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Side-selective self-assembly of graphene and FLG on piezoelectric PVDF from suspension

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Abstract

The deposition of few-layer graphene by self-assembly from suspension onto a piezoelectric polymer substrate is presented. The graphene self-assembles with negligible overlap between flakes, and with high selectivity for one of the faces of the substrate, an observation which is discussed and rationalized. A computational study on a model system further confirms the theory and supports the experimental results. The highest obtained degree of surface coverage was estimated to 77%.

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1. Introduction

Piezoelectric polymers offer a wide range of applications such as sensors, actuators and microelectronic devices. Polyvinylidene difluoride (PVDF) or its copolymer polyvinylidene fluoride-co-trifluoroethylene P(VDF-TrFE) are common in ultrasonic transducer designs as they have low acoustic impedance, are easy to tailor and offer a wider ultrasonic bandwidth compared to the traditional piezoceramic materials [1]. For many applications, the surface needs to be coated with an electrically conductive material with low surface resistivity, for example a thin layer of a metal. The metallization renders the surfaces optically reflective. If the optical transparency of the polymer film could be retained using an electrically conductive coating that is optically transparent, new applications of this group of polymers in e.g. sensors can be envisaged.

Graphene has excellent electrically conductive properties and optical transmittance [2]. Routes for manufacture include synthesis from a range of precursors by chemical vapour deposition (CVD) [3] and a range of graphite exfoliation strategies [4–7], of which sonochemical exfoliation of non-oxidized graphite into suspension has an attractive combination of simplicity, efficiency and quality of the exfoliated

graphene and few-layer graphene (FLG) [8]. Deposition of graphene from suspension can be achieved by spin- or spray-coating [9], or by self-assembly onto substrates immersed in the suspension [10]. Use of non-flexible substrates is well established [6, 8, 11–15], with polymer substrates as an emerging area [16–20]. In the present manuscript, we give an account of our results from room-temperature deposition of sonochemically exfoliated graphene and FLG onto commercially available films of poled PVDF [21], with non-poled PVDF, polytetrafluoroethylene (PTFE), and polyethylene (PE) as reference materials. To the best of our knowledge, deposition of FLG from suspensions has not been reported for piezoelectric polymers.

2. Deposition of FLG

Adsorption of graphene on PVDF was expected to be low as the polymer is structurally similar to PTFE. In line with the expectations, only minor amounts of graphene, less than 1% surface coverage, could be detected after dip deposition immersion of PTFE and non-poled PVDF substrates, very similar to the results obtained for PE (Table 1, entries 1-3). In contrast, the surface coverage of poled PVDF was approximately 20% after one immersion (Table 1, entry 5), enough for being visible to the naked eye as a weak grey tint.

The detailed analysis of the graphene-treated poled PVDF films with light optical microscopy (LOM) revealed that graphene adsorption occurs almost exclusively on the partially positive “-ve” face of the poled PVDF film, (Figure 1) [8]. Such selective adsorption of material on only one of the faces of the substrate without any chemical modification of the surfaces is interesting. A difference in adsorption properties between poled and non-poled PVDF has previously been noted for a PVDF-Fibronectin cell system, however without any mention of side preferences [22]. In this communication we use “-ve” and “+ve” as introduced by the manufacturer of the poled PVDF sheets. An alternative notation is “poled +” and “poled -”, respectively, referring to the partial charges of the faces [22].

Figure 1. LOM images of FLG flakes deposited on poled PVDF by dip deposition after one immersion: “+ve” face (left) and “-ve” face (right). The images were recorded focusing the instrument on one face of the substrate or another i.e. the substrate was not physically moved or rotated.

Table 1. Typical degrees of surface coverage by FLG flakes, observed for different polymeric substrates. The coverage is achieved through dip deposition (single or multiple, 10 seconds each) and calculated from LOM images using ImageJ software.

