

RECENT PROGRESS AND FUTURE OUTLOOK OF GRAPHENE-BASED SUPER CAPACITORS

MUHAMMAD ARSLAN HAIDER SHAH, USMAN BIN HASSAN & MUHAMMAD RAMZAN

ABSTRACT

With the growth of renewable energy sources, electric vehicles, and portable devices, there is a greater demand for efficient energy storage worldwide. Super capacitors have emerged as attractive alternatives due to their high power density, ability to charge and discharge quickly, and long cycle life. However, their lower energy density compared to batteries remains a significant obstacle. Graphene and its derivatives, particularly reduced graphene oxide (rGO), have sparked intense interest as electrode materials due to their high conductivity, huge surface area, and variable surface chemistry. This article provides a complete summary of recent achievements in graphene-based super capacitors, concentrating on basics, material strategy, synthesis methods, electrochemical performance, and the barriers to large-scale commercialization. The article discusses graphene-based hybrid composites with metal oxides, sulfides, conducting polymers, and metal-organic frameworks (MOFs), emphasizing their synergetic impact on performance enhancement. Finally, future views are presented for the logical design of graphene-based super capacitors to address the increasing energy demands of next-generation technology

KEYWORDS: *Graphene-based supercapacitors; Energy storage devices; Reduced graphene oxide (rGO); Electrode materials; Electrochemical performance;*

1. INTRODUCTION

The global energy crisis and growing environmental concerns arising from fossil fuel depletion have intensified research into renewable energy sources and efficient energy storage technologies [1,2]. Batteries are among the most energy-dense storage systems; however, they suffer from limited cycle life and relatively slow charge–discharge rates. Supercapacitors, also known as electrochemical capacitors, offer higher power density, rapid charging–discharging capability, and longer cycling stability [3,4]. These advantages make them attractive for

applications in electric vehicles, portable electronic devices, and renewable energy integration systems. Nevertheless, their comparatively low energy density remains a major limitation when compared to batteries [5].

The performance of supercapacitors is strongly dependent on the nature of the electrode materials. Carbon-based materials such as activated carbon, mesoporous carbons, and carbon nanotubes have been extensively investigated owing to their high surface area and good electrical conductivity [6]. Among these materials, graphene has emerged as a particularly promising candidate due to its unique two-dimensional (2D) structure, exceptionally high theoretical surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), superior electrical conductivity, and excellent mechanical strength [7,8].

Graphene derivatives, including graphene oxide (GO) and reduced graphene oxide (rGO), have attracted significant attention for supercapacitor applications. Although pristine graphene exhibits outstanding electrical conductivity, it tends to aggregate and restack during processing, which reduces the accessible surface area and limits ion transport pathways [9]. In contrast, rGO provides a favorable balance between electrical conductivity and oxygen-containing functional groups, enabling improved interaction with electrolytes and enhanced electrochemical performance [10,11]. To further enhance capacitance and cycling stability, graphene-based materials are often combined with pseudocapacitive components such as transition-metal oxides, sulfides, conducting polymers, and metal–organic frameworks (MOFs) [12,13].

This review focuses on recent developments in graphene-based supercapacitors, highlighting fundamental charge-storage mechanisms, advances in electrode materials, synthesis strategies, electrochemical performance, and the key challenges that must be addressed for future applications.

2. FUNDAMENTALS OF SUPERCAPACITORS

Supercapacitors are classified as electric double-layer capacitors (EDLCs) and pseudocapacitors [15]. EDLCs rely on the accumulation of electrostatic charge at the electrode-electrolyte interface and are often made of carbon-based materials like graphene or activated carbon [16]. In contrast, pseudocapacitors store charge using quick and reversible faradic redox processes involving transition metal oxides, sulfides, or conducting polymers [17].

EDLCs have lengthy cycling stability and a high power density, but they typically have a poor energy density [18]. Pseudocapacitors can increase capacitance and energy and energy density, but their long-term stability is frequently degraded [19]. Hybrid supercapacitor, which combine EDLC and pseudocapacitivity processes, provides a solution to these restrictions, with graphene acting as a conductive backbone to improve charge transport and mechanical integrity [20].

