

Review

# Cutting-Edge Green Polymer/Nanocarbon Nanocomposite for Supercapacitor—State-of-the-Art

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**Abstract:** Supercapacitors have attained a special stance among energy storage devices such as capacitors, batteries, fuel cell, and so forth. In this state-of-the-art overview on green synthesis approaches and green materials for supercapacitors, the cutting-edge green polymer/nanocarbon nanocomposite systems were explored by focusing on the design and related essential features. In this regard, various polymers were reconnoitered including conjugated polymers, thermosetting matrices, and green-cellulose-based matrices. Nanocarbon nanomaterials have also expanded research thoughtfulness for green-technology-based energy storage devices. Consequently, green polymer/nanocarbon nanocomposites have publicized fine electron conduction pathways to promote the charge storage, specific capacitance, energy density, and other essential features of supercapacitors. Future research directions must focus on the design of novel high performance green nanocomposites for energy storage applications.

**Keywords:** green; polymer; nanocarbon; nanocomposite; specific capacitance; supercapacitor



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## 1. Introduction

Currently, dynamically researching and developing green materials is positively altering future advanced technologies for industries [1]. In conventional industries, the abundant annual production of wastes, toxins, and pollutants frequently causes serious environmental problems. In this regard, green and efficient technologies have been developed for the production of sustainable materials. In the energy storage sector, green materials have been focused on to form supercapacitor electrodes [2]. Green materials with large surface areas and hierarchical porosity have been found most effective in supercapacitor application. Green materials have a low cost, light weight, fine capacitance, eco-friendliness, sustainability, and less corrosion occurrences. In this regard, green nanocomposites have been developed using nanocarbon or inorganic nanoparticles. Incidentally, green synthesis approaches have also been applied to form nanocomposites, such as conducting polymer-based nanomaterials, to minimize environmental pollution [3]. Green nanomaterials synthesized by green methods in a controlled manner enhance the desired supercapacitive performance.

Supercapacitors have been categorized as significant energy storage devices [4]. Generally speaking, supercapacitance devices have high charge storage capabilities, rapid charge–discharge processes, long-standing energy storage, and durability features. Polymers and polymeric nanocomposites have been espoused as successful energy storage

materials [5]. In this regard, various polymeric systems have been explored [6,7]. Conducting polymers have been successfully applied for energy storage applications [8]. Moreover, carbon nanoparticle insertion in a polymeric matrix may influence the essential physical properties of the nanocomposite [9]. Thermosets or thermosetting polymers such as epoxies, phenolic, and so forth have also been considered for supercapacitor electrodes [10,11]. These polymers have been filled with carbonaceous nanoparticles to form an advanced nanocomposite [12]. Recent trends in energy storage devices have inclined towards the use of green polymer/nanocarbon nanocomposite in supercapacitors [13]. The addition of nanocarbon nanoparticles such as graphene, graphene oxide, reduced graphene oxide, and so forth in polymeric matrices and have considerably supported the overall morphological, electrical, and mechanical characteristics of nanomaterials [14].

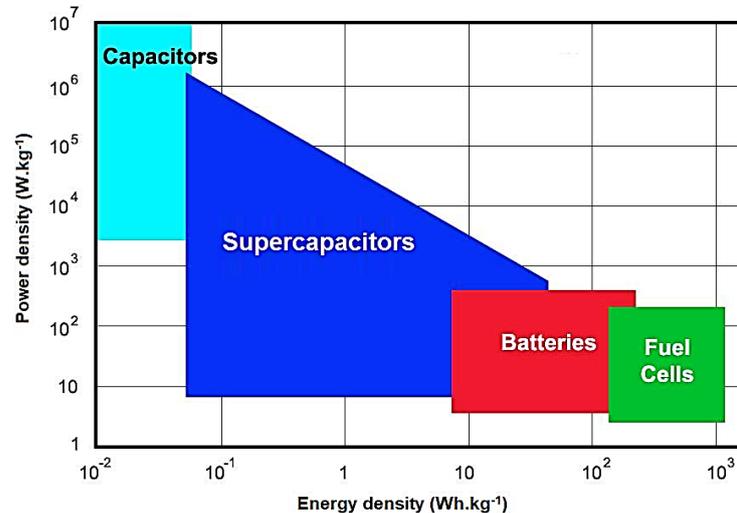
To convert supercapacitor technology to green energy storage technology, two effective approaches have been used, i.e., (i) the use of the green synthesis approach and (ii) the use of green polymers and modified nanofillers to form electrodes. In the first approach, various green methods have been seen to synthesize eco-friendly nanocomposites for supercapacitance application [15–17]. Consequently, the use of green synthesis approaches has avoided the use of any toxic or noxious chemicals during the fabrication of a supercapacitor electrode [18]. Green synthesis approaches have been used to form conducting polymers, epoxies, and nanocarbon nanoparticles, thereby avoiding the use of toxic organic solvents. In the second approach, green polymers and modified nanocarbons have been used to form green nanomaterials for the construction of a supercapacitor electrode. For example, a very famous green polymer for supercapacitor electrodes is cellulose [19]. Plus, the employment of nanocarbon with cellulose or nanocellulose has generated an advanced cellulose/nanocarbon nanocomposite for supercapacitors. However, the complete replacement of supercapacitor electrodes with green polymeric nanocomposite electrodes possesses the challenges of design limitation, sufficiently high conductivity, and a supercapacitance comparable to conjugated polymer-based supercapacitor electrodes.

This review proposes progress in the arena of green polymer/nanocarbon nanocomposite towards energy storage devices. Here, conducting polymers and thermosets have been found effective in the field of supercapacitors. Green polymer/nanocarbon nanocomposites have shown superior electron conduction and charge storage features. The inclusion of nanocarbon in conducting polymers thermosets, and green polymers like cellulose, using the green route has opened innovative doors to green supercapacitor technology. The present article highlights the significance of using green synthesis methods and green polymers and the main glitches in this direction.

