Supplementary Information for

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

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Infrared absorption spectrum of fluorinated compounds used in our experiments

The infrared spectra of 1H, 1H, 2H-perfluoro-dec-1-ene (PFD) neat liquid and Rf3PPhI neat powder were measured using an Attenuated Total Internal Reflectance accessory. Figure SI.1 shows the infrared spectrum of (a) PFD and (b) Rf3PPhI in the C—F stretching region, which displays three main peaks at 1240, 1200 and 1150 cm^{-1}.

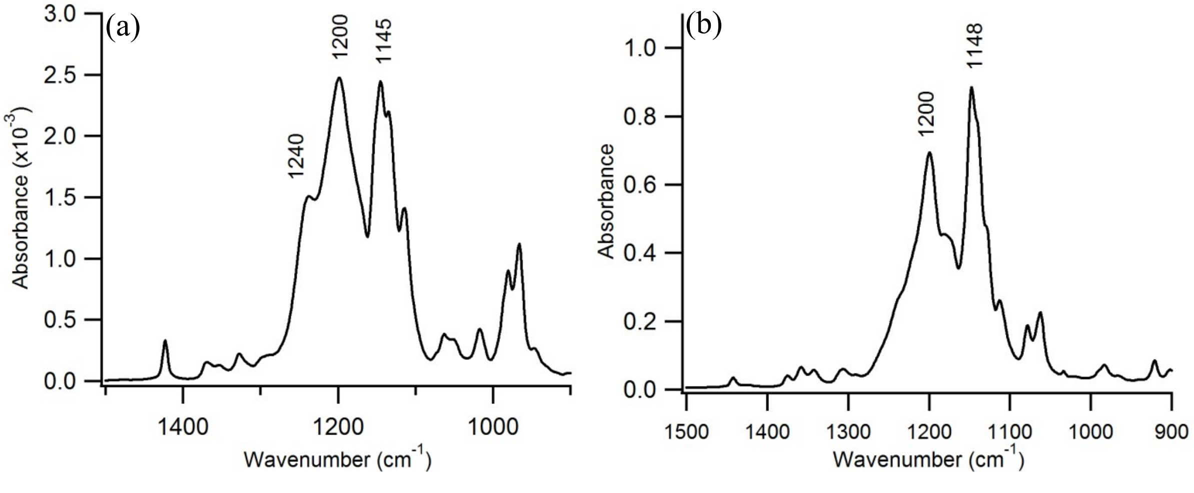

Figure SI.1. ATR-FTIR spectra of PFD (a) and Rf3PPhI (b) obtained from the neat liquid and powder, respectively.

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Grafting of PFD at 3 Hz and 10 Hz pulse rates

Figure SI.2 shows IRRAS spectra of PFD adlayers grafted at a-C substrates using 2700 pulses, at 16.5 mJ cm^{-2} fluence delivered using two pulse rates: 3 Hz and 10 Hz. A comparison of the two IRRAS spectra indicates that the two films display negligible differences.

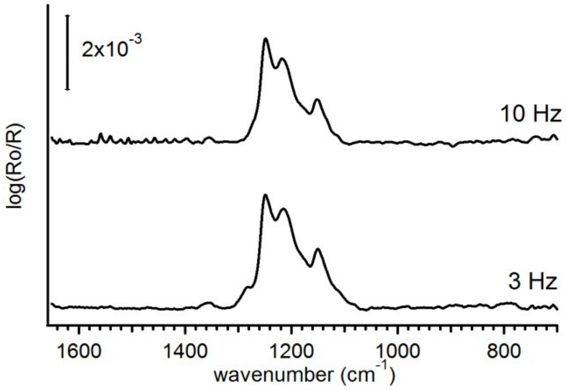

Figure SI.2. IRRAS spectra of PFD adlayers grafted by delivering 2700 pulses at 16.5 mJ cm^{-2} fluence.

Raman spectrum of carbon before and after exposure to laser

Figure SI.3 shows Raman spectra of a bare carbon substrate as deposited and after exposure to 5400 pulses at 16.5 mJ cm^{-2}. Raman spectra were measured in backscattering configuration using a Renishaw 1000 micro-Raman system and 514 nm excitation. The spectra show the characteristic D (~1350 cm^{-1}) and G (~1580 cm^{-1}) peaks of amorphous carbon which are diagnostic of graphitic content and graphitic cluster size.[1] The two spectra are identical thus showing no evidence of thermal damage to the carbon arising from exposure to the laser pulses at the maximum fluence used for our experiments.

