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Synthesis Processes of Carbonaceous Material/Conducting Polymer Nanocomposites in Relation to Grafting and Electrochemical Properties for Supercapacitor Application: A Review

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Abstract

Supercapacitors are the energy storage devices that have gained increased attention due to high charge storage capacity, fast charge-discharge rate, high specific power and excellent cycle stability. Recently, research on supercapacitors is focused on the development of new electrode materials prepared by surface engineering to obtain superior electrochemical performance. Carbonaceous materials (CM) such as graphene, graphene oxide (GO), reduced graphene oxide (rGO) and carbon nanotubes (CNTs) etc. and conducting polymer (CP) based composite materials have gained increased attention for their use in supercapacitors. The nanocomposites obtained by merely mixing these two components pose some serious drawbacks such as low conductivity or poor film forming ability. The conjugation of CPs to CMs through covalent bonds is able to address these drawbacks. This review mainly provide collective information about various synthetic strategies to obtain CP grafted CMs for supercapacitor application. Herein, we provide information on different CP-CM conjugation reactions for obtaining the composites and their effects on electrochemical performances. The analysis revealed the importance of CP-CM grafting is important for tuning the electrochemical properties of the materials.

Keywords

conducting polymers, carbonaceous materials, grafting, polymerization, supercapacitor

1 Introduction

High-performance energy storage systems are becoming more popular day by day due to their wide range of applications along with advancements in technology and massive energy usage [1]. Therefore, the development of energy storage devices with high specific capacitance, high energy density and high strength has become need of the hour [2]. Supercapacitors are considered as one of the most useful devices for storing energy and hence they have grabbed a lot of attention as high performance electrochemical energy source [3]. They deliver high capacitance, rapid charge-discharge cycles, excellent cycle life, and are cost-effective [4–6]. Supercapacitors are mainly classified into three types: electric double layer capacitor (EDLC), pseudocapacitor and hybrid [7]. Energy is stored electrostatically and electrochemically in EDLC and pseudocapacitive type of supercapacitors respectively. However, hybrid supercapacitors store charge by both electrostatically and electrochemically [8, 9]. A huge number of materials have been investigated to be used as electrode materials in supercapacitor. These materials are of various types, such as carbonaceous materials (CM), conducting polymers (CP), metal oxides or composites made of them [10]. The domain of CP-CM composites and related research has also increased drastically in last few years due to several advantages.

The CPs have grabbed significant attention due to their wide range of electrical conductivity and high pseudocapacitance [11, 12]. CPs are the class of organic compounds having electrical properties comparable to that of metals and inorganic semiconductors [13]. They are conjugated polymers having a band gap of 1 to a few eV which divides the highest occupied orbitals from the unoccupied orbitals. The negatively charged ions in the doped state balance out the positive electrical charges along the conjugated

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backbone (alternate arrangement of single and double bonds) to make the polymer conducting so that the conductivity values can exceed up to 1000 S cm^{-1}. Conjugated polymers due to their coupling and mixed transport of ions and electronic charges are desirable as polarizable bulk electrodes in electrical energy storage applications [14]. The very common examples of CPs include polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) and poly (3,4-ethylene dioxythiophene) (PEDOT), etc. [15]. Higher charge density, ease of synthesis and lower cost of CPs makes them attractive as electrode materials for supercapacitors. They have really fast charge–discharge kinetics, tuneable or suitable morphology and fast doping and de-doping processes [16]. Despite of these advantages they suffer from poor cycle life and mechanical properties [17]. Researchers have attempted various studies in order to overcome the drawback of CPs. Therefore, CPs are usually mixed with or grafted on carbon-based materials.

Carbonaceous materials (CMs) have become the key factor in the development of energy storage devices [18]. CMs can be classified according to their structure. Buckyballs (C60) are zero-dimensional material. Single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) represent one dimensional CM. Graphene is a two-dimensional material and activated carbon is a three-dimensional material [19]. The CMs show excellent properties such as good conductivity, high stability, low cost, wide potential windows and easy surface functionalization [20–23]. CNTs have high surface area (1300 $m^2 g^{-1}$) and high electrical conductivity [24]. Its unique porous or hollow structure can promote the diffusion of electrolyte ions and increase the interface area between the electrolyte and the electrode [25]. In graphene, nanosheets of carbon atoms are arranged in honeycomb like structure. It shows very high surface area (2630 m^2 g^{-1}) and high electrical conductivity which makes it possible to produce supercapacitors with high energy density [26].

As pointed out earlier CPs are desirable materials for pseudocapacitor because of their high specific capacitance, strong electrical conductivity, quick charge-discharge process and low price with environmental stability [27]. When compared with other electrode materials they have gained much attention as they are easy for processing and relatively flexible. With proper control, desired composition and thickness of the electrode material (film) could be obtained. Low cyclic stability of CPs during the charge-discharge process which results from expansion and contraction of the polymer backbone is the fundamental problem of CPs [28, 29]. Taking these issues into account, the design and suitable modification of the polymer properties in composites made from polymers and other materials has been recognized as a possible option to solve the problem. It is possible to improve the molecular chain segment structure, mechanical firmness, electron conductibility and machinability of CP based composite electrode materials [28]. CMs such as SWCNTs and MWCNTs have been employed as electrode materials for the supercapacitors as they have distinctive hollow structure, good electronic conductivity, thermal stability and mechanical strength [30]. CMs are one of the important nanofillers for the CPs to prepare interesting composite materials to be used as electrode materials. The possible application of CPs in electrochemical capacitors is dictated by their significant capacitance values. It is different than in activated carbons where only the surface of the material (interface with electrolyte) is used for charge accumulation, in the case of CPs, the total mass and volume is involved in charge storage [31]. The flexible and conductive nature of CPs when combined with the intrinsic layered structure of CM such as graphene results in a material with electrochemically active material for electrodes in supercapacitors. These composites have improved mechanical strength and conductivity as compared to each material individually. Compositing carbon nanomaterials with CPs having pseudocapacitance increases the energy density largely [32]. The benefits of double-layer capacitance in carbon materials as well as pseudo-capacitance in CPs can be fully combined in carbon and CP composites. As a result, these materials can offer high specific capacitance and working voltage as well as excellent cycle stability during the charge-discharge process.

Several reviews have been published on different supercapacitor electrode materials such as CM, CP, MO, CP-MO composites and carbon-MO composites in past few years. But grafting approach in the composites is not studied or dealt exclusively. As development in this field is very fast, new approaches in making composites should be studied. Hence, this review is focused on collective information about various strategies of grafting CPs on CMs and the use of resulting composites for supercapacitor application. The discussion is focused on the importance of grafting over conventional method of preparing composites by mere mixing of the materials.

