Covalently Attached Organic Monolayers from 1-Alkynes onto Chromium Nitride: Alkyl and Fluoroalkyl Termination

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1. Density Functional Theory (DFT)[1]

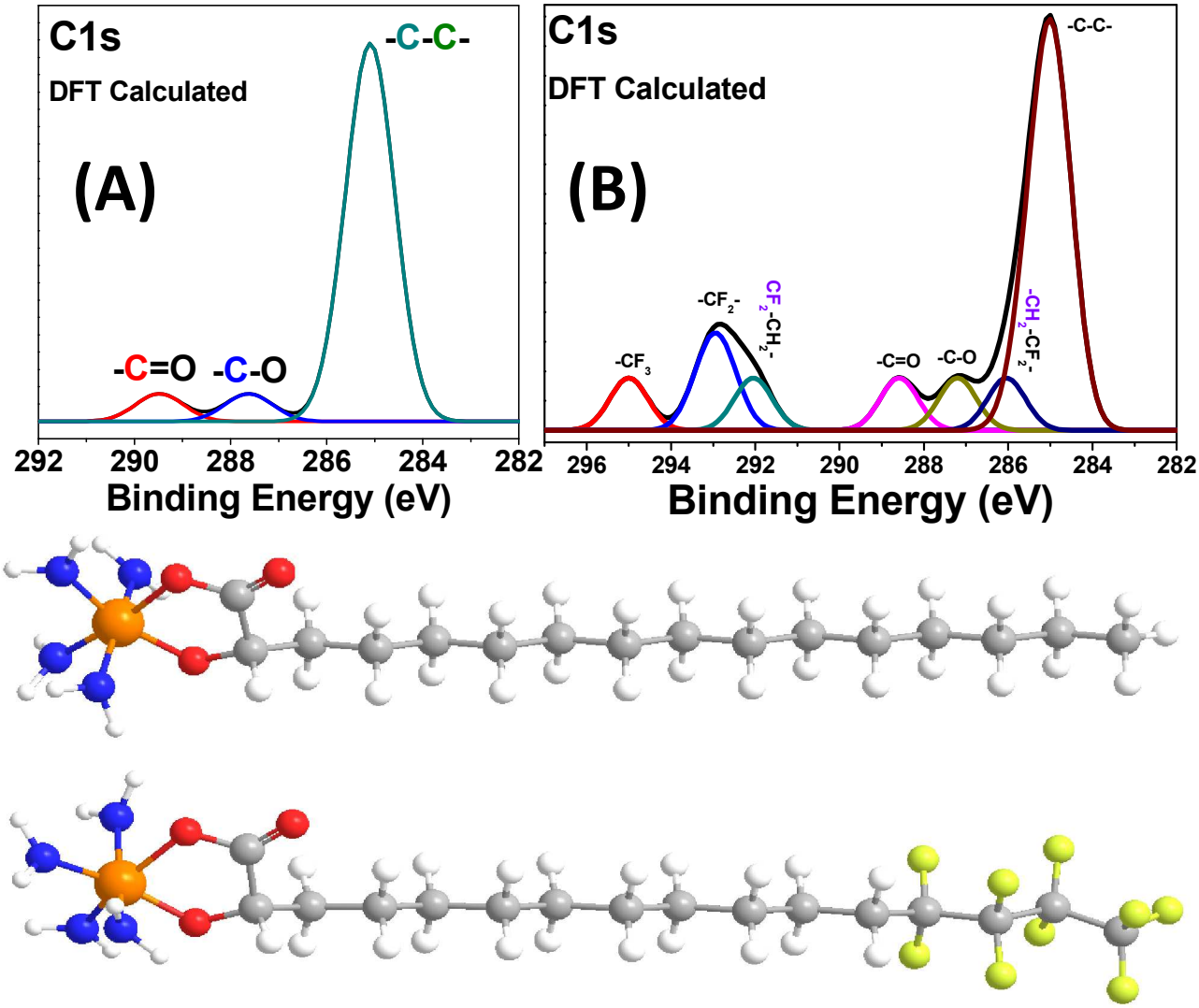

Figure 1S. (A) Simulated XPS spectra of C16YNE (A and C) and F9YNE (B and D) using the B3LYP/6-311G(d,p)-calculated binding energies corrected with slope and offset. Color code: blue (nitrogen), orange (chromium), red (oxygen), gray (carbon), white (hydrogen), and yellow (fluorine).

2. Kinetic study of the attachment of 1-alkynes and 1-alkenes onto plasma-activated CrN surface:

Table S1. Static water contact angle of organic monolayers derived from 1-hexadecene and 1-hexadecyne on hydroxyl-terminated CrN as function of reaction temperature at 12 h.

Contact angle : effects of temperature (Figure 3A)									
1-hexadecene					1-hexadecyne				
Temp. °C	Surf-I	Std(± °)	Surf-II	Std(± °)	**Temp. °C**	Surf-I	Std(± °)	Surf-II	Std(± °)
6	64.5	0.8	65.2	0.6	**6**	75.0	0.6	74.3	0.6
15	71.1	1.4	69.5	0.8	**15**	78.5	0.6	79.0	0.6
20	71.8	0.8	71.7	1.2	**20**	81.7	1.0	82.4	0.6
40	81.5	1.1	82.5	0.8	**40**	93.0	0.6	93.2	0.7
60	90.7	1.0	92.6	1.2	**60**	97.5	1.1	99.5	1.2
80	98.0	0.7	98.2	0.9	**80**	106.5	0.7	106.4	0.9
100	105.4	0.6	105.0	1.0	**100**	110.2	0.6	110.0	0.6
130	108.7	0.6	107.8	0.5	**130**	110.0	0.5	110.7	0.5
160	109.4	0.9	110.5	1.3	**160**	110.4	0.7	110.2	0.6

Table S2. Hexadecyne-derived monolayers on the CrN surface with different time at 100 °C for static water contact angle.

