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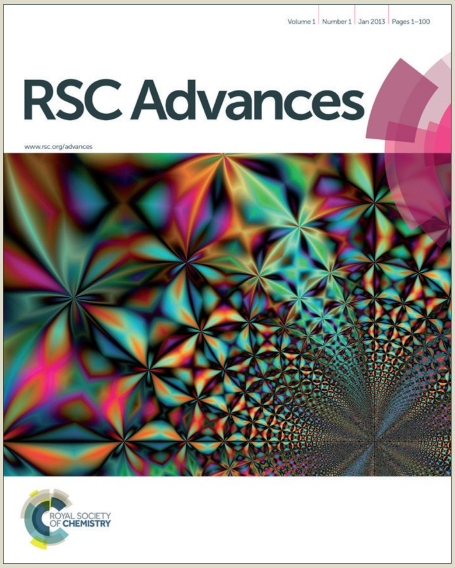

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Laser-driven rapid functionalization of carbon surfaces and its application to the fabrication of fluorinated adsorbers

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The use of laser sources can expand the range of applications of photochemical surface functionalization strategies, increasing reaction rate and sample throughput. However, high irradiances can result in thermal effects and/or changes in the mechanism of photoinduced reactions. In this work we report on the use of a pulsed UV laser source for the modification of carbon surfaces using fluorinated terminal alkenes. A perfluorinated alkene, 1H,1H,2H-perfluoro-dec-1-ene (PFD), was used to modify amorphous carbon surfaces using a pulsed excimer laser (248 nm). The rate and yield of photoinduced PFD chemisorption was measured using Infrared Reflectance Absorption Spectroscopy (IRRAS) and compared to that obtained using a continuous lamp source. Quartz Crystal Microbalance (QCM) measurements were also used to obtain quantitative estimates of surface coverage and quantum yields. We found that, under the experimental conditions investigated, PFD chemisorption rates at bare carbon are proportional to the rate of incident photons. Simulations indicated that thermal effects of laser irradiation are expected to be minor, thus supporting the conclusion that the pulsed source can be used to accelerate the reaction rate without leading to changes in reaction mechanism. However, we observed that the limiting chemisorption yield was ~30% higher for the laser source. We propose that this difference is due to photochemical formation of multilayers, a reaction that is slower than chemisorption at bare carbon, but that becomes evident when very high total fluence is applied via pulsed sources. Finally, we investigated the influence of reaction conditions on the ability of fluorinated carbon surfaces obtained via laser- and lamp-driven reactions to adsorb and capture fluorinated ligands via non-covalent fluorous-fluorous interactions.

Introduction

Photochemical grafting of terminal alkenes using UV excitation is a versatile strategy for the modification of surfaces. Previous work shows that it can be applied to the covalent immobilization of organic layers onto Si,[1-3] SiO_2,[4] GaN,[5] Ge,[6] TiO_2,[7] as well as a host of carbon materials.[8-12] Numerous studies suggest that more than a single mechanism can be at play depending on the specific substrate and molecule that are reacting.[6, 13-16] In the case of amorphous carbon, it has been shown that the reaction proceeds via photoemission of electrons from the substrate upon UV irradiation and subsequent capture by an electron accepting group. The terminal alkene can subsequently react with the hole created at the solid surface, resulting in a covalently grafted layer.[17]

There are a number of advantages in applying this technique to carbon substrates: the reaction conditions are mild and a strong C—C bond is formed between the alkene and the underlying carbon substrate, giving rise to a stable adlayer. Furthermore, such reactions are in principle selective, since light sources of varying wavelength could be used to selectively attach different moieties. Finally, this technique can be integrated with already established photolithographic methods. All of the above mentioned studies make use of continuous emission UV light sources to induce the grafting reaction; to the best of our knowledge, pulsed laser sources have not been utilised to trigger these reactions. The use of pulsed laser sources can expand the range of applications of this photochemical surface functionalization reaction because of the potential for delivering high incident photon rates and, consequently, increasing reaction rate and sample throughput. Furthermore, the use of these sources opens the possibility of simultaneously observing thermal processes in the case of substrates with high optical absorption, as in the case of graphitic carbons.

In this work we investigated reactions of a perfluorinated alkene, 1H,1H,2H-perfluoro-dec-1-ene (PFD) at amorphous carbon surfaces. PFD was chosen for several reasons; first, this molecule has high electron affinity which, based on proposed mechanisms, increases reaction rates and yields.[13, 17] Second, both photochemical[8, 10, 14] and thermal[18, 19] attachment of PFD

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Electronic Supplementary Information (ESI) available: Reference infrared spectra of fluorinated compounds and layers, IRRAS of PFD layers grafted at 3 and 10 Hz pulse rates, linear fits near time zero of chemisorptions curves, lamp power density spectrum, details of computational simulations and optical absorptivity of carbon films and organic compounds. See DOI: 10.1039/x0xx00000x has been demonstrated in the literature, thus allowing for the possibility of both processes to occur at the same time. Third, PFD is of interest because its highly fluorinated chains can be leveraged to control wetting behaviour[19, 20] and to modulate adsorption of fluorinated ligands in environmental remediation and catalyst recovery. Finally, PFD has the practical advantage of displaying strong IR active modes that can be used to detect PFD adlayers at the carbon surface via Infrared Reflectance Absorption Spectroscopy (IRRAS), thus providing a simple method to track adlayer formation as a function of reaction time.

