Supporting Information

The Influence of Nanoscale Roughness and Substrate Chemistry on the Frictional Properties of Single and Few Layer Graphene

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This document includes details on the deposition of graphene on oxidized SiO_2/Si(100) as a reference for comparison to the rough surfaces in the manuscript, along with adhesion mapping on rough surfaces as well as comparative AFM and Raman microspectroscopy studies of graphene on OTS modified supports.

Comparitive studies of graphene layers on oxidized SiO_2/Si(100) substrates

To calibrate the results from studies of graphene on the rough surfaces the same water-soluble tape method was used to fabricate graphene samples on thermally oxidized (~90 nm oxide thickness) SiO_2/Si(100) as a comparison. Figure S1a shows a Raman map of the 2D/G intensity ratio of an example graphene sample region shown as white and graphite as maroon. Figure S1b and S1c show the contact mode Atomic Force Microscopy (AFM) topography image and the corresponding friction map. The graphene region appears to have an overall higher friction than the multilayer regions with some areas displaying various friction domains due to differences in the crystallographic orientation of the lattice.[1] The relative friction signal was averaged from individual friction maps on different layers of graphene and normalized to the value for bulk graphite (determined *in situ* from thick layers on the surface). Figure S2 shows the normalized friction values comparing single-layer, bilayer and bulk-like graphene (greater than five layers) with friction decreasing with increasing layer thickness. Graphene is seen to have higher friction than multi-layers which is characteristic of the "puckering effect".[2] Figure S3a shows a contact mode AFM image containing one to three layers of graphene on silica nanoparticles and the corresponding adhesion map (S3b) generated from a grid array (32 x 32) of force-distance curves where the tip-surface pull-off force was measured.

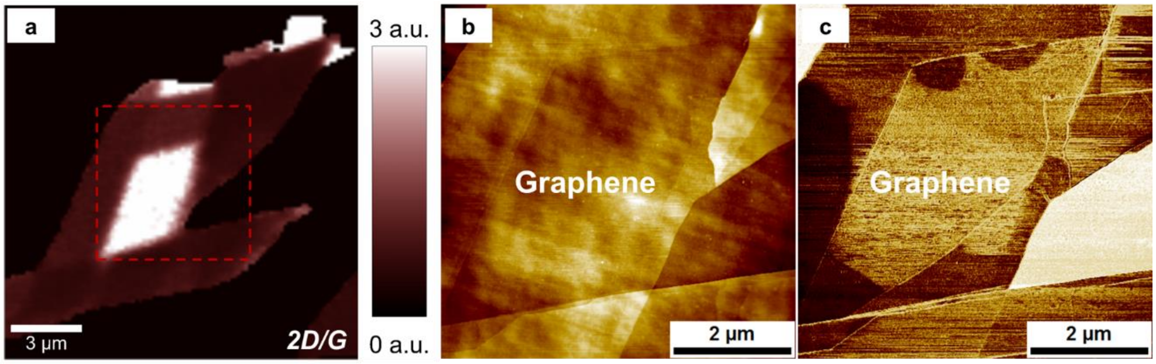

Figure S1. (a) Raman map of the 2D/G intensity ratio for a single and multi-layer graphene sample region on thermally oxidized (~90 nm oxide thickness) SiO_2/Si(100) with graphene having the highest intensity shown as white and graphite as maroon. (b) Contact AFM topography image of the sample region from the red box in (a) and the corresponding friction map (c).

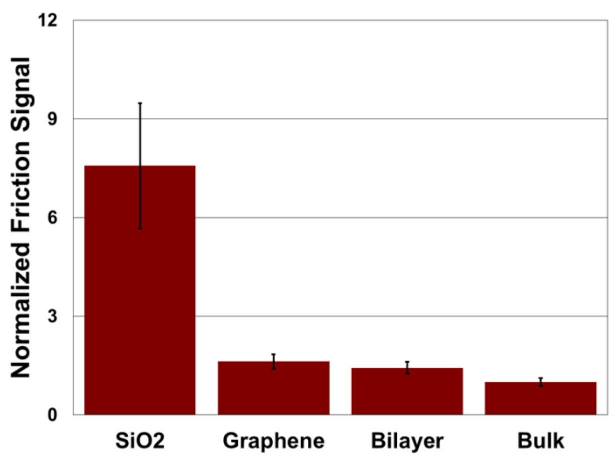

Figure S2. Friction values of SiO_2/Si(100) and graphene layers measured on an unfunctionalized substrate and normalized to that of bulk graphite. The friction trend shows the "puckering effect" with decreasing friction as the number of layers increase.

