Supplementary information

Impact of covalent functionalization by diazonium chemistry on the electronic properties of graphene on SiC.

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To estimate the molecule density, several scanning tunnelling microscopy (STM) images have been collected from different areas of the TMeOP-grafted graphene on SiC. The image, shown in Fig.S1, has been acquired in ambient condition after an annealing at 80°C in UHV. The bright structures, not present in the pristine graphene-SiC sample, are the fingerprint of the TMeOP-grafted units. The line profiles, collected along the coloured lines of Fig. S1, show that the average height of these bright structures is 0.30 ± 0.05 nm, in agreement with literature[1].

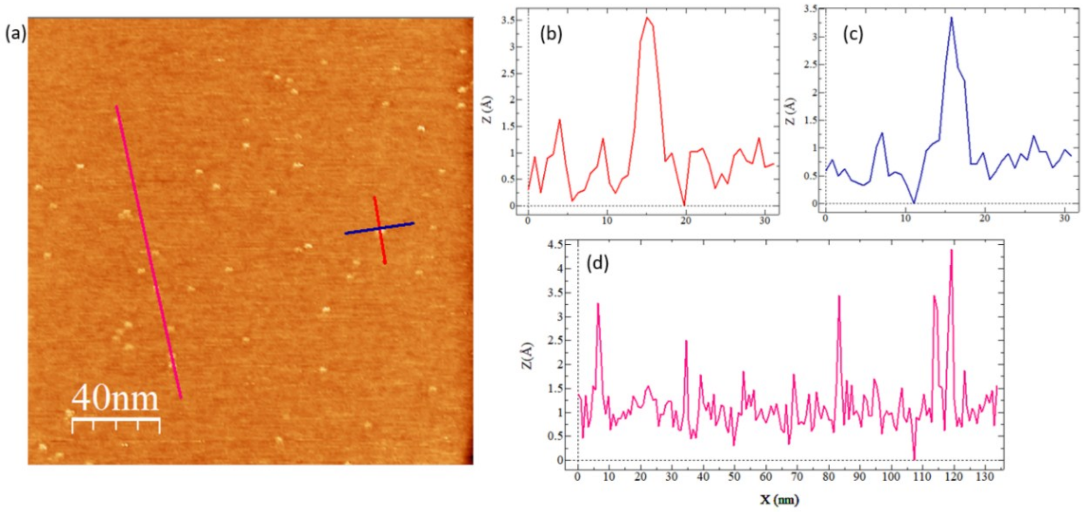

Fig. S1: 200 nm x 200 nm STM images of (a) 1 mM TMeOP-grafted units on graphene after an annealing at 80°C in UHV, acquired at I_{set} = 50 pA and V_{bias} = -0.3 V, (b-c-d) line profiles collected along the coloured lines of the image.

The density of these bright structures appears reduced of about 50% after the annealing at 220°C confirming the desorption of the molecule at high temperature. Two representative STM images collected after annealing at 80°C and 220°C are shown in Fig. S2.

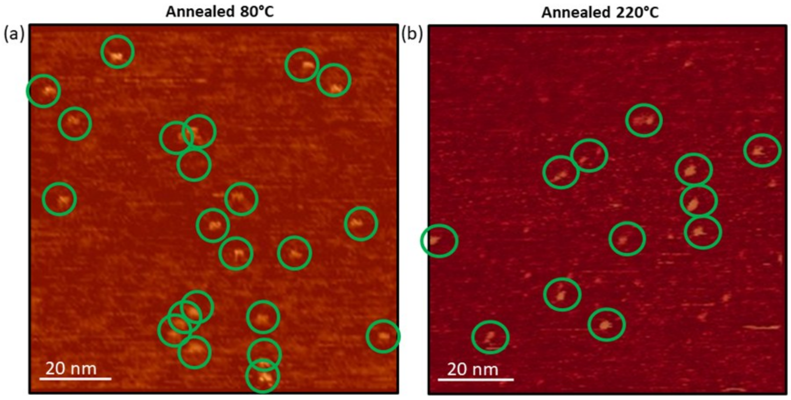

Fig. S2: 100 nm x 100 nm STM images of 1 mM TMeOP-grafted units on graphene after an annealing at (a) 80°C in UHV (b) 220°C. Both images are acquired at I_{set} = 50 pA and V_{bias} = -0.3 V. The green rings are a guide for eyes to distinguish the molecules.