We have used a combination of infrared spectroscopy, nanogravimetry and computational modelling in order to study the formation of PFD adlayers at amorphous carbons and whether they are affected by the nature of the UV source: pulsed laser or continuous lamp. The surface coverage was measured using ex situ Quartz Crystal Microbalance (QCM) and grafting rates/yields were compared. We also investigated potential applications of PFD adlayers for the patterning and recovery of fluorinated ligands via fluorous-fluorous interactions. Baker and co-workers[21] have demonstrated that a variety of fluorinated compounds could be immobilized via physisorption at perfluorinated self-assembled monolayers (SAMs) on gold substrates. They were able to correlate the amount of physisorbed species to the ligand structure, and suggested the possibility of leveraging these adsorptive interactions for solid phase extraction of toxic[22] and precious metals,[23] and for catalyst patterning and recovery. The use of photochemically grafted PFD films at carbon substrates would be advantageous for all of the above applications, since these films can be fabricated at much lower cost and display superior chemical and thermal stability compared to that of SAMs at Au.[12] We have therefore, carried out a study of surface adsorption of a perfluorinated ligand, Rf_3PPhI (Rf = $CF_3(CF_2)_9CH_2CH_2$-), at PFD films at carbon. We found that physisorption of perfluorinated ligands strongly depends on structure and organization of photochemically grafted PFD layers.

Experimental Methods

Chemicals and Materials. Dichloromethane (Fisher, analytical grade), methanol (Sigma-Aldrich, semiconductor grade), acetone (Sigma-Aldrich, HPLC grade), 1H, 1H, 2H-perfluoro-dec-1-ene (PFD, Sigma-Aldrich), sulfuric acid (Sigma-Aldrich, concentrated), and hydrogen peroxide (Sigma-Aldrich, 30%) were used without further purification. Rf_3PPhI (Rf = $CF_3(CF_2)_9CH_2CH_2$-) was synthesised as previously reported.[24]

Substrate preparation. Amorphous carbon (a-C) films with a thickness of 85 nm were deposited via DC magnetron sputtering at a base pressure of $\leq 1 \times 10^{-6}$ mbar and a deposition pressure of 7×10^{-3} mbar as previously described.[25] All depositions were carried out at 100 °C. Substrates thus prepared have been previously characterized via Raman and X-ray photoelectron spectroscopy and were found to consist of 80% sp^2 carbon centers. Films were deposited on 390 nm thick Ti sputtered layers on Si wafers. The Ti layer increases adhesion of the carbon film and serves as a metal substrate to enhance the IRRAS signal allowing for detection of grafted layers.[26]

Photochemical functionalization. a-C samples were introduced in a reaction cell equipped with a UV transparent window (fused quartz); they were covered with a thin liquid film of neat PFD and a quartz slide to prevent evaporation.[17] The cell was sealed and purged with Ar prior to starting illumination of the a-C surface with the UV source. Two light sources were used to induce grafting, a Mercury Grid lamp (UVP, main line λ = 254 nm) and a pulsed KrF excimer laser (λ = 248 nm, 26 ns, Coherent Inc.). Experiments using the lamp were performed for exposure times ranging between 10 and 360 min at a fixed sample distance of 11.5 cm away from the source. The irradiance of the 254 nm line was measured with a photodiode (Thorlabs, #DET10A) by separately measuring contributions from Hg characteristic lines above and below 305 nm using a long pass filter (Schott, #WG305); the 185 nm line contribution was assumed to be negligible based on lamp specifications (<3%). Laser induced grafting was performed using four different laser fluences: 1.6, 4, 10, and 16.5 mJ cm^{-2}; higher fluences were avoided since they resulted in visible damage to the carbon film. All experiments, unless otherwise stated, were performed at a laser pulse rate of 3 Hz for irradiation times between 1-60 min. Laser fluence was determined at the sample position with an energy meter. After irradiation, samples were washed and sonicated in dichloromethane and methanol.

Sample characterization. Infrared reflectance absorption spectra (IRRAS) of PFD modified carbon surfaces were collected on a Bruker Tensor 27 FTIR spectrometer equipped with a VeeMaxII variable angle specular reflectance accessory and a wire grid polarizer. Spectra were collected using p-polarized light at 80° incidence from the surface normal using a bare a-C substrate as background; 256 scans at 4 cm^{-1} resolution were collected for both background and sample.

A Quartz Crystal Microbalance (QCM) was used to determine the number of molecules grafted at the carbon surface using an ex situ method.[27] 10 MHz crystals with 100 nm thick vapour-deposited gold electrodes were used (International Crystal Manufacturing). Crystals were further coated with Ti (20 nm) and a-C (50 nm) layers. The QCM setup consists of a lever oscillator and a frequency counter (SR620, Stanford Research) connected to a computer for data recording using LabVIEW software. The frequency of the QCM prior to PFD grafting was recorded once the counter was stable within ±2 Hz over 10 min. After PFD functionalization using the photochemical approach, QCM crystals were gently rinsed in copious amounts of dichloromethane and methanol, followed by drying with Ar. The frequency of the functionalised crystals was then measured and the change in frequency due to grafting determined. Dark control experiments were also performed to provide an estimate of the accuracy of the ex situ QCM method.

