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Covalent functionalization of carbon materials with redox-active organic molecules for energy storage

Rizwan Khan *[a,b] and Yuta Nishina*[a,b]

[a] Graduate school of natural science and technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan
[b] Research Core for Interdisciplinary Sciences, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan
E-mail: nisina-y@cc.okayama-u.ac.jp.

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Abstract

Carbon-based materials (CBMs) have shown great versatility because they can be chemically combined with other materials for various applications. Chemical modification of CBMs can be achieved via either covalent or non-covalent interactions. Non-covalent interactions are weak and fragile, causing structural change and molecule dissociation. Therefore, in this review, we summarize the covalent modification of CBMs via organic chemistry techniques, aiming to form more robust and stable CBMs. Besides, applications as electrode materials in energy storage systems are also within the scope of this review. Covalently binding of redox-active organic molecules with CBMs improves the transfer rate of electron and prevents the dissolution of the redox-active molecules, resulting in good conductivity and cycle life. There are numerous amounts of papers on the functionalization of CBMs that have been published to date, but some of them lack scientific evidence and unable to understand chemically. Reliable and reasonable articles with adequate evidence are summarized in this review from a synthetic chemistry viewpoint.

1. Introduction

CBMs have attracted considerable interest in electrochemical applications due to their abundance, processability, stability, and relatively environmentally friendly characteristics.[1] CBMs has been widely used as electrode materials. Some of the useful properties of carbon-based electrodes include electrochemical stabilities and wide potential windows for repetitive redox reactions.[2] CBMs exist in different allotropic forms, such as 3-D diamond, 3-D graphite, 2-D graphene, 1-D carbon nanotubes (single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs)), and 0-D fullerenes; each of them has different physical and electrochemical properties. The sp^2 and/or sp^3 hybridized carbons and some of the oxygenated functional groups provide reactive sites for surface functionalization, which is beneficial to electrochemical applications, especially for electrode materials.

The covalent functionalization could significantly change the electrical structure and properties of the CBMs.[3,4] In particular, acid (*e.g.*, nitric acid or sulfuric acid)-promoted oxidation is one of the most commonly used methods for covalent functionalization.[5,6] The carbon atoms in CBMs can form robust covalent bonds with organic molecules, giving rise to a variety of composites with distinguished properties. The functionalization can be applicable for classic materials such as diamond, graphite, carbon black, and porous carbon, as well as for nanocarbons, which came at play in the last two decades. Nowadays, in addition to the fabrication of nano and porous CBMs, the surface functionalized CBMs have been used for a number of applications such as catalysis,[7,8] energy conversion,[9,10] sensing,[11,12] separation media,[13–17] and biomedicine.[18–20] However, most of the applications rely on the concept of electrochemistry.[21,22]

The fundamental components in electrochemical processes are the electrodes. CBMs show high chemical stability,[23] good mechanical properties,[24,25] and high electrical conductivity.[26,27] However, despite the potentials of CBMs, a common problem is the low surface wettability,[28] which lead to a low utilization rate of specific surface area, and result in low energy storage. Change of the surface chemistry by functionalization is a common route to optimize the interaction of the carbon surface with the external environment. The modification of the surface chemistry of CBMs strongly improves their interaction with aqueous and organic environments, providing improve performance as electrode materials in energy storage systems.

Covalent modification with organic molecules is expected to allow fine control of the function and physical properties at atomic or molecular levels. The covalent functionalization of CBMs with redox-active materials have been performed by nitrene and diazonium chemistry for sp^2 carbons, ring-opening reaction of epoxide group, etherification reaction, esterification reaction, amidation reaction and cyclization reaction.
The introduction of aziridine adduct onto the CBMs is obtained via a nitrene intermediate.[29–31] The nitrene is generated from a thermal- or photodecomposition of an azide group by eliminating a gaseous nitrogen molecule and is a highly reactive singlet species which subsequently undergoes a cycloaddition reaction on the sp^2 network of CBMs to provide an aziridine adduct (Figure 1a-A).
Surface modification of CBMs with diazonium chemistry has been achieved initially by an isolated diazonium salt and later by *in situ*-generated one. Although diazonium salt is unstable, it can be easily synthesized with an amine and $NaNO_2$ in an acidic aqueous solution,[32] *tert*-butyl nitrite, or $NOBF_4$.[33] Diazonium salt generates a radical with the elimination of nitrogen, then covalently reacts with CBMs (Figure 1a-B).[34–36] The radical formation can be initiated by electrochemical, thermal, or pH-dependent methods. Diazonium salts are important intermediates in organic chemistry, thus their derivatives are widely available.
The epoxide groups can be functionalized with nucleophilic molecules, which is well known as epoxy curing for the synthesis of epoxy resins. Oxidized CBMs, such as graphene oxide (GO), contain a large amount of epoxide.[37] Amine, thiol, or sodium azide can be used as a nucleophile for the ring-opening reaction (Figure 1b-A).[38–40] The reaction proceeds under the neutral and mild reaction condition without any additive or reagent; therefore, this is suitable for bonding unstable molecules such as biomolecules.[41,42]

The hydroxy groups can undergo etherification. The modified Claisen reaction allows functionalizing the hydroxy groups of CBMs through ether bond.[43,44] The Williamson reaction enables the formation of an ether bond from an organohalide and a deprotonated alcohol (alkoxide ion) via a substitution reaction (Figure 1b-B).[45] The Williamson synthesis gives the best yields with methyl or primary halides because the reaction occurs by an S_N2 displacement in which a halide ion is a leaving group. The yield is lower for secondary alkyl halides because they also react with the alkoxide ion in a competing elimination reaction.[46]

The esterification reaction is a way to functionalize the carboxylic acids on the surface of CBMs (Figure 1b-C).[47,48] For the activation of carboxylic acid, thionyl chloride is employed to obtain the acyl chloride. Then, alcohol is added in combination with base, resulting in the formation of an ester bond.[49] As another approach for esterification, a combination of *N,N′*-dicyclohexylcarbodiimide and *N,N*-dimethyl-4-aminopyridine is known as the Steglich esterification.[50] Similarly, carboxylic acid group can also be functionalized by thiol group using thiol-carboxylic-acid esterification.[51]

Amides are usually prepared by condensation of carboxylic acids and amines by using dehydration reagent,[52,53] or by prior conversion of the carboxylic acids into reactive derivatives.[54,55] Alternative procedures include the Staudinger ligation,[56] aminocarbonylation of aryl halides,[57] and oxidative amidation of aldehydes.[58] For the functionalization CBMs, thionyl chloride activation, coupling reagent, or simple heating have been employed (Figure 1b-D).

The cyclization reactions are promoted by the electrons moving in a circular way that includes bond cleavage and bond formation processes simultaneously (Figure 1b-E).[59]

CBMs-polymer composites are generally prepared through initiation site on CBMs. In the case of polyaniline (PANI) (Figure 1c-A) or polythiophene (Figure 1c-B), aniline or thiophene group is introduced by diazonium chemistry, epoxy ring-opening, amidation, or esterification, then oxidative polymerization is performed. Atom transfer radical polymerization is performed for the synthesis of an acrylate-type polymer (Figure 1c-C).

