



Preparation and Applications of Fluorinated Graphenes

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Abstract: The present review focuses on the numerous routes for the preparation of fluorinated graphene (FG) according to the starting materials. Two strategies are considered: (i) addition of fluorine atoms on graphenes of various nature and quality and (ii) exfoliation of graphite fluoride. Chemical bonding in fluorinated graphene, related properties and a selection of applications for lubrication, energy storage, and gas sensing will then be discussed.

Keywords: graphene; fluorination; fluorinated graphene; lubrication; energy storage; gas sensing

1. Introduction

Fluorination is one of the most used chemical treatments to add one or several properties to carbonaceous materials. The most evident quality is hydrophobicity because of the high electronegativity of fluorine element; once bonded to carbon atom, the high difference in electronegativity between the two elements results in high negative partial charge on F atom. Fluorination may be used to change the surface chemistry from hydrophilic to hydrophobic character [1–3]. Combination of hydrophobic surface due to C–F bonds and micro-texturing of the surface results in superhydrophobicity [4]. This occurs when polar oxygenated groups (C–O, COOH, COH, etc.) are converted into C–F bonds. C–F bonds are electrochemically active in primary lithium batteries and capacities as high as 865 mAh/g may be reached when the highest fluorine content is considered, i.e., with CF₁ composition [5–7]. Presence of fluorine atoms between carbon sheets in covalent graphite intercalation compounds F-GICs decreases both the energy needed for sheet cleavage and the friction energy, i.e., low friction coefficients are obtained for graphite fluorides, and in a general way, for fluorinated graphitized (nano)carbons. The low friction coefficients are achieved for medium and high fluorine content, e.g., CF_{0.20} for fluorinated nanofibers [8]. C-F bonds may favorably interact with some gases, such as ammonia, and fluorinated carbons with high specific surface area (SSA) appear to be promising active materials for gas sensing. Because of the numerous applications in energy storage, solid lubricant, gas sensing, but also as fillers in (nano)composites with hydrophobic polymer matrix because the differences between the surface energies of fillers and polymer are decreased, the fluorination of (nano)carbons has been extensively studied [5,9–17]. The main parameters that affect the reaction are well known: (i) the higher the graphitization degree, the higher the fluorination temperature; graphite is fluorinated at temperature higher than 350 °C in pure molecular fluorine F_2 and up to 600–650 °C to form the (CF)n structural type with FCF/FCF stacking sequence $((C_2F)_n; FCCF/FCCF stacking is formed at intermediate$ temperature range of 350–450 °C). (ii) because fluorination is a heterogeneous gas/solid reaction, materials with high SSA exhibit high reactivity towards fluorinating agents (FAs) such as F₂ but also gaseous xenon difluoride XeF₂, BF₃, IF₅, ClF₃, etc. When the carbon lattice exhibits a curvature, as for fullerenes and derivatives such as nanotubes, the reactivity towards FA is also increased. Graphene is a single-layer sheet of carbon atoms with



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). a high specific surface area, and the reactivity upon fluorination is expected to be very high. Molecular fluorine appears then to be a too strong oxidant to be used for the covalent functionalization of monolayer graphene. Because of the high reactivity, perfluorination of the sheet edges (saturation with formation of CF_2 and CF_3 groups) and decomposition in CF_4 , C_2F_6 , and other short fluorocarbon fragments may occur. If some solid fluorocarbon sheets are still maintained they are highly defected and applicative properties suffer from this degradation. Molecular fluorine must be diluted with an inert medium to avoid the decomposition or other FAs must be considered. The present review focuses only on fluorinated graphene (FG) without, of with a few other heteroatoms. Oxyfluorinated graphene is not under consideration. Traces of oxygen may still remain after fluorination when the precursor is graphite oxide or graphene oxide (GO) even reduced.

Whereas single layer graphene has a striking combination of unique properties [18–20], such as an exceptionally high charge carrier mobility and conductivity [21,22], while retaining excellent mechanical flexibility [23], and high optical transparency [24,25], graphene becomes a wide gap semiconductor when functionalized with fluorine [26–29]. The band gap of 4.2 eV is expected for 100% functionalization with fluorine through theoretical predictions (3.8 eV with hydrogen) [30,31]. With F atom addition saturated at C₄F for one-sided fluorination, the calculated band gap of optically transparent FG is 2.93 eV [22,32]. This single atomic layer holds the promise for future bendable and transparent all-graphene electronics, i.e., devices where insulating graphene is used as a host material in which conductive and semiconductive graphene channels can be opened. Chemical isolation was achieved by exposing the unmasked graphene nanoribbons to xenon difluoride XeF₂ gas to convert it to insulating fluorographene [33].

Chemical bonding in fluorinated graphene and related properties will be discussed in the present review after presenting the various synthesis routes. A selection of applications will also be discussed: lubrication, energy storage, electronic device, and gas sensing.

At the present time, the methods for preparing fluorinated graphene of general composition C_xF_y and fluorographene with CF_1 stoichiometry could be mainly divided into two groups regarding the starting material. Figure 1 summarizes the two strategies and their sub-divisions. On one hand, one method involves fluorination of graphene or reduced graphene oxide using various fluorinating agents including F_2 , HF, XeF₂, decomposition of fluoropolymers [34], or utilizing plasma such as CF_4 and SF_6 [35]. On the other hand, exfoliation of graphite fluorides appears as a top-down strategy [34,36].



Figure 1. The two strategies for preparing fluorinated graphene (FG) of general composition $C_x F_y$ and fluorographene with CF_1 stoichiometry.

2. The Conventional Direct Fluorination with Molecular Fluorine

A few studies have reported the use of diluted molecular fluorine and only on reduced graphene oxide (GO) in the form of multilayer. The presence of several graphene layers allows the fluorination to be favored in comparison with decomposition. Covalent grafting and decomposition always compete whatever the carbon lattice. Negligible for the case of graphite, decomposition dominates for graphene monolayer. As first examples, fluorinated graphenes were prepared from graphene oxide reduced in microwave plasma. N₂/F₂ mixture with 20% vol./vol. of F₂ at pressure of 3 bar has been used [37,38], with 70 kPa F₂/N₂ mixed gas (F₂ content is 10%) [39] or with F₂/N₂ (50 kPa) in the 180–210 °C range [40]. The work using F₂/N₂ (50 kPa) at 200 °C on GO evidences the role of oxygenated groups that facilitate the fluorination [41]. Nevertheless, a few oxygenated groups were still present in the final product. The same defects in FG are present with diethylaminosulfur trifuoride (DAST); this commercially available liquid fluorinating agent allows the chemical transformation of GO to FG under mild conditions [42]. The fluorine content can be easily tailored up to 23 at.% by altering the reaction medium.

