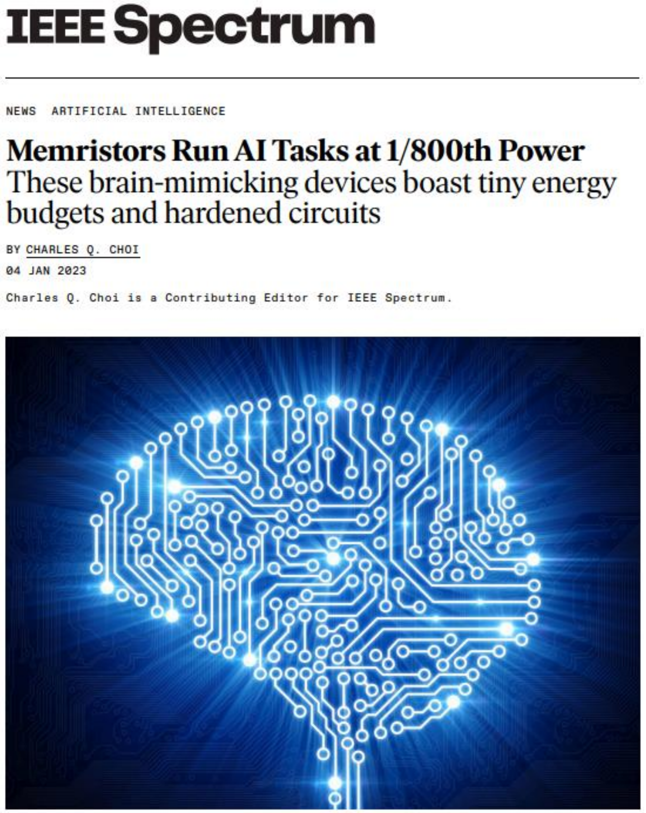
- 🟦 Networks (wireless and wired)
- 🟥 Production of ICT
- 🟨 Consumer devices (televisions, computers, mobile phones)
- 🟩 Data centres

Nature ***561***, *163-166 (2018); https://www.iea.org/reports/data-centres-and-data-transmission-networks; www.spglobal.com/; www.forbes.com/; www.technologyreview.com; Nature Climate Change* ***12***, *518–527 (2022).*

Data centers:

- 1–1.5% of global electricity demand
- ~0.3% overall carbon emissions
- Global Information and Communication Information sector: 1.4% greenhouse gas emissions

Memristors for Modern Computing



IEEE Spectrum

NEWS ARTIFICIAL INTELLIGENCE

Memristors Run AI Tasks at 1/800th Power

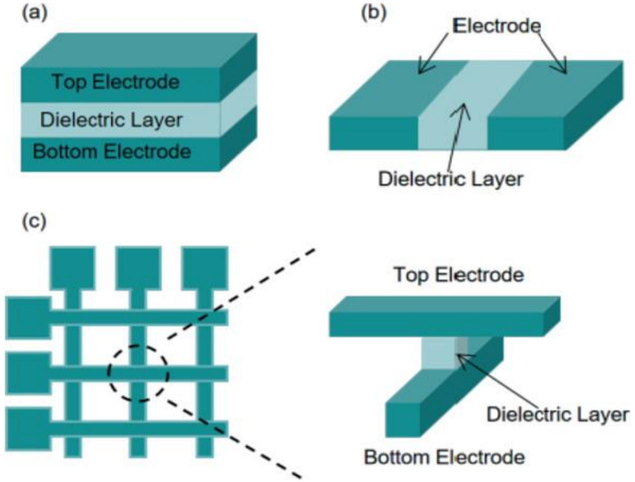
These brain-mimicking devices boast tiny energy budgets and hardened circuits

BY CHARLES Q. CHOI

04 JAN 2023

Charles Q. Choi is a Contributing Editor for IEEE Spectrum.

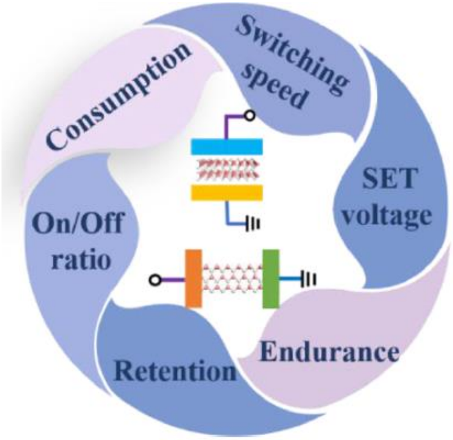
https://spectrum.ieee.org/memristor-devices-ai#:~:text=Memristors%2C%20or%20memory%20resistors%2C%20are,both%20compute%20and%20store%20data.



Memristor structure

(https://doi.org/10.1007/978-981-19-1673-1_77)

- Memristor, or memory resistor, is a two-terminal device consisting of a sandwiched structure of electrode/switching layer/electrode.
- The resistance of a memristor changes depending on the direction and amount of current flowing through it. A memristor's resistance value is maintained even after the power is turned off.



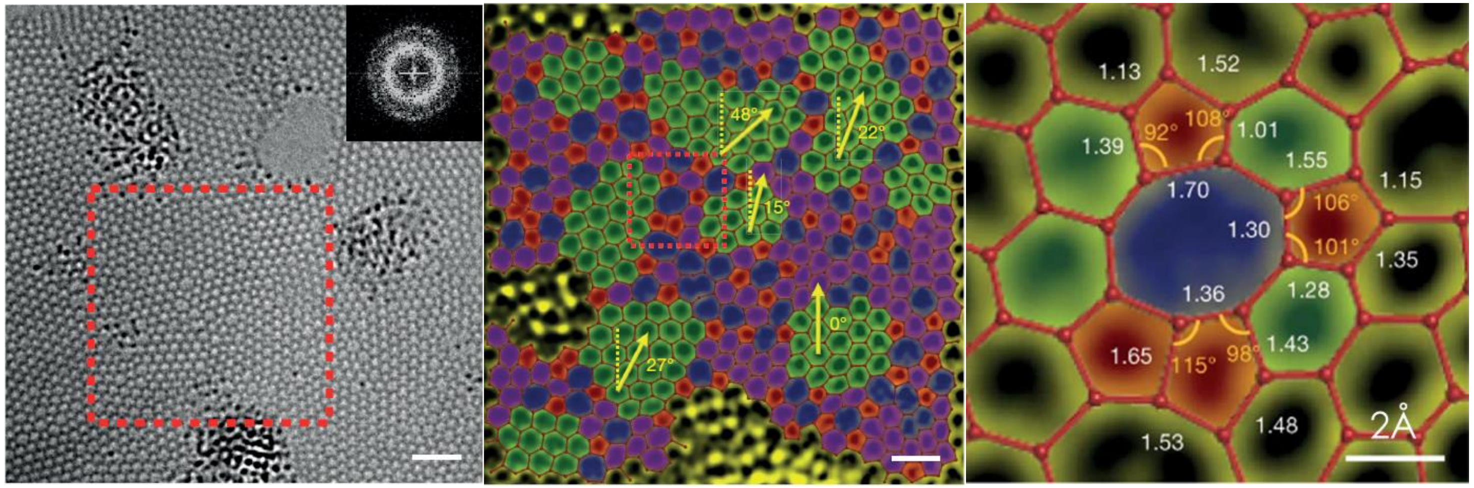
High performance of memristors based on 2D materials

(J. Phys. Chem. Lett. 2022, 13, 7130−7138)

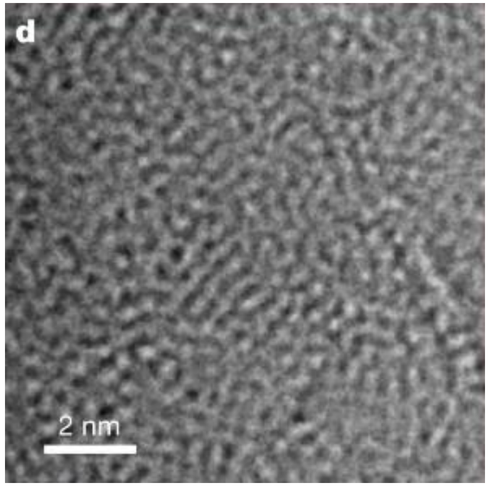
- Memristor's advantage: non-volatile, low energy consumption, fast reading and writing, high miniaturization.
- Atomically thin 2D materials are ideal switching layer with high-performance resistive switching characteristics, such as high on/off ratios, low set/reset voltages, good retention and endurance, fast switching speed, and low power and energy consumption.

2D Amorphous Dielectrics as Switching Layers

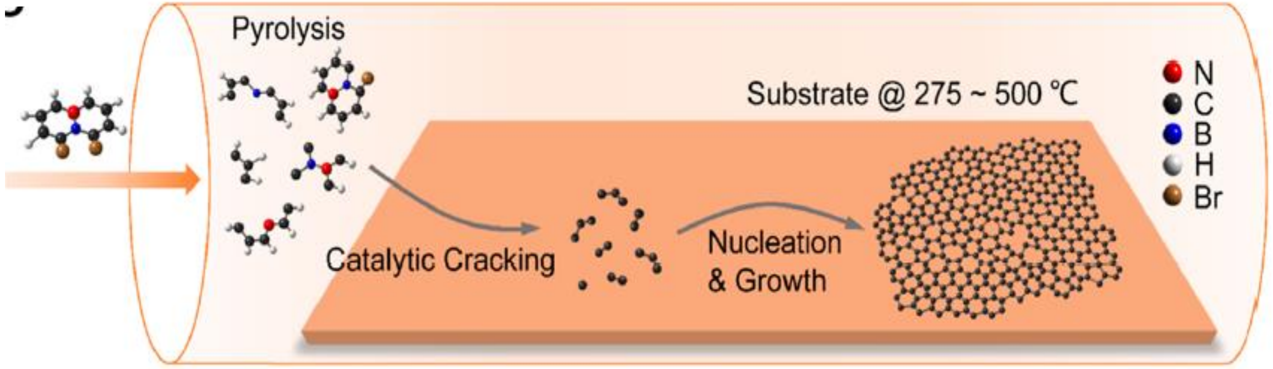
Significant Limitations of Existing Vacuum Deposition Methods



2D monolayer amorphous carbon (MAC).



2D amorphous boron nitride.



Schematic of the amorphous carbon growth using the cyclic aromatic molecule as the precursor.

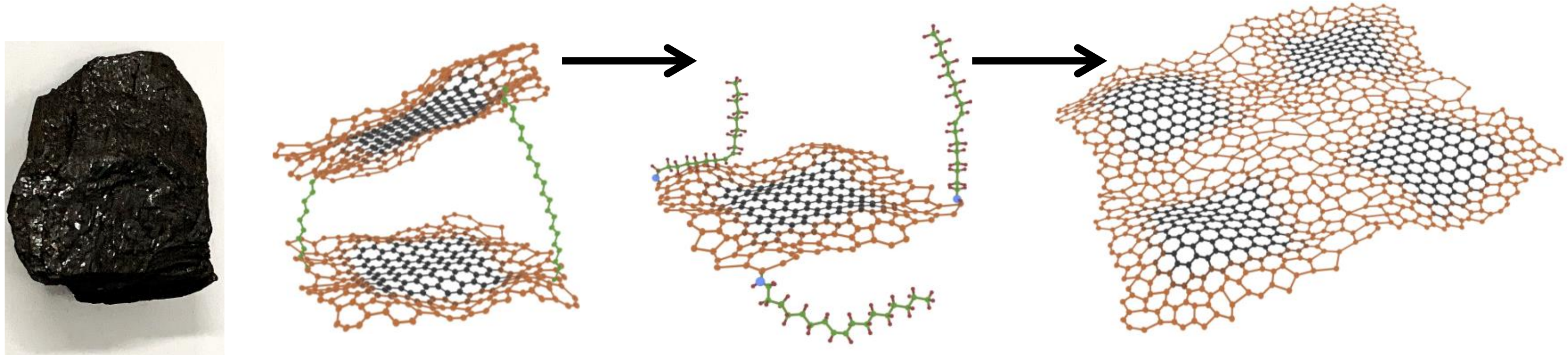
Significant limitations:

- Limited spatial uniformity and area coverage
- No precise control of film thickness, especially beyond first monolayer
- Limited demonstration for device applications

ACS Nano 2023, **17**, 24468–24478
Nature 2020, **577**, 199–203; *Nature* 582, 511–514 (2020)

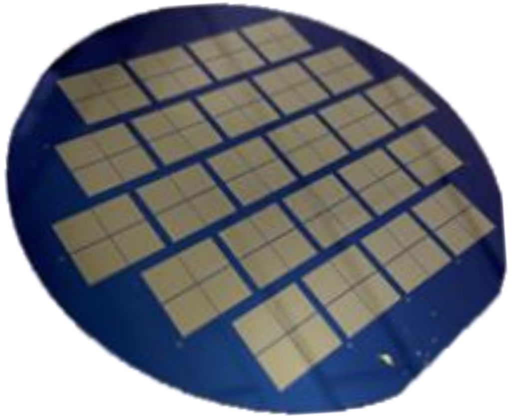
Can We Make Improved Electronic Materials from Coal?