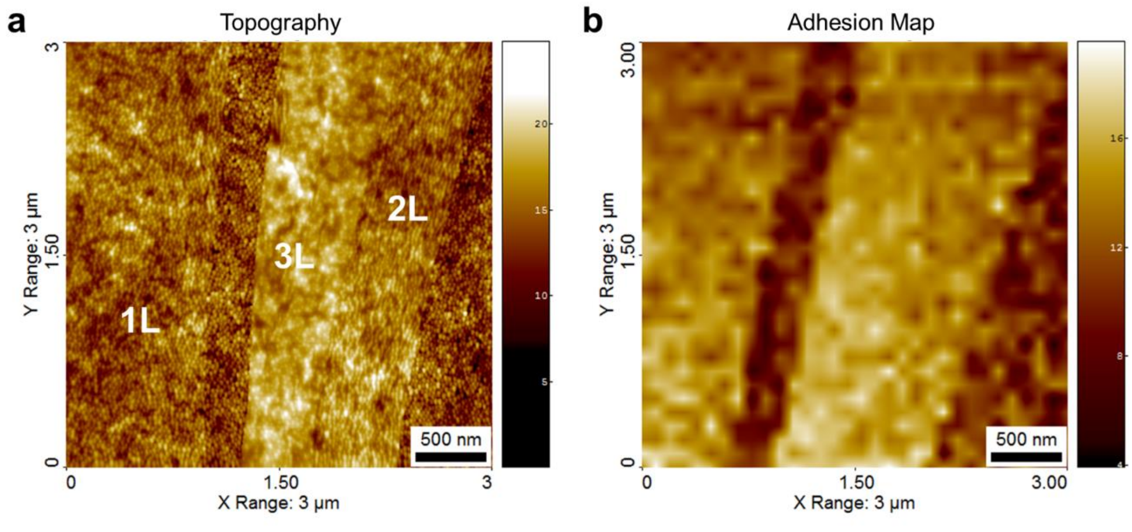

Figure S3. (a) Contact AFM topography image showing silica nanoparticles and one to three graphene layers. (b) Corresponding adhesion map of the sample region in (a) containing a 32 x 32 grid array of force-distance curves used to measure the pull-off force

Comparitive studies of graphene layers on OTS functionalized SiO_2/Si(100) and spincoated SiO_2 nanoparticle/Si(100) substrates

For reference samples to compare to the rough surfaces functionlaized with octadecyltrichlorosilane (OTS), thermally oxidized (~90 nm oxide thickness) SiO_2/Si(100) substrates were also functionalized with OTS and graphene was mechanically exfoliated on the surface using the water soluble tape method. OTS substrates were characterized with infrared spectroscopy before graphene transfer with a typical spectrum shown in Figure S5. Figure S6 is a contact mode topography image and line profile showing similar partial conformity and roughness changes on the functionalized rough surface as observed on the unfunctionalized silica nanoparticles. The partial conformity is due to strain which was measured using Raman microspectroscopy and the characteristic peak shifts to lower wavenumber on the rough substrates are shown in Figure S7.

Figure S8a shows a Raman map of the 2D/G intensity ratio of an example graphene sample on a thermally oxidized wafer with graphene shown as white and graphite as maroon. Figure S8b and 85c show the contact mode AFM topography image and the corresponding friction map comparing OTS, single-layer, bi-layer, tri-layer and bulk-like graphene. The relative friction signal was averaged from individual friction maps on the different layers of graphene and normalized to the value for bulk graphite (determined *in situ* from thick layers on the surface). Figure S9 shows the normalized friction values comparing single-layer, bi-layer and bulk-like graphene (greater than five layers) with friction decreasing with increasing layer thickness. Graphene on OTS is seen to also have higher friction than multi-layers which is characteristic of the “puckering effect”.[2]

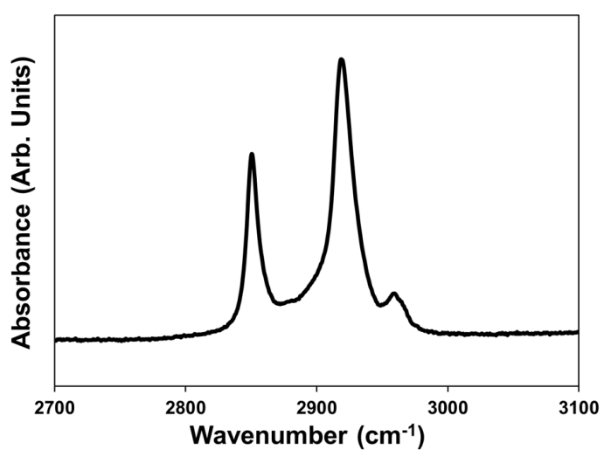

Figure S4. Example infrared spectrum of an OTS functionalized nanoparticle film showing the characteristic CH_2 asymmetric stretching band at 2918 cm^{-1}.