Nowadays, Raman spectroscopy is a powerful tool to understand the degree of disorder in carbon-based systems. We carried out Raman measurements, along with STM measurements, as preliminary analysis to understand the presence of covalent bonds on graphene on SiC after the functionalization with TMeOP units.

The Raman spectrum of single layer graphene consists of some peculiar well-studied features (Fig. S3). The G peak corresponds to the high frequency phonon at Γ point, the 2D peak originates from a process where momentum conservation is satisfied by two phonons with opposite wave vectors and the D peak originates from the same process of the 2D peak but it requires the presence of defects for the momentum conservation[2].

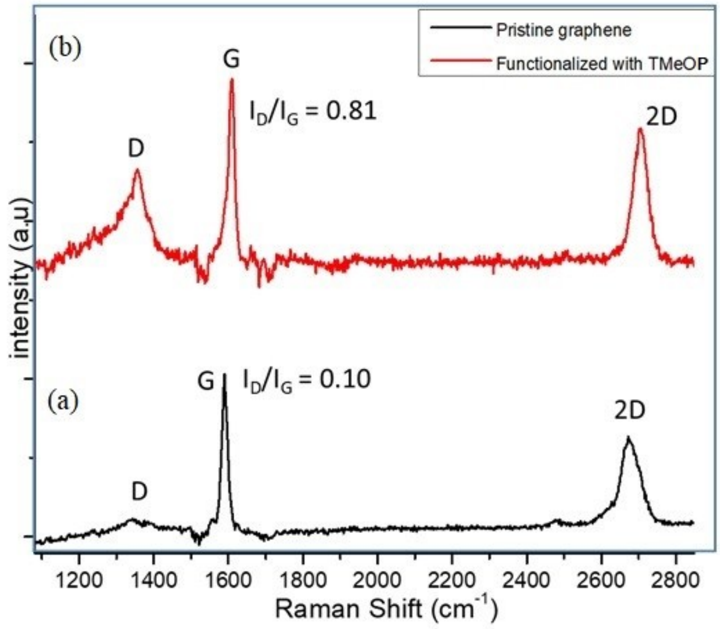

Fig. S3: SiC-background subtracted and normalized Raman spectra of (a) pristine graphene on SiC and (b) 1 mM TMeOP-grafted graphene on SiC after an annealing at 220°C.

In order to properly account for the Raman contribution of SiC substrate, the measurements were acquired by moving the optical lens in the out-of-plane/depth Z-direction. The depth of focus was varied at steps of 1.5 µm. Using this procedure, we obtained a spectrum with the sole contribution of the SiC substrate bulk signal, which finally is used to remove the SiC-background contributions in the graphene Raman spectra, recorded with the laser depth of focus point at the graphene interface. We have quantified the degree of covalent functionalization introduced by the grafted aryl units from the intensity ratio of the D and G peaks, I_D/I_G. In the pristine graphene on SiC this ratio is I_D/I_G =0.1 while in 1 mM grafted graphene it is eight times higher, i.e. I_D/I_G =0.8 due to a dislocation of the graphene layer after changing of hybridization.

Along with Raman, we carried out X-Ray photoemission measurements. The wide scan spectra of pristine graphene on SiC and TMeOP-grafted graphene on SiC are acquired after an annealing at 80°C, well below the desorption temperature of the molecules (120° C). In the survey spectra we can observe the silicon signal at lower BE, Si 2p at 100.7 eV and Si 2s at 152.2 eV, the carbon signal of graphene at 284.6 eV and the oxygen contamination along with its Auger peak at 532.2 eV and 978.2 eV, respectively (Fig. S4). Moreover, two peaks are observed in the spectrum of the TMeOP-grafted graphene: the fluorine F1s and nitrogen N1s core levels at 686.2 eV and 399.2 eV, respectively.