## 2. Polymer-Based Materials for Energy Storage

Energy storage devices include wide-ranging devices including capacitors, batteries, and fuel cells [20]. Amongst these expedients, supercapacitors have been used as competent energy storage devices [21]. Supercapacitors exposed performance predilections over the conformist storage devices [22]. The importance of supercapacitor devices among the energy devices is depicted Figure 1 [23]. According to the research analysis, the supercapacitor recital can be categorized somewhere between capacitors and batteries/fuel cells [24]. Supercapacitor devices usually have outstanding capacitance, power density, and energy density properties [25,26]. Amid polymeric materials, conjugated polymers possess high electron transfer and specific capacitance characteristics [27,28]. The most frequently engaged conjugated polymers comprise polyaniline, polypyrrole, polythiophene, and poly(3,4-ethylenedioxythiophene), and derivative polymers [29,30]. The conducting polymer-derived supercapacitors have high firmness, charge–discharge competence, and recyclability properties. The supercapacitor electrodes reported on polyaniline and polypyrrole revealed a high specific capacitance of  $360 \text{ Fg}^{-1}$  and  $190 \text{ Fg}^{-1}$ , respectively [31]. The inclusion of nanofillers has been found to develop the conducting network in these polymers to promote electron and charge transport [32]. Non-conjugated polymers such as thermosets have also been applied to develop supercapacitor electrodes. For example,

the epoxy resin/polyindole-based nanocomposite has been designed for conducting and charge-transport performance [33]. Hence, polymeric materials and nanomaterials have been successfully developed and characterized for supercapacitor application.



**Figure 1.** Ragone chart of power density vs. energy density for various energy devices [23]. Reproduced with permission from Elsevier.

### 3. Green Nanocomposite for Energy Storage

#### 3.1. Green Nanocomposite Derived from Conducting Polymer/Nanocarbon for Energy Storage

##### 3.1.1. Overview of Conjugated Polymer-Based Supercapacitive Nanomaterials

Energy storage devices have been used in the electronics and automobiles fields [34–36]. Moreover, supercapacitors have been applied in robotics and self-directed devices [37]. Supercapacitors have been deliberated as talented energy storage devices [38,39]. Supercapacitors have revealed recompenses over energy storage batteries [40–42]. Supercapacitors are inexpensive and have a high power generation [43]. Supercapacitors possess high resilience, energy density, and power density, compared with conformist capacitors [44]. High performance energy storage devices have shown the capability of charge storage [45,46]. Consequently, supercapacitance technology is a revolutionary way to create next-generation energy storage devices [47,48]. Incidentally, numerous energy storage devices have been designed and considered. Usually, a supercapacitor consists of electrodes (parted by dielectric substance). Supercapacitor electrodes have been fabricated, aiming at high surface area nanomaterials to enhance the electron transportation and charge mobility [49–51]. Consequently, polymer-derived materials have been used to design energy storage devices [52,53]. The frequently used and successful conjugated polymers for supercapacitor electrodes include polyaniline, polypyrrole, polythiophene, and so forth. These polymers possess high electron transportation and charge storage capabilities [54]. The conjugated polymers publicized a high constancy, charge–discharge, power density, recyclability, and other competent energy storage features [55]. Nanocomposites have been developed using the conjugated polymers and nanoparticles to support the electron transference trails assisting the charge transportation and capacitance physiognomies [56,57]. Inclusion of nanoparticles promoted the interactions with the polymers leading to high electron conductivity and charge mobilization [58]. Among conjugated polymers, polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT) have shown large pseudo capacitance properties. Moreover, these polymers have a high permanence, charge–discharge capability, reversibility, and recyclability for the supercapacitor. Conjugated polymers have been reinforced with graphene, carbon nanotubes, other nanocarbons, and inorganic nanoparticles [59]. Graphene has been commonly used in supercapacitor electrodes [60,61]. Using conjugated polymer/graphene nanocomposite, the supercapacitor electrodes have been fabricated [62]. The conducting



### 3.1.2. Use of Green Approaches to Form Conducting Polymer Nanocomposite for Supercapacitors

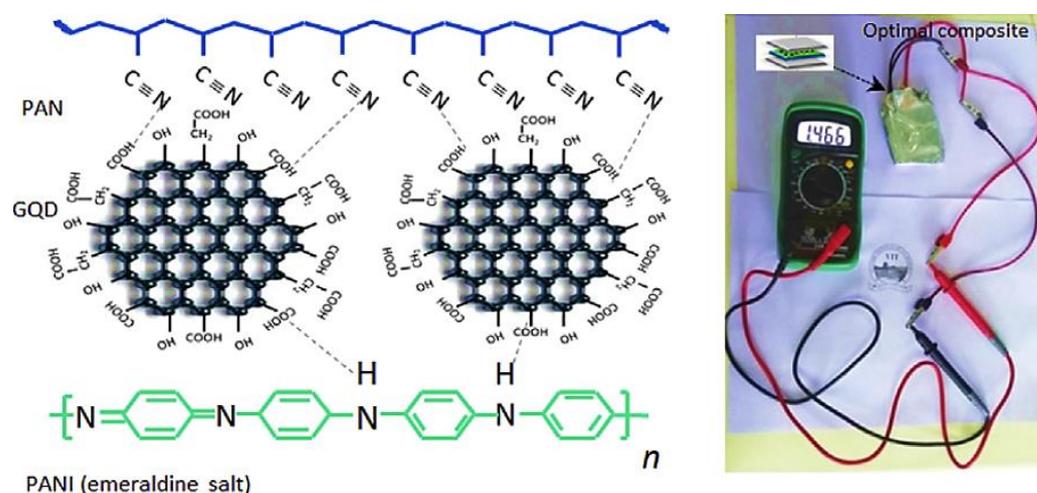
Polyaniline and other conducting polymers have a superior conductivity, mechanical strength, and performance as a supercapacitor electrode material [68]. The enhanced stability and high pseudocapacitance of polyaniline- and nanocarbon-based nanocomposites have been observed [69]. However, the preparation of these nanocomposites may require the use of environmentally toxic organic solvents, which may be detrimental to the environment. Therefore, the research has focused on the use of green technologies to form green conducting polymer nanocomposites.