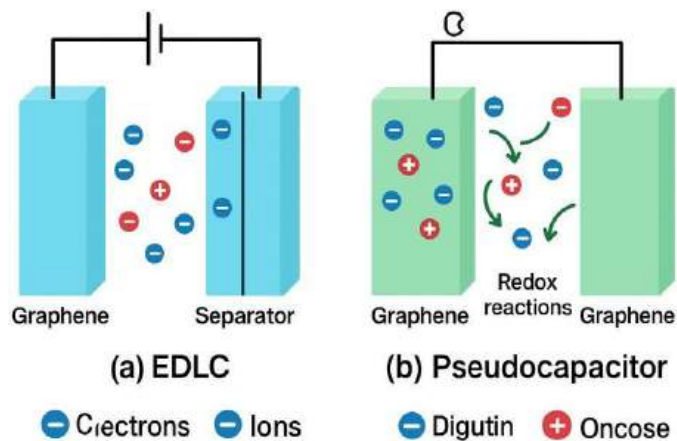


Figure 1. Schematic illustration of energy storage mechanisms in (a) electric double-layer capacitors (EDLCs) and (b) pseudocapacitors.

3. GRAPHENE AND ITS DERIVATIVES IN SUPERCAPACITORS

Graphene is a two-dimensional (2D) sheet of sp^2 -hybridized carbon atoms, possessing a predicted theoretical surface area of approximately $2630 \text{ m}^2 \text{ g}^{-1}$ and an electrical conductivity on the order of 10^4 S cm^{-1} [21]. These exceptional properties make graphene and its derivatives highly attractive electrode materials for supercapacitor applications. Qualities make it an excellent choice for EDLCs. However, clean graphene sheets tend to stack due to strong van der Waals interactions, considerably decreasing ion accessibility [22].

Graphene oxide (GO), which is commonly made using Hummers' technique, including many oxygen groups that improve solubility and process ability but decreasing conductivity [23]. Reduced graphene oxide (rGO) regains high conductivity while keeping some oxygen functional groups, making it an excellent candidate for hybrid supercapacitor electrodes [24, 26]. Despite these advantages, rGO alone frequently cannot offer the high capacitance needed for practical applications, promoting the development of composite methods [26].

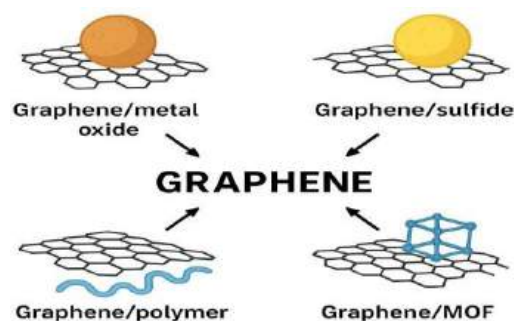


Figure 2. Graphene hybridized with metal oxides, sulfides, conducting polymers, and metal–organic frameworks (MOFs).

Table1.Graphene-Based Electrode Materials for Supercapacitors

Electrode Materials	Specific Capacitance (F/g)	Energy Density (Wh/Kg)	Power Density (W/Kg)	Cycling Stability(%)	References
Graphene	135–200	4–8	10,000	~95%(5000 cycles)	[4],[6]
Graphene Oxide(GO)	80–150	3–5	5000	~85% (3000 cycles)	[10],[23]
Reduced Graphene Oxide (rGO)	200–300	5–10	8000	~90%(5000 cycles)	[24],[26]
rGO/Ni Composite	~94	8	6000	92% (2000 cycles)	[46]
rGO/Co Composite	~204	12	7000	90% (3000 cycles)	[47]
Ni-Co Sulfide/rGO	~1000	25	10,000	88% (5000 cycles)	[31],[32]

4. COMPOSITE STRATEGIES FOR GRAPHENE-BASED SUPERCAPACITORS

4.1 Graphene/Metal Oxide Composites

Transition metal oxides such as MnO_2 , NiO , and Co_3O_4 possess high theoretical capacitance; however, their practical application is often limited by poor electrical conductivity and structural instability during cycling [27,28]. Hybridization with graphene significantly enhances electron transport, improves mechanical integrity, and facilitates efficient ion diffusion. For instance, MnO_2 /graphene composites have demonstrated high specific capacitance values exceeding 300 F g^{-1} along with excellent cycling stability [29]. Similarly, NiO/rGO and Co_3O_4 /graphene composites exhibit enhanced capacitance, improved rate capability, and superior electrochemical performance compared to their individual components [30].

4.2 Graphene/Metal Sulfide Composites

Metal sulfides, including NiS, CoS, and MoS₂, generally exhibit stronger redox activity and higher electrical conductivity than their oxide counterparts. In particular, Ni–Co sulfide/rGO composites have achieved remarkably high specific capacitance values of up to 1000 F g⁻¹ [31]. Despite these advantages, the dissolution of metal sulfides in electrolytes remains a critical challenge, leading to capacity fading and limiting their long-term cycling stability [32].

