Original Scientific Article

Highly Exfoliated Graphite Fluoride as a Precursor for Graphene Fluoride Dispersions and Films[†]

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Abstract. We synthesized highly exfoliated graphite fluoride of approximate composition C_2F by treating highly exfoliated graphite with ClF_3. The formed material was found to be dispersible in solvents giving 1 to 5 layered fluorinated graphene. Dispersions successfully formed in polar organic solvents capable of establishing hydrogen bonds. The highest stability is achieved in branched alcohols such as *tert*-butanol. The dispersions may be further processed into thin films by vacuum filtration technique. Also, composite multilayered films of graphene fluoride and graphene may be prepared. (doi: 10.5562/cca1972)

Keywords: graphite, fluoride, graphene, dispersion, film

INTRODUCTION

Graphene, a single layer of graphite, has emerged as a new material with outstanding properties of both fundamental and practical interest. Some unique features associated with these 2D crystals have been discovered.[1–4] In addition to single graphene sheets, double-layer or multiple-layer graphene sheets also exhibit unique and useful behaviors.[1,5–7] Several derivatives of graphene have been described in literature: (i) the long-known graphite oxide (GO) that disperses in solvents into individual layers[8–15] and may be further treated to attach various functionalities,[16–24] and the more recently synthesized analogues of graphene – (ii) graphane (hydrogenated counterpart)[25–27] and (iii) fluorographene.[28–32]

Fluorine has a number of influences on graphene modifying its electronic properties, introducing scattering centers and opening band gaps. The availability of processable fluorographene sheets in large quantities is essential to the success in exploiting its applications. Basically, there are two different approaches that have been followed to produce fluorinated graphenes: (1) fluorination of pre-synthesized graphene. This approach entails treating graphene prepared by mechanical exfoliation or by CVD growth with fluorinating agent such as XeF_2,[28,30] or F-based plasmas;[32] (2) Exfoliation of multi-layered graphite fluorides. Mechanical exfoliation of

commercial or laboratory-made[29,30] graphite fluoride was reported, but fragility of its monolayers made it difficult. More recently, in December 2010, liquid-phase exfoliation of graphite fluoride was described.[31] This approach to exfoliation was earlier developed for fluorinated carbon nanotubes.[33]

The latter synthetic strategy would be a good alternative to the consecutive graphene synthesis and fluorination. One obstacle to this is a high stability of commercial covalent graphite fluorides, and another is its big particle size (thickness).

The research of fluorinated carbon materials dates back to the first half of the 20th century.[34] Interaction of F_2 with graphite at high temperature leads to covalent graphite fluorides $(CF)_n$ or $(C_2F)_n$, while at low temperatures graphite intercalation compounds (GIC) C_xF ($2 \leq x \leq 24$) form.[35] In $(CF)_n$ carbon atoms are sp^3-hybridized and thus the fluorocarbon layers are corrugated consisting of trans-linked cyclohexane chairs. In $(C_2F)_n$ only half of the C atoms are fluorinated and every pair of the adjacent carbon sheets are linked together by covalent C–C bonds.[35,36] Systematic studies on the fluorination reaction showed that the resulting F/C ratio is largely dependent on the fluorination temperature, the partial pressure of the fluorine in the fluorinating gas, and physical characteristics of the graphite precursor, including the degree of graphitization, particle size, and

specific surface area. In addition to fluorine (F_2), other fluorinating agents may be used, although most of the available literature involves fluorination with F_2 gas, sometimes in presence of fluorides. Fluorinated counterparts of the new forms of carbon, *i.e.* nanotubes, fullerenes and graphene are also known.[37]

For exfoliating a layered precursor material to the state of individual layers or few-layers, it is necessary to overcome the attracting forces between adjacent layers and to further stabilize the layers. This may be achieved by either covalent modification of the graphene surface by functional groups[16–24] or by non-covalent modification using specific solvents,[38,39] surfactants,[40] polymers[41] or donor-acceptor aromatic molecules.[42] The processes for producing graphene by liquid-phase have been recently reviewed by our group.[43] Usually the process of liquid-phase exfoliation includes ultra-sonic treatment of a precursor in a reaction medium of choice as ultrasonic waves facilitate penetration of liquid into the layered graphene precursor and thus promote exfoliation. Finally, the dispersions may be centrifuged to remove aggregates.

In this study, we describe synthesis of highly exfoliated fluorographite material of composition C_2F by fluorinating exfoliated graphite and its dispersion in liquid medium with formation of few-layered fluorographenes.