Due to increasing environmental concerns, it is always preferred to look for alternate synthesis practices, where conducting polymers (polyaniline, polypyrrole, polythiophene, etc.) may hold all intrinsic valuable characteristic properties along with inexpensiveness and being less environmentally hazardous. The best way is to use eco-friendly solvents and minimize the use of toxic chemicals. There is always a need to develop facile and efficient green methods without employing toxic organic solvents. To overcome these environmental concerns, green solvents such as supercritical carbon dioxide and ionic liquids have been employed [70]. The use of green solvents not only solves environmental issues but also offers fine processability, low volatility, fine ionic conduction, and high thermal stability to the resulting green-processed nanocomposites. Nguyen et al. [71] used two green solvents, i.e., water and 1-butyl-3-methylimidazolium tetrafluoroborate for the fabrication of green-processed polyaniline/carbon nanotube nanocomposites. The green in situ interfacial polymerization method was used. This approach minimizes the use of toxic organic solvents. The polyaniline/carbon nanotube electrodes were characterized for electrochemical properties. Zhao et al. [72] employed eco-friendly tannic acid in the green synthesis of graphene oxide and nanocomposite with polyaniline. The green synthesis method produced offered a high surface area of graphene oxide for the homogeneous distribution of polyaniline. The high surface area of nanocarbon has been found to be important to develop a well-interacted nanocomposite with polyaniline. The functionalization of nanocarbon is also very important to develop interactions with the polymer. Graphene oxide is itself a functional form of graphene. The conversion of graphene to modified graphene oxide offers several functional groups for association with polyaniline and the subsequent charge and electron transportation. The introduction of functional groups may also produce defects on the surface of nanocarbons, which may further enhance the surface area of nanocarbons. The green-processed polyaniline/graphene oxide nanocomposite was used to prepare supercapacitor electrodes. The green-processed supercapacitor electrodes possess a well-compatible nanostructure to yield a high energy density and power density of  $1.68 \text{ Whkg}^{-1}$  and  $115 \text{ Wkg}^{-1}$ , respectively. Rahman et al. [73] adopted a simple and green synthesis route for the formation of a polyaniline-based supercapacitor electrode. The green chemical oxidative synthesis of the nanocomposite employed water as a solvent. In the green method, the synthesis was reduced without using toxic chemicals along with a fine dispersibility. The resulting supercapacitor electrode had a high conductivity up to  $10 \text{ Scm}^{-1}$  and a high specific capacitance in the range of  $528\text{--}832.5 \text{ Fg}^{-1}$ . The capacitance retention was also high at 95.3% after 1000 charge–discharge cycles. The green-processed nanocomposites have been suggested to form an inter-linked matrix-nanofiller network structure enhancing the electron transport, charge mobility, and supercapacitance properties.

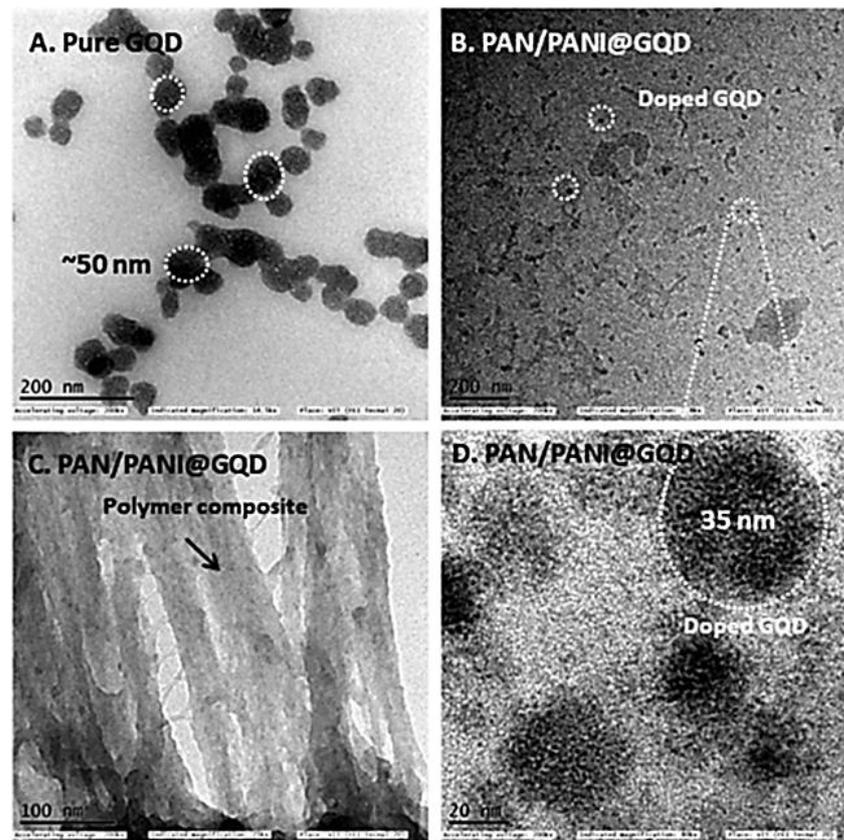
Simotwo and co-workers [74] fabricated a polyaniline/carbon nanotube-based electrode for supercapacitor application. The polyaniline/carbon nanotube-derived electrode possessed formability deprived of expending any binding material [75]. The electrode had PANI in a 93 wt.% and a carbon nanotube in a 12 wt.% configuration. The carbon nanotube that is usually reinforced in the conducting polymers is acid functionalized to create defects, improve the surface area, and form hydroxyl/acid functional groups on the nanotube surface. The generation of functional groups may form van der Waals and electrostatic interactions with the polyaniline. The well-interacted structure in turn promotes the charge/electron transport. The electrode owns porous interconnecting three dimensional

nanofibrous network structure. The three dimensional interlocking nanostructure has capability of fast electron and ionic conduction through the nanocomposite system. The neat PANI had specific capacitance of  $308 \text{ Fg}^{-1}$ , whereas the amalgamated nanomaterial had high specific capacitance of  $385 \text{ Fg}^{-1}$ . Song and co-researchers [76] developed a sulfonated polyaniline/graphene-derived nanocomposite electrode. The supercapacitor electrode had a reasonably high specific capacitance of  $\sim 262 \text{ Fg}^{-1}$ . The 87% capacitance was attained with the supercapacitor at 10,000 charge/discharge cycles.

