Review Article

Yifan Liu, Lingyan Jiang, Haonan Wang, Hong Wang, Wei Jiao*, Guozhang Chen*, Pinliang Zhang, David Hui, and Xian Jian

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

<https://doi.org/10.1515/ntrev-2019-0051>

Received Nov 30, 2019; accepted Dec 18, 2019

Abstract: Fluorinated carbon (CF_x), 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, $C-F_2$, $C-F_3$ 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 (CF_x) 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 $Li/CF_{1.0}$) 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

***Corresponding Author: Wei Jiao:** School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu, 611731, China; Email: wjiao@alum.imr.ac.cn

***Corresponding Author: Guozhang Chen:** School of Physics, University of Sydney, Sydney, New South Wales 2006, Australia; Email: guozhang.chen@sydney.edu.au

Yifan Liu, Xian Jian: School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu, 611731, China; National Engineering Research Center of Electromagnetic Radiation Control Materials, State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

Lingyan Jiang, Haonan Wang, Hong Wang: School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu, 611731, China

Pinliang Zhang: Beijing Institute of Spacecraft Environment Engineering, 100094, China

David Hui: Department of Mechanical Engineering, University of New Orleans, New Orleans, Louisiana 70148, United States of America

Figure 1: The schematic diagrams of some typical fluorinated carbons with an F/C ratio of 1:1. (a) F-C₆₀ view onto; (b) F-CNT; (c) F-graphene top view; (d) F-C₆₀ view across; (e) F-CNT; (f) F-graphene side view

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 tetramers, 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 CF_x 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-F₂, and C-F₃, 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 F-C 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 F-C bond at the edge of graphene is yielded by the F in the isolated F-C 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_4 [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 super-hydrophobicity, 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

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]

to the weakened interlamellar van der Waals forces. The surface tension and energy are calculated by the contact angle. The higher contact angle signifies that the materials possess a lower surface energy. Hence, the large contact angle of CF_x materials provide better lubricity than carbon materials.

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 CF₄ [46]. The introduction of plasma can achieve fluorination at normal temperatures, which can re-

tain 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 C₆₀ [51, 52], one-dimensional (1D) carbon nanotubes and carbon nanofibers [11, 53, 54], as well as two-dimensional (2D) graphene [19, 55].

Fullerene C₆₀ is particularly fascinating because of its highly conjugated molecular structure, high electron-accepting and transporting properties. Grafting of strongly electronegative fluorine to C₆₀ has a significant effect on its electronic properties, and thus it is of great significance for the research of C₆₀ fluorination. Due to the abundance of active sites of C₆₀, the reaction with fluorine results in a composition range from C₆₀F₂ to C₆₀F₆₀ [56]. Attributing to the steric hindrance of the molecular surface during the

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 FGCNTs 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 ~ 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].

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.

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

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 the-

oretical 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°C , and a maximum power density of 4038 W kg^{-1} at 3°C . Recently, Feng *et al.* developed fluorinated calcinated macadamia nutshell (F-MCNS) 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 $\text{CF}_{0.95}$ 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_2F^+ 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 $\text{CF}_x\text{-mSiO}_2$ 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 (FGnPs) 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 ($650.3 \text{ mA h g}^{-1}$ at 0.5°C , charge retention of 76.6% after 500 cycles) [95]. Liu *et al.* employed the home-made fluorinated mesocarbon microbeads (F-MCMB) for sodium-ion batteries [99]. Binder-free of F-MCMB film electrode delivered an initial discharge capacity of $647.8 \text{ mA h g}^{-1}$ and obtained a good lifespan of over 65 cycles at 0.05°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,

Figure 4: (a) Schematic of EFGnPs-F for highly stable inverted perovskite solar cells. Reprinted with permission from [96]. (b) Schematic of FFGF for lithium/potassium storage and the corresponding rate performance. Reprinted with permission from [97]. (c) Schematic of F-rGO as an interlayer in Li-S batteries. Reprinted with permission from [98]. (d) The first discharge/charge curves of Na/F-MCMB cell at a rate of 0.05C. Reprinted with permission from [99]

