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Highlights

- Recent developments of graphene-conducting polymer nanocomposites are overviewed.
- Material design, synthesis and applications in flexible supercapacitors are highlighted.
- Current challenges and future perspective are briefly commented.

Graphene-Conducting Polymer Nanocomposites for Enhancing Electrochemical Capacitive Energy Storage

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Abstract: The evolution of power generation, expansion of transportation and electrification, and popularization of portable electronic devices have altogether posed growing demands for more efficient energy storage systems. Supercapacitors, as one of major electrochemical energy storage devices, have recently received intensive attention. In this minireview, our focus is on graphene-conducting polymer nanocomposites and their applications in supercapacitors that have potential to perform high power and energy density, fast charge/discharge rate, low cost and eco-friendly operation conditions. We *first* introduce major types of supercapacitors and their working principles. We *then* overview several hybrid material systems combing graphene and various conducting polymers such as polyaniline, polythiophene, polypyrrole and their derivatives, with the emphasis on the composite design, synthesis methods, capacitive performance and current applications in flexible and bendable supercapacitors. *Finally*, the challenges and perspective of such composite electrode materials for supercapacitors are commented for perspective of further research directions.

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Keywords: *Supercapacitor, electrochemical energy storage, graphene, conducting polymer, nanostructured composite materials*

1. Introduction

An immense demand towards portable electronic devices and hybrid electric vehicles has raised unprecedented requirements to current energy storage systems (ESSs). As the most common energy storage devices, batteries have been the technology of choice for supplying power for most applications in the past long time, because they can store large amount of energy in a relatively small volume and less weight [1]. However, the low power density and short cycle life of batteries can hardly meet the demand of new energy sectors. Supercapacitors (SCs), with high power density, fast charge/discharge rate, long-cycle life and environmentally friendly operation, hold great potential to compensate the shortcomings of batteries and offer additional flexibility for storage of electricity [2]. Moreover, the combination of SCs (high power density) and batteries (high energy density) could further provide opportunity to build more advanced hybrid ESSs.

SCs, also called electrochemical capacitors (ECs), are rechargeable electrochemical energy storage devices capable of providing up to thousand times higher power output compared to the batteries of similar size [3]. Although SCs store lower amount of energy than batteries, in most cases, their energy density is still much higher than that of conventional capacitors [4]. In addition, SCs can be fully charged or discharged in seconds, while batteries take much longer time due to electrochemical kinetics through a polarization resistance [5]. The performance of various energy storage devices is compared in the Ragone plot (Figure 1). As seen from the plot, SCs could fill the gap between conventional capacitors and batteries. Therefore, SCs could play a crucial role in the development of new ESSs.
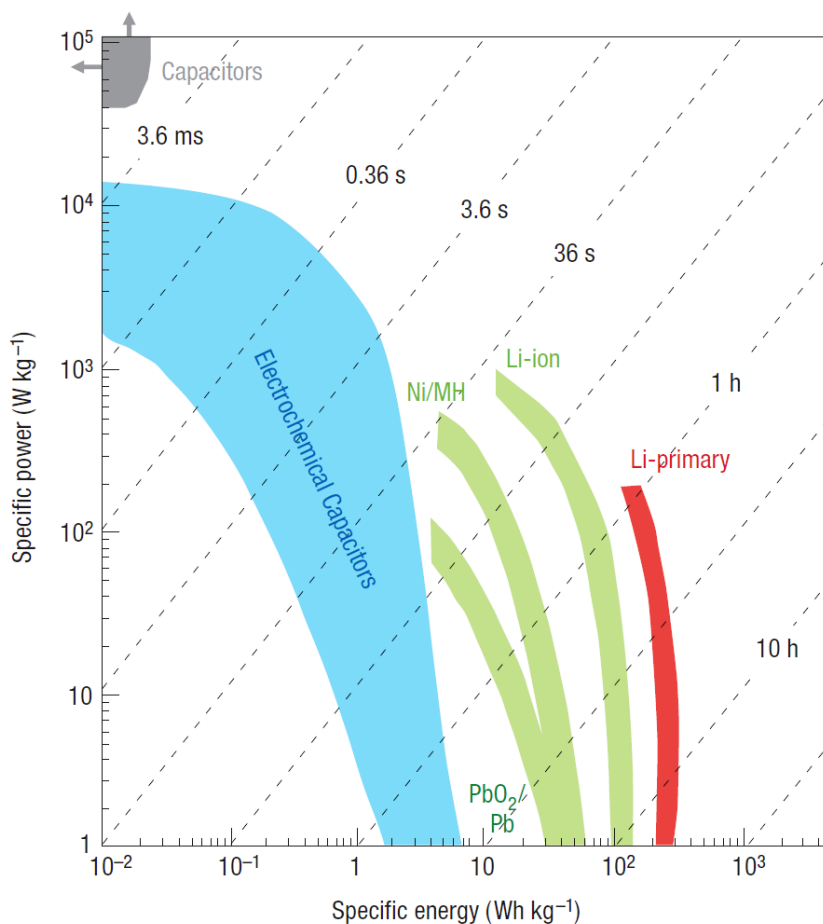
Figure 1. Ragone plot comparing specific energy and power capability of conventional capacitors, electrochemical capacitors (supercapacitors) and various batteries. Times shown are the time constants of the devices, obtained by dividing the energy density by the power. Adapted from ref. [6]

2. Working principles and classification

In a conventional capacitor, two electrically conductive electrodes are separated by an insulating dielectric material (Figure 2a), and the capacitance is originated in pure electrostatic charges. In contrast, SCs are composed of two electrodes mechanically separated by an ion permeable insulating membrane, but ionically connected to an electrolyte (Figure 2b). Each electrode/electrolyte interface represents a capacitor, a SC can thus be regarded as two capacitors in series. If two capacitors exhibit the same behavior, i.e. using the same material for both electrodes, then such SC is termed as a symmetric SC. Alternatively, two different electrodes can construct an asymmetric capacitor. The overall specific capacitance (C_S) of a SC can be calculated by Eq(1).

