# Supplementary Information
# Room-temperature Magnetic Ordering in Functionalized Graphene

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## STM Imaging of Pristine Graphene in the Presence of an External Magnetic Field

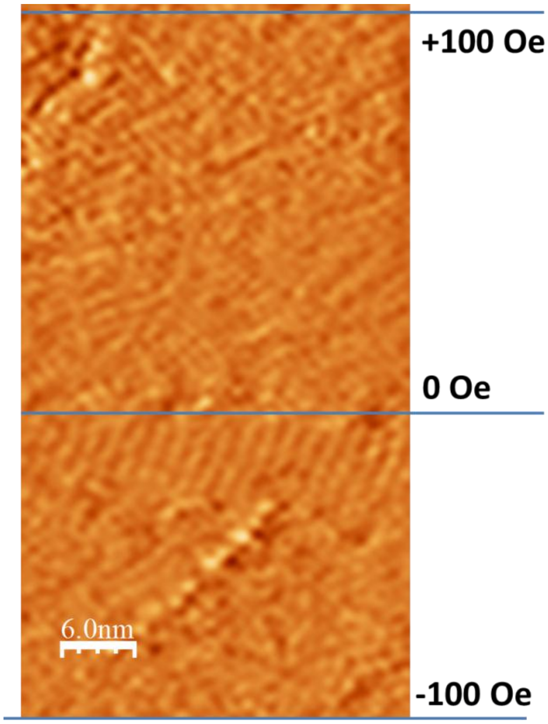

**Figure S1**: (A field-variable STM image of a pristine graphene surface. The field was varied in Y-direction from -100 to +70 Oe with a 10-Oe step.

As shown in Figure S1, according to the field measurement, no essential field dependence is observed in the case of the pristine graphene.

## Room-temperature M-H Hysteresis Loops of Functionalized Graphene

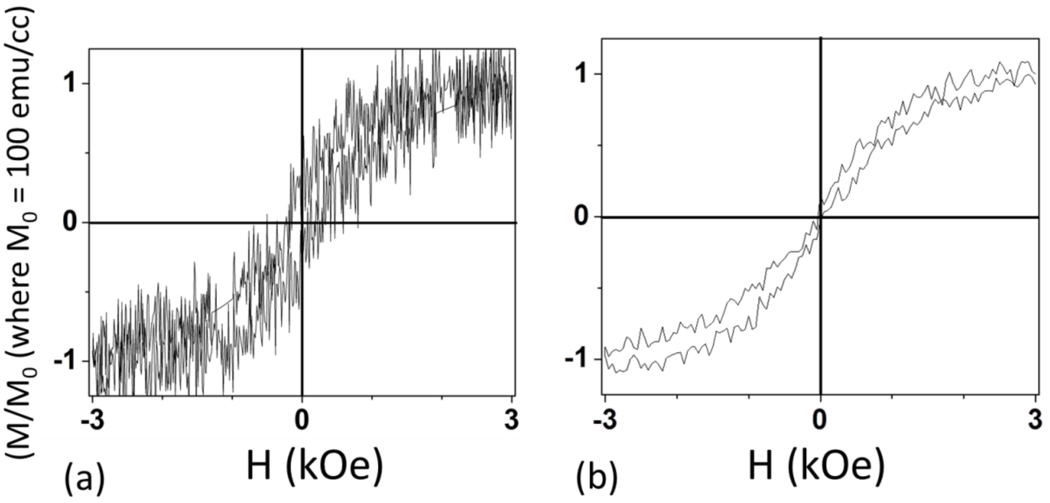

**Figure S2**: M-H Loops for a functionalized epitaxial graphene with a magnetic field with (a) in-plane and (b) out-of-plane directions at room temperature.

M-H hysteresis-loop measurements were performed using the VSM option of a Quantum Design cryogenic physical property measurement system (PPMS) with a 9.8-tesla superconducting magnet. Samples were mounted on quartz paddle and regular disk holders for the in-plane and out-of-plane measurements, respectively, with GE-7031 varnish to withstand thermal cycles during the measurements. To optimize the touchdown process, the samples were mounted with an offset of 35 mm from the bottom. To eliminate the background signal, each sample study was preceded by measurements of empty sample holders and silicon carbide substrates. The magnetic field was swept with a 10.13823 Oe/sec rate.

