

Patterned formation of enolate functional groups on the graphene basal plane.

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Supporting Information

Experimental Section

All experiments were conducted in ultra-high vacuum chambers with base pressure below 1E-9 mbar. The graphene sheet was prepared by temperature programmed growth at 1200 °C followed by chemical vapor deposition at 900 °C, using ethylene gas as the carbon source.^[1] Graphene samples were annealed to 900 °C to clean before experiments. In all experiments, unless otherwise stated, a complete monolayer of graphene was ensured by exposing the sample to a background pressure of CO and checking for evidence of CO adsorption on bare Ir. No CO adsorption was taken as evidence for complete graphene coverage of the Ir surface. The resulting pristine graphene sheet, once cooled to room temperature, was exposed, at normal incidence, to a flux of O atoms, produced by thermally cracking O₂ in an Ir capillary heated to 1750 °C. The cracker was thoroughly degassed prior to use. O₂ gas was backfilled through the capillary into the UHV chamber, to facilitate atomic dosing. In all cases the pressure in the main chamber during exposure to atomic oxygen was fixed at 2E-7 mbar.

STM images were recorded at room temperature using an Aarhus type STM,^[2] and were analysed using the Gwyddion SPM analysis software. All images were collected in constant current mode. Images were corrected for thermal drift and plane flattened.

XPS data were collected at beamline 11.0.2, at the Advanced Light Source, Lawrence Berkeley National Laboratory beamline. Photon energies of 490 eV, 275 eV and 725 eV were used to collect high-resolution data for C1s, Ir4f and O1s core levels respectively. Time resolved C1s data was recorded while irradiating the sample with O atoms and a photon energy of 725 eV were used to collect data for this experiment. The chamber geometry only permitted grazing incidence irradiation of the sample with the O atoms.

Vibrational and electronic spectra were obtained using high-resolution electron energy loss spectroscopy (HREELS) with a VSI delta 0.5 spectrometer, in Marseille. Data presented were collected using an incident electron beam with energy of 20 eV. The energy resolution, determined by the full-width half maximum of the elastic peak, was typically 4-7 meV.

Table S1. XPS fitting parameters

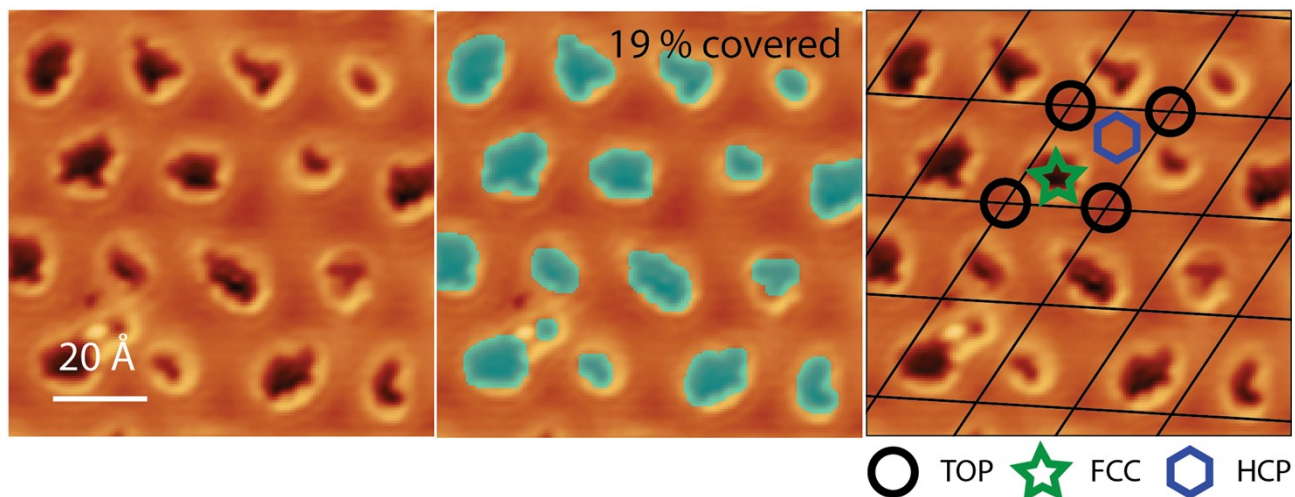
		GR/IR(111)				O-GR/IR(111)			
		BE (eV)	GFWHM (meV)	LFWHM (meV)	asym	BE (eV)	GFWHM (meV)	LFWHM (meV)	asym
C1S ¹	C _C	284.042	264	114	0.114	284.086	284	122	0.127
	C _O	-	-	-	-	284.326	931	122	0.127
	C _A	-	-	-	-	285.843	662	122	0.127
IR4F ²	Ir _B	60.801	217	249	0.159	60.813	217	249	0.159
	Ir _C	-	-	-	-	60.603	400	241	0.16
	Ir _S	60.291	256	250	0.214	60.303	266	250	0.214
O1S ³	O _A	-	-	-	-	531.07	2046	-	-
	O _B	-	-	-	-	528.83	1386	-	-