Green nanocomposite technologies have been continuously explored for supercapacitor applications [77–79]. Among the green approaches, Sarno et al. [80] designed Ag nanoparticle functionalized reduced graphene oxide to fabricate a green nanocomposite. The one-step green synthesis method was used to prepare the nanocomposite [81–83]. The eco nanomaterial was then used to make the supercapacitor electrode. The electrode had a consistent dispersal of the nanoparticles to support the supercapacitive properties. The supercapacitor revealed a fairly high specific capacitance of  $1850 \text{ Fg}^{-1}$  and electrical conductivity of  $1.3 \times 10^7 \text{ Sm}^{-1}$ . Nayak et al. [84] prepared the tungsten oxide-coated graphene using a facile green solvothermal method. The nanocomposite had a specific capacitance of  $465 \text{ Fg}^{-1}$  and capacitance retention of 97.7%. Arthisree et al. [85] developed a supercapacitor electrode based on the polyaniline, polyacrylonitrile, and green graphene quantum dot. The green synthesis method was used to form the graphene quantum dot and also the resulting nanocomposite to minimize environmental pollution. The green nanocomposite based on polyaniline/polyacrylonitrile/graphene quantum dot had an electrical conductivity of  $1.09 \times 10^{-7}$  to  $2.362 \times 10^{-6} \text{ Sm}^{-1}$ . The capacitance of the green nanomaterial was measured as  $105\text{--}589 \text{ Fg}^{-1} \text{ cm}^{-2}$  (Figure 3). The surface area of the nanocomposite electrode according to the Brunauer–Emmett–Teller (BET) method was found to be high with  $\sim 910 \text{ m}^2/\text{g}$ . The green nanoparticles synthesized revealed a surface area of  $\sim 220 \text{ m}^2/\text{g}$ . Their pore size distribution by the Barrett–Joyner–Halenda (BJH) method was found to be centered at  $\sim 4.5\text{--}38.8 \text{ nm}$ . The microporous volume was  $\sim 0.009 \text{ cm}^3/\text{g}$ . The surface area and pore size distribution showed finely prepared nanoparticles and nanocomposites using the green technique. Figure 4A shows TEM micrographs of the graphene quantum dot in the range of  $\sim 45\text{--}50 \text{ nm}$ . Figure 4B–D portrays TEM micrographs of 1.5 wt.% nanocomposite with finely dispersed nanoparticles in the polymeric matrix. At a higher loading level, the dot-like nanostructures of  $\sim 25\text{--}50 \text{ nm}$  were observed. The morphological analysis exposed a fine compatibility between the polymers and the quantum dot. The good nanoparticle dispersal and morphology positively influenced the electron and charge transport properties.

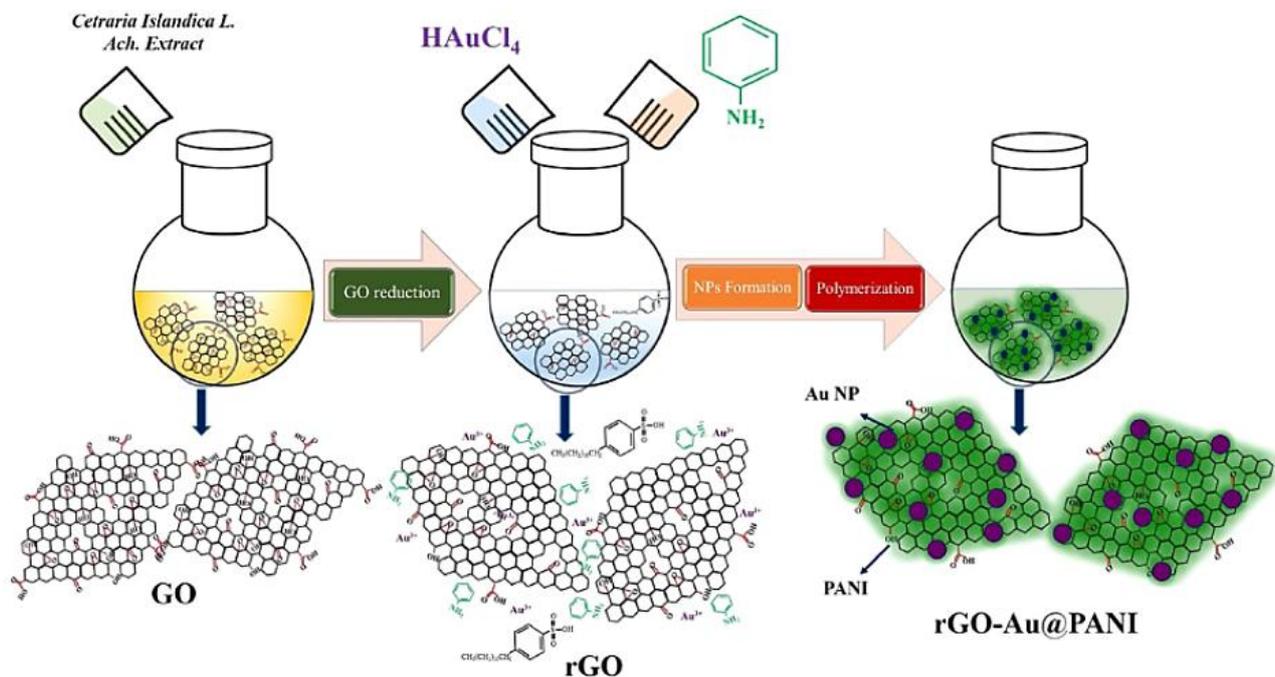


**Figure 3.** A green nanocomposite based on polyaniline (PANI), polyacrylonitrile (PAN), and a green graphene quantum dot (GQD) [85]. Reproduced with permission from Elsevier.