Adsorption experiments with fluorinated ligands. PFD modified carbon samples were immersed for 3 h in a 1 mM

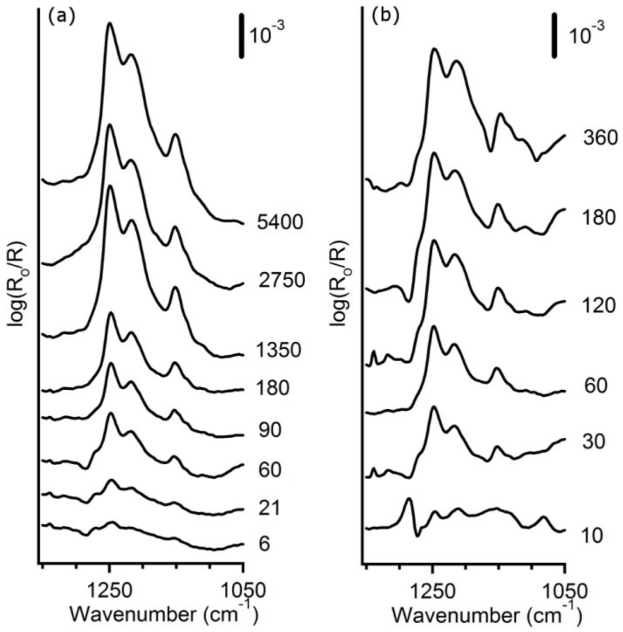


Figure 1. Evolution of the IRRAS spectra in the -CF2 stretching region of PFD layers obtained using laser (a) and lamp (b) irradiation; the numbers identifying each spectrum indicate the number of laser pulses incident on the sample (a) and the exposure time in minutes (b).

solution of Rf_3PPhI in acetone. They were then rinsed with acetone and dried under Ar prior to IRRAS characterisation. Afterwards they were sonicated in acetone for 10 minutes to remove physisorbed compounds, followed by further IRRAS spectra collection, according to published procedures.[21]

Results

Functionalization of amorphous carbon (a-C) surfaces

Figure 1a and 1b show IRRAS spectra in the C—F stretching region obtained for a-C films photochemically grafted with PFD over the full range of light exposure times, using an excimer laser (16.5 mJ cm^{-2} fluence, 248 nm) and a UV grid lamp, respectively. The IRRAS spectra display the characteristic C—F stretching absorbances of perfluorinated alkyl chains; the main peaks are similar whether PFD layers are obtained via continuous or pulsed illumination. The maxima at 1250, 1215, and 1150 cm^{-1} match the absorbance peaks of the parent PFD compound (see Supporting Information) and, based on previous studies are assigned to -CF_2 stretching modes.[28-30] IRRAS of a-C samples that were coated with neat PFD but not exposed to UV light yielded no absorbances in this region, thus indicating that the peaks observed in Figure 1 arise from photochemical reaction of PFD with a-C substrates.

The net absorbance of the -CF_2 stretching peak at 1250 cm^{-1} offers a semiquantitative method for monitoring the surface coverage.[17] Figure 2a shows the change in net absorbance at 1250 cm^{-1} versus the total number of laser pulses for all laser fluences used in our experiments. The peak height can be seen to level off, independently of laser fluence, at approximately the same value, 0.0036 ± 0.0003, as surface saturation is reached. However, the number of pulses at which this plateau is reached is smaller for higher fluences: for example, limiting coverage is obtained after only 2700 shots (15 min at 3 Hz pulse rate) at 16.5 mJ cm^{-2}, whereas 10800 shots (1 hour at 3 Hz pulse rate) are required at 1.6 mJ cm^{-2}. Also, the number of pulses required to reach limiting coverage appears to be independent of the pulse rate: for instance, we found that the same coverage is reached after 2700 pulses at 16.5 mJ cm^{-2} fluence whether the pulse rate used is 3 Hz or 10 Hz (see Supporting Information). This result suggests that the reaction reaches its limiting coverage after a threshold number of impinging photons. In order to test this hypothesis we plotted again the net peak absorbance at 1250 cm^{-1} vs. the number of incident photons as shown in Figure 2b. The results in Figure 2b show that the photon-normalized grafting rate does not depend on laser fluence, thus suggesting that there is no difference in the grafting mechanism as the pulse energy is increased within the investigated range. Fluences at or below 16.5 mJ cm^{-2} were found to cause no changes in the carbon substrate (see Supporting Information), however, above this threshold we observed visible and irreversible sample damage.

Figure 3a shows the net peak height versus exposure time for a-C samples grafted using a mercury lamp; the grafting curves show that the reaction is self-limited, in agreement with

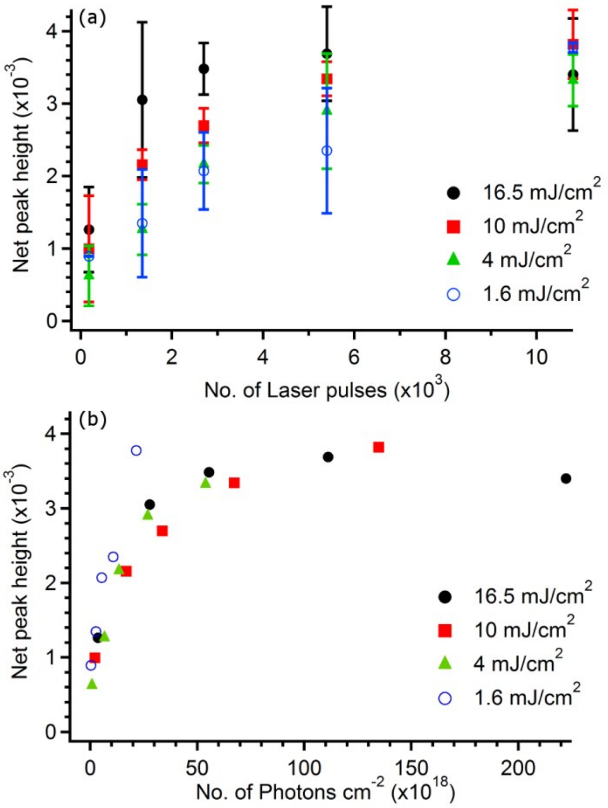


Figure 2. Net peak height of the -CF_2 peak observed in IRRAS spectra at 1250 cm^{-1} vs. number of laser pulses (a) and vs. number of photons (b) incident on the a-C sample at the four different laser fluences used in our experiments. Error bars represent one standard deviation; only the average value of the net peak height is reported in (b) for clarity.