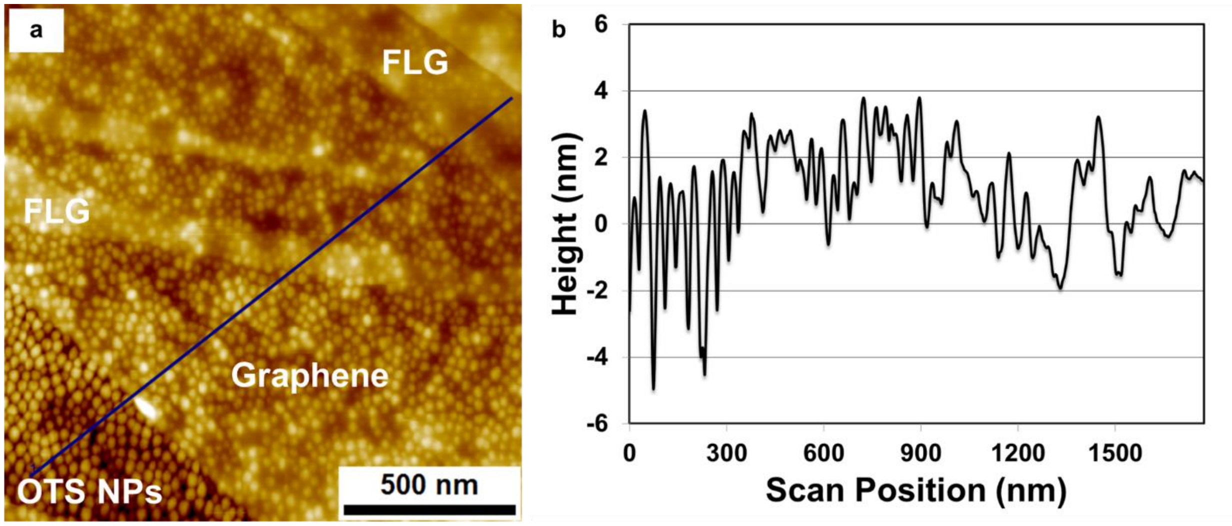

Figure S5. (a) Contact mode AFM topography image of graphene and multilayer graphene on a rough OTS nanoparticle surface. (b) Line profile from the blue line in (a) showing the decrease in roughness from the OTS nanoparticles to the different layers.