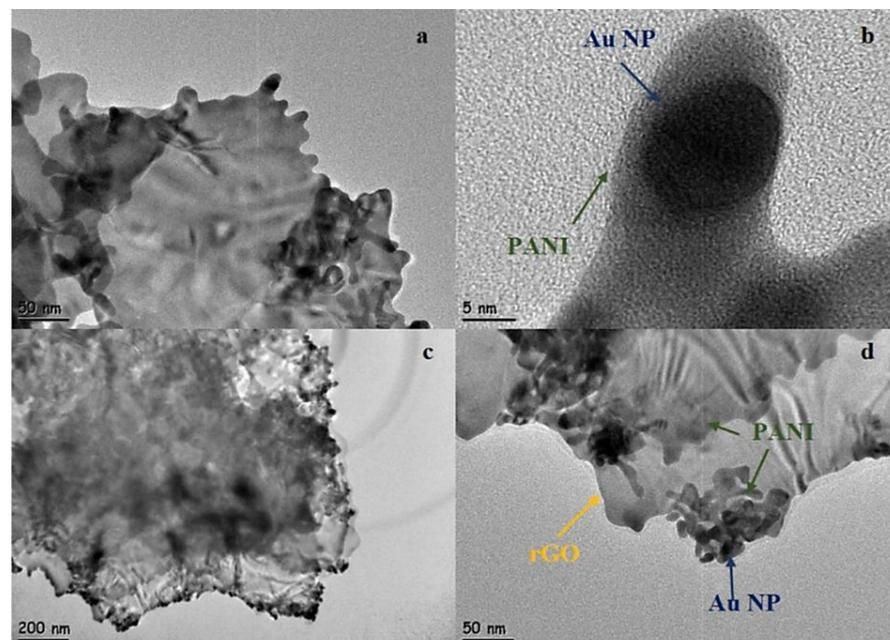


**Figure 4.** TEM images of (A) Pure GQD; (B–D) PAN/PANI@G –1.5 wt.% nanocomposite at different magnifications [85]. PAN/PANI@G = polyaniline/polyaniline/graphene quantum dot; GQD = graphene quantum dot. Reproduced with permission from Elsevier.

Çıplak et al. [86] produced a polyaniline and ternary-reduced graphene oxide-gold nanoparticle-based green nanocomposite. Graphene oxide and its derivatives were prepared using a green solvent, i.e., water. Furthermore, the polyaniline/graphene nanocomposites were prepared using a green strategy to minimize the use of environmentally noxious chemicals. Thus, a green approach was applied to prepare the reduced graphene oxide using a facile single-step method (Figure 5). Gold nanoparticles were consistently coated over the reduced graphene oxide surface. The green nanocomposite was prepared using the in situ polymerization of aniline monomer and gold-coated reduced graphene oxide nanoparticles. For the green-nanocomposite-based supercapacitor electrode, the specific capacitance of  $212.8 \text{ Fg}^{-1}$  was obtained. Figure 6a–d shows high-resolution transmission electron microscopy (HR-TEM) images of the reduced graphene oxide-gold nanoparticle@polyaniline (rGO-Au@PANI) nanocomposite. Gold nanoparticles of  $\sim 5\text{--}20 \text{ nm}$  were observed. The high surface area of the reduced graphene nanosheet and the gold nanoparticles developed fine interactions with the aniline monomers prior to polymerization. This resulted in the formation of a finely dispersible nanocomposite. The fine dispersion and morphology in turn affected the electrical conductivity and charge transport properties.



**Figure 5.** Schematic of green rGO-Au@PANI nanocomposite fabrication [86]. Reproduced with permission from Elsevier. GO = graphene oxide; rGO = reduced graphene oxide; rGO-Au@PANI = reduced graphene oxide-gold nanoparticle@polyaniline. Reproduced with permission from Elsevier.



**Figure 6.** (a–d) HRTEM images of rGO-Au@PANI nanocomposite scanned at various resolutions [86]. rGO-Au@PANI = reduced graphene oxide-gold nanoparticle@polyaniline. Reproduced with permission from Elsevier.

Similar to polyaniline, polypyrrole nanocomposites have also been prepared by green synthesis methods. Liu et al. [87] intended the PPy/graphene nanocomposite electrode for the supercapacitor. Figure 7 portrays the formation of the PPy/graphene nanocomposite through the green route and avoiding the use of toxic chemicals. To obtain the graphene and graphene oxide, peroxidation [88] and Hummer's method were adopted [89]. The electrode had a high conductivity, specific capacitance, and power density of  $1980 \text{ Sm}^{-1}$ ,

650  $\text{Fg}^{-1}$ , and 778.1  $\text{Wkg}^{-1}$ , respectively. The specific capacitance was  $\sim 95\%$  retained (5000 cycles). Figure 8 signifies the high capacitance of the PPy/graphene nanocomposite, relative to neat graphene or PPy electrodes [90]. Zhang et al. [91] fabricated a polypyrrole, graphene, and carbon nanotube nanocomposite electrode. The nanocomposite electrode has a fairly high specific capacitance of 1510  $\text{Fg}^{-1}$  [92,93]. The  $\pi$ -conjugated structure of polymers and incorporated nanocarbon facilitated the charge and electron conveyance. The conjugated polymeric nanocomposite had a significantly improved performance, compared with the neat conducting polymers.

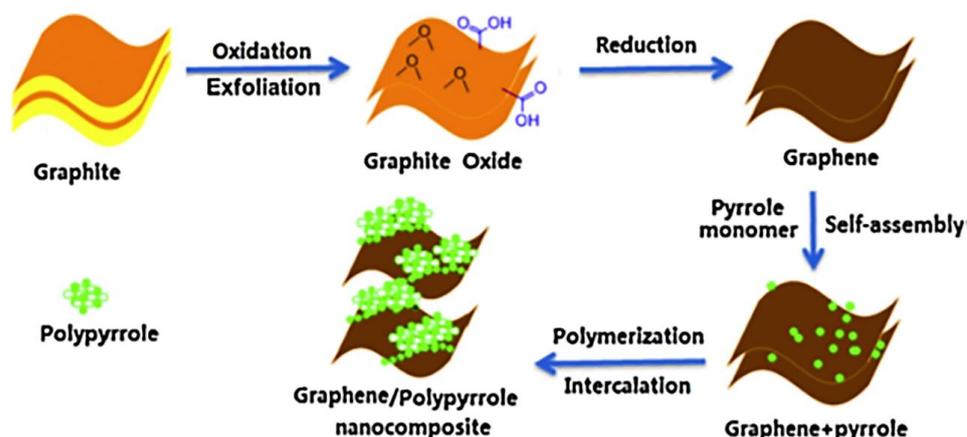


Figure 7. Synthesis of PPy/graphene nanocomposite [87]. PPy = polypyrrole. Reproduced with permission from Elsevier.