2 Advantages of CPs grafting on CMs

Grafting is an approach of synthesizing nanocomposites in which materials are bonded with polymers by making strong covalent bond between them. They are further categorized into three types: "grafting to", "grafting from" and "grafting through". In the "grafting to" approach, functional groups on the surfaces of CM are reacted with functional-polymers (polymers bearing functional groups) that have reactive end groups [29]. In the "grafting from" approach, polymer chains are grown from an initiator which is previously anchored on the CM surface by in-situ polymerization method. In the "grafting-through" approach, the surface of nanoparticles is functionalized with polymerizable groups which act as crosslinking agent. Then, the polymerization is initiated in the solution with initiator, monomers and functionalized NPs. Thus, polymerization of monomers takes place and the particles are incorporated inside polymer chains [33]. The advantage of this method is that the high reactivity of monomers makes efficient, controllable and designable and tailored grafting feasible [29]. This method mostly yield solid core polymer shell materials.

Grafting of CP is particularly important, as it does not alter the extended conjugated structure in the main chain, however, is capable of introducing and integrating the properties from the grafted materials. Grafting can potentially improve the properties of the conducting polymers beyond its charge transport [34]. The functionalization (grafting) with CPs such as PANI or PPy helps to improve the electric properties of CMs. The properties of CM-CP composites are enhanced due to the synergistic effect between the two components through covalent grafting. As compared to non-covalent mixing, the covalent linkage between CM and CP (grafting) can greatly improve the dispersibility, mechanical strength, and several morphological characteristics of CPs, by maintaining the electrical conductivity, chemical reactivity and the mechanical properties of CM [35]. Grafting proves to be an effective method for charge transfer process and also enhances ionic transport, ensuring better contact between the electrode material and electrolyte. It helps to overcome the low compatibility and low capacitance shown by weak interactions due to Van Der Waals forces and hydrogen bond between species in composites prepared by conventional methods. Ordered polymer chains are formed through grafting which helps in interfacial charge transfer between CP and CM. Sufficient diffusion channels are provided by grafting CP which helps to accommodate large volume changes during charge-discharge process. This improves the cyclic performance of composites [36]. The problem of dispersion of CM such as CNTs and interfacial adhesion between CNTs and Polymer matrices can also be solved by grafting [37]. Grafting also maintains the ideal structure of CM preserving its large surface area [36]. Covalent bonding of CP enhances interactions by reducing interfacial resistance of each component [38, 39]. The covalent functionalized groups on CNTs can avoid potential microscopic phase separations in the resulting nanocomposites and ensure enhanced electrochemical performance or properties [40]. Thus, CP grafted CM composites are emerging as new supercapacitive materials because of their high chemical and physical stability, increased conductivity, excellent film forming ability and high specific capacitance [40, 41].

3 Examples of CP grafted CM materials

There are considerable number of examples in the literature where conjugation of CPs to CMs is reported. Different condensation or conjugation reactions are used for the grafting purpose. The section below discusses different examples of CP conjugated CM materials together with their electrochemical parameters.

3.1 Graphene

Graphene, a 2-Dimentional nanostructured carbon allotrope is a single layer of graphite with the thickness of one atom of carbon. It is one of the remarkable material owing to its relative high surface area favorable for electrostatic charge storage and free electrons providing excellent conductivity for supercapacitor. Composites of CPs grafted with graphene has shown enhanced performance in case of capacitance, stability, energy density and power density.

Ensafi et al. [42] synthesized a new quaternary nanohybrid of graphene/PANI-benzimidazole grafted graphene/MnO_2 as an anode for supercapacitor. The synthesis scheme of quaternary nanohybrid is shown in Fig. 1(a). It shows the synthesis of two composites. One is graphene/PANI composite by polymerization method and other is graphene/MnO_2 composite by hydrothermal method. Final nanohybrid was prepared by sonicating these two composites. It exhibited a high specific capacitance of 675 F g^{-1} at current density of 50 A g^{-1}. The nanocomposite also showed excellent rate capability of 80% capacitance retention at 50 A g^{-1} and high cycling stability with of capacitance retention less than 13% after 2000 charge-discharge cycles. It exhibited a high columbic efficiency of 96% at a high discharge current of 50 A g^{-1} [42]. Mahdavi et al. [38] prepared FGA–PANI nanofibers in which graphene aerogel was functionalized with amino groups and it was grafted with PANI by grafting from approach and interfacial polymerization.

The synthesis procedure is shown in Fig. 1(b). The nanocomposite exhibited a high specific capacitance of 560 F g^{-1} at a current density of 1 A g^{-1}. It also showed good rate capability of 473 F g^{-1} at 10 A g^{-1} [38]. Wang et al. reported the synthesis of flake-like PPy grafted graphene nanosheets composites (PPy-g-GNS) which were fabricated by the in-situ chemical oxidative grafting polymerization of pyrrole in the presence of the 4-aminophenyl modified graphene nanosheets (AP-GNS). The synthesis scheme with principal and secondary reactions are shown of given composite are shown in Fig. 1(c). The composite showed specific capacitance of 191.2 F g^{-1} at the scan rate 10 mV s^{-1} which was higher than individual components of composite. It also exhibited excellent electrochemical stability even after 1000 cycles [43].

3.2 Graphene oxide (GO)

GO is a chemically modified form of graphene sheets with variety of functional groups having oxygen like alcohols, ethers, carboxylic acids, epoxides etc. on either sides of sheets. Presence of such polar functional groups on surface helps to enhance the pseudocapacitance and also facilitates the synthesis of different composites for various applivations.

