A brief review for fluorinated carbon: synthesis, properties and applications

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Abstract: Fluorinated carbon (CFₓ), a thriving member of the carbonaceous derivative, possesses various excellent properties of chemically stable, tunable bandgap, good thermal conductivity and stability, and super-hydrophobic due to its unique structures and polar C-F bonding. Herein, we present a brief review of the recent development of fluorinated carbon materials in terms of structures, properties and preparation techniques. Meanwhile, the applications in energy conversions and storage devices, biomedicines, gas sensors, electronic devices, and microwave absorption devices are also presented. The fluorinated carbon contains various types of C-F bonds including ionic, semi-ionic and covalent C-F, C-F₂, C-F₃ bonds with tunable F/C ratios. The controllable designing of C-F bonding and F/C ratios play a key role to optimize the properties of fluorinated carbon materials. Until now, the potential issues and future opportunities of fluorinated carbon are proposed. The present review will provide a direction for tuning C-F bonding and F/C ratios, developing a safe and efficient fluorination method and popularizing the applications of fluorinated carbon materials.

Keywords: fluorinated carbon, C-F bonds and F/C ratios, applications

1 Introduction

Fluorinated carbon (CFₓ) is a promising member of the carbon derivative family since graphite fluoride was synthesized by Ruff et al. in 1934 firstly [1]. Due to its extraordinary properties, such as good chemical stability, tunable bandgap, good thermal conductivity and stability, and super-hydrophobicity [2–6], fluorinated carbon materials attracts more and more attention. So, fluorinated carbon is a potential material in wide application fields such as self-cleaning, lubricants, super-hydrophobic coating and energy storage [7–11]. The synthesis methods of fluorinated carbon can be mainly classified into direct gas fluorination, indirect fluorination and plasma-assisted fluorination [12–14]. The C-F bonds and the F/C ratios deeply depend on the raw carbon materials and fluorination conditions including fluorinating agents, temperature and reaction time [15–17]. Thus, the key point of fluorinated carbon materials is mainly about the design of carbon materials and the optimization of fluoridation conditions.

The C-F bonds are formed based on the fluorination reactions between carbon materials and fluorinating agents. Because the F atom has extremely strong electronegativity, fluorinated carbon involves various C-F bonding characteristics of ionic, semi-ionic, and covalent bonds [18–20]. Besides, based on theoretical calculation, the C-F bonds depend on the fluorination levels (F/C ratios) [15]. The C-F bonds and F/C ratios have significant effects on the properties of fluorinated carbon materials. For instance, fluorinated carbon is considered as a promising cathode material for high-performance lithium batteries because of its high theoretical energy density of 2180 W h kg⁻¹ and specific capacity of 865 mA h g⁻¹ (for Li/CF₁₀) with a voltage platform of 4.5-5 V for a purely ionic C-F bond [21–23]. However, the low specific capacity is delivered due to an
extremely small F/C ratio when the ionic C-F bond is developed only [24]. In the case of ultra-high F/C ratio, the rate performance is deteriorated because of the large number of covalent bonds resulting in a poor conductivity [25]. Thus, optimizing the composition of C-F bonds and F/C ratios is an efficient approach to obtain fluorinated carbon with high performance.

Up to now, great progress has been achieved in the research of fluorinated carbon. In this brief review, we summarize the recent development of structure, properties, selection of carbon source and optimization of fluorination conditions during the preparation and applications of fluorinated carbon. Meanwhile, this paper also proposes the potential issues and future opportunities and provides the direction for the advances and applications of fluorinated carbon.

2 Synthesis of fluorinated carbon materials

2.1 Structure of fluorinated carbon

Typically, there are three types of fluorinated carbon as shown in Figure 1. The structure characteristics of fluorinated carbon mainly include C-F bonds and F/C ratios, which can determine the physical/chemical features of materials. Therefore, it is significantly important to deeply understand the structure for tuning the properties of fluorinated-carbon.