Graphene with a small amount of oxygen (8 at.%) typical of graphene samples prepared by chemical exfoliation was fluorinated with $20/80 \text{ vol.}\% \text{ F}_2/\text{N}_2$ at 2 bars for 5 h and 24 h at room temperature. Oxygen content remained approximately constant whatever the fluorination content [43].

As graphite oxide, graphene oxide (GO) exhibits the following functional groups: epoxides COC, COH, sp² carbon in oxidized environment, and carboxyl groups COOH; their relative amounts differ according to the synthesis route Hummers; Hummers modified improved synthesis [44]. The completion of the conversion of oxygenated groups into fluorinated groups may be questioned. A recent work on direct fluorination using F_2 gas at room temperature gives some information. The mild fluorination resulted in homogeneous fluorine dispersion when precursor was graphite oxide. Mild fluorination of GO for duration in between 15 and 90 min results in a triphasic oxyfluoride/fluoride/graphite material, while longer fluorination duration (240 min) leads to a biphasic oxyfluoride/fluoride material [45]. The decomposition temperature, higher than for raw GO, was related to the presence of fluorinated groups with high thermal stability as seen with graphite fluorides. The profile attested to a continuum of functions with superimposed thermal decompositions. The diversity of functions contained in the oxyfluoride was evidenced by solid state NMR evidence. Chemical shifts are measured at 59, 87, 110, 138, and 165 ppm vs TMS, respectively assigned to isotropic bands of functional groups COC, CF, CF₂, sp² C, and COOH. COH are missing because of their quasi-total conversion into C-F during the fluorination. Fluorine atoms coexist with oxygen ones in fluorinated GO or fluorinated graphene oxide.

3. Other Fluorinating Agents

Xenon difluoride XeF₂ was often used because its reaction with graphene resulting in any routes occurs at low temperature (from room temperature to 250 °C) [46]. The sublimation equilibrium between solid and gaseous XeF₂ is used to generate the gas that reacts with graphene. The amount of FA may be perfectly controlled contrary to gas F₂. Several works used the XeF₂ route either with chemical vapor deposition (CVD)grown graphene [47,48], with graphene films grown on Cu foils then transferred to either silicon-on-insulator or SiO₂/Si substrates [29,32], with the graphene-on-Cu sample and the Cu foil [49], or with graphene on SiC(0001) and then converted into quasi-freestanding graphene by hydrogen intercalation [50].

The efficiency of XeF₂ fluorination is changed by generating defects within the graphene layer, e.g., by an oxygen plasma etcher [51]. Whereas the reactivity of the single layer graphene is not significantly affected, the case of graphene bilayers is different; either a decrease in the reactivity was reported for a small number of new defects or an increase in reactivity was reported for a larger number of defects. This complex behavior results from a balance between the increase in reactivity towards the FA for some defects,

as expected, and stabilization of some parts of graphene (charge inhomogeneities) via formation of more stable groups.

 SF_6 may be used as the etching gas, as exemplified on chemical CVD-grown graphene in a reactive ion etching [52]. To avoid adverse etching with SF_6 plasma of graphene (deposited on the Ge (110) substrate by atmospheric pressure chemical vapor deposition), samples were placed upside-down on the pedestal in SF_6 plasma environment [53].

In a two-step process, the first step consisted in the electrochemical exfoliation of highoriented pyrolytic graphite (HOPG) with its additional processing with ultrasound. The fluorination of this suspension was proceeded in a weak (~3–7%) solution of hydrofluoric acid [54]. The fluorination duration was adjusted to the initial sizes of graphene particles. Low fluorine contents were achieved with this route, i.e., F/C atomic ratio lower or equal to 0.23. With the same two-step strategy involving aqueous HF, chemical exfoliation may be used to prepare the starting suspension [55]. Mechanical crushing of natural graphite, dimethylformamide (DMF) intercalation, ultrasonic treatment intended for splitting the intercalated particles, followed by centrifugation in order to remove non-split graphite particles was then carried out to prepare the suspension before the fluorination.

A one-step hydrothermal process using HF (40 w.%) as the fluorination source has been used to convert GO in aqueous dispersion [56]. During a hydrothermal process, the fluorination and reduction processes of GO occurred simultaneously. In order to reduce the surface energy of graphene nanoflake, fluorinated graphene nanoflake was prepared by solvo-thermal reaction between GO and HF [57].

An alternative for the use of reactive fluorinating agents has been reported by Lee et al. [58]. Graphene has been selectively fluorinated by irradiating fluoropolymer-covered graphene with a laser. The active fluorine radicals produced by photon-induced decomposition of the fluoropolymer (CYTOP) reacted with the sp²-hybrized carbons and C–F bonds were formed. Because the reactive species are the same, atomic fluorine, FG from this route exhibits similarities with the ones obtained with XeF₂.

Plasma technology allows the control of the fluorination whatever the graphene type. Numerous parameters may be tailored for this aim, i.e., gas pressure in the chamber, power for the plasma discharge ignition, exposure time. Different reactive gases may be used for plasma fluorination, e.g., CF_4 and SF_6 , and then different fluorinated groups are then introduced. Indeed, ions drive chemical reactions at the surface when reactive species are present during irradiation. Using CF_4 plasma treatment, adatom clustering occurs but it can be avoided when higher kinetic energy is supplied to the ions [35]. Careful attention must be paid to the interaction of the reactive gas with the graphene substrate. Using SF_6 plasma, the sulfur atoms tend to bond to bare copper areas (substrate) instead of changing the graphene chemistry. Monolayer graphene grown by CVD using Cu foil was treated with controllable SF_6 plasma treatment and F content close to 25 at.% was then achieved [59]. Such conditions result in the formation of covalent C–F bonds, which are perpendicular to the basal plane of FG, as evidenced by angle-dependent near edge X-ray absorption fine structure (NEXAFS).