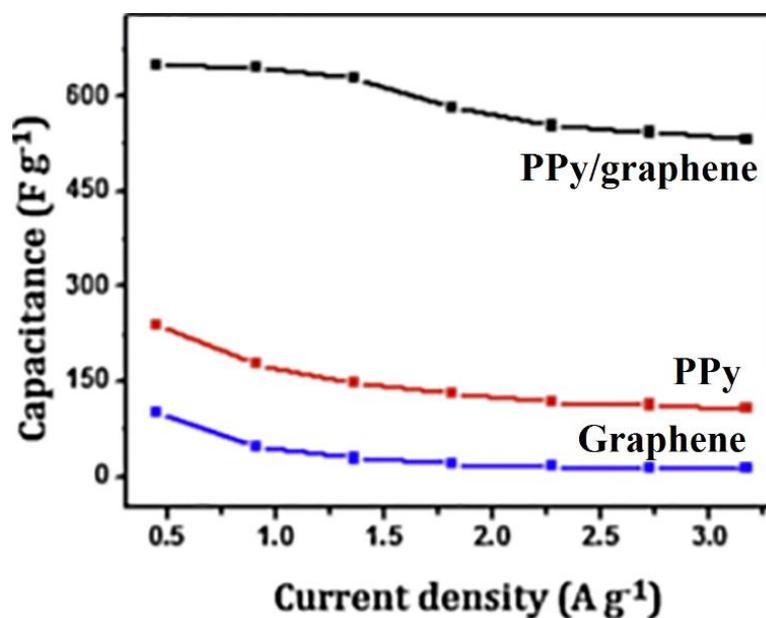


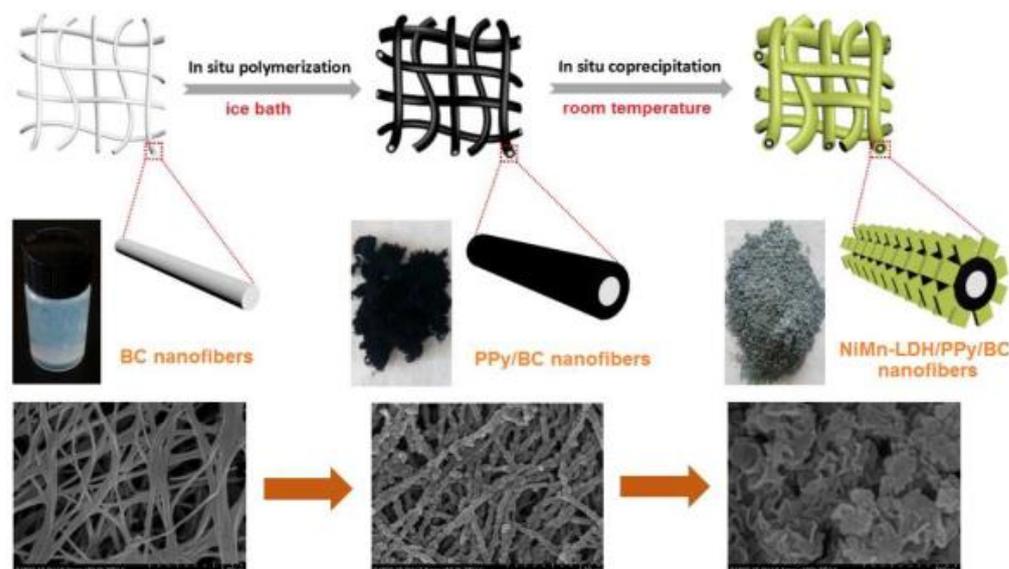
Figure 8. Specific capacitance curves of graphene, PPy, and PPy/graphene at varying current densities [87]. PPy = polypyrrole. Reproduced with permission from Elsevier.

### 3.2. Green Cellulose/Nanocarbon Nanocomposites for Energy Storage

Another imperative category of green-nanocomposite-based supercapacitor fabrication belongs to nanocellulose [94]. Nanocellulose-based green nanocomposites have shown potential for renewable materials for technical resolves. Graphene has been included in the green nanocomposites aiming at high performance applications [95]. The high-tech green nanocellulose/graphene nanocomposites have a fine dispersion, functionality, and interaction with polymers. Malho et al. [96] formed nanofibrillar nanocellulose and graphene-based nanocomposites. The addition of graphene (1.25 wt.%) in nanofibrillar

nanocellulose yielded a high strength and Young's modulus of 351 MPa and 16.9 GPa, respectively. Song et al. [97] fabricated microcrystalline cellulose nanofiber/graphene oxide nanocomposites. The green nanocomposite had a large surface area, leading to application in electrochemical energy storage devices [98]. The cellulose nanofibers had hydrogen bonding interactions between the nanostructures, leading to a better charge transport for energy storage purposes [99]. Table 2 depicts the specific capacitance of cellulose-based green nanocomposite electrodes for supercapacitors.

In supercapacitor application, cellulose or nanocellulose has been used as a precursor, substrate, and electrode binder [100]. Yuan et al. [101] applied nanocellulose, polypyrrole, and bimetallic hydroxide (NiMn-LDH)-based green material for a supercapacitor electrode. Figure 9 shows the successive layer deposition assembly to form the nanocomposite. The capacity of  $653.1 \text{ Cg}^{-1}$  at  $1 \text{ Ag}^{-1}$  was attained. SEM analysis revealed the fibrous morphology of nanocellulose, while the dense structure for the nanocomposite formed. The well-compatible nanocomposite morphology caused high electrical conductivity and charge transportation features. Song et al. [102] formed a cellulose-, polyaniline-, and graphene-based green nanocomposite for a supercapacitor. The areal capacitance and energy density of  $630 \text{ mFcm}^{-2}$  and  $2.8 \text{ mWh kg}^{-1}$ , respectively, were obtained. Yao et al. [103] developed a cellulose- and carbon-nanotube-based green nanomaterial. The green-nanocomposite-based supercapacitor electrode had an energy density and power density of  $8.3 \text{ Wh kg}^{-1}$  and  $47.3 \text{ Wkg}^{-1}$ , respectively. The fine capacitance, energy density, and power density of cellulose-based green nanocomposites depicted the formation of a well-intermixed nanostructure for the passage of charge and electrons through the system.