Entry	Substrate	Number of immersions	Estimated surface coverage
1	PE ^{*,a}	1	2 %
2	PTFE ^{*,b}	1	< 1 %
3	Non-poled PVDF [*]	1	3 %
4	Poled PVDF, “+ve”	1	< 1 %
5	Poled PVDF, “-ve”	1	20 %
6	Poled PVDF, “+ve”	3	< 1 %
7	Poled PVDF, “-ve”	3	30%
8	Poled PVDF, “+ve”	5	< 1 %
9	Poled PVDF, “-ve”	5	40 %
10	Poled PVDF, “+ve”	10	< 1 %
11	Poled PVDF, “-ve”	10	68%
12	Poled PVDF, “+ve”	15	< 1 %
13	Poled PVDF, “-ve”	15	77%

^{*}) Without net dipole moment; a) model of “-ve” face of poled PVDF; b) model of “+ve” face of poled PVDF.

The Raman spectra of the larger graphene flakes on poled PVDF provide proof of the expected FLG of approximately 5-8 layers (Figure 2). The 2D band at 2730 cm⁻¹ shows some asymmetry typical for FLG flakes, and has a typically lower intensity than the G band. The intensity of the D band is very small indicating low degree of damage and few defects. From the thicker graphitic flakes, also signals from residual intercalated bromine can be observed at low wave numbers, all in line with the previous observations [8]. Due to substrate fluorescence (at both

514 and 785 nm irradiation) the Raman signals of flakes of less than 5 layers were barely distinguishable.

Figure 2. Raman spectrum of a large FLG flake on the “-ve” face of poled PVDF.

Further immersions increased the surface coverage, with new flakes of graphene adsorbing at previously unoccupied areas of the “-ve” face, rather than on top of already deposited flakes (Figure 3). In the present study, the highest surface coverage obtained was 77% (Table 1, entry 13). The transmittance of samples with 70-77% surface coverage in the 400-800 nm range was around 70% of what was recorded prior to the treatment.

Figure 3. LOM images of FLG flakes deposited on the “-ve” face of poled PVDF after: a) 1, b) 2, c) 3, d) 5, and e) 10 immersions.

The levelling out of additional adsorbed material per immersion is not due to lack of material in the suspension. The absorbance of a FLG suspension at 600 nm was monitored over consecutive immersions of several substrates. The most significant drop in absorbance was observed after the first immersion of new plate of poled PVDF. The each following immersion of the same plate withdrew less material from the suspension. When a new substrate plate was immersed in the partially depleted suspension, the same “stairway” pattern was observed. Sedimentation deposition, with the PVDF substrate placed horizontally with the “-ve” side up in a settled suspension for four weeks, resulted in a surface coverage of 60%. In order to estimate how firmly the FLG flakes attach to the poled PVDF, the surface coverage was determined by LOM before and after bath sonication of samples in toluene (Supplementary). Loosely bound FLG flakes (mainly thick and/or aggregated) are desorbed in the initial 60-100 seconds. Longer sonication times, up to 3.5 minutes, results in further desorption, however at a much slower rate. Maximum observed desorption was 37% of the initial coverage.

The high-resolution scanning electron microscopy (HR-SEM, Figure 4) as well as atomic force microscopy (AFM, Figure 5) images visualize mono- and multilayer regions, folding and to some extent rolling of the flakes, commonly found in exfoliated graphene. The FLG flakes adsorbed over the entire substrate with minimal overlap. In agreement with the LOM analyses, flake areas were found to be in the 0.1 to 400 μm^2 range and the flakes were well distributed over the substrate with no tendency towards stacking. The vast majority of the flakes were not in contact with one another but appeared to occupy the available polymer surface in such a way that minimizes interactions with the neighbouring flakes. It was therefore not surprising that the surface resistivity of selected samples with different surface coverage measured using a four-point probe at ten different positions at each sample indicated resistivity close to the surface resistivity of the PVDF material itself for all samples.

Figure 4. HR-SEM images of FLG flakes deposited on the “-ve” face of poled PVDF. These images were chosen to illustrate: a) surface coverage; b) a low degree of overlap between flakes; c) a high-resolution view of thin flakes; d) a close-up of the previous image.