4.3 Graphene/Conducting Polymer Composites

Conducting polymers such as polyaniline (PANI) and polypyrrole (PPy) exhibit high pseudocapacitance but suffer from significant volumetric expansion and contraction during repeated charge–discharge cycles, which leads to poor cycling stability [33]. Incorporation of these polymers with graphene effectively enhances electrical conductivity, buffers volumetric changes, and improves structural stability. As a result, graphene–conducting polymer composites have demonstrated specific capacitance values exceeding 600 F g⁻¹ along with improved cycling performance [34,35].

4.4 Graphene/MOF-Derived Composites

Metal–organic frameworks (MOFs) serve as versatile templates and precursors for the fabrication of highly porous carbon materials. Graphene/MOF-derived composites integrate the high surface area and tunable porosity of MOFs with the excellent electrical conductivity of graphene. This synergistic combination facilitates rapid ion transport and efficient charge storage, leading to enhanced electrochemical performance in supercapacitor applications [36–38].

Table 3. Hybrid strategies and performance comparison of graphene-based composite electrodes.

Composite Type	Example Material	Best Reported Capacitance F/g	Cyclic Stability (%)	References
Graphene/Metal Oxides	MnO ₂ /Graphene, NiO/rGO	300-350	90-95% (5000 cycles)	[27],[28],
Graphene/Metal Sulfides	Ni-Co Sulfides/rGO, MoS ₂ /rGO	>1000	~88% (5000 cycles)	[31],[32]
Graphene/Conducting Polymers	PANI/rGO, PPy/rGO	600-650	80-90% (2000 cycles)	[33],[34,35]

Graphene/MOFs MOF-derived Graphene 400-500 ~90%
(3000 cycles) [36],[38]

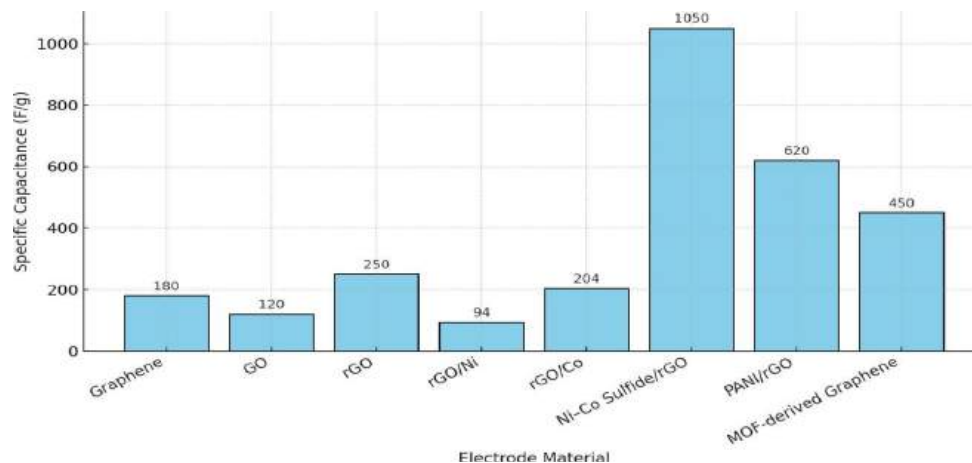


Figure 3. Comparison of specific capacitance values for various graphene-based electrode materials, including pristine graphene, graphene oxide (GO), reduced graphene oxide (rGO), rGO/metal composites, rGO/polymer composites, and MOF-derived hybrid materials.

Table 3. Synthesis methods for graphene and graphene-based composites.

Methods	Precursors/	Advantages	Limitations	References
Chemical Reduction	GO+Hydrazine, Ascorbic Acid	Simple,scalable, cost-effective	Toxic reagents, partial reduction	[9]
Hydrothermal/ Solvothermal	GO+MetalSalts, Sulfur Sources	Strongbonding, uniform nanostructures	High Temperature, batchprocess	[40]
RefluxMethod	GO + Transition MetalPrecursors	Cost-effective, easy setup	Lesscontrol on morphology	[41]

MOF-Derived Synthesis	Graphene+MOFs	Tunable Porosity, high surface area	Complex synthesis, costly precursors	[42]
Electrochemical Exfoliation	Graphite+ Electrolyte	Green, fast production	Poor layer control; defects	[10]

5. CHARACTERIZATION AND ELECTROCHEMICAL PERFORMANCE

A comprehensive understanding of supercapacitor behavior requires detailed structural, morphological, and electrochemical characterization of electrode materials. These techniques provide critical insights into material composition, surface chemistry, and charge-storage mechanisms.

