Graphene-Based Carbon Electrode Material for Improving the Performance of Supercapacitors

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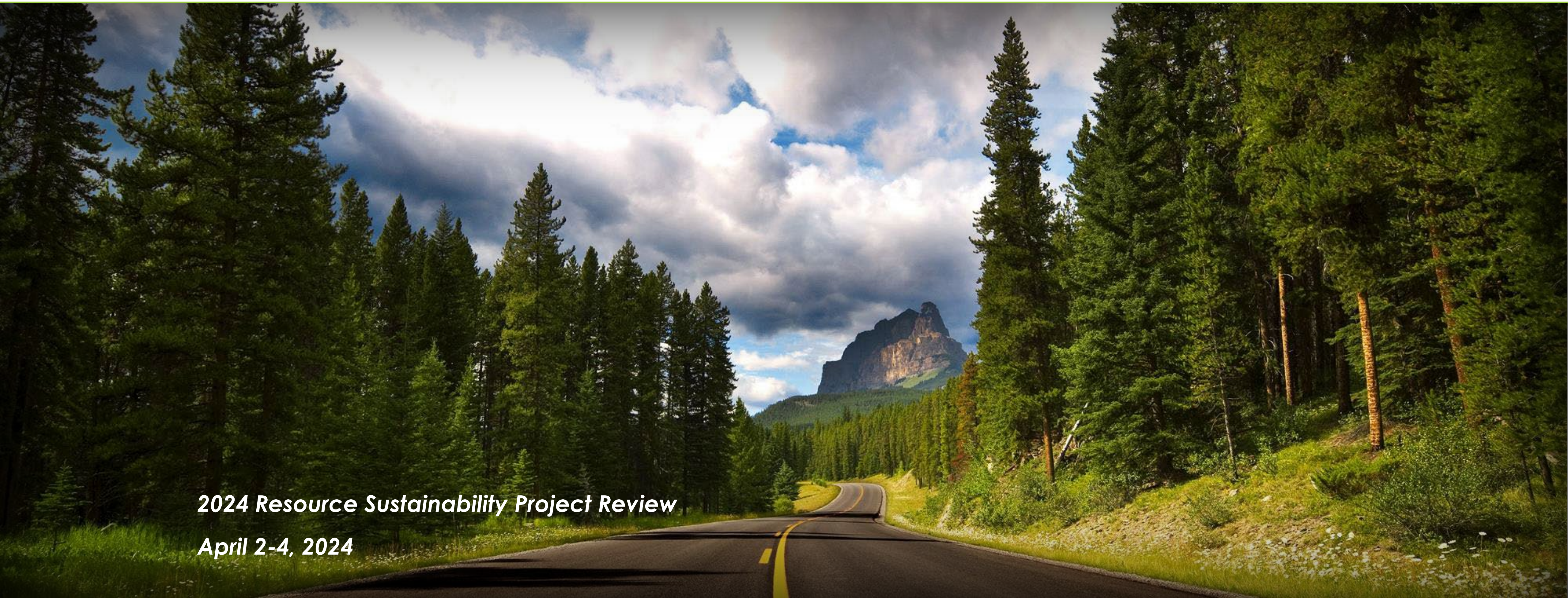

2024 Resource Sustainability Project Review

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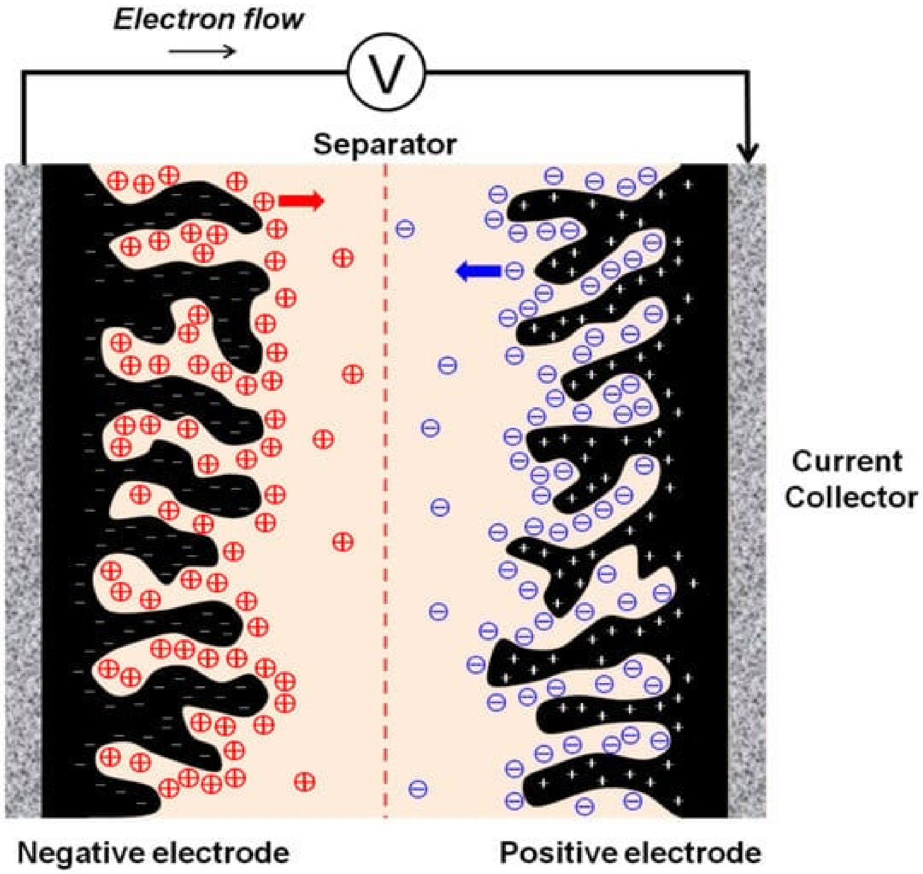
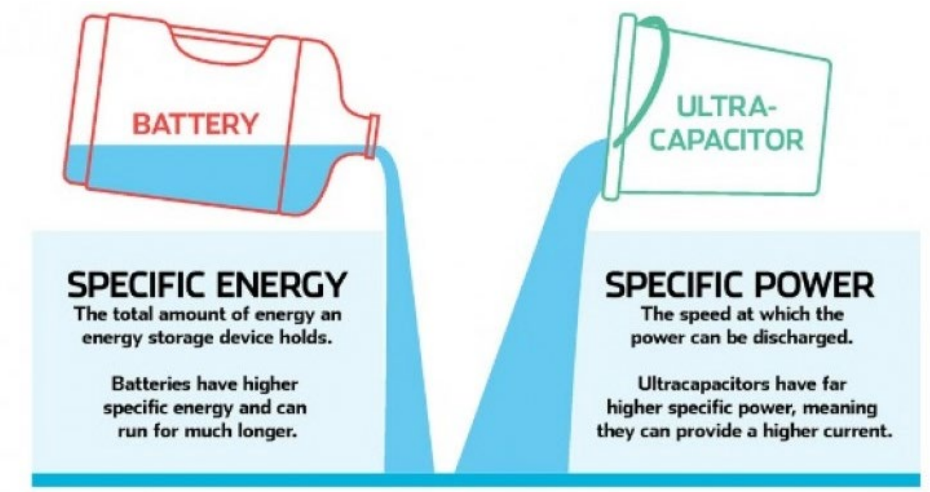
Outline