Coal as Feedstock for Low-Cost, Scalable Production of 2D Dielectrics



Nanoscale graphitic domains → **Acids/functionalization** → **Assembly/annealing**

1 L of Carbon Quantum Dots.



3-inch Memristor Prototype (~24,000 devices).

Advantages:

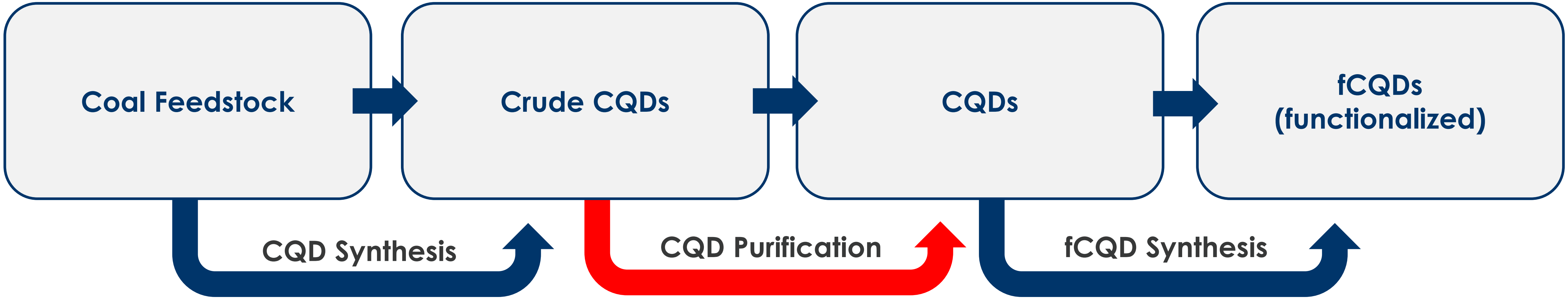
- Coal = small graphitic/aromatic domains, easy to extract
- Size/chemistry/properties ideal for thin film, non-conductive materials
- Solution precursors for scalable production with precise control of thickness
- Inexpensive, can make 1000s of prototypes
- Domestically sourced feedstock

U.S. patent application No. 17/707,521
Communications Engineering **2**, 93 (2023).

Synthesis and Functionalization of CQDs

Optimizing Processes to Produce the Perfect Precursor for 2D Carbon

Synthetic Pathway for Carbon Materials for Microelectronics



Coal Feedstock

Crude CQDs

CQDs

fCQDs
(functionalized)

CQD Synthesis

CQD Purification

fCQD Synthesis

Challenges:

- Impurities of coal feedstock → purification needed
- Variation in size of as-synthesized carbon quantum dots (CQDs) → non-uniform carbon film →size exclusion needed
- Highly oxygenated, highly hydrophilic → not compatible with semiconductor device fabrication process → functionalization needed

Synthesis and Functionalization of CQDs

Synthesis and Purification of CQDs

Coal feedstock.

Concentrated H_2SO_4 + HNO_3, 100 ^{o}C, 24 h

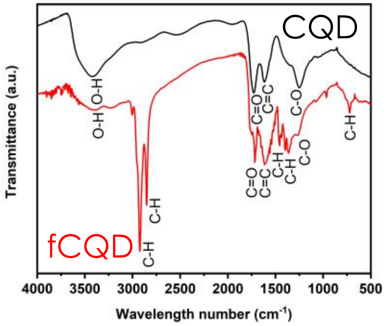
Purification (acid washing + cross-flow ultrafiltration 8 times → removing 99.9999% contaminants)

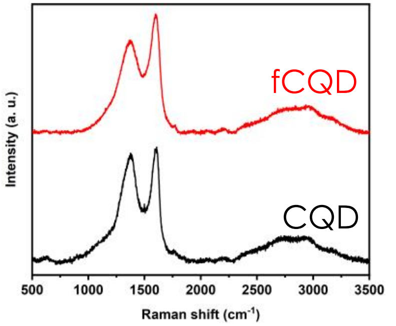
CQDs solution.

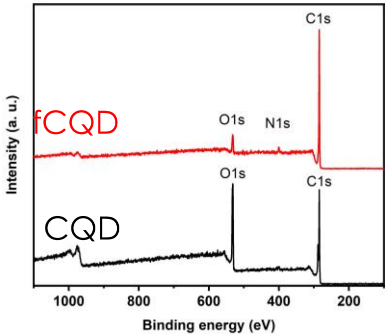
wt.%	Blue Gem Coal Fine	Coal Char*
Fixed C	61.68	95.89
Volatiles	36.66	1.52
Ash	1.66	2.59
C	81.19	94.82
O	9.39	0.08
N	2.12	1.67
H	4.88	0.31
S	0.76	0.53
SiO_2	0.61	0.72
Cl, F, Hg	trace	trace
Al	0.19	0.31
Ti	0.015	0.017
Fe	0.20	0.42
Ca	0.084	0.16
Mg	0.019	0.028
K	0.027	0.032
Na	0.023	0.022
P	0.0023	0.0028
Sr	0.011	0.018
Ba	0.0077	0.010
Mn	0.00031	0.0029

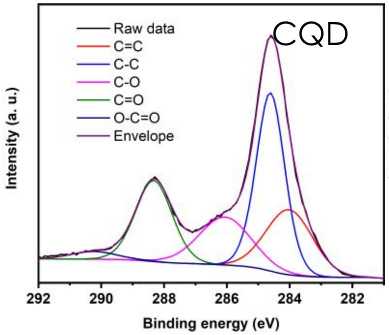
wt.%**	CQD	fCQD
C	61.7	85.1
O	38.3	11.1
N	-	3.8

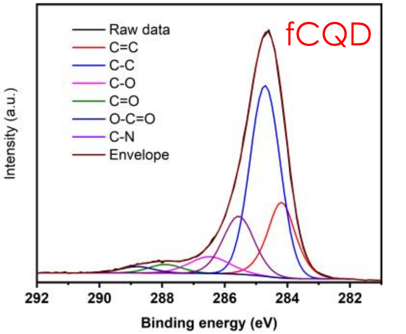
**H not analyzed.





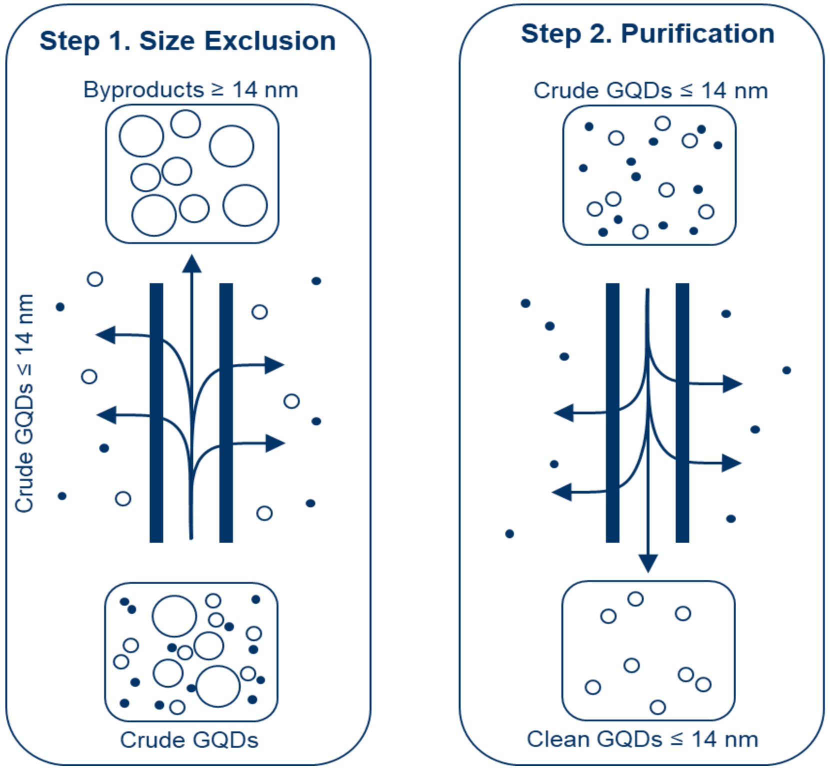






Synthesis and Functionalization of CQDs

Size Exclusion and Purification Using Cross-Flow Ultrafiltration



○ Oxidized carbon particles, large CQDs, insolubilized minerals.

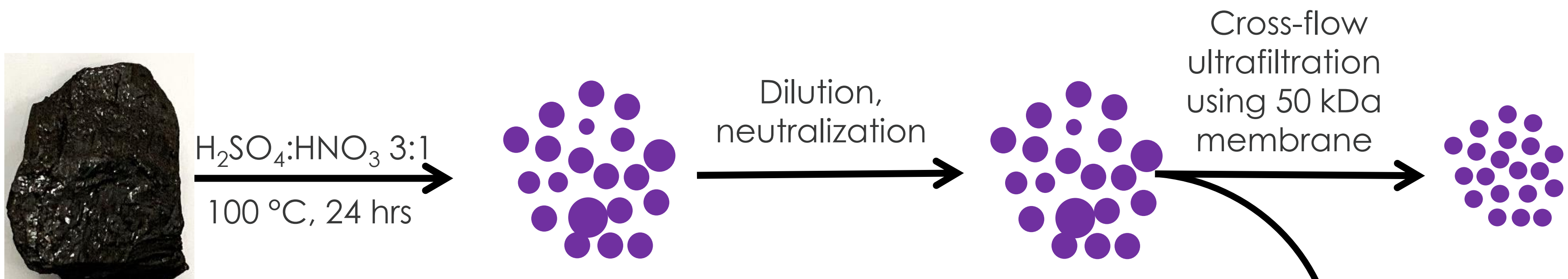
○ CQDs.

● Water soluble mineral salts and oxidized polycyclic aromatic hydrocarbons (PAHs).

- **Step 1. Size exclusion:** cross-flow ultrafiltration using 50 kDa membrane with pore size of ~14 nm and collecting solution passed through membrane.
- **Step 2. Purification:** multiple cycles washing with acid (HCl) and then with water with cross-flow ultrafiltration using 3 kDa membrane with pore size of ~1.5-2.0 nm. 99.9999% of contaminants could be removed by repeating washing 8 times.

Synthesis and Functionalization of CQDs

Size Exclusion by Cross-Flow Ultrafiltration

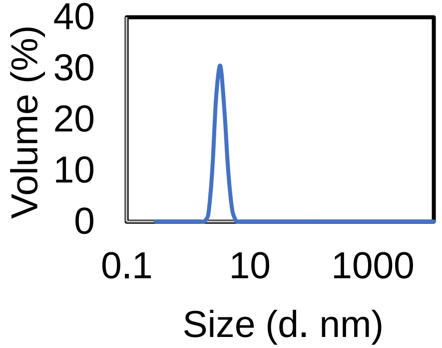


$H_2SO_4:HNO_3$ 3:1

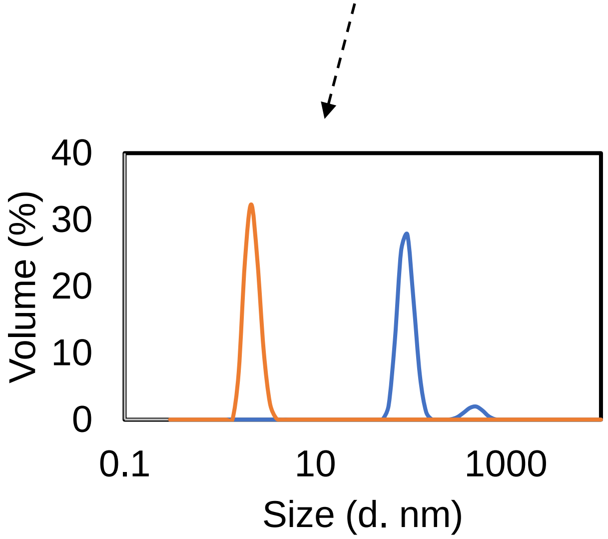
100 °C, 24 hrs

Dilution, neutralization

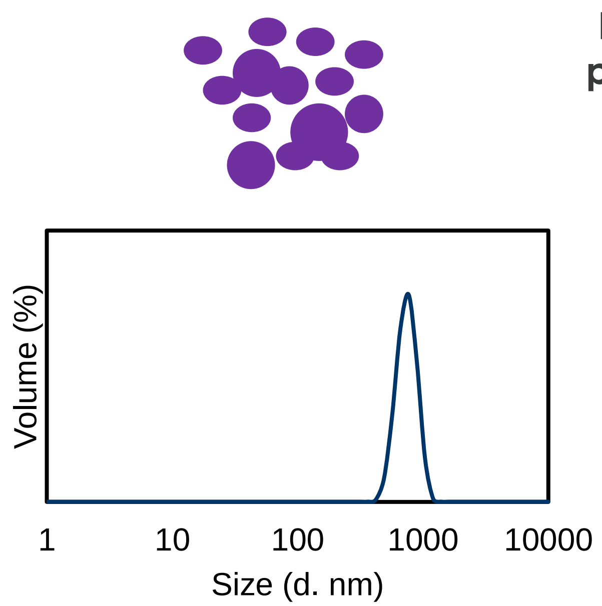
Cross-flow ultrafiltration using 50 kDa membrane



Particle size distribution of purified GQDs analyzed by DLS.