Figure 5. AFM height images of FLG flakes deposited on the “-ve” face of poled PVDF. These images illustrate: a) surface coverage and a low degree of overlap between flakes; the appearing streaks reflect roughness of the PVDF surface; b) a close-up of a folded FLG flake.

3. Explanation of the experimental results

The differences in adsorption properties observed for poled PVDF vs non-poled PVDF, PTFE, and PE as well as the side-selectivity observed for the poled PVDF (Table 1, entries 1-5) are due to the properties of poled PVDF. In contrast to PE and PTFE that are

overall non-polar, the PVDF polymer chains can adopt conformations of different net polarity, which in the solid phase gives rise to different phases in the material. The dominating phases are alpha, with no resulting dipole moment, and the polar beta phase [23]. In a non-poled material, the distribution of alpha and beta regions is expected to be randomized. After poling by a process involving heating and stretching the film in an electric field [21,24], a higher proportion of the chains will adopt the conformation giving rise to the beta phase, and the chains will become aligned with the electronegative fluorine atoms towards the positive anode, creating the “+ve” face and the hydrogen atoms towards the negative cathode, producing the “-ve” face. This arrangement of chains creates a permanent dipole in the poled PVDF film giving the material piezoelectric properties. Using FT-IR absorbance spectroscopy, the proportions of beta phase in the commercial substrates used were determined to be 34% for the non-poled PVDF, and 86-88% for the poled material, with very small differences between the “+ve” and the “-ve” faces, well in accordance with the literature [25,26].

The “+ve” and the “-ve” faces carry the negative and the positive charge respectively. Graphene possesses an extensive system of π -electrons delocalized over the entire graphene sheet. Flakes readily adsorb on the “-ve” face due to polar- π interactions while being repelled by the negative charge of the “+ve” side. For non-poled PVDF, the surface displays a random distribution of regions with alpha phases as well as positive and negative beta phases. The relatively large surface area of an average flake implies that attraction and repulsion would cancel each other out resulting in equally low degree of deposition on both faces. PE and PTFE are net non-polar and the interaction forces between the polymer surfaces and the suspension of graphene therefore too weak for any significant self-assembly of graphene during dip-deposition. The fraction of beta phase in poled PVDF substrates (ca 85%) is a likely upper limit for adsorption of FLG flakes. This agrees well with the highest observed degree of coating (ca 77%).

Once a graphene flake has adsorbed on the “-ve” face, the positively charged surface is blocked and the surface at this particular area will be dominated by the graphene π -electrons, which does not attract additional FLG as strongly as the bare “-ve” surface. As a result, any additional flakes would adsorb on the unoccupied surface of the H-enriched face of the substrate rather than on top of already deposited flakes, which is in line with the experimental results. As the surface area of the substrate is limited and the mobility of flakes once adsorbed is low, flakes with a large area are primarily deposited in the initial immersions.

The qualitative explanations have initial support from a computational study of a highly simplified

inverted system, in which the interaction between perfect graphene and difluoromethane, a small molecule model of poled PVDF was studied by ab initio density functional theory for a system at $T=0$ K with no solvent included. The relaxed structures with fluorine pointing towards the graphene were at higher energy than the ones with the hydrogen end closer to the graphene. However, a deeper study using more realistic models is needed to better mimic a polymer material that interacts with a larger area of graphene.

4. Conclusions and outlook

The chosen method of preparation of FLG suspensions in combination with a simple dip deposition technique provided an efficient and reliable way of partially coating the “-ve” side of the chosen poled PVDF substrates with a monolayer FLG. The maximum coverage achieved for multiple dip depositions was approximately 77% after 15 immersions. The FLG flakes did not show any significant tendency of stacking even when left in suspension over long time for sedimentation. Instead an even distribution over the surface of the substrate was obtained, except for some “coffee ring” aggregation at the edges of the substrate. The transparency of the material was around 70% at surface coverage of 70-77%. The observations can be rationalized from the properties of poled PVDF: the material has a net dipole moment caused by alignment of the polymer chains. The negatively charged fluorine atoms are oriented towards one face of the sheet, repelling the graphene flakes. The positively charged hydrogens are oriented towards the other side attracting the π -electron systems of graphene flakes. Overall, the observations give an interesting insight into adsorptive properties of graphene with regard to an important piezoelectric polymer material.