For C-F bonds of fluorinated carbon, the extremely high electronegativity of fluorine endows the C-F bonds varying from ionic bonds, through semi-ionic bonds, to covalent bonds, which results in more electrostatic character in the C-F bonds [26]. It was found that the ionic C-F
Figure 2: F-C bond length (ordinates) and F1s core-level energy shift (abscissa) of fluorine species chemisorbed on graphene in various bonding environments. From left to right, F bonded to edge C atoms of an armchair-type graphene edge, energetically most stable F-C tetraters, trimers, and dimers, and an individual fluorine species chemisorbed on a pristine region of graphene (bottom) and nearby a tightly packed agglomerate of F−C bonds on graphene (top). The color (dash) and the number of the vertical segments and open circles are used to establish the correspondence between core-level energy shift and the fluorine species drawn in the ball-and-stick illustration. The height of the vertical segments is used to show the length of the F−C bonds in the various bonding environments. The F1s core-level binding energies calculated from DFT are referred to that as F in single F−C species (8) chemisorbed on a pristine region of graphene. The core-level energy shift of an F anion in bilayer graphene is also reported on the right (vertical dashed segment). Reprinted with permission from [15].

bonds are typically only formed when the percentage of F in fluorinated carbon is extremely small (e.g., x<0.05 in CFx for graphite fluoride), which makes no sense for its applications, especially for energy storage. The semi-ionic C−F bonds are of great significance to the properties of fluorinated carbon. Sato et al. demonstrated the existence of semi-ionic C−F bonds in first stage fluorine-graphite intercalation [27]. Moreover, Zhu et al. confirmed that the formation of semi-ionic C−F not only enhanced the discharge capacity and plateau but also provided good conductivity for significant power density [28]. Covalent C−F bonds own the characteristics of sp^3 C, where the angle of F−C−C is greater than 90° and the length of the neighboring C−C bond is about ~ 0.153 nm. So, a high covalent C−F ratio might destroy the conductive network of conjugate double bonds [29]. Meanwhile, the covalent C−F includes C−F, C−F_2, and C−F_3, the ratio of those bonds also have an effect on the properties of fluorinated carbon. Thus, reasonable tuning of the type of C−F bonds is one of the key factors in the regulation of fluorinated carbon properties.

The semi-ionic C−F bonds are essentially covalent, which differs from bonding formation and bond length [29]. In terms of theoretical calculation, Zhou et al. calculated the shifts in F1s energy level for various fluorine modes on graphene utilizing the core-excited pseudopotential technique [15]. Figure 2 exhibits the relationship between the level shift calculated for an isolated F and the C−F bond length. The shorter the bond, the higher the shift. And the authors concluded that the ionicity of the C−F bond depends strongly on the local chemical environment. The calculation shows that the core binding energy chemisorption of fluorine on graphene is about 3.5 eV and an intermediate core layer binding energy between the F anion in graphite and the covalent C−F bond at the edge of graphene is yielded by the F in the isolated C−F species. When the bonds loss some ionicity, they are closed to a highly fluorinated region of graphene. In the case of F−C
bonds forming orderly, the semi-ionic and semi-covalent F-C bonds packed domains of fluorinated graphene. Meanwhile, the C-F bonds with the length larger than 1.5 Å can be also attributed to semi-ionic bonds with diverse interaction strength.

Additionally, precise control of the F/C ratio of fluorinated carbon is also significant for tuning the bandgap and electrical conductivity as well as understanding the structural transformation such as type of bonds. In order to design the F/C ratios, many factors should be considered including fluorination time and temperature, fluorination agents (e.g. F$_2$, CF$_4$, XeF$_2$ and etc.), and carbon source (e.g. CNT, graphene graphite and etc.). Yu et al. reported that the F/C ratio of fluorinated graphene was controlled by the treatment time of CF$_4$-plasma [30]. Besides, Ahma et al. presented that higher fluorination temperature could result in a higher F/C ratio under a certain range [31]. Meanwhile, different F/C ratios could be controlled by direct fluorination with F$_2$ and indirect fluorination with TbF$_6$ [31].

2.2 Preparation methods of fluorinated carbon

Carbon is a precursor to synthesize fluorinated carbon materials. The main preparation methods including direct gaseous fluorination, wet chemical, and plasma fluorination were developed to synthesize fluorination carbon.