Both the in-plane and out-plane measurements at room temperature showed a relatively small value for the saturation magnetization of the pristine samples (below 2 emu/cc). Functionalization increased this value by a factor of about 50 at room temperature. The M-H loops for the in-plane and out-of-plane measurements of the functionalized sample are shown in Figures S2a-b, respectively. The room-temperature value of approximately 100 emu/cc for the saturation magnetization corresponds to about 0.1 $\mu_B$ (Bohr magnetons) per carbon atom for the NP-EG samples. Considering that there are approximately five carbon atoms per nitrophenyl group, we could make an order of magnitude estimate that each functionalized site contributes approximately 0.5 $\mu_B$ (the saturation magnetization of iron is about 2.2 $\mu_B$ per atom). The M-H loops indicate the potential presence of both ferromagnetic and antiferromagnetic regions in the functionalized samples. The in-plane measurements show hysteresis loops similar to those of either a ferromagnetic or antiferromagnetic material, with some remnant magnetization and an easy axis normal to the plane. However, the out-of-plane measurements display smaller remnance and instead show double loops typical of an antiferromagnetically coupled material with the easy axis normal to the plane. The fact that the general shapes of the two curves look similar indicates a relatively small out-of-plane anisotropy field. Figure S3 provide a trivial schematic to explain the mechanism of the spin switching in the hysteresis loops observed in the antiferromagnetic case. The relatively “noisy” opening in the in-plane case is likely due to the hysteresis in the exchange coupling process when the spins are rotated with respect to each other as the field is applied normal to their axis. Similarly, the two symmetric openings in the out-of-plane case can be explained by the hysteresis in the exchange coupling dynamics as the field along the axis flips one of the two spins. According to this model, the characteristic field in the two cases is defined by the exchange coupling field (of the order of 100 Oe).

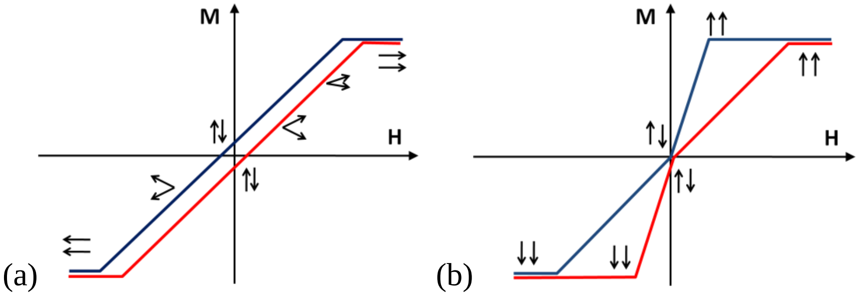

**Figure S3**: **Schematic of the spin switching sequence in the antiferromagnetic regions, as the field is applied**: (a) in-plane, and (b) out-of-plane directions. The easy axis is assumed to be normal to the plane. The red and blue lines show the sides of the loop in the forward and reverse direction of the field, respectively.