Experimental section

Suspensions of graphene/FLG in toluene were prepared from graphite foil by the intercalation-exfoliation methodology previously developed in the group [8,27]. Toluene stabilizes the graphene/FLG suspensions, has a suitable vapour pressure and is compatible with the polymers used in the study. The presence of FLG facilitates evaluation of deposition outcome. Poled and non-poled PVDF polymer sheets were purchased from Precision Acoustics. The sheets were degreased with acetone, iso-propanol and ethanol. The degreased substrates were treated with graphene/FLG suspensions, primarily by vertical immersion of the substrates in the settled suspension, the absorbance of which was monitored by UV-vis absorption spectroscopy (at 600 nm in toluene). LOM was used to estimate the degree of substrate surface coverage using colour threshold settings. Selected samples were analysed also by Raman spectroscopy,

HR-SEM and by AFM. For further experimental details, see supporting information.

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References

- [1] B. Reyes-Ramírez, C. García-Segundo, A. García-Valenzuela, *J. Phys. Conf. Ser.*, 2013, **450**, 012032.
- [2] A. K. Geim, K. S. Novoselov, *Nat. Mater.* 2007, **6**, 183–191.
- [3] S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, et al., *Nat. Nanotechnol.* 2010, **5**, 574–578.
- [4] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339.
- [5] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon N. Y.* 2007, **45**, 1558–1565.
- [6] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'ko, et al., *Nat. Nanotechnol.* 2008, **3**, 563–568.
- [7] K. S. Novoselov, A. K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, I. V Grigorieva, A. A. Firsov, *Science (80-.)*. 2004, **306**, 666–669.
- [8] E. Widenkvist, D. W. Boukhvalov, S. Rubino, S. Akhtar, J. Lu, R. A. Quinlan, M. I. Katsnelson, K. Leifer, H. Grennberg, U. Jansson, *J. Phys. D-Applied Phys.* 2009, **42**, **11**, 112003.
- [9] S. Watcharotone, D. A. Dikin, S. Stankovich, R. Piner, I. Jung, G. H. B. Dommett, G. Evmenenko, S.-E. Wu, S.-F. Chen, C.-P. Liu, et al., *Nano Lett.* 2007, **7**, 1888–1892.
- [10] E. Widenkvist, Fabrication and Functionalization of Graphene and Other Carbon Nanomaterials in Solution, *Acta Universitatis Upsaliensis* 2010.
- [11] A. N. Sidorov, M. M. Yazdanpanah, R. Jalilian, P. J. Ouseph, R. W. Cohn, G. U. Sumanasekera, *Nanotechnology* 2007, **18**, 135301.
- [12] A. Banerjee, H. Grebel, *Nanotechnology* 2008, **19**, 365303.
- [13] T. Moldt, A. Eckmann, P. Klar, S. V Morozov, A. A. Zhukov, K. S. Novoselov, C. Casiraghi, *ACS Nano* 2011, **5**, 7700–7706.
- [14] E. Ou, Y. Xie, C. Peng, Y. Song, H. Peng, Y. Xiong, W. Xu, *RSC Adv.* 2013, **3**, 9490.
- [15] W. Li, W. Shimin, W. Xianbao, D. Binhai, X. Zuxun, Z. Xiuhua, Y. Bing, P. Simin, W.