4. Exfoliation of Graphite Fluoride

4.1. Mechanical

Mechanical exfoliation from a graphite fluoride appears to be an easy route to prepare FG without drastic defluorination. Nevertheless, the quantities of high-quality few-layer graphene are often low and lateral size of the layer is significantly decreased in comparison with graphite fluoride granulometry. FG flakes may be obtained by mechanical cleavage of graphite onto adequate substrate, e.g., SiO_2/p -doped Si substrate (which acts as a back gate for electrical transport measurements). The homogeneity of the fluorine atoms distribution is of primary importance. As a matter of fact, when this distribution is highly homogenous, the probability of producing fluorinated monolayer is high [27,28]. On the contrary, when the dispersion is less homogenous, exfoliation efficiency appeared to be lower and few layers of FG were then obtained [60]. Regarding the smaller radius and thus

higher diffusion rate in the interlayer space of graphite of atomic F[•] released by XeF₂, this FA must be favored for homogenous dispersion of F atoms in graphite fluoride precursor and then the preparation of monolayer FG. The ability to use mechanical exfoliation to control the fluorine content of graphene is promising for engineering different electronic properties in graphene materials. The prepared FG provides evidence of the possibility to tune the electronic transport properties of graphene mono-layers and multilayers by functionalization with fluorine. For mono-layer samples, by increasing the fluorine content, a transition from electronic transport through Mott variable range hopping (VRH) in two dimensions to Efros–Shklovskii VRH has been evidenced. Multi-layer fluorinated graphene with high concentration of fluorine shows two-dimensional Mott VRH transport, whereas $CF_{0.28}$ multi-layer flakes exhibit thermally activated transport through near neighbor hopping [27,28]. Another way to tune the electoral transport is electron beam irradiation [60]; the resistivity of insulating FG can be progressively decreased by several orders of magnitude simply (Figure 2). The electron-irradiated fluorinated graphene ultimately exhibited the resistance per square of pristine graphene.



Figure 2. Nanopatterning of fluorinated graphene by electron beam irradiation (**a**) (adapted with permission from ref [60], Copyright, 2011, American Chemical Society). The defluorination resulted in a decrease of both the interlayer distance and the height from SiO₂ substrate in atomic force microscopy (AFM) measurements (**b**). The surface resistance of FG connected to Cu/Au plots (**c**) decreased according to the electron dose (**d**).

4.2. Thermal Exfoliation

Graphite fluorides of any type appear to be excellent precursors to formed multi-layer graphene. Thanks to the presence of a high amount of fluorine atoms in covalent $(CF)_n$, the exfoliation of fluorinated graphite by a very fast thermal treatment has proved to be efficient. Both exfoliation and restructuring of the graphitic regions occurred simultaneously during the flash; conductive graphene with a low fluorine content was then prepared. Contrary to GO, the reduction step to obtain pure graphene could be easier because of the low amount of residual fluorinated groups. Another strategy involved semi-covalent graphite fluoride

synthesized at room temperature thanks to a catalytic gaseous mixture, based on a thermal shock induced by a flame [61]. The starting material exhibited a weakened covalence (called also semi-covalent) for the C–F bonding that favored the exfoliation. Moreover, residual catalysts such as IF₅, IF₆⁻, and IF₇, which were still intercalated after the room temperature synthesis, acted also on the exfoliation because of their fast deintercalation (Figure 3).



Figure 3. Schematic view of the thermal exfoliation of graphite fluoride containing semi-covalent (weakened covalence) and covalent regions (reproduced/adapted with permission from ref [61], Copyright, 2014, Elsevier). Colors before and after exfoliation (**a**), FTIR spectra of the gases involved into the reactor during the thermal shock (**b**) and TEM images (**c**) of the resulting sample are also shown. The FTIR spectra were recorded as a function of the duration (3, 6, 9, and 12 min) after the connection of the reactor to the measurement cell.

Graphite fluoride obtained with a two-step process, i.e., synthesis of a bromineintercalated graphite followed by long fluorination (14 days at room temperature with 10 vol.% solution of BrF₃ in Br₂) was thermally exfoliated with a fast increase of temperature at 800 °C [62]. It is to be noted that the reactive species are fluorine atoms released from BrF₃. The resulting material consisted of flat particles with an average basal plane size of a few microns and low concentration of defects. Residual bromine and fluorine species as well as oxygen-containing groups were still present.

Using thermal treatments or microwave plasma exfoliation of GO in atmospheres containing SF₆, SF₄, and MoF₆ as fluorinating agents, fluorographene was prepared. Process with SF₆ at 800 $^{\circ}$ C results in the highest F content (4.25 at.%) [63].

4.3. In Liquid Media

Liquid-phase exfoliation of layered materials is a simple and versatile method for preparing two-dimensional single- or few-layer materials in large quantities. Graphite fluoride can be easily exfoliated under shear force that facilitates the intercalation of solvent molecules into the interlayer galleries, weakening the van der Waals attraction between two adjacent layers and resulting in an expanded interlayer distance and thus separation of single- or few-layers in colloidal suspensions. The stability of the resulting graphene fluoride strongly depends on the temperature used in the process, i.e., room temperature treatment allows exfoliated graphene fluoride to retain its original chemical composition; high temperature leads to partial decomposition despite a higher yield of single- or fewlayer. In addition, the use of intercalating molecules and reaction condition (time and pressure) are important for facilitating the exfoliation process and the quality of product. That said, the precise control over the size and thickness (number of layers) of graphene fluoride is still challenging, which leads to a relatively poor selectivity of the exfoliation.