$$C_S = \frac{C_1 * C_2}{C_1 + C_2} \tag{1}$$

where C_1 and C_2 are the specific capacitance of two electrodes, respectively. In addition, the energy (E) density that a SC enables to store can be expressed by Eq(2).

$$E = \frac{1}{2} C V^2 \tag{2}$$

where V is the applied cell voltage. Equation (2) shows that the specific capacitance and the applicable cell voltage determine the output energy of a SC. In order to enhance the energy density of a SC, we need to design electrode materials that enable to increase the device capacitance or expand the applicable voltage window. The maximum power (P_{max}) of a SC can be calculated according to Eq(3).

$$P_{max} = \frac{V^2}{4R} \tag{3}$$

where R is the equivalent series resistance. Hence, the power output is determined by the cell voltage and internal resistance.
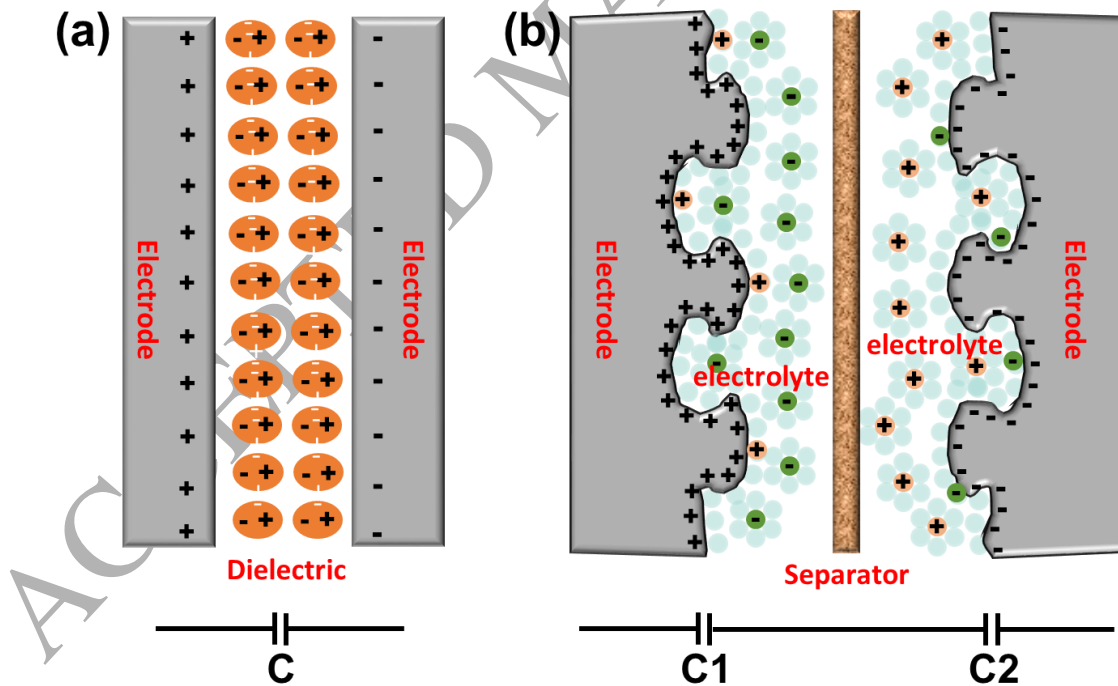
Figure 2. Schematic diagrams of (a) a conventional capacitor and (b) structure and working principles of a symmetric supercapacitor

To sum up, the capacitance mainly depends on the electrode materials, and the available cell voltage window depends on both of electrode material and electrolyte. Therefore, the electrode materials and electrolytes are two critical factors to the specific energy and power of SCs. Some electrode materials are discussed in detail in the following sections. As for the electrolytes used in SCs, briefly, aqueous electrolytes have high ionic conductivity (up to ~1 S cm^{-1}) but relatively low decomposition voltage (~1.23 V); while organic electrolytes allow the use of cell operating voltage up to ~3-4 V but they could induce higher electrical resistivity, resulting in a higher internal resistance [7].
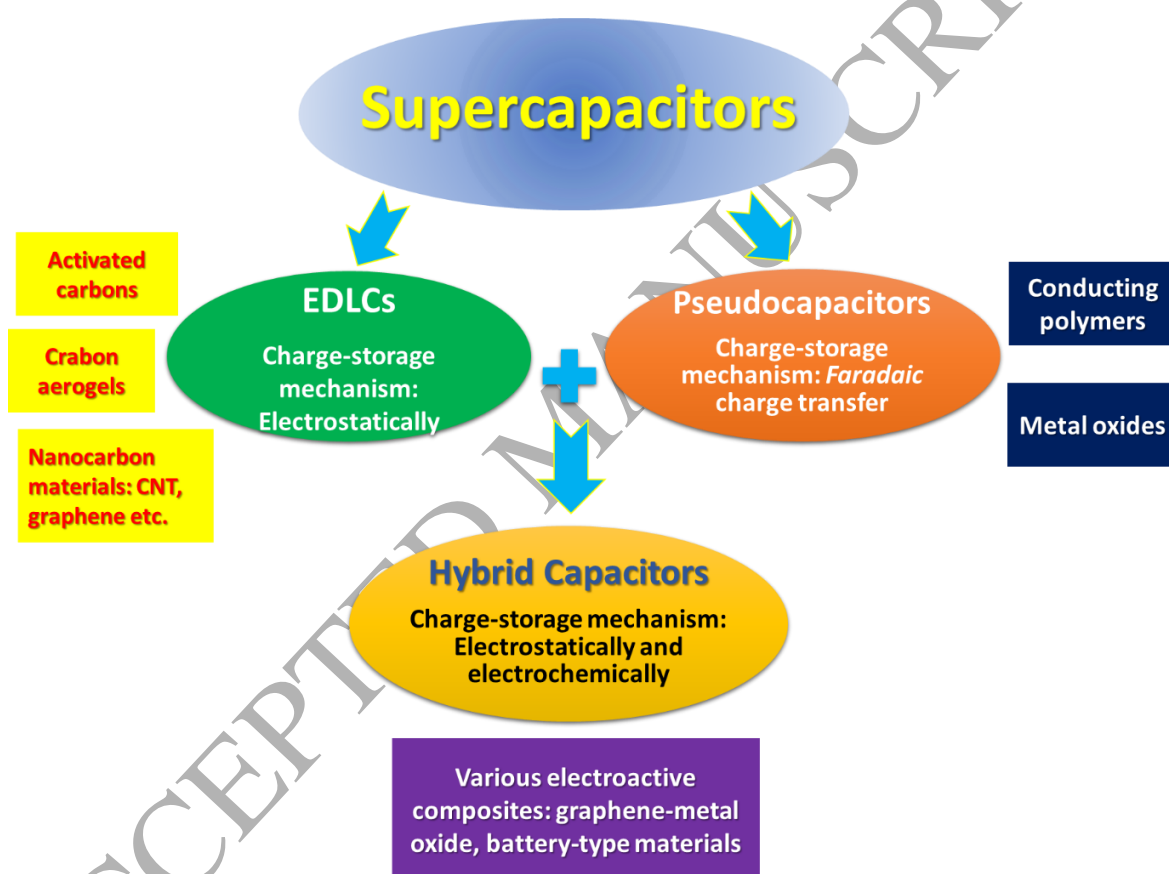
Figure 3. Diagram representations for three types of supercapacitors and corresponding most common materials used in the construction.

