Synthesis of Microscopic 3D Graphene for High-Performance Supercapacitors with Ultra-High Areal Capacitance

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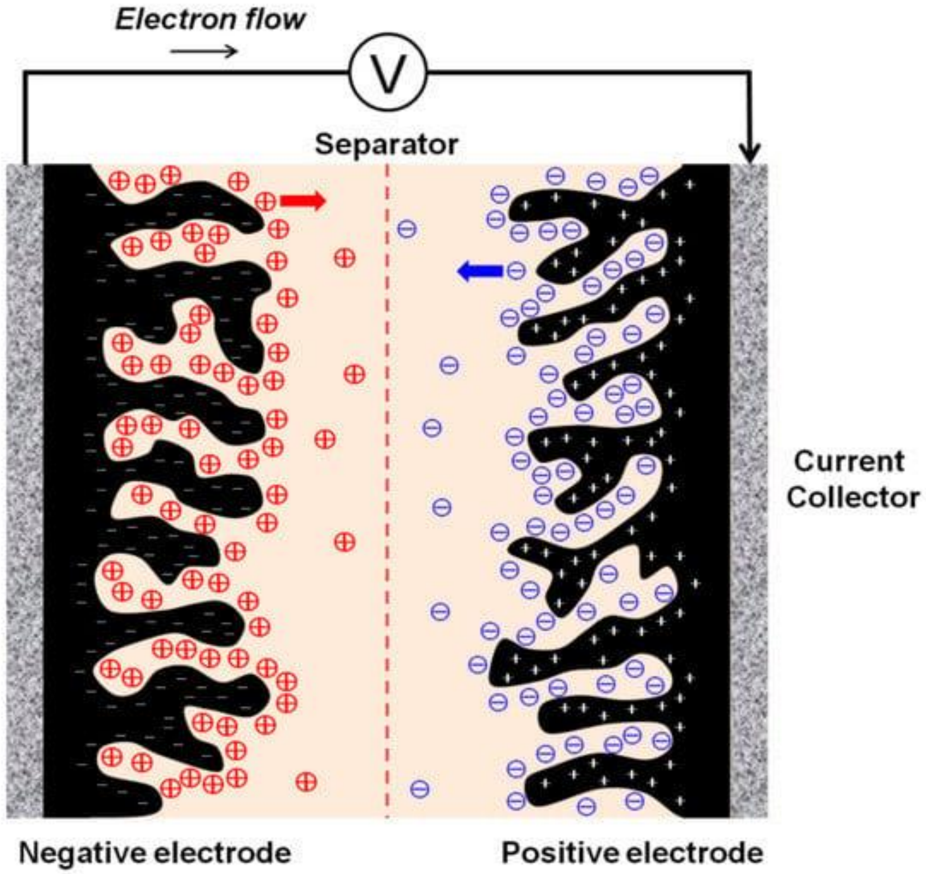
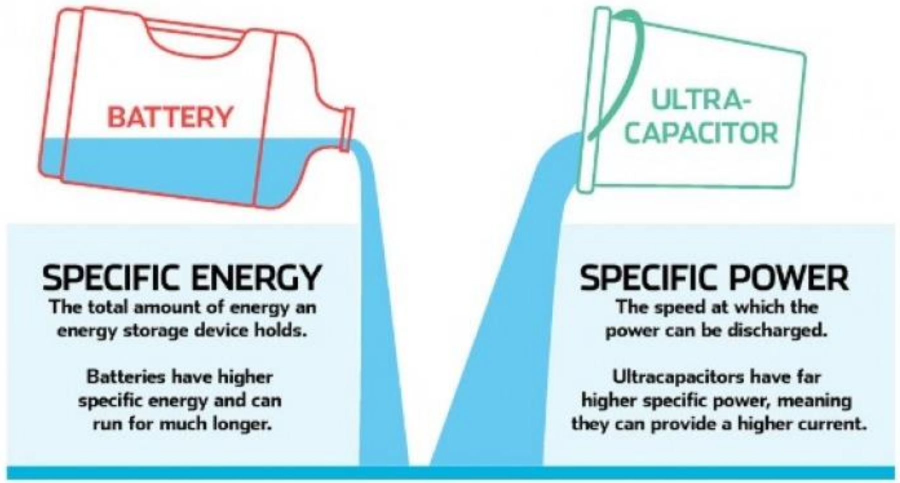
Outline

- Introduction of Supercapacitor and Its Application
- DOE Technical Assessment on Supercapacitors
- How to Make a Better Supercapacitors
- High Mass Loading Supercapacitors
- 3D Graphene From Coal Tar Pitch Feedstock and Its Application as Supercapacitor Electrode Materials
- Recycling Chemical Activator Toward Sustainable Production
- Summary

What is a Supercapacitor?



Schematic illustration of the porous carbon-based supercapacitor (Materials 2020, 13(18), 4215).

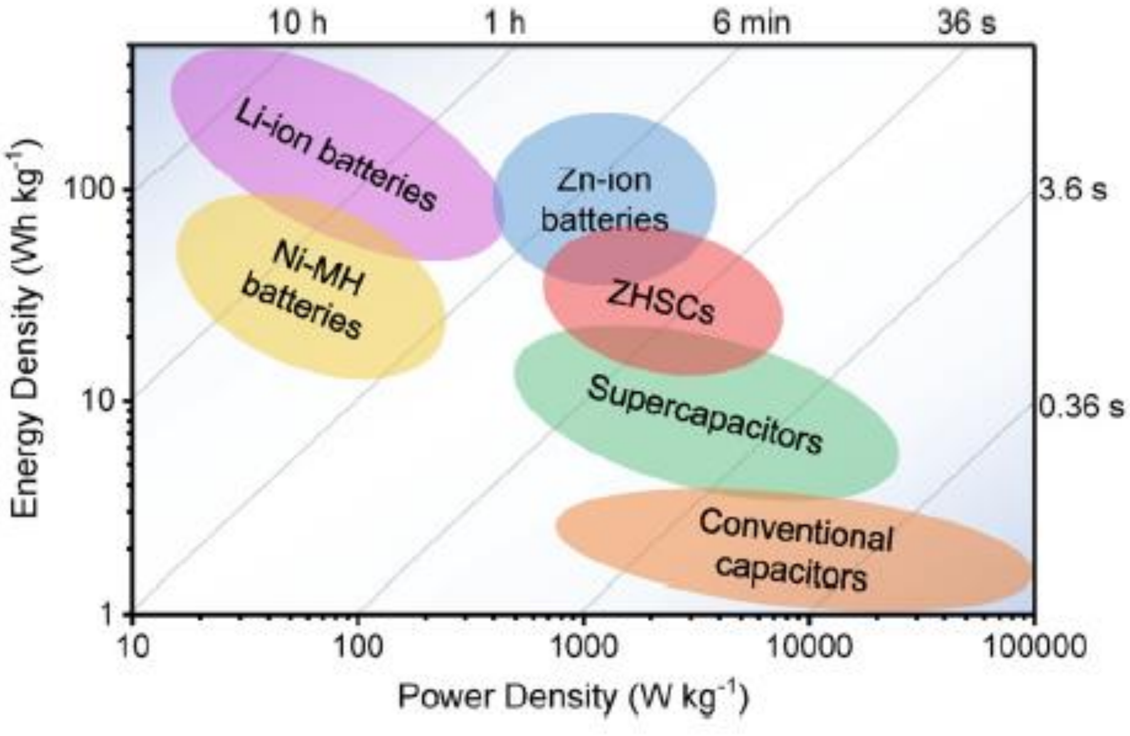


(https://interestingengineering.com/science/could-ultracapacitors-replace-batteries-in-future-electric-vehicles.)