- **X-ray diffraction (XRD):** Used to identify crystalline phases, structural integrity, and phase composition of graphene-based composites [43].
- **Scanning electron microscopy (SEM) and transmission electron microscopy (TEM):** Employed to examine surface morphology, particle size, and dispersion of active nanoparticles on graphene sheets [44].
- **Fourier transform infrared (FTIR) and Raman spectroscopy:** Utilized to detect functional groups, bonding interactions, defect density, and the degree of reduction in graphene derivatives [45].
- **Electrochemical characterization:** Cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) are commonly applied to evaluate capacitive behavior, rate capability, charge–transfer resistance, and cycling stability. Representative specific capacitance values reported in the literature include approximately 94 F g^{-1} for rGO/Ni, 204 F g^{-1} for rGO/Co, and values exceeding 1000 F g^{-1} for Ni–Co sulfide/rGO hybrid electrodes [46–48].

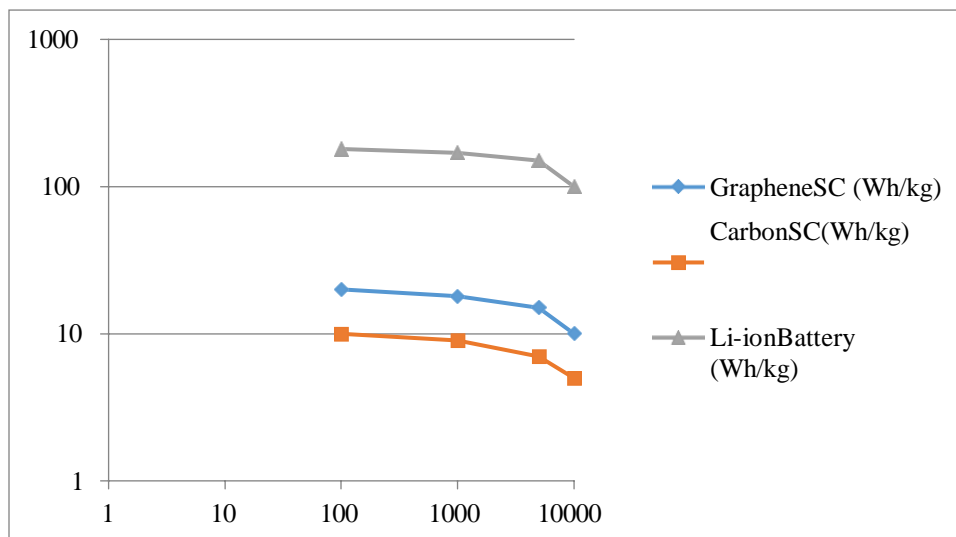


Figure 4. Ragone plot comparing energy density (X-axis) and power density (Y-axis) of graphene-based supercapacitors with conventional carbon-based supercapacitors and lithium-ion batteries.

6. CHALLENGES AND FUTURE DIRECTIONS

Despite remarkable progress in graphene-based supercapacitors, several critical challenges must be addressed to enable their large-scale practical application.

- **Energy density:** The energy density of graphene-based supercapacitors remains significantly lower than that of lithium-ion batteries, limiting their use in long-duration energy storage applications [49].
- **Scalability:** The synthesis of high-quality graphene with controlled structure and reproducible properties remains costly and difficult to scale for industrial production [50].
- **Cycling stability:** Electrode materials incorporating conducting polymers and metal sulfides often suffer from structural degradation and capacity fading during prolonged charge–discharge cycling [51].
- **Device integration:** Further optimization in device design and packaging is required to achieve efficient flexible, wearable, and solid-state supercapacitors [52].

Future research directions include heteroatom doping (e.g., N, S, and P) to enhance electrical conductivity and pseudocapacitive behavior [53], the use of bio-derived and sustainable precursors for environmentally friendly graphene synthesis [54], and the integration of graphene-based electrodes into flexible and wearable electronic systems [55].