- ❖ Introduction of Supercapacitor and Its Application
- ❖ DOE Technical Assessment on Supercapacitor
- ❖ How to Make a Better Supercapacitor
- ❖ 3D Graphene From Coal Tar Pitch Feedstock and Its Application as Supercapacitor Electrode Materials
- ❖ Recycling Chemical Activator Toward Sustainable Production
- ❖ Potential Environmental Impact (Elemental Analysis of Feedstock)
- ❖ Summary

What is 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

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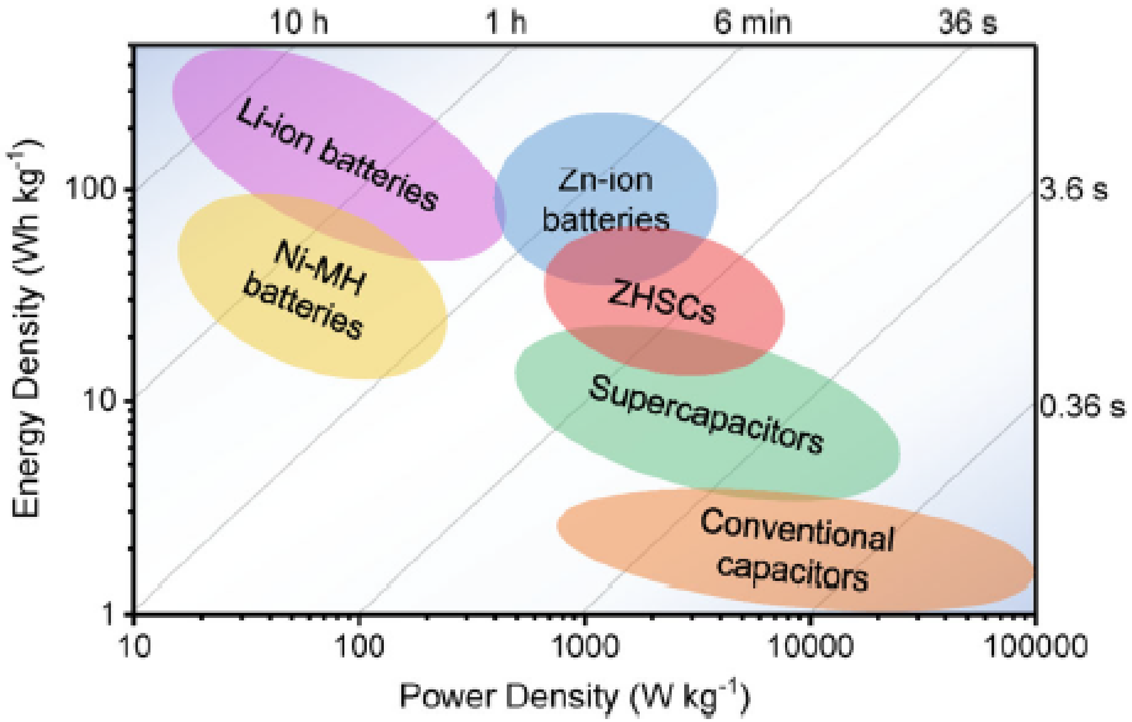
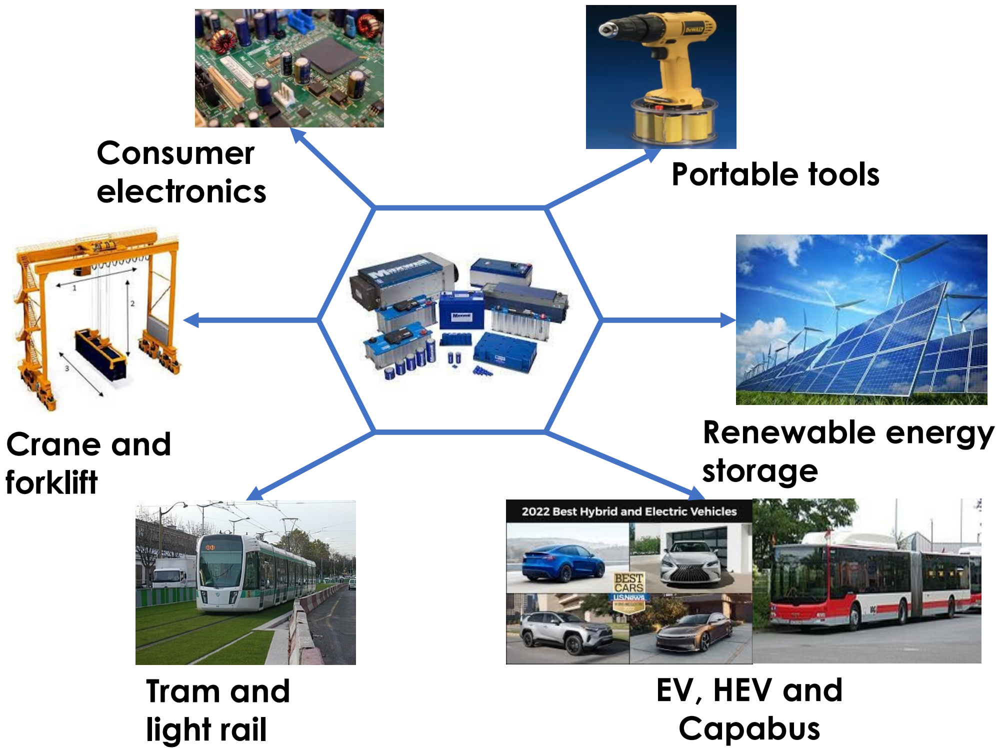
Supercapacitors vs. other electrochemical storage devices