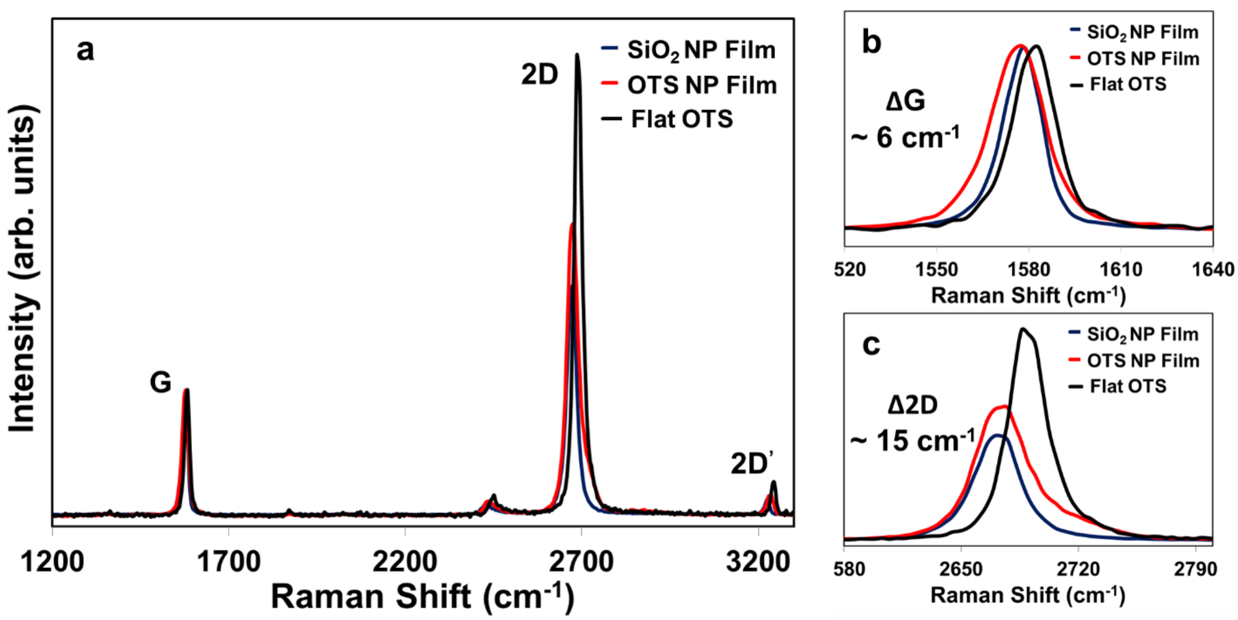

Figure S6. (a) Raman spectra of graphene on an unfunctionalized and an OTS functionalized nanoparticle surface compared to a flat OTS functionalized surface showing the shift to lower wavenumbers on rough surfaces due to strain in the graphene lattice. (b) and (c) are larger views of the G and 2D peak shifts. The Raman spectra were normalized to the intensity of the G peak.

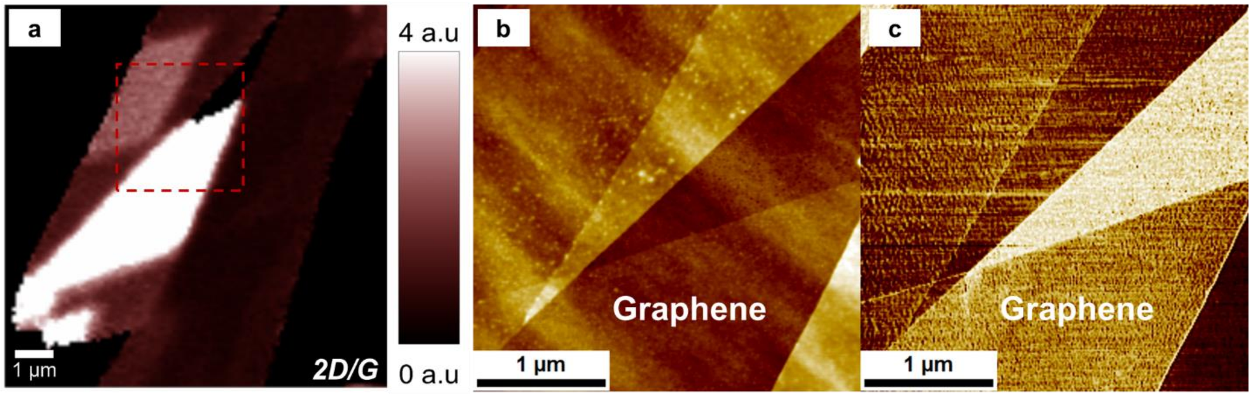

Figure S7. (a) Raman map of the 2D/G intensity ratio for a single and multi-layer graphene sample region on an OTS functionalized SiO_2/Si(100) substrate with graphene having the highest intensity shown as white and graphite as maroon. (b) Contact AFM topography image of the sample region from the red box in (a) and the corresponding friction map (c).

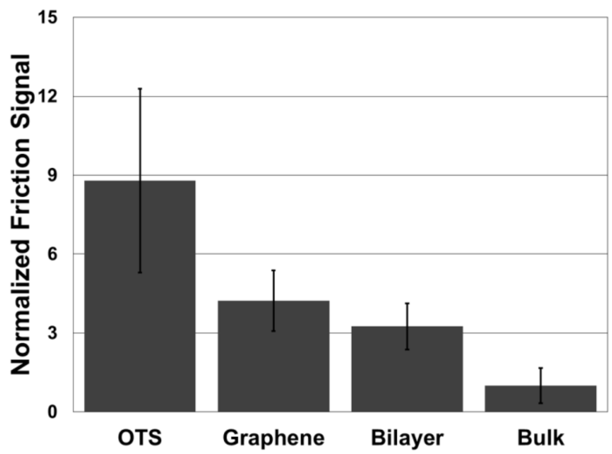

Figure S8. Friction values of graphene layers on a flat OTS functionalized substrate normalized to that of bulk graphite. The friction trend shows the "puckering effect" with decreasing friction as the number of layers increase.

References

1. M. V. Rastei, B. Heinrich and J. L. Gallani, *Physical Review Letters*, 2013, **111**, 084301.
2. C. Lee, Q. Li, W. Kalb, X.-Z. Liu, H. Berger, R. W. Carpick and J. Hone, *Science*, 2010, **328**, 76-80.