2.2.1 Wet chemical fluorination

The wet chemical method relays on a chemical reaction between the fluorine-containing solution and carbon-based solution to synthesis fluorinated carbon. The F/C ratios, size, and shape of the fluorocarbon are controlled by adjusting the concentration of the fluorine-containing solution and the reaction temperature.

2.2.2 Plasma fluorination

The plasma fluorination method has been investigated to generate free radicals to adsorb on the carbon substrate to form a C-F bond. Zhang Hui et al. synthesized a large-area single-layer fluorinated graphene (FG) by a controllable SF$_6$ plasma treatment method [32]. His research found that plasma treatment changes the fluorine content, and the maximum fluorine content reaches ~24.6 at% F for a 20s plasma treatment.

2.2.3 Chemical vapor deposition

The direct gaseous fluorination method is a method in which fluorocarbon material is synthesized in a gas atmosphere by using F$_2$-containing gas as a fluorinating agent. According to the different fluorine source addition methods and the reaction environment, three preparation methods were divided including dynamic fluorination method, static fluorination method, and thermal decomposition method. The dynamic fluorination method uses the flowing gases like F$_2$ and XeF$_2$ as fluorinating agents and fills them into the chemical vapor deposition (CVD) furnace to form a fluorocarbon bond. The formation of C-F bonds increases the number of defects on the surface and leads to structural variations of SWCNTs like an increase in diameter and a modification in chirality. The static fluorination method and the thermal decomposition method are both carried out in the closed vessels, but the fluorinating agents are added in different ways. The agent is employed via a continuous addition way to fluorinate the carbon substrate in the former method and the later method adopts a heating mix of solid agent and carbon substance to get the fluorination carbon substrate.

2.3 Properties of fluorinated carbon

Fluorinated carbon, owing to the properties of chemically stable, non-toxic, non-flammable, non-corrosive, excellent solvent-resistant, weather-resistant, as well as superhydrophobicity, is a promising insulating, waterproof and lubricating materials [33–36]. The low surface energy of fluorinated carbon results in a good lubricity. Moreover, it is difficult to break C-F bonds at high temperature, high pressure and different gaseous due to the large bonding energy, which endows and excellent lubricating properties under high temperature, high speed and high load conditions [34]. In addition, fluorinated carbon exhibits the highest theoretical specific capacity (865 mA h g$^{-1}$) for primary lithium battery, tunable bandgap, and good thermal stability and conductivity [37–39]. Fluorinated carbon with such remarkable properties has been widely researched and applied in the field of self-cleaning, lubricants, super-hydrophobic coating and energy storage, et al. Here, we give a simple comparison of the performances for fluorinated carbon and carbon materials applied in different fields in the Table 2. Compare to the properties of carbon and fluorinated carbon, CF$_x$ materials possess a lower friction coefficient than carbon, which demonstrates that the CF$_x$ materials have longer wear lives, lower friction coefficients and superior load-carrying capacities due
3 Two main factors for the preparation of fluorinated carbon

The synthesis methods of fluorinated carbon are typically classified into direct fluorination, indirect fluorination, and plasma-assisted fluorination. The direct fluorination refers to a method in which a fluorine gas or mixture of gases containing fluorine element is used as a fluorinating agent to direct reaction with carbon materials at a certain temperature and pressure [44]. Whereas, the indirect fluorination corresponds to a fluorination reaction in which fluorine radicals are generated at a decomposition temperature of a fluorine-containing solid or liquid substance [45]. The plasma-assisted method utilizes a plasma fluorine-containing gas, and commonly the fluorine source is CF$_4$ [46]. The introduction of plasma can achieve fluorination at normal temperatures, which can retain the structural characteristics of the carbon materials to the utmost extent. Fluorinated carbon prepared by different methods and conditions are summarized in Table 1. It can be drawn from the above methods that the carbon source and the fluorination conditions are two important factors determining the performance of the fluorinated carbon.