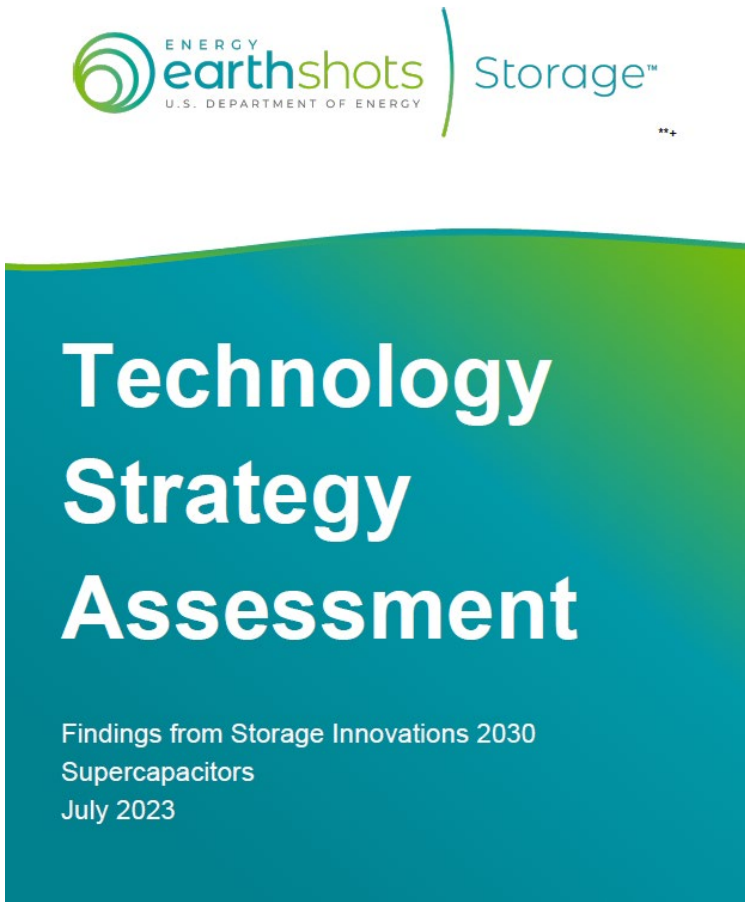


(Carbon Energy, 2020, 2, 521–539)