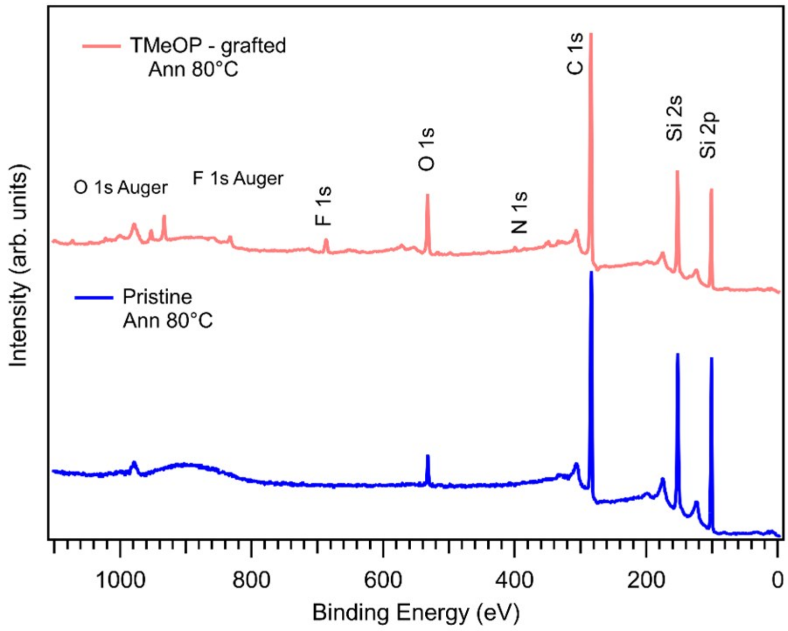

Fig. S4: (a) Survey spectra of pristine graphene on SiC annealed at 80°C and 1 mM TMeOP-grafted graphene on SiC annealed at 80°C.

In agreement with Ambrosio et al.[3], the N 1s are not ascribed to unreacted diazonium molecules but to N-groups, released from the growth solution (acetonitrile) and anchored to the graphene sp^2 defects created by the electrochemical process. Likewise, the presence of fluorine could be ascribed to fluorine groups, coming from the HF acid in the growth solution.

The contribution of oxygen and carbon increases after the grafting procedure according to the presence of oxygen and carbon of the benzene ring of the molecules: the oxygen ratio $\frac{I_{grafted}^{o}}{I_{pristine}^{o}} = 5$ and carbon ratio $\frac{I_{grafted}^{c}}{I_{pristine}^{c}} = 2.5$, where $I_{grafted}^{o}$ and $I_{grafted}^{c}$ are the peak intensity of carbon and oxygen after the functionalization while $I_{pristine}^{o}$ and $I_{pristine}^{c}$ are the peak intensity of carbon and oxygen of the pristine graphene on SiC.

Fig.S5 shows the C1s core level spectrum of the TMeOP-grafted graphene, before and after the annealing at 80°C, at two different electron take-off angles in order to be more (take-off angle = 20°) or less (take-off angle = 80°) sensitive to the surface. The C 1s lineshape in the grafted sample remains virtually unperturbed upon annealing up to 80°C. This is consistent with a previous study on grafted graphene on copper[3], where the grafting procedure itself seems to remove adventitious oxygen from the surface.

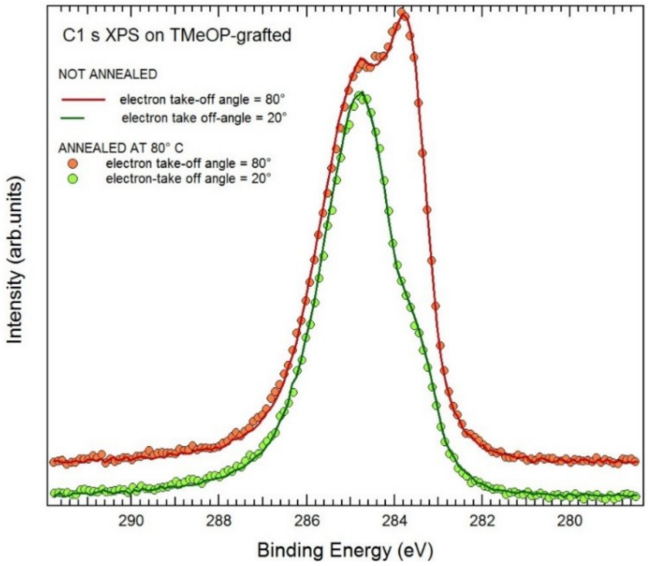

Fig. S5: C 1s spectra of 1mM TMeOP-grafted units before and after an annealing at 80°C. For both temperatures, the measurements are acquired at nearly-normal (80°) and nearly-grazing (20°) electron take-off angles with respect to the sample surface.

As discussed in the manuscript, C 1s core level of pristine and 1mM TMeOP-grafted graphene, collected at grazing angle, has been fitted, after removing a Shirley background, by a sum of Voigt functions, one for each component, being the latter the convolution of a Lorentzian with a Gaussian function, which mainly accounts for the experimental resolution. The width of the Gaussian has been set to 0.9 eV, at least. The results of the fitting procedure are shown in Table S1. The binding energies have been locked to the value reported in literature.