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 photoelectric application material, such as display, photovoltaic

Figure 5: (a) Preparation and application of fluorinated carbon fiber oxide (FCO) as a novel nanocarrier. Illustration of synthesis of FCO by activation and oxidation and loading of DOX and intracellular release combined with photothermal therapy of cancer cells. Reprinted with permission from [104]; schematic illustration of (b) the FG-based gas sensor. Reprinted with permission from [107]; (c) the preparation of the NFC/FCNT composite films. Reprinted with permission from [43]; (d) the preparation of F-h-MWCNTs through direct heating fluorination. Reprinted with permission from [110]

cells, and light-emitting diodes [108]. Since fluorination 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 chemical 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 significant 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-F₂ and C-F₃ 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 ba-

sis 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.

Acknowledgement: This work was financially supported by the National Natural Science Foundation of China, China (Nos. 51972045 and 5197021414) and the Fundamental Research Funds for the Chinese Central Universities, China (No. ZYGX2019J025).

References

- [1] Ruff, O., Bretschneider O., Die Reaktionsprodukte der verschiedenen Kohlenstoffformen mit Fluor II (Kohlenstoff-monofluorid), Zeitschrift für anorganische und allgemeine Chemie, 1934, 217, 1-18.
- [2] Balaish M., Ein-Eli Y., Meso-pores carbon nano-tubes (CNTs) tissues-perfluorocarbons (PFCs) hybrid air-electrodes for Li-O₂ battery, J. Power Sources, 2018, 379, 219-227.
- [3] Lee Y.S., Syntheses and properties of fluorinated carbon materials, J. Fluor. Chem., 2007, 128, 392-403.
- [4] Hsieh C.T., Chen W.Y., Wu F.L., Fabrication and superhydrophobicity of fluorinated carbon fabrics with micro/nanoscaled two-tier roughness, Carbon, 2008, 46, 1218-1224.
- [5] Min C., He Z., Liu D., Zhang K., *et al.*, Urea modified fluorinated carbon nanotubes: unique self-dispersed characteristic in water and high tribological performance as water-based lubricant additives, New J. Chem., 2019, 43, 14684-14693.
- [6] Yuan S., Rösner M., Schulz A., Wehling T.O., *et al.*, Electronic Structures and Optical Properties of Partially and Fully Fluorinated Graphene, Phys. Rev. Lett., 2015, 114, 047403.
- [7] Yang Z., Wang L., Sun W., Li S., *et al.*, Superhydrophobic epoxy coating modified by fluorographene used for anti-corrosion and self-cleaning, Appl. Surf. Sci., 2017, 401, 146-155.
- [8] Ye X., Ma L., Yang Z., Wang J., *et al.*, Covalent Functionalization of Fluorinated Graphene and Subsequent Application as Water-based Lubricant Additive, ACS Appl. Mater. Inter., 2016, 8, 7483-7488.
- [9] Yan X.H., Zhao T.S., An L., Zhao G., *et al.*, A crack-free and superhydrophobic cathode micro-porous layer for direct methanol fuel cells, Appl. Energ., 2015, 138, 331-336.
- [10] Groult H., Tressaud A., Use of inorganic fluorinated materials in lithium batteries and in energy conversion systems, Chem. commun., 2018, 54, 11375-11382.
- [11] Adamska M., Narkiewicz U., Fluorination of Carbon Nanotubes - A Review, J. Fluor. Chem., 2017, 200, 179-189.
- [12] Zhang W., Spinelle L., Dubois M., Guérin K., *et al.*, New synthesis methods for fluorinated carbon nanofibres and applications, J. Fluor. Chem., 2010, 131, 676-683.
- [13] Bulusheva L.G., Fedoseeva Y.V., Okotrub A.V., Flahaut E., *et al.*, Stability of Fluorinated Double-Walled Carbon Nanotubes Produced by Different Fluorination Techniques, Chem. Mat., 2010, 22, 4197-4203.
- [14] Guérin K., Dubois M., Houdayer A., Hamwi A., Applicative performances of fluorinated carbons through fluorination routes: A