Supercapacitor applications



DOE Technology Assessment


ENERGY earthshots U.S. DEPARTMENT OF ENERGY | Storage™

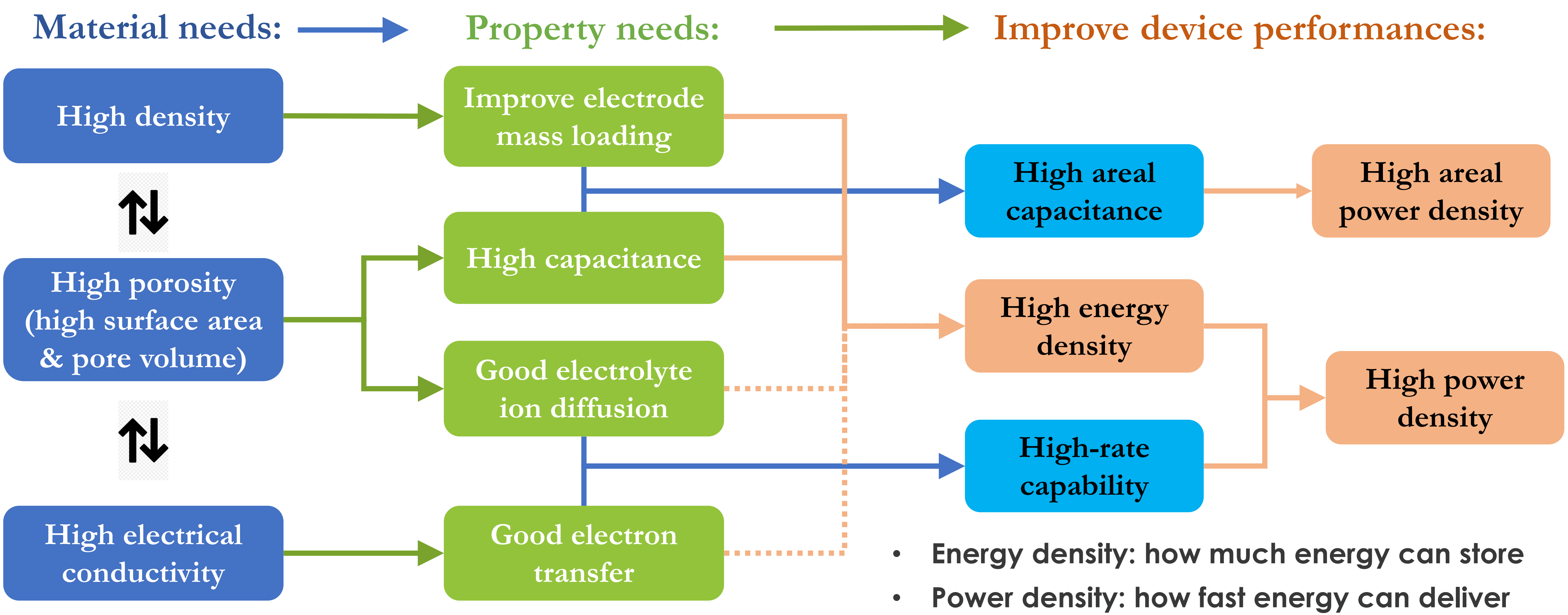
Technology Strategy Assessment

Findings from Storage Innovations 2030
Supercapacitors
July 2023

- Released as part of the Long-Duration Storage Shot, contains the findings from the Storage Innovations 2030 strategic initiative
- Current state-of-the-art: activated carbon, offshore supply chains
- Materials: ~ 71% of device cost, with activated carbon as most significant component
- Graphene could improve performance by >72%, but is expensive, industrial-scale sources do not exist
- Graphene electrodes identified as 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



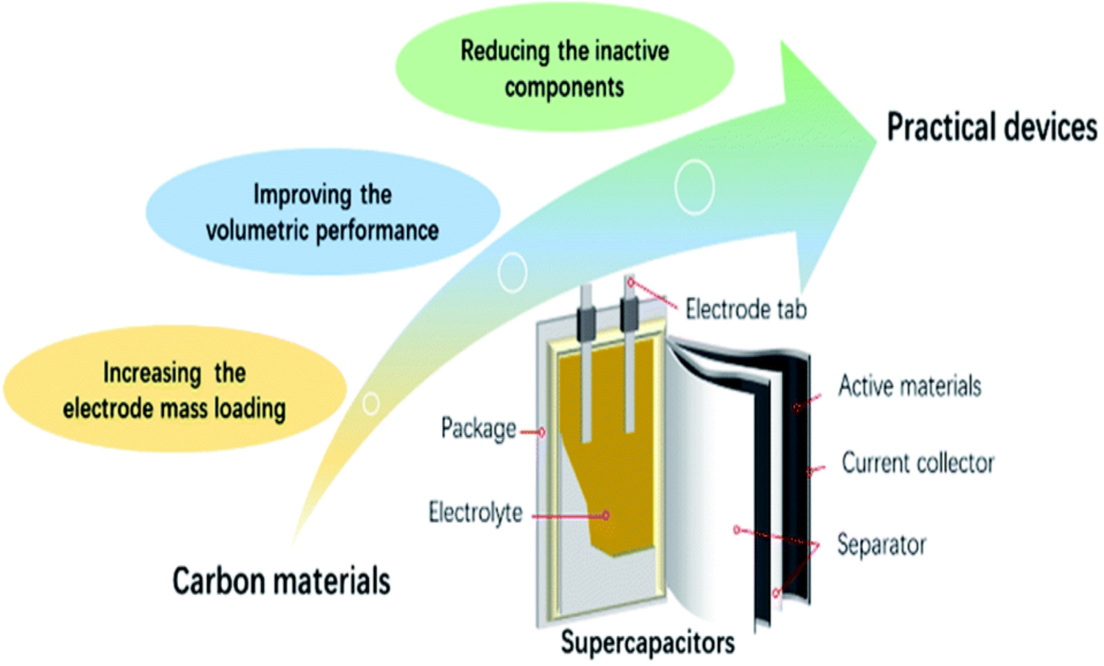
- Energy density: how much energy can store
- Power density: how fast energy can deliver
- High-rate capability: large amount of energy can be fast delivered

Synthesis of 3D Graphene 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	**Highly potential – research stage**

- **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

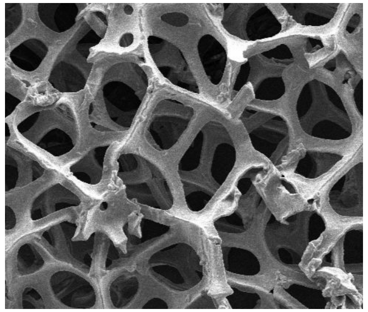


An overview of the design of carbon materials for practical application, and a scheme of full supercapacitors (*J. Mater. Chem. A, 2020, 8, 21930*)

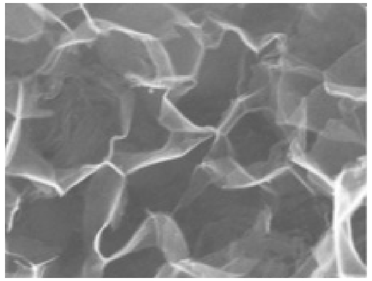
Synthesis of 3D Graphene for Supercapacitors