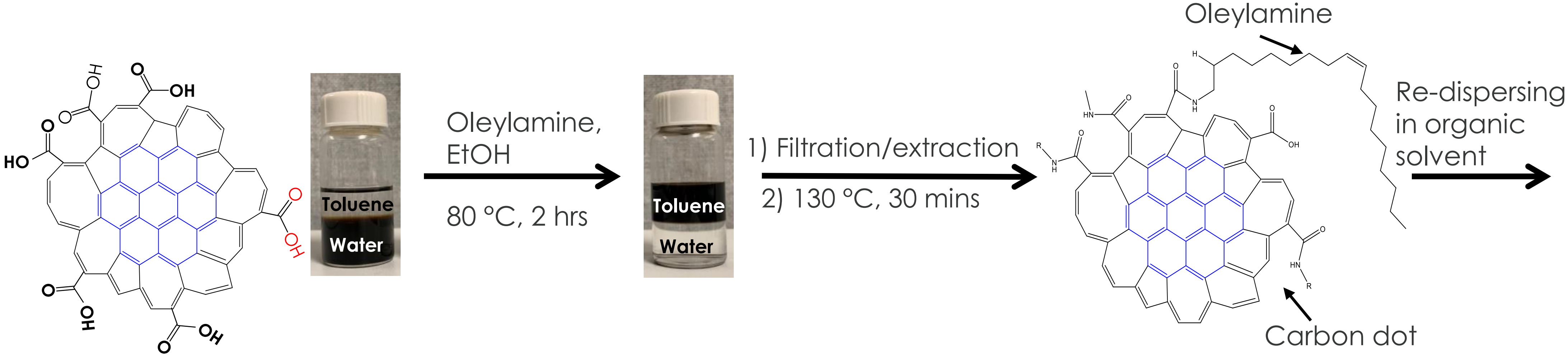


Particle size distribution of crude GQDs analyzed by dynamic light scattering (DLS).



Synthesis and Functionalization of CQDs

Functionalization of CQDs



Oleylamine, EtOH

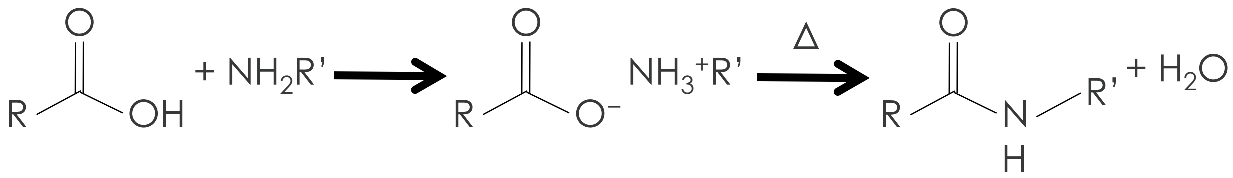
80 °C, 2 hrs

1) Filtration/extraction

2) 130 °C, 30 mins

Re-dispersing in organic solvent

Optimized precursor ink.

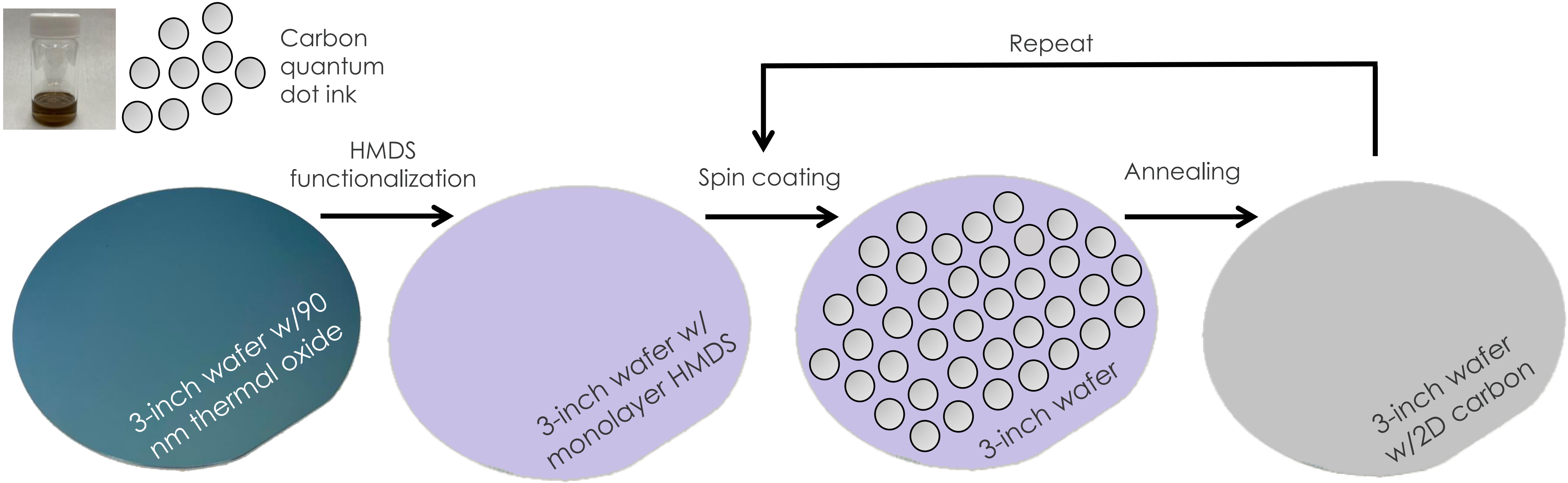


$$RCOOH + NH_2R' \rightarrow RCOO^- \; NH_3^+R' \xrightarrow{\Delta} RC(O)NHR' + H_2O$$

- Functionalization to achieve right surface chemistry for stable dispersion in organic solvents compatible with device fabrication.

Scalable Production of 2D Amorphous Carbon

Low-Cost Fabrication of Large Area Continuous 2D Amorphous Carbon

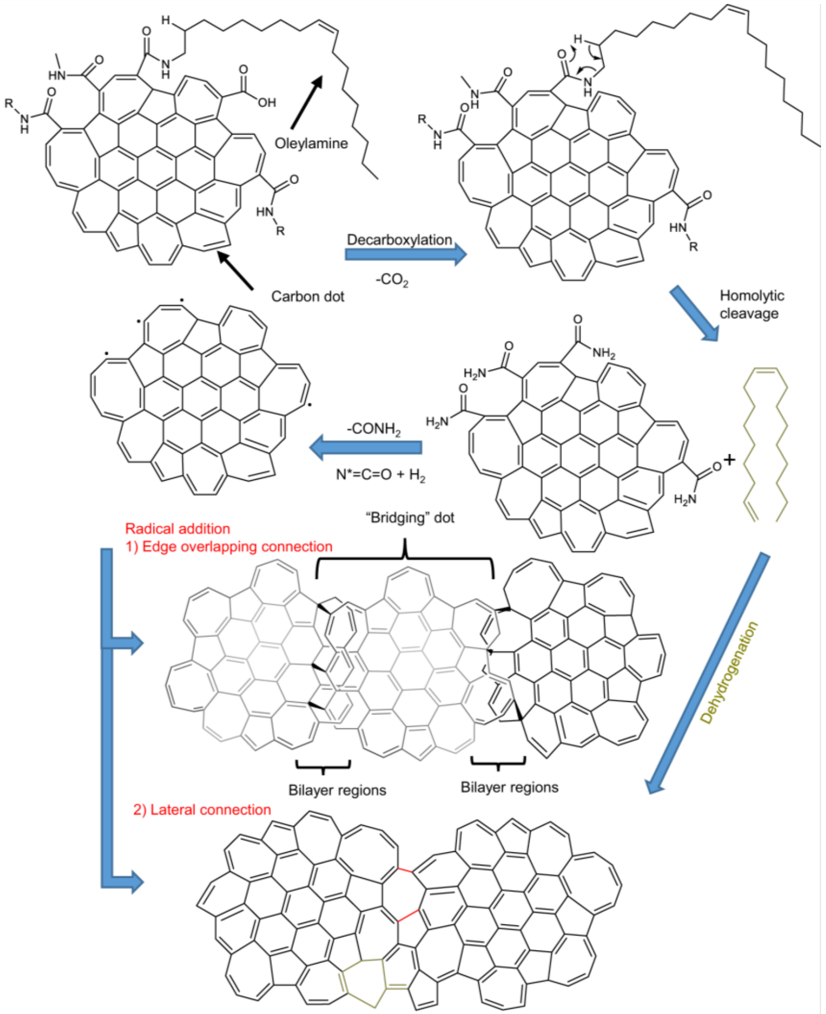


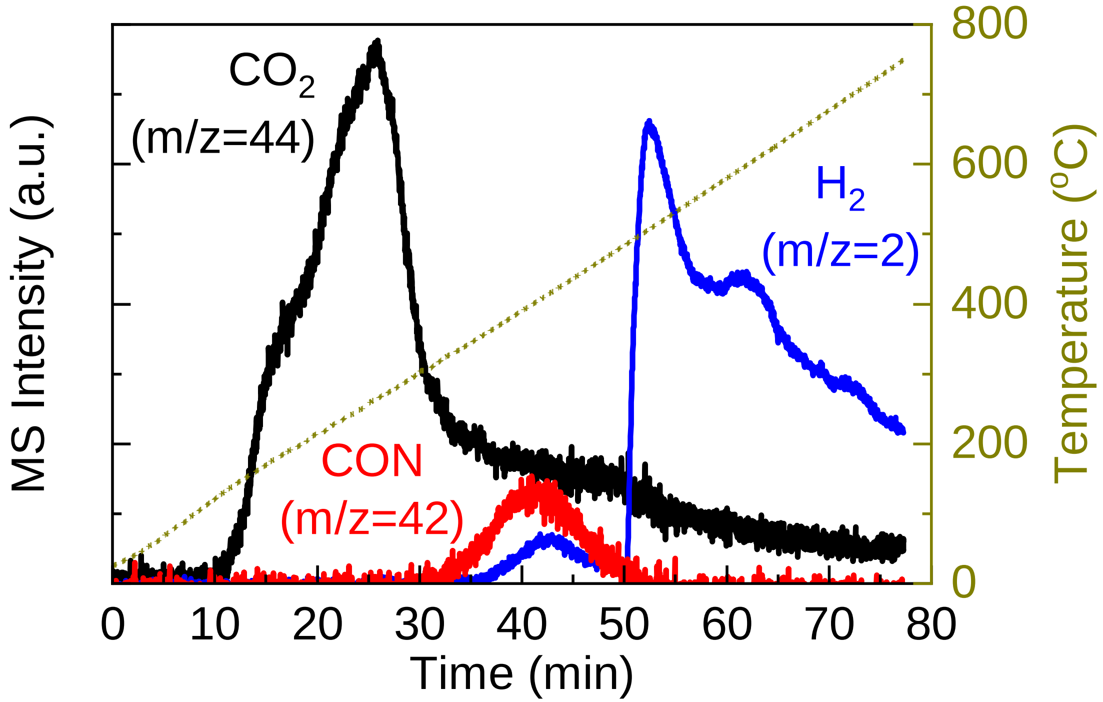
Favorable interaction with hexamethyldisilazane (HMDS) promotes alignment of CQDs parallel to the wafer surface.

Carefully controlled surface chemistry and meticulously formulated precursor ink for the formation of high quality, continuous 2D amorphous films and device fabrication.