- Jingchao, X. Chunhui, *Solid State Sci.* 2011, **13**, 468-475.
- [16] V. P. Verma, S. Das, I. Lahiri, W. Choi, *Appl. Phys. Lett.* 2010, **96**, 203108.
- [17] J. H. Yu, P. K. Jiang, C. Wu, L. C. Wang, X. F. Wu, *Polym. Compos.* 2011, **32**, 1483-1491.
- [18] V. Eswaraiah, K. Balasubramaniam, S. Ramaprabhu, *J. Mater. Chem.* 2011, **21**, 12626-12628.
- [19] M. Ataur Rahman, G.-S. Chung, *J. Alloys Compd.* 2013, **581**, 724-730.
- [20] J.-Y. Hong, K.-Y. Shin, O. S. Kwon, H. Kang, J. Jang, *Chem. Commun.* 2011, **47**, 7182-7184.
- [21] K. Chelakara Satyanarayana, K. Bolton, *Polymer (Guildf)*. 2012, **53**, 2927-2934.
- [22] C. Ribeiro, J. A. Panadero, V. Sencadas, S. Lanceros-Méndez, M. N. Tamaño, D. Moratal, M. Salmerón-Sánchez, J. L. Gómez Ribelles, *Biomed. Mater.* 2012, **7**, 035004.
- [23] Y. Y. Zhang, S. L. Jiang, Y. Yu, Y. K. Zeng, G. Z. Zhang, Q. F. Zhang, J. G. He, *J. Appl. Polym. Sci.* 2012, **125**, E314-E319.
- [24] E. Erdtman, K. C. Satyanarayana, K. Bolton, *Polymer (Guildf)*. 2012, **53**, 2919-2926.
- [25] Jr. R. Gregorio, M. Cestari, *J. Polym. Sci. B: Polym. Phys.* 1994, **32**, 859-870.
- [26] M. M. D. Ramos, H. M. G. Correia, S. Lanceros-Méndez, *Comput. Mater. Sci.* 2005, **33**, 230-236.
- [27] W. Yang, E. Widenkvist, U. Jansson, H. Grennberg, *New J. Chem.* 2011, **35**, 780.

Supporting information

Side-selective self-assembly of graphene and FLG on piezoelectric PVDF from suspension

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1. General**1.1. Materials**

The graphite foil (99.8%, metal basis) with thickness of 0.5 mm was purchased from Alfa Aesar, the poled and non-poled polyvinylidene difluoride (PVDF) substrates were purchased from Precision Acoustics as 110 and 52 μm films. DuPont Teflon® 0.09 mm thread seal tape was used as polytetrafluoroethylene (PTFE) substrate. Toluene was purified at the department with Innovative Technology inc. Solvent Purification System PureSolv PS-MD-4-EN. Bromine was purchased from Sigma-Aldrich and used as supplied.

1.2. Instrumentation

UV-vis absorption and transmittance measurements were performed on a Varian 3 Bio spectrophotometer using 10 mm quartz cuvettes (Hellma Analytics). Ultrasonication was performed in a VWR USC500T ultrasonic bath. The output frequency was 45 kHz and the output power was 100 W. The contact angle measurements were performed at ambient temperature on an in-house contact angle system, based on Narishige EG-400 Micro Grinder, using the sessile drop method with deionized water (drop volume 3.0 μL). Contact angle was calculated as an average of three measurements using ImageJ and Low-Bond Axisymmetric Drop Shape Analysis measurement plugin [1]. Infrared (IR) absorption and transmittance measurements were performed on a Perkin-Elmer Spectrum 100 Using Fourier transform infrared (FT-IR) spectrometer. Raman spectroscopy was performed on a Renishaw micro-Raman system 200 at an excitation wavelength of 514 and 785 nm. Scanning electron microscopy (SEM) characterization was performed using a high-resolution scanning electron microscope Merlin HR-SEM (Carl Zeiss, Germany). All atomic force microscopy (AFM) images were collected in intermittent contact mode (tapping mode) with an NTEGRA Prima AFM (NT-MDT). Images were collected in both closed and open loop using a 100 μm sample scanner (NT-MDT) equipped with capacitive sensors or a 14 μm sample scanner (NT-MDT) with additional equivalent closed-loop. Sensor height values were used for overall large scale height imaging. Silicon cantilevers NSG01 (NT-MDT) and NCH-50 (Pointprobe, Nanoworld) were both used to image the surfaces with scanning velocities ranging between 6 and 35 $\mu\text{m/s}$. Many of the collected raw height images were subjected to flattening by subtracting a first order plane or, when appropriate, a curve fit to each line in the fast scan direction. Light optical microscopy (LOM) was performed with a Leitz Laborlux S light optical microscope.