Sample		SiC	C-sp^2	S1	S2	C=O	C-sp^3	O-CH$_3$

Pristine	BE (eV)	**283.7**[4]	**284.7**[4,5]	**285.1**[4]	**285.7**[4]	**287.0**[6]	/	/
	FWHM (± 0.1 eV)	1.5	1.5	1.5	1.7	1.7	/	/
	AREA ((± 0.05) x 10^5)	4.39	12.5	1.23	2.73	0.46	/	/
TMeOP-grafted	BE (eV)	**283.7**[4]	**284.7**[4,5]	**285.1**[4]	**285.7**[4]	**287.0**[6]	**285.2**[4]	**286.3**[3]
	FWHM (± 0.1 eV)	1.5	1.5	1.5	1.7	1.7	1.3	1.7
	AREA ((± 0.05) x 10^5)	2.69	9.94	0.78	1.51	0.14	0.25	1.38

Table S1: Results of the fitting procedure carried out, as discussed in the text, on C1s core level (shown in Fig. 3a-b of the manuscript) obtained from the XPS spectra of pristine and 1Mm TMeOP-grafted.

From the ARPES measurements, we estimate the charge transferred (*CT*) from a molecule to graphene using the following relation:

$$CT = \frac{n_{pristine} - n_{grafted}}{\rho}$$

where *n* is the charge density obtained by the azimuthal scan data and *ρ* is molecular density measured by STM measurements. The value obtained is *CT* = (1.87 ± 0.43) molecules $^{-1}$ times the electron charge.

A solution of 3,4,5-trimethoxybenzenediazonium salt (1.0 mM) in acetonitrile (5.0 mL) was prepared in a sample tube. After 3 min from addition of the diazonium solution to the electrochemical cell with the graphene-SiC as working electrode, EC reduction was carried out using a cyclic voltammetry mode. In the cyclic voltammetry, we applied two cycles with a potential window from +1.0 V to −1.0 V (vs. Ag/AgCl reference electrode) and a sweeping speed of 50 mV/sec. After EC treatment, the TMeOP modified graphene samples were rinsed with acetonitrile to remove any physisorbed material from the surface and dried in an argon stream. Mainly, the large irreversible reduction peak observed around 0 V is assigned to the aryldiazonium activation (Fig. S6).

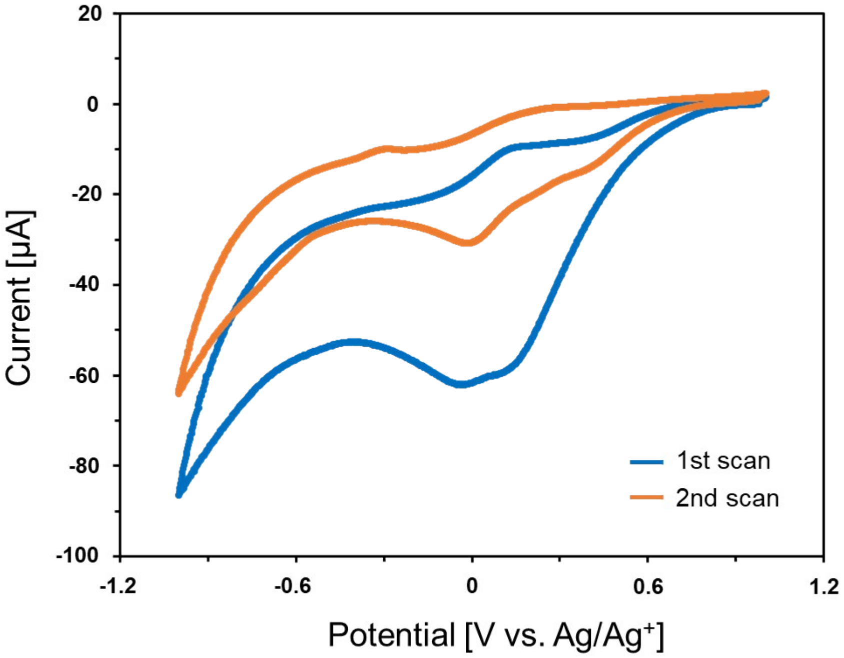

Fig. S6: Cyclic voltammogram recorded during electrochemical grafting of single layered graphene on SiC using 1.0 mM of 3,4,5-trimethoxybenzenediazonium salt.

References

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