Mechanism

Coalescence of CQDs via Cleavage of Amide Bond





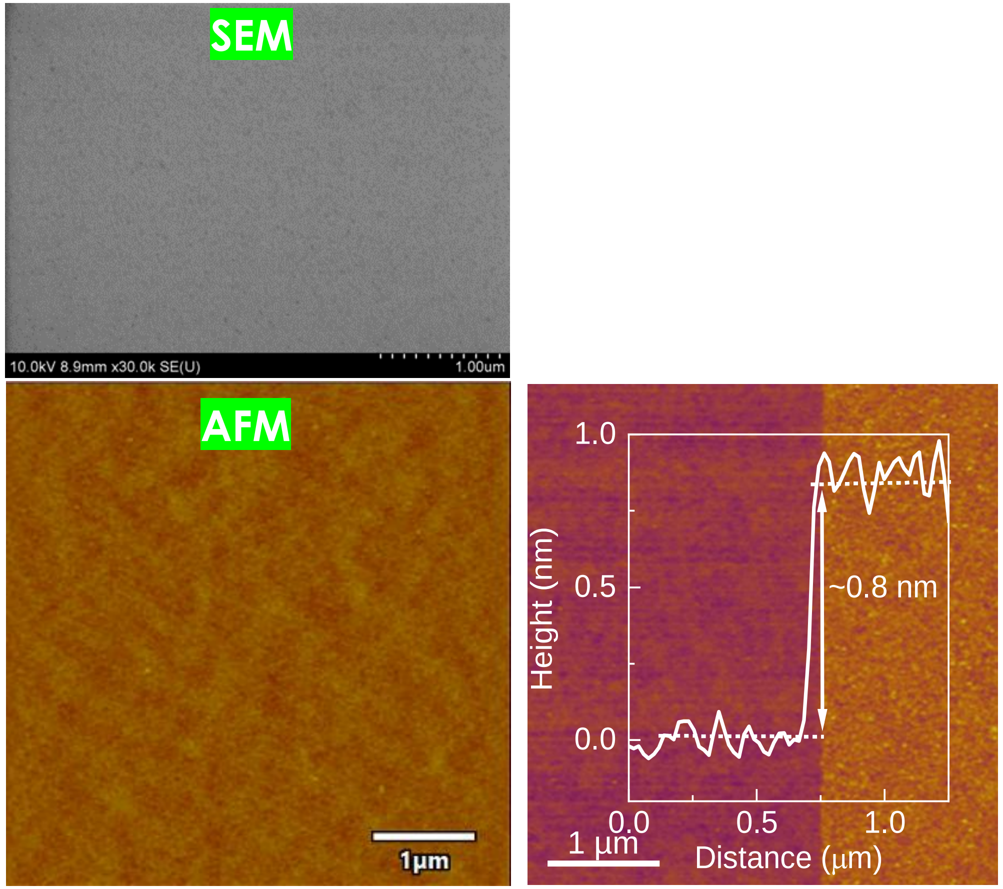
Similar to pyrolytic nylon decomposition:

- NH–CH_2 bond cleaved in the β position
- Cleavage of the C–CO amide bond and evolution of a $CONH_2$ fragment
- Radical addition to form film

Variation in 2D Carbon Film Quality

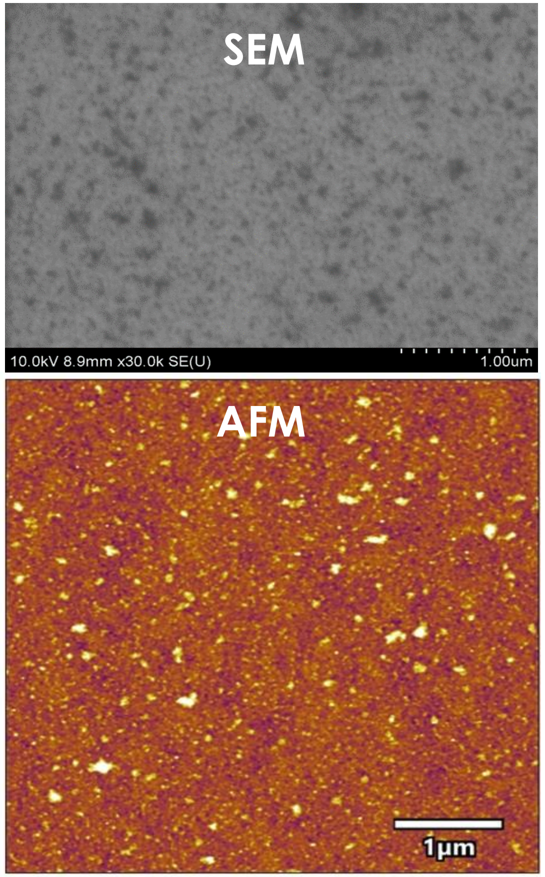
Inconsistent 2D Carbon Quality from Variation in CQD Precursors

Representative high quality 2D amorphous carbon from size exclusive, high purified fCQDs



Root mean square (RMS) ~ 0.1 – 0.2 nm

Representative low quality 2D amorphous carbon from as-synthesized fCQDs

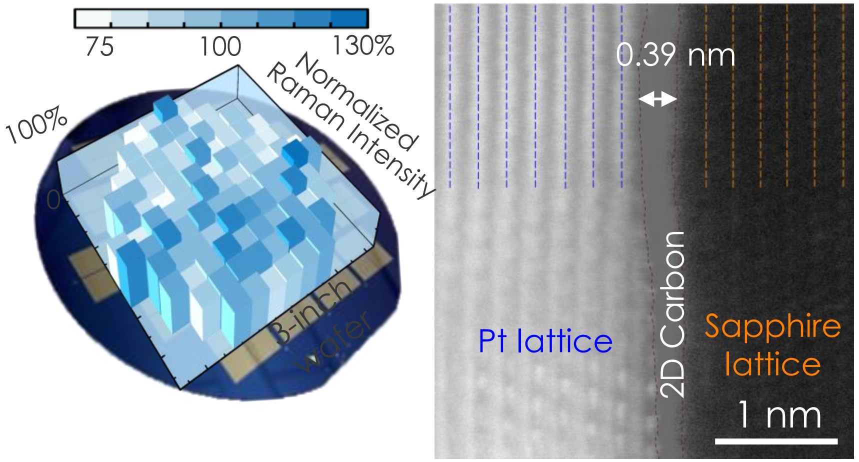


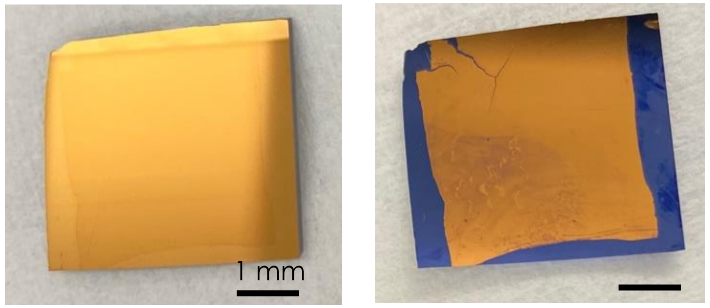
RMS ~ 2 nm.

Wafer-Scale Uniformity and Precise Layer Control

Low-Cost, Scalable Method of 2D Amorphous Carbon Fabrication

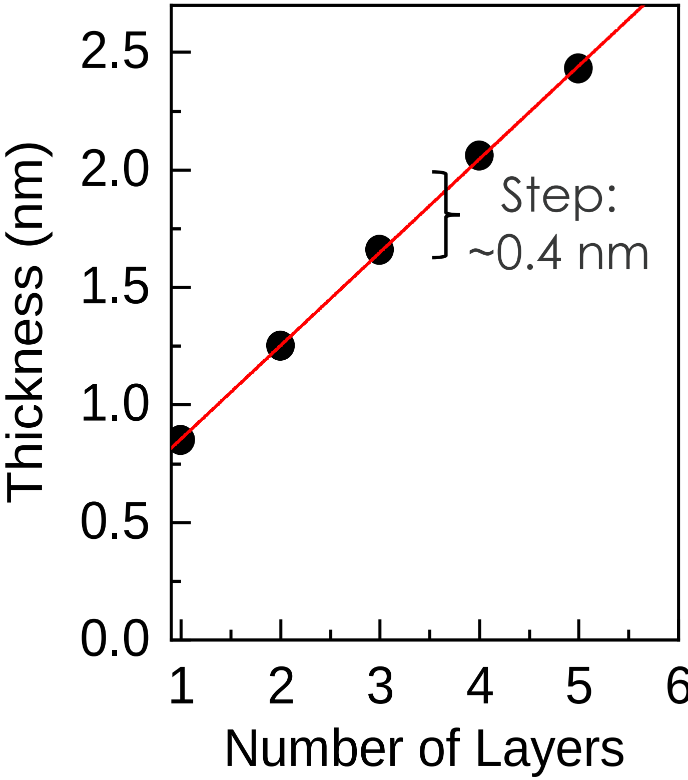
Atomically uniform thickness

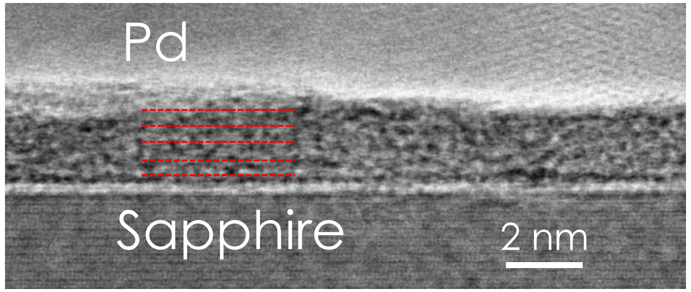


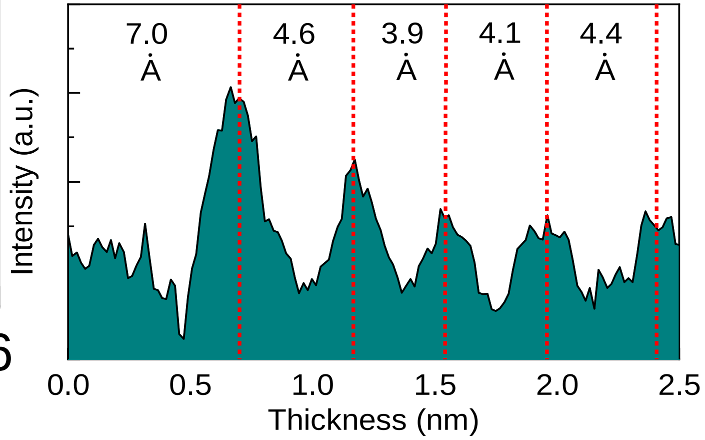


Efficient transfer to different substrates.