1.3. Image analysis

LOM image editing was handled using ImageJ 1.49v image processing and analysis software. Typically the LOM images were edited by adjusting the brightness and contrast, and adding a sharpening filter. Degree of coating was then determined using colour threshold settings.

1.4. Preparation of graphene suspension

Suspensions of few-layer graphene FLG flakes in toluene were prepared according to a previously reported method with minor modifications [2]. A piece of graphite foil (typically 4×5 mm) was cut out and intercalated with bromine by placing in a vial with 4 ml of saturated bromine water in the dark for at least 48 hours. The graphite foil was then removed, thoroughly washed with water and dried in air for at least 2 hours. The dried piece of graphite foil was placed in a vial together with 4 ml of solvent (toluene) and the sealed vial subjected to ultrasonication for 10 minutes. After the sonication, the remaining piece of graphite was removed and the suspension allowed to settle for at least 2 hours, yielding a grey suspension with black sediment on the bottom.

1.5. Deposition of graphene

The PVDF and PTFE polymer substrates were degreased by 15 minutes immersion in acetone, followed by 15 minutes immersion in iso-propanol followed by rinsing with ethanol and drying in a stream of nitrogen. The polyethylene (PE) substrates were degreased by the same procedure but without use of acetone. The dip deposition was performed by manually vertically dipping the degreased substrates in settled suspension of graphene flakes for 10 seconds. After dipping the substrates were allowed to dry in air while hanging vertically. In experiments studying multiple depositions, the dipping was repeated after drying of the substrate. The drop deposition was performed by applying a drop of suspension on a horizontally aligned degreased substrate plate. After application the substrate was allowed to dry in air. The sedimentation deposition was performed by placing a poled PVDF substrate horizontally with ‘-ve’ face up in a vial followed by applying a settled suspension of FLG in toluene to the height of 2 cm, sealing the vial and allowing the sedimentation to proceed for 1 month. After removal of the substrate it was allowed to dry in air.

The deposition process was followed by measuring the absorption of the graphene suspension at 600 nm as a function of the number of performed dipping steps. The deposited graphene flakes were studied by Raman spectroscopy at 514 nm. Finally, the overall degree of deposition was determined by LOM studies of the substrates after each deposition steps, using simple image editing software (ImageJ 1.49v).

2. Experimental results

The surface of the poled PVDF film was inhomogeneous with randomly distributed areas of the film with a lower affinity for graphene. On some samples, these areas were observed as bands through the film. The inhomogeneities are likely to originate from uneven pulling during the poling [3] of the bulk polymer. For drop deposition, isolated aggregates of FLG with pronounced ‘coffee rings’ were observed.

2.1. Substrate characterization

Contact angle measurements were performed to compare wettability of the different substrates. Figure S1 shows the results for the different substrates. PE, PTFE and non-poled PVDF substrates were in good agreement with the literature [4,5]. Both the ‘+ve’ and the ‘-ve’ faces of the poled PVDF were found to be more hydrophobic than stated in the literature [6,7]. This can be largely attributed to differences in the manufacturing procedures. Importantly, the ‘+ve’ face was found to be more hydrophobic (73.6°) than the ‘-ve’ (55.2°), in complete agreement with the literature [6,7].

Figure S1. Contact angle measurements of the different polymer substrates.

The fraction of alpha and beta phase in the poled and non-poled PVDF substrates were estimated by FT-IR through comparing the absorbance of the bands at 766 cm^{-1} and 840 cm^{-1} , characteristic for the respective phases [8,9]. The absorbance values were obtained as an average of four measurements. The proportion of beta-phase was estimated to 34% for non-poled PVDF and 88 and 86% for '+ve' and the '-ve' respectively. These results are in line with typical values reported in the literature [8,9] and confirm conversion of PVDF from alpha to beta phase through poling. Figure S2 illustrates the differences in absorption spectra of the studied substrates.