previous reports.[17] The 254 nm irradiance at the sample distance was measured to be 5.9 mW cm^{-2} and this value was used to calculate the total number of photons delivered to the sample surface which is indicated in the top axis of Figure 3a. After 2 h of irradiation the net peak height plateaus at 0.0027 ± 0.0006; this result indicates that the self-limited PFD coverage is statistically different from that obtained using laser irradiation (90% C.I.) and approximately 25% lower. In order to directly compare grafting rates, the total number of photons per area incident on the sample during grafting experiments was determined for lamp driven reactions and compared to that of laser driven reactions. The emission spectrum of the UV lamp consists of the Hg characteristic lines at 185, 254, 312, 365, and 404 nm, but effectively only 254 nm photons result in PFD chemisorption. Experiments carried out using only the visible region of the lamp output did not result in PFD grafting; similarly, control reactions using a fused quartz window confirmed that the 185 nm line does not contribute significantly to PFD grafting. Figure 3b shows PFD grafting curves as a function of total incident photons for reactions carried out using the UV lamp and laser pulses at the four different fluences. The two curves suggest that the grafting efficiency at bare carbon might be higher for laser than for lamp driven reactions: a linear fit of the two curves near time zero indicates that chemisorption rates are 1.8 ± 0.4 times larger when using the pulsed source, however, it remains challenging to statistically distinguish the two rates (see Supporting Information).

The intensity of peaks observed in IRRAS spectra can depend, not only on surface coverage, but on molecular orientation and substrate optical constants.[26, 31] In order to determine whether the difference observed between the two limiting net absorbances from IRRAS spectra in Figures 2 and 3 is due to PFD surface coverage exclusively, we carried out mass density measurements using Quartz Crystal Microbalance (QCM). Briefly, the resonant frequency of a carbon coated QCM crystal was measured in air before and after grafting, and the difference, Δf, was used to calculate the mass change, Δm, at a crystal via the Sauerbrey equation.[32] The mass change was then converted to surface number density values via normalization by the PFD molecular weight. Table 1 shows the surface number densities thus calculated, obtained from samples modified with PFD using lamp irradiation for 2 h and laser irradiation at 4 mJ cm^{-2} for 1 h; under these conditions both reactions have reached limiting coverage. Surface density values were found to be 8.1 × 10^{14} and 1.0 × 10^{15} molecules cm^{-2} for lamp and laser irradiated samples, respectively; control measurements yielded an uncertainty of 1 × 10^{14} molecules cm^{-2}. Table 1 also shows IRRAS net absorbance values obtained from two samples prepared under the same conditions. The lamp/laser density ratio found using QCM is 0.81, which is in excellent agreement with the 0.82 value calculated from IRRAS net absorbances.

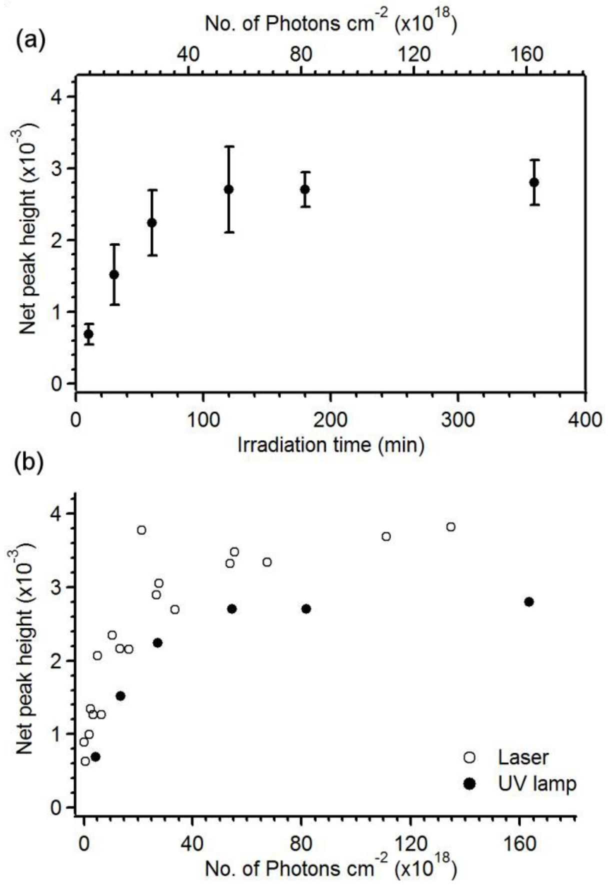


Figure 3. (a) Net peak height of the -CF$_2$ peak observed in IRRAS spectra at 1250 cm^{-1} vs. irradiation time and incident photons obtained using the UV lamp source; error bars represent one standard deviation. (b) Comparison of the net peak height of -CF$_2$ IRRAS peaks vs. the total number of UV photons impinging on a-C samples when irradiated using a UV lamp (●) and a pulsed UV laser (○).

Table 1. QCM and IRRAS results obtained for lamp and laser driven reactions of PFD at a-C surfaces. QCM surface coverage and IRRAS net absorbance for laser grafted layers were obtained after 1 h of irradiation using 4 mJ cm^{-2} laser fluence at 3 Hz.