7. CONCLUSION

Graphene and its derivatives, particularly reduced graphene oxide (rGO), have significantly advanced the design of high-performance supercapacitors. Their exceptional physicochemical properties, when combined with various hybridization strategies, have led to specific capacitance values that far exceed those of conventional carbon-based electrodes. Despite existing challenges such as limited energy density and issues related to large-scale, cost-effective production, continuous progress in composite engineering, synthesis techniques, and heteroatom doping

strategies indicates a promising future for these materials. With sustained research and technological innovation, graphene-based supercapacitors are expected to play a crucial role in next-generation energy storage systems.

REFERENCES

- [1] M. S. Halper and J. C. Ellenbogen, *Supercapacitors: A Brief Overview*, The MITRE Corporation, Technical Report, 2006.
- [2] D. Qu, "Studies of the activated carbons used in double-layer supercapacitors," *Journal of Power Sources*, vol. 109, no. 2, pp. 403–411, 2002.
- [3] J. Fernández, T. Morishita, M. Toyoda, M. Inagaki, F. Stoeckli, and T. A. Centeno, "Performance of mesoporous carbons derived from poly(vinyl alcohol) in electrochemical capacitors," *Journal of Power Sources*, vol. 175, no. 1, pp. 675–679, 2008.
- [4] C. Liu, Z. Yu, D. Neff, A. Zhamu, and B. Z. Jang, "Graphene-based supercapacitor with ultrahigh energy density," *Nano Letters*, vol. 10, no. 12, pp. 4863–4868, 2010.
- [5] B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Springer, New York, 1999.
- [6] S. R. C. Vivekchand, C. S. Rout, K. S. Subrahmanyam, A. Govindaraj, and C. N. R. Rao, "Graphene-based electrochemical supercapacitors," *Journal of Chemical Sciences*, vol. 120, no. 1, pp. 9–13, 2008.
- [7] A. Burke, "Ultracapacitors: Why, how, and where is the technology," *Journal of Power Sources*, vol. 91, no. 1, pp. 37–50, 2000.
- [8] P. Simon and Y. Gogotsi, "Materials for electrochemical capacitors," *Nature Materials*, vol. 7, pp. 845–854, 2008.
- [9] E. Frackowiak and F. Béguin, "Carbon materials for the electrochemical storage of energy in capacitors," *Carbon*, vol. 39, no. 6, pp. 937–950, 2001.
- [10] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, and R. S. Ruoff, "Graphene and graphene oxide: Synthesis, properties, and applications," *Advanced Materials*, vol. 22, no. 35, pp. 3906–3924, 2010.
- [11] M. D. Stoller and R. S. Ruoff, "Best practice methods for determining an electrode material's performance for ultracapacitors," *Energy & Environmental Science*, vol. 3, pp. 1294–1301, 2010.
- [12] H. Wang, H. S. Casalongue, Y. Liang, and H. Dai, "Ni(OH)₂ nanoplates grown on graphene as advanced electrochemical pseudocapacitor materials," *Journal of the American Chemical Society*, vol. 132, no. 21, pp. 7472–7477, 2010.
- [13] H. Chen *et al.*, "Electrochemical performance of graphene/metal oxide composites as electrode materials for supercapacitors," *Electrochimica Acta*, vol. 55, no. 23, pp. 6596–6602, 2010.