The working principles of SCs also depend on the type of electrode materials, which is electroactive or not. The charge storage of SCs arises from electric double layer (ELD) induced by ion adsorption or/and faradic redox processes of electroactive species at the electrode/electrolyte interface (Figure 2b). According to the charge-storage mechanism, SCs

can be generally classified into three types, i.e. electric double layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors (Figure 3). In the first-type SCs, reversible electrostatic attraction occurs between the ions from electrolytes and the charged surface of electrodes. This kind of supercapacitors can be called as EDLCs, which have much higher capacitance values than conventional capacitors due to the large surface area of electrodes (up to thousands of m^2 g^{-1}) and the extremely thin double-layer distance (e.g. a few tenths of nanometer) [8]. The double layer capacitance of an EDLC can be expressed as:

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \qquad (4)$$

where ε_r and ε_0 are the dielectric constant of electrolyte and free space (or vacuum), respectively; A is the specific surface area of electrode, and d is the thickness of electric double layer. Carbonaceous materials have so far been the most widely used electrode substrate, due to their high specific surface area, high chemical stability and relatively low cost (Figure 3). During the charging process, cations are driven to accumulate on the negative electrode and anions on the positive electrode forming a double layer for energy storage. During the discharging process, in contrast, ions travel away from the surface of electrode and mixed in electrolyte. There is no charge transfer in the process, which guarantees very fast charge/discharge rate and better power performance of EDLCs. However, this kind of SCs normally suffer from low energy density.

In pseudocapacitors, fast and reversible faradic reactions take place at the interface during the energy storage and delivery process accompanied by double layer charge storage; hence, they generally exhibit much higher specific capacitance and energy density than EDLCs. For a pseudocapacitor, its capacitance can be described as:

$$C = \frac{\Delta Q}{\Delta V} \qquad (5)$$

where Q is the accumulated charge and V is the applied voltage. As the redox processes in a pseudocapacitor occur mainly at the electrode surface, the charge/discharge rates are faster than that of a battery where redox reactions occur within the electrode itself [9]. Conducting polymers and metal oxides/sulfides are among the most common electroactive materials used in constructing pseudocapacitors (Figure 3). Compared to metal oxides/sulfides, conducting polymers have shown some unique physicochemical properties, such as larger theoretical specific capacitance, better electrical conductivity, lower cost and ease of large-scale

production [10]. In conducting polymers based pseudocapacitors, the charge/discharge processes are associated with the doping/de-doping processes of conducting polymers. There are two types of doping organic polymers, i.e. p-doping (oxidation) and n-doping (reduction), which could enhance the overall conductivity of a polymer up to the metallic level [11]. The p-doping of polymers normally refers to the partial oxidation of the polymers (P), and counter-anions (A$^-$) are intercalated to preserve electrical neutrality in the system, Eq(6). In contrast, the n-doping of polymers involves the partial reduction of the polymer and insertion of counter-cations (M$^+$) to preserve electrical neutrality, Eq(7).

$$P_m - xe^- + xA^- \xleftrightarrow{Charge/Discharge} P_m^{x+}A_x^- \qquad (6)$$

$$P_m + xe^- + xM^+ \xleftrightarrow{Charge/Discharge} P_m^{x-}M_x^+ \qquad (7)$$
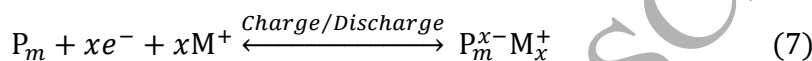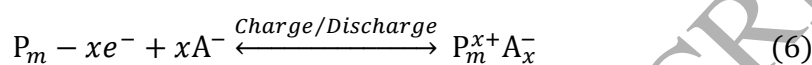
where m is the polymerization degree and x is the number of charges transferred. However, only using these redox materials in capacitors encounters other problems such as poor stability and low power density.

In order to overcome the drawbacks of EDCLs and pseudocapacitors, both electrode materials (carbonaceous materials and redox-active materials) can be used in construction of a SC. Such SCs is normally termed a hybrid SC (Figure 3). In general, carbon materials are used as the scaffold to support electroactive components, and their composites act as electrodes of a hybrid SC. Hybrid SCs could display enhanced energy density, high power density and relatively high stability. In the following sections, we will focus on highlighting recent advances in the development of graphene-conducting polymer nanocomposite based SCs and their potential applications in flexible electronics.