Source	Surface density (molecules cm-2)	Net absorbance
Grid lamp	8.1 × 10^{14}	0.0027
Pulsed laser	10 × 10^{14}	0.0033
Lamp/Laser	0.81	0.82

These results suggest that the net absorbance in IRRAS spectra provides a good estimate of relative surface coverage, likely because photochemically grafted PFD films lack a preferred molecular orientation. Assuming that PFD layers are densely packed, and considering that Godet and co-workers estimate the surface coverage for a densely packed monolayer to be 4 × 10^{14} cm^{-2},[33, 34] we can estimate that the limiting surface coverage of PFD layers is equivalent to 2 ML and 2.5 ML in the case of lamp and laser sources, respectively. These values are higher than the maximum surface coverage obtained by thermal grafting, 2 × 10^{14} cm^{-2} (~0.5 ML),[35] and comparable to the thickness measured by Downard and co-workers via atomic force microscopy (1-2 ML) after 1 h of exposure to a Hg lamp.[8]

Based on the optical absorption of a-C, the QCM quantitative data, and chemisorption curves shown in Figure 3b it is also possible to estimate the efficiency of the photochemical chemisorption reaction. A straight-line fit of the curves shown in Figure 3b (see Supporting Information) indicates that a 4 × 10^{14} cm^{-2} (1 ML) coverage is reached after irradiating the surface with approximately 5 × 10^{18} photons cm^{-2}.

The optical absorptivity of a-C films in the range 248-254 nm was found to be ~218 × 10^{3} cm^{-1} (see Supporting Information), therefore ~84% of incident photons are absorbed in the 85 nm thickness of a-C. This estimate indicates that ~10^{-4} of the incident photons results in a chemisorption event.

Laser induced heating at amorphous carbon substrates

Godet and co-workers have found that PFD can be covalently attached to amorphous carbon and silicon via thermal grafting,[18, 19, 34, 36] whereby covalent modification could be achieved above a threshold temperature of 160 °C. Irradiation of carbon films with a high energy pulsed laser will result in an increase in sample temperature, which could, if high enough, induce thermal grafting at the film surface. In order to understand whether the observed molecular coverage differences could arise from thermal contributions to the grafting process, we modelled the temperature rise at the sample surface. The temperature change upon excimer laser irradiation through the whole material stack (a-C/Ti/Si) was modelled using COMSOL Multiphysics software. The PFD liquid layer was omitted and it was assumed that the a-C surface was covered with quartz. The temperatures reached during laser induced heating depend upon the thermophysical and optical properties of the irradiated materials;[37] the values used in the model for each material layer and details of heat flow equations used in the model are listed in the Supporting Information. Figure 4a shows the calculated temperature increase as a function of sample depth during one laser pulse at the maximum fluence used in our grafting experiments (16.5 mJ cm^{-2}). The profile is split into three regions, where I, II, and III, denote a-C, Ti, and Si films. A maximum temperature increase of 70 K occurs in the a-C film, followed by a sharp drop in temperature in the Ti layer, before tailing off in the Si substrate. Figure 4b shows how the temperature changes as a function of time at the surface of a-C. The maximum increase is once again 70 K and occurs at 17 ns, which is within the width of pulses used in our experiments (26 ns), and then decreases asymptotically towards initial temperature value over time. The maximum temperature reached remains well below the boiling point of PFD (419 K) and the threshold temperature for thermal grafting (433 K). Thus, it seems unlikely that laser induced heating of the carbon substrate contributes to the grafting process.

Adsorption of fluorinated ligands from solution at PFD modified carbon surfaces

Work carried out by Baker et al.[21] using IRRAS, showed that fluorinated surfaces prepared via self-assembly of 1H,1H,2H,2H-perfluorodecanethiol at gold surfaces could be used for solid phase extraction of a number of perfluorinated compounds via surface physisorption. We therefore investigated whether (a) PFD modified a-C surfaces could be used for similar applications, and (b) whether the molecular density of photografted layers prepared using both light sources had an effect on their performance in solid phase extraction. The compound chosen for the study shall be referred to as Rf_3PPhI (Scheme I); the fluorinated tails of Rf_3PPhI yield strong absorbances in the C—F stretching regions, with $-CF_2$ symmetric and antisymmetric stretching modes displaying maxima at 1148 and 1200 cm^{-1}, respectively (see Supporting Information). Figure 5 shows a typical set of IRRAS spectra obtained for a PFD modified a-C substrate illuminated for 30 minutes with the UV lamp (trace a), after 3 h immersion in a 10 mM solution of Rf_3PPhI in acetone (trace b), and the same surface after 10 min sonication in acetone (trace

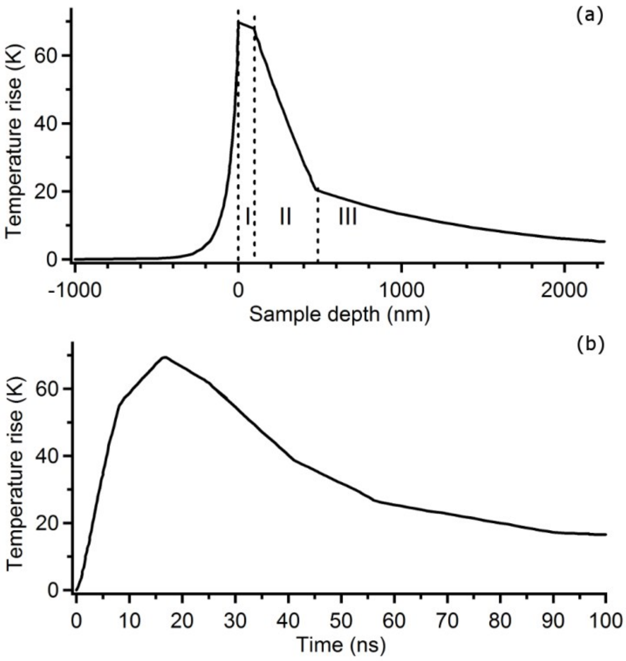


Figure 4. (a) Temperature increase through the a-C/Ti/Si material stack 17 ns after irradiation with a 16.5 mJ cm^{-2} laser pulse; where region I, II, and III, correspond to a-C, Ti, and Si, respectively. (b) Temperature change as a function of time at the carbon surface, after irradiation with a 26 ns laser pulse at 16.5 mJ cm^{-2} fluence.