Monolayer by monolayer deposition

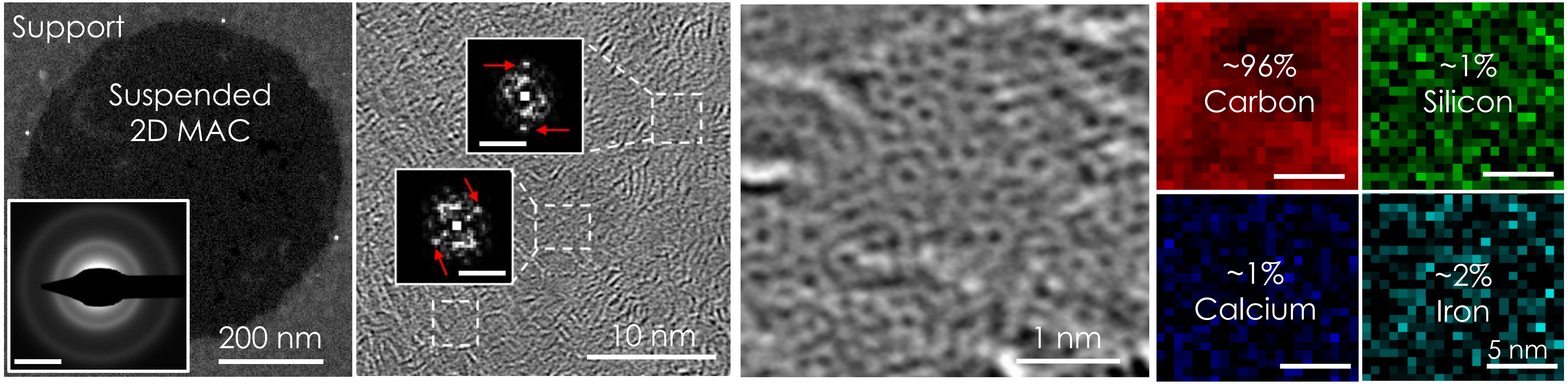


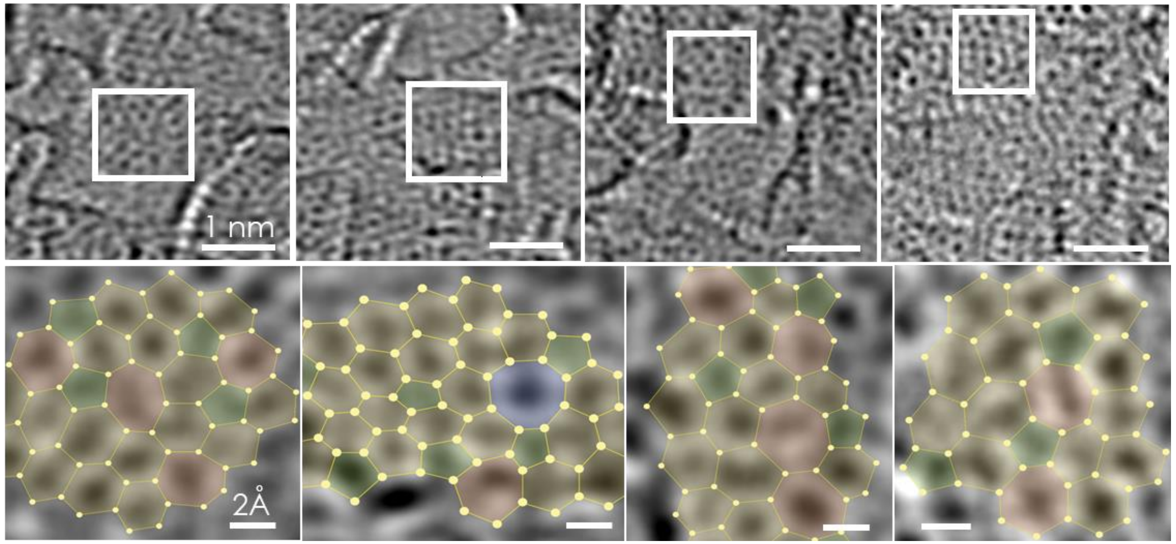


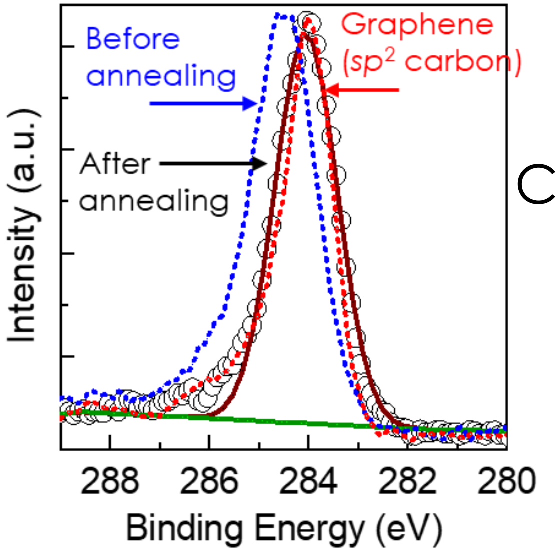


Amorphous Atomic Structures of the 2D Carbon

Large Area, Continuous 2D Amorphous Carbon



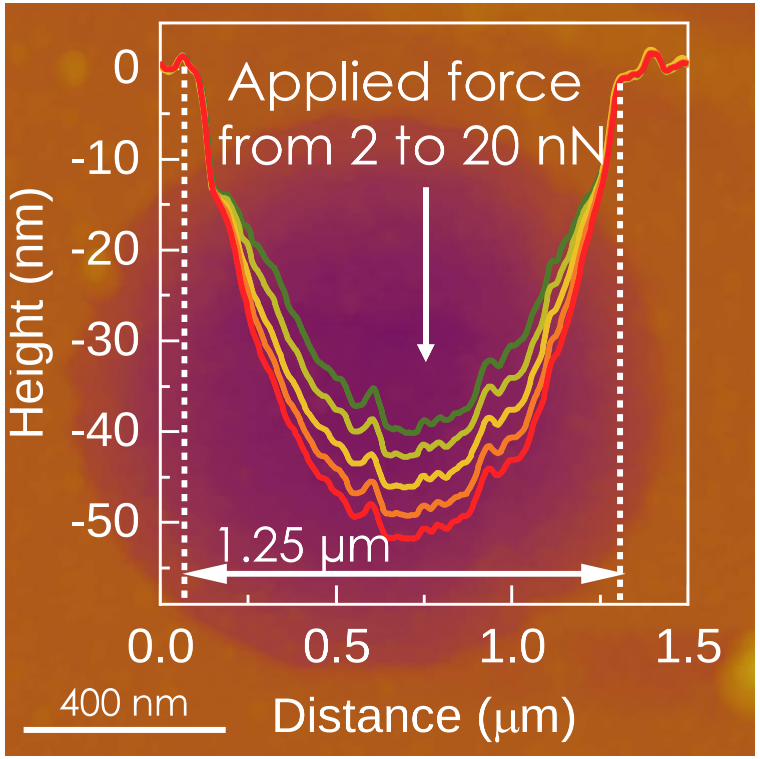


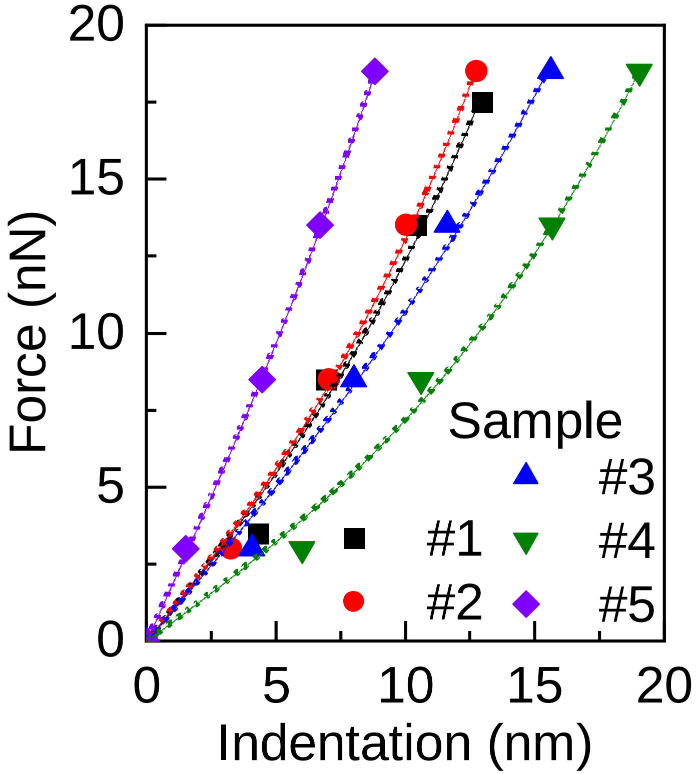


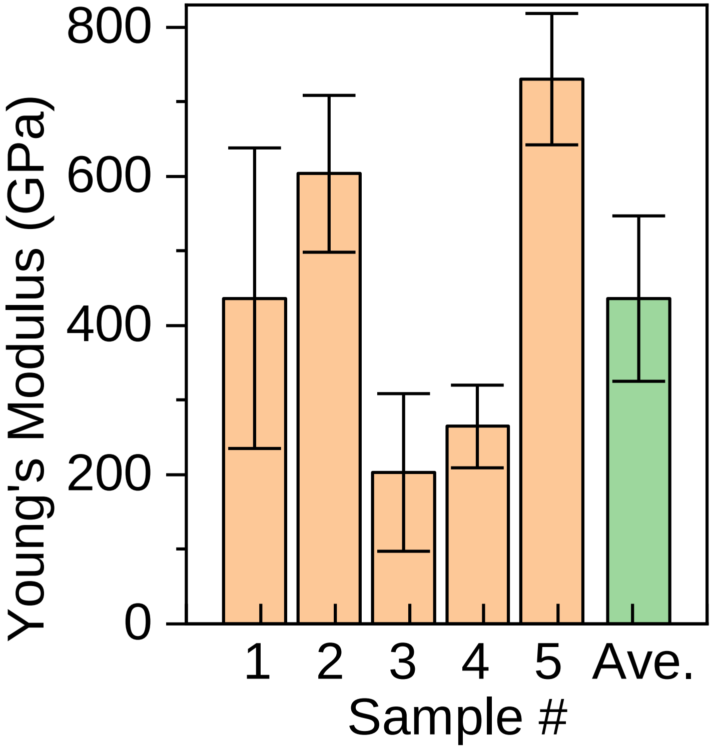
C-C

Mechanical Properties of 2D Amorphous Carbon

Young's Modulus Comparable to That of Crystalline Graphene



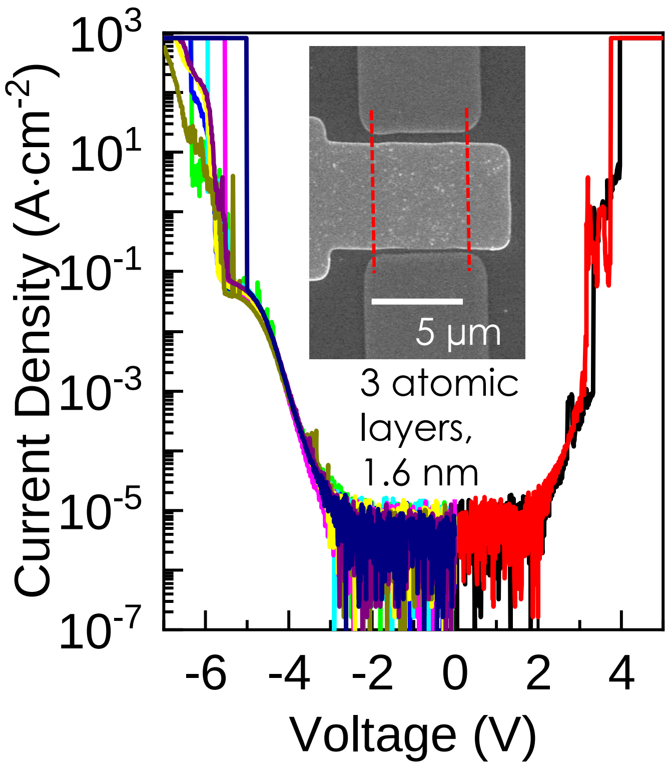




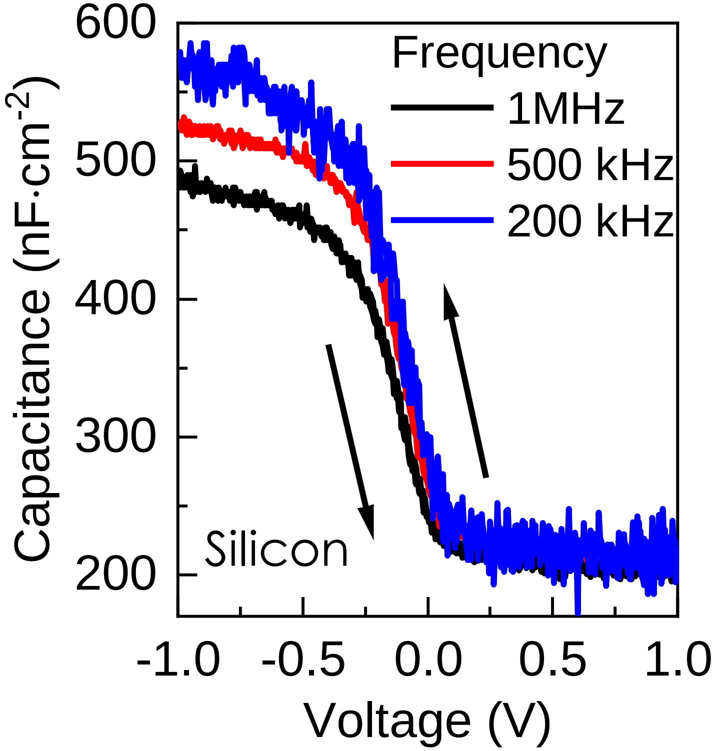
Electrical Properties of 2D Amorphous Carbon

