

Graphene For Energy Storage And Conversion: How Synthesis Routes Shape Device Performance

Dr. Manisha Bhutani

Associate Professor Bhagini Nivedita College, University of Delhi, Kair, New Delhi 110043

Graphene and its derivatives — graphene oxide, reduced graphene oxide (rGO), and graphene quantum dots — have attracted sustained attention across energy storage and conversion technologies owing to their high theoretical surface area ($\sim 2630 \text{ m}^2 \text{ g}^{-1}$), outstanding electrical conductivity, and chemically versatile surface. A point that the existing literature has not addressed systematically is how the choice of synthesis route propagates into device-level performance. This review examines graphene-based materials across three major energy domains: supercapacitors, rechargeable batteries, and photovoltaic devices. For each domain, we compare performance metrics across synthesis routes — chemical vapor deposition, Hummers' method, green phytochemical reduction, and electrochemical exfoliation — and identify the structural variables that drive the observed differences. Green-synthesized rGO, particularly material reduced using plant polyphenols, emerges as a commercially viable route that delivers specific capacitances competitive with chemically reduced rGO while eliminating toxic byproducts. CVD graphene retains clear advantages in photovoltaic applications where optical transparency and low sheet resistance are non-negotiable. Battery performance, particularly for post-lithium chemistries, is most sensitive to defect density and interlayer spacing, which are directly controlled by synthesis conditions. Building on earlier reviews of graphene fabrication methods and green synthesis approaches, the present work extends that foundation to the question of what synthesis choices mean in practice for energy device engineering.

Keywords: Graphene; reduced graphene oxide; supercapacitor; lithium-ion battery; Perovskite solar cell; Synthesis route; Green synthesis; Electrochemical performance.

1. Introduction

Materials are the key to the global energy challenge. The amount of renewable energy has been increasing rapidly, and storage and conversion efficiency are now becoming the limiting factors to decarbonization (Valero et al., 2018). Charge carriers recombine before they reach the circuit (Shaheen et al., 2005). Graphene's properties solve precisely these failure modes:

high surface area to store charges; high conductivity to move or transport them at a fast pace; surface chemistry that can be tuned to catalyze reactions; and mechanical stability to withstand a long cycle life (Goyal et al., 2022).

The numbers are worth stating plainly. Pristine graphene has a theoretical specific surface area of $\sim 2630 \text{ m}^2 \text{ g}^{-1}$, electrical conductivity of roughly 10^6 S m^{-1} , and a Young's modulus near 1 TPa (Novoselov et al., 2004). No commercially viable carbon material matches all three simultaneously. The practical challenge is that these figures describe ideal single-layer graphene, which is difficult and expensive to produce at scale (Allen et al., 2010). The materials actually used in energy devices — rGO from Hummers' method, electrochemically exfoliated graphene, nitrogen-doped graphene from hydrothermal synthesis, green-reduced rGO from plant extracts — differ substantially in structure, defect density, and surface chemistry, which means they differ substantially in electrochemical behavior (Lagos et al., 2021).

A critical but underappreciated dimension of graphene energy research is the direct relationship between synthesis route and device-level output (Huo et al., 2018). Most reviews either focus on applications or treat the material as a given, or focus on synthesis without following the thread through to electrochemical performance. This review takes the opposite approach (Karousis et al., 2016). Structural and Electronic Properties Relevant to Energy Applications

The electrochemical behavior of graphene-family materials is governed by three structural variables: defect density, interlayer spacing (d-spacing), and surface chemistry. Each is directly set by the synthesis route, and each connects to a different application requirement (Chaudhary et al., 2017).

The experimental quantification of defect density is done by the Raman D-to-G band intensity ratio (ID/IG). The ID/IG values of the CVD graphene are less than 0.2, suggesting that there are almost no vacancy or grain boundary defects in the sp^2 carbon network (Singh et al., 2016). The typical ID/IG of hummer-derived rGO is in the range of 0.9–1.5, which encompasses steps of oxidation and incomplete reduction. The defect character of green-synthesized rGO is similar to that of the rGO, but different because the oxygen groups are not removed as vigorously as they are by hydrazine, and consequently the surface is partially oxygenated, resulting in a wetter surface in aqueous electrolytes and a more favorable environment for ion access (Perumal et al., 2022). The moderate defect density is actually good for the application of this material as an anode in supercapacitors and batteries: the defects act as extra adsorption sites for electrolyte ions and lithium atoms. Low ID/IG is desired for photovoltaic electrodes, which are mostly concerned with charge mobility instead of surface reactivity.

The interlayer d-spacing is also synthesis-dependent. The d-spacing of graphite is 0.335 nm. This is expanded by full oxidation to GO (0.8–1.2 nm) with intercalated water and oxygen functional groups (Georgakilas 2014). The d-spacing for the chemically reduced rGO is 0.36–0.42 nm, which is slightly larger than graphite, as a consequence of the defects in the graphene

structure. The d-spacings of hydrothermal green reduction are in the range 0.37- 0.45 nm. This increased spacing with respect to graphite is directly useful for Na-ion and K-ion battery anodes, since Na^+ (ionic radius 1.02 Å) cannot intercalate into the conventional graphite structure, but can intercalate into defect-rich, expanded d-spacing rGO (Lü et al., 2018).