Li et al. [44] studied the effect of grafting by synthesizing covalently grafted PANI/GO nanocomposites and noncovalently-grafted nanocomposites. Among them the synthesis procedure of covalently grafted nanocomposite is shown in Fig. 2(a). It involves grafting of GO with aniline and further in situ oxidative polymerization to form PANI/GO nanocomposite. The covalently-grafted PANI/GO composites (6:1) showed the highest capacitance of 422 F g^{-1} at a current density of 1 A g^{-1}. It exhibited 83% capacitance retention after 2000 cycles at 2 A g^{-1}. The excellent electrochemical performance of covalently-grafted PANI/GO composites was observed due to higher surface area and larger pore volume as compared to noncovalently-grafted PANI/GO composites. These features favoured more exposure of PANI to the electrolyte ions which results in increased redox reaction species and faster ion transport [44]. Li et al. [45] prepared PD4ET-g-GO nanocomposite in which alkoxy substituted polythiohene poly[3-(2-(2-(2-(2-(diethanolamino)ethoxy)ethoxy)ethoxy)ethoxy)thiophene] (PD4ET) was chemically grafted to GO nanosheets via esterification. The synthesis procedure of nanocomposite is shown in Fig. 2(b). PD4ET-g-GO electrode showed remarkable electrochemical performance with a maximum specific capacitance of 971 F g^{-1} at a current density of 1 A g^{-1} which was much higher as compared to individual components of nanocomposite and the physical mixture. It achieved high energy and power density up to 66.11 Wh kg^{-1} and 350 W kg^{-1} and of 38.11 Wh kg^{-1} and 7000 W kg^{-1} respectively with excellent cycling stability of 98% initial capacitance retention within 10000 consecutive charge-discharge cycles [45]. He et al. reported the synthesis of GO@PPy nanosheets which is represented in Fig. 2(c) in which PPy was grafted on GO during in situ oxidative polymerization of pyrrole. The GO@PPy nanosheets showed a higher areal specific capacitance of 1532 mF cm^{-2} at 0.88 mA cm^{-2}. It also revealed better rate capability (capacitance retention rate of 41% from 0.88 to 44 mA cm^{-2}) with excellent cycling stability i.e., only 10% capacitance loss after 1000 cycles. Solid-state symmetrical supercapacitor device fabricated showed high energy density of 114 µWh cm^{-2} at a power density of 500 µW cm^{-2} and high power of 20,000 µW cm^{-2} at an energy density of 70 µWh cm^{-2} [46].

3.3 Reduced graphene oxide (rGO)

rGO i.e., reduced form of GO is extensively known and most used electrode material for suppercapacitor as it has notably high surface area, high carrier mobility and great chemical stability. Its surface features like easy, simple surface functionalization and other modifications helps to form composites with other materials like CPs which boosts electrochemical performance.

Male et al. [47] synthesized PANI-grafted rGO via azobenzene pendants for supercapacitor. For this rGO-Azo composite was first synthesized by reducing GO-Azo with hydrazine and then PANI was grafted by in situ chemical polymerization of aniline to form PANI/rGO-Azo composites. The detailed synthesis reaction of composite is represented in Fig. 3(a). The effect of grafting was observed by increase in specific capacitance. It showed specific capacitance of 328 F g^{-1} which is higher than that of rGO-Azo was 114 F g^{-1} [47]. Wang et al. synthesized a hierarchical nanocomposite (PANI-frGO) of PANI nanowire arrays covalently bonded on rGO. For this synthesis, firstly nitrophenyl groups were grafted on rGO via C-C bond and then reduced to aminophenyl for the growth of PANI arrays on rGO. The synthesis reaction of PANI-frGO composite is shown in Fig. 3(b). The nanocomposites showed high capacitance of 590 F g^{-1} at 0.1 A g^{-1}, and no capacitance loss was observed up to 200 cycles at 2 A g^{-1} [48]. Kumar et al. prepared PANI-g-rGO in which amine-protected 4-aminophenol was initially grafted to

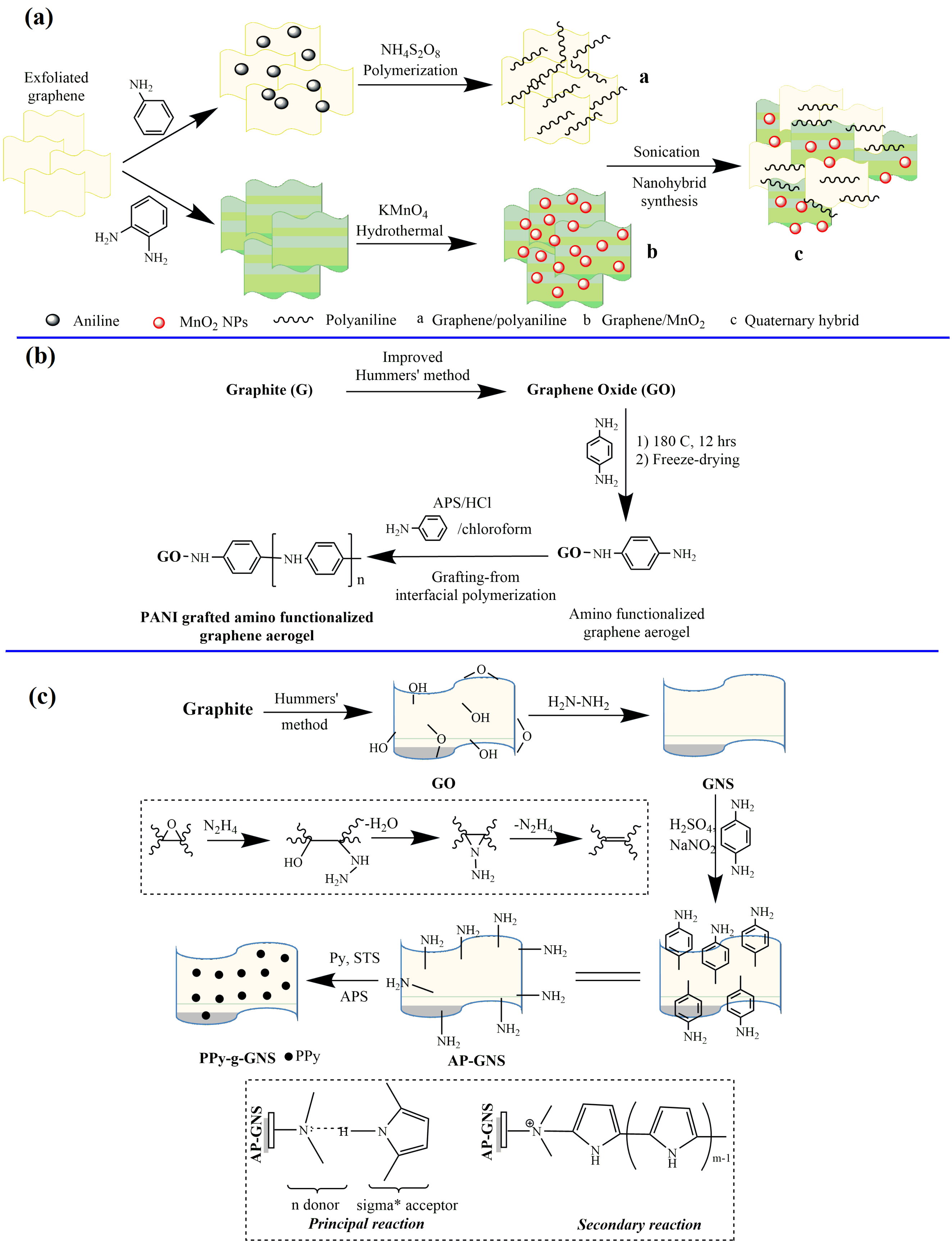

Fig. 1 (a) Schematic of the nanohybrid synthesis. Reproduced with suitable modification and permission from Ensafi et al. [42]. (b) Schematic procedure for synthesis of FGA–PANI electrode materials. Reproduced with suitable modification and permission from Mahdavi et al. [38]. (c) Schematic illustration for the fabrication of the PPy-g-GNS nanocomposites. Reproduced with suitable modification and permission from Wang et al. [43].