- Supercapacitors, also called ultracapacitor or electrochemical capacitors, consist of two electrodes separated by an ion-permeable membrane (separator), and an electrolyte ionically connecting both electrodes
- Porous carbons are dominated electrode materials
- Supercapacitors vs. batteries = high power density vs. high energy density

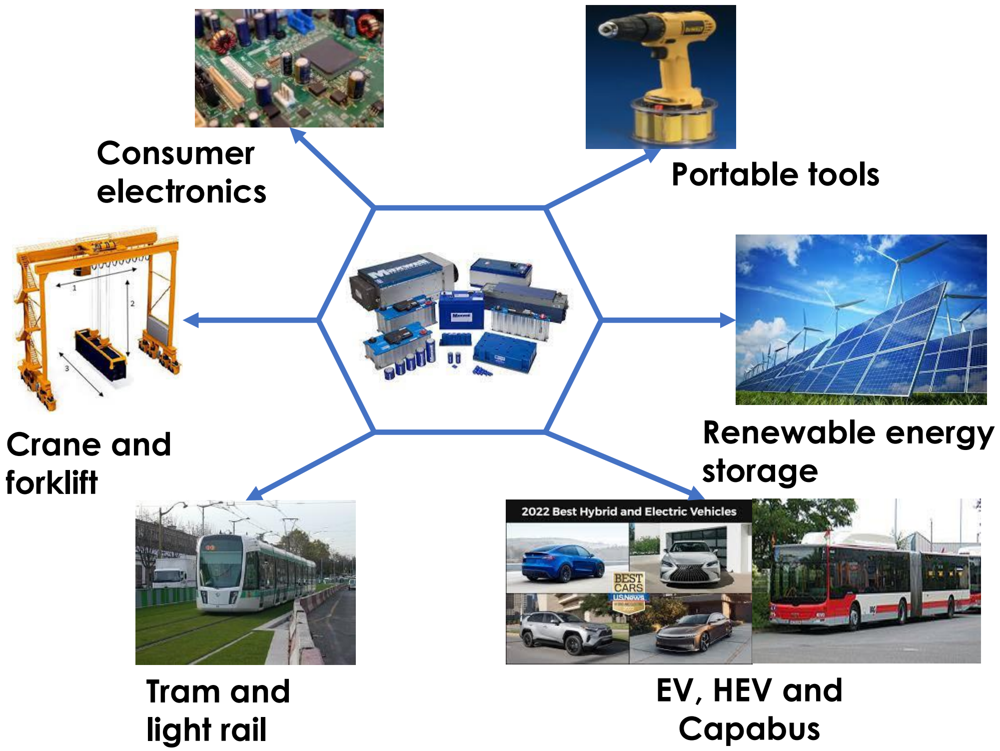
Supercapacitor's Application

Supercapacitors vs. other electrochemical storage devices

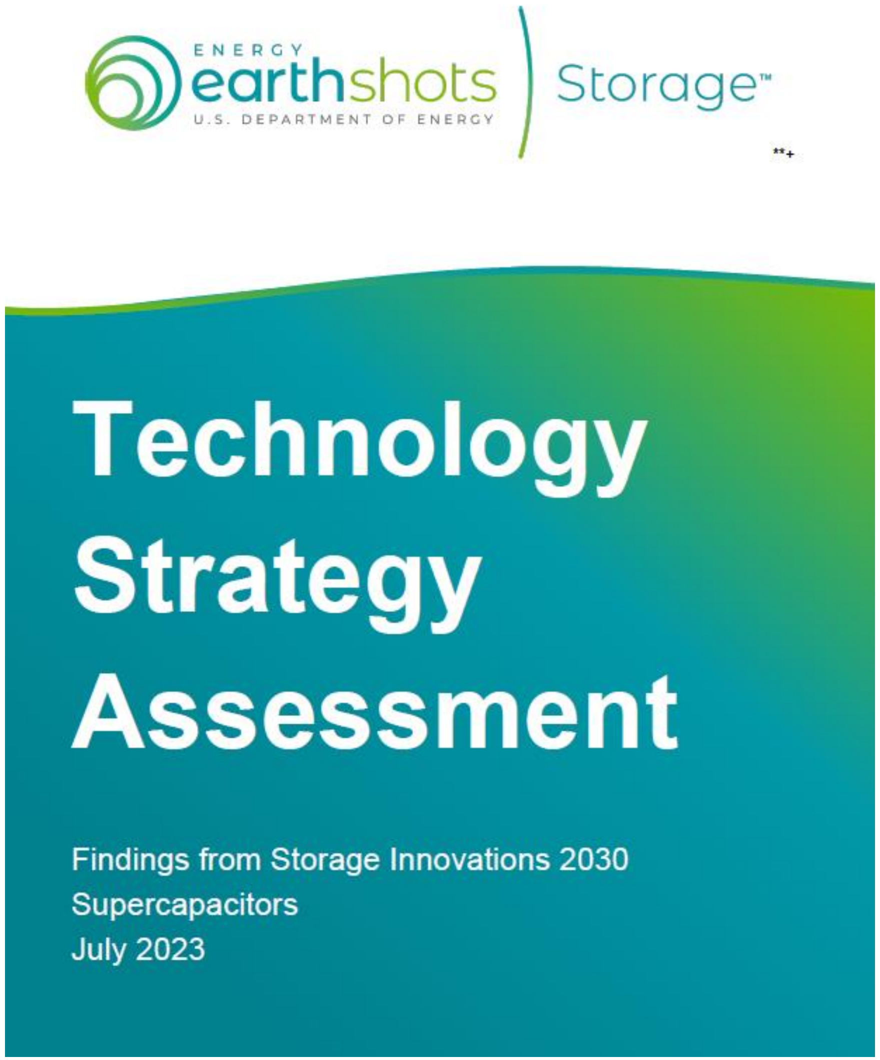


(Carbon Energy, 2020, 2, 521–539.)

