Perspective

A perspective on graphene for supercapacitors: Current status and future challenges

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Supercapacitors, also known as ultracapacitors or electrochemical capacitors, possess intriguing merits of high power density (10–100 times higher than that of batteries), long life expectancy (millions of cycles), wide operation temperature range (−40 °C to 70 °C), environmental friendliness, and high energy efficiency (90%–95%). Therefore, supercapacitors have drawn great attention in various applications, such as public transportation, hybrid heavy vehicles, rail network, wind blades, back power, and portable consumer electronics. Currently, searching high-performance electrode materials is still the key for the development of supercapacitors. Recently, two-dimensional (2D) materials have exhibited superior capacitive or pseudocapacitive performance due to the increased surface area and enriched electrochemically active sites [1,2]. Among these materials, graphene, a 2D monolayer of sp^2-bonded carbon atoms with the unique combination of large specific surface area (SSA, 2630 m^2 g^{-1}), extraordinary conductivity, physicochemical stability and mechanical properties, holds great promise for multiple types of high-performance and new-concept supercapacitors (Fig. 1). In principle, graphene can serve as (1) a highly active material, (2) an ideal substrate for hybrids, and (3) a flexible structural material (binder) and conductive additive in electrodes.

Electric double layer capacitors (EDLCs) store energy by electrostatic ion adsorption on the surface of active materials. The large SSA endows graphene with high theoretical EDL capacitance of 550 F g^{-1} [3]. However, in the pioneering work, graphene-based supercapacitors only deliver capacitances of 135 F g^{-1} and 99 F g^{-1} in aqueous and organic electrolytes respectively [4], owing to the restacking of graphene sheets caused by the π–π interaction and Van der Waals force, which results in the limited access of electrolyte ions to the surface. To increase the ion-accessible surface area, various graphene derivatives pillared by nanospacers (e.g., carbon nanotube, nanoparticles, and nonvolatile solvent) and porous graphene architectures (e.g., curved graphene, activated graphene, holey graphene, vertically aligned graphene, and porous graphene assemblies) are developed. Consequently, the capacitances increase to 200–300 F g^{-1} in aqueous electrolytes and 120–280 F g^{-1} in nonaqueous electrolytes. Besides, graphene offers the possibility of constructing hierarchical porous frameworks with controllable porosity that allow superior pore connectivity and accessibility to targeted electrolytes and surpass the limitation of activated carbon with a broad pore distribution and some unavailable pores.

Pseudocapacitors utilize fast surface or near-surface faradaic reactions for charge storage. Transition metal oxides and conducting polymers are two main kinds of pseudocapacitive materials, but plagued by poor electronic conductivity. An effective approach is to hybridize these redox-active species with graphene. The graphene in the hybrids can provide a highly conductive path and work as a stabilizing agent to significantly reduce the charge transfer resistance and maximize the utilization of pseudocapacitive
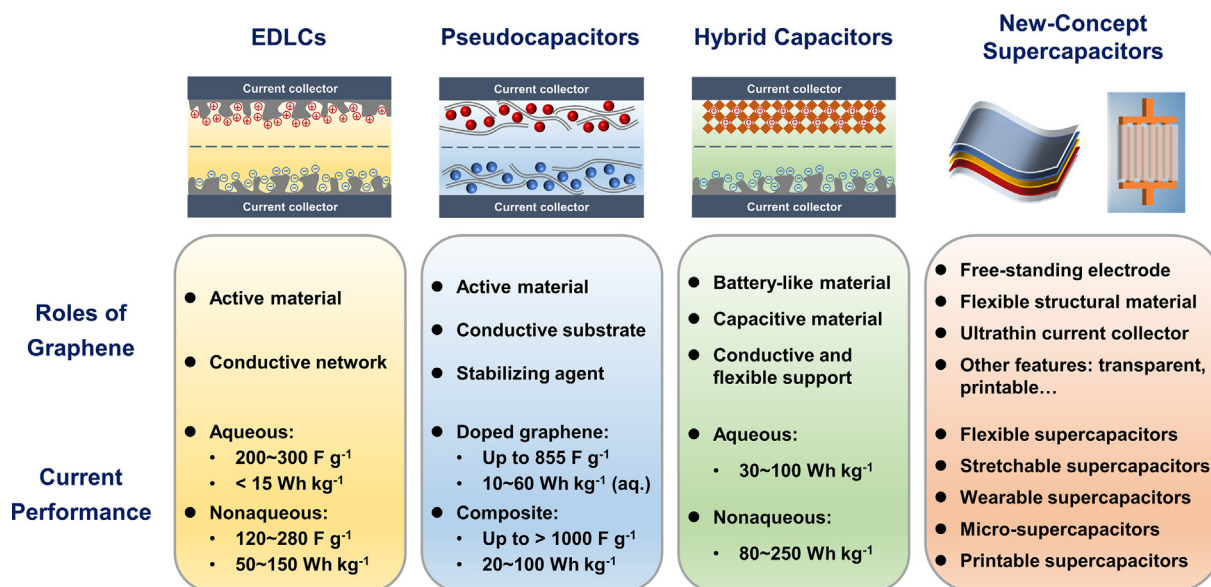
Fig. 1. Roles of graphene in different types of supercapacitors and the corresponding performance (based on electrode materials).