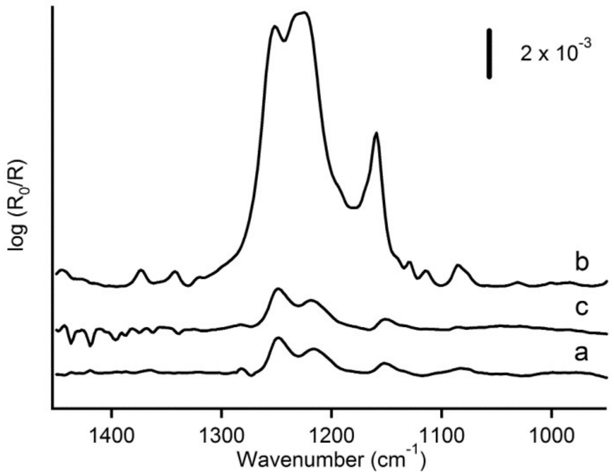
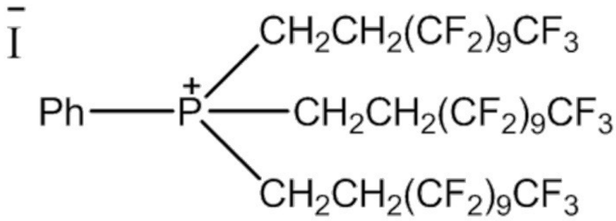


Figure 5. IRRAS spectra of a PFD film (trace a), of a PFD film after adsorption of Rf_3PPhI (trace b), and after vigorous sonication to remove physisorbed material (trace c). Spectra have been offset for clarity.



Scheme I. Chemical structure of compound Rf3PPhI.

c). There is a clear increase in C—F stretching peak intensities in trace (b) thus indicating that Rf_3PPhI remains physisorbed at the PFD modified surfaces; physisorption however appears to be reversible, since the original peak intensity is recovered after prolonged sonication in acetone. These observations indicate that photochemically grafted PFD layers behave like solid phases for fluorinated ligand extraction, in a similar manner as perfluorinated SAMs on gold.[21]

All PFD films examined were found to effectively physisorb Rf_3PPhI ligands; however, we observed that the adsorption capacity of PFD adlayers was strongly dependent on the photochemical grafting conditions used for their preparation. Figures 6a and 6b show a comparison of the relative Rf_3PPhI adsorption capacity of PFD films grafted for progressively longer times using lamp and laser (4 mJ cm^{-2}) sources, respectively; the adsorption capacity of bare a-C surfaces is shown for comparison purposes on both Figures. The relative Rf_3PPhI adsorption values were obtained by integrating the total intensity of $–CF_2$ stretching peaks, according to previously published methods.[21] For samples modified with the lamp (Fig. 6a), the integrated absorbance was found to reach a maximum at surfaces that were illuminated for 30 – 60 min, suggesting that maximum Rf_3PPhI physisorption occurred on these samples. Surprisingly, after longer reaction times (e.g. 120, and 180 minutes) the amount of physisorbed Rf_3PPhI decreases. A similar trend is observed at laser modified surfaces (Fig. 6b), with Rf_3PPhI physisorption increasing for PFD layers synthesized with exposures up to 2700 laser pulses, followed by a decrease for PFD layers grafted for longer reaction times. It is interesting to notice that maximum Rf_3PPhI physisorption is observed, in both Figures 6a and 6b, for surfaces where PFD coverage yielded a net absorbance for C—F stretching peaks of ~0.0022 (see Figures 2a and 3a), which based on results in Table 1 would be equivalent to ~1.6 ML.

Since the adsorption of perfluorinated ligands has been shown to depend on the organization of perfluorinated tails,[21] these results indicate that there are significant differences in the ability to pack and accommodate perfluorinated chains depending on PFD grafting reaction times. Surprisingly, when comparing PFD layers that display relatively small differences in PFD coverage, it is possible to observe remarkable differences in Rf_3PPhI adsorption capacity. This indicates that, even when surface coverage reaches its self-limiting value, structural changes continue to take place in grafted layers at longer reaction times.