Supercapacitor applications



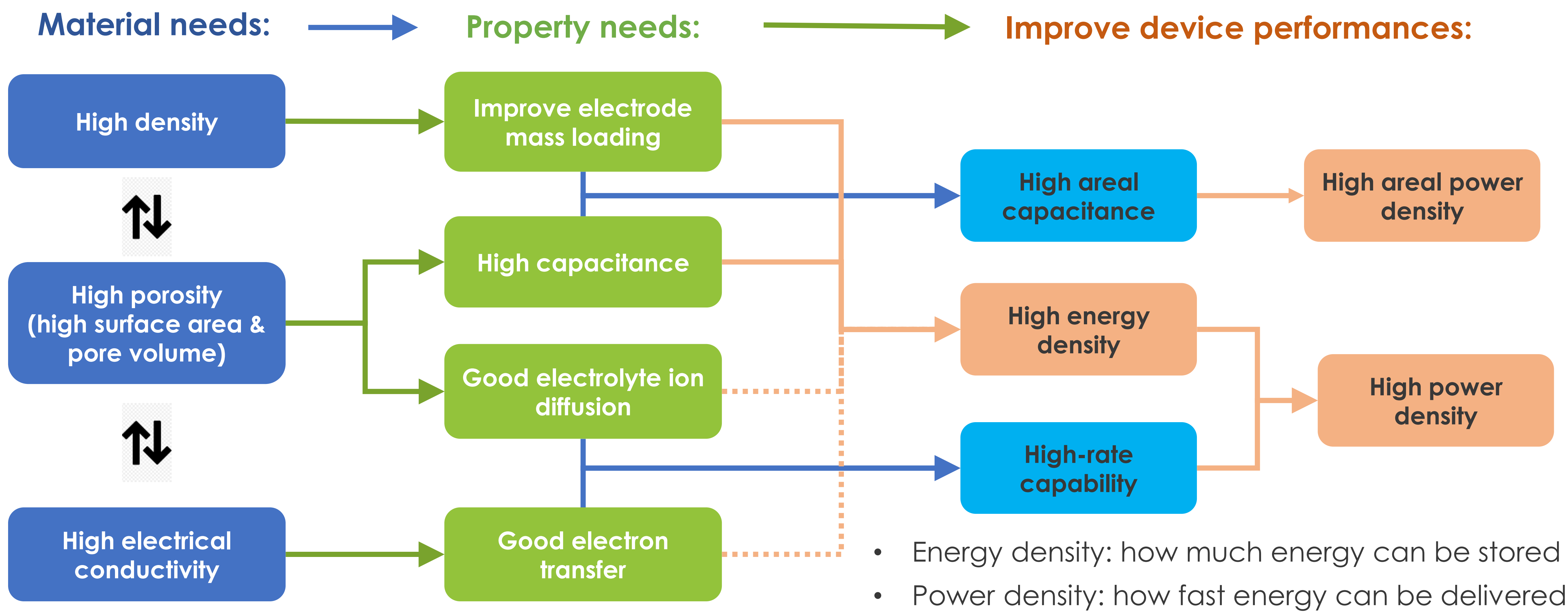
DOE Technology Assessment



- Current state-of-the-art (SOTA): activated carbon, offshore supply chains
- Materials: ~71% of device cost, with carbon as most significant component
- Graphene improves performance by >72%, but is expensive, industrial-scale sources do not exist
- Graphene electrodes identified as a key innovation for improving performance and levelized cost of storage (LCOS)

(https://www.energy.gov/sites/default/files/2023-07/Technology%20Strategy%20Assessment%20-%20Supercapacitors_0.pdf)

How to Make a Better Supercapacitor Device

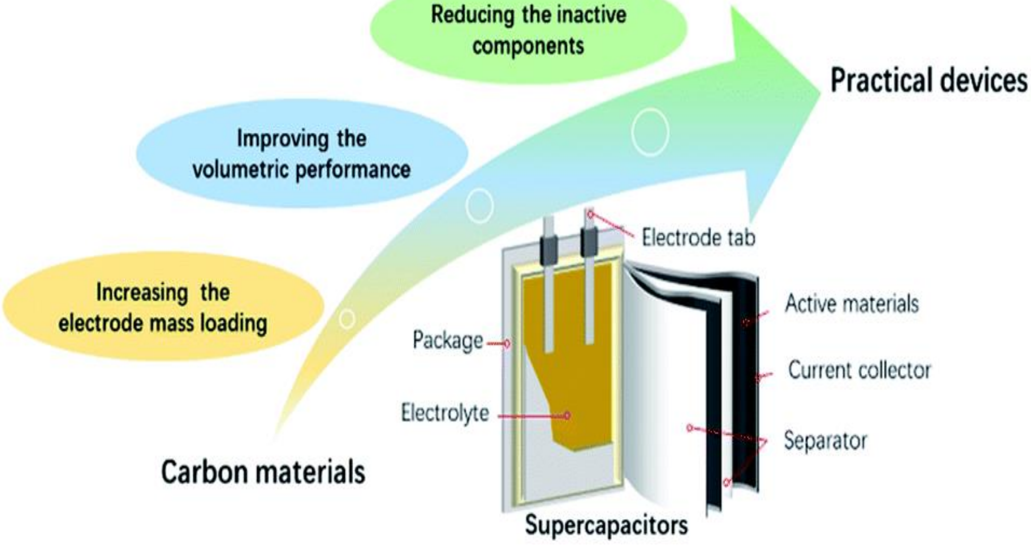


- Energy density: how much energy can be stored
- Power density: how fast energy can be delivered
- High-rate capability: large amount of energy can be delivered fast

Electrode Materials for Supercapacitors

Most supercapacitor electrode materials are *high surface area carbons*:

	Activated Carbon	Carbon Nanotube	Graphene
Surface area (m^2/g)	1,000–3,000	100–1,300	200-2,600
Electrical conductivity	Low	Medium to high	Medium to high
Density	Low to medium	Low	Low
Potential application	Commercial practice	Research only	**High potential – research stage**

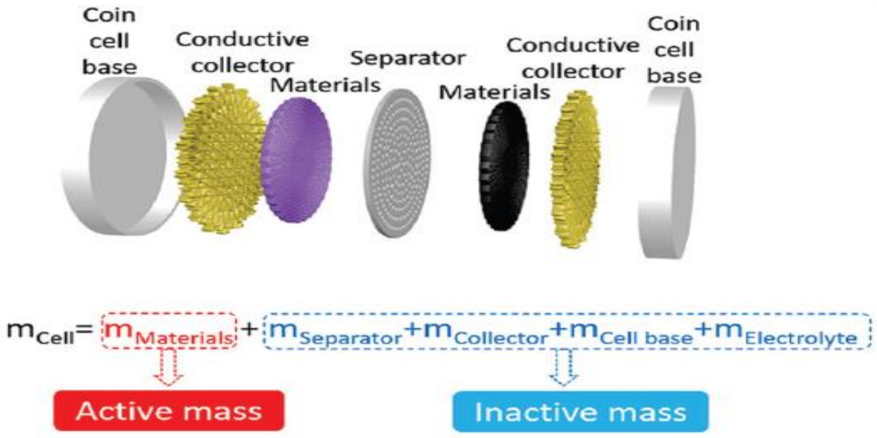


An overview of the design of carbon materials for practical application, and a scheme of full supercapacitors (*J. Mater. Chem. A, 2020, 8, 21930*).

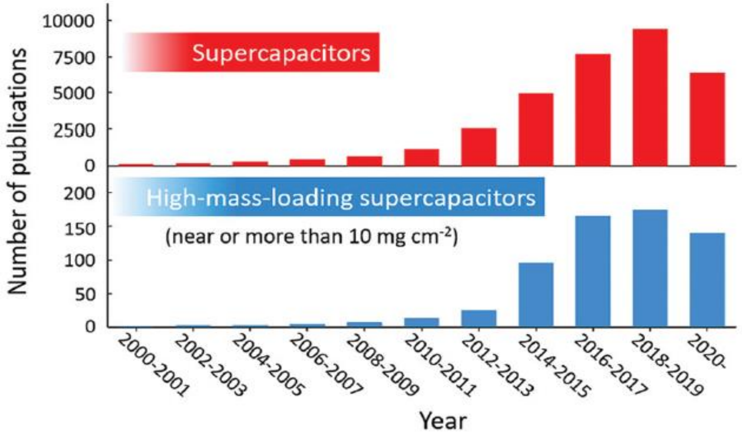
Commercial device requirements for electrode materials:

- Electrode mass loading: ≥10 mg/cm^2
- Electrode thickness: ≥200 μm
- Areal capacitance: ≥2 F/cm^2
- Active material is about 30% mass of supercapacitor cell