To date, exfoliation of single- or few-layer graphene fluoride from graphite fluoride using sonication in various liquid media has been reported, including sulfolane, isopropanol (IPA), ethanol, ionic liquids, N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), chloroform, acetonitrile, and aqueous solutions in the presence of surfactant. Zbořil et al. prepared graphene fluoride using a one-step exfoliation process, which involved suspending graphite fluoride in sulfolane, followed by sonication [64]. It is found that the high polarity of sulfolane is capable of stabilizing the exfoliated layers in the solution. The product consisted of a large fraction of single layers, although multi-layers (2–4 nm in thickness) were also observed. Cheng et al. [26] reported the exfoliation of fluorinated HOPG crystals into thin sheets in IPA using sonication, which were deposited onto a TEM grid for characterizing the structure of the fluorinated compounds. Similarly, graphene fluoride was fabricated by sonicating graphite fluoride in IPA [65,66] or ethanol [67,68] at room temperature. Chang et al. prepared a colloidal dispersion of single- and few-layer graphene fluoride in ionic liquid (1-butyl-3-methylimidazolium bromide) using sonication at room temperature [69]. The formation of graphene fluoride is attributed to surfaceenergy matching between the ionic liquid and the graphene sheets in graphite fluoride. As a consequence, ionic liquid molecules can intercalate into the layers and absorb on the surface, leading to a significant decrease in van der Waals interaction between neighboring layers. The exfoliated graphene fluoride was 1–4 nm in thickness and 2–10 μ m in lateral size. The exfoliation of graphene fluoride in NMP has been reported, which involved refluxing the mixture of graphite fluoride and NMP, followed by sonication at room temperature [70–74]. Similar to the exfoliation in ionic liquid, surface energy matching and intercalation of NMP into the graphite fluoride layers might contribute to the exfoliation. Strong shear force caused by ball milling in the presence of NMP also resulted in the exfoliation of graphene fluoride, which gave a high yield of 38% compared to other liquid-phase methods [75]. The exfoliated sheets were assembled into a flexible film showing ultrahigh thermal conductivity and good electrical insulation. Exfoliation of graphene fluoride has also been achieved with DMF using sonication or microwave-assisted methods [76,77]. A one-pot sonochemical preparation of graphene fluoride in chloroform was reported by Zhu et al. [78]. The exfoliated nanosheets had a lateral size of 200-500 nm and an average thickness of 0.8 nm. The use of chloroform and acetonitrile as liquid media for the exfoliation was also studied by Sun et al. [79]. Wrinkled few-layer graphene fluoride sheets with disordered edges and poor stacking order were observed. It was found that the intercalation of chloroform resulted in partial transformation of C-F bonds from covalent to semi-ionic bonds. Wang et al. prepared graphene fluoride by adding graphite fluoride, dopamine, and cetyl-trimethyl-ammonium bromide (CTAB) into Tris-HCl solution. The mixture was subjected to sonication to produce the exfoliated sheets [80]. The exfoliation of fluorinated graphene oxide can also be performed in deionized water with sonication [81]. The presence of hydrophilic oxygen-containing groups on the surface of fluorinated graphene oxide facilitated its dispersion in water.

Table 1 shows a summary of the conditions used in those reports, including the boiling points and surface tensions of the solvents, relative polarity, exfoliation methods and temperatures, and post-processing. Note that there are roughly two groups of liquid media used depending on their boiling points and surface tensions: solvents with relatively lower boiling points (61–82 °C) and surface tensions (22–30 mN/m) such as ethanol, IPA, chloroform, and acetonitrile; and solvents with higher boiling points (153–285 °C) and surface tensions (37–46 mN/m) such as sulfolane, NMP, and DMF. The latter typically involves additional post-processing steps, e.g., washing with water/ethanol and/or freezedrying to remove the solvents. The use of water as the liquid exfoliation medium could be more attractive for sustainable applications. In addition, polar solvents are typically used for the intercalation and exfoliation. Note that some of the polar aprotic solvents such as NMP and DMF have been found to induce partial defluorination due to the interaction between graphene fluoride and the solvent molecules [72,77,79].

Solvent	Boiling Point (°C)	Surface Tension at 20 °C (mN/m)	Relative Polarity	Exfoliation Method	Exfoliation Temperature (°C)	Post-Processing	Ref
Sulfolane	285	46.0 (50 °C)	0.41	Sonication (B)	50	Separate supernatant	[64]
IPA	82.5	23.0	0.55	Sonication	-	-	[26]
IPA	82.5	23.0	0.55	Sonication	-	Centrifuge; Freeze drying	[65]
IPA	82.5	23.0	0.55	Sonication (B)	-	Centrifuge	[66]
Ethanol	78.4	22.1	0.65	Sonication	-	-	[67]
Ethanol	78.4	22.1	0.65	Sonication (B)	-	Remove sediment using separatory funnel	[68]
[bmim]Br	-	-	-	Sonication (B)	-	Centrifuge; Wash with ethanol	[69]
NMP	202	40.8	0.36	Sonication (B)	RT	-	[70]
NMP	202	40.8	0.36	Sonication (B)	RT	Wash with water; Freeze drying	[71]
NMP	202	40.8	0.36	Sonication (B)	RT	Filtration; Freeze drying	[72]
NMP	202	40.8	0.36	Sonication (B)	RT	Filtration; Freeze drying	[73]
NMP	202	40.8	0.36	Sonication (B)	-	Centrifuge; Washing; Freeze drying	[74]
NMP	202	40.8	0.36	Sonication (B)	RT	-	[111]
NMP	202	40.8	0.36	Ball milling	RT	Centrifuge; Washing; Freeze drying	[75]
DMF	153	37.1	0.39	Sonication	-	Separate supernatant	[76]
DMF	153	37.1	0.39	Sonication	-	Centrifuge	[77]
Chloroform	61.2	29.9 (0 °C)	0.26	Sonication (P)	0	Centrifuge	[78]
Chloroform Acetonitrile	61.2 82	27.5 28.9	0.26 0.46	Sonication	RT	Re-disperse in NMP; Centrifuge; Filtration	[79]
Water (surfactant)	100	-	1.00	Sonication	RT	Filtration; Wash with water; Freeze drying	[80]
Water	100	72.8	1.00	Sonication	-	-	[81]

Table 1. A summary of the conditions used in liquid-phase exfoliation strategies.

Sonication (B), bath sonication; Sonication (P), probe sonication; RT, room temperature.

4.4. Electrochemical Exfoliation

The simultaneous fluorination and exfoliation of graphite may be achieved by electrochemical method in electrolytes containing HF as fluorinating agent (10 w.%) [82]. Fluorine content, defect density morphology and structure of the prepared powders, mainly multilayered graphene sheets, can be tailored according to the applied voltages. It is to be noted that HF solution is not a proper electrolyte for the preparation of few-layered graphene sheets. Moreover, the addition of TiO₂ (2.5 g/L) in the HF solution had positive effects on both exfoliation and fluorination of graphene sheets. TiO₂ particles can be dissolved in HF solutions, forming TiF₆⁻ ions, which may favor the exfoliation.

5. F-Diamane

Atomically thin diamond, namely "diamane", has recently emerged as a new twodimensional carbon allotrope. Unlike graphite which has a layered structure, diamond possesses a three-dimensional crystalline structure that becomes unstable when thinned down to the thickness comparable to the dimensions of diamond's unit cell. Chemical modifications of the surface carbons with specific functional groups using fluorination (F-diamane) or hydrogenation (H-diamane) are necessary to stabilize the structures at ambient conditions. Recently, theoretical studies predicted the conversion of graphene layers into ultrathin diamond films by attaching fluorine atoms (or hydrogen atoms or hydroxyl groups) to the surface of graphene [65,83–85]. For example, complete fluorination of a monolayer graphene can yield a thermodynamically stable sp³-bonded layer [86]. The evidence of fluorination of monolayer graphene membranes has been shown experimentally. Later, Odkhuu et al. [87] showed that when a one-side surface of a supported graphene bilayer grown/coated on a transition metal surface is fluorinated, the energetics for the conversion to sp³-bonded films were significantly lower than that for the free-standing bilayer [87].