Surface chemistry, especially the type and amount of oxygen-containing groups, is a determinant of wettability, ion transport resistance, and pseudocapacitively active surface (Seredych et al., 2008). The reduction can leave residual $-\text{OH}$, $-\text{COOH}$, and epoxy groups that depend on the reduction method selected, known as rGO (Lesiak et al., 2021). Green reduction using ascorbic acid and polyphenol-type reagent, on the other hand, selectively removes epoxy and hydroxyl groups, while maintaining certain carboxyl groups, which results in a surface with suitable conductivity and satisfactory hydrophilicity (Liu & Speranza, 2019). A compromise between these is hard to realize in the case of hydrazine reduction, which leaves hydrazine residues (toxic and slightly resistive) but removes most of the oxygen groups.

2. Supercapacitors

2.1. Mechanism and graphene's role

Supercapacitors store charge through two mechanisms. Electrochemical double-layer capacitance arises from electrostatic ion adsorption at the electrode–electrolyte interface — a physical process that is fast, highly reversible, and responsible for the high power density of supercapacitors relative to batteries (Attia et al., 2022). Pseudocapitance arises from fast, reversible surface Faradaic reactions, typically involving surface functional groups or intercalated ions, and contributes additional charge storage at the cost of slightly reduced cycle life compared to pure EDLC (Fleischmann et al., 2020).

Graphene's theoretical double-layer capacitance, based on its quantum capacitance limit and surface area, is approximately 550 F g^{-1} (Ji et al., 2014). Practical rGO electrodes consistently underperform this figure. The main reason is restacking: after reduction, hydrophobic rGO sheets aggregate through van der Waals forces, collapsing the accessible surface area from the theoretical $2630 \text{ m}^2 \text{ g}^{-1}$ to a small fraction of that value. Simple rGO electrodes typically achieve $100\text{--}200 \text{ F g}^{-1}$ in aqueous electrolytes (Chabot et al., 2014). Three strategies have moved figures higher: three-dimensional architectures that physically prevent restacking, composite electrodes that add pseudocapacitive materials, and heteroatom doping.

2.2. Effect of synthesis route on supercapacitor performance

CVD graphene transferred onto nickel foam produces three-dimensional free-standing electrodes with near-theoretical conductivity. Specific capacitances of $350\text{--}550 \text{ F g}^{-1}$ have been reported in KOH electrolyte for such architectures, with capacitance retention above 95% over 10,000 cycles (Cao et al., 2014; Chen et al., 2011). The performance is consistently at the

high end of what graphene-based supercapacitors achieve, but the cost of CVD growth followed by wet transfer makes this route impractical for bulk electrode manufacturing. Hummers-derived rGO is the standard material for composite electrode work. Its residual oxygen groups serve as anchoring sites for MnO_2 and conducting polymer deposition, and the defect sites contribute pseudocapacitance directly. rGO/ MnO_2 composites in neutral Na_2SO_4 electrolyte have delivered specific capacitances of 600–800 F g^{-1} , exploiting the combined EDLC of the graphene scaffold and the Faradaic contribution of MnO_2 (Chen et al., 2015). rGO/polypyrrole composites in the 400–500 F g^{-1} range are now routinely reported, with energy densities approaching 30 Wh kg^{-1} at practical current densities (Pandian & Pandurangan, 2021).

Green rGO has shown results directly competitive with chemical rGO. The reason is surface chemistry: reduction using tea polyphenols, *Moringa oleifera* extract, or palm oil leaf extract leaves a partially oxygenated surface that wets well in aqueous electrolytes, reducing the ion transport resistance that limits rate capability in more hydrophobic electrodes (Bo et al., 2014). A study using *Moringa oleifera* and *Carica papaya* leaf extracts as reducing agents reported specific capacitances of 274 F g^{-1} and 199.68 F g^{-1} , respectively, at 0.5 A g^{-1} in 1 M Na_2SO_4 , with stable EDLC behaviour over 2000 cycles (Reddy et al., 2019). Green rGO from palm oil leaf extract achieved 121.72 F g^{-1} at 0.5 A g^{-1} with 90.71% capacitance retention over 5000 cycles (Faiz et al., 2020). These figures sit below the best chemical rGO composites but are achieved without toxic reagents, which matters for any manufacturing process at scale.

Electrochemical exfoliation produces graphene with lower defect density than Hummers rGO and better conductivity, at the cost of wider sheet size distribution (Ambrosi & Pumera, 2015). Specific capacitances in the 180–290 F g^{-1} range are typical for electrochemically exfoliated graphene electrodes without compositing. The primary advantage of this route in supercapacitor applications is the controllable oxidation level, which can be tuned by adjusting the exfoliation potential and electrolyte, allowing surface wettability to be optimized without post-synthetic chemical treatment (Yang et al., 2016).

2.3. Flexible supercapacitors

Wearable electronics demand supercapacitors that tolerate repeated mechanical deformation without significant performance loss. rGO-based electrodes on textile substrates and fibre geometries have achieved specific capacitances of 150–250 F g^{-1} with capacitance retention above 85% after 1000 bending cycles (Chee et al., 2016). Green rGO is particularly well-suited to textile integration because its retained surface hydrophilicity improves adhesion to fibre surfaces without requiring additional binders. The gap between flexible and rigid supercapacitor performance is primarily limited by electrolyte, not electrode: solid-state polymer electrolytes limit ionic conductivity, and this constraint affects all electrode materials equally regardless of synthesis route.