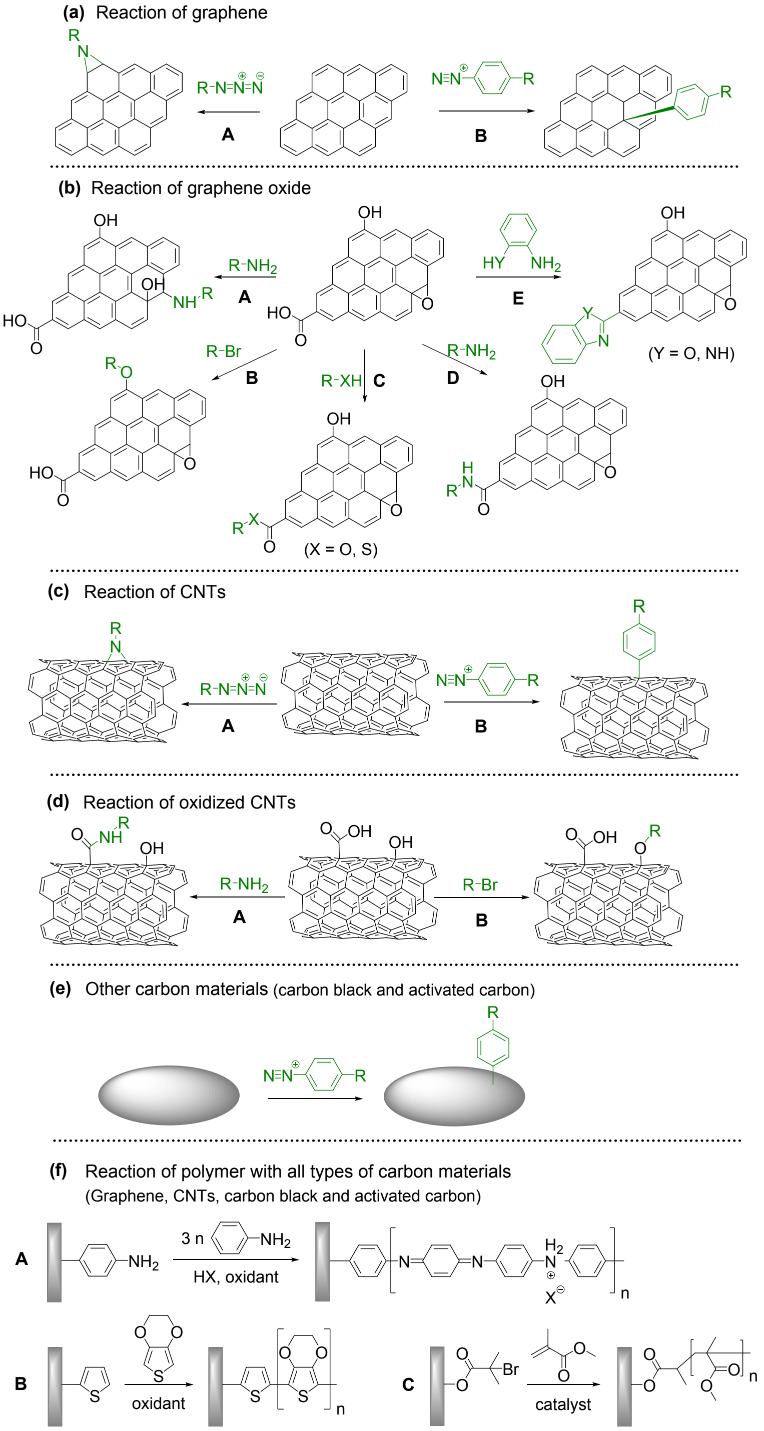

Figure 1: Various functionalization routes of CBMs with redox-active molecules (a) toward sp^2 carbons and (b) toward oxygenated functional groups on carbon. (c) Preparation strategies of CBMs-polymer composites.

1.1. Redox-active organic molecules and their operating mechanism

To solve the problems of global energy consumption, the development of high-performance and low-cost clean energy devices is required. According to the growth of renewable energy utilization, demands for advanced energy storage devices with high efficiency are increasing. Lithium-ion batteries (LIBs) and supercapacitors (SCs) are two of the most promising energy storage devices due to their notable characteristics, such as high energy density,[60] high power density,[61] and long cycle life.[62] For instance, widespread success has been achieved for LIBs since their commercialization in the 1990s.[63] Current commercial LIBs are constructed with metal-based materials, such as $LiMn_2O_4$,[64] $LiCoO_2$,[65] and $LiFePO_4$,[66] on the cathode side and CBMs such as graphite on the anode side. In the case of SCs, pseudocapacitive materials, such as metal oxides, sulfides, selenides and phosphides, are widely explored to enhance energy density.[67] However, the concerns of high cost, limited availability, and electronic hazards of transition metals, as well as poor cycling stability, would hinder their practical use.[68] Thus, metal-free redox-active materials for the fabrication of electrodes have been widely studied and can be potential candidates for the next-generation energy storage.

The first organic electrode was introduced by Williams using dichloroisocyanuric acid as an active material for a primary battery in 1969.[69] After this study, a variety of redox-active organic molecules have been studied, including small organic molecules such as quinones and dianhydrides and conjugated polymers such as polypyrrole and polyacetylene. The reported redox-active organic molecules can be categorized into carbonyl compounds,[70] organic radicals,[71] organosulfur compounds,[72] phenazine derivatives,[73] and conductive polymers (Figure 2).[74]

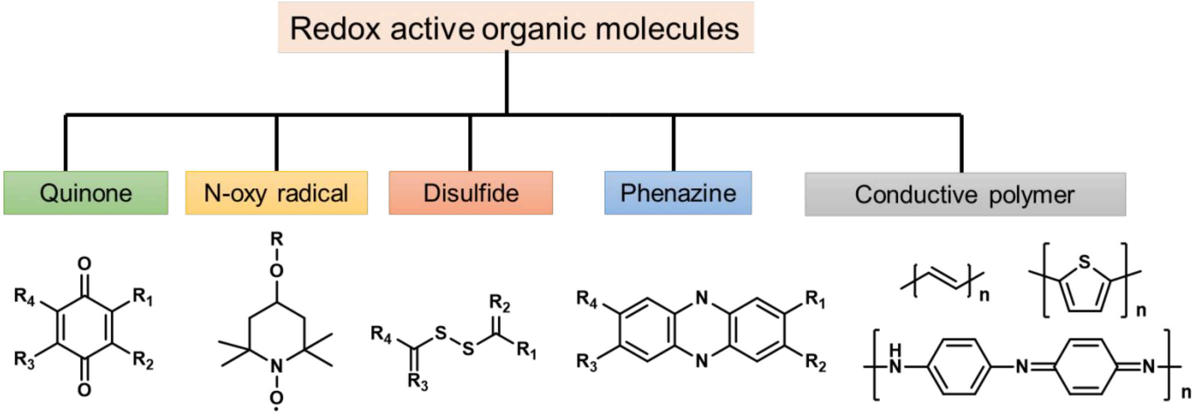

Figure 2: Classification of organic redox-active molecules

Redox-active organic molecules have attracted more and more interest recently, due to their intrinsic and reliable redox behavior, which can be readily utilized for charge-storage memory applications. A redox-active molecule contains a redox component acting as the charge-storage center surrounded by insulators/barriers. The electrons tunnel through the barrier during the oxidation and reduction processes. Typically, the application of an oxidation voltage will cause electron loss in the redox molecules; reversely, the electrons will be driven back to the molecules by applying a reduction voltage. Generally, the redox molecules have multiple stable states. The switching between these states is dynamically reversible through the loss or capture of a charge, that is, oxidation and reduction of the redox centers (Figure 3).