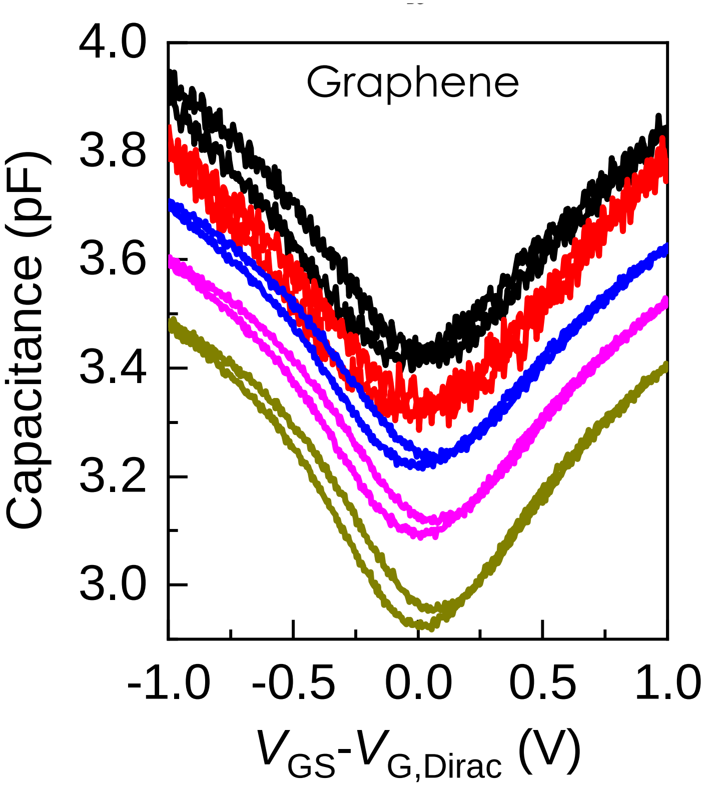
Exceptional Electrical Properties

Low leakage current <10^{-4}A/cm² (1000x lower than borone nitride (BN)) high breakdown field >20 MV/cm (2x higher than BN)



Good interface with Si and graphene (no hysteresis in cyclic voltammetry (CV) curves)

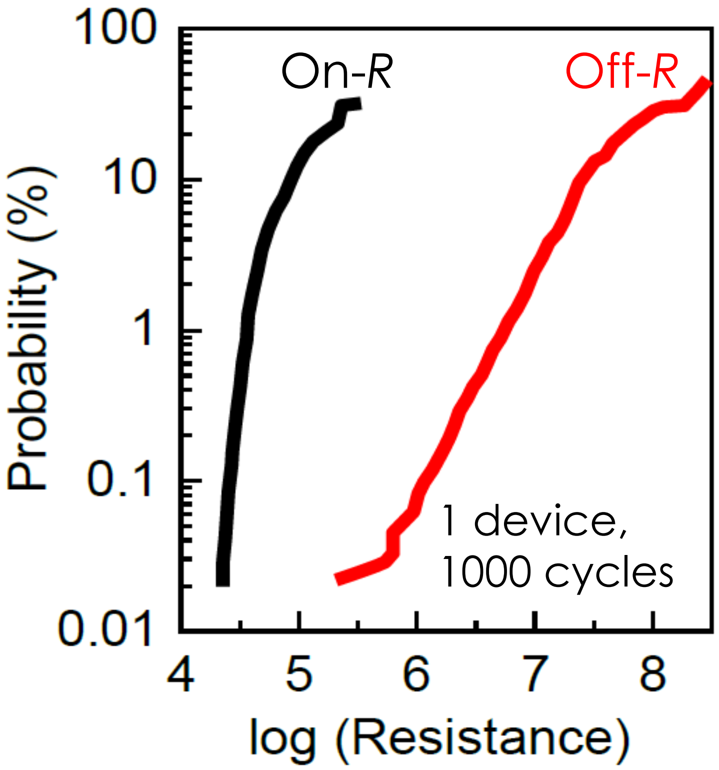




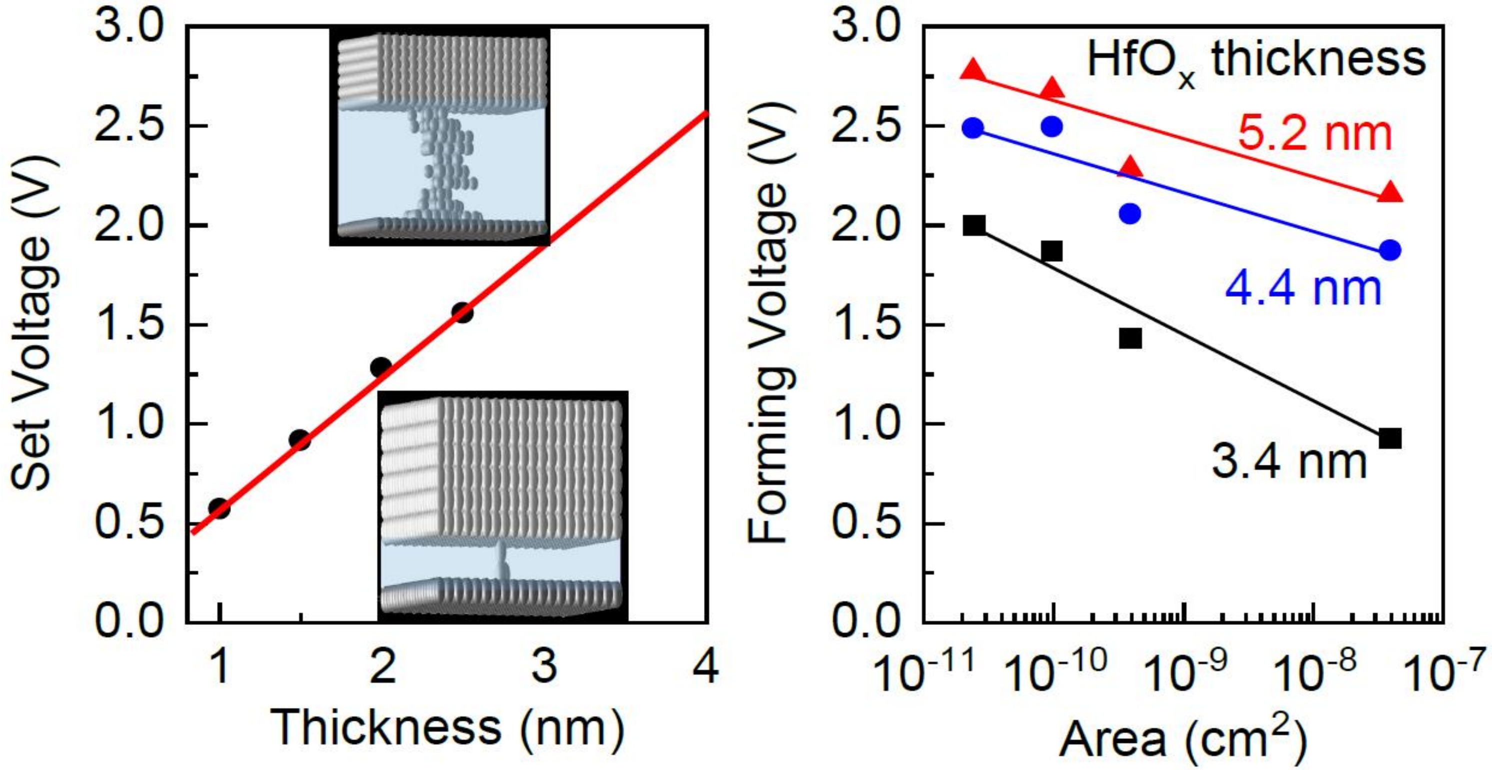
Device Application: Memristor

Significant Problems Limiting Memristor's Commercial Success

High variability (cell-to-cell and cycle-to-cycle)