Recent advances in the growth of large-area, high-quality graphene films with a precisely controlled number of layers have suggested promising pathways for experimental conversion of graphene into "diamane" films. Bakharev et al. [88] reported that chemisorption of fluorine on chemical vapor deposition grown bilayer graphene resulted in the formation of an F-diamane film [88]. In their experiment, bilayer graphene films grown on CuNi (111) surface were fluorinated at 65 °C under 50–60 Torr vapor pressure of XeF₂. It was found that, by changing the fluorination conditions (temperature, XeF_2 partial pressure, and exposure time), the fluorinated graphene structures can be controlled to have different C/F ratios. The F-diamane film was found to be an ultra-thin wide-band gap semiconductor. Rajasekaran et al. reported experimental evidence that hydrogen adsorption could induce partial phase transition of few layers of graphene to a diamond-like structure on Pt(111) [89]. Hot filament process has been used to expose bilayer graphene to hydrogen radicals for the preparation of diamane films [90–92]. UV Raman spectroscopy was used in their studies to track the structure conversion, which showed the presence of a sharp sp³-bonded carbon stretching mode and absence of sp²-bonded carbon peak. Based on the experimental studies of diamane, density functional theory (DFT) simulations have also been used to explore the stability, mechanical, electronic, and optical properties of diamane nanosheets [93]. Zheng et al. [94] studied the vibrational properties of diamane nanoribbons [94]. Compared with graphene, diamane resonator showed a higher natural frequency and a larger quality factor on the order of 105, and it could be useful for developing ultra-sensitive resonator-based nanosensors.

6. Chemical Bonding and Related Properties

The C–F bonding in FG has been extensively discussed in the in-depth review from Feng et al. [34]. As in graphite fluorides, the C–F bonding is highly versatile in FG and strongly depends on both the fluorine content (F/C atomic ratio) and the distribution of F atoms along the graphene layer(s). The C–F bonds in FG are mainly covalent but their weakening may occur when non-fluorinated sp² carbon atoms are located around the C–F bonds. Hyperconjugation between C–F and sp² C occurs [95,96]. The terms of weakened covalence appear more significant than semi-covalent (semi-ionic). The C–F bond length is close to 0.17 nm, as in room temperature graphite fluoride, whereas a C–F bond in fully fluorinated neighbor is 0.14 nm long [24]. A recent study using polarized attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR) evidenced two types of C–F bonds (Figure 4): the first are linked at the coplanar carbon atoms in the weakly fluorinated region (C_xF, x ≥ 2), whereas the second type are in cluster at the strongly deformed carbon framework with an F/C ratio of about 1 [97]. The coplanar structure of weakly fluorinated graphene sheets (weakened covalence) is more likely to transform to the planar aromatic ring with the breaking of the C–F bond more easily as compared with

the strong fluorinated nonplanar region (covalent). In comparison with C–F bonds with weakened covalence, semi-ionic C–F bonds have a higher discharge voltage and a more excellent rate capability compared to covalent C–F bonds. The C–F bond with weakened covalence can be selectively reduced, leading to the recovery of conductivity [98]. By comparison, the covalent C–F bonds exhibit higher stability and higher bond dissociation energy, which is equal to 460 kJ/mol. The coplanar structure of the weakly fluorinated region tends to transform to the planar aromatic ring with the breaking of the C–F bond as compared with the strong fluorinated nonplanar region [97].



Figure 4. Changes of the F/C ratio and color during the fluorination of rGO with F_2/N_2 mixture (**a**); scheme of polarized ATR-FTIR acquisition (**b**) and data (**c**) related to C–F bonding (reproduced/adapted with permission from ref [97], Copyright, 2016, American Chemical Society).

The energies required for homo- and heterolytic cleavage of the C–F bond were rather high (418 kJ/mol). As an additional proof of the hyperconjugation, the energy required for homolytic cleavage decreased significantly as the fluorine content decreased in FG [99]. This may result in spontaneous loss of fluorine atoms from FG with low F content. We strongly agree with the authors of this work who claimed that FG appears as a "viable precursor for the synthesis of graphene derivatives and cannot be regarded as a chemical counterpart of Teflon".

The difference in stability affects the electrochemical performances in energy storage devices, as discussed thereafter.

The decrease in stability of C–F bonds with weakened covalent may favor other functionalization of graphene. Defluorination assists the N-doping of graphene with a large doping degree [100]. In comparison with GO, FG possesses a higher reactivity with ammonia, enabling nitrogen doping to proceed efficiently at a lower temperature via substitution of C–F bonds by C–NH₂ groups followed by the cyclization to the three-membered ring of ethylenimine of these groups. The dissociation and migration of C–F bonds the dissociating of C–C bonds and the recombining of C–N bonds.

The C–F bonding may be estimated by the stability under electron beam irradiation. The double-sided fluorinated graphene exhibited a much stronger stability than the single-sided fluorinated graphene under the same irradiation dose [29]. According to DFT calculations, the configuration of double-sided fluorinated graphene has a negative and

low formation energy and then an energetically stable structure contrary to single-sided fluorinated graphene.

7. Applications

7.1. Tribological Performances

In today's world, so much energy is lost due to friction in mechanical components. To address this issue, lubricant is added because it not only removes the friction heat but also reduces unnecessary energy loss by reducing the wear and friction [101,102]. In order to enhance the performance of the lubricant, adding lubricant additives is an indispensable strategy. The lubricant additive owns many different functionalities, such as anti-wear, anti-oxidation, anticorrosion, defoaming capability, viscosity modifier, dispersant, etc. [103–105].