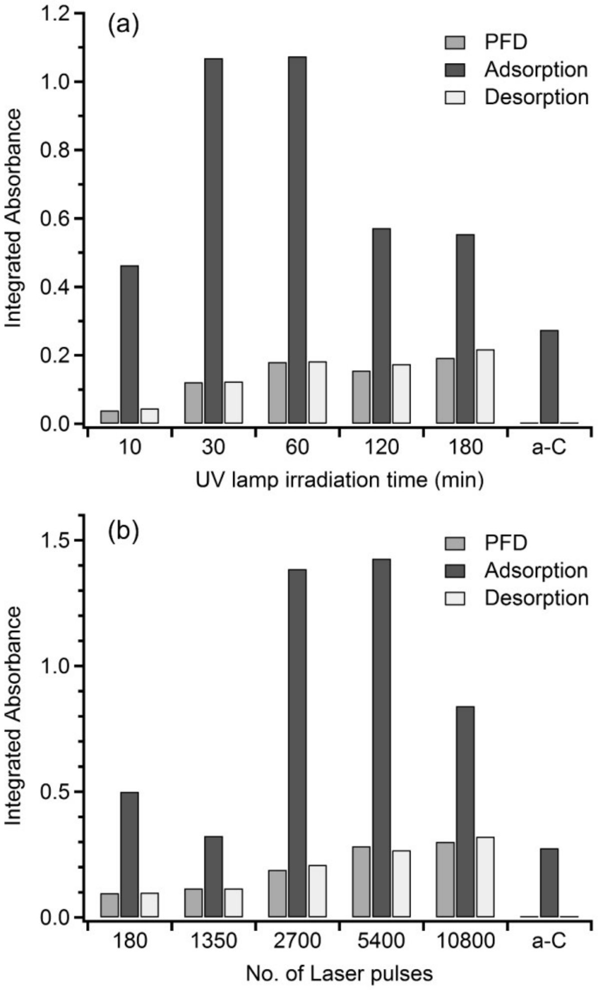


Figure 6. Integrated absorbances obtained from IRRAS spectra in the region 1400–1000 cm^{-1} for (a) lamp and (b) laser (4 mJ cm^{-2}) grafted PFD films, as deposited (▨), after Rf_3PPhI physisorption (■) and after desorption of Rf_3PPhI via sonication (□).

Discussion

Our results indicate that both the pulsed laser and the lamp source lead to PFD grafting at a-C surfaces. It is clear that the laser can be used for the preparation of functionalized surfaces over very short times; for instance, at the highest fluence tested and 3 Hz a 1 ML coverage was obtained in 1 min while lamp exposure requires approximately 20 min. The ability of the pulsed laser source to deliver photons at larger rates than the UV lamp therefore translates into significant practical advantages that might be leveraged for fast functionalization of surfaces.

Significant differences were observed in chemisorption yields between the two types of sources, with the limiting surface coverage being 25-30% higher when the pulsed laser source is used. Also, grafting efficiency appears to be enhanced when using the pulsed laser source. A simulation of the temperature changes expected using pulsed laser irradiation both over the depth of the sample and over the time following an incident pulse, suggests that thermal effects are unlikely to affect reaction rates or be responsible for observed differences in reaction yield. The fact that fluences above 16.5 mJ cm^{-2} led to irreversible and visible changes in the carbon sample, indicates that it might not be possible to achieve simultaneous thermal and photochemical grafting via laser excitation at thin graphitic carbon films without also affecting the carbon properties. Therefore, it is reasonable to interpret PFD chemisorption results obtained via pulsed laser irradiation in terms of photochemical effects solely.

In the case of carbon materials such as amorphous carbon and diamond, the photochemical reaction with terminal alkenes is initiated by electron photoemission from the surface to an acceptor level in the liquid phase.[14, 17] Photoemission at the carbon/liquid interface is an effective pathway for the creation of persistent holes with sufficiently long lifetimes to allow for subsequent nucleophilic attack reactions with terminal olefins.[38-40] Wavelength dependent photocurrent measurements by Hamers and co-workers[13, 39] demonstrated indeed that both an increase in photon energy and the presence of electron acceptors such as fluorinated groups,[17, 39, 41, 42] increase grafting yields. The two UV sources used in our experiment emit at slightly different photon energies of 4.88 and 5.00 eV for excimer laser and grid lamp, respectively. A difference in incident photon energy can potentially result in differences in (a) photon absorption, (b) electron photoemission yield and (c) kinetic energy of photoemitted electrons at the carbon/PFD interface. Absorptivity of a-C films had previously been measured via UV-Vis spectroscopy,[25] and found to be (216 ± 22) × 10^3 cm^{-1} and (221 ± 22) × 10^3 cm^{-1} at 254 and 248 nm, respectively (see Supporting Information). Given a thickness of 85 nm, a-C films would be expected to absorb only 0.7% more photons at 248 nm than at 254 nm. Also, the optical absorption of liquid PFD is negligible and remains constant in the range 245-263 nm (see Supporting Information). Therefore, a difference in optical absorptivity is unlikely to be at the origin of the observed 20-30% difference in reaction yield.

It appears therefore more important to examine the impact that (b) and (c) might have on rates and limiting layer thickness obtained via these reactions. For photon energies above the photoemission threshold (E_{thr}), the electron photoemission yield depends on photon energy; the yield at the solid/vacuum and solid/liquid interface has been shown to follow the following relationship:[43-45]

$$Y \propto (h\nu - E_{thr})^{\gamma} \ (1)$$

where an exponent γ = 2.5 has been found to satisfactorily describe reaction trends at the carbon/alkene interface.[17, 39] Given a change in photon energy from 4.88 eV (lamp) to 5.00 eV (laser) it is possible to estimate the expected change in electron photoemission yield using equation (1) if E_{thr} is known. The position of the acceptor level of a perfluoroalkane chain has been determined electrochemically, and its reduction potential (E_{red}) is positioned at -2.4 V relative to SHE in N,N-dimethylformamide (DMF).[46] Given that the valence band edge of the a-C film (E_V) was found to be positioned at -4.8 eV[47] and that the SHE is positioned at -4.43 eV[48] (E_{SHE}) with respect to vacuum, the threshold energy for photoemission into PFD acceptor levels can be estimated in DMF as $E_{thr} = E_{SHE} – E_{red} – E_V = 2.8$ eV. Given that the photochemical reaction takes place at the carbon/PFD interface, it is reasonable to expect a higher threshold due to lower solvent stabilization of charged species in PFD when compared to DMF: the Born solvation energy[49] for PFD should be ~40% that in DMF given the much lower dielectric constant of perfluoroalkanes (ε = 1.81 vs. 37.06).[50] Considering that Born energies for anions in DMF range between 1.7-2.6 eV[51] the E_{thr} energy for photoemission into the neat PFD liquid is expected to range between 3.8 and 4.4 eV, in good agreement with previous threshold energies for fluorinated alkenes calculated by Wang et al. from photocurrent experiments.[39]