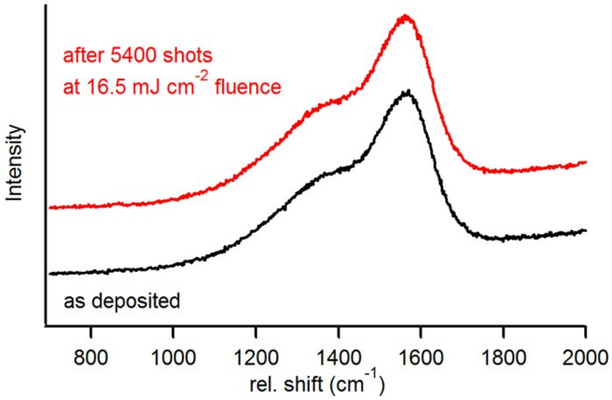

Figure SI.3. Raman spectrum (514 nm exc.) of carbon before and after exposure to laser pulses.

Spectral irradiance of UV grid lamp

Figure SI.4 shows the spectral irradiance of the UV grid lamp used in our experiments at the sample position. The spectrum was calibrated as described in the main text.

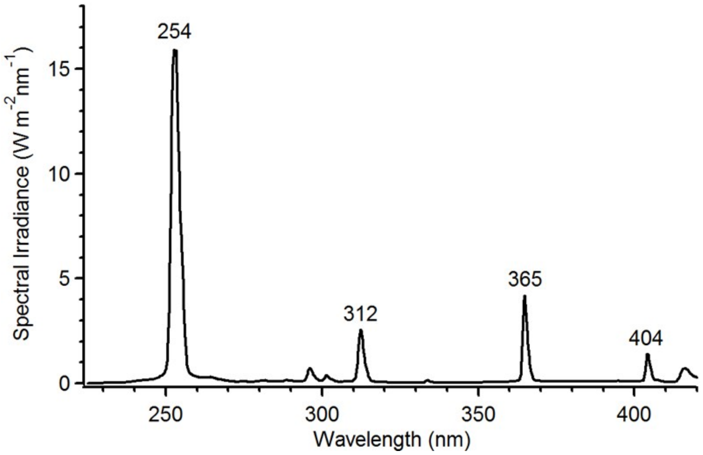

Figure SI.4. Spectral irradiance of the UV grid lamp used in PFD grafting experiments.

Linear fits of chemisorption rates at time zero

The chemisorption curves reported in Figure 3b of the main text were fitted to a line near time zero to compare grafting rates using the two sources. The intercept was fixed at the origin and datapoints were weighted by the standard deviation calculated over the IRRAS spectra of three distinct samples; the average standard deviation across data points was 0.0005 which is close to the experimental spectral noise. The slopes were used in the text to estimate the number of photons needed to obtain 1 ML coverage, equivalent to net peak height ~0.0013.

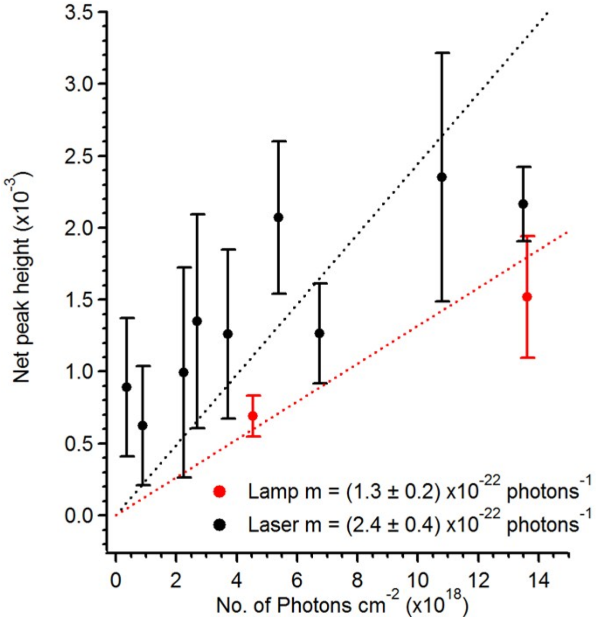

Figure SI.5. Linear fit of the chemisorption curves reported in Figure 3b near time zero.