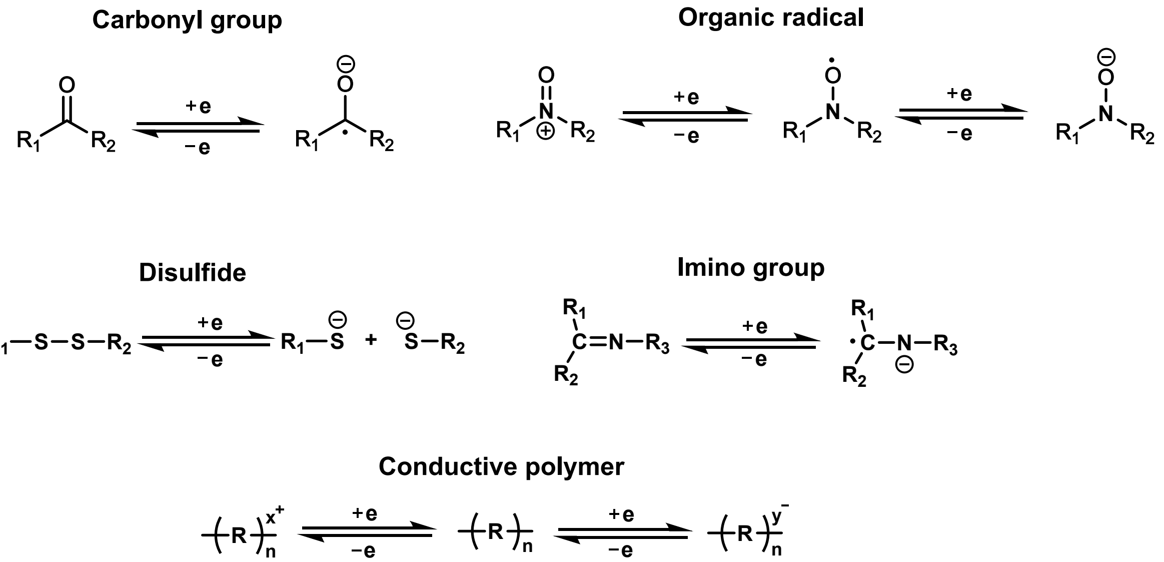

Figure 3: Redox mechanisms of various types of organic redox-active molecules

Up to now, several reviews were published on the organic electrode for energy devices; Schon,[75] Shanmukaraj,[76] Shea,[77] Han,[78] and Song,[79] independently reported the progress of the organic-based electrode for SCs and LIBs, all of which have mentioned difficulties in the development of organic electrodes. First, the organic molecules on electrodes tend to dissolve into the electrolytes, which results in a poor cycle life.[80] Second, their poor conductivity, resulting in limited electrochemical performance; as a result, their potential cannot be withdrawn completely due to the insulative effect.[81] Covalent functionalization strategy is expected to solve these problems.

1.2. Scope of this review

The organic modification of nanocarbons can be classified into covalent,[82] non-covalent,[83] and ionic bond[84] formations. Organic molecules have been functionalized on nanocarbon through non-covalent interactions and ionic bonding; as a result, high capacity, energy density, and power density were obtained.[85] Li,[86] Yuan,[87] Notarianni,[88] and Iqbal[89] independently reviewed the progress of the carbon-based composites as electrode materials for SCs and LIBs (Figure 4), focusing mainly on physical (non-covalent) interactions. However, since physical interactions are weak, molecular dissociation occurs readily.[90,91] Also, the rapid fading of electrode performance due to the volume change during charge–discharge cycles is a problem that needs to be addressed. The covalent functionalization of CBMs results in the formation of durable materials.[92] The electrochemical performance of redox-active organic molecules can be properly regulated by introducing redox-active molecules via diverse organic reactions. Covalent binding of redox-active organic molecules with CBMs improves the transfer rate of electron and prevents the dissolution of the redox-active material, resulting in good conductivity and long cycle life.[93,94] In this review, we will summarize and discuss the reported literature based on the covalent modification of redox-active organic molecules on CBMs and their electrochemical stability as electrode material in SCs and LIBs.

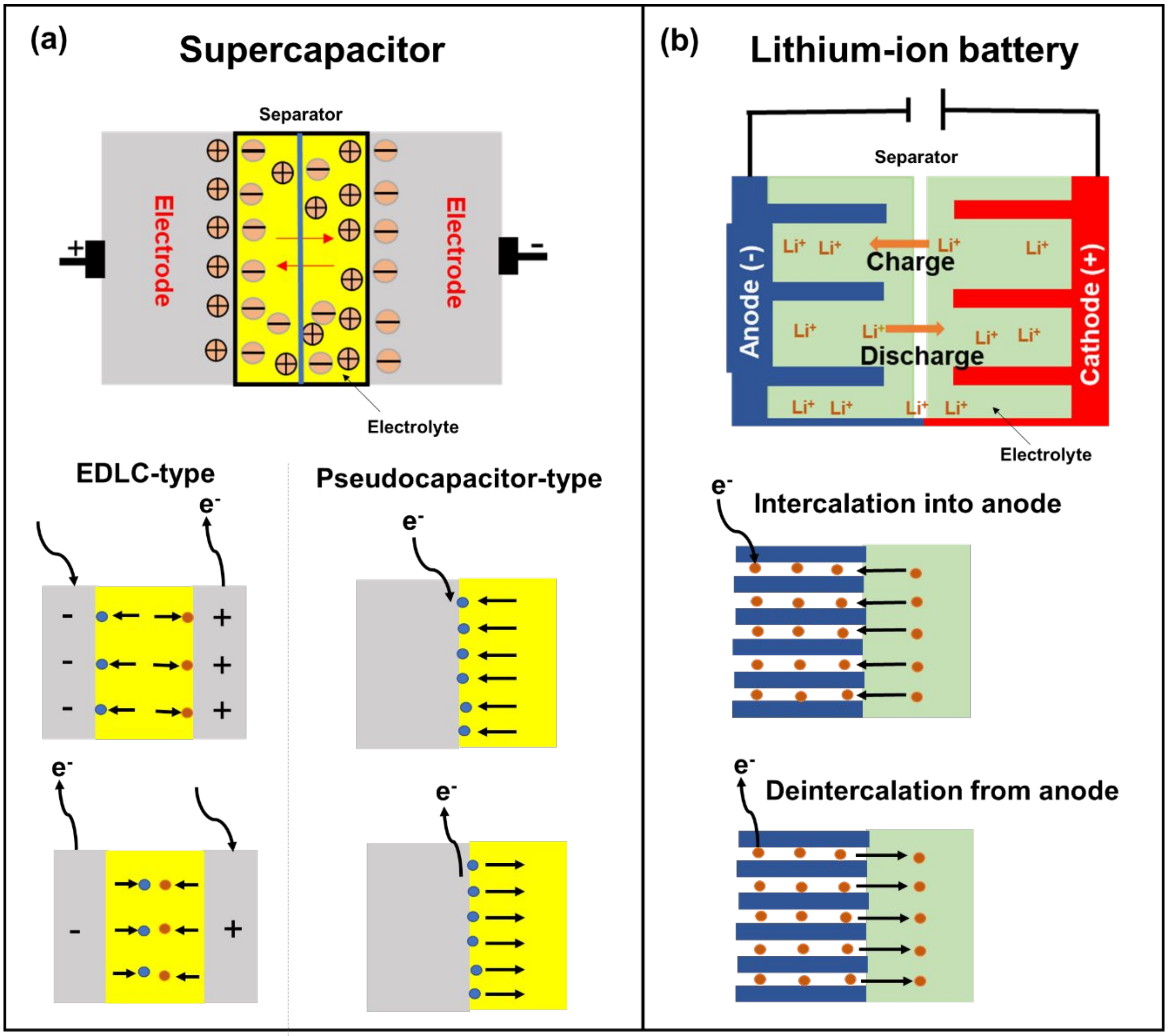

Figure 4: Schematic representation of the working principle of (a) SCs and (b) LIBs.