- [14] Z. Fan, J. Yan, L. Zhi, Q. Zhang, T. Wei, J. Feng, M. Zhang, W. Qian, and F. Wei, "A three-dimensional carbon nanotube/graphene sandwich and its application as electrode in supercapacitors," *Advanced Materials*, vol. 22, no. 33, pp. 3723–3728, 2010.
- [15] P. Simon and A. Burke, "Nanostructured carbons: Double-layer capacitance and more," *Electrochemical Society Interface*, vol. 17, no. 1, pp. 38–43, 2008.
- [16] F. Béguin, V. Presser, A. Balducci, and E. Frackowiak, "Carbons and electrolytes for advanced supercapacitors," *Advanced Materials*, vol. 26, no. 14, pp. 2219–2251, 2014.
- [17] J. Jiang and A. Kucernak, "Electrochemical supercapacitor material based on manganese oxide: Preparation and characterization," *Electrochimica Acta*, vol. 47, no. 15, pp. 2381–2386, 2002.
- [18] B. Xu, F. Wu, R. Chen, G. Cao, S. Chen, Z. Zhou, and L. Yang, "Mesoporous activated carbon fiber-based electrochemical capacitors with high energy density," *Electrochimica Acta*, vol. 52, no. 14, pp. 4595–4598, 2007.
- [19] M. Toupin, T. Brousse, and D. Bélanger, "Charge storage mechanism of MnO₂ electrode used in aqueous electrochemical capacitor," *Chemistry of Materials*, vol. 16, no. 16, pp. 3184–3190, 2004.
- [20] L. L. Zhang and X. Zhao, "Carbon-based materials as supercapacitor electrodes," *Chemical Society Reviews*, vol. 38, no. 9, pp. 2520–2531, 2009.
- [21] K. S. Novoselov, A. K. Geim, S. V. Morozov *et al.*, "Electric field effect in atomically thin carbon films," *Science*, vol. 306, no. 5696, pp. 666–669, 2004.
- [22] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nature Materials*, vol. 6, pp. 183–191, 2007.
- [23] W. S. Hummers and R. E. Offeman, "Preparation of graphitic oxide," *Journal of the American Chemical Society*, vol. 80, no. 6, p. 1339, 1958.
- [24] S. Pei and H. M. Cheng, "The reduction of graphene oxide," *Carbon*, vol. 50, no. 9, pp. 3210–3228, 2012.
- [25] K. Yang, L. Feng, X. Shi, and Z. Liu, "Nano-graphene in biomedicine: Theranostic applications," *Chemical Society Reviews*, vol. 42, no. 2, pp. 530–547, 2013.
- [26] L. L. Zhang, R. Zhou, and X. Zhao, "Graphene-based materials as supercapacitor electrodes," *Journal of Materials Chemistry*, vol. 20, no. 29, pp. 5983–5992, 2010.
- [27] R. Kötz and M. Carlen, "Principles and applications of electrochemical capacitors," *Electrochimica Acta*, vol. 45, no. 15–16, pp. 2483–2498, 2000.
- [28] J. Yan, Q. Wang, T. Wei, and Z. Fan, "Supercapacitor electrodes based on graphene and carbon nanotube composites," *Electrochimica Acta*, vol. 55, no. 24, pp. 6973–6978, 2010.
- [29] J. Wu, Z. Li, Z. Xu, M. Zhai, and J. Li, "Facile synthesis of MnO₂/graphene composite for supercapacitor applications with enhanced electrochemical performance," *Electrochimica Acta*, vol. 55, no. 25, pp. 7470–7475, 2010.

- [30] H. Zhang, G. Cao, Z. Wang, and Y. Yang, "Electrochemical capacitive properties of Co_3O_4 nanocrystals with different morphologies as electrode materials for supercapacitors," *Electrochimica Acta*, vol. 52, no. 16, pp. 5209–5214, 2007.
- [31] X. Zhao, B. Zheng, X. Xie, J. Jiang, and Y. Tian, "Graphene/ MoS_2 nanocomposites for supercapacitor applications," *Electrochimica Acta*, vol. 107, pp. 219–227, 2013.
- [32] L. Li, Z. Wu, S. Yuan, and X. Zhang, "Ni Co_2S_4 nanostructures for high-performance supercapacitors: Pseudocapacitive mechanism and asymmetric cell performance," *Chemistry – A European Journal*, vol. 19, no. 49, pp. 16537–16545, 2013.
- [33] A. Ghosh and Y. H. Lee, "Carbon-based electrochemical capacitors," *ChemSusChem*, vol. 5, no. 3, pp. 480–499, 2012.
- [34] G. Wang, L. Zhang, and J. Zhang, "A review of electrode materials for electrochemical supercapacitors," *Chemical Society Reviews*, vol. 41, no. 2, pp. 797–828, 2012.
- [35] X. Dong *et al.*, "3D graphene–polymer hybrid for high-performance supercapacitor," *ACS Nano*, vol. 6, no. 4, pp. 3206–3213, 2012.
- [36] J. Xu, K. Wang, S. Zu, B. Han, and Z. Wei, "Hierarchical nanocomposites of polyaniline nanowire arrays on graphene oxide sheets with synergistic effect for energy storage," *ACS Nano*, vol. 4, no. 9, pp. 5019–5026, 2010.
- [37] Y. Zhai *et al.*, "Carbon materials for chemical capacitive energy storage," *Advanced Materials*, vol. 23, no. 42, pp. 4828–4850, 2011.
- [38] Z. Lei, J. Zhang, and X. Zhao, "Ultrathin MnO_2 nanoflakes grown on graphene oxide sheets for supercapacitors," *Journal of Materials Chemistry*, vol. 22, no. 1, pp. 153–160, 2012.
- [39] C. Gómez-Navarro *et al.*, "Electronic transport properties of individual chemically reduced graphene oxide sheets," *Nano Letters*, vol. 7, no. 11, pp. 3499–3503, 2007.