### 3.1 The reasonable design of carbon sources

In terms of carbon sources, a series of carbonaceous nanomaterials were investigated for fluorination such as zero-dimensional (0D) fluorinated fullerene C$_{60}$ [51, 52], one-dimensional (1D) carbon nanotubes and carbon nanofibers [11, 53, 54], as well as two-dimensional (2D) graphene [19, 55].

Fullerene C$_{60}$ is particularly fascinating because of its highly conjugated molecular structure, high electron-accepting and transporting properties. Grafting of strongly electronegative fluorine to C$_{60}$ has a significant effect on its electronic properties, and thus it is of great significance for the research of C$_{60}$ fluorination. Due to the abundance of active sites of C$_{60}$, the reaction with fluorine results in a composition range from C$_{60}$F$_2$ to C$_{60}$F$_{60}$ [56]. Attribution to the steric hindrance of the molecular surface during the

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**Table 1: Preparation methods and conditions for fluorinated carbon**

| Preparation method       | Carbon materials | Fluorinating agents | F/C ratios | Fluorination temperature | Fluorination time | Ref. |
|--------------------------|------------------|---------------------|------------|--------------------------|------------------|------|
| Direct fluorination      | MWCNTs           | F$_2$               | 0.983      | 450°C                    | 24 h             | [47] |
| Direct fluorination      | Graphene         | F$_2$               | 0.65       | 300°C                    | 1 h              | [37] |
| Direct fluorination      | Honeycomb GO     | F$_2$               | 1.02       | 180°C                    | 20 min           | [48] |
| Indirect fluorination    | carbon nanodiscs | TbF$_5$             | 0.95       | 550°C                    | 20 h             | [31] |
| Indirect fluorination    | SWCNTs           | XeF$_2$             | 0.05-0.32  | 180°C                    | 12 h             | [49] |
| Plasma fluorination      | MWCNTs           | CF$_4$              | 0.07-0.29  | RT                       | 0.5-45 min       | [50] |
| Plasma fluorination      | GO               | CF$_4$              | 0.17-0.27  | RT                       | 5-20 s           | [30] |

**Table 2: Comparing the properties of fluorinated carbon and carbon materials in different applications**

| Properties              | Carbon                      | Fluorinated carbon                          | Ref. |
|-------------------------|-----------------------------|---------------------------------------------|------|
| Band gap                | 0 (graphen)                 | 0-3.8 eV (fluorinated graphen)              | [38] |
| Contact angle           | 0° ethanol-derived carbon   | 168° (fluorinated carbon nanoparticle)      | [40] |
| Tribological            | 0.17 (Friction coefficient for graphene) | 0.08 (Friction coefficient for fluorinated graphene) | [41] |
| Mechanical              | Young’s modulus 340 ± 50 N m$^{-1}$ (graphene) | Young’s modulus 100 ± 30 N m$^{-1}$ (fluorinated graphene) | [42] |
| Thermal conductivity    | 6.2 W m$^{-1}$ K$^{-1}$ (reduced graphene oxide) | 14.1 W m$^{-1}$ K$^{-1}$ (fluorinated carbon nanotubes) | [43] |
fluorination process, it is considered that the compound composed of $C_{60}F_{48}$ with the highest fluorine content synthesized by the direct fluorination of $F_2$ [57]. Further fluorination inclined to cause internal fracture at the carbon skeleton level. Matsuo et al. reported that the synthesis of fluorinated fullerenes with compositions between $C_{60}F_{15}$ and $C_{60}F_{47}$ using $F_2$ [51]. Furthermore, different fluorinating agents also successfully employed to synthesize highly fluorinated $C_{60}$, such as $XeF_2$ ($C_{60}F_{60}$) [58].