3D graphene as the most potential electrode material for supercapacitors

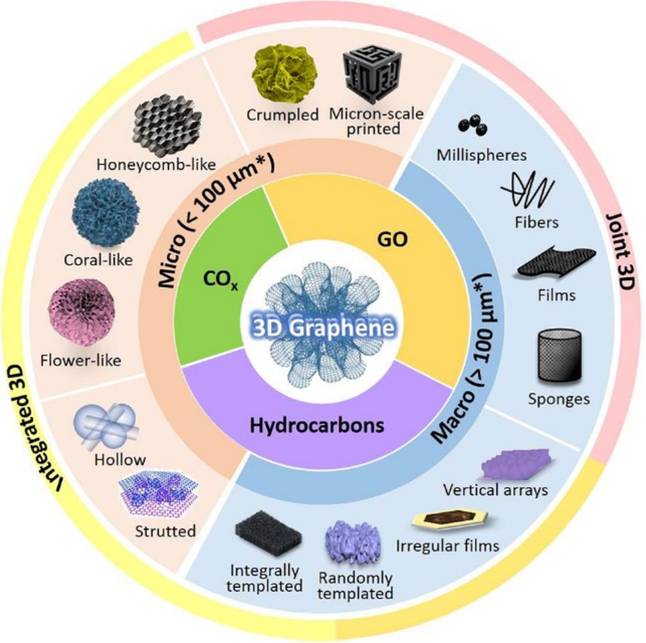
- **3D graphene assembling based on graphene oxide (GO)**
  - Self-assembling of GO
  - Reduction of 3D GO assembly
  - Concurrent reduction and 3D construction



- **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

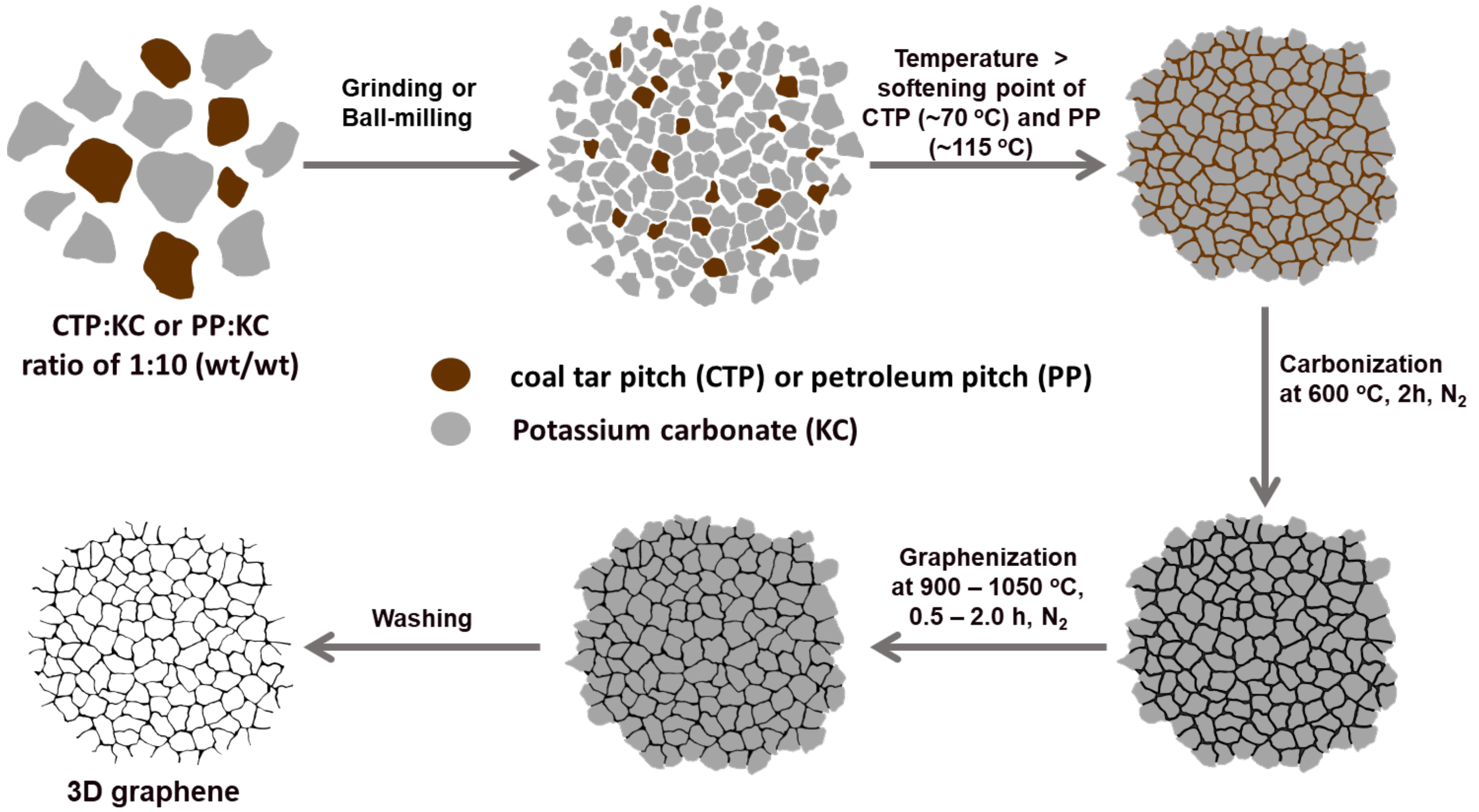


General diagram about the types of 3D graphene materials (Chem. Rev. 2020, 120, 10336−10453)