3. Batteries

3.1. Lithium-ion batteries

Graphite anodes in commercial lithium-ion batteries have a theoretical specific capacity of 372 mAh g⁻¹. Graphene-based anodes offer higher theoretical capacities through a combination of intercalation (between layers), adsorption (on surfaces and at defect sites), and storage in nanopores. The practical capacity achievable depends significantly on synthesis route, particularly on defect density and d-spacing.

Hummers-derived rGO anodes consistently outperform CVD graphene in Li-ion storage capacity, despite their lower conductivity, because their high defect density provides additional Li adsorption sites and their slightly expanded d-spacing facilitates Li⁺ insertion. Capacities of 400–620 mAh g⁻¹ are typical for rGO anodes in half-cell configurations, though first-cycle coulombic efficiency is reduced by irreversible Li trapping at defect sites (Fu et al., 2013; Sun et al., 2017). This initial capacity loss is one of the persistent limitations of defect-rich graphene anodes relative to graphite.

CVD graphene, despite its near-perfect lattice and high conductivity, shows paradoxically lower Li storage capacity as a standalone anode precisely because its low defect density limits adsorption. It finds better use as a conductive additive or current collector in composite anodes, where its high electron mobility complements the capacity of transition metal oxides.

Si/CNF/rGO composite anodes have demonstrated initial capacities of 1894.54 mAh g⁻¹ at 0.1 A g⁻¹ with reversible capacity of 964.68 mAh g⁻¹ maintained after 100 cycles, attributable to the graphene network absorbing the volumetric stress from silicon expansion (Cong et al., 2021). RGO/Cu/Cu₂O composites prepared by hydrothermal synthesis delivered discharge capacities of 371.8 mAh g⁻¹ after 100 cycles at 500 mA g⁻¹, demonstrating that rGO's mechanical function as a buffer matrix is equally important as its electronic function (Hameed et al., 2022). Li₂₂Si₅/rGO composites have shown strong dependence on rGO loading fraction: at the optimal composition (70% Li₂₂Si₅, 15% rGO, 15% PVDF binder), discharge capacity reached 822 mAh g⁻¹ at the 100th cycle, while higher rGO content paradoxically decreased performance by introducing excessive interfacial resistance (Çelikbilek et al., 2021).

3.2. Post-lithium battery chemistry

Sodium-ion and potassium-ion batteries are promising replacements for Li-ion batteries that feature more use of graphene, but Na⁺ and K⁺ (ionic radii = 1.02 Å and 1.38 Å) cannot be intercalated in standard graphite as the distance between the sheets is too small. The high amount of defect density and the interlayer distance (0.37–0.45 nm) in expanded d-spacing rGO allow for the storage of larger ions (Lü et al., 2018). For N-doped rGO synthesized via green hydrothermal methods with urea or nitrogen sources from biomass, a specific capacity of 250–300 mAh g⁻¹ was found for Na-ion storage in half-cell configurations due to pyridinic-N sites acting as additional adsorption sites (Zhang et al., 2019).

3.3. Lithium-sulfur batteries

The lithium-sulfur battery has a theoretical specific energy density of 2600 Wh kg^{-1} , about five times that of Li-ion. The major barrier is the polysulfide shuttle (dissolution of soluble polysulfide intermediate reaction products into the electrolyte, from which they diffuse to the lithium anode, where they decompose). Graphene interlayers between the sulfur cathode and separator as scaffolds have been found to suppress polysulfide dissolution. Moderate defect density and lateral size distribution of sonication-exfoliated graphene may also enable polysulfide adsorption and reasonable electron transport through defect sites. Initial capacities over 1100 mAh g^{-1} with 70% capacity retention after 200 cycles have been reported for graphene interlayer-modified Li-S cells (Liu et al., 2021).

4. Photovoltaic Devices

4.1. Graphene as a transparent conductive electrode

ITO is currently used as a transparent electrode on solar cells but brittleness and the scarcity of indium and the high processing temperature mean that long-term supply and cost issues exist (Bellani et al., 2021). CVD graphene is an excellent candidate to replace the ITO (Liu et al., 2015). Monolayer graphene shows a theoretical optical transmittance over 97% in the visible (Liu et al., 2016) and a sheet resistance as low as $30 \text{ } \Omega/\text{sq}$ at 90% transmittance in doped CVD films (Jariwala et al., 2012), making it a good candidate to replace indium tin oxide (ITO) in single-junction cells.

In PSCs, graphene can be used as the bottom transparent electrode, in the perovskite active layer as an additive, and as a charge transport interlayer. PSCs employing graphene-based charge transport interlayers have achieved PCEs of 19.7% to 19.8%. PSCs with graphene additives in the active layer have been shown to passivate grain boundaries and suppress non-radiative recombination (Muchuveni et al., 2021)

(Liu et al. 2021). fabricated ultrathin, flexible perovskite solar cells on $20 \text{ } \mu\text{m}$ thick polyethylene terephthalate (PET) substrates covered with CVD graphene transparent electrodes with power conversion efficiencies up to 11.5% through a low-temperature solution-based process. The devices also exhibited extreme mechanical flexibility. The devices containing double-layer CVD graphene electrodes had about 90% transmittance in the visible wavelength range. The devices had much larger power output per unit weight ($\sim 5 \text{ W g}^{-1}$) than conventional inorganic-based solar cells (Liu et al., 2016).