2. Covalent functionalization of graphene with redox-active organic molecules for SCs.

2.1. Small redox-active molecules-functionalized graphene for SCs

SCs are attractive for high power applications because of their ability to rapidly store/release electrical energies.[95–97] High-performance SCs should have large specific capacitances, high-power capabilities, and ultra-long cycle lives. Among the proposed applications of graphene-based materials, SCs, also known as electrochemical capacitors, have attracted much attention for the past decade. Compared with secondary batteries, graphene-based SCs are electrochemical energy storage devices that promise outstanding power density, charge/discharge rate, cycling stability, and operational safety.[98] SCs are often utilized individually or in tandem with batteries for energy storage and supply. Based on their energy storage mechanisms, SCs are mainly classified into electrical double-layer capacitors (EDLCs) and pseudocapacitor.[99,100] EDLCs store energy by electrostatic charge accumulation at electrode/electrolyte interfaces, while the pseudocapacitance is mainly attributed to the redox reactions at electrode surfaces (Figure 4a).

The covalent attachment of redox-active molecules to graphene has been proven to be a viable means of increasing electron transfer rates and preventing the dissolution of redox-active material, leading to a good cycle life.[101] When redox-active molecules are covalently attached on graphene, they can represent reversible reactions; therefore, electrodes can have both pseudocapacitance and EDLC mechanism simultaneously. Thus, the energy density of the electrode enhances and results in a stable behavior without any structural disturbance. Selected examples are summarized in Table 1. Reduced graphene oxide (RGO) was functionalized with phenylenediamine (RGO-PD),[102] 2-aminoanthraquinone (RGO-AAQ),[103] and 2-aminopyrene-3,4,9,10-tetraone (RGO-PYT)[104] through nucleophilic ring-opening reaction of epoxide group and applied for SCs. The resulting composite materials showed a capacitance retention of 92%, 100%, and 100%, respectively. The covalently bonded redox-active moieties contribute to the pseudocapacitance. Graphene provides a large specific surface area for forming electric double layers, works as a host material for the redox-active molecules, and promotes charge transfer and electrolyte diffusion. Edges of graphene can be functionalized by cyclization reaction at carboxylic groups.[59,105] The prepared composite material displays a capacitance retention of 98% after 9000 cycles. The cyclization reaction does not destroy the in-plane sp^2 framework of graphene, allowing better electrical conductivity. However, this functionalization method requires phosphoric acid catalyst and multistep reactions. Thiourea functionalized GO (RGO-TU) was prepared through amide bond.[106] The specific capacitance of the material increases slightly in the initial cycles and then become stable with no obvious loss in specific capacitance after long cycling. We assume that the sulfur-containing thiourea is activated in the first few cycles and undergoes redox reaction. In another report, adenine (AD) was functionalized on GO (GO-AD) through amide bond.[107] The GO-AD electrode exhibited excellent cycling retention of 100% after 1000 cycles. But, the reaction was performed at room temperature; therefore, the functionalization might occur only at the epoxide groups instead of carboxyl groups. Another approach for graphene functionalization is diazonium chemistry. Anthraquinone (AQ) molecules were grafted on graphene through diazonium chemistry, forming covalently linked graphene framework (G-AQ). Covalently linked AQ molecules worked as pillars to construct graphene framework and prevented the restacking of graphene sheets during fabrication processes. The capacitance retention of G-AQ was 96% after 5000 cycles.[108] Similarly, 2-amino-3-chloro-1,4-naphthoquinone (ACNQ) molecules were introduced onto graphene via diazonium chemistry (G-CNQ).[109] The electrode exhibited a long cycling life, nearly no loss after 10,000 cycles. Diazonium chemistry is simple, fast, and efficient. The key species of the reaction is an aryl radical, which readily adds to carbon frameworks at the basal planes and edges, achieving a sufficient introduction of functional groups. To summarize this section, the order of the desirable functionalization is diazonium chemistry > cyclization > amidation reaction > reaction through epoxide group (Figure 5), although the investigation may not be comprehensively performed.

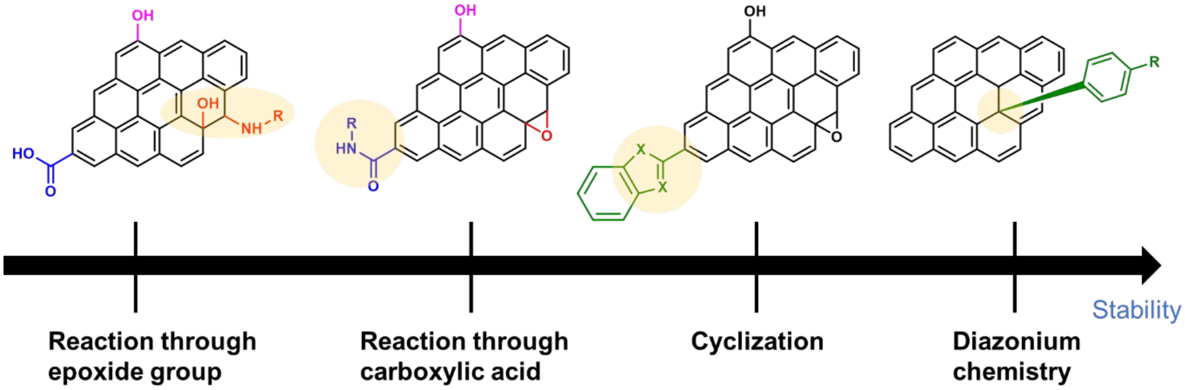

Figure 5: Comparison of different covalent functionalization methods toward electrochemical stability.

Table 1: Small redox-active molecules-functionalized graphene for SCs

Material	Functionalization reaction	Cycle number	Capacity retention	Ref
RGO-PD	Ring opening of epoxide	1000	92%	[102]
RGO-AAQ	Ring opening of epoxide	1000	100%	[103]
RGO-PYT	Ring opening of epoxide	25000	100%	[104]
G-BBO	Cyclization (phosphoric acid-catalyzed cyclization reaction)	9000	98%	[59]
G-BO	Cyclization (phosphoric acid-catalyzed cyclization reaction)	2000	100%	[105]
RGO-TU	Amidation and ring opening of epoxide	10000	100%	[106]

GO-AD	Amidation (mixing and heating)	1000	100%	[107]
G-AQ	Diazonium chemistry	5000	96%	[108]
G-CNQ	Diazonium chemistry	10000	100%	[109]