In recent years, 2-dimensional (2D) layered materials including tungsten disulfide (WS₂), molybdenum disulfide (MoS₂), graphitic materials, and hexagonal boron nitride (h-BN) have been widely used as solid lubricants owing to their easy shear between lattice layers [106–108]. These 2D materials have been extensively investigated for a better adaptability to extreme environmental conditions and contact pressures [106]. In addition, there have been consistent efforts by the researchers worldwide to improve their tribological performance, i.e., anti-wear and friction reduction performance [108]. Among various 2D materials, graphene has attracted worldwide attention because it exhibits excellent electrical, thermal, mechanical, stable chemical properties [109], as well as tribological properties [110]. Thanks to these unique properties, graphene-based materials are widely used as lubricant additives. In fact, graphene film can significantly decrease the friction coefficient between friction pairs [111,112]. Furthermore, the small-sized nanosheets with only a few nanometer thickness allow graphene to easily enter the friction contact surfaces [113,114]. Despite its interesting properties, pristine graphene has some disadvantages including structural defects and chemical inertness which is induced by the delocalized π electron system [115]. The strong $\pi - \pi$ interaction between graphene layers restricts the interlayer slippage of graphene [111]. The chemical inertness of graphene hinders the stable formation of a solid tribofilm on the friction pairs [116], limiting the lubrication and wear-resistance performances of graphene at the macroscale. Moreover, the friction coefficient of graphene is not sufficiently low at the macroscale. To overcome these shortcomings, the design of novel graphene-based materials has become a critical component of emerging technologies. Therefore, researchers have focused on functionalizing pristine graphene to form free radicals or functional groups which could improve the overall properties of the material, i.e., surface activity, structural integrity, and processability without altering the unique carbon conjugated structures of graphene [111,117]. In the literature, several types of functionalization methods have been reported and the modified graphene nanosheets showed an excellent performance of friction reduction and anti-wear as lubricant additives. Covalent functionalization has been commonly used to obtain functionalized graphene, including graphene oxide (GO) [118], polydopaminefunctionalized GO [119], hydrogenated graphene [120], and acid-grafted graphene [121]. Furthermore, the functionalized graphene exhibited worse chemical and thermal stabilities compared to graphene, owing to the large contents of surface substituents or defects [34]. The functionalized graphene structures such as GO and hydrogenated graphene exhibited higher frictions attributed to their higher surface energies [122,123]. In addition, the tribological performances of graphene-related materials are largely restricted by the external environment [124–126]. Fluorographene is another important class of graphene-derived material, and has attracted an immense research interest since its introduction in 2010 [32] due to its excellent performances [32,42,46,64,67,115,127–133]. FGs not only hold the properties of graphene but also possess the characteristics of fluorine-based materials such as excellent thermal and chemical stability, mechanical strength, and larger interlayer distance compared to pristine graphene [134]. FG inherits the excellent mechanical properties of graphene even though fluorination disrupts the van der Waals forces between the FG

sheets [135]. Thus, FG is widely used as lubricant additive thanks to its outstanding tribological performance [32,136,137]. For instance, Ye et al. [138] reported that FG can be used to enhance the mechanical properties of polymers; also Liu et al. [111] evidenced that FG coating on a stainless-steel substrate exhibited an excellent lubrication performance, which reduced the friction by a factor of 2. Kwon et al. [47] investigated the effect of fluorination on friction, adhesion, and the charge transport properties of chemical vapor deposition (CVD)-grown graphene using ultrahigh vacuum friction force microscopy and their 2D characteristic spring model; the friction measured on FG was modulated up to 6 times larger than on pristine graphene, while fluorination slightly reduced the adhesion force [47]. In addition, Hou et al. [73] prepared FG by liquid-phase exfoliation of graphite fluoride, and the friction tests confirmed that FG could greatly enhance the anti-wear property compared with pure base oil. Furthermore, Liu et al. [111] fabricated a fluorinated graphene (FG) coating on a stainless-steel substrate by a simple electrophoretic deposition in ethanol. The FG coating exhibited excellent lubrication performances under different contact pressures which reduced the friction coefficient by 54.0% and 66.2% compared to those of pristine graphene and GO coatings, respectively. The authors attributed the lubrication enhancement of FG coating to its extremely low surface energy and interlaminar shear strength [111]. However, although FG possesses numerous excellent properties, it cannot be really applied in aqueous environments due to its high hydrophobicity [59]. To address this issue, Ye et al. [72] have reported the covalent functionalization of FG by urea via part replacement of fluorine (UFG), and such replacement can change the surface wettability of FG from hydrophobicity to hydrophilicity. The authors have evidenced that the prepared UFG has a very good dispersibility in water, which allows UFG, as an effective lubricant additive, to enhance the tribological property of the water. Tribological tests have demonstrated that the sample of UFG-1 exhibited the best antiwear ability with a 64.4% decrease of wear rate compared with that of the pure water (UFG-0) [72]. Li et al. [139] combined experiments and molecular dynamics simulations to propose a novel mechanism in which friction can be altered over a wide range by fluorination; the friction force between silicon atomic force microscopy tips and monolayer fluorinated graphene can range from 5-9 times higher than for graphene. The proposed mechanism suggests that the dramatic friction enhancement results from increased corrugation of the interfacial potential due to the strong local charge concentrated at fluorine sites, consistent with the Prandtl-Tomlinson model. The monotonic increase of friction with fluorination in experiments also demonstrates that friction force measurements provide a sensitive local probe of the degree of fluorination [139]. Recently, an interesting contribution by Fan et al. [140] reported the development of a novel and simple means to achieve lossless covalent functionalization of FG by activating dormant radicals, improving its water dispersibility, and simultaneously maintaining intrinsic self-lubricating ability with limited commensurate stacking and weak interlayer interactions. The obtained materials present excellent tribological performances as a water-based lubricant additive and are regarded as an ecofriendly and sustainable system, whose friction coefficient and wear rate have about 66% and 82% decrease compared to that of polyethylenimine (PEI) grafted fluorinated graphene (FG-PEI), respectively [140].

A low fluorine content CF_{0.05} in FG resulting from thermal exfoliation using a thermal shock is enough to achieve low friction coefficient remarkably as soon as the first friction cycle (Figure 5) [141]. Although there is massive defluorination during exfoliation, the comparison of raw and exfoliated graphite fluorides evidenced that exfoliation does not deteriorate the excellent lubricating performances because of the weakening of the interparticles' interactions due to the exfoliation process. Exfoliated structure may facilitate the formation of a homogeneous and stable tribofilm even if the fluorine content is low.



Figure 5. Friction coefficients after 10 cycles (**a**) and as a function of cycle number (**b**) of raw graphite fluoride (F-Gr) and thermally exfoliated graphite fluoride (Exf-FG), evaluated under air atmosphere using a ball-on-plane tribometer in which a ball describes a reciprocating motion on a static steel plane (**c**) (reproduced/adapted with permission from ref [141], Copyright, 2016, Royal Society of Chemistry).

According to the fluorination route, the friction properties differ. Compared with FG synthesized using exfoliation method, FG prepared by direct gas fluorination has uniform size distribution and similar thickness. Furthermore, F/C ratios of FG synthesized by gas fluorination could be controlled easily by regulating the heating temperature. FG with higher F/C ratio significantly enhanced the friction reduction and anti-wear properties as lubricant additive because more covalent C–F bonds are present that could ensure steady chemical properties during the friction process [116]. On the other hand, the size of FG was reduced with the increase of F/C ratio because of the special properties of synthesizing method. The small size made it possible for FG to enter the contact area easily, thus improving the good tribological properties of FG.