EXPERIMENTAL

Fluorination of Highly Exfoliated Graphite

In a typical procedure, highly exfoliated graphite (HEG) was prepared from intercalated compound $C_2F \cdot x ClF_3$ according to the method reported earlier.[44] HEG was further fluorinated by vapors of chlorine trifluoride to yield fluorinated highly exfoliated graphite (FHEG). Pre-cooled Teflon reactor was filled with 20–30 mL of liquid pre-cooled ClF_3, the reactor was closed and cooled to liquid nitrogen temperature. Then, no more than 1 g of HEG was put in a container with holes for ClF_3 gas to access and situated inside the reactor. In 7–10 days a gray-beige product with approximate formula C_2F was formed.

Liquid-phase Dispersion of Highly Exfoliated Fluorinated Graphite and Film Preparation

A small amount of FHEG (approximately 0.5mg) was mixed with 20–30 mL of an organic solvent (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, *tert*-butanol, isoamyl alcohol) and subjected to ultrasound treatment (280 W) for 5–60 min. It led to formation of homogeneous yellowish dispersions. Five minutes of sonication was enough to obtain a seemingly homogenous solution, but more lengthy times ensured better stability. Upon filtration through a membrane filter (ex. Anodisc 25 0.02 μm) a brownish film formed on the filter surface. By dissolv-
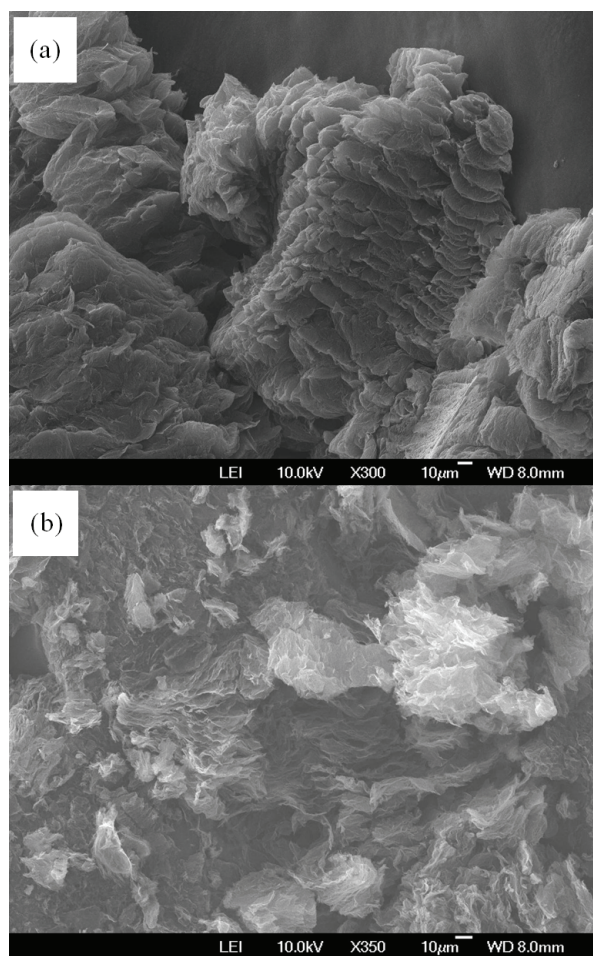
Figure 1. SEM images of highly exfoliated graphite before (a) and after (b) fluorination with ClF_3 vapor.

ing the membrane in an appropriate medium (3 mol dm^{-3} NaOH) and consequent washes with water, it is possible to obtain a film floating on the water surface and recapture it on a substrate of choice. Alternate filtrations of HEG and FHEG dispersions may lead to composite films of multilayered graphene and graphene fluoride.

Characterization

Samples were studied by Scanning electron microscopy and energy dispersive analysis (SEM/EDX), Atomic