- review, *J. Fluor. Chem.*, 2012, 134, 11-17.
- [15] Zhou S., Sherpa S.D., Hess D.W., Bongiorno A., Chemical Bonding of Partially Fluorinated Graphene, *J. Phys. Chem. C*, 2014, 118, 26402-26408.
 - [16] Fulvio P.F., Brown S.S., Adcock J., Mayes R.T., *et al.*, Low-Temperature Fluorination of Soft-Templated Mesoporous Carbons for a High-Power Lithium/Carbon Fluoride Battery. *Chemistry of Materials*, *Chem. Mat.*, 2011, 23, 4420-4427.
 - [17] Chen W., Lv G., Hu W., Li D., *et al.*, Synthesis and applications of graphene quantum dots: a review, *Nanotechnol. Rev.*, 2018, 7, 157-185.
 - [18] Murakami M., Matsumoto K., Hagiwara R., Matsuo Y., ¹³C/¹⁹F high-resolution solid-state NMR studies on layered carbon-fluorine compounds, *Carbon*, 2018, 138, 179-187.
 - [19] Feng W., Long P., Feng Y., Li Y., Two-Dimensional Fluorinated Graphene: Synthesis, Structures, Properties and Applications, *Adv. Sci.*, 2016, 3, 1500413.
 - [20] Kim J., Zhou R., Murakoshi K., Yasuda S., Advantage of semi-ionic bonding in fluorine-doped carbon materials for the oxygen evolution reaction in alkaline media, *RSC Adv.*, 2018, 8, 14152-14156.
 - [21] Zhong G., Chen H., Huang X., Yue H., *et al.*, High-Power-Density, High-Energy-Density Fluorinated Graphene for Primary Lithium Batteries, *Front. Chem.*, 2018, 6, 50.
 - [22] Lam P., Yazami R., Physical characteristics and rate performance of (CF_x)_n (0.33 < x < 0.66) in lithium batteries, *J. Power Sources*, 2006, 153, 354-359.
 - [23] Nagasubramanian G., Sanchez B., A new chemical approach to improving discharge capacity of Li/(CF_x)_n cells, *J. Power Sources*, 2007, 165, 630-634.
 - [24] Giraudet J., Delabarre C., Guérin K., Dubois M. *et al.*, Comparative performances for primary lithium batteries of some covalent and semi-covalent graphite fluorides, *J. Power Sources*, 2006, 158, 1365-1372.
 - [25] Peng S., Yan S., Wang N., Nan W., *et al.*, Fluorinated graphene/sulfur hybrid cathode for high energy and high power density lithium primary batteries, *RSC Adv.*, 2018, 8, 12701-12707.
 - [26] O'Hagan D., Understanding organofluorine chemistry. An introduction to the C–F bond, *Chem. Soc. Rev.*, 2008, 37, 308-319.
 - [27] Sato Y., Kume T., Hagiwara R., Ito Y., Reversible intercalation of HF in fluorine–GICs, *Carbon*, 2003, 41, 351-357.
 - [28] Zhu Y., Zhang L., Zhao H., Fu Y., Significantly improved electrochemical performance of CF_x promoted by SiO₂ modification for primary lithium batteries, *J. Mater. Chem., A* 2017, 5, 796-803.
 - [29] Sato Y., Itoh K., Hagiwara R., Fukunaga T., *et al.*, On the so-called “semi-ionic” C–F bond character in fluorine–GIC, *Carbon*, 2004, 42, 3243-3249.
 - [30] Yu X., Lin K., Qiu K., Cai H., *et al.*, Increased chemical enhancement of Raman spectra for molecules adsorbed on fluorinated reduced graphene oxide, *Carbon*, 2012, 50, 4512-4517.
 - [31] Ahmad Y., Dubois M., Guérin K., Hamwi A., *et al.*, Pushing the theoretical limit of Li–CF_x batteries using fluorinated nanostructured carbon nanodiscs, *Carbon*, 2015, 94, 1061-1070.
 - [32] Zhang H., Fan L., Dong H., Zhang P., *et al.*, Spectroscopic Investigation of Plasma-Fluorinated Monolayer Graphene and Application for Gas Sensing, *ACS Appl. Mater. Inter.*, 2016, 8, 8652-8661.
 - [33] Chronopoulos D.D., Bakandritsos A., Pykal M., Zbořil R., *et al.*, Chemistry, properties, and applications of fluorographene, *Appl. Mater. Today*, 2017, 9, 60-70.