materials. Given the synergistic effect, these hybrids exhibit enhanced capacitance and cycling stability. Besides, heteroatoms (e.g., N, B, S and P) doping of graphene itself has proven to be capable of changing its chemical state and introducing additional pseudocapacitance. Notably, the doped mesoporous graphene-like few-layer carbon delivers landmark capacitance of 855 F g^{-1} in aqueous electrolyte [5].

Hybrid supercapacitors composed of a capacitive electrode and a battery-like electrode are proposed to combine the merits of high power density of supercapacitors and high energy density of batteries, but still hindered by the mismatch of electrode kinetics and capacity of these two-type electrodes. In this regard, graphene with tailored structure can offer superior capacitance for capacitive electrodes, and meanwhile exhibit extraordinary lithium-ion storage capability for battery-like electrodes. Impressively, the non-aqueous dual-graphene lithium-ion hybrid supercapacitors simultaneously achieve high energy density and power density profiting from the alleviated imbalance of electrode kinetics. Moreover, graphene can serve as a conductive, flexible yet inactive support for stably anchoring nano-crystallized battery materials to substantially overcome their sluggish reaction kinetics and buffer their volumetric strain during charge and discharge, which is of crucial importance for the development of hybrid supercapacitors with "double-high" characteristics of energy density and power density.

Multitasking graphene also pushes the exploration of new-concept supercapacitors with diverse features (e.g., flexible, miniaturized, stretchable, wearable and transparent) to meet the requirements of next-generation smart electronics. Graphene can act as a flexible structural material or binder to improve the mechanical integrity of electrode, and also as building blocks for the assembly of graphene macroscopic architectures (e.g., 1D fiber, 2D film, 3D network) that can be facilely processed into free-standing electrodes for flexible and wearable supercapacitors. Besides, the excellent physicochemical stability facilitates the use of graphene in durable supercapacitors for stable power output under harsh electrochemical, thermal and mechanical conditions [6]. Notably, graphene is more suitable for planar micro-supercapacitors due to perfect match of 2D graphene with planar geometry for rapid ion transport in horizontal direction and effortless processing of graphene films into patterned micro-electrodes and micro-arrays. Furthermore, highly conductive and atomically

thin graphene has been applied as active material, ultrathin and lightweight current collector, and metal-free interconnect for printable and integrated supercapacitors with shape conformality and tunable voltage/capacitance output.

To realize the practical application, graphene for supercapacitors is still facing huge challenges. First, the low-cost mass production of graphene with controlled microstructure and surface chemistry is the key challenge for the utilization of graphene in commercial devices. Second, it should be noted that ion diffusion is possibly impeded by the large basal plane of graphene sheets, especially in the thick electrodes. Therefore, the amount, lateral size, and in-plane nanopores of graphene in the electrodes must be systematically optimized to ensure the accessibility of the active materials while retaining efficient electron conducting network. Third, porous graphene architectures usually possess large pore volume that consumes an extra amount of electrolyte, worsening the capacitance at device level, and low packing density that leads to unsatisfactory volumetric performance. To simultaneously achieve high gravimetric and volumetric performance, the porosity and mass density should be well balanced, and precise synthetic methods need to be further developed for better control on SSA, pore size and distribution of graphene-based materials. Fourth, graphene sheets often tend to agglomerate and lose their intrinsic properties during the fabrication process. Besides, it is still challenging to fabricate graphene-based electrodes by standard manufacturing techniques used in current supercapacitor industries, and most reported processing methods are limited to the laboratories. Therefore, it is crucial to develop compatible and cost-effective electrode processing techniques that allow high mass loading and packing density and can be scaled up from laboratory to industry. Fifth, when used as anode for nonaqueous hybrid supercapacitors, graphene exhibits a low initial coulombic efficiency due to the formation of solid electrolyte interface on the huge surface of graphene sheets. A facile and efficient pre-lithiation method is highly needed to compensate the large irreversible capacity.

