Studies of Friction and the Mechanochemical Reactivity of 2D Nanomaterials

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Control of friction and wear is a ubiquitous challenge in numerous machined interfaces ranging from biomedical implants, to engines, to nano- and micro-scaled electromechanical systems (MEMS) devices. Control of friction is also essential to reducing energy waste.¹ Central to developing boundary lubrication schemes for such applications is how to reduce wear at the rough surfaces of such surfaces, where nanoscaled asperities dominate the interfacial contacts that can lead to wear. The robust mechanical properties and general chemical inertness of twodimensional (2D) nanomaterials, such as graphene and MoS₂, has made them of interest as friction modifiers. While single layer graphene and MoS₂ can readily adapt to surface structure on the atomic scale, when deposited on substrates with nanoscopic roughness of ~ 10 nm rms (as is common in many machined interfaces) a conformal coating generally cannot be fully formed, due to competition between adhesion to the substrate nanoscopic asperities and the bending rigidity of the material.^{2,3} This often leaves a mixture of supported and unsupported regions which respond differently to applied load, with spatial variations in mechanical properties and chemical bonding. Modification of the frictional properties may also be tuned by controlling substrate interactions using self-assembled monolayers.^{4,5} It has also been observed that increased strain in these materials on rough surfaces has also been seen to increase their chemical reactivity.⁶ This has recently led us to examine force-driven chemical reactions with graphene as a model approach to understanding mechanochemical reactions at surfaces. Here, we describe a combination of AFM nanomechanical, confocal Raman microspectroscopic and near-field IR scattering studies of graphene and MoS₂ on silica surfaces with controlled nanoscopic roughness, to examine the how this impacts their frictional properties, and alters their electronic properties and chemical reactivity, where strain dependent reactions can be driven by applied forces. Studies of MoS_2 on metal surfaces, such as Au(111) will also be described, where even within single layer MoS₂, varying phases of the MoS₂ are found to occur.⁷

1. J.C. Spear, B.W. Ewers and J.D. Batteas, "2D-Nanomaterials for Controlling Friction and Wear at Interfaces," **10** *Nano Today* (2015) 301-314.

2. M.B. Elinski, Z. Liu, J.C. Spear and J.D. Batteas, "2D or not 2D? The impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene and MoS₂," *J. of Phys. D: Appl. Phys.* **50** (2017)103003.

3. J.C. Spear, J.P. Custer and J.D. Batteas, "The Influence of Nanoscale Roughness and Substrate Chemistry on the Frictional Properties of Single and Few Layer Graphene," *Nanoscale* **7** (2015) 10021-10029.

4. M.B. Elinski, B.D. Menard, Z. Liu and J.D. Batteas, "Adhesion and Friction at Graphene/Self-Assembled Monolayer Interfaces Investigated by Atomic Force Microscopy," *J. Phys. Chem.* C **121** (2017) 5635-5641.

5. M. Negrito, M.B. Elinski, N. Hawthorne, M.P. Pedley, M. Han, M. Sheldon, R.M. Espinosa-Marzal, and J.D. Batteas, "Using Patterned Self-Assembled Monolayers to Tune Graphene-Substrate Interactions," *Langmuir* **37** (2021) 9996-10005.

6. S. Raghuraman, M. B. Elinski, J. D. Batteas and J. R. Felts. "Driving Surface Chemistry at the Nanometer Scale Using Localized Heat and Stress," *Nano Lett.* **17** (2017) 2111-2117.

7.F. Wu, Z. Liu, N. Hawthorne, M. Chandross, Q. Moore, N. Argibay, J. Curry and J.D. Batteas, "Formation of Coherent 1H-1T Heterostructures in Single Layer MoS₂ on Au(111)," ACS Nano **14** (2020) 16939-16950.