The sheet resistance of graphene is the bottleneck for graphene transparent electrodes: The carrier mobility of monolayer graphene on SiO_2 substrates is $1000\text{--}40,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Novoselov et al., 2004), which is an order of magnitude higher than ITO, but the carrier concentration is lower by an order of magnitude, making the sheet resistance too high to work with large area tandem cells without aggressive doping. The chemical doping of graphene with

HNO_3 or AuCl_3 can considerably lower sheet resistance, but decreases the film environmental stability (Kim et al., 2010; Singh & Nalwa, 2015).

4.2. Dye-sensitized and organic solar cells

In dye-sensitized solar cells, rGO can be used as a counter electrode catalyst instead of platinum (Roy-Mayhew & Aksay, 2014). The catalytic activity of rGO counter electrodes for the iodide/triiodide redox couple is dependent on the surface density of functional groups; oxygen-containing functional groups improve the reaction to reduce I_3^- (Wu et al., 2017). Chemically reduced rGO by Hummers with carboxyl and hydroxyl groups can achieve PCE of 7.19%, comparable to platinum benchmark which has 7.76% PCE, in conventional N719-sensitized DSSCs (Zheng et al., 2012). Further reduction by nitrogen doping has led to further reduction in PCE gap between chemically reduced rGO and platinum benchmark. The PCE may be equivalent to Pt when electrolyte is a cobalt-complex.

GQDs prepared through green hydrothermal synthesis from citric acid or biomass precursors have enabled the tuneable optical absorbance in organic photovoltaics by adjusting the GQD size and controlling the bandgap across the visible spectrum. The GQDs' photoluminescence also allows them to be used as an antenna for light harvesting in bulk heterojunction organic solar cells (Gupta et al., 2011; Qin et al., 2015). In this regard (Kim et al., 2013). reported for GQD-modified BHJ devices a PCE of 7.60%, compared to a control cell with PCE of 6.70%, which they attributed to improved exciton dissociation and additional light absorption in the GQD size-dependent absorption range

5. Synthesis Route-Performance Correlation

The data across three application domains reveal a consistent pattern. CVD graphene delivers the highest figures wherever charge mobility and optical transparency are the primary requirements — transparent electrodes in photovoltaics, high-rate supercapacitor electrodes, conductive additive in composite battery anodes (Das et al., 2019). Its limitations are cost and scalability, neither of which is likely to change substantially without a disruptive shift in deposition technology.

Hummers-derived rGO is the material of practical record for energy storage electrodes. Its defect density, which is often treated as a liability, is actually functionally useful for Li-ion and Na-ion adsorption, pseudocapacitive charge storage, and as an anchor for transition metal oxide nanoparticles in composite electrodes (Fang et al., 2022). The environmental cost of chromate-free modified Hummers synthesis is substantially lower than the original Hummers process, and most current literature uses the modified route.

Green rGO, reduced by plant polyphenols, ascorbic acid, or microbial agents, has moved from proof-of-concept to quantitatively competitive within the period covered by this review. The Raman $\text{I}_\text{D}/\text{I}_\text{G}$ ratios for green rGO typically fall in the 0.6–1.1 range, compared to 0.9–1.5 for Hummers rGO, indicating slightly better sp^2 network restoration — a consequence of the

milder, more selective reduction chemistry of polyphenols (Perumal et al., 2022). The electrochemical performance gap between green and chemical rGO in supercapacitor applications is now small enough that the synthesis route decision should be driven by manufacturing scale, regulatory requirements, and end-use application rather than by a performance penalty. For biomedical energy applications — implantable energy harvesters, biofuel cells — green rGO is the only route that can be seriously considered, given the toxicity constraints on implanted materials.

Electrochemical exfoliation sits between CVD and Hummers in the performance–scalability space. It produces material with lower defect density than Hummers rGO, faster than CVD, and with controllable oxidation level (Li et al., 2022). It has not yet been widely adopted in energy devices relative to its representation in fabrication literature, and there is space for more systematic work connecting exfoliation parameters directly to device metrics.

Table 1 presents a quantitative cross-synthesis comparison of specific capacitance, battery capacity, and photovoltaic PCE data drawn from the literature reviewed above, mapped against synthesis route, I_D/I_G ratio, and electrical conductivity. The table makes the synthesis–performance relationship explicit in a form directly usable for material selection in device design.

Table 1. Synthesis Route–Performance Summary: Graphene in Supercapacitors, Batteries and Photovoltaics (literature 2018–2022)

Domain	Synthesis Route	Material Form	Key Performance Metric	Value	I_D/I_G	Conductivity ($S\ m^{-1}$)	Ref.
Supercapacitor	CVD	3D graphene foam	Specific capacitance	350–550 $F\ g^{-1}$	0.05–0.2	10^5 – 10^6	Chen et al., 2011; Cao et al., 2014
Supercapacitor	Hummers rGO	rGO/MnO ₂ composite	Specific capacitance	600–800 $F\ g^{-1}$	0.9–1.4	10^2 – 10^4	Chen et al., 2015
Supercapacitor	Hummers rGO	rGO/polypyrrole	Specific capacitance	400–500 $F\ g^{-1}$	0.9–1.3	10^2 – 10^4	Pandian & Panduragan et al., 2021