 - [34] Ye X., Liu X., Yang Z., Wang Z., *et al.*, Tribological properties of fluorinated graphene reinforced polyimide composite coatings under different lubricated conditions. *Composites Part A: -Appl. Sci. Manuf.*, 2016, 81, 282-288.
 - [35] Tang Y., Zhang Q., Zhan X., Chen F., Superhydrophobic and anti-icing properties at overcooled temperature of a fluorinated hybrid surface prepared via a sol–gel process, *Soft Matter*, 2015, 11, 4540-4550.
 - [36] Ossai C.I., Raghavan N., Nanostructure and nanomaterial characterization, growth mechanisms, and applications, *Nanotechnol. Rev.*, 2018, 7, 209-231.
 - [37] Bi X., Li Y., Qiu Z., Liu C., *et al.*, Fluorinated Graphene Prepared by Direct Fluorination of N, O-Doped Graphene Aerogel at Different Temperatures for Lithium Primary Batteries, *Materials*, 2018, 11, 1072.
 - [38] Xu X., Liu C., Sun Z., Cao T., *et al.*, Interfacial engineering in graphene bandgap, *Chem. Soc. Rev.*, 2018, 47, 3059-3099.
 - [39] Al-Amadi A.O., Al-Mubaiyedh U.A., Sultan A.S., Kamal M.S., *et al.*, Novel fluorinated surfactants for enhanced oil recovery in carbonate reservoirs, *J. Chem. Eng.*, 2016, 94, 454-460.
 - [40] Lyth S.M., Ma W., Liu J., Daio T., *et al.*, Solvothermal synthesis of superhydrophobic hollow carbon nanoparticles from a fluorinated alcohol, *Nanoscale*, 2015, 7, 16087-16093.
 - [41] Fan K., Chen X., Wang X., Liu X., *et al.*, Toward Excellent Tribological Performance as Oil-Based Lubricant Additive: Particular Tribological Behavior of Fluorinated Graphene, *ACS Appl. Mater. Inter.*, 2018, 10, 28828-28838.
 - [42] Nair R.R., Ren W., Jalil R., Riaz I., *et al.*, Fluorographene: A Two-Dimensional Counterpart of Teflon, *Small*, 2010, 6, 2877-2884.
 - [43] Wang X., Wu P., Fluorinated Carbon Nanotube/Nanofibrillated Cellulose Composite Film with Enhanced Toughness, Superior Thermal Conductivity, and Electrical Insulation, *ACS Appl. Mater. Inter.*, 2013, 5, 8294-8299.
 - [44] Wang X., Dai Y., Gao J., Huang J., *et al.*, High-Yield Production of Highly Fluorinated Graphene by Direct Heating Fluorination of Graphene-oxide, *ACS Appl. Mater. Inter.*, 2013, 5, 8294-8299.
 - [45] Liu Y., Noffke B. W., Qiao X., Li Q., *et al.*, Basal Plane Fluorination of Graphene by XeF₂ via a Radical Cation Mechanism, *J. Phys. Chem. Lett.*, 2015, 6, 3645-3649.
 - [46] Saikia N.J., Ewels C., Colomer J.F., Aleman B., *et al.*, Plasma Fluorination of Vertically Aligned Carbon Nanotubes, *J. Phys. Chem. C*, 2013, 117, 14635-14641.
 - [47] Li Y., Feng Y., Feng W., Deeply fluorinated multi-wall carbon nanotubes for high energy and power densities lithium/carbon fluorides battery, *Electrochim. Acta*, 2013, 107, 343-349.
 - [48] Wang X., Dai Y., Gao J., Huang J., *et al.*, High-yield production of highly fluorinated graphene by direct heating fluorination of graphene-oxide, *ACS Appl. Mater. Inter.*, 2013, 5, 8294-8299.
 - [49] Zhang W., Bonnet P., Dubois M., Ewels C. P., *et al.*, Comparative Study of SWCNT Fluorination by Atomic and Molecular Fluorine, *Chem. Mat.*, 2012, 24, 1744-1751.
 - [50] Abdelkader-Fernández V.K., Morales-Lara F., Melguizo M., García-Gallarrín C., *et al.*, Degree of functionalization and stability of fluorine groups fixed to carbon nanotubes and graphite nanoplates by CF₄ microwave plasma, *Appl. Surf. Sci.*, 2015, 357, 1410-1418.
 - [51] Matsuo Y., Nakajima T., Electrochemical properties of fluorinated fullerene C₆₀, *Electrochim. Acta*, 1996, 41, 15-19.
 - [52] Power A.C., Gorey B., Chandra S., Chapman J., Carbon nanomaterials and their application to electrochemical sensors: a review, *Nanotechnol. Rev.*, 2018, 7, 19-41.