**Figure 9.** Schematic of layer-by-layer deposition of bacterial cellulose (BC)-supported nanocomposites and respective SEM micrographs [101]. PPy/BC = polypyrrole/bacterial cellulose; NiMn-LDH/PPy/BC = bimetallic hydroxide/polypyrrole/bacterial cellulose. Reproduced with permission from Elsevier.

**Table 2.** Electrochemical performance comparison of bacterial cellulose electrode/nanocarbon for a supercapacitor.

Material	Nanofiller	Specific Capacitance	Capacitance Retention (%)	Ref.
Bacterial cellulose	Graphene	1274.2 $\text{Fg}^{-1}$	96.4	[104]
Bacterial cellulose	Graphene oxide	160 $\text{Fg}^{-1}$	90.3	[105]
Bacterial cellulose	Carbon nanotube	50.5 $\text{Fg}^{-1}$	99.5	[106]
Bacterial cellulose	Polypyrrole	153 $\text{Fg}^{-1}$	93.0	[107]
Bacterial cellulose	Carbonization	216 $\text{Fg}^{-1}$	97.6	[108]
Bacterial cellulose	Carbonization	204.9 $\text{Fg}^{-1}$	90.0	[109]
Bacterial cellulose	Carbonization	422 $\text{Fg}^{-1}$	113	[110]
Bacterial cellulose	Polypyrrole; Carbon nanotube	228 $\text{Fg}^{-1}$	88.0	[103]
Bacterial cellulose	Polypyrrole; Graphene	1.93 $\text{Fcm}^{-2}$	56.3	[111]
Bacterial cellulose	Polypyrrole; Graphene	4.16 $\text{Fcm}^{-2}$	91.5	[112]
Bacterial cellulose	Polypyrrole; reduced graphene oxide	3.66 $\text{Fcm}^{-2}$	73.5	[113]
Bacterial cellulose	Reduced graphene oxide	2106–2544 $\text{mFcm}^{-2}$	100	[114]

### 3.3. Green Nanocomposite Derivative of Thermosetting Polymer/Nanocarbon for Energy Storage

Green nanocomposites have been designed using thermosetting resin and derived nanomaterials [115–117]. Amongst thermosets, epoxy resin has been commonly used to form the materials [118]. Epoxy nanocomposites have been designed using various nanoparticles in the matrix [119,120]. The dispersal state and interaction with epoxy resin may determine the final nanocomposite properties [121–123]. The nanofillers can be incorporated in thermosets in a modified or non-modified form [124,125]. Similar to the green synthesis attempts for conducting polymers in the previous sections, epoxy-based materials have also been prepared by green technologies to reduce environmental effluents. Zabihi and co-workers [126] industrialized the epoxy- and nano-polythiophene-derived nanocomposite by a green synthesis approach without using any organic solvent. The electrical conductivity behavior of the nanocomposite is given in Figure 10. The 1–20% nanoparticle-loading considerably enhanced the electrical conductivity. Wang et al. [127] used a green in situ technique (no organic solvent involved) for the formation of an epoxy/graphene oxide nanocomposite. The green epoxy/graphene nanocomposite revealed a fine wear resistance performance. Seok et al. [128] designed a green nanocomposite from epoxy-coated soybean oil and cellulose nanocrystal. Green epoxy/soybean oil/cellulose nanocrystals have revealed high mechanical features. Tang et al. [129] designed a green epoxy/graphene oxide nanocomposite by employing the glycidylamine epoxy resin. The eco-friendly nanocomposite was prepared without employing any toxic organic solvent. The enhanced dispersion of graphene oxide in the green nanocomposite led to extraordinarily enhanced mechanical characteristics. A phenolic resin nanocomposite with carbon nanoparticles has been

developed using the green route [130]. Figure 11 displays the synthesis protocol for the nanocomposite. In the phenolic-resin derived nanomaterial-based supercapacitor, a power density of up to  $14.5 \text{ kW kg}^{-1}$  was attained. Ma and co-researchers [131] designed a phenolic resin/polyvinylpyrrolidone and a carbide-based nanofiber through electrospinning and avoided toxic chemicals through green synthesis technology. Due to the formation of an interconnecting network nanostructure, electron and charge transportations were facilitated. Figure 12 demonstrates the specific capacitance of, i.e.,  $102\text{--}128 \text{ Fg}^{-1}$  [132]. The nanomaterial had a high surface area of  $416 \text{ m}^2\text{g}^{-1}$ . The specific capacitance was found at  $143\text{--}171 \text{ Fg}^{-1}$ .