Table 1. Elemental composition of fluorinated highly exfoliated graphite by SEM/EDX and XPS analysis

| Element	w / %		Weight uptake
	SEM/EDX	XPS	
C	66.55	67.13	-
F	32.79	28.13	-
Cl	0.67	1.68	-
O	-	3.07	-
Empirical formula	$C_2F_{0.99}Cl_{0.02}$	$C_2F_{0.84}Cl_{0.05}$	$\approx C_2F$
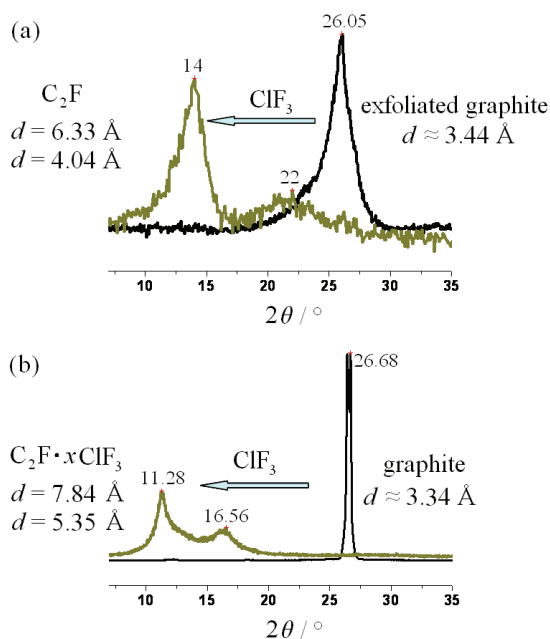
Figure 2. XRD patterns of the products before and after fluorination of (a) highly exfoliated graphite (b) natural graphite.

Force Microscopy (AFM), X-Ray Diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Ultraviolet-visible absorption spectroscopy (UV-Vis).

RESULTS AND DISCUSSION

Fluorination of highly exfoliated graphite by ClF_3 vapors gives a product with stoichiometry corresponding to C_2F as was determined by mass uptake measurements, SEM/EDX ($C_{2.03}F_{0.99}Cl_{0.02}$) and XPS ($C_2F_{0.84}Cl_{0.05}$) (Table 1). The product has a fluffy morphology
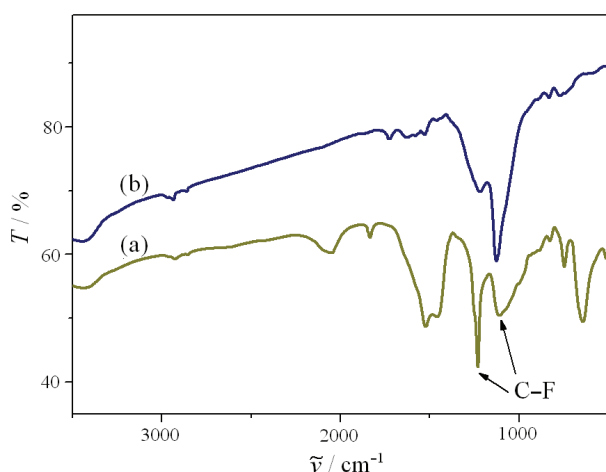
Figure 3. IR spectra of (a) $C_{1.97}F\cdot0.13ClF_3$ (product of natural graphite fluorination with ClF_3) and (b) C_2F (product of highly exfoliated graphite fluorination with ClF_3).
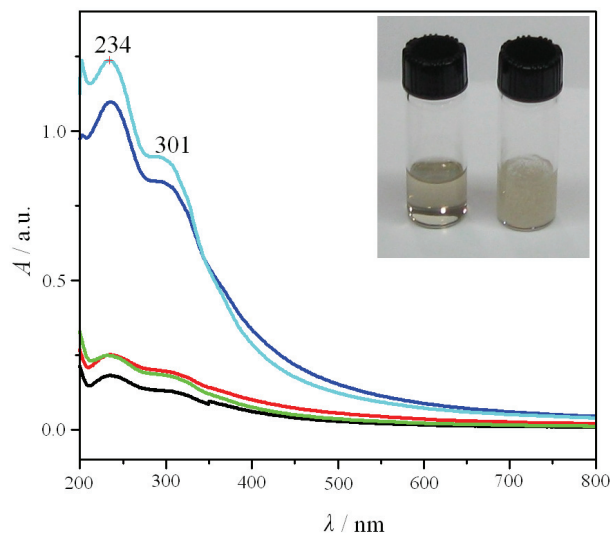
Figure 4. UV-vis spectra of C_2F (FHEG) alcohol dispersions (up down: *tert*-butanol, 1-butanol, 2-propanol, ethanol, methanol). Inset shows a dispersions of FHEG in ethanol/*tert*-butanol mixture and in pure *tert*-butanol at 20 °C.

similar to the parent highly exfoliated graphite as indicated by SEM (Figure 1).