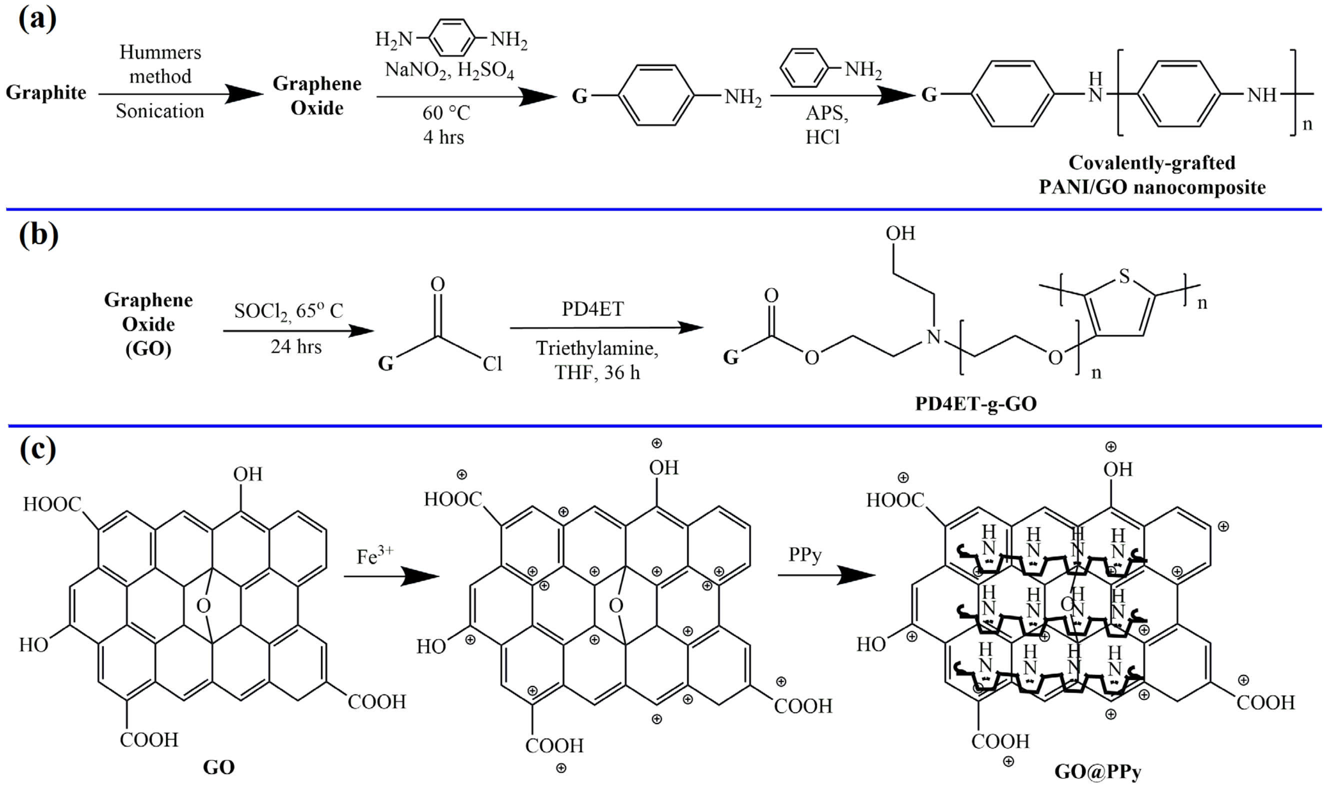

Fig. 2 (a) Schematic illustration of the three-step preparation of covalently-grafted PANI/GO nanocomposites. Reproduced with suitable modification and permission from Li et al. [44]. (b) Schematic diagram for the covalent grafting PD4ET side chains to GO. (c) Illustration of synthesis procedure of GO@PPy.

GO via acyl chemistry. It was followed by in situ chemical oxidative grafting of aniline in the presence of an oxidizing agent ammonium persulphate (APS) to yield highly conducting PANI-g-rGO which is represented in Fig. 3(c). The composite revealed electrical conductivity as high as 8.66 S cm^{-1} and a specific capacitance of 250 F g^{-1} [49]. Nguyen et al. [50] in their work synthesized RGO-g-PANI composite by two step method. In first step RGO was surface-modified with 1,3-diaminopropane, which provided reactive NH_2 groups. In second step, it was reacted with aniline to form polymer chain grafting on RGO. The chemical reaction of composite synthesis is shown in Fig. 3(d). It showed the specific capacitance 1337 F g^{-1} at a very high current density of 15 A g^{-1} [50]. Hoa et al. [51] prepared 3D RGO-g-PANI aerogel composite and tested it for supercapacitor application. It was done by grafting PANI chains on RGO sheets further it was heated and dried to obtain aerogel. The composite exhibited an excellent specific capacitance of 1600 F g^{-1} at a very high current density of 12 A g^{-1} and an excellent cycle stability with 91.3% capacitance retention after 3000 cycles [51].

Vijaya Sankar and Kalai Selvan [52], in their work prepared $CoFe_2O_4$/rGO/PANI (CCGP) ternary composite for supercapacitor. It was prepared by in-situ chemical oxidative polymerization method in which binary composite $CoFe_2O_4$/rGO was covalently grafted with PANI through unreduced oxygen functional groups. The synthesis scheme of given composite is shown in Fig. 4(a). A hybrid supercapacitor formed with β-$Co(OH)_2$ as positive electrode and ternary composite as negative electrode exhibited a high specific capacitance of 1.41 F m^{-1}, with high energy density of 270×10^{-8} Wh cm^{-1} and excellent cycling stability [52]. Li et al. [53] prepared PANI covalently grafted to isocyanate functionalized rGO (PANI-IPDI-rGO) nanocomposite for supercapacitor. The synthesis of nanocomposite is shown in Fig. 4(b). It was prepared by simultaneous reduction and functionalization of GO nanosheets by isophorone diisocyanate (IPDI) and followed by grafting PANI to produce a novel PANI-IPDI-rGO nanocomposite. It showed excellent specific capacitance of 1415 F g^{-1} without compromising rate capability. Also all-solid-state supercapacitor device fabricated with PANI-IPDI-rGO as positive electrode showed a remarkable gravimetric specific capacitance of 485 F g^{-1} with maximum energy density of 113.8 Wh kg^{-1}. An excellent capacitance retention of 95 % after 2000 consecutive charge-discharge cycles