So far, tremendous efforts have been devoted to architectural design and chemical modification of graphene-based materials to improve the performance of supercapacitors under practical conditions. Regarding to the preparation approaches of graphene, liquid-phase exfoliation of graphite and reduction of graphite oxide are promising for large-scale production of graphene. In particular, graphene oxide is regarded as a competitive starting material to

construct various graphene-based materials for supercapacitors due to its superior processability.

Constructing porous graphene architectures with interconnected in-plane and/or out-of-plane pores is an effective way to boost the EDL capacitance. In-plane pores generated through carbon erosion reactions using oxidizer (*e.g.*, HNO_3, H_2O_2), strong base (*e.g.*, KOH), metal oxide/salt (*e.g.*, Fe_2O_3, $ZnCl_2$), and gases (*e.g.*, steam, air) as etching agent offer numerous ion migration pathways to the surface and edges of graphene even in a compact film. Impressively, a holey graphene framework with a packing density of 0.71 g cm^{-3} displays a capacitance of 298 F g^{-1} [7]. Moreover, 3D porous graphene assemblies can provide 3D efficient electron transport network and facilitate electrolyte penetration, enabling superior surface utilization for charge storage. To further improve the areal and volumetric performance, capillary compression combined with pore generation or electrolyte-mediated techniques is developed to yield densely packed graphene monoliths with tailored nanoporous structure and tortuosity, achieving rapid ion diffusion in thick compact electrodes [8,9]. As demonstrated, a supercapacitor based on two 400-µm-thick electrodes with a packing density of 0.87 g cm^{-3} delivers remarkable energy density of 65 Wh L^{-1} [8]. Besides, layer-by-layer assembly is another versatile strategy to fabricate compact electrodes for high volumetric performance. Typically, a densely stacked graphene-conducting polymer hybrid film for micro-supercapacitors exhibits ultrahigh volumetric capacitance of 736 F cm^{-3} [10].

Surface chemistry is also a key parameter that determines the physicochemical properties (*e.g.*, electronegativity, carrier concentration, and surface energy) and electrochemical performance of graphene. Heteroatom doping can change the chemical state and improve the electronic conductivity and wettability. Oxygen-containing functional groups are also reported to enhance the wettability of graphene-based electrodes and incorporate faradaic charge storage, but they are not stable enough in most cases. It should be noted that, to improve the stability at high voltage, high-quality graphene with low-content or free defects is more favorable. Recently, a symmetric supercapacitor based on seamless sheets consisting of graphene meso-sponge with few edge sites achieves ultrahigh working voltage up to 4.4 V [11], demonstrative of great potential for high-energy supercapacitors.