## AFM and MFM Images of Functionalized Epitaxial Graphene

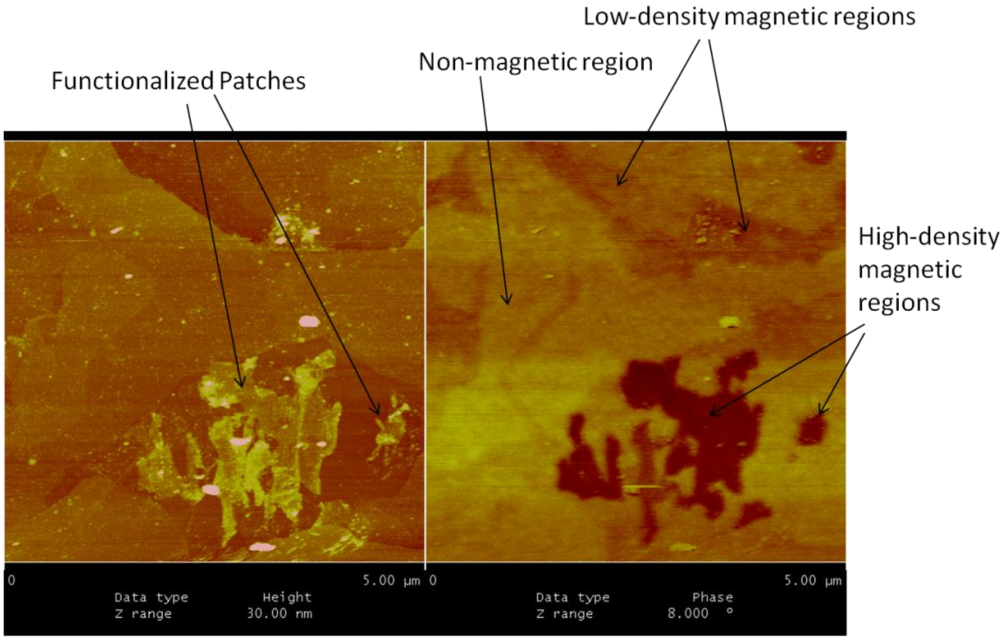

**Figure S4:** AFM (left) and MFM (right) images of the surface of epitaxial graphene (EG) which includes both pristine graphene planes and functionalized patches of EG; the average thickness of the densely functionalized patches is about 1.5 nm.

An AFM / MFM study was performed in a non-contact mode with a Veeco Dimension 3100 system. MFM measurements were conducted in a dynamic lift mode with a lift-off distance of 30 nm.

In order to support the idea of magnetic order in functionalized graphene, we directly examined the effect of the chemistry on the epitaxial graphene surface in a combined AFM and MFM study in order to correlate the functionalization with the pronounced increase in magnetism. Simultaneous measurements of the images allowed us to match the observed local magnetic properties with the surface topology of the EG. Also, such direct AFM/MFM study automatically eliminated one of the main concerns in magnetometry studies related to the misleading contribution of mostly iron based magnetic impurities. The left and right images in Figure S1 show AFM and MFM images, respectively, of a graphene region including patches of functionalized graphene. The average height of the functionalized patches was found to be approximately 1.5 nm; the dark color of the functionalized patches in the MFM image indicates a relatively strong magnetic moment in these regions. The graphene in these patches act as a soft magnetic material relative to the field generated by the probe (of the order of 1 kOe). It may be noted that the (apparently) pristine areas also show non-zero magnetic moments in certain regions, though the signal in these areas is substantially weaker (by a factor of 10) than the signal in the functionalized areas. The relatively weak signal from the pristine areas might be due to the difference in the number of graphene layers between different EG areas.[1]

## Comparison of STM Images Taken by Pt-Ir Probe from Different Non-magnetic and Magnetic Surfaces

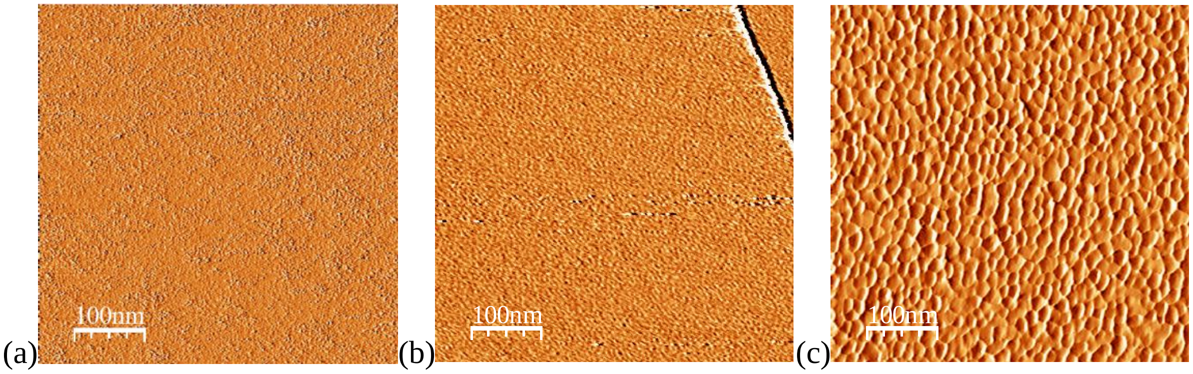

**Figure S5**: STM images by Pt-Ir probe of non-magnetic, (a) amorphous C and (b) graphite (HOPG) surfaces, and (c) magnetic CoCr-based media.

To understand whether the observed effect was inherent to graphene (and particularly the functionalized graphene), we used the same technique to image various types of media, both non-magnetic and magnetic. Figures S5a-d show typical STM images by the Pt-Ir probe of (a) amorphous C surface, (b) graphite (HOPG) surface, (c) perpendicular CoCr-based media. It can be noted that no noticeable contrast (beyond the known texture) can be observed in either of these cases.

## References

1. Yazyev, O. V.; Helm, L., Defect-Induced Magnetism in Graphene. *Phys Rev. B* **75**, 125408 (2007)