3. Advantages of graphene-conducting polymer nanocomposites as supercapacitor electrode materials

Graphene (Gr), a two-dimensional monolayer of sp^2-bonded carbon atoms, exhibits a range of remarkable physical properties, *including* high elastic modulus and fracture strength ($\sim$1 TPa and $\sim$130 GPa, respectively), good electrical conductivity ($\sim$10^4 - 10^5 S m^{-1}), and very high surface area ($\sim$2600 m^2 g^{-1}) [12]. Double layer capacitance of pristine single-layered graphene was reported to be about 21 μF cm^{-2} [13], therefore the maximum specific capacitance of ~550

F g^{-1} can be expected if the entire specific surface area of graphene nanosheets are effectively used. A specific capacitance of 513 F g^{-1} has recently been achieved for the three-dimensional (3D) reduced graphene oxide (rGO) networks fabricated on a copper foam surface [14]. Doping of Gr nanosheets with heteroatoms, *e.g.* N, B, or S, can modify the charge distribution and hence further enhance the specific capacitance and power density of graphene supported SCs [15–17].

Conducting conjugated polymers (CPs), *e.g.* polyaniline (PAni), polythiophene (PT), polypyrrole (PPy) and their derivatives, are prospective materials for charge- and energy-storage applications due to their relatively low cost, good electrical conductivity (up to $4.6 \cdot 10^5$ S m^{-1} [18]) and high capacitance, mainly related to the pseudo-faradaic phenomena (up to 2000 F g^{-1} for PAni [19], 485 F g^{-1} for PT [20], 620 F g^{-1} for PPy [21], dependent on the doping level). Although CPs hold promising characteristics for electrochemical energy storage, however, their low stability under charge/discharge conditions has limited practical applications [20]. The rapid decayed stability is mainly caused by considerable mechanical degradation (e.g. swelling and shrinking) and irreversible structural changes occurred during the charge-discharge processes.

Recent studies have shown that Gr can affect the molecular conformation and orientation of CP chains, leading to the positive synergistic effect on their composites to achieve higher electrical conductivity and higher stability than individual components [22]. Other advantages of Gr-CP composite materials include high surface area (for enhancement of the specific capacitance), considerable structural diversity, small size of particles and short distance for ion transfer, structural uniformity and controllable morphology [23, 24]. Moreover, the integration of CP with Gr prevents self-aggregation or re-stacking of graphene nanosheets to avoid decrease in the specific surface area and irreversible capacitance loss arising from changes in the nanocomposite morphology.

3.1. Material Design, Synthesis methods, and Performance

Several crucial aspects have to be considered in the development of Gr/CP nanocomposites, including *i*) appropriate methods of synthesis, *ii*) surface compatibility of CP with Gr, *iii*) controlling thickness and morphology of the CP film, and *iv*) surface properties of the nanocomposite material (e.g. surface roughness, hydrophilicity) [25].

There are two major strategic approaches for preparation of Gr/CP nanocomposites, *viz.* through incorporation of the CP between the Gr sheets (2D nanocomposites) and employment of Gr nanosheets as a matrix for the synthesis of CP or Gr/CP nanostructures with various morphology (3D networked materials) [26]. This can be achieved by direct incorporation of CP nanostructures during the GO reduction, *in situ* polymerization of monomers on rGO surface or template synthesis, in which metal or polymer with micro-/nano structures are used for layer-by-layer assembly of Gr and CP followed by sequent removal of templates [27]. A variety of methods can be used for the synthesis of CPs, including chemical routes, electrochemical deposition and photo-induced polymerization. These approaches have their own advantages and drawbacks (Figure 4).
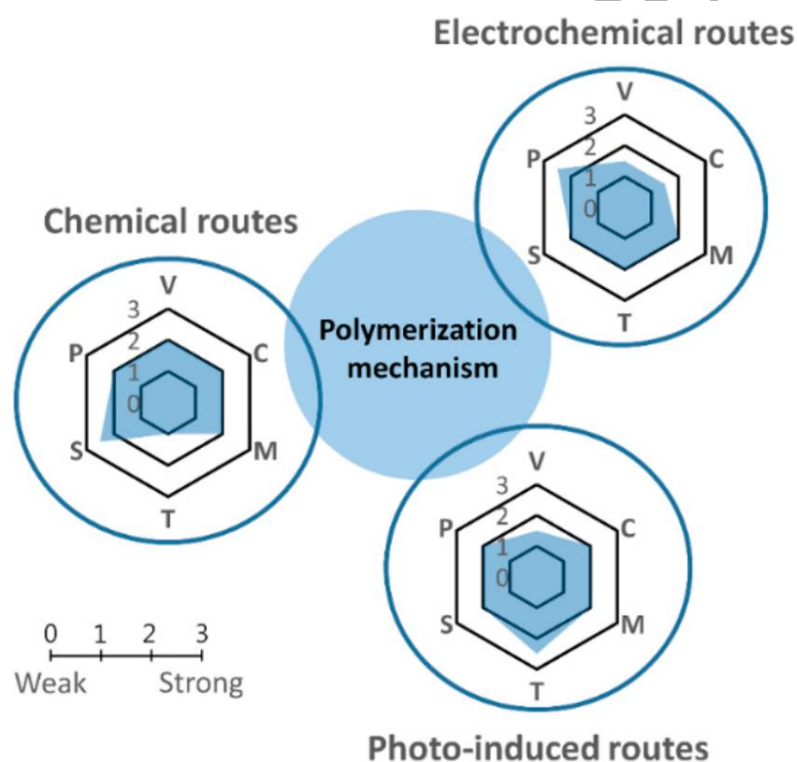
Figure 4. Schematic comparison of the main methods for CPs synthesis in terms of relative number of key variables in the synthesis process (V), cost effectiveness (C), morphology control (M), reaction time (T), scalability (S), and the product purity (P). Adapted from [28].