Details of computational modeling of temperature changes using COMSOL

The temperature rise due to laser irradiation through the whole material stack (a-C/Ti/Si) was modelled using COMSOL Multiphysics software. A graphite layer was chosen to represent the a-C film both in terms of optical absorption and heat transport. The parameters used are shown in Table SI.1. The wavelength and fluence chosen were 248 nm and 16.5 mJ cm^{-2}, respectively. The electromagnetic simulation uses the wave equation:

$$\nabla \times (\nabla \times \vec{E}) - k_0^2 \in_r \vec{E} = 0 \qquad \text{(SI1)}$$

where $\epsilon_r = (n - ik)^2$ is the complex relative dielectric permittivity accounting for absorption and $k_0 = 2\pi/\lambda$. The laser heating in the material is given by:

$$Q = \omega \operatorname{Im}[\in_r] \in_0 |E|^2 = \omega(2nk) \in_0 |E|^2 \qquad \text{(SI2)}$$

The incoming field is modelled as a plane wave of the form:

$$\vec{E} = \vec{E}_0 \exp(ikx) \qquad \text{(SI3)}$$

The calculated laser heating is then input into the heat equation:

$$\rho C_p \frac{\partial T}{\partial t} + \nabla(-\kappa \nabla T) = Q(\vec{x}, t) \qquad \text{(SI4)}$$

where ρ is the density, C_p the heat capacity at constant pressure and κ the thermal conductivity. This yields $T(x,t)$ as a solution, i.e. the temperature as a function of position and time.

Layer	***n***	***k***	***ρ*** **g/cm³**	**C**$_p$ **J/mol K**	***κ*** **W/m K**
Si	1.57 [2]	3.565 [2]	2.33 [3]	19.789 [3]	124 [3]
Ti	1.24 [3]	1.21 [3]	4.51 [3]	25.06 [3]	21.9 [3]
C	1.51 [4]	0.71 [4]	2.2 [5]	8.517 [3]	191 [6]

Table SI.1. The parameter values chosen for Si, Ti, and graphite layers, where n is the refractive index, k is the extinction coefficient, ρ is the density, C_p is the specific heat capacity, and κ is the thermal conductivity.

Optical absorption of a-C and PFD thin films in the UV-Vis region

The optical absorption of PFD and a-C films was measured using a UV-Vis spectrophotometer in transmission mode. The absorption of PFD neat liquid was measured using a 3 mm pathlength cell. The absorptivity of a-C films was calculated from the measured absorbance of a film of known thickness deposited on quartz, neglecting reflection losses.

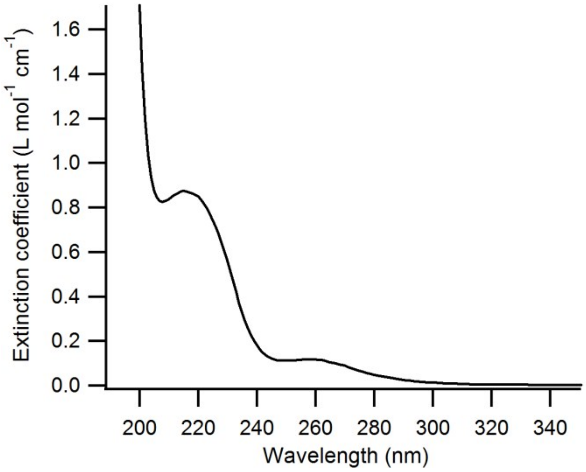

Figure SI.6. Absorption spectrum of PFD in the UV region.

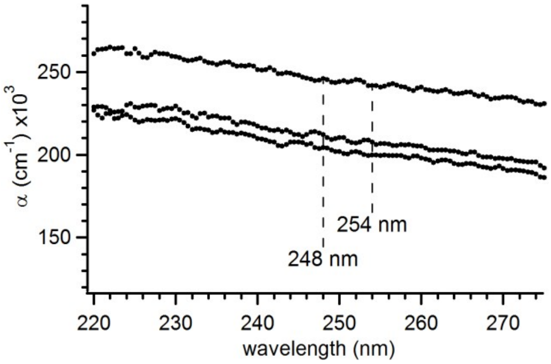

Figure SI.7. Absorptivity of three a-C thin films in the UV region.

References

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