Contact angle : Time (hr) at 100 oC (Figure 3C)				
1-hexadecyne				
Time (hr)	Surf-I	Std(± °)	Surf-II	Std(± °)
0.0	0.0	0.0	0.0	0.0
1.0	80.1	*0.4*	*81.0*	0.8
2.0	92.7	*0.6*	*92.5*	1.2
3.0	95.2	*0.7*	*95.0*	0.8
4.0	99.0	*0.6*	*98.0*	1.2
8.0	105.3	*0.5*	*105.4*	0.9
12.0	109.6	*0.6*	*109.4*	1.0
16.0	110.0	*1.0*	*110.0*	0.5
24.0	110.2	0.6	110.0	1.3

3. AFM image and roughness:

Figure S2 shows the AFM topographical height image of CrN substrates after various activation processes and alkyne modification: Bare (before activation) acetone cleaning of CrN (Figure S2A), 10 min air plasma activation (Figure S2B), after modification with C16YNE (Figure S2C), and after modification with F9YNE (Figure S2D). We found that the surface roughness decreases to 5.9 ± 0.1 nm after air plasma activation 10 min. After monolayer grafting, the roughness slightly reduced again in both C16YNE and F9YNE to 5.8 ± 0.1 nm and 5.7 ± 0.1 nm, demonstrating that the formation of a cushioning monolayer. The similar effect we observed in the SiC surfaces.[2]

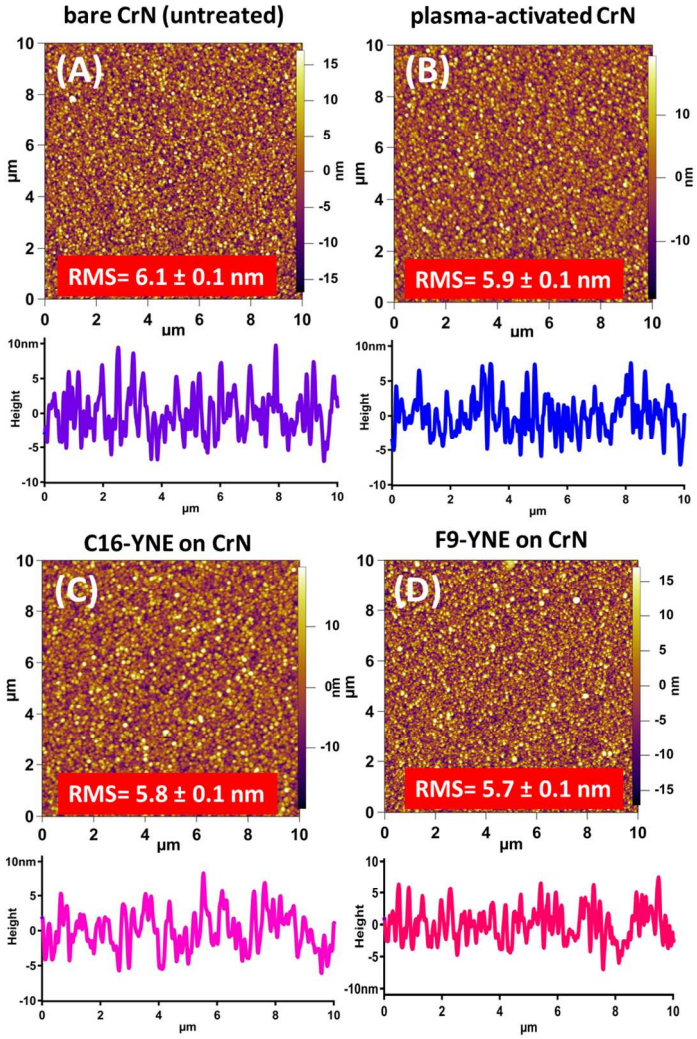

Figure S2. AFM tapping mode topographic images of CrN surface. (A) bare CrN (untreated) surface, (B) air plasma activation for 10 min, (C) after modification with C16YNE on CrN surfaces, and (D)

after modification with F9YNE on CrN surfaces. Section Analyses for corresponding surfaces shown in below.

1. Giesbers, M.; Marcelis, A. T. M.; Zuilhof, H., Simulation of XPS C1s Spectra of Organic Monolayers by Quantum Chemical Methods. *Langmuir* **2013,** 29, (15), 4782-4788.
2. Pujari, S. P.; Scheres, L.; Weidner, T.; Baio, J. E.; Stuart, M. A. C.; Rijn, C. J. M. v.; Zuilhof, H., Covalently Attached Organic Monolayers onto Silicon Carbide from 1-Alkynes: Molecular Structure and Tribological Properties. *Langmuir* **2013,** 29, (12), 4019–4031.