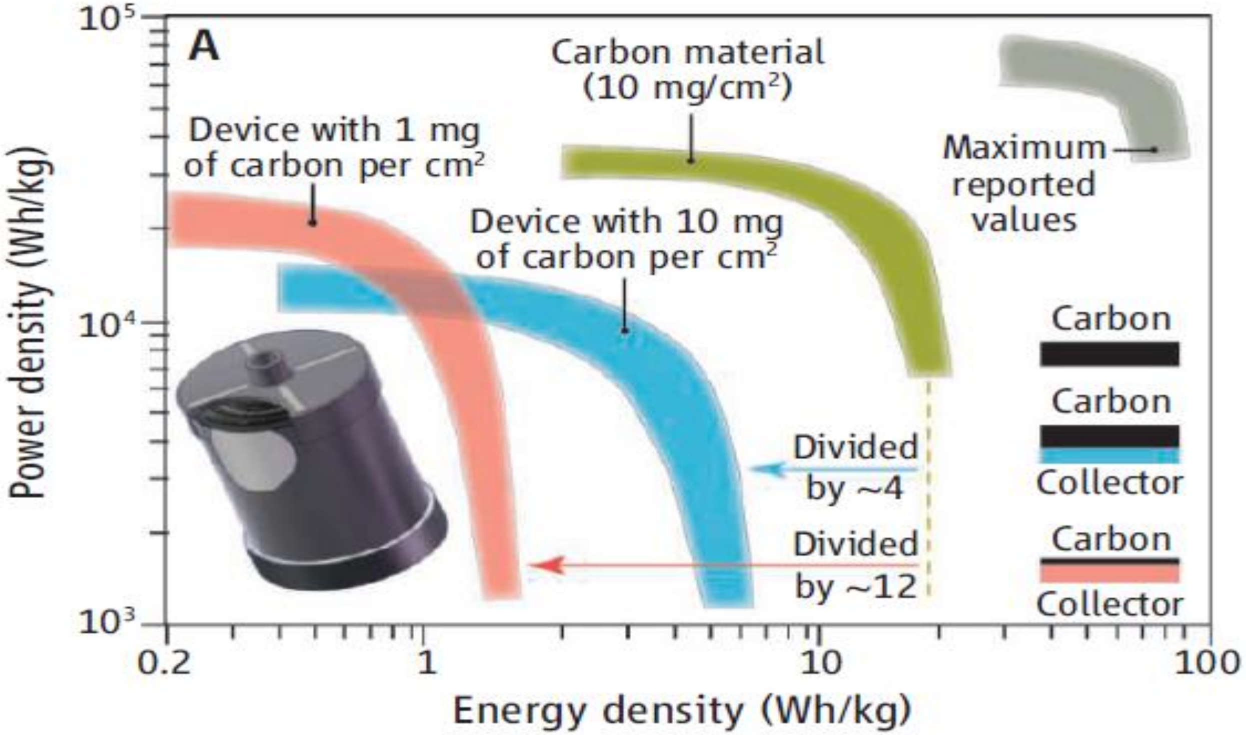
High Areal Mass-Loading Supercapacitors



Schematic illustration of the construction of the coin cell.
(Energy Environ. Sci., 2021, 14, 576601)



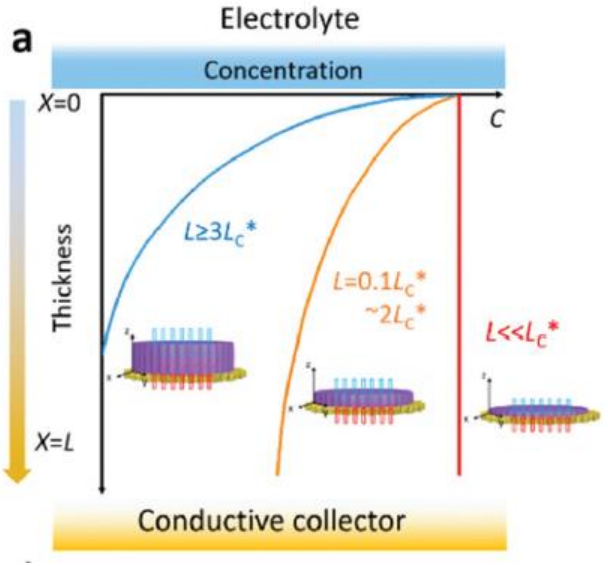
Number of publications about "supercapacitors" and "high mass-loading supercapacitors."



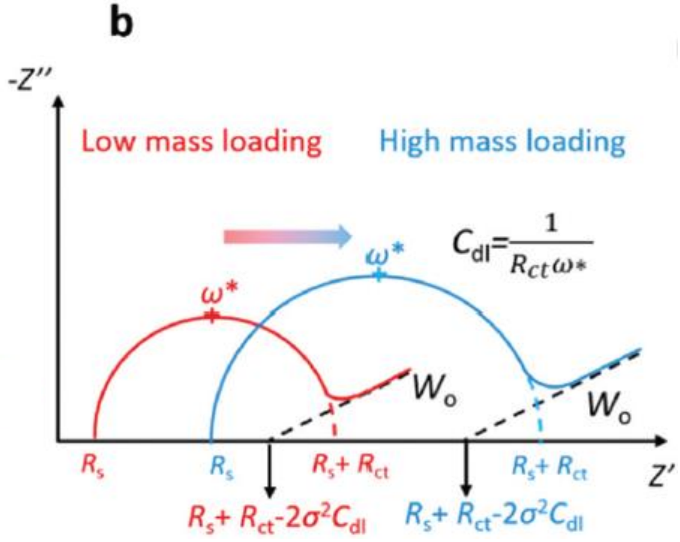
Ragone plot of supercapacitor cells with different areal mass loading.
(Science, 2011, 334, 917-918)

High Areal Mass-Loading Supercapacitors

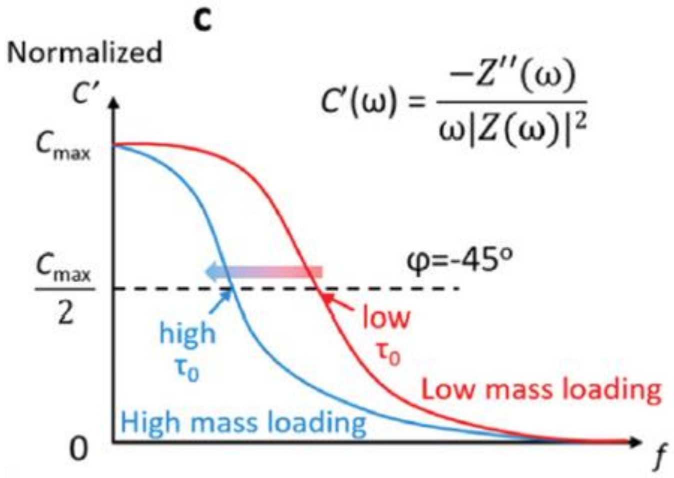
Challenges associated with high mass loading supercapacitors:



Concentration distributions of electrolyte ions for electrodes with different thicknesses.



The Nyquist curves.



The frequency response curves.

Electrode materials for high mass-loading supercapacitors:

- High surface area → improving specific capacitance
- Hierarchical macro-, meso-, and micropores distribution → improving electrolyte ion diffusion
- High electrical conductivity → improving electron transfer

(Energy Environ. Sci., 2021, 14, 576601.)