Non-homogeneous structure of thin CP layer on the Gr/CP interface negatively affects the overall conductivity of the composite material [12, 29]. According to the multi-core model proposed by Tanaka *et el.* [30], the structure of Gr-CP/electrolyte interfaces consists of three layers: *the bounded layer*, where CP and graphene sheets are interconnected by covalent, ionic

or electrostatic forces; *the interfacial region,* which interacts with the surface of the nanomaterials, and *the external loosely coupled layer* with enhanced mobility and conformational changes of the CP chain [24]. These structural features of multiple interfaces are illustrated in Figure 5. Variation of the interfacial layer structures during charge/discharge polarization must occur in many cases and plays a critical role in charge-storing performance as well as stability of Gr/CP composites and devices, since both double-layer capacitance and pseudocapacitance originate in the near-surface phenomena. As reported by Islam *et al.* [29], for example, the structure of Gr sheets uniformly covered with CP followed by subsequent stacking in a parallel manner can be denoted as series of parallel resistance-capacitor components. However, such a structure leads to additional dielectric loss [29] and should be replaced with more effective architecture for achieving better performance.
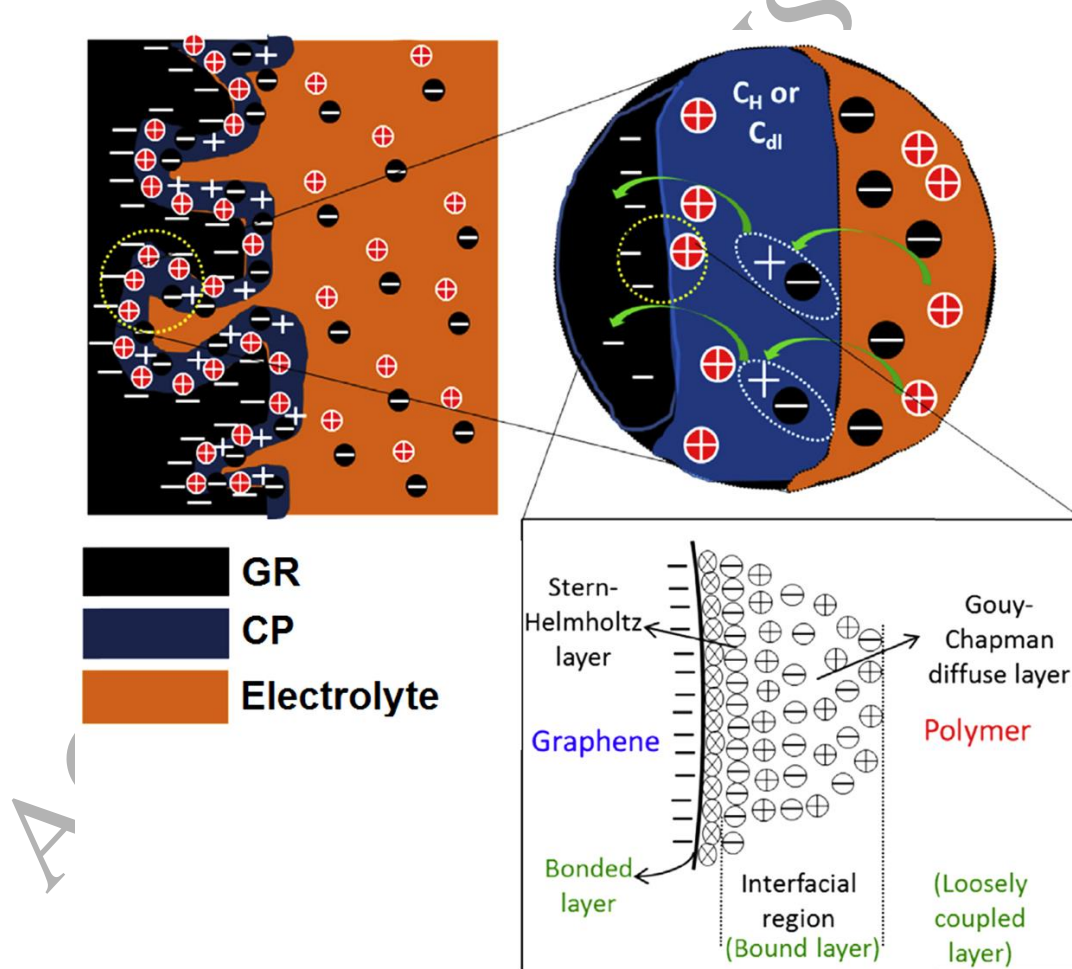

Figure 5. Schematic illustration of the interfaces between the graphene-polymer composite and electrolyte reproduced from [24].

High specific capacitance values of 520 F g^{-1} and 253 F g^{-1} were achieved, when PAni nanowires or PPy nanotubes, respectively, were incorporated in rGO [31] or GO sheets [32] acting as spacers. These values can be duplicated using additional coverage of Gr with CP nanoparticles [33]. Incorporation of hollow PPy nanoparticles leads to a specific capacitance of about 500 F g^{-1} with excellent stability at 5 A g^{-1} after 10000 charge-discharge cycles [34]. Freestanding sandwich-structured rGO/PAni/rGO nanocomposite paper reported by Xiao *et al*. has reached a specific capacitance of 580 F g^{-1} with a good perspective for scalable fabrication, outperforming many analogous composites [35].