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

Synthesis of 3D Graphene for Supercapacitors

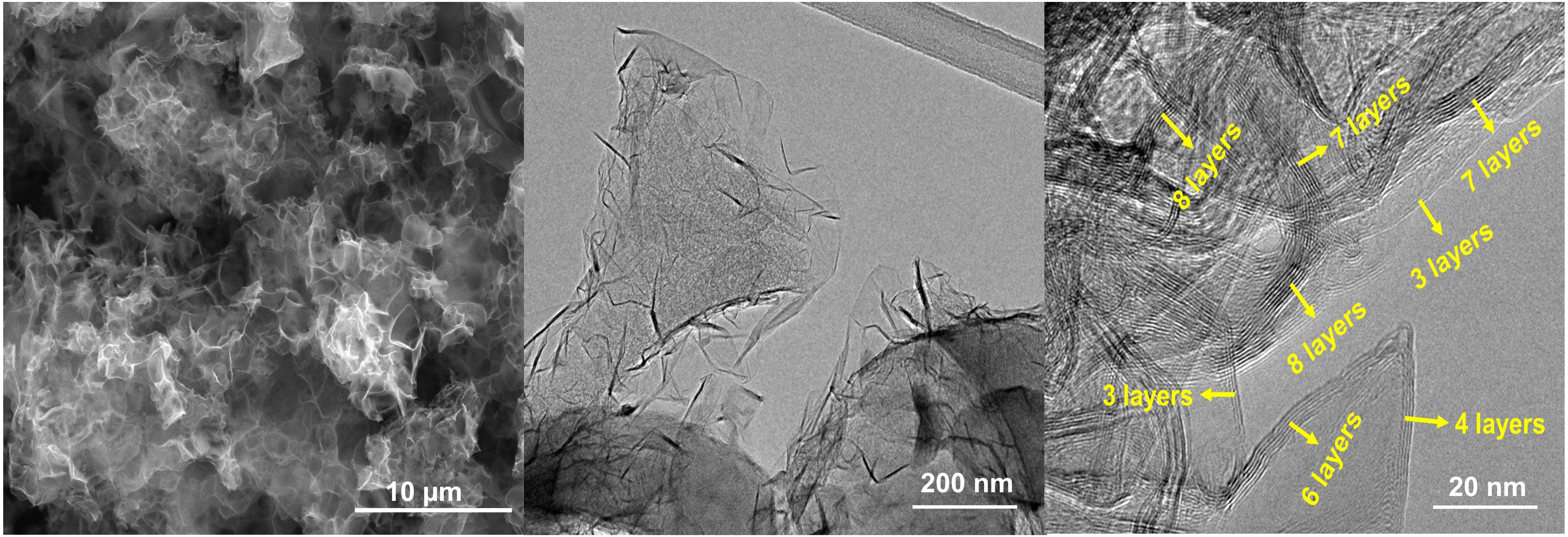
Synthesis of 3D graphene using coal tar pitch and petroleum pitch feedstocks:



Photograph of ~ 3.0 g of 3DG-900 in 100 mL petri dish (tap density ~0.035 g/cm^3)

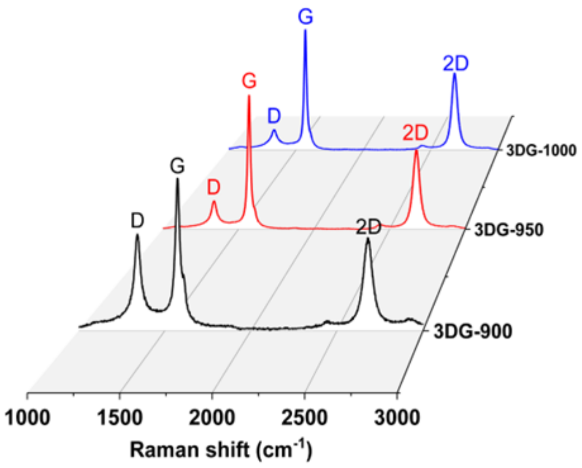
- Low cost and scalable method to produce high-quality 3D graphene
- Recycling 95% KC for at least 10 times without compromise quality of 3D graphene

Synthesis of 3D Graphene for Supercapacitors



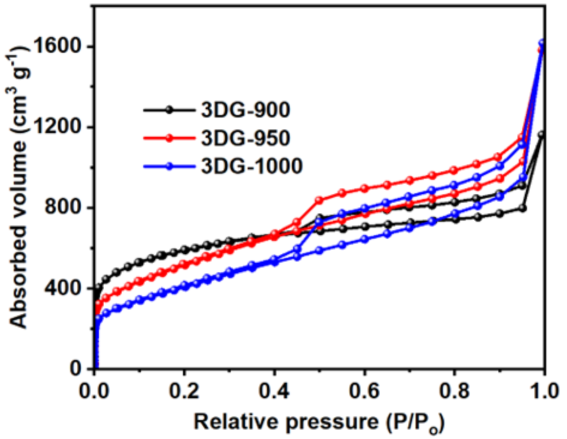
SEM and TEM images of 3DG-900

Synthesis of 3D Graphene for Supercapacitors



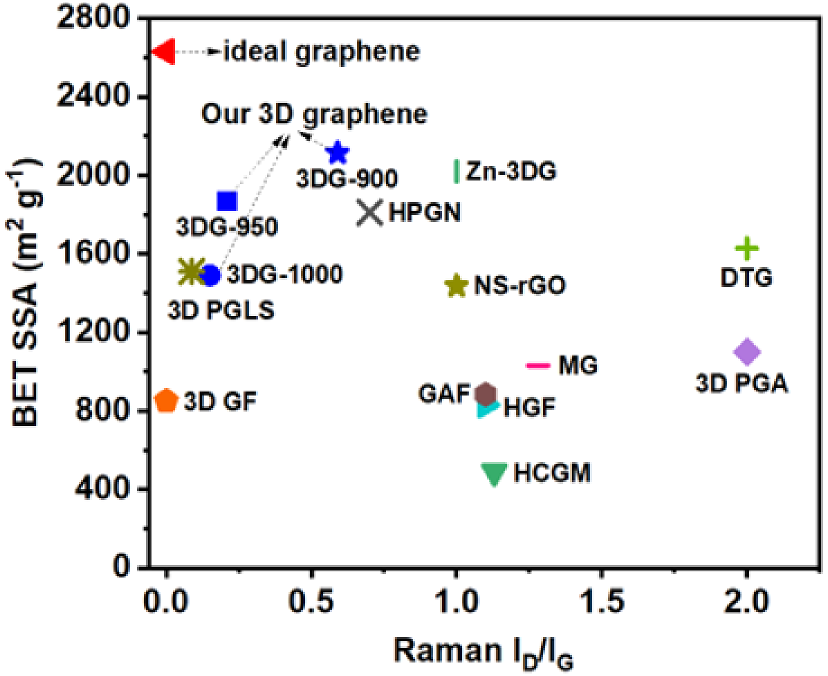
- Raman I_D/I_G: 0.15 – 0.7
- Raman I_{2D}/I_G: 0.60 – 0.67