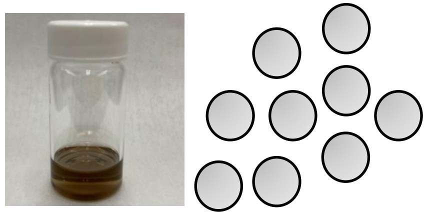


High operation voltage

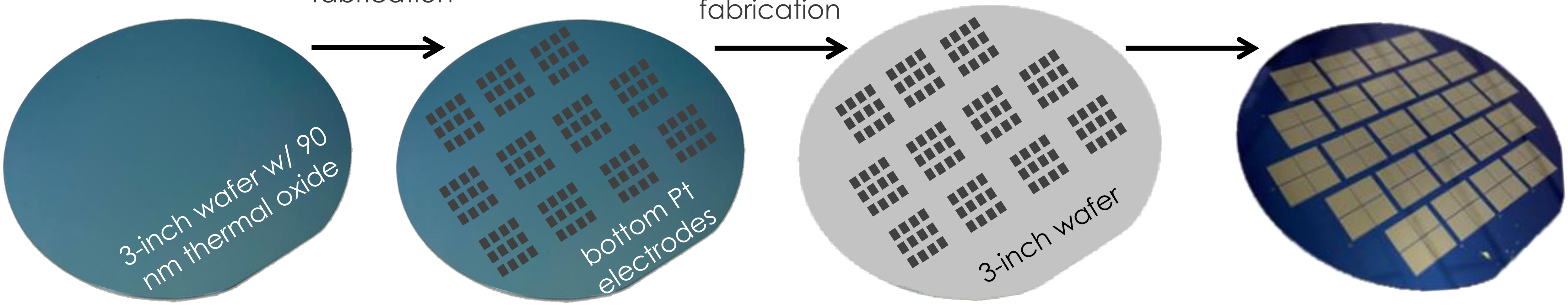


Fabrication of Memristors

Low-Cost Fabrication of 2D Amorphous Carbon Films as Ion-Transport Medium



Carbon quantum dot ink



Bottom Pt electrode fabrication

HMDS functionalization/2D amorphous carbon fabrication

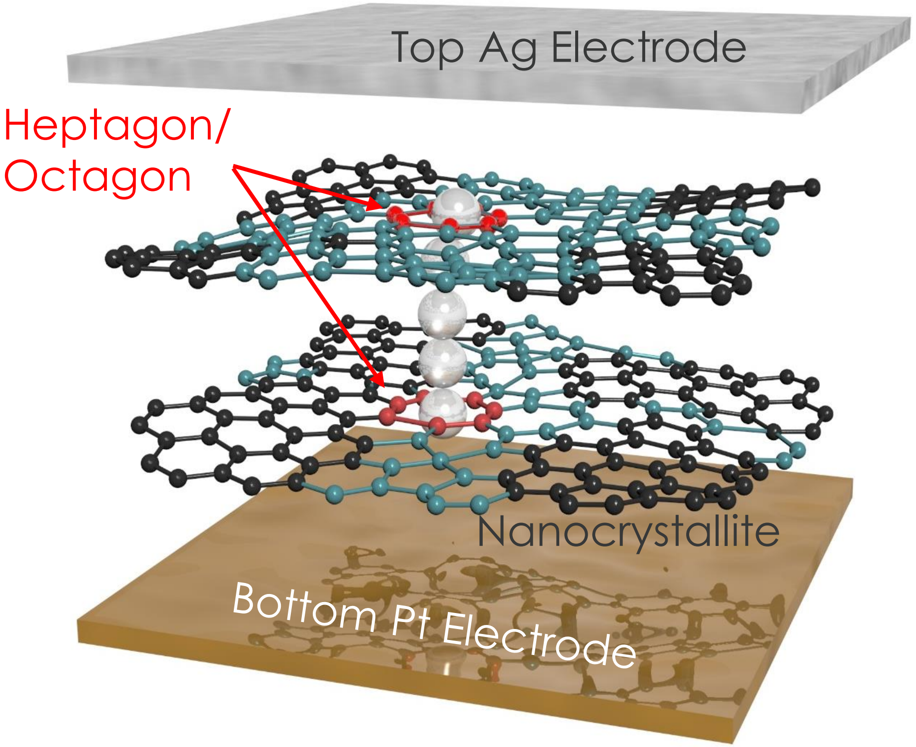
Top Ag electrode fabrication

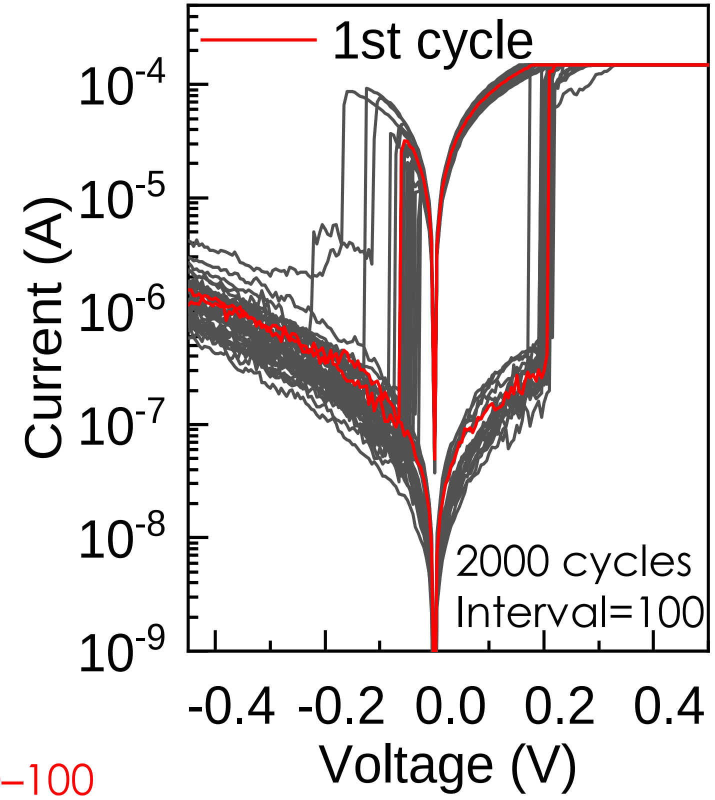
Memristors

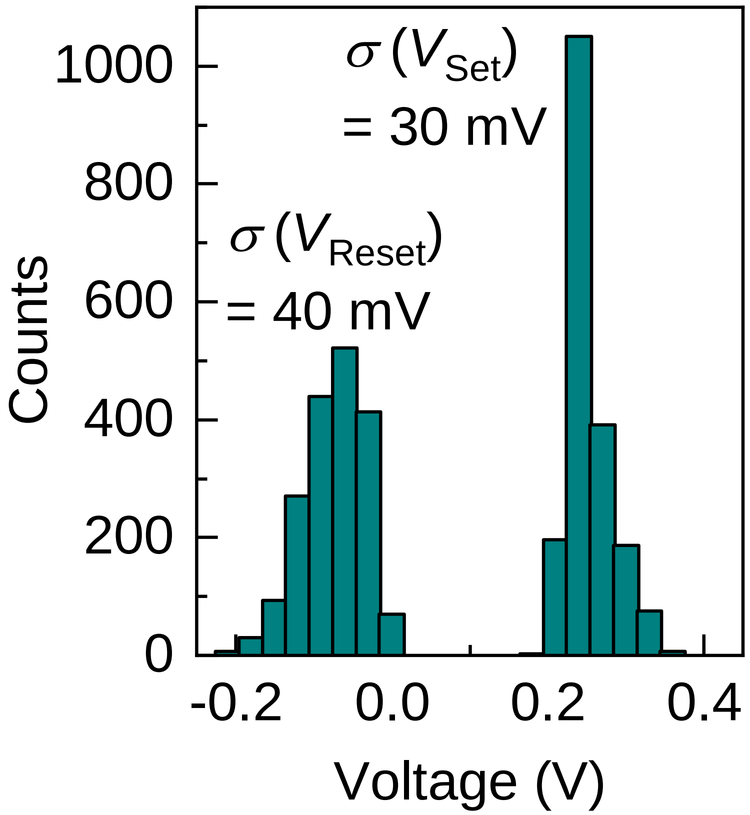
2D Amorphous Carbon for Memristors

Atomically Thin 2D Amorphous Carbon as the Switching Media for Resistive Random-Access Memories (RRAMs)

Low operating voltage (<0.4 V), small cycle-to-cycle variability



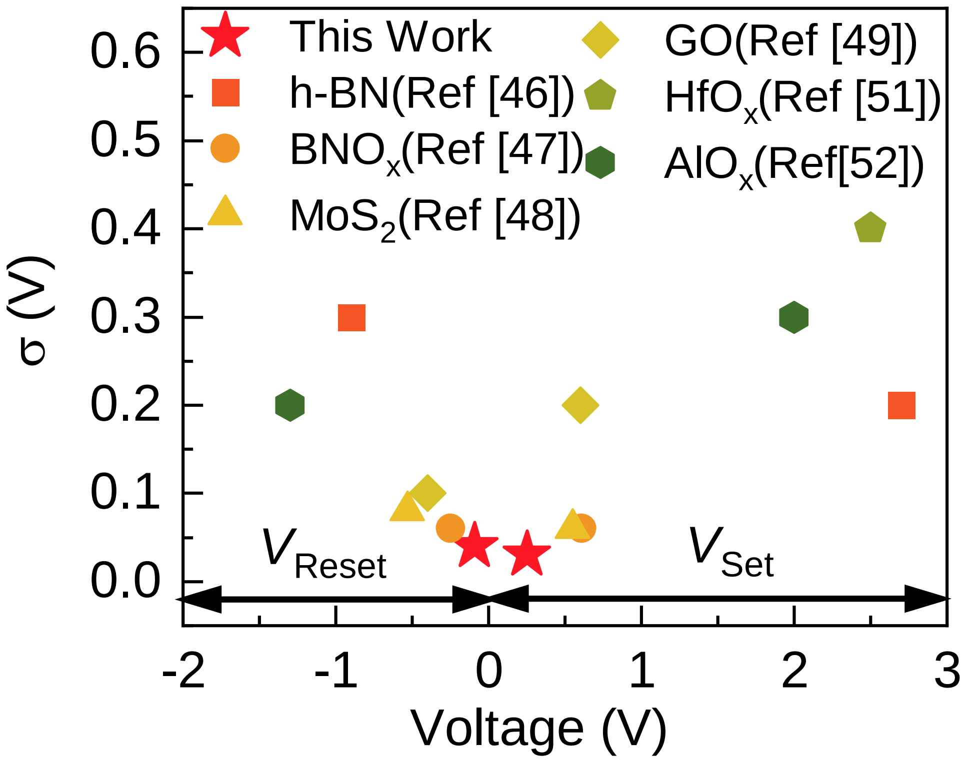


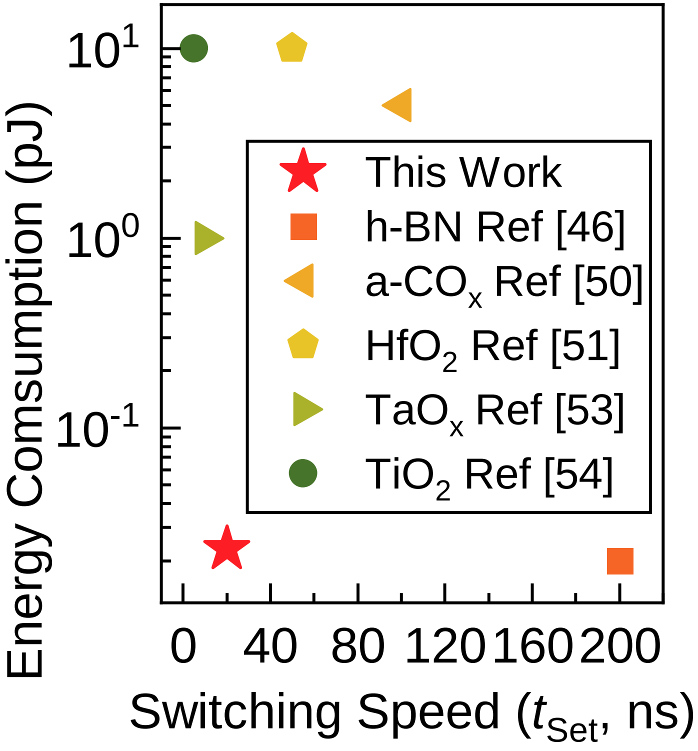


Energy consumption <20 fJ per operation, 10–100 times lower than the only truly commercial RRAM.

Comparison with Memristor Literature

One of the Best Performing Memristors Enabled by 2D Amorphous Carbon



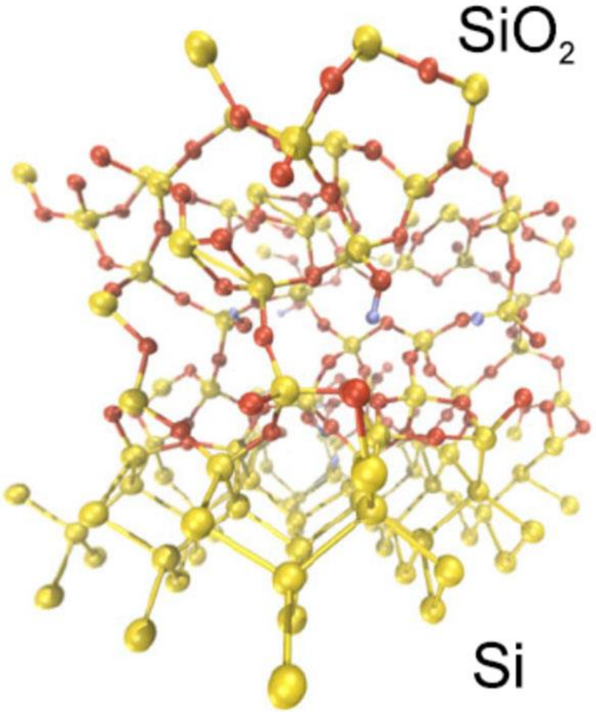


- One of the lowest operation voltage reported (left figure X axis, red stars).
- One of the smallest variations in operation voltage reported (left figure Y axis, red stars).
- One of the fastest and lowest energy consuming devices reported (right figure, red star).

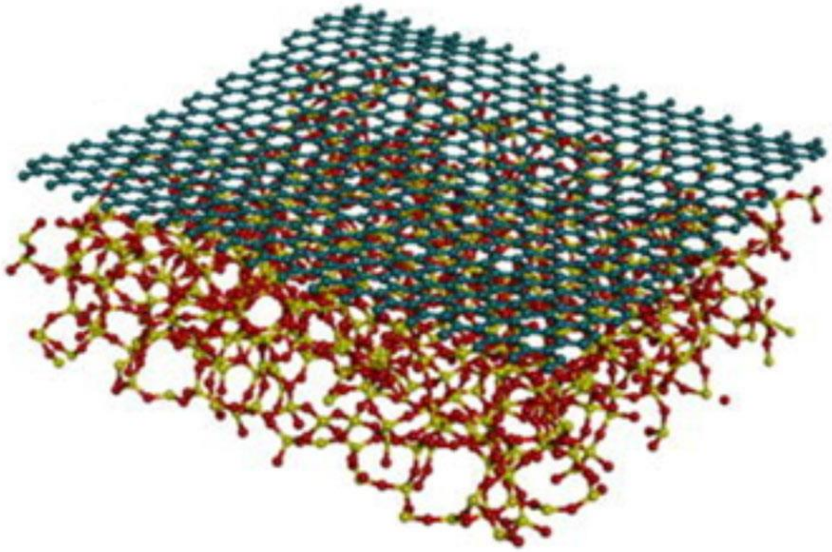
Device Application: Field Effect Transistor (FET)

Existing Dielectric Materials Not Tailored for 2D Electronic Materials

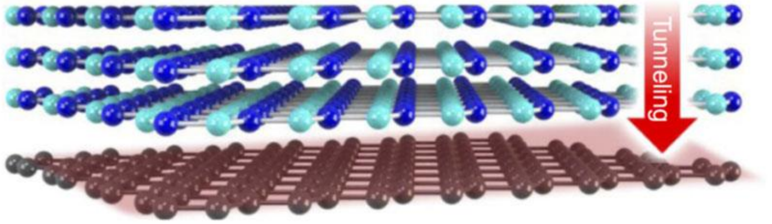
Nearly perfect interface between Si and SiO_2