The X-Ray diffraction pattern of FHEG (Figure 2a) showed an intensive reflection at $2\theta \approx 14$ corresponding to $d \approx 6.3$ Å (a broad shoulder around $2\theta \approx 22$ is from the XRD holder). Noticeably, fluorination of natural graphite under the same conditions (ClF_3, room temperature) produced an intercalated compound of composition $C_{1.97}F\cdot0.13ClF_3$ (Figure 2b). No reflections of intercalated compounds are detected for HEG fluorination.

IR spectra of FHEG (Figure 3) showed features typically attributed to C-F bonds (1126 cm^{-1}, 1251 cm^{-1}), but did not show bands characteristic of ClF_3 molecules (642 cm^{-1} and 750 cm^{-1}). Stretching mode of covalent C–F bonds is usually found around 1220 cm^{-1}, and of "semi-ionic" C–F bonds – around 1100 cm^{-1}.[45] These data imply that fluorination of HEG with ClF_3 differs significantly from fluorination of bulk graphite materials. It seems that very low thickness of graphitic domains in HEG may be responsible for the fact that no ClF_3 intercalation takes place and the formed product (FHEG) is graphite fluoride and not a fluorinated GIC.

We found that FHEG is easily dispersible in alcohol solvents under mild sonication (280 W) for 5–60 min (inset of Figure 4). The tested solvents include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, *tert*-butanol, *tert*-isoamyl alcohol. Almost instantly, the mixture appeared homogenous and demonstrated Tyndall effect (light scattering) typical for colloids. The longer sonication times produced more stable dispersions. However, care should be taken with long sonication times if fluorine is to be preserved in the samples, since it was found for F-carbon nanotubes that it may be removed under long sonication.[33]
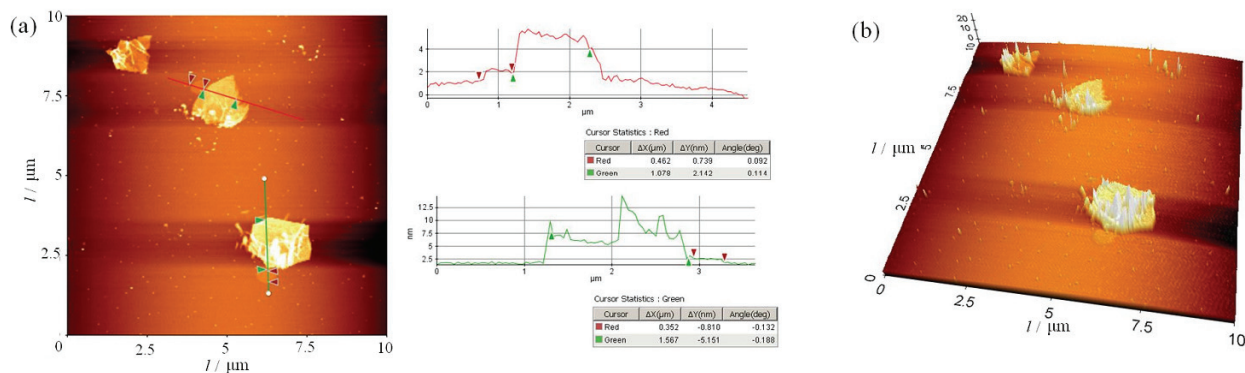
Figure 5. AFM images of nano graphene fluorinated platelets deposited from *tert*-butyl alcohol dispersion of C_2F (FHEG) on freshly cleaved mica (a) image and height profiles; (b) 3D view.

Dispersions in short-chain alcohols (methanol, ethanol) were metastable and precipitated after several hours. The best solvents were alcohols with branched chain such as *tert*-butanol. Consistently with these observations, UV-Vis spectra of the dispersions showed higher absorbance for *t*-BuOH dispersions with maxima at ≈234 and ≈301 nm (Figure 4).

An interesting fact was observed for tert-butanol dispersions: because of the high melting point of the solvent (25 °C) in winter time the dispersions freeze and thus may be stored in a frozen state. They may be melt-ed down easily by light heating or dilution with another alcohol, *i.e.* ethanol (inset of Figure 4).