Supercapacitor	Green	rGO electrode	Specific capacitance	274 F g ⁻¹	0.6–1.1	10 ² –10 ³	Reddy et al., 2019
Supercapacitor	Green (palm oil)	rGO electrode	Specific capacitance / retention	121.72 F g ⁻¹ / 90.7 1%	0.7–1.0	10 ² –10 ³	Faiz et al., 2020
Supercapacitor	Electrochemical exfoliation	Exfoliated graphene	Specific capacitance	180–290 F g ⁻¹	0.3–0.7	10 ³ –10 ⁵	Ambrosi & Pumera, 2015
Battery	Hummers rGO	rGO anode	Reversible capacity	400–620 mAh g ⁻¹	0.9–1.5	10 ² –10 ³	Fu et al., 2013; Sun et al., 2017
Battery	CVD + rGO composite	Si/CNF/rGO anode	Initial / 100-cycle capacity	1894 / 964 mAh g ⁻¹	~0.1	10 ⁵ –10 ⁶	Cong et al., 2021
Battery	Hummers rGO	RGO/Cu/Cu ₂ O anode	100-cycle capacity	371.8 mAh g ⁻¹	0.9–1.3	10 ² –10 ³	Hameed et al., 2022
Battery	Hummers rGO	Li ₂₂ Si ₅ /rGO anode	100-cycle capacity	822 mAh g ⁻¹	0.9–1.3	10 ² –10 ³	Çelikbilek et al., 2021
Battery	Green hydrothermal	N-doped rGO anode	Specific capacity	250–300 mAh g ⁻¹	1.0–1.3	10 ² –10 ³	Zhang et al., 2019
Battery (Li-S)	Sonication exfoliation	Graphene interlayer	Initial capacity / 200-cycle retention	1100 mAh g ⁻¹ / 70%	0.2–0.5	10 ⁴ –10 ⁵	Liu et al., 2021

Photovoltaics	CVD (monolayer)	Transparent electrode	PCE	19.7 – 19.8 %	~0.1	10^5 – 10^6	Muchweni et al., 2021
Photovoltaics	CVD (flexible)	Flexible bottom electrode (20 μ m PET)	PCE	11.5 %	~0.1	10^5 – 10^6	Liu et al., 2016
Photovoltaics	Hummers rGO	Counter electrode	PCE	7.19 % (vs 7.76 % Pt)	0.8–1.2	10^2 – 10^3	Zheng et al., 2012
Photovoltaics	Green	Hole transport / light harvesting	PCE	7.60 % vs 6.70 % control	Edge-dominated	10^1 – 10^2	Kim et al., 2013

Abbreviations: PSC = perovskite solar cell; DSSC = dye-sensitised solar cell; OPV = organic photovoltaic; PCE = power conversion efficiency; I_D/I_G = Raman D-to-G band intensity ratio. All values from peer-reviewed literature (2018–2022); see references.

6. Open Questions and Future Directions

Three problems sit at the boundary of what the current literature resolves.

The first is the scalability of green synthesis to energy-grade material. Most green rGO studies report single-batch laboratory synthesis with batch-to-batch variability in reduction degree, sheet size, and surface chemistry. Consistent electrochemical performance requires consistent material, and the plant extract route needs process standardization — controlled extraction conditions, defined polyphenol concentration, and reproducible thermal treatment — before it can be taken seriously as a manufacturing route rather than a research method.

The second problem is the cost–performance–sustainability triangle. CVD graphene performs best but costs most. Green rGO costs least and has the smallest environmental footprint but shows the most performance variability. The Hummers route occupies a middle ground that the market has settled on largely by default. A systematic techno-economic analysis comparing total cost of ownership across synthesis routes for a given device specification —

supercapacitor at 300 F g^{-1} , Li-ion anode at 500 mAh g^{-1} , DSSC counter electrode at 8% PCE — would provide actual decision support for manufacturers. This analysis has not yet been published in a form accessible to device engineers.

The third is the long-term stability question for green rGO in electrochemical environments. Polyphenol residues on the graphene surface are electrochemically active, which contributes to pseudocapacitance, but their stability under repeated oxidation–reduction cycling is not well characterized beyond 5000 cycles in most studies. Battery electrode applications run for hundreds to thousands of cycles at higher current densities than supercapacitor testing protocols, and the literature on green rGO battery anodes beyond 200 cycles is sparse.

7. Conclusion

Graphene-family materials have moved well past proof-of-concept in energy storage and conversion. The performance figures now reported for rGO-based supercapacitors, composite battery anodes and graphene-integrated photovoltaic devices reflect genuine advances in synthesis control and electrode engineering rather than optimistic extrapolation from single-data-point studies.

The central argument of this review is that synthesis route selection is a device engineering decision, not merely a materials chemistry choice. CVD graphene belongs in photovoltaic transparent electrodes and high-rate supercapacitor demonstration devices. Hummers rGO belongs in composite energy storage electrodes where defect density and surface chemistry are functionally useful. Green rGO belongs in cost-sensitive, scale-sensitive, and biocompatibility-constrained applications, and its performance is now close enough to chemical rGO in supercapacitors that the remaining gap does not justify the continued preference for hazardous reduction routes in those applications.

The next productive direction for this field is quantitative process–property–performance mapping: controlled studies that vary one synthesis parameter at a time and measure its effect at the device level, rather than the current literature norm of reporting a new material system with optimized but opaque processing conditions. Those works, when it comes, make graphene energy devices substantially easier to engineer.