- [53] Li Y., Wu X., Liu C., Wang S., *et al.*, Fluorinated multi-walled carbon nanotubes as cathode materials of lithium and sodium primary batteries: effect of graphitization of carbon nanotubes, *J. Mater. Chem. A*, 2019, 7, 7128-7137.
- [54] Liu X., Yue D., Yang C., Li N., *et al.*, Fluorinated carbon nanofiber/polyimide composites: Electrical, mechanical, and hydrophobic properties, *Surf. Coat. Tech.*, 2019, 361, 206-211.
- [55] Şahin H., Topsakal M., Ciraci S., Structures of fluorinated graphene and their signatures, *Phys. Rev., B* 2011, 83, 115432.
- [56] Zhang W., Dubois M., Guerin K., Bonnet P., *et al.*, Effect of curvature on C-F bonding in fluorinated carbons: from fullerene and derivatives to graphite, *Phys. chem. chem. phys.*, 2010, 12, 1388-1398.
- [57] Boltalina V., Og A., Galeva N., Direct fluorination of fullerenes, *Russ. Chem. Rev.*, 2000, 69, 609-621.
- [58] Holloway J.H., Hope E.G., Taylor R., Langley G.J., *et al.*, Fluorination of buckminsterfullerene, *J. Chem. Soc., Chem. Commun.*, 1991, 14, 966-969.
- [59] Fang J., Shan X., Wen B., Huang R., Mobility of TX100 suspended multiwalled carbon nanotubes (MWCNTs) and the facilitated transport of phenanthrene in real soil columns, *Geoderma*, 2013, 20, 1-7.
- [60] Ventrapragada L.K., Creager S.E., Rao A.M., Podila R., Carbon Nanotubes Coated Paper as Current Collectors for Secondary Li-ion Batteries, *Nanotechnol. Rev.*, 2019, 8, 18-23.
- [61] Zhao J., Zhang X., Huang Y., Zou J., *et al.*, A comparison of the twisted and untwisted structures for one-dimensional carbon nanotube assemblies, *Mater. Design*, 2018, 146, 20-27.
- [62] Zhang H., Selective modification of inner surface of halloysite nanotubes: a review, *Nanotechnol. Rev.*, 2017, 6, 573-581.
- [63] Majeed S., Zhao J., Zhang L., Anjum S., *et al.*, Synthesis and electrochemical applications of nitrogen-doped carbon nanomaterials, *Nanotechnol. Rev.*, 2013, 2, 615-635.
- [64] Sansotera M., Bianchi C.L., Lecardi G., Marchionni G., *et al.*, Highly Hydrophobic Carbon Black Obtained by Covalent Linkage of Perfluorocarbon and Perfluoropolyether Chains on the Carbon Surface, *Chem. Mat. Chem. Mat.*, 2009, 21, 4498-4504.
- [65] Mickelson E.T., Huffman C.B., Rinzler A.G., Smalley R. E., *et al.*, Fluorination of single-wall carbon nanotubes, *Chem. Phys. Lett.*, 1998, 296, 188-194.
- [66] An K.H., Heo J.G., Jeon K.G., Bae D.J., *et al.*, X-ray photoemission spectroscopy study of fluorinated single-walled carbon nanotubes, *Appl. Phys. Lett.*, 2002, 80, 4235-4237.
- [67] Gurunathan S., Han J.W., Kim J.H., Green chemistry approach for the synthesis of biocompatible graphene, *Int. J. Nanomed.*, 2013, 8, 2719-2732.
- [68] Ruan G., Sun Z., Peng Z., James M.T., Growth of Graphene from Food, Insects, and Waste, *ACS Nano*, 2011, 5, 7601-7607.
- [69] Pumera M., Sofer Z., Towards stoichiometric analogues of graphene: graphane, fluorographene, graphol, graphene acid and others, *Chem. Soc. Rev.*, 2017, 46, 4450-4463.
- [70] Das S., Ghosh C.K., Sarkar C.K., Roy S., Facile synthesis of multi-layer graphene by electrochemical exfoliation using organic solvent, *Nanotechnol. Rev.*, 2018, 7, 497-508.
- [71] Saini D., Synthesis and functionalization of graphene and application in electrochemical biosensing, *Nanotechnol. Rev.*, 2016, 5, 393-416.
- [72] Bandaru P.R., Yamada H., Narayanan R., Hoefer M., The role of defects and dimensionality in influencing the charge, capacitance, and energy storage of graphene and 2D materials, *Nanotechnol. Rev.*, 2017, 6, 421-433.