2.2. Conductive polymer functionalized graphene for SCs

Polymer-based SCs offer some unique properties such as controllable solubility, precise optimization of potential, variety of counter ions, flexible or even bendable electrodes and, subsequently, devices can be fabricated.[110] Various graphene–polymer composites with non-covalent and covalent interaction have been synthesized, and high capacitive performances have been achieved. The non-covalent interaction between graphene and polymers limits charge transfer at their interface and causes volumetric change during the charge-discharge cycles, reducing the cycling stability when applied for electrode materials.[111–114] To overcome this issue, polymers were introduced on graphene through covalent bond. At the same time, the polymer structure plays important roles, both in stability and capacitance. Various types of polymers have been introduced on graphene through covalent bond and applied for SCs. PANI was functionalized on RGO (RGO-PANI) through introduction of carboxyl group on RGO, amidation, followed by oxidative polymerization. Diazonium chemistry is widely employed for the covalent functionalization of RGO, because it can prevent the graphene sheets from aggregating during the functionalization. In addition, RGO can provide an excellent conducting path to the grafted PANI and improve the charge transport of PANI. The cycling stability of nanocomposite after 1000 cycles was 72% of the initial capacitance.[115] Similarly, poly(3,4-ethylenedioxythiophene) was covalently grafted onto RGO, which was prefunctionalized with thiophene by diazonium chemistry (RGO-PEDOT). Thiophene was used as linker, followed by chemical polymerization. Thiophene unit on GO promotes the selective polymerization with EDOT at the 2- and 5-positions of thiophene, forming covalently grafted GO-PEDOT. The prepared material showed a capacitance retention of 80% after 1000 cycles.[116] Also, PANI was introduced on RGO using PD as an linker. The capacitance retention in a range of 82%-90% was obtained.[117–119] These results suggest that the type of linker affect the electrochemical stability. Using cyclization reaction, 1,3-bis(2-benzimidazolyl)-5-aminobenzene was functionalized on RGO (RGO-BOA). The capacitance retention of electrode materials was 87% after 5000 cycles.[120] Through amide linkage, melamine was functionalized on RGO (RGO-M), and then nanocomposite with polyorthoaminophenol was prepared (RGO-M-PAP). The prepared material was applied as an electrode, with a capacity retention of 90% after 1000 cycles.[121] This result suggests that nitrogen-containing RGO has the potential to improve the electrochemical behavior of SCs. In another work, PPD was functionalized on RGO (RGO–

PPD) through amide bond, using thionyl chloride activation method, followed by polymerization. The composite exhibits excellent cycling stability, maintaining 90% of its initial capacitance after 1000 cycles.[122] The excellent supercapacitor properties rely on the polymer nanoparticles wrapped within or on the graphene surface, providing a large surface area and high pore volume of RGO. To further improve the electrochemical performance, organic dopant was introduced into the structure of PANI which is covalently functionalized on the surface of graphene (G-PANI) through diazonium chemistry. The resulting material showed high electrochemical stability in cycling, with 95% of capacitance retention after 1000 cycles.[123] The synthesized composites showed a unique hierarchical morphology, which increased the accessible surface area for the redox reaction and allowed faster ion diffusion for excellent electrochemical performance. Recently, we reported graphene–polymer composite through ring opening reaction of epoxides (RGO-SBP). The composite was synthesized using a three-step reaction involving a cross-linker, initiator, and monomer. The prepared material demonstrated a cycling stability of 98% after 1000 cycles.[124] Furthermore, RGO was functionalized with a redox-active thiourea-formaldehyde polymer (TF), yielding a multifunctional hybrid system (RGO-TF). The functionalization of the RGO was performed by thiol-carboxylic-acid esterification. The presence of multiple functional groups comprising sulfur, nitrogen, and oxygen provide additional contribution of faradaic redox reaction in SCs, leading to effective pseudocapacitances. The prepared material exhibited good cycling stability with a capacitance retention of 100% after 5000 cycles.[125] The literature reveals that the most important point for the electrochemical stability is the structure of polymer along with covalent connection. The introduction of proper linker, and construction of multifunctional polymer increase the stability as well as the specific capacitance of polymer-graphene composites.

Table 2: Conductive polymer functionalized graphene for SCs.

Materials	Functionalization reaction	Cycle number	Capacity retention	Ref
RGO-PANI	Diazonium chemistry	1000	72%	[115]
RGO-PEDOT	Diazonium chemistry	1000	80%	[116]
RGO-PANI	Diazonium chemistry	2000	83%	[117]
RGO-PANI	Ring opening of epoxide	10000	82%	[118]
RGO-PANI	Ring opening of epoxide	1000	81%	[119]
RGO-BOA	Cyclization	5000	88%	[120]
RGO-M-PAP	Amidation	1000	90%	[121]
RGO-PPD	Amidation ($SOCl_2$ activation)	1000	90%	[122]
G-PANI	Diazonium chemistry	1000	95%	[123]
RGO-SBP	Ring opening of epoxide	1000	98%	[124]
RGO-TF	Esterification	5000	100%	[125]

3. Covalent functionalization of graphene with redox-active organic molecules for LIBs

3.1. Small redox-active molecules-functionalized graphene for LIBs

Small organic molecules covalent grafted onto the surface of graphene can result in a high capacity and maintain excellent cycling stability in LIBs. To date, several approaches for covalent functionalization of graphene have been reported (Table 3). AQ was grafted on RGO (RGO-AQ) through nitrene chemistry. The material showed a capacity retention of

70% after ten cycles in LIBs.[126] The cycling stability of the material decreases significantly, indicating the formation of RGO-AQ via nitrene is not ideal. To further improve the electrochemical stability, graphene was functionalized with an organic radical, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy-TEMPO), through esterification reaction. This composite has an electrically conductive network of graphene sheets with abundant electrochemically active nitroxide radical functionalities. However, when the prepared material was applied as an electrode, the capacity decreases in the first few cycles, suggesting the instability of the ester bond.[127] Esterification was also investigated for the functionalization of tetrahydroxybenzoquinone (THBQ) on GO (GO-THBQ). GO-THBQ was applied as electrode for LIBs and demonstrated a cycling stability of 68% after 2000 cycles.[128] Similarly, carboxyl-enriched RGO was functionalized with nitroxide radical (RGO-NO) via one-step esterification. The capacity retention of RGO-NO was 89% after 2000 cycles, derived from the folded RGO-NO structure that shortens the distance of electron transport between radicals.[129] These results suggest that ester bonding is not stable. In another report, *N,N′*-diamino-1,4,5,8-naphthalenetetracarboxylic bisimide (DNTCB)-functionalized GO (GO-DNTCB) was prepared by amidation. The resulting material showed a capacity retention of 85% after 50 cycles in LIBs electrode.[130] Similarly, GO was functionalized with naphthalenediimide diamine (NDIDA) through amide bond (GO-NDIDA), using conjugating linker. GO-NDIDA exhibits a capacity retention of 100% after 50 cycles with the aid of conjugated linker (aniline).[131] These results suggested that the introduction of a conjugated linker between graphene and redox-active molecules can improve the electrochemical stability. The functionalization of graphene through the amide bond is the better approach to achieve stability under electrochemical reactions. This is because amide is the most stable form in carboxyl acid derivatives.

To summarize this section, the order of the desirable functionalization is amidation > esterification > nitrene chemistry (Figure 6), although there is still room for consideration.