The mechanism of C_2F (FHEG) stabilization may be related to the increased ionic character of C–F bond in this material facilitating the formation of hydrogen bonds between fluorine atoms of C_2F and hydrogen atoms of alcohols. Such an interaction was suggested to promote dissolution of carbon nanotubes in alcohols.[33]

The dispersions of C_2F in solvents were studied by AFM by depositing a drop of solution on freshly cleaved mica (Figure 5). AFM images show flat platelets with
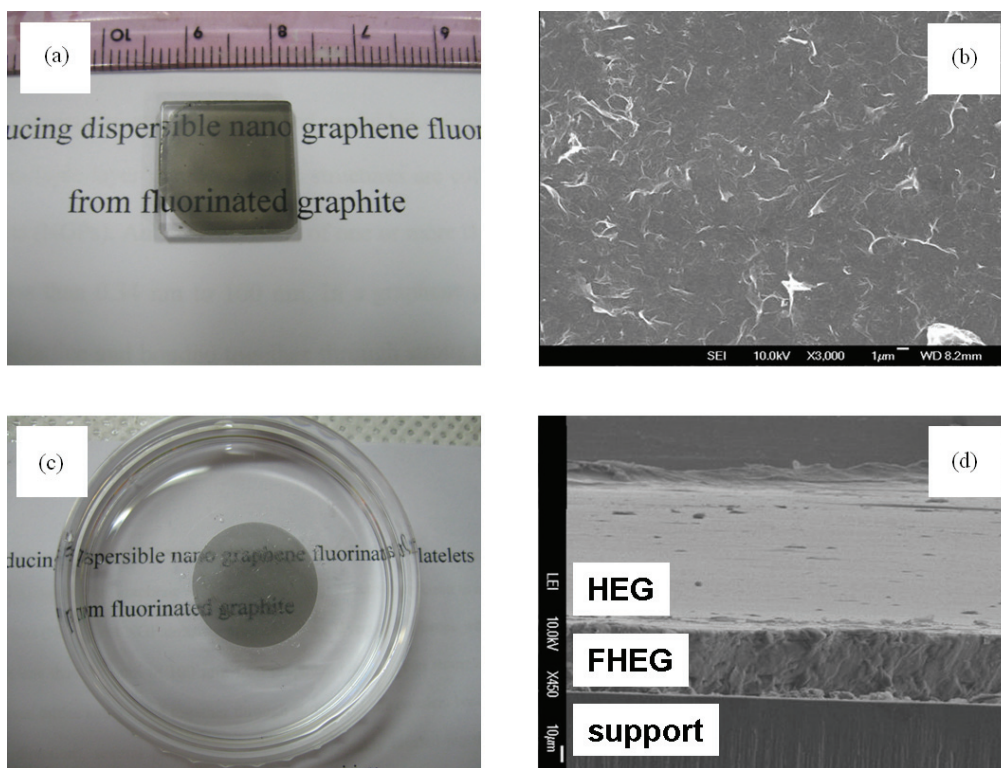
Figure 6. (a) photograph of a multilayered film of graphene fluoride on quartz substrate; (b) SEM image of the multilayered film of graphene fluoride; (c) photograph of a floating composite film of multilayered graphene fluoride and graphene after supporting membrane dissolution; (d) SEM image of the composite film of multilayered graphene fluoride and graphene (side view).

micrometer scale lateral sizes. Thickness ranges from 0.7 nm (one fluorographene layer, taking into account interlayer distance of C_2F) to 4–5 nm (up to ≈8 layers).

It should also be noted, that sonication of C_2F samples in the solvents typically used for dispersing graphene, such as dimethylformamid or *N*-methylpyrrolidone does not yield a stable dispersion. Rather, these reagents seem to interact chemically with C_2F, because we observed swelling and blackening of the samples.

Filtration of the dispersions over a membrane filter yields a fluorographene film deposited on the filter. After the membrane dissolution in 3 mol dm^{-3} NaOH and consequent water washes, the film floats on the water surface and may be transferred to other substrates such as quartz, PET, *etc*. (Figure 6). It has a light brown color and seems half-transparent. It is possible to control its thickness by varying filtration volume of the dispersions. SEM shows some surface wrinkles, as often observed for the films prepared by vacuum filtration. We also prepared composite films by filtering first FHEG dispersion, and then HEG dispersion. SEM shows layered structure of this material that may have interesting and unusual properties.

CONCLUSION

Well-exfoliated graphite fluoride was prepared by fluorination of highly exfoliated graphite by ClF$_3$ vapors. The material has a composition of C_2F but its structure is different from the reported C_2F prepared with help of fluorine gas. Treatment in certain solvents leads to further exfoliation of the graphite fluoride to one and few-layered graphene fluoride platelets. Vacuum filtration methods allow to assemble them into films, including composite films graphene/graphene fluoride.

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