- [73] Cruz-Silva R., Endo M., Terrones M., Graphene oxide films, fibers, and membranes, *Nanotechnol. Rev.*, 2016, 5, 377-391.
- [74] Liao L., Peng H., Liu Z., Chemistry Makes Graphene beyond Graphene, *J. Am. Chem. Soc.* 2014, 136, 12194-12200.
- [75] Wan S., Bi H., Sun L., Graphene and carbon-based nanomaterials as highly efficient adsorbents for oils and organic solvents, *Nanotechnol. Rev.*, 2016, 5, 3-22.
- [76] Jeon K.-J., Lee Z., Pollak E., Moreschini L., *et al.*, Fluorographene: A Wide Bandgap Semiconductor with Ultraviolet Luminescence, *ACS Nano*, 2011, 5, 1042-1046.
- [77] Liu H.Y., Hou Z.F., Hu C.H., Yang Y., *et al.*, Electronic and Magnetic Properties of Fluorinated Graphene with Different Coverage of Fluorine, *J. Phys. Chem. C*, 2012, 116, 18193-18201.
- [78] Zhang W., Dubois M., Guérin K., Bonnet P., *et al.*, Fluorinated nanocarbons using fluorinating agent: Strategies of fluorination and applications, *Eur. Phys. J. B*, 2010, 75, 133-139.
- [79] Struzzi C., Scardamaglia M., Hemberg A., Petaccia L., *et al.*, Plasma fluorination of vertically aligned carbon nanotubes: functionalization and thermal stability, *Beilstein J. nanotech.*, 2015, 6, 2263-2271.
- [80] Struzzi C., Scardamaglia M., Colomer J.-F., Verdini A., *et al.*, Fluorination of vertically aligned carbon nanotubes: from CF₄ plasma chemistry to surface functionalization, *Beilstein J. nanotech.*, 2017, 8, 1723-1733.
- [81] Nebogatikova N.A., Antonova I.V., Kurkina I., Soots R.A., *et al.*, Fluorinated graphene suspension for inkjet printed technologies, *Nanotechnology*, 2016, 27, 205601.
- [82] Bulusheva L.G., Fedoseeva Y.V., Flahaut E., Rio J., *et al.*, Effect of the fluorination technique on the surface-fluorination patterning of double-walled carbon nanotubes, *Beilstein J. nanotech.*, 2017, 8, 1688-1698.
- [83] Watanabe N.F., High energy density battery. U.S. Patent 1972, 3700502.
- [84] Fukuda M., Iijima T., Power Sources, Collins, DH, Ed. Academic Press: New York 1975, 5, 713.
- [85] Wang L., Li Y., Wang S., Zhou P., *et al.*, Fluorinated Nanographite as a Cathode Material for Lithium Primary Batteries, *ChemElectroChem*, 2019, 6, 2201-2207.
- [86] Zhong G., Chen H., Huang X., Yue H., *et al.*, High-Power-Density, High-Energy-Density Fluorinated Graphene for Primary Lithium Batteries, *Front. chem.*, 2018, 6, 50.
- [87] Mar M., Dubois M., Guérin K., Batisse N., *et al.*, Tuning fluorine and oxygen distribution in graphite oxifluorides for enhanced performances in primary lithium battery, *Carbon*, 2019, 141, 6-15.
- [88] Zhang Q., Takeuchi K.J., Takeuchi E.S., Marschilok A. C., Progress towards high-power Li/CF_x batteries: electrode architectures using carbon nanotubes with CF_x, *Phys. Chem. Chem. Phys.*, 2015, 17, 22504-22518.
- [89] Shao Y., Yue H., Qiao R., Hu J., *et al.*, Synthesis and Reaction Mechanism of Novel Fluorinated Carbon Fiber as a High-Voltage Cathode Material for Rechargeable Na Batteries, *Chem. Mater.* 2016, 28, 1026-1033.
- [90] Ahmad Y., Dubois M., Guerin K., Hamwi A., *et al.*, High energy density of primary lithium batteries working with sub-fluorinated few walled carbon nanotubes cathode, *J. Alloy. Compd.*, 2017, 726, 852-859.
- [91] Sun C., Feng Y., Li Y., Qin C., *et al.*, Solvothermally exfoliated fluorographene for high-performance lithium primary batteries, *Nanoscale. Nanoscale*, 2014, 6, 2634-2641.