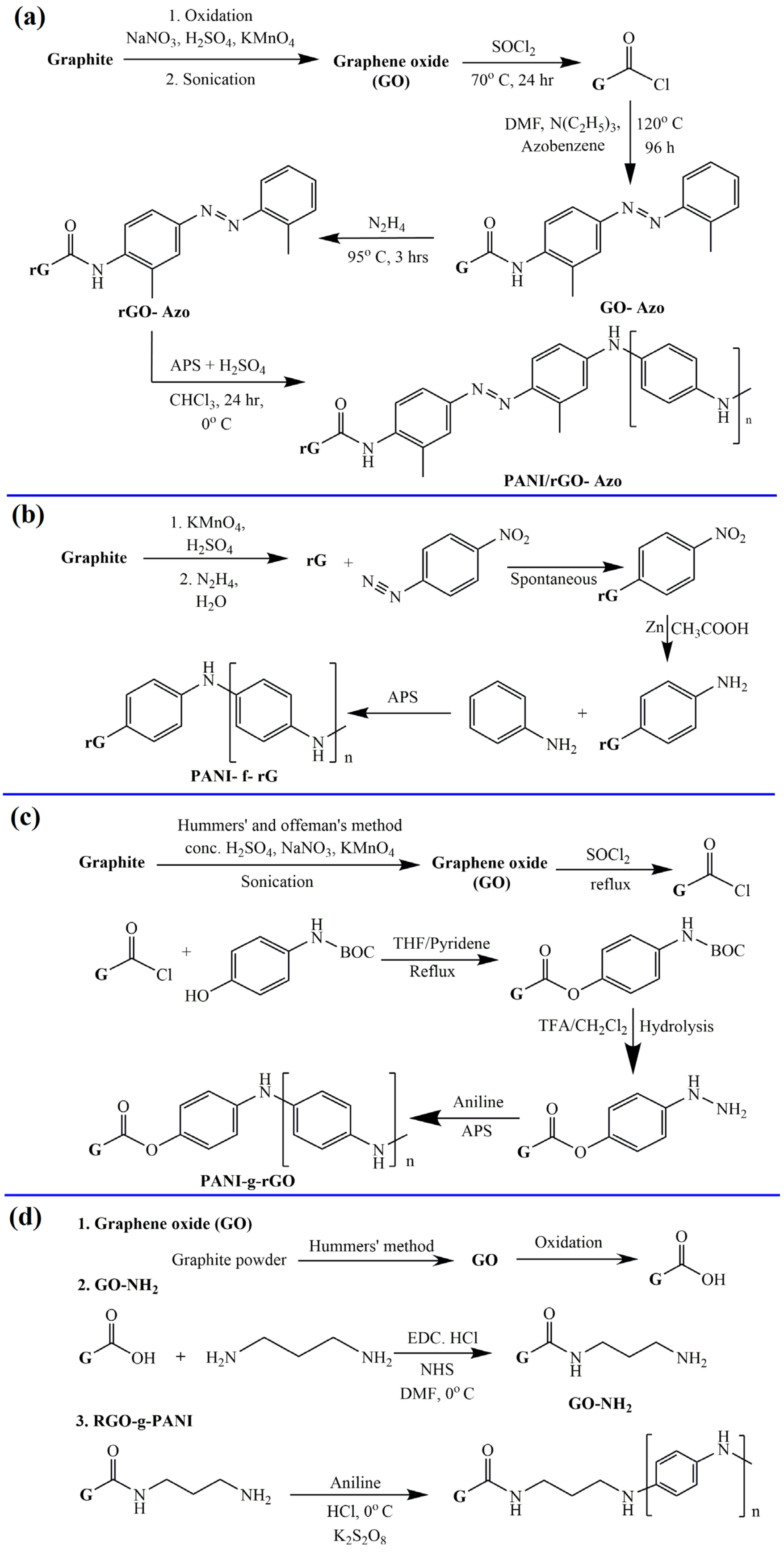

Fig. 3 (a) Schematic representation for the synthesis of PANI-rGO-Azo. Reproduced with suitable modification and permission from Male et al. [47]. (b) Procedure for the fabrication of PANI-frGO [48]. (c) Schematic governing the preparation of PANi-g-rGO. Reproduced with suitable modification and permission from Kumar et al. [49]. (d) Step by step synthesis of RGO-g-PANI.