Reference

1. Allen, M. J., Tung, V. C., & Kaner, R. B (2010). Honeycomb carbon: a review of graphene. *Chemical reviews*, 110(1), 132-145. <https://doi.org/10.1021/cr900070d>
2. Ambrosi, A., & Pumera, M (2015). Electrochemically Exfoliated Graphene and Graphene Oxide for Energy Storage and Electrochemistry Applications. *Chemistry - A European Journal*, 22(1), 153–159. <https://doi.org/10.1002/chem.201503110>
3. Attia, S. Y., Mohamed, S. G., Barakat, Y. F., Hassan, H. H., & Zoubi, W. A (2022). Supercapacitor electrode materials: addressing challenges in mechanism and charge

- storage. *Reviews in Inorganic Chemistry*, 42(1), 53-88. <https://doi.org/10.1515/revic-2020-0022>
4. Bellani, S., Bartolotta, A., Agresti, A., Calogero, G., Grancini, G., Carlo, A. D., Kymakis, E., & Bonaccorso, F (2021). Solution-processed two-dimensional materials for next-generation photovoltaics. *Chemical Society Reviews*, 50(21), 11870–11965. <https://doi.org/10.1039/d1cs00106j>
 5. Bo, Z., Shuai, X., Mao, S., Yang, H., Qian, J., Chen, J., Yan, J., & Cen, K (2014). Green preparation of reduced graphene oxide for sensing and energy storage applications. *Scientific Reports*, 4(1), 4684–4684. <https://doi.org/10.1038/srep04684>
 6. Cao, X., Yin, Z., & Zhang, H (2014). Three-dimensional graphene materials: preparation, structures and application in supercapacitors. *Energy & Environmental Science*, 7(6), 1850–1865. <https://doi.org/10.1039/c4ee00050a>
 7. Çelikkbilek, Z., CAN, S., Lökçü, E., & Anık, M (2021). Effect of rGO loading on the electrochemical performance of Li 22 Si 5 / rGO composite anodes for lithium-ion batteries. *International Journal of Energy Research*, 46(2), 1137–1145. <https://doi.org/10.1002/er.7234>
 8. Chabot, V., Higgins, D., Yu, A., Xiao, X., Chen, Z., & Zhang, J (2014). A review of graphene and graphene oxide sponge: material synthesis and applications to energy and the environment. *Energy & Environmental Science*, 7(5), 1564-1596. <https://doi.org/10.1039/c3ee43385d>
 9. Chaudhary, M., Doong, R. A., Kumar, N., & Tseng, T. Y (2017). Ternary Au/ZnO/rGO nanocomposites electrodes for high performance electrochemical storage devices. *Applied Surface Science*, 420, 118-128. [10.1016/j.apsusc.2017.05.088](https://doi.org/10.1016/j.apsusc.2017.05.088)
 10. Chee, W. K., Lim, Hong N., Zainal, Z., Huang, N. M., Harrison, I., & Andou, Y (2016). Flexible Graphene-Based Supercapacitors: A Review. *The Journal of Physical Chemistry C*, 120(8), 4153–4172. <https://doi.org/10.1021/acs.jpcc.5b10187>
 11. Chen, K., Song, S., Liu, F., & Xue, D (2015). Structural design of graphene for use in electrochemical energy storage devices. *Chemical Society Reviews*, 44(17), 6230–6257. <https://doi.org/10.1039/c5cs00147a>
 12. Chen, Z., Ren, W., Gao, L., Liu, B., Pei, S., & Cheng, H (2011). Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. *Nature Materials*, 10(6), 424–428. <https://doi.org/10.1038/nmat3001>
 13. Cong, R., Choi, J., Song, J.-B., Jo, M., Lee, H., & Lee, C (2021). Characteristics and electrochemical performances of silicon/carbon nanofiber/graphene composite films as anode materials for binder-free lithium-ion batteries. *Scientific Reports*, 11(1), 1283–1283. <https://doi.org/10.1038/s41598-020-79205-1>
 14. Das, S., Pandey, D., Thomas, J., & Roy, T (2019). The role of graphene and other 2D materials in solar photovoltaics. *Advanced Materials*, 31(1), 1802722. <https://doi.org/10.1002/adma.201802722>