→ Highly crystalline → high electrical conductivity (1300 – 2400 S/m)



- Hierarchical pore size distribution
- BET specific surface area (SSA): 1,500–2,100 m^2/g
- Total pore volume: 1.8 – 2.5 cm^3/g

Raman and N_2 isotherms of 3DGs



Comparison of BET SSA and Raman I_D/I_G of 3D graphene with other graphenes with high SSA in literature. (Holey graphene framework (HGF), 3D porous graphene-like sheets (3D PGLS), highly compressible graphene monolith (HCGM), 3D-printed graphene aerogels (3D PGA), wet-spun graphene core-shell aerogel fiber (GAF), non-stacked rGO (NS-rGO), 3D graphene foam (3D GF), unstacked double layer templated graphene (DTG), hierarchical porous graphene networks (HPGN), microporous graphene (MG), Zn-guided 3D graphene (Zn-3DG)).

Synthesis of 3D Graphene for Supercapacitors

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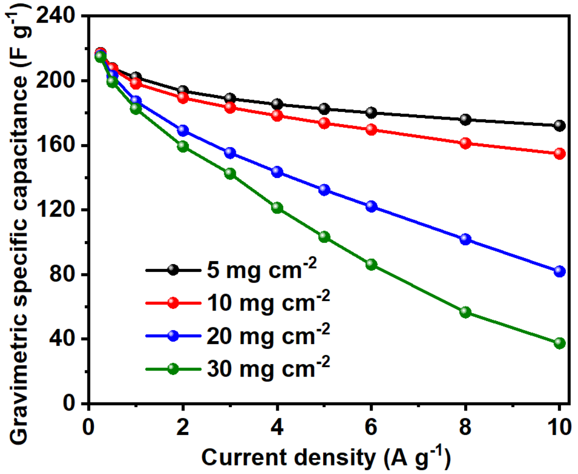
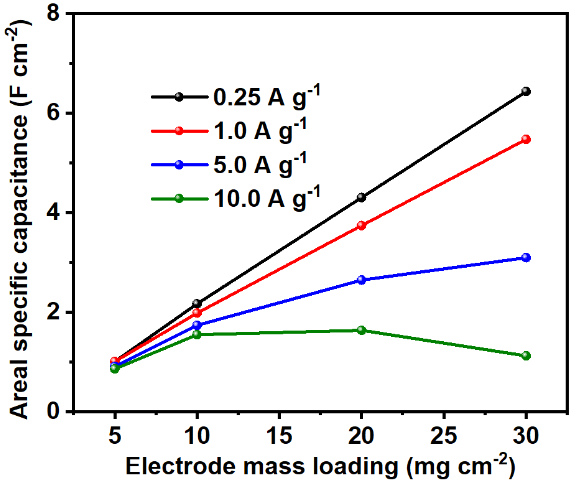
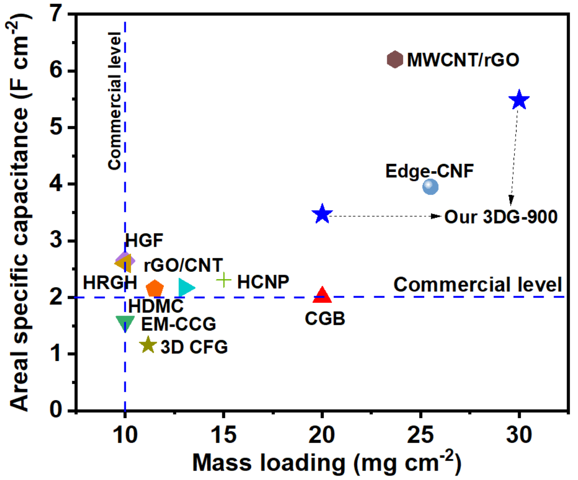
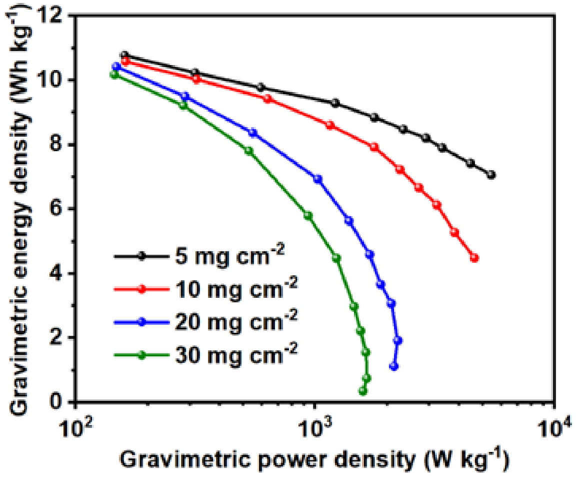
3D graphene as electrode material for supercapacitors with ultrahigh areal capacitance :









- The microscopic 3D structure with hierarchical pore size distribution (which does not collapse during electrode fabrication) + high surface area + high electrical conductivity → ultrahigh mass loading, up to 30 mg/cm^2 → ultrahigh areal capacitance, up to 6.44 F/cm^2, one of the highest value reported in literature
- 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
- Excellent cycling stability with ~80% capacitance retention after 20,000 cycles, even at extended working voltage

Synthesis of 3D Graphene for Supercapacitors

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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)
NETL 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

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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
NETL 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	
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

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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 recyle K_2CO_3 up to 95% for at least 10 cycles