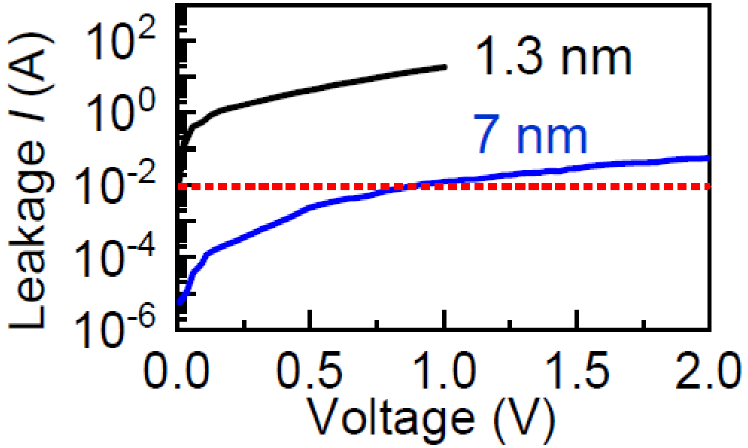


High density of traps and scattering centers at the interface



Leakage current through tunneling and grain boundaries

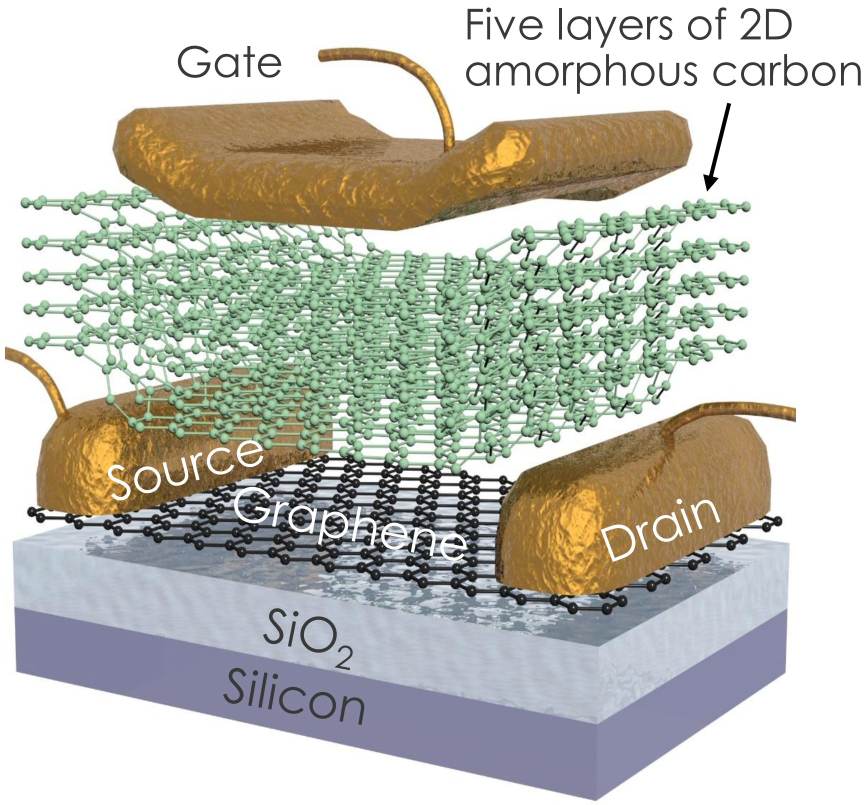


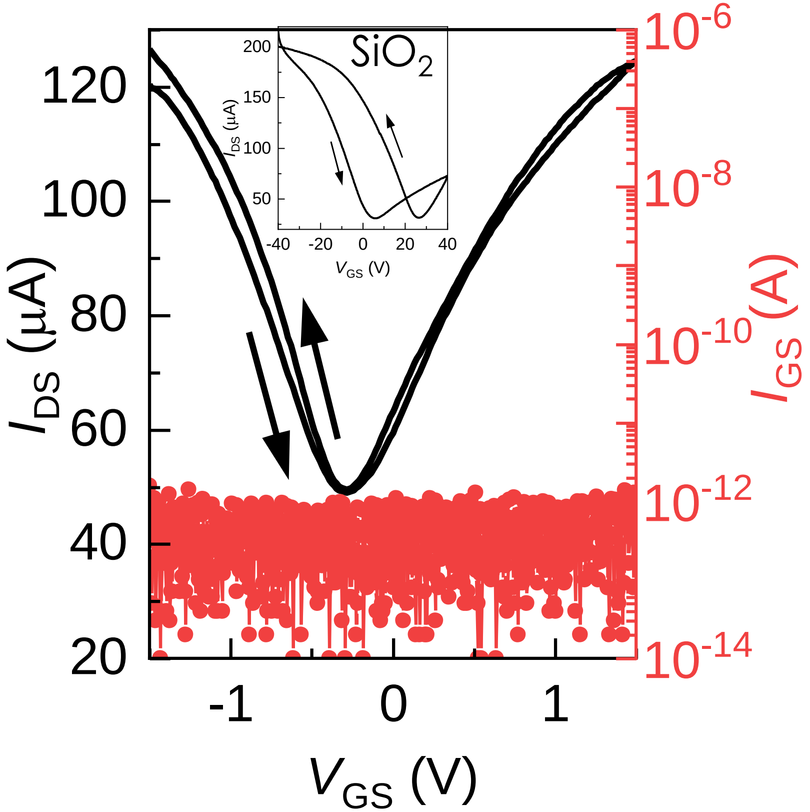


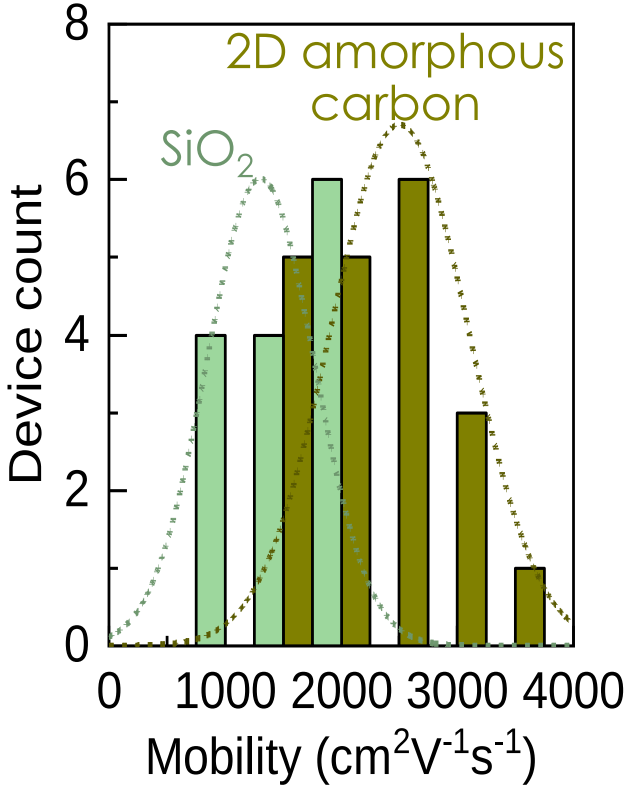
Nature Commun. ***11***, *3385 (2020).*
Nature Electron. ***4***, *98-108 (2021).*

Device Application: Gate Dielectric for Graphene FETs

Low Leakage Current, Reduced Hysteresis and Operation Voltage, High Effective Mobility



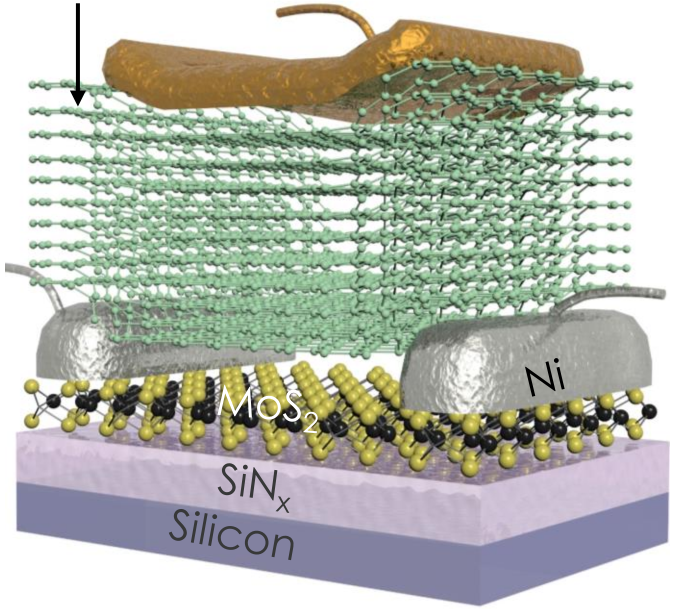


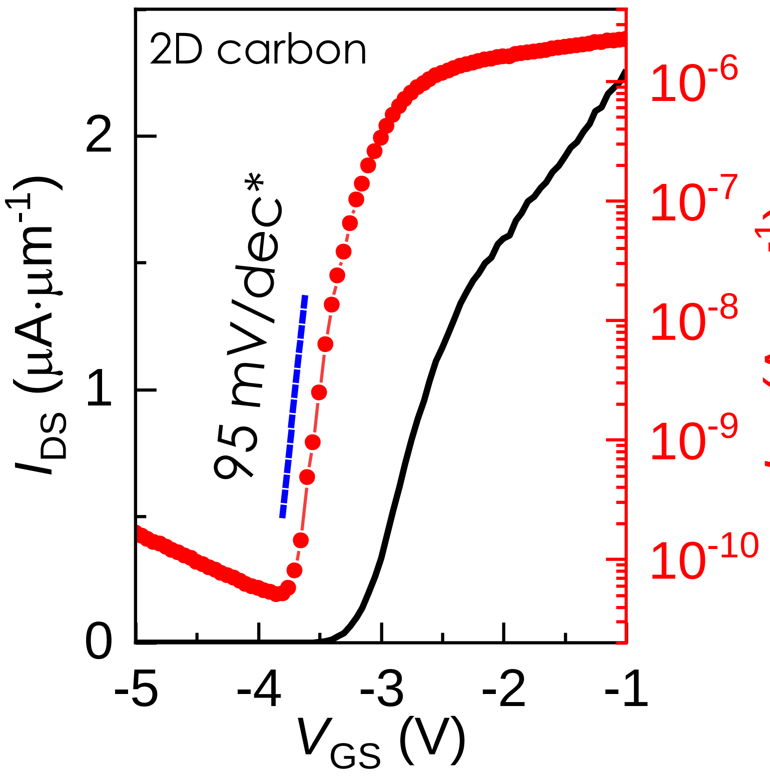


Gate Dielectric for High-Performance 2D MoS_2 Transistors

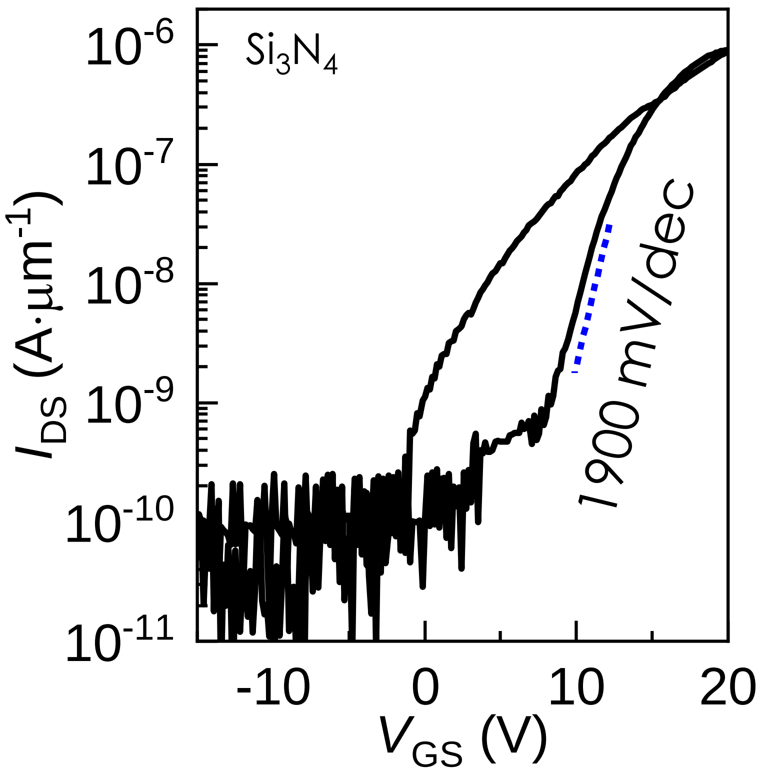
Reduced Hysteresis and Operation Voltage, Steeper subthreshold swing, High Effective Mobility

Transferred 10 layers of 2D amorphous carbon





$\mu = 15\ cm^2 \cdot V^{-1} \cdot s^{-1}$.



$\mu = 9\ cm^2 \cdot V^{-1} \cdot s^{-1}$.

Summary

Carbon Ore for Advanced Electronic Materials

- Synthesis and control of surface chemistry enable the production of the ideal solution precursor for the scalable fabrication of high performance 2D amorphous carbon.
- 2D amorphous carbon exhibits extraordinary mechanical and electrical properties that can enable next generation solid state electronic devices beyond the limit of existing technology with dramatically improved performance and reduced energy consumption.
- When implemented as the switching layer in memristors, the 2D amorphous carbon enables one of the best performing memristors with ultrafast switching time, low energy consumption, robust endurance, stable data retention, and reduced device spatiotemporal variability.
- Because of the ultrathinness and clean interface with 2D materials, the 2D carbon dielectric leads to dramatically improved device performance that compares favorably against state-of-the-art h-BN and high-κ oxides for FETs.

Coal: Don’t Burn It, Compute With It › A certain fossil fuel works well as a 2D insulating film for transistors

BY TAMMY XU | 24 JAN 2024 | 4 MIN READ

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Acknowledgments

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