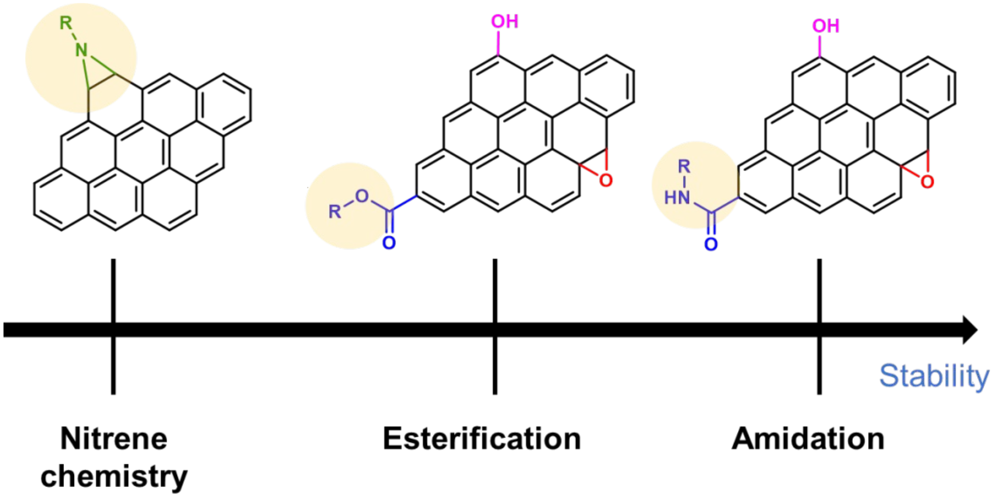

Figure 6: Comparison of different covalent functionalization methods of graphene toward electrochemical stability.

Table 3: Small redox-active molecules-functionalized graphene for LIBs

Material	Functionalization reaction	Cycle number	Capacity retention	Ref
RGO-AQ	Cyclization (nitrene chemistry)	10	70%	[126]
GO-TEMPO	Esterification ($SOCl_2$ activation)	400	65%	[127]
GO-THBQ	Esterification (simple mixing)	2000	68%	[128]
RGO-NO	Esterification ($SOCl_2$ activation)	200	89%	[129]
GO-DNTCB	Amidation (coupling reagent)	50	85%	[130]
GO-NDIDA	Amidation (coupling reagent) and conductive linker	50	100%	[131]

3.2. Conductive polymer functionalized graphene for LIBs

Surface covalent functionalization of graphene sheets by polymers has been verified as an effective approach to keep the sheets from restacking in the composite materials, which is a different solution to allow utilization of the surface groups of graphene sheets.[132,133] Covalently grafted graphene with polysulfur (G-PS) was synthesized through inverse vulcanization, and applied for ultra-high loading Li−polyS batteries.[134] The prepared material showed a capacity retention of 67% after 100 cycles. Graphene sheets improve the conductivity and stability of polysulfides matrix. The nitroxide radical polymer, poly(2,2,6,6-tetramethylpiperidinyloxy-4-ylmethacrylate) (PTMA), gains attention as a promising cathode material for high-rate, organic radical batteries, which is also called as organic radical polymer battery.[135] Graphene covalently functionalized with radical polymer (G-PTMA), via surface-initiated atom transfer radical polymerization, and applied for LIBs. After 250 cycles, the capacity retention of the prepared material was almost 70%. The covalently bonded PTMA could interact with graphene sheets at a molecular level, improving electron and ion transportation. G-PTMA could also inhibit the restacking of graphene sheets during the electrode fabrication process.[136] However, this method requires several preparation steps, which is time-consuming and requires metallic catalyst.

To summarize this section, atom transfer radical polymerization reaction showed relatively good electrochemical stability than synthesis and grafting of polymer through inverse vulcanization.

Table 4: Conductive polymer functionalized graphene for LIBs

Materials	Functionalization reaction	Cycle number	Capacity retention	Ref
G-PS	Ring opening of epoxide and Inverse vulcanization	100	67%	[134]
G-PTMA	Diazonium chemistry and atom transfer radical polymerization	250	70%	[136]

4. Covalent functionalization of other CBMs with redox-active organic molecule for SCs

4.1. Small redox-active molecules-functionalized other CBMs for SCs

Chapters 2 and 3 dealt with the covalent functionalization of graphene. In this section, covalent functionalizations of other CBMs are summarized. Covalent functionalization of other CBMs with redox-active molecules improved the stability and the electrochemical performance of electrode materials. MWCNTs were functionalized with aromatic azides via nitrene chemistry and applied for SCs. Capacitive retention was above 85% after 1000 charge/discharge cycles in different electrolytes.[137] Organic molecules having specific functional groups enhance the dispersion stability of MWCNTs in different electrolytes and device performance. Catechol was grafted on high surface area Black Pearls 2000 carbon using spontaneous reduction of catechol diazonium salt in situ prepared in aqueous solution from the corresponding amine (BP-cat). The capacitance retention of the prepared composite was 89% after 2000 cycles.[138] Ali et al. functionalized MWCNTs with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (MWCNTs-TEMPO), using oxidized MWCNTs and followed by amide bond formation with amino-TEMPO. The capacity retention of the composite was 90% after 4000 cycles in symmetrical SCs.[139] The covalent functionalization of MWCNTs with redox-active material ensures good cycling stability. Carbon nano-onions (CNOs) was functionalized through an amidation reaction that occurs between the oxidized CNOs and 4-(pyren-4-yl)butanehydrazide (Pyr) and used as electrode materials for SCs. The CNO-Pyr electrodes exhibited 99% retention from its initial value after 1000 cycles.[140] The functionalization of carbon material through amidation reaction is stable under electrochemical conditions. The reason for high stability for amide bond is also discussed in Section 3.1.

To summarize this section, the order of the desirable functionalization in the viewpoint of electrochemical stability is amidation reaction > diazonium chemistry > nitrene chemistry (Figure 7).

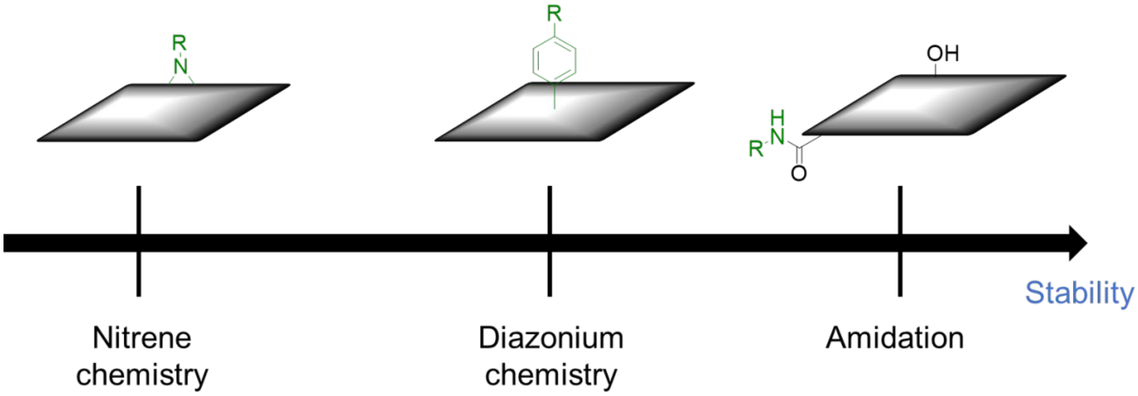

Figure 7: Comparison of different covalent functionalization methods of other CBMs toward electrochemical stability.