Synthesis of 3D Graphene for Supercapacitors

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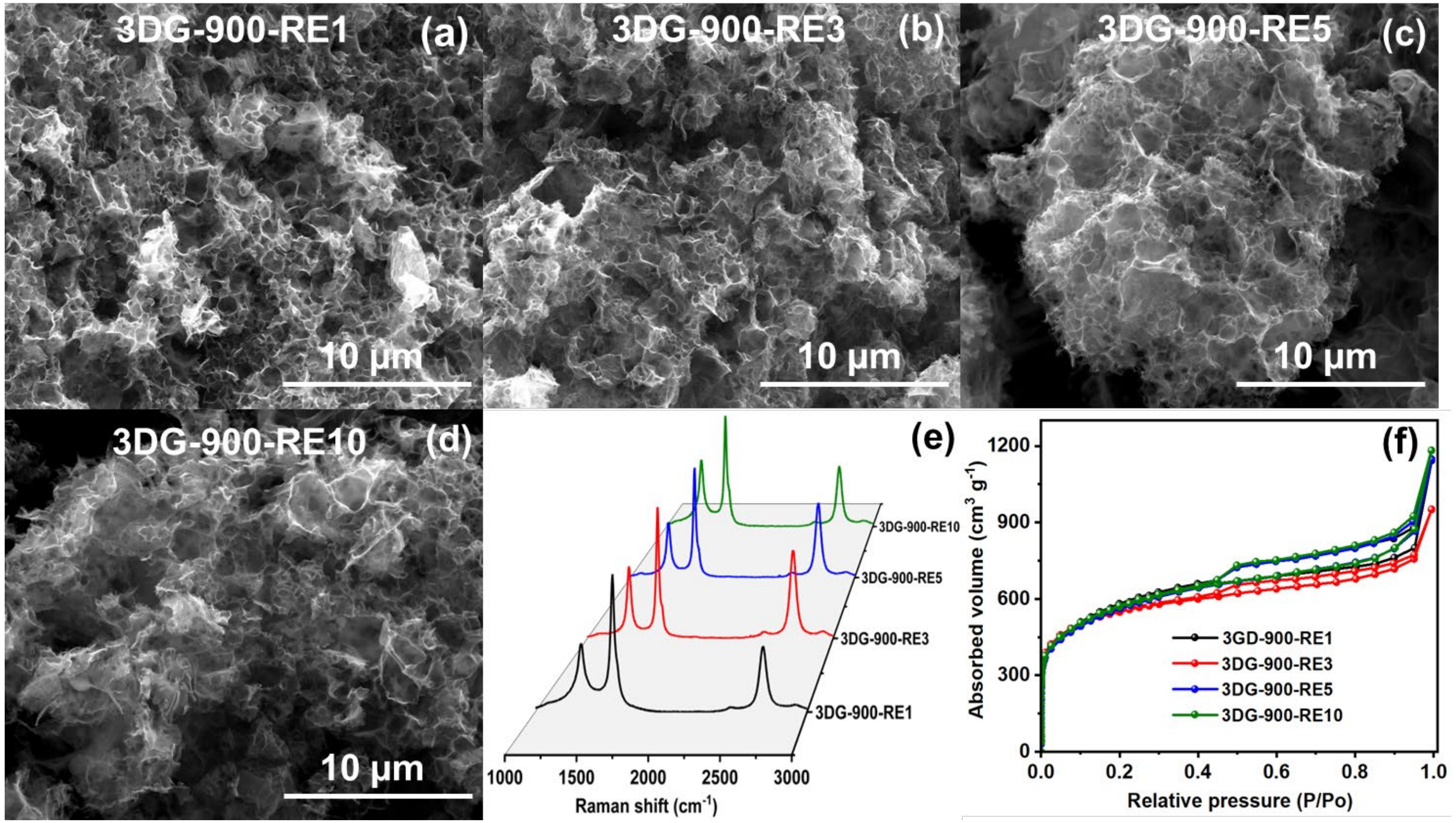
Recycling K_2CO_3 for 10 cycles:



(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 current density of 1.0 A/g (F/g)	Energy Density (Wh/kg)
3DG-900	2,113	198	9.52
3DG-900-RE1	2,058	182	8.78
3DG-900-RE3	2,002	185	8.89
3DG-900-RE5	2,005	179	8.64
3DG-900-RE10	2,043	180	8.71
Commercial SOTA YP-50F	1,746	126	6.08

Potential Environmental Impact (Elemental Analysis of Feedstock)

Element	Analysis Method	Coal Tar Pitch Feedstock	Washing Filtrates (Intermediate Processing Steps)*	3D Graphene (Final Product)	Drinking Water Standard
Hg	AAS	< 0.250 ppm (<reporting limit)	-	-	≤2 ppb
As	ICP-MS	0.583 ppm	-	-	≤10 ppb
Se	ICP-MS	2.8 ppb	-	-	≤ 50 ppb
Cd	ICP-MS	25.5 ppb	-	-	≤ 3 ppb
Sb	ICP-MS	46.6 ppb	-	-	≤ 6 ppb
Pb	ICP-MS	0.11 ppm	-	-	≤15 ppb
Cl	XPS	Not detected	-	Not detected	
F	XPS	Not detected	-	Not detected	
Br	XPS	Not detected	-	Not detected	
S	EA/XPS	0.22 wt.% (EA)	-	Not detected (XPS)	250 ppm (sulfate)
N	EA/XPS	1.02 wt.% (EA)	-	<0.1 wt.% (XPS)	10 ppm (nitrate)

** At 100 mL of water is needed to process 1.0 g of coal tar pitch feedstock.*

Summary

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- ❖ Simple and scalable method to convert coal tar pitch into high-quality 3D graphene with high surface area and hierarchical pore size distribution + high electrical conductivity → supercapacitor electrode with ultrahigh mass loading (30 mg/cm^2) → ultrahigh areal capacitance
- ❖ NETL 3DG-900 graphene improves electrochemical capacitive performance over SOTA Kuraray YP-50F ~ 50%
- ❖ Recycling K_2CO_3 for at least 10 times → low-cost and sustainable production

Acknowledgments

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