Fabrication of multilayered composites consisting of the Gr/CP bilayers is another strategy to create regular structures with attractive properties. For example, multilayer films of PAni and GO were deposited on indium tin oxide (ITO) surface exhibiting specific capacitance of 429 F g^{-1} [36]. However, it should be noted that increasing the number of layers could lead to the decrease of specific capacitance [24]. Figure 6 highlights some intriguing fabrication methods and structures of CP-Gr composites obtained by different architectures.
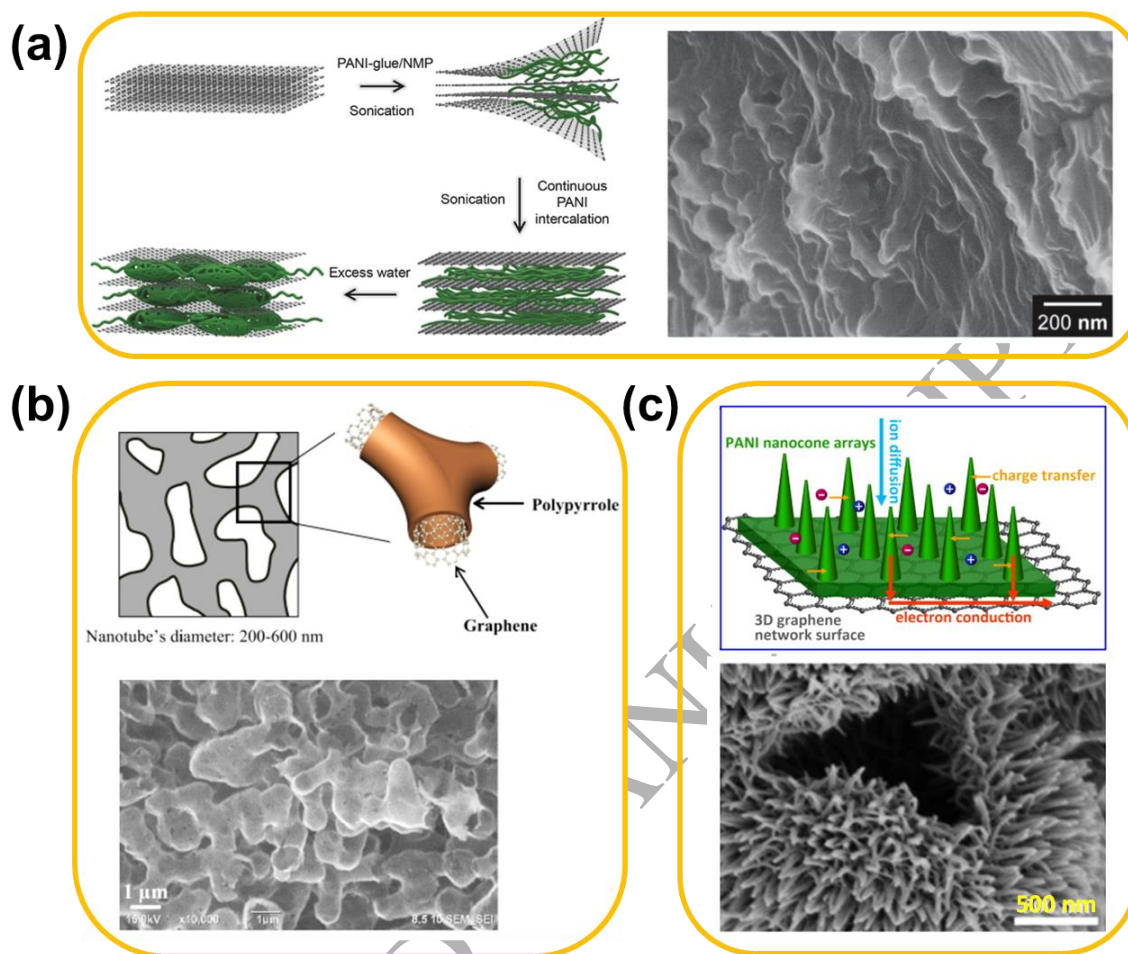
Figure 6. Schematic representation and SEM images of different Gr/CP nanocomposite architectures synthesized by: (a) incorporation of CP between rGO sheets [37], (b) synthesis of uniform CP layer on the 3D Gr surface [38] and (c) fabrication of 3D CP nanofeatures on Gr surface [39, 40].

Highly developed graphene surface is a common platform to fabricate Gr/CP composites. However, randomized 3D geometry may produce a tortuous path for diffusion of ions in the nanocomposite structure and consequently cause irreversible capacitance loss. This means that the pore size should match optimal relationship between the maximum surface area and the sizes of ions in the electrolyte [41]. Hierarchically ordered Gr/CP structures with continuous conductive skeleton display significantly higher specific capacitance compared to the intermittent designs. Wrapping of PAni nanofibers inside the rGO skeleton allows achievement of tight contact between rGO and CP, resulting in a high capacitance of 921 F g^{-1} [42]. Bicontinuous nanotubular graphene–PPy hybrids synthesized using a nanoporous Ni template to create a stable 3D morphology with subsequent etching of the metal part display

capacitance up to 509 F g^{-1} with excellent cycling stability [43], whereas bicontinuous Gr/PAni composite exhibits outstanding areal capacitance of over 1.7 F cm^{-2} [44]. Utilization of polymer particles as an alternative to the metal removable template looks promising taking into account charge-storing ability, but the operation stability of this type of nanocomposite still needs to be improved [44–46]. Employment of MnO_2 nanowires simultaneously acting as a template and oxidant for the rGO/PAni synthesis results in high capacitance of 956 F g^{-1} [47]. It should be noted that other materials with highly developed surface area, such as kitchen sponge [48], can also be used as a template for Gr/PAni synthesis with similar values of capacitance. Utilization of the 3D sponge-like ionic liquid-graphene assembly as a matrix for CP electropolymerization demonstrates capacitance up to 662 F g^{-1} with excellent cycling stability of about 93% at 10 A g^{-1} after 5000 consecutive cycles [49]. Fabrication of PAni-modified 3D graphene frameworks with rapid mixing of the oxidant and monomer solutions allows avoiding the CP film overgrowth and achieving extraordinarily high specific capacitance and energy density, ~1000 F g^{-1} and ~120 W h kg^{-1}, respectively [50], which is the highest energy density achieved so far for all Gr-based nanocomposites for pseudo-SCs [51]. These findings are in good relationship with results of the recent study of Gr/PAni layered composites with different morphology, where pore connectivity and accessibility to the electrolyte was shown as the dominant factor determining fast ion transport and kinetics of the pseudo *faradaic* redox process [52].