3D Graphene for Supercapacitors

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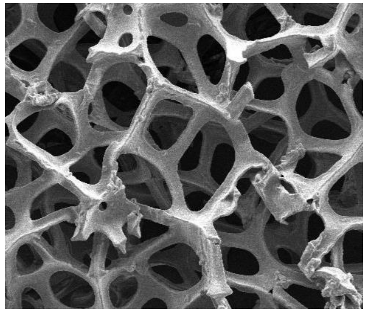
3D Graphene as the Most Potential Electrode Material for Supercapacitors

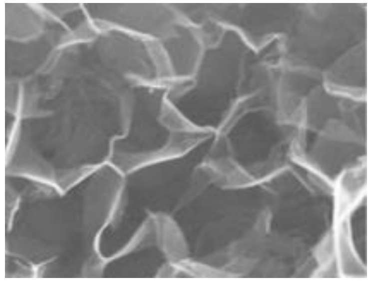
3D graphene assembling based on graphene oxide (GO)

- Self-assembling of GO
- Reduction of 3D GO assembly
- Concurrent reduction and 3D construction



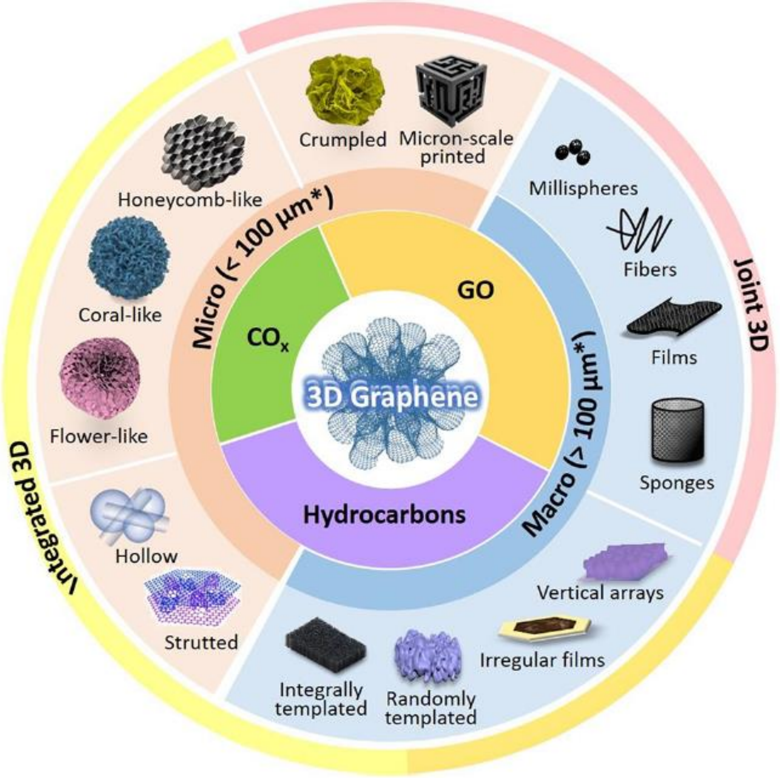
3D graphene construction from hydrocarbons

- Chemical vapor deposition (CVD)
- On-site polymerization (OSP) of nongaseous hydrocarbons



3D graphene building with inorganic carbon compounds

- Alkali metal oxide and CO
- Alkali metal and CO/CO_2

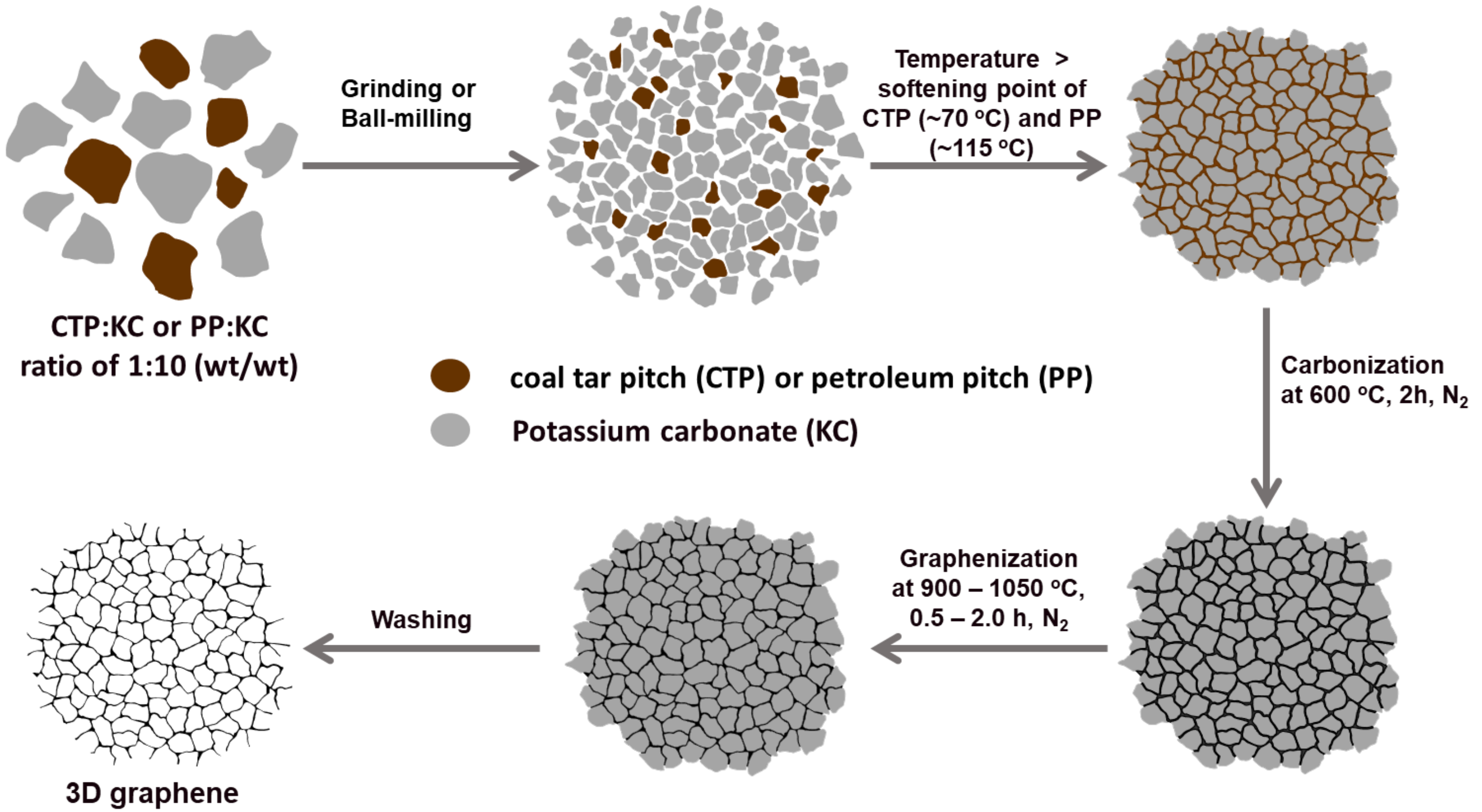


General diagram about the types of 3D graphene materials (Chem. Rev. 2020, 120, 10336–10453).