Using equation (1) and a 2.5 exponent, the photoemission yield ratio Y_{248}/Y_{254} should range between 1.2 and 1.6. If the chemisorption rate were solely controlled by the electron photoemission yield, these ratios should translate into 20-60% faster reaction rates when using the laser source as opposed to the lamp source. This is indeed close to the 1.8 factor difference in chemisorption rates that emerges from results in Figure 3b thus suggesting that electron photoemission is rate-limiting during the initial stages of PFD chemisorption at bare amorphous carbon surfaces.

At a later stage during the chemisorption process, grafting rates are drastically reduced. Hamers and co-workers observed that, once organic layers reach a limiting thickness of approximately 5 nm (~3 ML), the rate of photoinduced chemisorption of terminal alkenes is significantly reduced. They proposed that the limiting thickness of organic layers is controlled by the attenuation length of the photoemitted electrons: chemisorption rates decrease after the formation of 2-3 layers because photoemission into acceptor levels and any charge neutralization necessary for sustained electron emission, must occur on or through an organic layer. It is therefore possible that a difference in photon energy could translate into a different attenuation length for photoemitted electrons, and in turn into a different limiting thickness of the PFD adlayer. Considering the photon energies used and the estimated E_{thr} range, photoelectron kinetic energies are expected in the range 0-1.2 eV which, based on determinations by Monjushiro and Watanabe for hydrocarbon films,[52] should result in escape depths in the range 1-2 nm. Importantly, the variations in escape depth due to a change of only 0.1 eV in photon energy are negligible and at most translate into a change of 0.2 nm in escape depth.

The discussion above suggests that photon energy differences could translate into differences in photoemission rates at bare carbon but are not likely to determine the limiting thickness of PFD adlayers, and therefore cannot explain the observed differences in yield between excimer laser and UV lamp reactions. It is therefore likely that the difference arises from secondary radical reactions which are known to take place during photochemical grafting of alkenes and that become evident in the multilayer regime. Franking and Hamers have in fact shown that cross-linking reactions are involved in multilayer chemisorption of alkenes at TiO_2 surfaces;[7] also, dissociative electron attachment at perfluorinated chains has been shown by Vurens et al.[53] to lead to chain cross-linking reactions. Radical anions formed via photoemission within the organic layer can either dissipate their charge or dissociate causing further radical side-reactions, such as bond breaking and/or cross-linking.[7, 40] The large incident photon rates that can be achieved during a laser pulse would facilitate cross-linking once the primary alkene chemisorption reaction has slowed down due to the presence of a multilayer. Rf_3PPhI adsorption experiments suggest that cross-linking reactions take place and affect the structure of the chemisorbed adlayer at high molecular coverage. Physisorption of Rf_3PPhI, which is favoured by the ability of fluorinated chains to interact and pack at the surface, reaches a maximum as the molecular coverage reaches its limiting value. After that point the molecular coverage of the layer stabilizes but the Rf_3PPhI adsorption capacity diminishes, thus indicating decreased intermolecular interactions between Rf_3PPhI and PFD fluorinated chains.

Conclusions

The photochemical grafting of a perfluorinated terminal alkene, PFD, onto amorphous carbon substrates driven by UV pulsed laser irradiation was investigated and compared to the same reaction driven by a UV lamp. Differences in chemisorption rates and yields of reactions were observed, however, these differences could be interpreted on the basis of established photochemical mechanisms of reaction. We propose that the somewhat faster chemisorption rate observed for laser driven reactions might be explained by differences in photon energy between the two sources, which are predicted to result in higher photoemission yields for the excimer laser. A higher self-limiting surface coverage was observed when laser pulses vs. lamp irradiation were used; we attribute this to faster rates of cross-linking reactions that take place and often dominate in the multilayer regime. Interpretation of our results on the basis of established photochemical processes alone is supported by computational results that indicate that, despite the high optical absorption of carbon substrates in the UV range, only a modest temperature rise is expected.

Our results indicate that pulsed laser sources can be used for fast functionalization of surfaces. These results have important implications for the development of new rapid methods for the modification of surfaces with both time and spatial resolution. Such methods could find applications in, for instance, high throughput device processing or, interestingly, dynamic systems such as microreactors and fluidic devices in general. Finally, we demonstrate that fluorinated carbon surfaces offer a good alternative to, for example, fluorinated SAMs as adsorbers for fluorinated ligands or pollutants.

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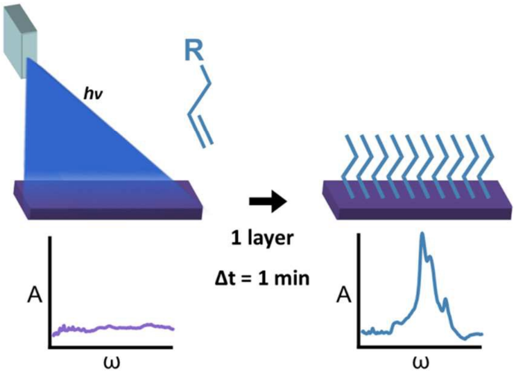

Rapid functionalisation of carbon surfaces using pulsed UV lasers offers a novel method for capturing fluorinated ligands or pollutants.