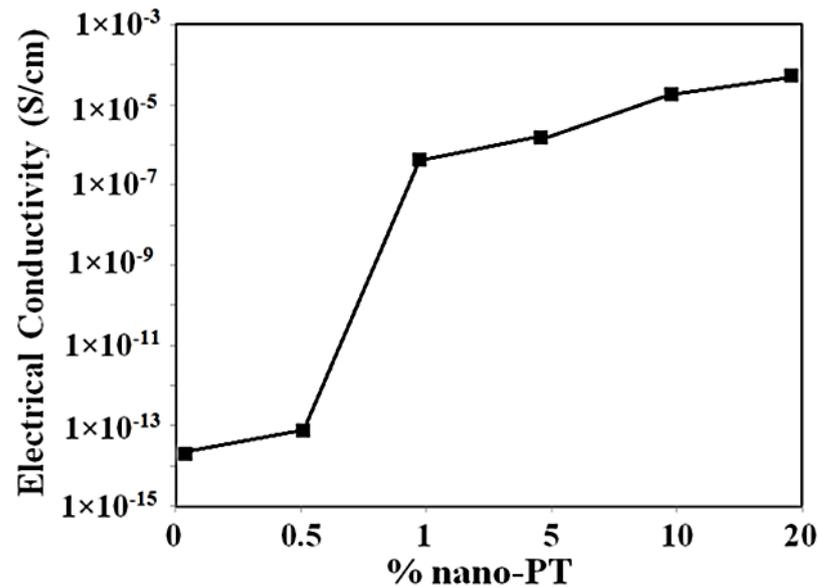
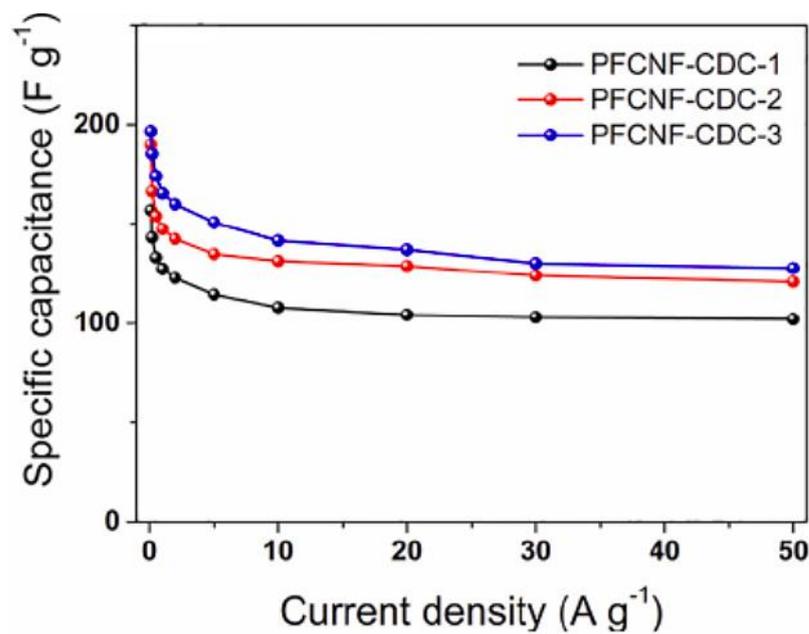


Figure 10. Electrical conductivity of epoxy/nano-polythiophene vs. % nano-polythiophene nanoparticle [126]. Reproduced with permission from Elsevier.



Figure 11. Schematic of phenolic-based nanocomposite synthesis [130]. Reproduced with permission from Elsevier.



**Figure 12.** Specific capacitances of phenolic nanocomposite at different current densities [131]. PFCNF-CDC = phenolic resin/polyvinylpyrrolidone blend carbon nanofiber and carbide-derived carbon. Reproduced with permission from Elsevier.

#### 4. Opportunities, Challenges, and Summary

Supercapacitors have gained an important stance among energy storage devices [133]. Newfangled designs, processing, and feature alterations have been found desirable for advanced supercapacitor electrodes. The supercapacitors possess sturdiness, high capacitance, and power density features. Various polymeric materials and nanoparticles have been derived to form nanocomposites for energy storage application (Figure 13). Conducting polymers and thermosets have been used to form high-performance nanocomposites. The progressive energy storage devices need to be designed using a polymer/nanocarbon nanocomposite. Nanoparticles such as carbon nanotube, graphene, graphene oxide, and so forth have been applied in conjugated polymers and thermosets towards the supercapacitors. Conjugated polymers such as PANI, PPy, PEDOT, and so forth have been frequently applied. Among thermosets, epoxy resins and phenolics have been used. Technology has successfully turned towards the use of green synthesis methods to fabricate cutting-edge nanocomposite systems for supercapacitors. Constancy, capacitance, power density, charge/discharge, and other supercapacitive parameters have been found to be enriched by using green nanocomposites. However, the design of green-nanocomposite-based supercapacitors has been found to be challenging. The electrical conductivity and charge storage capabilities of green nanocomposites have been attributed to the conducting network generation for the passage of electrons and charges through the system. The synergistic effects in the polymer and nanoparticles may further enhance the supercapacitive features.



**Figure 13.** Green polymer/nanocarbon for supercapacitors.

A safe solution to the use of energy storage devices is to convert the processing technologies towards green approaches. In this regard, the use of environmentally friendly solvents and environmentally friendly materials such as cellulose have been preferred. The use of non-toxic solvents such as water, ionic liquid, tannic acid, and so forth during the formation of nanocarbons (graphene, carbon nanotube) and the resulting nanocomposites have solved the environmental concerns to a great extent. The use of green solvents have revealed less toxicity and fine material processability. However, challenges still exist in the complete implementation of green nanotechnologies for supercapacitor electrodes. It has been observed that green solvents and green synthesis routes cannot be adopted for all combinations of conducting polymer/nanocarbon nanocomposites. Furthermore, using green solvents such as water sometimes may deteriorate the nanofiller dispersion, conductivity, and supercapacitance performance. This challenge can be overcome by researching and developing some new eco-friendly green solvents. For example, innovative green solvents based on ionic liquids can be invented to resolve the issue of using toxic chemicals. Moreover, there are hurdles in the complete transference of supercapacitor electrodes to green electrodes. In this regard, comprehensive efforts are needed to use cellulose, nanocellulose, cellulose nanofibers, and cellulose nanocrystals in the supercapacitor electrode structure and completely replace the non-degradable polymers. Moreover, nanocarbons such as carbon nanotube and graphene can be functionalized to transform into green nanocarbon nanomaterials.

Therefore, this review encompassed essential aspects of green polymer/nanocarbon nanocomposites and green-processed nanomaterials for supercapacitor application. Moreover, the crucial facets of conjugated polymers, thermosets, and green-polymer-based nanocomposites for supercapacitors have been stated. The green-technology-derived nanocomposites revealed superior processability, electrical conductivity, and charge storage characteristics. The inclusion of nanoparticles through the green processing routes have been found to support the electron transport, charge transference, and other supercapacitive properties. The focus of future efforts has been anticipated to include the development of progressive green nanocomposites for next-generation supercapacitors and other energy storage maneuvers.

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