Employment of Gr surface as a conductive support to create nanostructured CP architectures is also a perspective strategy to fabricate freestanding flexible materials with outstanding charge-storing ability. rGO/PAni paper exhibits enhanced ion diffusion due to the shortened pathways of ion migration compared to the pristine PAni and high capacitance of 763 F g^{-1} [53] and 939 F g^{-1} for controllably grown PAni nanowires [40] or 751.3 F g^{-1} for PAni nanocones [39]. Similar performance was achieved when low temperature oxidation polymerization method was used on the 4-aminophenyl pre-crafted rGO [54] and further improved by utilization of the sulfonated triazine to initiate the growth of PAni nanorods [55]. Another nanocomposite of Gr nanomesh coated with PAni nanorods exhibits extraordinarily high-rate capability with 98% of capacitance retention when current density was increased from 1 A g^{-1} to 50 A g^{-1} [56]. It should be mentioned that Gr itself does not contribute significantly to the overall capacitance of this type of materials; instead, the Gr matrix mainly provides attractive mechanical and

electrical properties to fabricate the freestanding SC electrodes. Therefore, similar capacitance values can be achieved using alumina oxide [57] or stainless steel [58] substrates.

Recent achievements in the specific capacitance of Gr/CP nanocomposites described above indicate a limiting value of *ca*. 1000 F g^{-1}, which is close to the best results obtained at those SCs electrodes based on metal oxides and hydroxides [59, 60], confirming the competent capability of Gr/CP nanocomposites among mostly targeted materials for electrochemical energy-storing purposes.

3.2 Applications of Gr/CP nanocomposites in *flexible* supercapacitors

Materials based on Gr/CP nanocomposites are attractive candidates for high-performance *thin* and *flexible* microsystems for energy storage, which can be used as a lightweight power source for portable electronics, electronic papers, bendable displays, *etc*. [20, 61−63].

Utilization of PAni nanofibers wrapped with rGO sheets results in a volumetric capacitance of 25.6 F cm^{-3} at 0.12 A cm^{-3} with excellent cycling stability without structural failure and loss of performance in their bended state [42]. In another example, flexible all-solid-state SCs based on the GO/PAni composites were constructed [64]. Resulting wave-shaped bendable and stretchable SCs exhibited the maximum specific capacitance up to 1095 F g^{-1} at 1 A g^{-1} with an energy density of 24.3 W h kg^{-1} and a maximum power density of 28.1 kW kg^{-1} (Figure 7). The SCs have excellent retention of properties after mechanical treatment (Figure 7c).

Assembled flexible and all-solid-state supercapacitor employed rGO paper with incorporated PANI-PSS nanoparticles has a volumetric specific capacitance of 217 F cm^{-3} at 0.37 A cm^{-3} [65], which is significantly larger than the values obtained for CNTs/CP-based designs [66, 67] and close to the value obtained for the symmetrical SC based on the 3D foam of rGO/PAni nanowires [68]. Bendable micro-SC comprised of the electrodes fabricated by incorporation of PAni nanofibers between rGO sheets also offered remarkable volumetric capacitance of 436 F cm^{-3} at 10 mV s^{-1} [69].
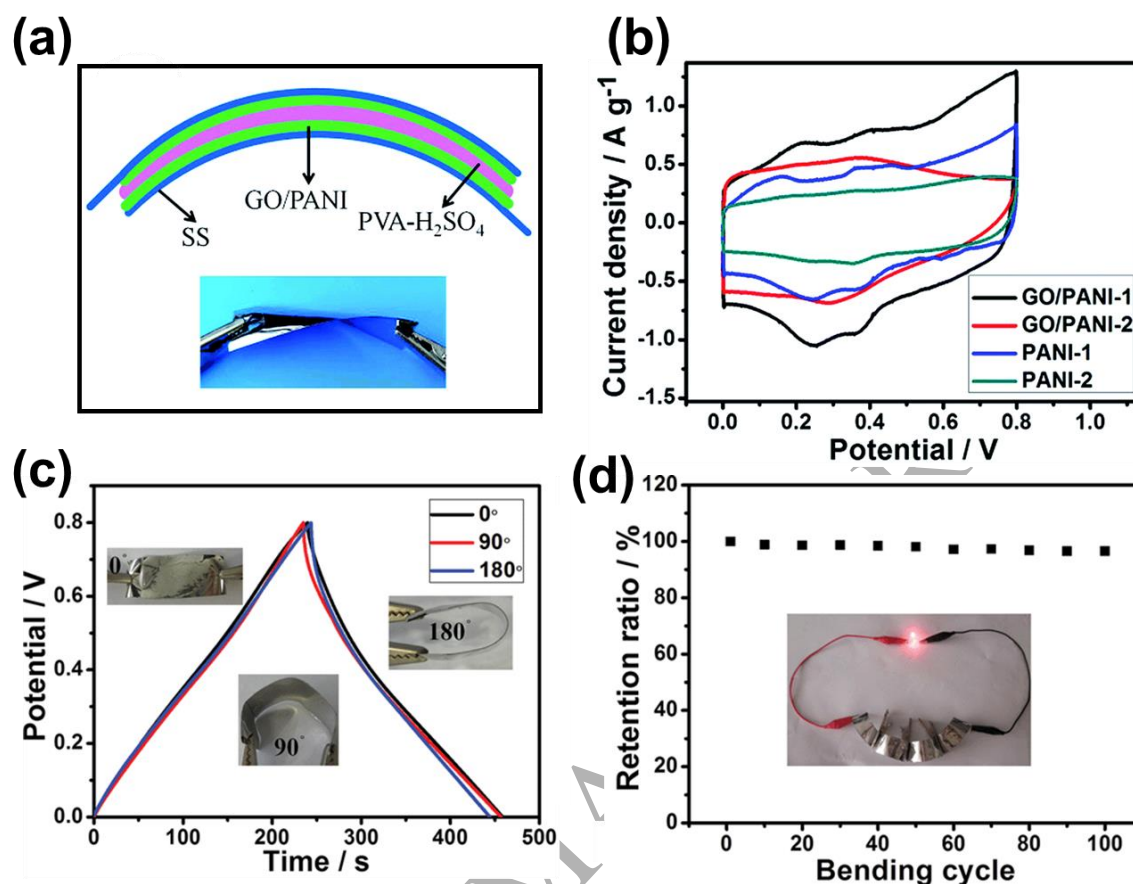
Figure 7. Example of graphene-conducting polymer composite based flexible and bendable SCs: (a) schematic representation of the structure and optical image, (b) comparison of cyclic voltammograms (CVs) of various materials obtained at 5 mV s^{-1}, (c) comparison of Galvanostatic charge–discharge curves (1 A g^{-1}) of GO/PANI based flexible supercapacitors obtained at various bending angles, and (d) evaluations on the bending cycle stability of GO/PANI based SCs. Insets in (c) are photographs of bended SCs with different angles, and inset in (d) is an LED illuminated by the device units connected in series. Adapted from Ref. [64].