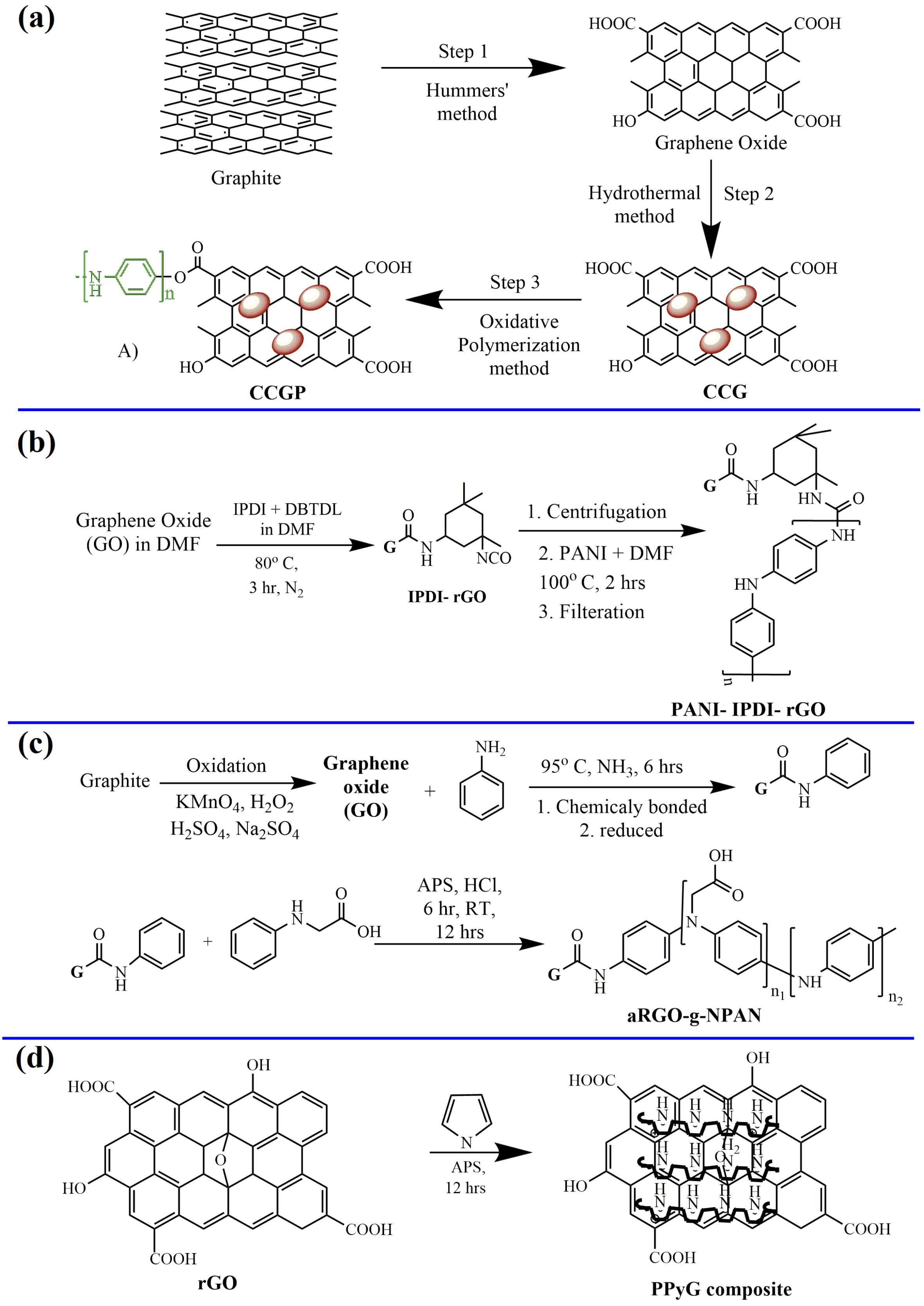

Fig. 4 (a) Schematic representation of preparation of CCGP composite. Reproduced with suitable modification and permission from Vijaya Sankar and Kalai Selvan [52]. (b) Schematic illustration for the PANI covalently grafted on rGO nanosheets. Reproduced with suitable modification and permission from Li et al. [53]. (c) Schematic Diagram of synthesis of aRGO-g-NPAN Hybrid. Reproduced with suitable modification and permission from Zhang et al. [54] (d) Schematic flow diagram of the preparation of PPyG composite based sandwich electrodes.

was observed [53]. Zhang et al. [54] prepared N-substituted Carboxyl PANI (NPAN) Covalent Grafting RGO (aRGO-g-NPAN) Nanocomposites and studied its application in supercapacitor. For the synthesis of this nanocomposite, first RGO was bonded with aniline via the nucleophilic ring-opening reaction of epoxy group of GO. It was further polymerized with N-phenylglycine (NAN) monomer to get aRGO-g-NPAN nanocomposites. The reaction is for the preparation of nanocomposite is shown in Fig. 4(c). Electrochemical tests of this nanocomposite was compared with traditional physical mixture. It revealed that the specific capacitance of the aRGO-g-NPAN hybrids was 654.3 F g^{-1} at 1 A g^{-1}, while for physical mixture it was 418.5 F g^{-1} for traditional physical mixture. Also capacitance retention for the successive 1000 charge/discharge cycles for composites was 79.1%, while the traditional physical mixture showed 67.4% capacitance retention. Thus increase in electrochemical performance highlighted the effect of covalent grafting [54]. Akhtar et al. studied charge transport and electrochemical performance of PPyG supercapacitor. PPyG composite was prepared by grafting PPy on RGO sheets. The synthesis scheme of PPyG composite is illustrated in Fig. 4(d). The grafting occurred due to mutual oxidation/reduction process of pyrrole monomer and GO respectively. The composite obtained large value of specific capacitance i.e., ~ 931 F g^{-1}. It exhibited an excellent energy density of 46.6 Wh kg^{-1} at an ultra-high power density 469 W kg^{-1} [55].

3.4 Carbon nanotubes (CNTs)

CNTs are tubular form of graphene sheets whose diameter lies in the nanometer range. The unique structure of CNTs with increased surface area, poor resistivity and greater stability makes it potential material for supercapacitor application. CPs incorporated with CNTs have attracted researchers owing to the given reasons: its novel structure gives exposure of active materials efficiently, honeycomb like mesoporous nanotubes aloows diffusion of ions and its flexible structure makes it easily adaptable for volumetric changes during charging and discharging.

Chang et al. [56] used plasma modification to synthesize PANI grafted CNT embedded carbon nanofiber electrodes for high performance supercapacitors. The Plasma treatment modified the surface with free radicals which further treated with aniline to form PANI-g-CNF. It is represented in Fig. 5(a). The synthesized material has a high specific capacitance value of 606 F g^{-1} and good cyclic stability up to 1000 cycles with no capacitance loss at 1 A g^{-1} of current density [56]. Che et al. [57] synthesized a porous PANI/CNT composite for supercapacitor applications. It was synthesized by chemically grafting PANI on CNTs and producing interfacial porosity via synthesizing with $CaCO_3$ nanoparticles. The synthesis reaction is shown in Fig. 5(b). Due to the porous morphology of PANI, ions have more space for transportation, resulting in a high capacitance value of 1266 F g^{-1} at a current density of 1 A g^{-1}, as well as 864 F g^{-1} at a current density of 128 A g^{-1}. It also has an excellent cyclic performance of 10,000 cycles with 83% capacitance retention [57]. Faraji et al. successfully fabricated binder-free PANI-g-MWCNT/TiO_2NTs/Ti electrodes by electrodeposition of aniline-functionalized MWCNT (An-fMWCNT) onto TiO_2 nanotubes/Ti, followed by grafting of PANI chains via aniline in situ chemical polymerization on the sites of An-fMWCNT. Among the electrode material, synthesis scheme of PANI-g-MWCNT is shown in Fig. 5(c). The produced electrode material has a specific capacitance of 708 F g^{-1}, good cyclic stability up to 1000 cycles with 88% at 5 A g^{-1} current density [40]. Jin et al. prepared a P-MWNT/PANI electrode composite by covalently bonding a multi amino dendrimer on MWNTs as a bridge to promote PANI covalent grafting. The synthesis scheme of the composite is represented in Fig. 5(d). The electrode material showed a specific capacitance of 568 F g^{-1} and exhibited good cyclic stability [39].