Carbon nanotubes (CNTs) possess excellent mechanical, optical, and electrochemical properties. Meanwhile, there are many deficiencies on the surface of them [59–63]. Fluorination is one of the efficient approaches to modifying CNTs [64]. Mickleson et al. investigated the fluorination of single-walled carbon nanotubes (SWCNTs) at different temperatures using $F_2$ [65]. It demonstrated that a temperature above 150°C is essential for the formation of C-F bonds. Meanwhile, the obtained fluorinated SWCNTs transferred to an insulated state under temperatures above 250°C, while the structure collapsed when the temperature exceeds 500°C. Furthermore, An et al. calculated that the $F/C$ ratio of fluorinated SWCNTs could reach up to 1 from 0.25 with increasing temperature [66]. Recently, Li et al. presented two series of F-CNTs are prepared from ordinary CNTs and graphitized CNTs [53]. It is confirmed that the graphitization treatment of CNTs could increase the structural stability under high-temperature fluorination. The resulted FG-CNTs possessed a weaker C-F bonding leading to higher performance.

Graphene exhibits tremendous potential in advanced electronic devices due to its unique electronic properties [67–73]. On the other hand, the zero band gap of graphene restricts its application [74, 75]. It is believed that the fluorination of graphene-based materials is an efficient technique to open the bandgap by transforming the structure of the chemical bonds from $sp^2$ to $sp^3$ configuration. Theoretically, the bandgap of fluorinated graphene could be tuned from 0 to 3.8 eV by controlling the fluorination degree with different C-F bonding characters [38]. The high bandgap of $\sim$ 3.8 eV also reported to a fluorinated graphene practically [76]. Liu et al. investigated the different $F/C$ ratios of fluorinated graphene concluding that the bandgap increasing with $F/C$ ratios [77].

3.2 The control of fluorination conditions

The fluorination conditions, such as fluorination temperature, fluorination time, gas flow rate and fluorinating agent, also determine the properties of fluorinated carbon [78]. Ahmad et al. investigated the effect of different fluorination temperatures and fluorinating agents ($F_2$ and $TbF_4$) on fluorinated carbon preparation [31]. After the temperature of fluorination increased, higher homogeneity of the materials were obtained from the indirect fluorination of $TbF_4$ in comparison with the direct fluorination using $F_2$. This can be interpreted by the slow kinetics of $TbF_4$ decomposition, which allows for the continuous addition of fluorine to the carbon matrix and makes the fluorination process more gradual. Struzzi et al. used a plasma-assisted method to fluorinate vertically oriented multi-walled carbon nanotubes (VCNTs) in a magnetron sputtering chamber with mixed gas (Ar/$F_2$=95:5) atmosphere [79]. The role of high dilution fluorine in the precursor gas mixture was investigated by studying the nanotube structure change and the electrical properties during plasma processing. Then, the authors used $CF_4$ plasma to fluorinate VCNTs and studied the influence of different plasma parameters (power, time and distance) on the fluorination reaction [80]. Similarly, Nebogatikova et al. used the HF aqueous solution to fluorinate graphene suspension to investigate the influence of suspension composition, fluorination time, temperature and thermal stress on the crushing process of graphene [81]. Bulusheva et al. produced fluorinated double-walled carbon nanotubes (DWCNTs) by using fluorine $F_2$ (200°C), room temperature gaseous $BrF_3$ and $CF_4$ radio frequency plasma, respectively [82]. The fluorinated DWCNTs produced by $F_2$ and $BrF_3$ have smaller per-fluorinated regions and shorter fluorinated chains. $CF_4$ plasma induced different adsorbing groups, including single or paired fluorine atoms and $-CF_3$ group. These results imply that fluorinating agents could partly decide the structure of fluorinated carbon.

Overall, different reaction conditions are applied in different applications, correspondingly. For example, in the case of the lithium-ion primary battery, if the higher energy density requires then the higher fluorination degree should be chosen. But for the higher power density, a $F/C$ ratio of 0.7-0.9 requires. When the fluorinated carbon materials are applied in the field of superhydrophobic surface (insulation property), the higher $F/C$ ratio requires and the corresponding fluorination conditions including reaction temperature, time, fluorine concentration should choose the large values.
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Figure 3: (a) Schematic of FCNT primary lithium/sodium battery, galvanostatic discharge curves of FCNT and FGCNT at different current density of 10, 100, 500, 1000, 2000 mA g\(^{-1}\) for primary lithium battery. Reprinted with permission from [53]. (b) Schematic illustration of the preparation of FG nanosheets by the intercalation and exfoliation, the galvanostatic discharge curves at different discharge rates and the Ragone plot of FG. Reprinted with permission from [91]. (c) The galvanostatic discharge curves, Ragone plot and gravimetric energy densities at different discharge rates. Reprinted with permission from [28]