Figure S2. IR-absorbance spectra of the PVDF substrates, the bands of interest are 766 cm^{-1} (alfa phase) and 840 cm^{-1} (beta phase).

2.2. Deposition on substrates with zero net charge

Figure S3. LOM images of FLG flakes deposited on the two faces of non-poled PVDF substrate by dip deposition after one immersion (10 seconds).

Figure S4. LOM images of FLG flakes deposited on the two faces of PTFE substrate by dip deposition after one immersion (10 seconds).

Figure S5. LOM image of FLG flakes deposited on the PE substrate by dip deposition after one immersion (10 seconds).

2.3. Deposition on poled PVDF substrate

The LOM analysis of PVDF plates after 1, 3 and 5 immersions reveal that large flakes of FLG adsorb readily at fresh plates. During subsequent immersions additional but smaller flakes are adsorbed. The plates used in the depletion study (figure S6) are shown in figure S8, each after five or six consecutive immersions. The first substrate plate accumulated most of the large flakes while the third one almost exclusively adsorbed uniformly small flakes. In suspension, the graphene flakes are surrounded by solvent molecules (toluene in the studied case), the larger the flake the more solvent molecules are organized around it. Adhesion to a substrate surface releases solvent molecules, which is entropically favourable. As a larger flake releases more of the organized solvent molecules, the entropy increase is larger than would be the case for a small flake.

Figure S6. Removal of FLG flakes from suspension, displayed as absorption of the suspension of FLG flakes in toluene in a 1 cm quartz cuvette at 600 nm, monitored over consecutive immersions of 5×10 mm 52 μm PVDF substrates (10 seconds each).

Figure S7. UV-vis transmittance of a sheet of poled PVDF after 15 consecutive immersions in FLG suspension (coating estimated to 75%).

Figure S8. LOM images of FLG flakes deposited on the '-ve' faces of three plates of poled PVDF after: (a) 6, (b) 5, (c) 5 consecutive immersions in the same FLG suspension.

In order to estimate the strength of adsorption of the FLG flakes to the substrate, the surface coverage before and after bath sonication of a substrate in toluene was determined using LOM. The results are presented in table S1 and figure S9. During the first 60-100 seconds a proportion of the initially deposited flakes (ca 30%) desorbs at a constant rate. Longer sonication times cause further desorption at a significantly slower rate. Analysis of LOM images revealed that the aggregated and thick flakes are more easily removed than thin non-aggregated flakes.

Table S1. Surface coverage by FLG flakes, at the '-ve' face of a poled PVDF substrate upon sonication in toluene.

Entry	Sonication time (s)	Estimated surface coverage ^b	Proportion desorbed ^c
1	0	54 % ^a	0 %
2	10	52 %	3 %
3	20	51 %	5 %
4	30	49 %	9 %
5	60	45 %	17 %
6	90	39 %	27 %
7	150	36 %	34 %
8	210	34 %	37 %

^a FLG flakes were deposited on the PVDF substrate by dip deposition prior to the desorption study.

^b Surface coverage is calculated from LOM images using ImageJ software.

^c Decrease of estimated covered surface area in % (relative initial coverage).

Figure S9. Desorption of FLG from the '-ve' face of a poled PVDF substrate upon sonication in toluene over time.

2.4. Characterization by AFM

Further confirmation of the estimated degree of coverage of the surface of poled PVDF ('-ve' face) was obtained using AFM (figure S10). Flakes of FLG are seen on the surface of the substrate with little to no tendency towards stacking. The overall coverage is well in line with LOM and SEM measurements. Individual flake size and height profile (images b and c) are typical for folded few-layer graphene flake. The height profile values are affected by surface of PVDF, which is known to be rough [10]; height variations of up to 200 nm are not uncommon. Therefore the measured height variations reflect a combination of FLG flake height and substrate roughness.