All these methods are highly expensive, multi-steps, and hardly scalable

Synthesis of 3D Graphene for Supercapacitors

Synthesis of 3D Graphene Using Coal Tar Pitch and Petroleum Pitch Feedstocks

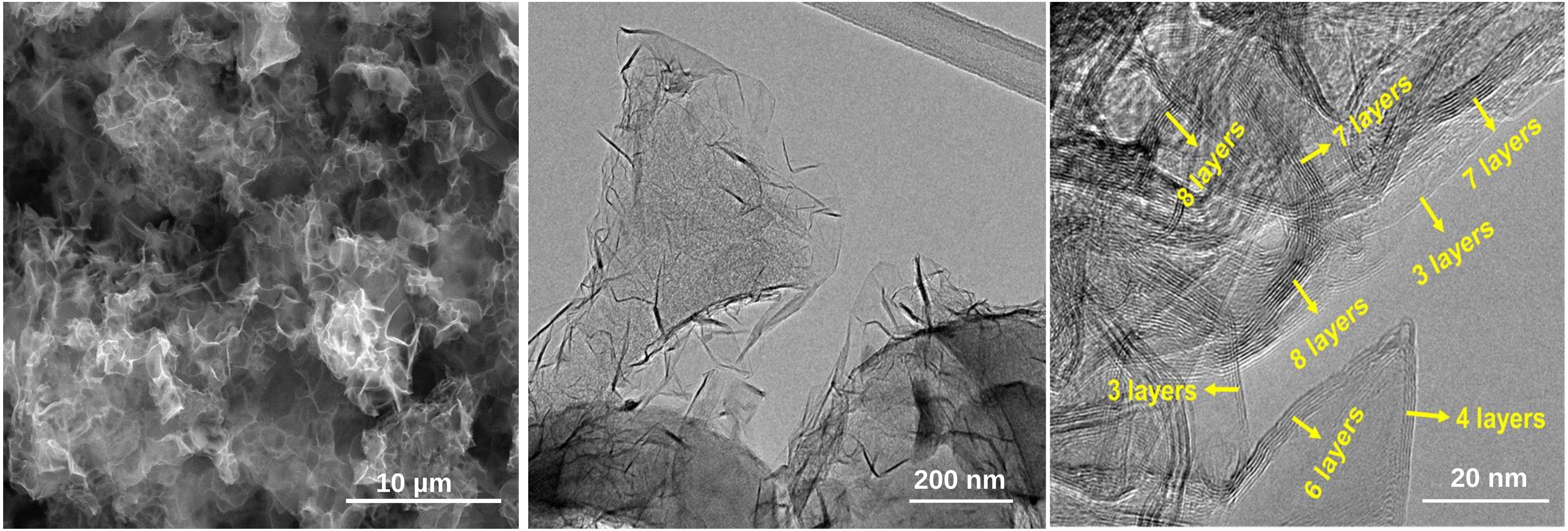


Photograph of ~3.0 g of 3DG-900 in 100 mL petri dish.

- Low cost and scalable method to produce high-quality 3D graphene
- Recycling 95% KC for at least 10 times without compromising the quality of 3D graphene

Synthesis of 3D Graphene for Supercapacitors

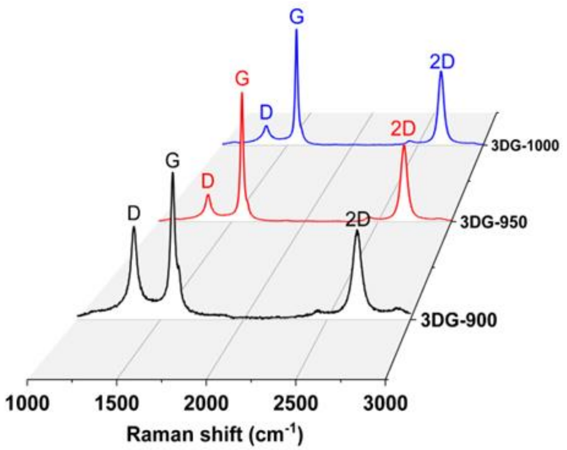
Characteristics of 3D Graphene



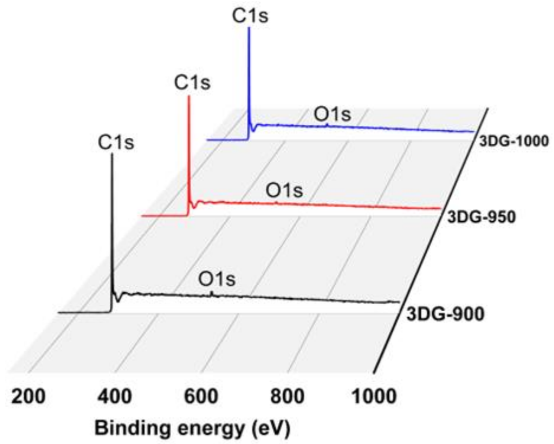
SEM and TEM images of 3DG-900.

Synthesis of 3D Graphene for Supercapacitors

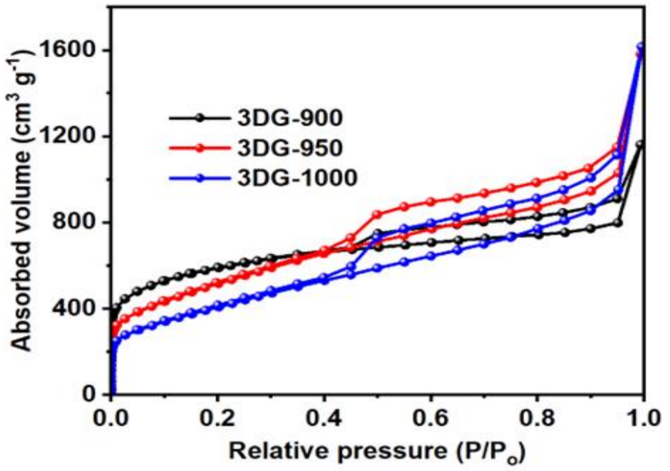
Characteristics of 3D Graphene



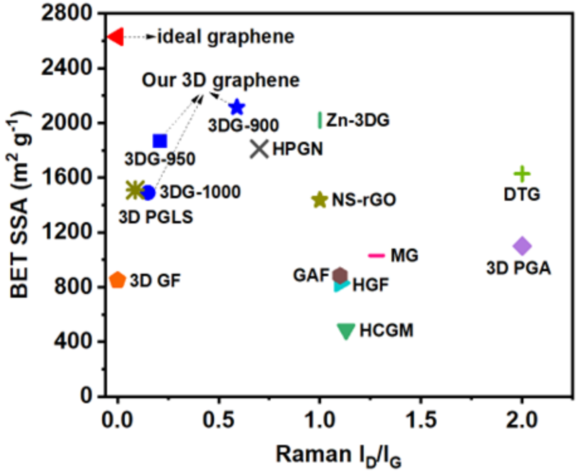
Raman of 3DGs.



XPS of 3DGs.



N_2 isotherms of 3DGs.



3DGs vs. literature.

- Raman I_D/I_G of 0.15 – 0.7 and I_{2D}/I_G of 0.60 – 0.67 → highly crystalline
- Prominent XPS C1s and minor O1s → C/O atomic ratio of 44.6 – 61.5 → very low defect → high electrical conductivity of 1,300 – 2,700 S/m
- N_2 isotherms = type I(b) + type IV(a) characteristics → a hierarchical pore structure consisting of macro-, meso-, and micro-pores. BET SSA of 1,500 – 2,100 m^2/g
- BET SSA and Raman I_D/I_G of 3DGs approaching ideal graphene → high quality