Other challenges and opportunities lie in fundamental understanding of the charge storage mechanisms and further performance improvement of graphene-based supercapacitors (Fig. 2). First, a well-designed regulation of critical factors such as wettability by electrolyte, high voltage stability, pore connectivity and accessibility is required for further boosting the EDL capacitance, but restricted by the limited understanding of the ionic kinetics and EDL formation inside pores as well as the interaction between electrode and electrolyte. In this regard, stacked-layer graphene films as a fundamental model can provide straightforward 2D ionic channels with adjustable interlayer distance and defect engineering for the in-depth understanding of the ion population, adsorption and transport in the confined space and the charge separation at the active material/electrolyte interface. To this end, a combination of in-situ or operando characterization experiments (*e.g.*, nuclear magnetic resonance spectroscopy, electrochemical quartz crystal microbalance, infrared spectroscopy and scattering approaches) that offer direct information about microscopic kinetics and computational methods (*e.g.*, molecular dynamics, density functional theory and mean field theory) that provide theoretical basis for precise description of ion-ion and ion-carbon interactions is highly recommended to fully elucidate the charge storage mechanisms. Second, the effects of the dopants on their contribution to capacitive performance are complicated in different electrolytes, which need to be further confirmed. Based on the fundamental understanding of the origins of the changed physicochemical properties and the faradaic charge storage, an exact manipulation of heteroatom configuration would enable EDLC electrodes with enhanced wettability, conductivity and stability, and promote the utilization of doped graphene in pseudocapacitors, especially those in nonaqueous electrolytes. Third, the illumination of the molecular-level coupling interaction between graphene and loaded materials will provide guidance on designing novel hybrids with enhanced synergy to improve their charge storage capability and cycling stability. Fourth, the sluggish reaction kinetics of battery-like electrodes imposes great restriction on the performance of hybrid supercapacitors. To solve this issue, dispersing nano-structured battery materials into 3D porous graphene architectures with efficient electron transport network and shortened ion diffusion path would be an effective choice to maximize the extrinsic pseudocapacitive charge storage behavior of battery-like electrodes. Fifth, autonomous microsystems consisting of energy harvester, energy accumulator and functional circuits are of profound importance for wearable electronics and the Internet of Things. The new-concept graphene-based micro-supercapacitors are particularly useful in these applications due to their superior reliability and robustness under dynamic operating conditions with varied current, voltage or deformation.
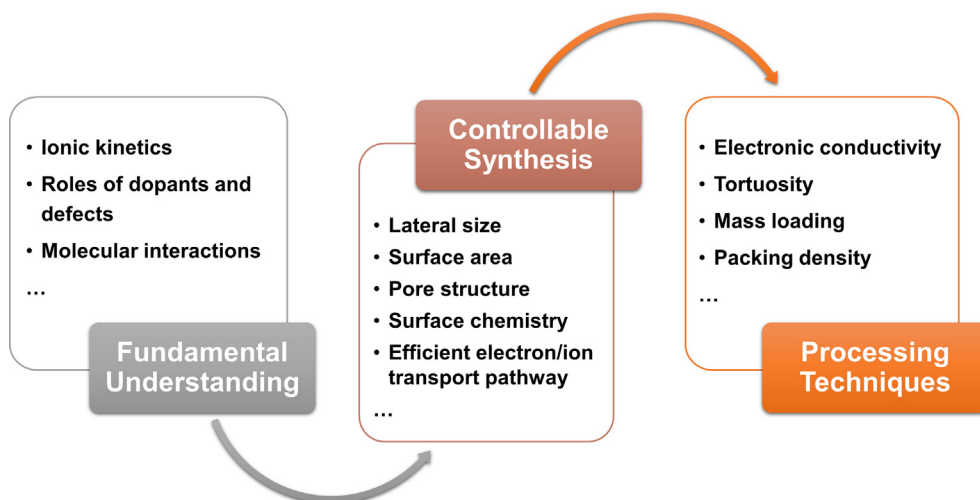

Fig. 2. A schematic illustration showing the challenges and opportunities in graphene-based materials for supercapacitors.

Nevertheless, the controllable fabrication of multi-functional graphene-based materials and complex system engineering towards compatible integration of different components are crucial for the development of the new-concept supercapacitors and their integrated systems.

In summary, notable breakthroughs have enabled graphene-based supercapacitors with superior performance beyond current commercial ones in terms of energy density, power density, cycle life, mechanical flexibility and other features. Nevertheless, extending the availability of these remarkable properties from laboratory to industry is of vital importance in near future, and it will take the collaborative efforts of scientists, engineers and entrepreneurs. Meanwhile, it should be emphasized that the performance of graphene-based supercapacitors needs continuous improvement to match the stringent criteria for specific applications. To this goal, a systematic optimization of the key factors is highly necessary and should be based on the fundamental understanding of electrochemical processes in graphene-based electrodes and devices. Moreover, the unique properties of graphene would open many intriguing opportunities to create new-concept supercapacitors, such as ultrathin, flexible, wearable, miniaturized, integrated and customized supercapacitors for unconventional smart electronics and the Internet of Things.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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