¹ A Doniach-Šunjić function convoluted with a Gaussian, using a linear background

² A Doniach-Šunjić function convoluted with a Gaussian, using a Shirley background

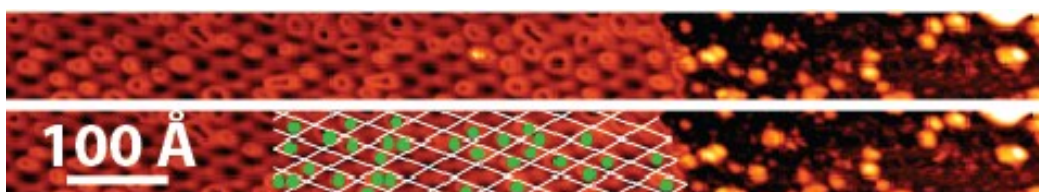
³ A Gaussian function, using a linear background

Figure S1. O-atom coverage estimate using STM imaging.



Gr/Ir(111) was exposed to a low flux of O atoms for 60 s. The same image from the resulting surface is shown here 3 times; on the left as recorded, in the center with the sites where O atoms have attached to the graphene basal plane highlighted in blue, and on the right with the moiré lattice superimposed. In this region of the graphene basal plane, O atom defects are clustered, with one cluster site per moiré unit cell and O atoms selectively adsorbed at FCC sites. We can estimate the O-atom coverage by counting the number of pixels highlighted in blue in the center image and such an analysis reveals that 19 % of the surface is covered in O atoms. This figure concurs with the level of coverage, at saturation under similar conditions, estimated from an analysis of XPS data in Figure 2 in the main text. $V=-390$ mV, $I=0.11$ nA.

Figure S2. Identifying the reactive sites in the moiré unit cell.



It has previously been established that the dark areas imaged in STM scans of the Gr/Ir(111) moiré unit cell represent the TOP site regions of the moiré unit cell, as described in the main text. Hence, the bright areas represent the HCP and FCC regions.^[3] To further support this assignment we include, in Figure S2, an STM image of submonolayer coverage of Gr/Ir(111) meeting an Ir step edge, following exposure to atomic O. The left hand side of the image is covered in O-graphene while the right hand side is O-Ir. The boundary between the two represents the boundary at the edge of the graphene island on the Ir surface. The same image is presented twice, and in the bottom version a moiré lattice has been added with the crossing points of the white lines representing the TOP sites. The green dots mark the areas that have been

functionalised with O atoms. The white lines have been added to the image following the procedure explained by N'Diaye et al.^[4], which determines that for submonolayer graphene, the graphene areas protruding toward the Ir are TOP regions. As expected, the TOP regions are imaged as dark circles and the green dots do not fall on these TOP regions. Hence we safely label the functionalised areas as the HCP and FCC areas. $V=1.1$ V, $I=0.30$ nA.

References

- [1] A. T. N'Diaye, M. Engler, C. Busse, D. Wall, N. Buckanie, F.-J. Meyer zu Heringdorf, R. van Gastel, B. Poelsema, T. Michely, *New J. Phys.* **2009**, *11*, 023006.
- [2] E. Lægsgaard, F. Besenbacher, K. Mortensen, I. Stensgaard, *J. Microsc.* **1988**, *152*, 663.
- [3] A. T. N'Diaye, J. Coraux, T. N. Plasa, C. Busse, T. Michely, *New J. Phys.* **2008**, *10*.
- [4] A. T. N'Diaye, T. Gerber, C. Busse, J. Mysliveček, J. Coraux, T. Michely, *New J. Phys.* **2009**, *11*.