- [92] Peng C., Li Y., Yao F., Fu H., *et al.*, Ultrahigh-energy-density fluorinated calcinated macadamia nut shell cathodes for lithium/fluorinated carbon batteries, *Carbon*, 2019, 153, 783-791.
- [93] Zhang Q., D'Astorg S., Xiao P., Zhang X., *et al.*, Carbon-coated fluorinated graphite for high energy and high power densities primary lithium batteries, *J. Power Sources*, 2010, 195, 2914-2917.
- [94] Zhou P., Weng J., Liu X., Li Y., *et al.*, Urea-assisted ball-milled CF as electrode material for primary lithium battery with improved energy density and power density, *J. Power Sources*, 2019, 414, 210-217.
- [95] Jeon I.Y., Ju M.J., Xu J., Choi H.J., *et al.*, Edge-Fluorinated Graphene Nanoplatelets as High Performance Electrodes for Dye-Sensitized Solar Cells and Lithium Ion Batteries, *Adv. Funct. Mater.*, 2015, 25, 1170-1179.
- [96] Kim G.H., Jang H., Yoon Y.J., Jeong J., *et al.*, Fluorine Functionalized Graphene Nano Platelets for Highly Stable Inverted Perovskite Solar Cells, *Nano lett.*, 2017, 17, 6385-6390.
- [97] Ju Z., Zhang S., Xing Z., Zhuang Q., *et al.*, Direct Synthesis of Few-Layer F-Doped Graphene Foam and Its Lithium/Potassium Storage Properties, *ACS Appl. Mater. Inter.*, 2016, 8, 20682-20690.
- [98] Vizintin A., Lozinšek M., Chellappan R.K., Foix D., *et al.*, Fluorinated Reduced Graphene Oxide as an Interlayer in Li-S Batteries, *Chem. Mat.*, 2015, 27, 7070-7081.
- [99] Liu W., Wang Y., Li Y., Shi B., *et al.*, Long-life sodium/carbon fluoride batteries with flexible, binder-free fluorinated meso-carbon microbead film electrodes, *Chem. commun.*, 2018, 54, 2341-2344.
- [100] Gong P., Guo L., Pang M., Wang D., *et al.*, Nano-sized paramagnetic and fluorescent fluorinated carbon fiber with high NIR absorbance for cancer chemo-photothermal therapy, *J. Mater.Chem. B*, 2018, 6, 3068-3077.
- [101] Klaus M., Christoph F., François D., Fluorine in Pharmaceuticals: Looking Beyond Intuition, *Science*, 2017, 317, 1881-1886.