Table 5: Small redox-active molecules-functionalized other CBMs for SCs

Materials	**Functionalization reaction**	**Cycle number**	**Capacity retention**	**Ref**
MWCNTs-AZ	Cyclization (nitrene chemistry)	1000	85%	[137]
BP-cat	Diazonium chemistry	2000	89%	[138]
MWCNTs-TEMPO	Amidation (coupling reagent)	4000	90%	[139]
CNO-Pyr	Amidation	1000	99%	[140]

4.2. Conductive polymer-functionalized other CBMs for SCs

Physical mixing of polymer tends to degrade during the long-term charge-discharge process and leads to peeling off from CBMs, deteriorating the electrodes’ performance. The physical contact between CBMs and polymer may also slow down the charge transfer, causing a decrease in the overall performance of electrodes. In addition, phase-separation generally occurs for polymers, which hampers the formation of uniform composites. Covalent connection of polymers with CBMs are expected to solve these problems. PANI was grafted on MWCNTs through multi-amino dendrimer (PAMAM) linker, affording MWCNTs-PANI electrode composites for SCs. Under the successive charging-discharging cycle, the specific capacitance of MWCNTs-PANI retained 85% after 50 cycles.[141] Covalently functionalized PAMAM on MWCNTs provides more reaction sites for in-situ polymerization of ordered PANI, which can shorten the ion diffusion length and lead to full use of redox-active materials. In order to further improve the electrochemical stability, poly(benzodithiophenylcarbazole) (PBDTC) was grafted on MWCNTs through Williamson reaction. The capacitance retention of the prepared composite (MWCNTs-PBDTC) was 96% after 5000 cycles.[142] However, this method employed several preparation steps and metallic catalyst, which make this process less efficient. In another report, crosslinked C-CNTs/PANI composite was prepared by diazonium chemistry. In the first step, PD was functionalized with CNTs through diazonium chemistry. In the second step 1,4-benzoquinone was introduced as a spacer between the functionalized CNTs. Finally, aniline monomer was added and performed oxidative polymerization on cross linked CNTs. The composite retains 95% of its initial specific capacitance after 1000 cycles.[143] This result suggest that the introduction of redox-active molecule as a spacer, improving the electrochemical stability and electrochemical performance. Redox-active molecules as a spacer avoid the aggregation of CNTs and contribute in electrochemical reaction at a same time. The order of the desirable functionalization in the viewpoint of electrochemical stability is etherification ≥ diazonium chemistry > amidation reaction (Figure 8).

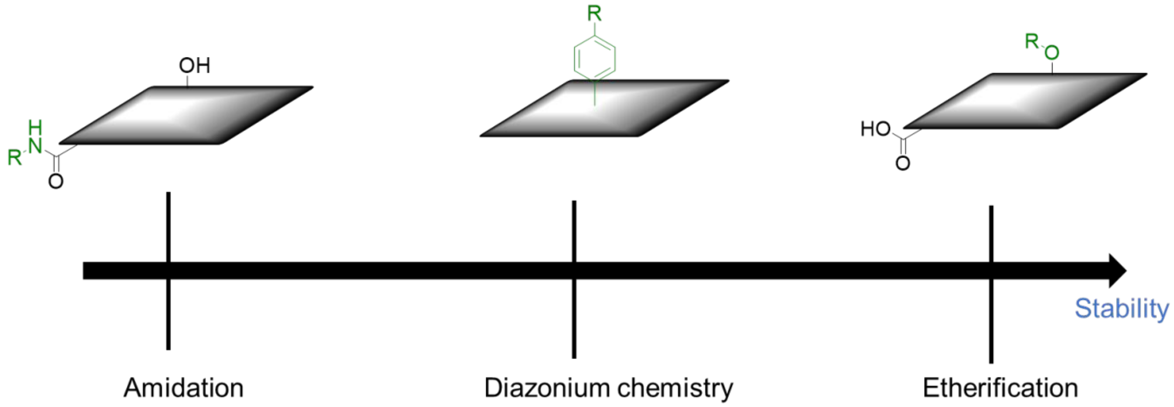

Figure 8: Comparison of different covalent functionalization methods of other CBMs toward electrochemical stability.

Table 6: Conductive polymers functionalized other CBMs for SCs

Materials	**Functionalization reaction**	**Cycle number**	**Capacity retention**	**Ref**
MWCNTs-PANI	Amidation ($SOCl_2$ activation)	2000	85%	[141]
MWCNTs–PBDTC	Etherification (Williamson reaction)	5000	96%	[142]
C-CNTs/PANI	Diazonium chemistry	1000	95%	[143]

5. Covalent functionalization of other CBMs with redox-active organic molecules for LIBs.

CBMs show high electronic conductivity and serve as support materials for covalent immobilization of the redox-active molecules for LIBs application, however, there reported only a few examples. 9,10-phenanthrenequinone (PAQ) was functionalized on Ketjen black (KB-PAQ) through diazonium chemistry and applied for LIBs. The electrode is capable of charging and discharging for 500 cycles, preserving 71% of the initial capacity.[94] Covalent functionalization improves the cycling stability of the electrode. MWCNTs were functionalized with a disulfide molecule (DS) through diazonium chemistry (MWCNTs-DS). The electrode material includes disulfide bonds that can react with lithium during the discharge of the batteries. The MWCNTs play the double role of scaffold for the functionalization and of electronic conductor in the electrodes. The covalently functionalized system presents 95% of the initial capacity after 50 cycles.[144] By grafting anthraquinone diazonium salts to MWCNTs (MWCNTs-AQ), 98% of the initial capacity was retained after 50 cycles.[145] Besides covalent functionalization, the structure of redox-active molecules also plays great role in the stability of electrode.

Table 7: Small redox-active molecules-functionalized other CBMs for LIBs

Materials	**Functionalization reaction**	**Cycle number**	**Capacity retention**	**References**
KB-PAQ	Diazonium chemistry	500	71%	[94]
MWCNTs-DS	Diazonium chemistry	50	95%	[144]
MWCNTs-AQ	Diazonium chemistry	50	98%	[145]

6. Conclusive remarks in the viewpoint of electrochemical stability

6.1 Covalent interaction vs non-covalent interaction

The stability and electrochemical performance of the CBMs electrodes rely on the functionalization methods. Chemical functionalization of CBMs has been performed via either covalent or non-covalent (including π–π, ionic, and hydrophobic interaction etc) bonding to improve the performance of the electrode materials. Here, we take PANI as an example. The covalently grafted GO-PANI by diazonium chemistry showed a capacitance retention as high as 83% over 2000 charge-discharge cycles, while non-grafted (physically mixed) PANI/GO only retained 68% of capacitance after 2000 cycles.[117] Further, PANI covalently functionalized with MWCNTs through amide bond, which retained a capacitance of 85% after 2000 cycles, while non-covalently bonded PANI on MWCNTs retained only 61% after 2000 cycles.[141] These results suggest that covalent binding of redox-active organic molecules with CBMs improves stability.

6.2 Covalent functionalization of small redox-active molecules on CBMs

The dissolution of the redox-active component into electrolyte results in low cycling stability and inadequate electrochemical performance, which have limited the practical use of organic electrode materials. To solve the problem, several strategies have been proposed to alleviate the dissolution, such as using the solid-state electrolytes, optimizing molecular structure, and polymerization of small molecules into insoluble materials. Covalent binding of redox-active organic molecules to CBMs has been demonstrated to be a promising strategy, which improves the transfer rate of electron and prevents the dissolution of the redox-active material. For example, GO was functionalized with THBQ through covalent bond and applied for LIBs. The covalently functionalized material (GO-THBQ) showed a capacity retention of 68% after 2000 cycles. The cycling stability of THBQ was decreased significantly after a few cycles due to dissolution in the electrolyte.[128] Similarly, GO-DNTCB composite was prepared through covalent bond and applied for LIBs. The covalent composite demonstrated a capacity retention of 85% after 50 cycles. In comparison, the capacity retention of DNTCB electrode without covalent binding was 16%, after 50 cycles, due to a significant dissolution in the electrolyte.[130] Thus, organic molecules covalently grafted onto the surface of CBMs show excellent cycling stability.