7.2. Energy Storage

Modified graphenes have been successfully considered for energy and storage applications over the years [142–144]. In particular, fluorinated graphene is one of the most promising materials for energy application thanks to its tunable electrochemical properties, its lightweight, high in-plane conductivity and mechanical strength which make FG a promising material for energy applications. FG used as cathode material for primary lithium battery could open the way for high-performance Li primary cells for large-scale applications. FG obtained through chemical exfoliation of graphite fluoride ($CF_{0.25}$)_n exhibited enhancements in both energy density and power capability along with exceptional faradaic yield, all achieved in a single step [145]. As claimed by the authors, the obtained specific capacity for FG derived from ($CF_{0.25}$)_n was comparable to the theoretical capacity of ($CF_{0.75}$)_n. Further improvements in electrochemical performances could be achieved

by optimizing the fluorine content in the starting material. Meduri et al. [130] studied the effect of fluorine content in fluorinated graphene on the structure and electrochemical properties when these materials were used as cathode materials in primary lithium battery. FG used was synthesized by partial fluorination of graphene having high and moderate fluorine content, i.e., F/C = 0.47, 0.66, and 0.89; the material with the highest fluorine content ($CF_{0.89}$) consisted of stacked graphene layers with surface insulating groups such as CF₂ and CF₃ which were considered as structural defects that hindered the electrochemical performance. In contrast, $CF_{0.47}$ composed of fluorine primarily on the surface with small amounts of CF_2 and CF_3 groups led to the lowest overall resistance [130]. Compared to graphite fluoride, the transport of solvated Li⁺ ions within fluorinated graphene was greatly improved, benefiting the high-rate performance. In addition, the large amounts of residual graphene domains along with defective sites also contributed to the greatly improved performance of CF_{0.47}. The distribution of the discharge product LiF clearly indicated the original location of C–F bonding, and thus appears as a good electrochemical approach to probing fluorine atoms on graphene (providing information for the indirect detection of functional groups) [78].

Lim et al. [37] also showed the importance of the amount of fluorine if FG is considered for energy and sensing applications. The electrochemical and electrocatalytic properties of three FGs, namely, $CF_{0.02}$, $CF_{1.02}$, and $CF_{1.39}$ were investigated in order to evidence the impact of different fluorine levels. FGs exhibited enhanced electrochemical sensing in various biomarkers, including uric acid, ascorbic acid, and dopamine, and also in energy applications, such as hydrogen evolution and oxygen reduction over the bare glassy carbon electrode surface [37]. The higher the fluorine level, the higher the electrochemical and electrocatalytical performance [71].

FG use is of concern not only as cathode materials in primary Li batteries but also as anodic material in lithium ions batteries. Cheng et al. [146] reported a fluorinated graphenemodified Li negative electrode (LFG) for high-performance lithium–oxygen (Li $-O_2$) cells; only 3 w.% FG introduction leads to a significant enhancement on rate capability and cycling life of Li electrodes. Compared with the half cells with bare Li, the cells with LFG exhibit much more stable voltage profiles even at a large areal capacity up to 5 mAh cm⁻² or a large current density up to 5 mA cm⁻² [146]. Two significant improvements were achieved: (i) Li–O₂ cells with the LFG anode show a longer cycle life than the cell with the pristine lithium anode, (ii) a LiF-rich layer could be in situ built upon cycling when FG is used, which ensures uniform Li stripping/ plating and effectively suppresses Li dendrite growth [146]. In fact, lithium dendrite growth is harmful for the battery performances as the incessant lithium dendrite growth during charge/discharge cycles of the battery will pierce the separator, and the Li dendrite will finally reach the cathode, leading to cell short circuit [147]. It also induces cracking and collapsing of the solid electrolyte interphase (SEI) layer, rendering a more exposed fresh Li surface and more parasitic reactions with the electrolyte, causing low coulombic efficiency and short cell life [148,149].

In spite of the relatively high fluorine content achieved during hydrothermal process [56], high electrical conductivity may be maintained thanks to the predominance of C–F bonds with weakened covalence. High pseudo-capacitance and improved specific capacitance (227 F/g), power density as high as 50 kW/kg (at the current density of 50 A/g) as well as good rate capability were achieved in supercapacitor. The hydrothermal temperature of 150 °C appeared to be the best to reach those performances. Maintaining the C–F bonds with weakened covalence appears as a key point to achieve good performances in supercapacitors. The fluorination time is a parameter to both favor those bonds and limit the formation of groups (such as CF₂, CF₃, etc.) in fluorine-rich surface; those ones are electrochemically inactive. This was clearly evidenced for FG obtained with hydrothermal fluorination of a GO suspension and used as electrode materials for supercapacitors [150]. An impressive specific capacitance of 1222 F/g at 1 A/g has been reported when a fluorinated graphene (GF) obtained at the optimal fluorination was included in composite with CoAl-layered double hydroxide (LDH) with a thermal process too. LDH crystals were in

situ anchored on the surface of FG. The electronic conductivity and transport performance of C-F bonds with weakened covalence allow the high performances to be reached.

In spite of their high specific surface area, a low capacitance of thermally exfoliated graphite fluorides was recorded in supercapacitor with an aqueous electrolyte (about 21 F/g), which was related with the hydrophobic behavior [63]. With such an aqueous electrolyte, the presence of C–F bonds is detrimental and the surface chemistry must be changed in order to improve the wettability of the electrode by adding redox active oxygen species as the authors of this work did; the specific capacitance increased to 158 F/g after a mild oxidation in a mixture of concentrated H_2SO_4/HNO_3 .