CNT woven film (CNWF)@vinyltrimethoxysilane (VTMS)/PANI was synthesized by Li et al. [58]. The CNT woven film CNWF obtained by floating catalytic chemical vapour deposition (FCCVD) was treated with nitrating mixture and VTMS to form CNWF@VTMS composite functionalized with CH_2=CH- group. It was further grafted with PANI by in-situ oxidative polymerization method which is represented in Fig. 6(a). The material (CNWF@VTMS/PANI) demonstrated the best specific capacitance of 531.3 F g^{-1} and the maximum energy density of 26.5 Wh kg^{-1} at a current density of 1 A g^{-1}, as well as 96.6% capacitance retention after 2000 consecutive cycles [58]. Potphode et al. reported the synthesis of partially exfoliated Px-MWCNT/PANI nanocomposites by grafting PANI on Px-MWCNT in equal amount. The synthesis reaction of given nanocomposite is shown in Fig. 6(b). The symmetric supercapacitor fabricated with given nanocomposite achieved the highest specific capacitance of 809.6 F g^{-1} at 25 mV s^{-1}. It showed good charge-discharge rate capability and electrochemical stability of 78% capacitive retention after 2000 cycles [59].

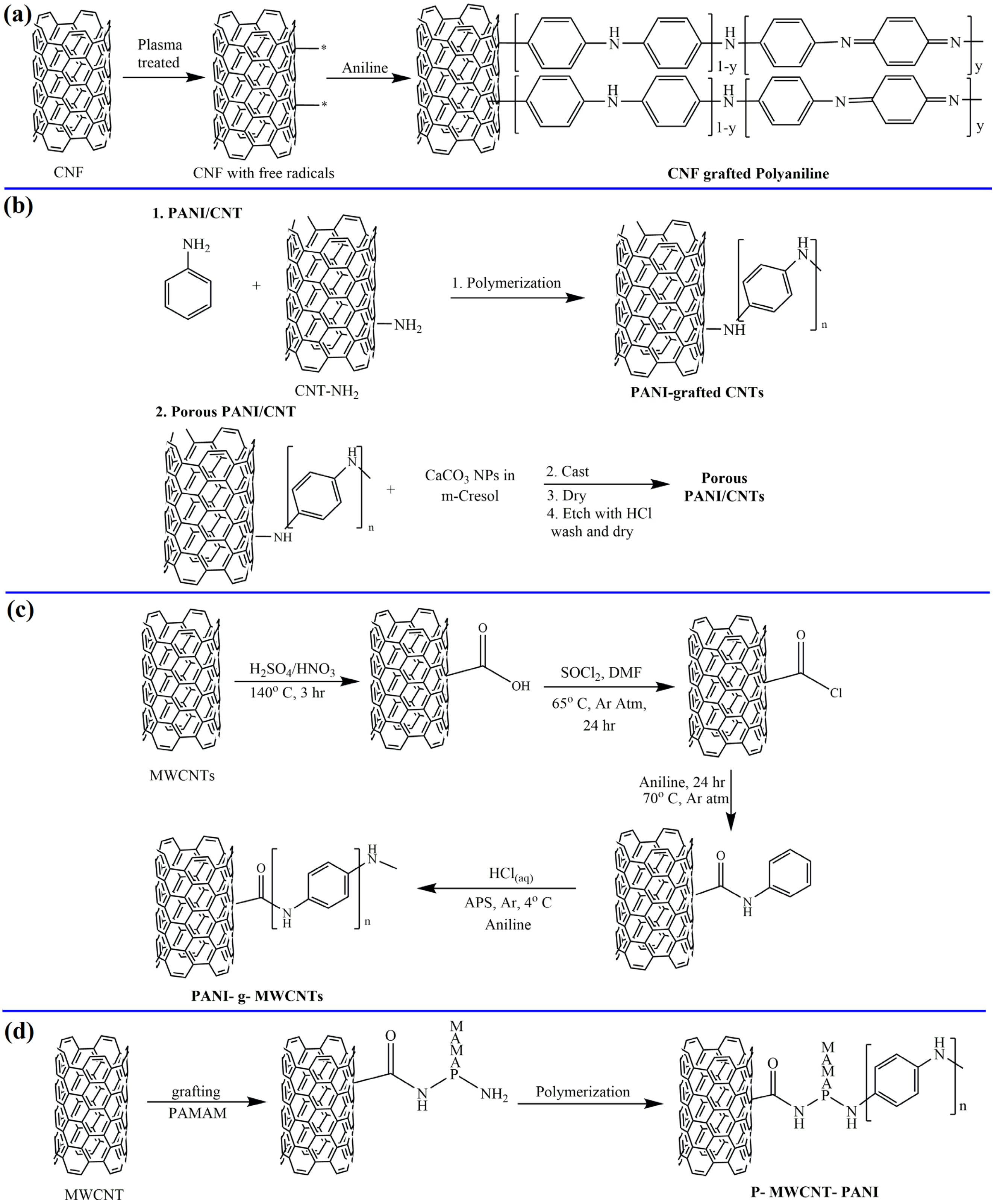

Fig. 5 (a) Plasma induced polyaniline grafted on the CNT embedded CNF. Reproduced with suitable modification and permission from Chang et al. [56]. (b) Schematic of preparation process of porous PANI/CNT. Reproduced with suitable modification and permission permission from Che et al. [57]. (c) Preparation of functionalized MWCNTs by different agents and PANi-g-MWCNT. Reproduced with suitable modification and permission from Faraji et al. [40]. (d) Schematic representation for preparation of P-MWNT-PANI [39].