Figure S10. AFM images of FLG flakes deposited on the '-ve' face of poled PVDF: (a) large-scale phase image as an overview of the substrate surface with deposited FLG; (b) height image illustrating the surface coverage and a low degree of overlap between flakes; (c-d) height images and cross sections showing the low degree of overlap and height profiles of the FLG flakes. The panel below each image in (c-d) shows the cross section along the solid and dashed lines, note the magnified vertical scale. Step heights measured on flakes and to the substrate are typically 2.5 – 15 nm.

3. Computational study

All the calculations have been performed using plane wave based density functional code VASP [11, 12]. The structures were optimized using the conjugate gradient method with forces calculated from the Hellman-Feynman theorem. Difluoromethane was placed on top of a freestanding graphene

layer with a 5x5 supercell structure. Two adsorption sites on the graphene lattice were chosen. The first one was the bridge position. 2 F, 2 H, or 1 H and 1 F atoms were placed on top of two bridge C atoms and the structure was fully relaxed. The starting molecule-graphene distance was 2.5 Å, which finally converges to 3.2 Å. Similar treatment was done for the hexagonal site. In all cases, van der Waals interaction was considered within the vdw-DF scheme. The molecule was allowed to rotate and change position in a restricted volume until an energy minimum was reached. The initial and final structures are given in figures 11-16 below (top-view), C-atoms are in blue, while H and F atoms are in yellow and orange colours respectively. The energies are presented in table S2.

Table S2. Relative stability of CH₂F₂ on graphene.

Adsorption site	Relative energy / cell (eV)
BridgeF	0.082
BridgeH	0.059
BridgeHF	0.000
HexH	0.031
HexF	0.069
HexHF	0.009

Figure S11. BridgeF: initial (left) and final (right) structures.

Figure S12. BridgeH: initial (left) and final (right) structures.

Figure S13. BridgeHF: initial (left) and final (right) structures.

Figure S14. HexF: initial (left) and final (right) structures.

Figure S15. HexH: initial (left) and final (right) structures.

Figure S16. HexHF: initial (left) and final (right) structures.

References

- [1] Stalder A F, Melchior T, Müller M, Sage D, Blu T, Unser M 2010 *Colloids Surf. A: Physicochem. Eng. Asp.* **364** 72–81
- [2] Widenkvist E, Boukhvalov D W, Rubino S, Akhtar S, Lu J, Quinlan R A, Katsnelson M I, Leifer K, Grennberg H, Jansson U 2009 *J. Phys. D-Applied Phys.* **42** 112003
- [3] Chelakara Satyanarayana K, Bolton K 2012 *Polymer (Guildf)*. **53** 2927–34
- [4] Razmkhah K, Chmel N P, Gibson M I, Rodger A 2014 *Analyst* **139** 1372–82
- [5] Sun P, Lu H, Yao X, Tu X, Zheng Z, Wang X 2012 *J. Mater. Chem.* **22** 10035
- [6] Pärssinen J, Hammarén H, Rahikainen R, Sencadas V, Ribeiro C, Vanhatupa S, Miettinen S, Lanceros-Méndez S, Hytönen V P 2015 *J. Biomed. Mater. Res. A* **103** 919–28
- [7] Ribeiro C, Panadero J A, Sencadas V, Lanceros-Méndez S, Tamaño M N, Moratal D, Salmerón-Sánchez M, Gómez Ribelles J L 2012 *Biomed. Mater* **7** 035004
- [8] Gregorio Jr R, Cestari M 1994 *J. Polym. Sci. B: Polym. Phys.* **32** 859–70
- [9] Ramos M M D, Correia H M G, Lanceros-Méndez S 2005 *Comput. Mater. Sci.* **33** 230–6
- [10] Lee H, Cooper R, Wang K, Liang H 2008 *Sensors* **8** 7359–68
- [11] Kresse G, Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15–50
- [12] Kresse G, Furthmüller J 1996 *Phys. Rev. B* **54** 11169–86