4 Applications

4.1 Primary lithium-ion battery

Fluorinated carbon (CF\(_x\)) firstly used as cathode materials for primary lithium batteries in 1972 [83], and Matsushita Electric Co. in Japan firstly commercialized Li/CF\(_x\) batteries in 1975 [84]. Fluorinated carbon used as cathode materials for primary lithium batteries have attracted extensive attention because of its various unique properties, including high energy density (2180 Wh kg\(^{-1}\) for \(x=1\)), average operating voltage, long shelf life, operation stability and wide range of operating temperature [10, 53, 85, 86]. More important, fluorinated carbon owns the highest theoretical specific capacity (865 mA h g\(^{-1}\) for \(x=1\)) among primary lithium battery systems [87, 88]. Note that the type of C-F bond and F/C ratio are closely related to the electrochemical properties of fluorinated carbon. Thus, recently, tremendous efforts have been made to achieve the theoretical capacity of fluorinated carbon in the respect of tuning the type of C-F bond and F/C ratio by designing the raw materials and fluorination conditions [89, 90].

Feng et al. investigated deeply fluorinated multi-wall carbon nanotubes (F-MWCNTs), where the F/C ratio is controlled to be approximate to 1 [47]. The as-obtained F-MWCNTs was able to support the high discharge rate up to 5C delivering a maximum power density of 7114.1 W kg\(^{-1}\) and a high energy density of 1923 W h kg\(^{-1}\), owing its
conductive networks and the intrinsic fast rate capability of one-dimensional nanostructures. Later, they reported a fluorographene, solvothermal exfoliated of fluorinated graphite by acetonitrile and chloroform [91]. As a cathode of primary lithium battery, it exhibited a remarkable discharge rate performance because of good Li\(^+\) diffusion and charge mobility through nanosheets. The fluorographene with semi-ironic C-F bonds delivered a high specific capacity of 520 mA h g\(^{-1}\) at 1\(^\circ\)C, and a maximum power density of 4038 W kg\(^{-1}\) at 3\(^\circ\)C. Recently, Feng et al. developed fluorinated calcinated macadamia nutshell (F-cMNS) delivering a specific capacity exceeding 900 mA h g\(^{-1}\), associated with a discharge potentials exceeding 3.0 V (vs. Li/Li\(^+\)) and an unprecedented energy density of 2585 W h kg\(^{-1}\) [92]. Such unique electrochemical performance endowed by the vigorous destruction of the periodic carbonaceous lattice of the basal plane, which substantially alters the electron distribution within the C-F bonds. Thus, the structural features of fluorinated carbon have a significant influence on electrochemical performance. In addition, although the theoretical capacity of CF\(_{0.95}\) sample was calculated as 847 mA h g\(^{-1}\), Ahmad et al. synthesized the fluorinated carbon nanodiscs (CND) to push the theoretical limit capacity to a high one of 1180 mA h g\(^{-1}\) [31]. The reinforcement effect of the central discs and the presence of a shell of LiF allowed the diffusion of the lithium ions through the sheet edges or the surface cracks, leading to the extra-capacity. The authors explained that the formation of Li\(_2\)F\(^+\) species play a vital role in the achievement of the extra-capacity.

Surface modification of the fluorinated carbon is an effective pathway to improve the performance of Li/CF\(_x\) batteries. Carbon coating CF\(_{x}x=1\) materials delivered a higher energy and power density [93]. When the fluorinated carbon materials are treated by a ball milling with urea, the maximum power density reaches 10309 W kg\(^{-1}\) at 5000 mA g\(^{-1}\) [94]. The ball milling effect enlarged the interlayer distance, decreased particle size and increased surface area of CF\(_x\) materials, which results in improving the electrochemical reaction activity, decreasing the reaction resistance and promoting the lithium ions diffusion. Furthermore, the composition of fluorinated carbon and oxides like CF\(_x\)-mSiO\(_2\) also delivered a significantly higher power density of 9689 W kg\(^{-1}\) [28].