Small Methods 2024, 2301426

Synthesis of 3D Graphene for Supercapacitors

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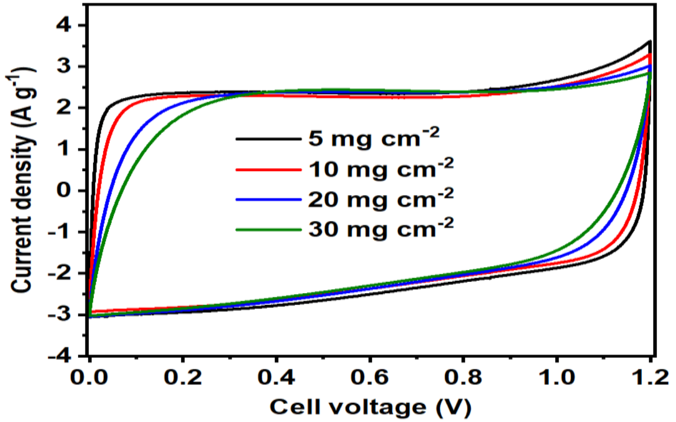
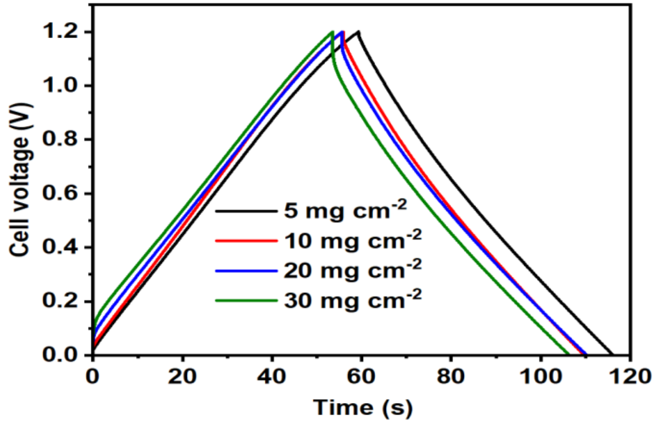
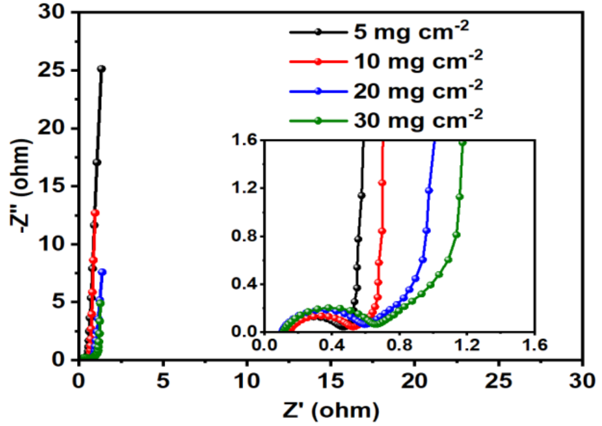
3D Graphene as Electrode Material for Supercapacitors with Ultra-High Areal Capacitance



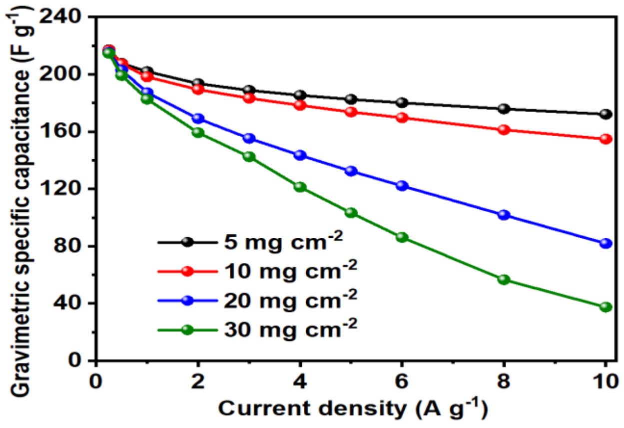
Cyclic voltammetry curves at 25 mV/s.



Charge-discharge curves at 1.0 A/g.



Nyquist plots.



Gravimetric specific capacitance.

- The microscopic 3D structure with hierarchical pore size distribution (which do not collapse during electrode fabrication) + high surface area + high electrical conductivity → ultra-high mass loading, up to 30 mg/cm^2
- High C/O ratio (44.6) → chemically inert surface → extending working voltage of supercapacitors using aqueous 6M KOH electrolyte from 1.0 to 1.2 V → 44% improving energy density

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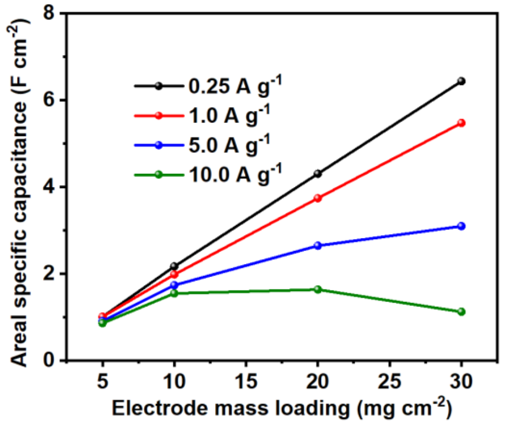
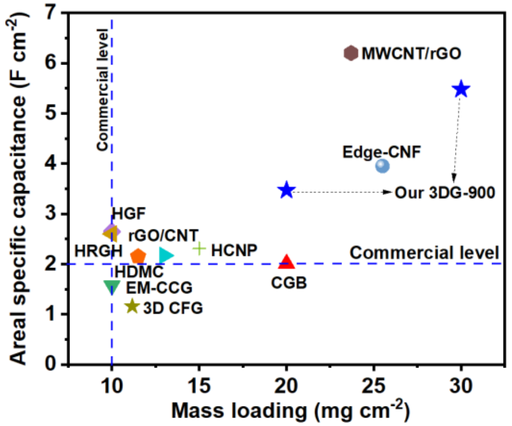
Synthesis of 3D Graphene for Supercapacitors

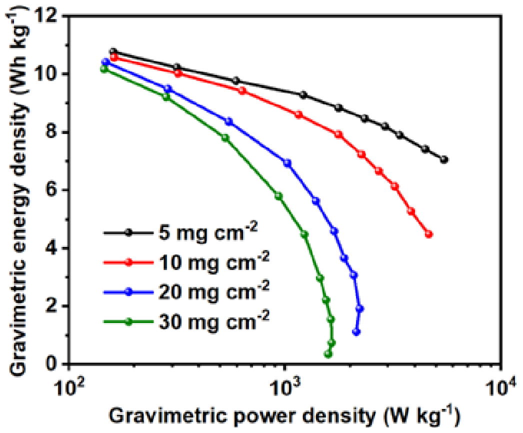
3D Graphene as Electrode Material for Supercapacitors with Ultra-High Areal Capacitance



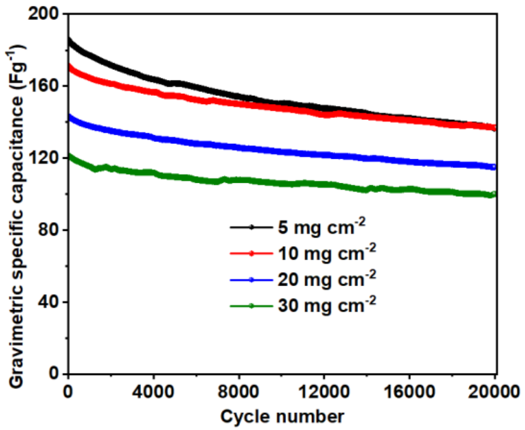
Areal specific capacitance.



3D graphene vs. literature.



Ragone plots.



Cycling stability at 4.0 A/g.

- High specific capacitance + ultra-high mass loading → ultra-high areal capacitance, up to 6.4 F/cm^2, more than 3 times commercial requirement
- High specific capacitance + extended working voltage of 1.2V → excellent energy density of ≥ 10 Wh/kg
- Excellent cycling stability with ~80% capacitance retention after 20,000 cycles, even at extended working voltage

Small Methods 2024, 2301426.