6.3 Covalent functionalization of conducting polymers on CBMs

Similarly, conductive polymers suffer from the retention of specific capacitance because of their large volume change and ion dissolution during the charge–discharge processes. To address these shortcomings, polymers are combined with CBMs through covalent bond, to improve its cycle life. For example, GO-PEDOT was prepared through covalent bonding using diazonium chemistry. Electrochemical analysis suggested that GO-PEDOT showed relatively good cycling stability with capacitance retention of 80% after 1000 cycles than 69% of PEDOT without grafting.[116] MWCNTs was functionalized with polymer through covalent bond and applied for SCs. The covalently functionalized MWCNTs (MWCNTs-PANI) showed a capacity retention of 85% after 2000 cycles. The capacitance of PANI without covalent grafting continued to decrease throughout the cycling process; the value decreased to 35% of its initial value.[141] The covalent functionalization provides a high surface area, uniform distribution, and unique structure, which compensate for the swelling and shrinking of the polymer network during cycling.

7. Conclusion and future prospective

We have summarized the covalent functionalization of CBMs with redox-active small molecules and polymers and compared their performances for SCs and LIBs. CBMs have been functionalized by diazonium chemistry, amidation reaction, ring-opening reaction of epoxide group, cyclization reaction, esterification reaction, nitrene chemistry, etherification reaction and radical reaction (Table 8). Among these reactions, diazonium chemistry has been mostly employed for the functionalization of CBMs because many types of aromatic amines, which are the precursors of diazonium, are commercially available, and the synthesis and use of diazonium salts only necessitates one or a few steps. Amidation is another useful functionalization method of CBMs. The reason may be the well-established carboxyl group transformations; however, amide bonds can be cleaved under acidic conditions by hydrolysis.

The covalently bonded composites prevent the dissolution of small redox-active molecules, stabilize the polymer structure, and show better electrochemical stability than non-covalently bonded ones. The literature survey reveals that comprehensive research has not been done on the covalent functionalization of CBMs for SCs and LIBs applications, despite the development of various types of organic transformations in recent years. Only a few traditional reactions have been employed for the functionalization of CBMs (Figure 9). Interestingly, there reported quite a limited number of papers on the covalent functionalization of classic carbons, such as carbon black, ketjen black, and activated carbon; most of the studies focused on the functionalization of novel nanocarbons, such as graphene and CNTs. Therefore, further investigation is needed combining traditional and latest chemical transformations and classical carbons and nanocarbons for developing advanced electrochemical electrode materials.

Table 8: Characteristics and issues of each covalent functionalization method.

Methods for functionalization of CBMs	**Characteristics**	**Issues**
Diazonium chemistry	Simple, stable, basal-plane functionalization	Disrupt the sp^2 framework, side reactions can occur
Amidation	Preserve the sp^2 framework, well-established chemistry, stable	Functionalization only at the edge, harsh reaction condition, hydrolysis can occur
Ring opening of epoxide	Simple, mild condition, basal-plane functionalization	Disrupt the sp^2 framework, less stable
Cyclization	Stable, preserve the sp^2 framework	Harsh reaction conditions (phosphoric acid), multistep reaction
Esterification	Preserve the sp^2 framework, strong	Harsh reaction condition ($SOCl_2$ activation), less stable (hydrolysis), functionalization only at the edge
Nitrene chemistry	Simple, basal-plane functionalization	Harsh reaction conditions (180 °C), less stable
Etherification	Stable, basal-plane functionalization	Harsh reaction condition, disrupt the sp^2 framework

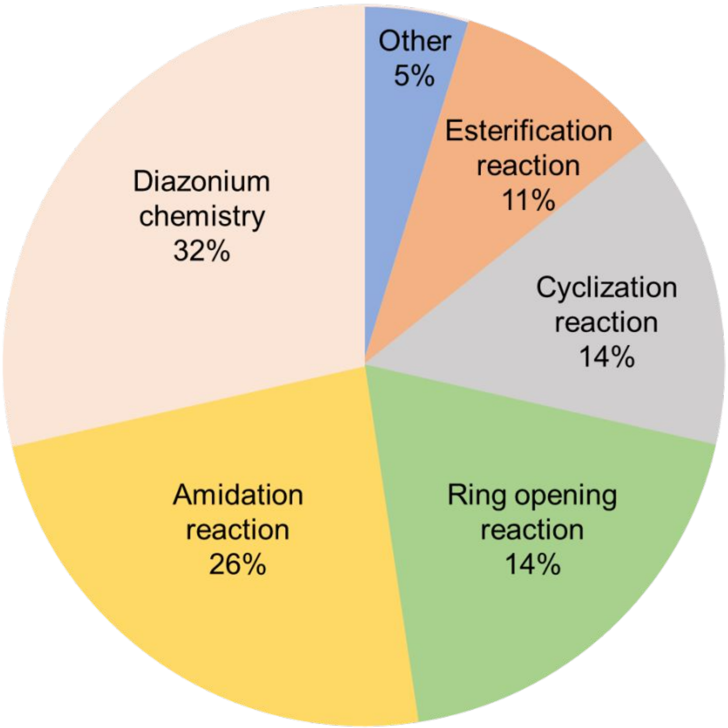

Figure 9: Methods for the covalent functionalization of CBMs with redox-active molecules,

Table 9: List of abbreviation

Full name	Abbreviation
Carbon-based material	CBMs
Graphene oxide	GO
Reduced graphene oxide	RGO
Carbon nanotubes	CNTs
Single-walled carbon nanotubes	SWCNTs
Multi-walled carbon nanotubes	MWCNTs
Supercapacitors	SCs
Electrical double-layer capacitors	EDLCs
Lithium ion batteries	LIBs
Polyaniline	PANI
Phenylenediamine	PD
Poly(phenylenediamine)	PPD
Amino-anthraquinone	AAQ
Anthraquinone	AQ
2-amino-3-chloro-1,4-naphthoquinone	ACNQ
3-chloro-1,4-naphthoquinone	CNQ
2-aminopyrene-3,4,9,10-tetraone	PYT
Thiourea	TU
Adenine	AD
Benzobisoxazole	BBO
Benzoxazole	BO
Poly(3,4-ethylene dioxythiophene)	PEDOT
1,3-bis(2-benzimidazolyl)-5-aminobenzene	BOA
Polyorthoaminophenol	PAP
N,N′-bissulphinyl-m-benzenediamine-p-phenylenediamine	SAB
Thiourea-formaldehyde	TF
2,2,6,6-tetramethylpiperidin-1-oxyl	TEMPO
Tetrahydroxybenzoquinone	THBQ
Nitroxide	NO

Naphthalenediimide diamine	NDIDA
N,N′-diamino-1,4,5,8-naphthalenetetracarboxylic bisimide	DNTCB
Polysulfur	PS
Poly(2,2,6,6-tetramethylpiperidinyloxy-4-ylmethacrylate	PTMA
Carbon nano-onions	CNO
4-(pyren-4-yl)butanehydrazide	Pyr
poly(benzodithiophenylcarbazole)	PBDTC
9,10-phenanthrenequinone	PAQ
Ketjen black	KB
Disulfide	DS

Conflicts of interest

The authors declare no conflict of interest.

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