### 4.2 Other batteries

Except for primary lithium batteries, fluorinated carbon is also widely investigated in the field of solar cells, lithium/sodium-ion batteries, and lithium-sulfur batteries [95–99]. Jeon et al. reported an edge-selectively fluorinated graphene nanoplatelets (FGnP) with a maximized charge polarization and an enhanced chemical stability, which demonstrates superb stability/cycle life for dye-sensitized solar cells (FF: 71.5%; Jsc: 14.44 mA cm\(^{-2}\); Voc: 970 mV; PCE: 10.01%) and lithium-ion batteries (650.3 mA h g\(^{-1}\) at 0.5\(^\circ\)C, charge retention of 76.6% after 500 cycles) [95]. Liu et al. employed the home-made fluorinated mesocarbon microbeads (F-MCM) for sodium-ion batteries [99]. Binder-free of F-MCM film electrode delivered an initial discharge capacity of 647.8 mA h g\(^{-1}\) and obtained a good lifespan of over 65 cycles at 0.05\(^\circ\)C. The results demonstrated that micro-structure design could improve the electrochemical performance of Na/CF\(_x\) cells. In terms of lithium-sulfur batteries, Vizintin et al. synthesized fluorinated reduced graphene oxide (F-rGO) used as an interlayer additive supported by a glass fiber separator in lithium-sulfur batteries, which can block the diffusion/migration of polysulfides from the porous positive electrode to the metallic lithium electrode and to prevent the redox shuttle effect [98]. The results illustrated that the additive of F-rGO resulted in better reversibility of the sulfur electrochemical reaction and capacity retention upon cycling.

Although fluorinate carbon materials are applied and developed widely in the field of primary lithium ion battery, the unique materials also are utilized in other fields like biomedicines, gas sensors, electronics devices and microwave absorption devices [43, 100–105].

### 4.3 Biomedicine

In recent years, due to the largest electronegativity of the fluorine atom, the strong polarity of the C–F bond is expected to induce biological responses, especially, 50% of drugs contain fluorine element [101]. Compared to other carbon materials without fluorine, FC\(_x\) materials have higher paramagnetism and can be used as a contrast agent of magnetic resonance imaging (MRI) in biological fields [102]. Since the distribution of fluorine in the human body is very small, the contrast medium is very ideal, so the observed signal is stable and shows an excellent degree of specificity. Then, the conjugated structure makes the fluorinated carbon ready for the loading of the aromatic drugs [103]. All these properties make FC\(_x\) a potentially valuable candidate for imaging, drug delivery, and photothermal responses. Sun et al. developed fluorinated carbon fiber (FC) based nano-carrier with good biocompatibility, high drug-loading capacity and enhanced photo-thermal performance [104]. As a novel nano-carrier,
it shows low toxicity and exhibits excellent cancer therapy effects deriving from a good combination of chemotherapy and photothermal therapy (Figure 5a).

4.4 Gas sensor

Gas monitoring technology has recently become a critical issue since they are some of the most common air pollutants, such as toxic gas handling plants and laboratories, urban areas filled with vehicles and plants that generate energy by combustion of fossil fuels [105]. Thus, the development of a gas sensor is an important goal that will reduce damage to human life. The development of a gas sensing material is the most important step in the development of such a gas sensor. In the past few years, nanoscale materials such as carbon materials, have been used as gas sensing materials, due to high specific surface area for enhanced gas adsorption, excellent electrical properties for high sensitivity and chemical stability for resistance to acidic and high-temperature conditions [106]. Zhang et al. showed monolayer fluorinated graphene (FG) synthesized by a controllable plasma treatment that could be applied as a gas-sensing material [107]. The FG-based gas sensor exhibited better performance for ammonia detection compared to pristine graphene, in which the fluorine species and defects in FG play key roles in the function of the gas sensor. According to the density functional theory simulation results, the superior sensing performance of FG was attributed to enhanced physical absorption due to the C-F covalent bonds on the surface of FG (Figure 5b).