Synthesis of 3D Graphene for Supercapacitors

Comparison of 3DG-900 with commercial SOTA Kuraray YP-50F for high mass loading supercapacitors using 6M KOH electrolyte

Electrode Material	Electrolyte	Working Voltage	Mass Loading (mg/cm^2)	Current Density (A/g)	Specific Capacitance (F/g)	Areal Capacitance (F/cm^2)	Gravimetric Energy Density (Wh/kg)
3DG-900	6M KOH	1.2 V	30	1.0 A/g	182	5.48	10.1
Commercial SOTA (Kuraray YP-50F)	6M KOH	1.2 V	30	1.0 A/g	124	3.58	6.9

NETL 3DG-900 graphene improves performance over SOTA:

- Specific Capacitance by ~47%
- Areal Capacitance by ~53%
- Gravimetric Energy Density by ~46%

Synthesis of 3D Graphene for Supercapacitors

Comparison of 3DG-900 with representative carbon electrode materials for high mass loading supercapacitors, testing in two-electrode configuration in recent literature

Electrode Material	BET SSA (m^2/g)	Electrolyte	Mass Loading (mg/cm^2)	Current Density (A/g) or (mA/cm^2)	Gravimetric Capacitance (F/g)	Areal Capacitance (F/cm^2)	Maximum Gravimetric Energy Density (Wh/kg)	Reference
3DG-900	2,113	6M KOH	30	1.0 A/g	182	5.48	10.1	NETL
Commercial SOTA (YP-50F Activated Carbon)	1,700	6M KOH	30	1.0 A/g	124	3.58	6.9	NETL
Holey graphene framework	830	6M KOH	10	1.0 A/g	250	2.5	9.2	1
MWCNT/rGO ten-bilayer hybrid	166	5M LiCl	23.7	20 mA/cm^2 (~0.84 A/g)	262	6.20	5.8	2
GQD assembled porous carbon	1,323	6M KOH	20.0	1.0 A/g	215	4.30	6.5	3

References: 1. Nat. Commun., 2014. 5, 4554.
2. Adv. Mater, 2017. 29, 1606679.
3. Carbon, 2020. 161, 89-96.

Synthesis of 3D Graphene for Supercapacitors

Recycling K_2CO_3

During thermal treatment process:

- A small quantity of K_2CO_3 is consumed during the activation redox reaction with CTP at above 600 °C :

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \qquad (1)$$

- Partial decomposition of K_2CO_3 also occurs above 800 °C

$$K_2CO_3 \rightarrow K_2O + CO_2 \qquad (2)$$

During washing process:

$$2K + 2H_2O \rightarrow 2KOH + H_2 \qquad (3)$$

$$K_2O + H_2O \rightarrow 2KOH \qquad (4)$$

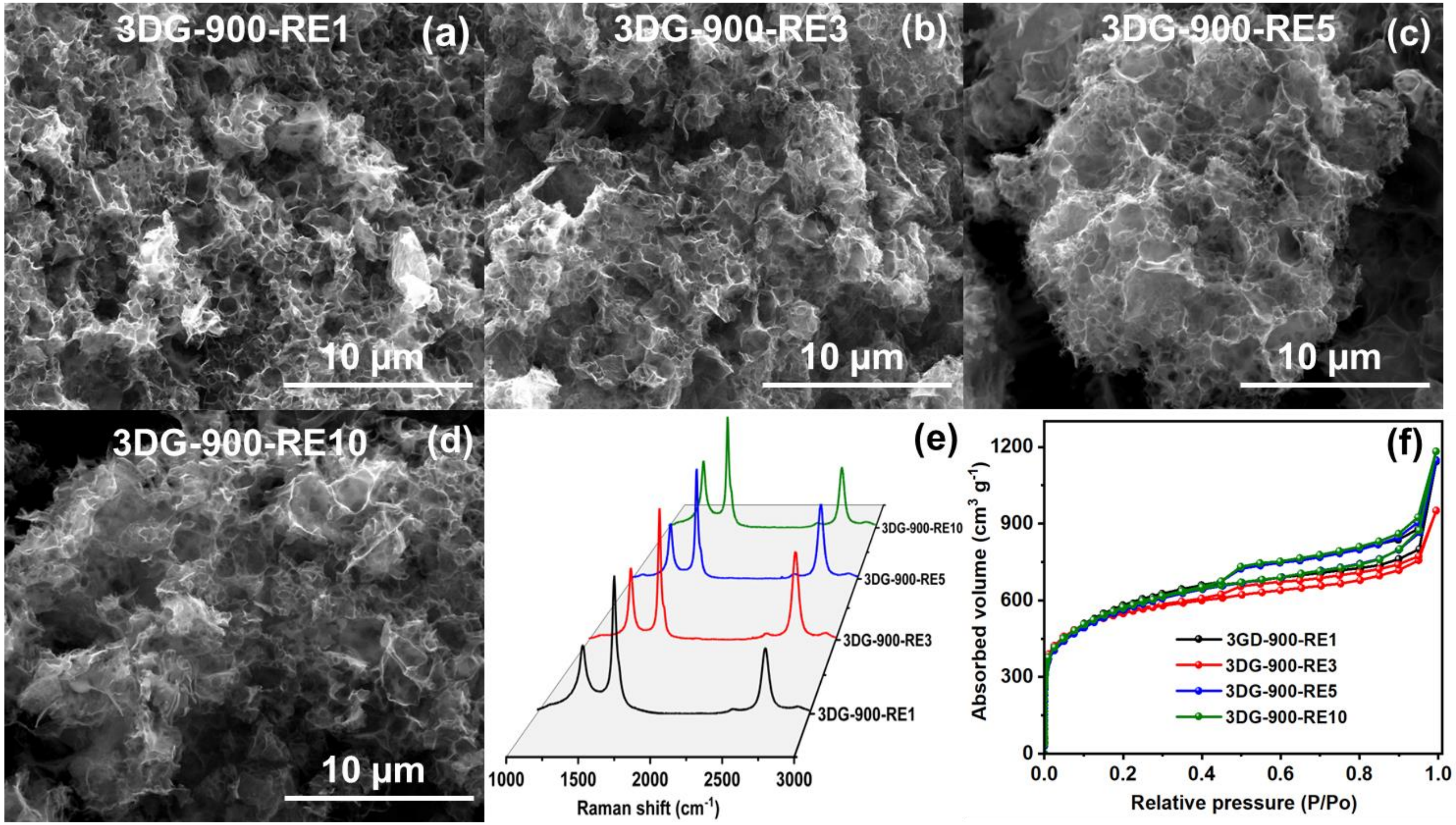
During recycling process:

$$KOH + KHCO_3 \rightarrow K_2CO_3 + H_2O \qquad (5)$$

It is possible to recycle K_2CO_3 up to 95% for at least 10 cycles.

Synthesis of 3D Graphene for Supercapacitors

Recycling K_2CO_3 for 10 Cycles



(a-d) SEM images, (e) Raman spectra, and (f) N_2 isotherms of 3DG-900-Rex using recycled K_2CO_3.

Synthesis of 3D Graphene for Supercapacitors

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Electrochemical Capacitive Properties of 3D Graphene Using Recycled K_2CO_3

Electrode Material	BET SSA (m^2/g)	Gravimetric Capacitance at 1.0 A/g (F/g)	Energy Density (Wh/kg)	Capacitance Retention After 10,000 Cycles (%)
3DG-900	2,113	198	9.52	86.2
3DG-900-RE1	2,058	182	8.78	85.9
3DG-900-RE3	2,002	185	8.89	88.2
3DG-900-RE5	2,005	179	8.64	89.7
3DG-900-RE10	2,043	180	8.71	85.6
Commercial SOTA YP-50F	1,746	126	6.08	93.4

Summary

- This study developed a low-cost and scalable method to convert coal tar pitch into high-quality 3D graphene with high surface area, hierarchical pore size distribution, and high electrical conductivity which allows the supercapacitor electrode to be fabricated with ultra-high mass loading (30 mg/cm^2), leading to ultra-high areal capacitance.
- The NETL 3DG-900 graphene improves electrochemical capacitive performance over the SOTA Kuraray YP-50F by ~50%.
- Recycling K_2CO_3 for at least 10 times led to potentially low-cost and sustainable production of 3D graphene.

Acknowledgments

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