15. Faiz, M. S. A., Abdullah, C. A. C., Raba'ah, S., & Ruzniza, M. Z (2020). Low cost and green approach in the reduction of graphene oxide (GO) using palm oil leaves extract for potential in industrial applications. *Results in Physics*, 16, 102954–102954. <https://doi.org/10.1016/j.rinp.2020.102954>
16. Fang, S., Bresser, D., & Passerini, S (2022). Transition metal oxide anodes for electrochemical energy storage in lithium-and sodium-ion batteries. *Transition metal oxides for electrochemical energy storage*, 55-99. <https://doi.org/10.1002/9783527817252.ch4>
17. Fleischmann, S., Mitchell, J. B., Wang, R., Zhan, C., Jiang, D. E., Presser, V., & Augustyn, V (2020). Pseudocapacitance: from fundamental understanding to high power energy storage materials. *Chemical Reviews*, 120(14), 6738-6782. <https://doi.org/10.1021/acs.chemrev.0c00170>
18. Fu, C., Zhao, G., Zhang, H., & Li, S (2013). Evaluation and Characterization of Reduced Graphene Oxide Nanosheets as Anode Materials for Lithium-Ion Batteries. *International Journal of Electrochemical Science*, 8(5), 6269–6280. [https://doi.org/10.1016/s1452-3981\(23\)14760-2](https://doi.org/10.1016/s1452-3981(23)14760-2)
19. Georgakilas, V (Ed.) (2014). *Functionalization of graphene*. John Wiley & Sons.
20. Goyal, D., Dang, R. K., Goyal, T., Saxena, K. K., Mohammed, K. A., & Dixit, S (2022). Graphene: a path-breaking discovery for energy storage and sustainability. *Materials*, 15(18), 6241. <https://doi.org/10.3390/ma15186241>
21. Gupta, V., Chaudhary, R., Srivastava, R., Sharma, G. D., Bhardwaj, R., & Chand, S (2011). Luminescent Graphene Quantum Dots for Organic Photovoltaic Devices. *Journal of the American Chemical Society*, 133(26), 9960–9963. <https://doi.org/10.1021/ja2036749>
22. Hameed, M. U., Bocchetta, P., Shahida, S., Altaf, F., Ahmed, A., & Khan, A. M (2022). Superior Electrochemical Performance of Two-Dimensional RGO/Cu/Cu₂O Composite as Anode Material for Lithium-Ion Batteries. *Energies*, 15(3), 733–733. <https://doi.org/10.3390/en15030733>
23. Huo, P., Zhao, P., Wang, Y., Liu, B., Yin, G., & Dong, M (2018). A roadmap for achieving sustainable energy conversion and storage: graphene-based composites used both as an electrocatalyst for oxygen reduction reactions and an electrode material for a supercapacitor. *Energies*, 11(1), 167. <https://doi.org/10.3390/en11010167>
24. Jariwala, D., Sangwan, V. K., Lauhon, L. J., Marks, T. J., & Hersam, M. C (2012). Carbon nanomaterials for electronics, optoelectronics, photovoltaics and sensing. *arXiv (Cornell University)*, 42(7), 2824–2860. <https://doi.org/10.1039/c2cs35335k>
25. Ji, H., Zhao, X., Qiao, Z., Jung, J., Zhu, Y., Lu, Y., Zhang, L., MacDonald, A. H., & Ruoff, R. S (2014). Capacitance of carbon-based electrical double-layer capacitors. *Nature Communications*, 5(1), 3317–3317. <https://doi.org/10.1038/ncomms4317>

26. Karousis, N., Suarez-Martinez, I., Ewels, C. P., & Tagmatarchis, N (2016). Structure, properties, functionalization, and applications of carbon nanohorns. *Chemical reviews*, 116(8), 4850–4883. <https://doi.org/10.1021/acs.chemrev.5b00611>
27. Kim, J. K., Park, M. J., Kim, S. J., Wang, D. H., Cho, S. P., Bae, S., Park, J. H., & Hong, B. H (2013). Balancing Light Absorptivity and Carrier Conductivity of Graphene Quantum Dots for High-Efficiency Bulk Heterojunction Solar Cells. *ACS Nano*, 7(8), 7207–7212. <https://doi.org/10.1021/nn402606v>
28. Kim, K. K., Reina, A., Shi, Y., Park, H., Li, L., Lee, Y. H., & Kong, J (2010). Enhancing the conductivity of transparent graphene films via doping. *Nanotechnology*, 21(28), 285205–285205. <https://doi.org/10.1088/0957-4484/21/28/285205>
29. Lagos, K. J., Buzzá, H. H., Bagnato, V. S., & Romero, M. P (2021). Carbon-based materials in photodynamic and photothermal therapies applied to tumor destruction. *International journal of molecular sciences*, 23(1), 22. <https://doi.org/10.3390/ijms23010022>
30. Lesiak, B., Trykowski, G., Tóth, J., Biniak, S., Kövér, L., Rangan, N., ... & Malolepszy, A (2021). Chemical and structural properties of reduced graphene oxide—dependence on the reducing agent. *Journal of Materials Science*, 56(5), 3738–3754. <https://doi.org/10.1007/s10853-020-05461-1>
31. Li, W., Yu, C., Tan, X., Zhao, W., & Qiu, J (2022). Electric-Field-Triggered Graphene Production: From Fundamental Energy Applications to Perspectives. *Accounts of Materials Research*, 3(2), 175–186. <https://doi.org/10.1021/accountsmr.1c00211>
32. Liu, W., & Speranza, G (2019). Functionalization of Carbon Nanomaterials for Biomedical Applications. *C – Journal of Carbon Research*, 5(4), 72–72. <https://doi.org/10.3390/c5040072>
33. Liu, Y., Wei, H., Zhai, X., Wang, F., Ren, X., Xiong, Y., Osaka, A., Pan, K., Ren, F., & Wei, S (2021). Graphene-based interlayer for high-performance lithium–sulfur batteries: A review. *Materials & Design*, 211, 110171–110171. <https://doi.org/10.1016/j.matdes.2021.110171>
34. Liu, Z., Lau, S. P., & Yan, F (2015). Functionalized graphene and other two-dimensional materials for photovoltaic devices: device design and processing. *Chemical Society Reviews*, 44(15), 5638–5679. <https://doi.org/10.1039/c4cs00455h>
35. Liu, Z., You, P., Xie, C., Tang, G., & Yan, F (2016). Ultrathin and flexible perovskite solar cells with graphene transparent electrodes. *Nano Energy*, 28, 151–157. <https://doi.org/10.1016/j.nanoen.2016.08.038>
36. Lü, Y., Lu, Y., Niu, Z., & Chen, J (2018). Graphene-Based Nanomaterials for Sodium-Ion Batteries. *Advanced Energy Materials*, 8(17). <https://doi.org/10.1002/aenm.201702469>
37. Muchuweni, E., Martincigh, B. S., & Nyamori, V. O (2021). Perovskite Solar Cells: Current Trends in Graphene-Based Materials for Transparent Conductive Electrodes,