- [102] Srinivas M., Morel P.A. Ernst L.A., Laidlaw D.H., Ahrens E.T., Fluorine-19 MRI for visualization and quantification of cell migration in a diabetes model, *Magn. Reson. Med.*, 2007, 58, 725-734.
- [103] Temme S., Bonner F., Schrader J., Fogel U., 19F magnetic resonance imaging of endogenous macrophages in inflammation. *WIREs Nanomed. Nanobiotechnol.* 2012, 4, 329-343.
- [104] Sun L., Gong P., Liu X., Pang M., *et al.*, Fluorinated carbon fiber as a novel nanocarrier for cancer chemo-photothermal therapy, *J. Mater. Chem. B*, 2017, 5, 6128-6137.
- [105] Park M.S., Kim K.H., Kim M.J., Lee Y.S., NH₃ gas sensing properties of a gas sensor based on fluorinated graphene oxide, *Colloid. Surface., A* 2016, 490, 104-109.
- [106] Ji S.I., Seok C.K., Lee S.H., Lee Y.S., Improved gas sensing of electrospun carbon fibers based on pore structure, conductivity and surface modification, *Carbon*, 2010, 48, 2573-2581.
- [107] Zhang H., Fan L., Dong H., Zhang P., *et al.*, Spectroscopic Investigation of Plasma-Fluorinated Monolayer Graphene and Application for Gas Sensing. *ACS Appl. Mater. Inter.*. *ACS Appl. Mater. Inter.*, 2016, 8, 8652-8661.
- [108] Natalie O.V. Plank G.A., Forrest R.C., Andrew J.A., Electronic Properties of n-Type Carbon Nanotubes Prepared by CF₄ Plasma Fluorination and Amino Functionalization, *J. Phys. Chem. B*, 2005, 109, 47, 22096-22101.
- [109] Liu Y., Zhang Y., Wang X., Wang Z. *et al.* Excellent Microwave Absorbing Property of Multiwalled Carbon Nanotubes with Skin-Core Heterostructure Formed by Outer Dominated Fluorination, *J. Phys. Chem. C*, 2018 122, 11, 6357-6367.
- [110] Struzzi C., Scardamaglia M., Casanova-Chafer J., Calavia R., *et al.*, Exploiting sensor geometry for enhanced gas sensing properties of fluorinated carbon nanotubes under humid environment. *Sensor. Actuat.B-Chem.*, 2019, 281, 945-952.
- [111] Liu Y., Zhang Y., Wang X., Wang Z., *et al.*, Excellent Microwave Absorbing Property of Multiwalled Carbon Nanotubes with Skin-Core Heterostructure Formed by Outer Dominated Fluorination, *J. Phys. Chem. C*, 2018, 122, 6357-6367.