Micro-SCs based on sandwich-like layered mesoporous Gr/CP nanosheets with uniform and densely packed structure can deliver a volumetric capacitance of 736 F cm^{-3} and 436 F cm^{-3} at 10 mV s^{-1}, respectively using water and poly(vinyl alcohol) in electrolyte [70]. This is the highest specific capacitance obtained at 2D thin-film micro-SCs, regardless of electrode materials [71].

In addition to fabrication of SCs, attractive pseudocapacitive properties of Gr/CP materials can also be used in other systems or devices, for example the devices for capacitive water deionization with an enhanced salt removal performance [72].

4. Perspective and challenges

Perspectives of the further development of Gr/CP nanomaterials for the capacitive energy storage purposes can be related to two main directions. The first one is concerned with the improvement of intrinsic properties of Gr/CP nanomaterials, *e.g.* utilization of new derivatives, copolymers or even more complex conjugated structures, *e.g.* proteins [73], introduction of additional components to the Gr/CP nanocomposites, development of novel architectures, methods of synthesis *etc*. Recent advances in this field rest on the use of additional carbon or metal nanomaterials to facilitate electron transfer process and improve capacitive performance [74,75].

The second direction is related to a variety of ways using complete Gr/CP-based electrodes in SCs. Combination of nanocomposite-based electrodes into asymmetric SCs, which display superior properties compared to the symmetric design [76], or to more complex battery-SC hybrids [77, 78], leads to significantly higher energy density and voltage compared to the conventional approach.

The appealing properties of Gr/CP nanocomposites can also be utilized in currently expanding field of dual-feature self-charging SC/power cell hybrids for mechanical- [79, 80], chemical- [81] or solar-to-electric energy conversion [82] coupled with electrochemical energy storage within a singular contrivance. Nanostructured Gr/CP surfaces, being a promising matrix for the entrapment of various bioelements (living cells [83], protein complexes [84], redox enzymes [85], *etc*.), offer further opportunities for the development of supercapacitive biofuel cells [86, 87] and photo-bioelectrochemical cells [88] (in other words, self-charging biosupercapacitors (BioSCs) and photo-BioSCs) with improved performance and prospects for miniaturization of devices.

Alternative application of Gr/CP materials is not limited to particular capacitive storage of electric charges but expanding to the broad field of energy storage. For instance, Gr/CP nanocomposites were successfully utilized in various types of organic batteries to demonstrate promising features [89].

In spite of the numerous advantages of many Gr/CP composites, complicated procedures of synthesis and limited ability for mass production remain a bottleneck for their broad applications. More recently, some cost-effective and template-free methods for the scale-up or mass fabrication of 3D Gr frameworks under mild conditions have been proposed [90, 91]. A number of composites, fabricated by further modification of the structures with CPs, have

shown promising performances. These latest advances may open new ways to use Gr/CP nanostructured composite materials for the development of inexpensive and scalable capacitive charge-storing devices.

Acknowledgements

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• Paper of special interest

•• Paper of outstanding interest

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TOC graphic abstract
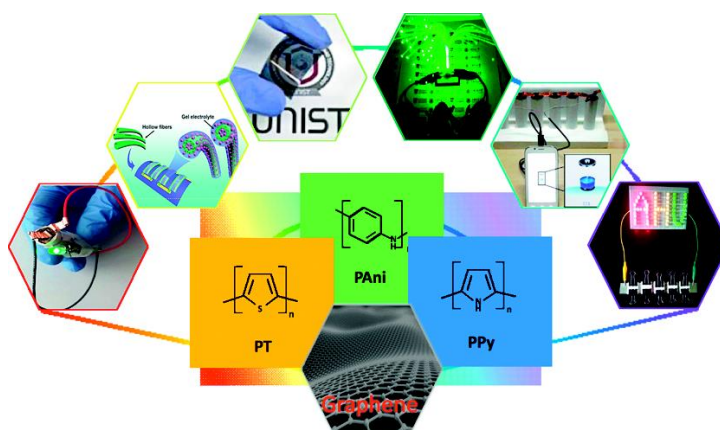
Synopsis: This minreview presents recent advances and our comments on the research subject of graphene-conducting polymer nanocomposite based supercapacitors. We emphasize material design, controlled assembly and nanoscale engineering of relevant composites, and their applications in flexible and bendable supercapacitors.