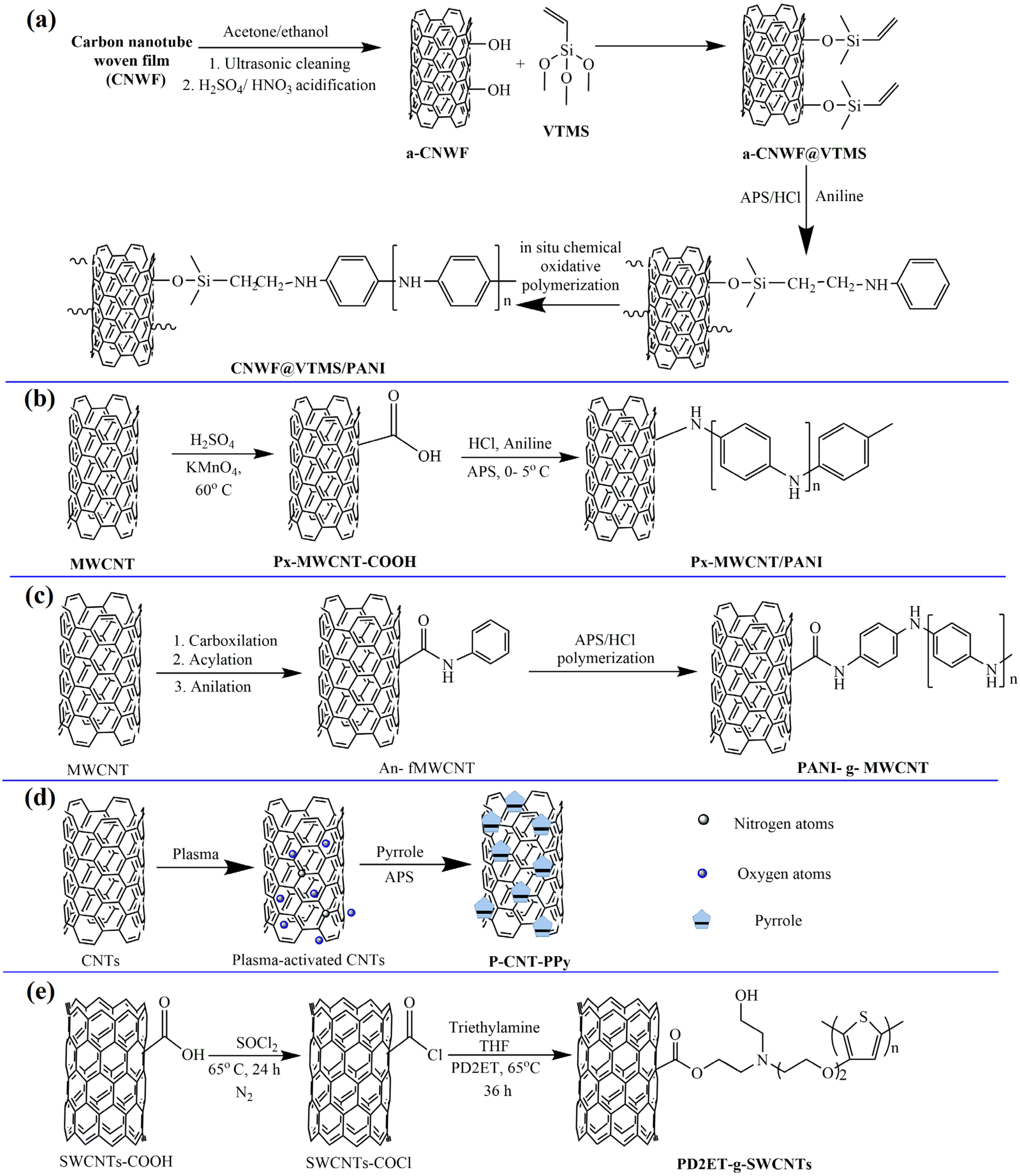

Fig. 6 (a) Schematic illustration of the preparation of CNWF@VTMS/PANI flexible self-supporting composites. Reproduced with suitable modification and permission from Li et al. [58]. (b) Synthesis of Px-MWCNT/PANI nanocomposites. (c) Detailed fabrication o of PANI-g-MWCNT/VOGN/G. Reproduced with suitable modification and permission from Dadashi et al. [41]. (d) Schematic diagram of synthesis of plasma-activated CNT and P-CNT-PPy composite. Reproduced with suitable modification and permission from Yang et al. [60]. (e) Synthesis scheme for preparation of PD2ET-g-SWCNTs hybrids. Reproduced with suitable modification and permission from Zhou et al. [36].

Dadashi et al. [41] synthesized a binder-free PANI grafted MWCNT composite that was deposited on vertically oriented graphene nanosheets on a graphite sheet via anodizing, electrodeposition and polymerization which is shown in Fig. 6(c). The prepared electrode material demonstrated the maximum specific capacitance of 880 F g^{-1} at a current density of 1.5 A g^{-1}, as well as an energy density of 68.4 m Wh g^{-1} and power density of 895.4 mW g^{-1}. It possess excellent cyclic stability upto 10,000 cycles after 80.6% of capacitance retention [41]. In an experiment performed by Yang et al., novel Ppy bonded CNT composite (P-CNT-PPy) was synthesized. It was prepared by grafting PPy on using air-plasma activated CNT by in situ chemical oxidative polymerization. The synthesis scheme is represented in Fig. 6(d). The composite P-CNT-Ppy exhibited specific capacitance of 188 F g^{-1} in 1M KCl and 264 F g^{-1} in 1M H_2SO_4 and excellent cyclic stability i.e., 89% capacitance retention at 5 mA cm^{-2} after 1000 consecutive cycles [60]. An experiment performed by Zhou et al. proposed PTh grafted on SWCNTs via oligo(ethylene oxide) linkages by using esterification reaction which is represented in Fig. 6(e). It exhibited specific capacitance of 399 F g^{-1} at a current density of 1 A g^{-1} and excellent cycling stability i.e., 91% capacitance retention after 8000 charge discharge cycles. The electrode also showed high energy density 22.5 Wh kg^{-1} at a power density of 500 kW kg^{-1} [36]. A summary of different chemical bonding reactions of all examples explained in this report is presented in Table 1.

4 Conclusion

This review highlighted different CP grafted CM composites with their synthesis procedures and information about their electrochemical performances. CPs are being used as electrode materials in supercapacitors but their poor cyclic performance and mechanical properties limits their application. The various examples from literature discussed in this review prove that these limitations can be overcome by grafting CPs on CMs. As a result of grafting of CP on various CMs, improved electrochemical properties such as high capacitance and cyclic stability was observed. The CP-CM composites prepared by mixing the materials does not ensure uniformity of the composite. Grafting creates strong covalent bond between CM and CP which helps in improving their electrochemical performance.

The future research in this area may be directed along following main directions:

1. Synthesis of functional CMs by inventing new and economical process that include less energy consuming synthesis methods by using green or easily available starting materials.
2. Development and optimization of the synthesis methods to obtain high yield of CMs.
3. The continuous demand for CMs such as Graphene, GO, CNTs etc. has increased exponentially in various technological fields. Therefore, to meet the demand, new methods that yield higher quantities of these materials need to be developed.

Table 1 Common conjugation bonds between CP and CM

Sr. No.	CM	CP	Conjugation bond	Specific capacitance (F g^{-1})
1.	Graphene	PANI	-NH-C-	560
		PPy	-C-N+	191
2.	GO	PANI	-CO-NH--CO-	422
				971
		PPY	-C-N+	1532*
3.	rGO	PANI	-CO-NH-NH-C-COO-	1337
				590
				250
		PPy	-C.-C.-	931
4.	CNTs	PANI	-CO-NH-NH-C-O-Si-C.-C.-	568
				809
				531
				606
		PPy	-C.-C.-	264
		PTh	-COO-	399

* mF cm^{-2}

4. From CPs side, the synthesis and development of functional polymers that can be easily conjugated to not only CMs but also to other materials such as metal oxides will be needed. The development of in situ polymer synthesis and conjugation or grafting methods will be welcomed as they will save time needed for the post synthesis polymer grafting processes. The developments in modern synthetic organic chemistry may come up with new grafting strategies for various CPs on CMs.

Conflict of interest

There are no conflicts of interest to declare.

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