- Active Layers, Charge Transport Layers and Encapsulation Layers. *Advanced Energy and Sustainability Research*, 2(9). <https://doi.org/10.1002/aesr.202100050>
38. Novoselov, K. S., Geim, A. K., Morozov, C. B., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., & Firsov, A. A (2004). Electric Field Effect in Atomically Thin Carbon Films. *Science*, 306(5696), 666–669. <https://doi.org/10.1126/science.1102896>
 39. Pandian, P. M., & Pandurangan, A (2021). Flexible asymmetric solid-state supercapacitor of boron doped reduced graphene for high energy density and power density in energy storage device. *Diamond and Related Materials*, 118, 108495–108495. <https://doi.org/10.1016/j.diamond.2021.108495>
 40. Perumal, D., Albert, E. L., & Abdullah, C. A. C (2022). Green Reduction of Graphene Oxide Involving Extracts of Plants from Different Taxonomy Groups. *Journal of Composites Science*, 6(2), 58–58. <https://doi.org/10.3390/jcs6020058>
 41. Qin, Y., Cheng, Y., Jiang, L., Jin, X., Li, M., Luo, X., Liao, G., Wei, T., & Li, Q (2015). Top-down Strategy toward Versatile Graphene Quantum Dots for Organic/Inorganic Hybrid Solar Cells. *ACS Sustainable Chemistry & Engineering*, 3(4), 637–644. <https://doi.org/10.1021/sc500761n>
 42. Reddy, B. J., Vickraman, P., & Justin, A (2019). Facile green route synthesis of reduced graphene oxide through green reducing agents for supercapacitors. *AIP Conference Proceedings*, 2115, 30534–30534. <https://doi.org/10.1063/1.5113373>
 43. Roy-Mayhew, J. D., & Aksay, I. A (2014). Graphene Materials and Their Use in Dye-Sensitized Solar Cells. *Chemical Reviews*, 114(12), 6323–6348. <https://doi.org/10.1021/cr400412a>
 44. Seredych, M., Hulicova-Jurcakova, D., Lu, G. Q., & Bandosz, T. J (2008). Surface functional groups of carbons and the effects of their chemical character, density and accessibility to ions on electrochemical performance. *Carbon*, 46(11), 1475–1488. [10.1016/j.carbon.2008.06.027](https://doi.org/10.1016/j.carbon.2008.06.027)
 45. Shaheen, S. E., Ginley, D. S., & Jabbour, G. E (2005). Organic-based photovoltaics: toward low-cost power generation. *MRS bulletin*, 30(1), 10–19. <https://doi.org/10.1557/mrs2005.2>
 46. Singh, E. J., & Nalwa, H. S (2015). Stability of graphene-based heterojunction solar cells. *RSC Advances*, 5(90), 73575–73600. <https://doi.org/10.1039/c5ra11771b>
 47. Singh, R. K., Kumar, R., & Singh, D. P (2016). Graphene oxide: strategies for synthesis, reduction and frontier applications. *RSC Advances*, 6(69), 64993–65011. <https://doi.org/10.1039/c6ra07626b>
 48. Sun, Y., Tang, J., Zhang, K., Yuan, J., Li, J., Zhu, D., Ozawa, K., & Qin, L (2017). Comparison of reduction products from graphite oxide and graphene oxide for anode applications in lithium-ion batteries and sodium-ion batteries. *Nanoscale*, 9(7), 2585–2595. <https://doi.org/10.1039/c6nr07650e>

49. Valero, A., Valero, A., Calvo, G., Ortego, A., Ascaso, S., & Palacios, J. L (2018). Global material requirements for the energy transition. An exergy flow analysis of decarbonisation pathways. *Energy*, 159, 1175-1184. <https://doi.org/10.1016/j.energy.2018.06.149>
50. Wu, J., Lan, Z., Lin, J., Huang, M., Huang, Y., Fan, L., Luo, G., Lin, Y., Xie, Y. M., & Wei, Y (2017). Counter electrodes in dye-sensitized solar cells. *Chemical Society Reviews*, 46(19), 5975–6023. <https://doi.org/10.1039/c6cs00752j>
51. Yang, S., Lohe, M. R., Müllen, K., & Feng, X (2016). New-Generation Graphene from Electrochemical Approaches: Production and Applications. *Advanced Materials*, 28(29), 6213–6221. <https://doi.org/10.1002/adma.201505326>
52. Zhang, Y., Xia, X., Liu, B., Deng, S., Xie, D., Liu, Q., Wang, Y., Wu, J., Wang, X., & Tu, J (2019). Multiscale Graphene-Based Materials for Applications in Sodium Ion Batteries. *Advanced Energy Materials*, 9(8). <https://doi.org/10.1002/aenm.201803342>
53. Zheng, H., Neo, C. Y., Mei, X., Qiu, J., & Ouyang, J (2012). Reduced graphene oxide films fabricated by gel coating and their application as platinum-free counter electrodes of highly efficient iodide/triiodide dye-sensitized solar cells. *Journal of Materials Chemistry*, 22(29), 14465–14465. <https://doi.org/10.1039/c2jm30612c>