7.3. Gas Sorption and Sensing

Molecular simulations have been used to reveal the effect of fluorination of graphene surfaces on the adsorption of various gases. Studies suggested that fluorine-modified porous graphene membrane might provide excellent selectivity for the separation of CO_2/N_2 [151]. DFT calculations and experimental studies revealed that the C–F bonds in graphene fluoride improved adsorption of NH₃ molecules and provided a higher sensitivity compared to pristine graphene [59]. Fluorinated graphene also showed sensitivity to ethanol, methane, and formaldehyde gases [152]. The introduction of fluorine into graphene-based materials can improve gas-sensing properties given that the fluorine could modify the surface chemistry and electrical properties of the materials. Fluorinated graphene oxide-based sensors have been reported for sensing NH₃, showing improved sensitivity, selectivity, and reversibility with a significantly low theoretical detection limit of ~6 ppb at room temperature [153–155]. DFT calculations revealed the role of fluorine in changing the charge distribution on the functional groups in graphene oxide, leading to selective adsorption and desorption of NH₃ molecules. In addition, the effects of chemical modifications of graphene fluoride with hydrazine [155] or hydroxyl species [156] on the adsorption of gas molecules have been revealed. The fluorinated graphene sensor showed a much better regeneration after simply purging with Ar at room temperature. DFT calculations indicated that NH₃ and NO₂ molecules are adsorbed on fluorine, hydroxyl groups, and the carbon atoms close to the functional groups. Oxyfluorinated graphene is expected to have a stronger adsorption energy for NH_3 due to the short N/H(O) contact.

Graphene fluoride has been used for electrochemical sensing of ascorbic acid and uric acid. It was found that increasing the level of fluorination up to $CF_{0.75}$ led to improved performance on both the response linearity of the electrode and resolution of the oxidation peaks of the sensing molecules [37,157]. Graphene fluoride has also been used in a biosensor platform for electrochemical detection of NADH and dopamine [43]. Fluorinated graphene functionalized with thiol groups showed an effective DNA impedimetric sensitivity. This is attributed to the interactions between the DNA strands and thiol groups. DFT calculations showed that the thiol-modified graphene derivatives were thermodynamically stable only when fluorine adatoms were present on the graphene [158]. The use of fluorinated graphene oxide as a sensing material for the simultaneous detection of various heavy metal ions has been reported [159]. Recently, fluorinated graphene oxide sensor was also used for detecting caffeic acid in wine [160].

Taking benefit of hydrogen bonding between FG and water molecules, a resistive humidity sensor with FG as sensitive material was developed. According to DFT calculations, the hydrogen atoms of the water molecule move towards the fluorine atom of the FG during the relaxation process [161].

7.4. Nanocomposites and Coating

Presence of fluorine atoms allows the surface energy to be adjusted at a value closer than the one of hydrophobic polymer matrix (e.g., polypropylene) for the preparation of composites. Thanks to the improved exfoliation and dispersion of the filler in the polypropylene (PP) matrix, the composites with FG showed little improvement in mechanical properties and a sharp drop in elongation at break [57]. With the same strategy

of filler/matrix tailoring of their surface energy, fluorinated graphene/polyimide (PI) nanocomposite films were prepared. Because of their individual graphitized planar structure, their high surface area, and the presence of some oxygen-containing functional groups, excellent dispersion of the FG nanosheets in the PI matrix has been achieved. The hydrophobicity, which is provided by F atoms, associated with low dielectric constant, low dissipation factor, and good optical properties makes these films promising for advanced electronic packaging of fan-out wafer level package (FO-WLP).

Highly thermally conductive and electrically insulating materials for heat dissipation are required for portable and flexible electronic devices. FG-based composite films with well-organized alignment of fluorocarbon layers along the in-plane direction exhibit the needed characteristics, i.e., ultrahigh in-plane thermal conductivity ($61.3 \text{ W m}^{-1} \text{ K}^{-1}$) and mechanical flexibility [66]. Polyvinyl alcohol was added to FG (from graphite fluoride sonically exfoliated) in order to both facilitate the uniform dispersion of FG in water and enhance the linking between adjacent FG nanosheets.

FG coating on Cu plain surface is able to enhance the boiling heat transfer performance [48]. The heat transfer performance was enhanced thanks to the hydrophobicity of C–F bonds' surface against the nonpolar molecule of refrigerant that created more boiling active sites and increased the bubble size. In other words, the vaporization is catalyzed on the fluid/graphene interface. The chemical stability of FG during harsh thermal cycling operation is higher than conventional polymer coating.

8. Conclusions

The aim of the present review was to exhaustively present the synthesis routes of fluorinated graphenes. The fluorinating agent for fluorination or exfoliation must be chosen according to the precursor and its quality (number of layers, i.e. monolayer, few-layers, presence of defects, functional groups with oxygen). The direct fluorination of graphene oxide with molecular fluorine appears to be the easier route to produce fluorinated graphene at large-scale but the resulting materials contain residual oxygenated groups. The quality of the resulting FG depends on the quality of the precursor; methods other than direct fluorination with F_2 , such as fluorinating agent (XeF₂) must be used and the cost is significantly increased. Thermal and liquid phase exfoliations appear to be intermediate in terms of cost and quality. The thermal exfoliation results in low fluorine content because of simultaneous exfoliation/defluorination. On the contrary, exfoliation in the liquid phase allows high fluorine content to be maintained but the use and removal of organic solvents complicate the method and acts in the final yield. The main applications are also discussed, for energy storage, lubrication, gas sorption and sensing, and nanocomposites.

Whatever the use, careful attention must be paid to the C–F bonding in addition to the fluorine content. Figure 6 summarizes the main application as a function of the F/C ratio. Most of those applications may be planed only if cytotoxicity of fluorinated graphene is fixed. The cytocompatibility of fluorinated graphene has been studied by comparing the biological responses of cells to graphene treated by SF₆ plasma at different F contents [53]. Thanks to the presence of C–F bonds, biological response to rat bone mesenchymal stem cells (rBMSCs) and cytotoxity are good as well as the facilitation to cell adhesion at early stage. However, for the case of fully fluorinated graphene, the cell viability decreased. In a general way, the biological response depends on the fluorine content, i.e., on both the C–F bonding and the maintaining of sp² carbon providing possible π - π interaction between the surface of FG and biologic component. The adhesion and aggregation of blood platelets is reduced. Favorable antibacterial ability against *E. coli* of partially fluorinated graphene was also evidenced in this work.



Figure 6. Some applications of fluorinated graphenes, in supercapacitors ((**a**) reproduced with permission from [162], Copyright, 2014, American Chemical Society), conductive films ((**b**) reproduced with permission from [66], Copyright, 2019, American Chemical Society), electronic devices ((**c**,**d**), reproduced with permission from [60], Copyright, 2011, American Chemical Society and [33] Copyright, 2010, American Chemical Society), lubricants ((**e**) reproduced with permission from [47], Copyright, 2012, American Chemical Society), lithium ions battery ((**f**) reproduced with permission from [163], Copyright, 2016, Wiley) and gas sensors (here NH₃) ((**g**) reproduced with permission from [59], Copyright, 2016, American Chemical Society).

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