4.5 Electronics device

Carbon has excellent electronic, optical and mechanical properties, which be used in new-generation devices. For example, the high mobility of charge carriers has aroused great interest in the field of high-speed electronics. In addition, due to the unique combination of high conductivity and optical transparency, graphene is a promising photovoltaic...
cells, and light-emitting diodes [108]. Since fluoridation is one of the most effective chemical methods to modify and control physicochemical properties in a wide range, fluorination of new forms of carbon materials is of great interest. The tunable electronic structure in fluorinated carbon is sufficiently utilized in electronic devices. Wang et al. firstly used fluorinated carbon nanotube (FCNT) as a thermally conductive filler to prepare composite film with nano fibrillated celluloses (NFCs) [43]. The presence of FCNT induces the excellent thermal conductivity, favorable electrical insulation property, enhanced toughness, reliable mechanical strength, and flexibility. These outstanding comprehensive properties guaranteed that the prepared composite film containing FCNT has promising applications in the heat dissipation of electronic devices (Figure 5c).

4.6 Microwave absorption

The demand for broadband microwave absorbing materials is increasing to prevent electromagnetic radiation from most modern electronic devices, such as computers and mobile phones. Due to their unique tubular nanostructure with extremely large aspect ratio, CNTs possess larger excluded volume, a smaller percolation threshold, and a lower additive amount, which endows CNTs with great potential as lightweight microwave absorbers [109].

In order to reduce electromagnetic interference (EMI), Liu et al. synthesized a novel fluorinated multi-walled carbon nanotubes (F-MWCNTs) with skin-core heterostructure to possess a minimal reflection loss up to −69 dB at a thickness of 1.5 mm [110]. During the fluorination process, the preformed CF₂ bonds prevent the F₂ gas permeating into the inner tubes, which results in an intact structure of the inner tubes. The intact inner tubes provide a
good attenuation of electromagnetic waves. However, the outer skin is the fluorinated layer with good impedance matching, which helps the transmission of electromagnetic waves (Figure 5d).

5 Conclusion and outlook

In this review, a general overview of the structure, properties, as well as the effects of different carbon sources and fluorination conditions of fluorinated carbon that can be utilized for energy conversion/storage devices, biomedicines, gas sensors, electronic devices, and microwave absorption devices has been provided. Fluorinated carbon possesses various excellent properties such as chemically stability, tunable bandgap, good thermal conductivity, thermal stability as well as superhydrophobicity. We have emphasized that the features of C-F bonds and F/C ratios are significance for tuning the properties of fluorinated carbon. Importantly, the selection of carbon source and fluorination conditions can efficiently control the structure of fluorinated carbon, including morphology, C-F bonding, and F/C ratios. A series of carbonaceous nanomaterials and fluorinating agents were employed to synthesize fluorinated carbon with different morphology and structural features, further demonstrating the effects of raw materials.

Although significant progress has been achieved in the development and application of fluorinated carbon materials, it is necessary to address high-volume synthesis/production, precision fluorination, uniformity of C-F bonding character, controllability of C-F bond types and wider range of F/C ratio (>1.3). In the fluorination process, the mechanism of formation of different C-F bonding is equivocal. Normally, the fluorinated carbon consists of different proportions of ionic, semi-ionic as well as covalent C-F, C-F$_2$ and C-F$_3$ bonds with different ratios. Thus, it is difficult to achieve precisely tunable of specific C-F bonds. Moreover, pushing the theoretical limit of the F/C ratio is of great significance in specific applications, such as increasing the energy density of primary lithium batteries.

By designing fluorinated carbons with different structures, such as core-shell, porous, nanostructures (nanotube, nanofiber, nanosheet, etc.), the intrinsic association between structural characteristics and the fluorinated carbon can be deeply understood. The structure of fluorinated carbon deeply depends on the selection of carbon source and fluorination method. Therefore, the development of different carbon sources and suitable fluorination method is still a hot topic in the future. On the basis of structural control and optimization, fluorinated carbon will exhibit excellent performance in large-scale applications of electronics, energy conversion/storage devices, and special protective coatings.

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