

Nanolithographic Chemical Patterning on Graphene Using Local Stress and Heat

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Here we investigate the chemical dynamics of local graphene oxide reduction during thermochemical nanolithography using a heated atomic force microscope (AFM) tip. Figure 1.a shows a schematic of the technique, where a silicon AFM cantilever with an embedded Joule heater applies both local stress and heat to the graphene oxide surface during tip sliding. Figure 1.b shows a measure of measured tip friction along lines of reduced GO, and figure 1.c shows a measured friction reduction of $\sim 2x$ due to the reduction of oxygen groups on the graphene surface. Monitoring friction force during chemical reduction thus provides an *in situ* measure of oxygen functionality on the surface over time. Figure 2 shows friction measurements as a function of tip dwell time for tip temperatures between 310 – 355 °C at a low load of < 40 nN. Calculating reaction rate as a function of temperature assuming a first order reaction provided an activation energy for bond scission of 0.7 ± 0.3 eV, where measurement noise contributed significantly to error and precluded determination of reaction order. In an effort to reduce measurement time and error, friction was measured as a function of load during linear temperature ramps of the tip heater (figure 3). Such a measurement is analogous to thermogravimetric analysis (TGA), which is governed by

$$\frac{df}{dT} = \frac{\nu}{\beta} f^n e^{-\frac{(E_a - \sigma V_a)}{kT}} \quad (\text{eqn 1})$$

where β is the temperature ramp rate, ν is an exponential pre-factor, f is the measured friction, n is the order of the reaction, E_a is activation energy for bond removal, σ is stress at the tip-surface contact, V_a is the activation volume of the reacted molecules, k is Boltzmann's constant, and T is temperature. Numerically curve fitting the solution to this equation with the measured friction response provided an activation energy of 0.62 ± 0.07 eV, an activation volume of 40 ± 10 Å³, a reaction order $n \sim 1$, and a pre-exponential factor between $10^1 - 10^4$ s⁻¹. It was further shown that applied force linearly reduces the observed activation barrier. Quantitatively, the results are at odds with many theoretical and experimental works showing that graphene oxide reduces via a 2nd order recombination reaction with activation energies significantly exceeding 1 eV. We propose an alternative reduction mechanism where the local temperature rise at the tip drives diffusion of molecules away from the tip. Monte Carlo simulations (figure 4) of particle surface diffusion (with a barrier to surface diffusion of 0.6 eV) shows 1st order local reduction under the tip. In contrast, considering desorption under the tip with an equal activation barrier results in a 2nd order reaction. The results are physically intuitive, as adsorbed species can no longer contribute to friction once excited above the diffusion energy barrier. Further, the measured pre-exponential factor depends on the time required for a molecule to diffuse over the scan area, resulting in values of $10^{-1} - 10^4$ s⁻¹, quantitatively agreeing with experimental observation. Thus, we showed that heated AFM tips can simultaneously drive and measure chemical reactions on 2D surfaces, provide quantitative measures of the kinetics of those reactions, and induce reactions which would otherwise not be possible during bulk processing. Such exquisite thermomechanical control over local surface chemistry will greatly improve the fabrication of a many 2D nanoscale devices.

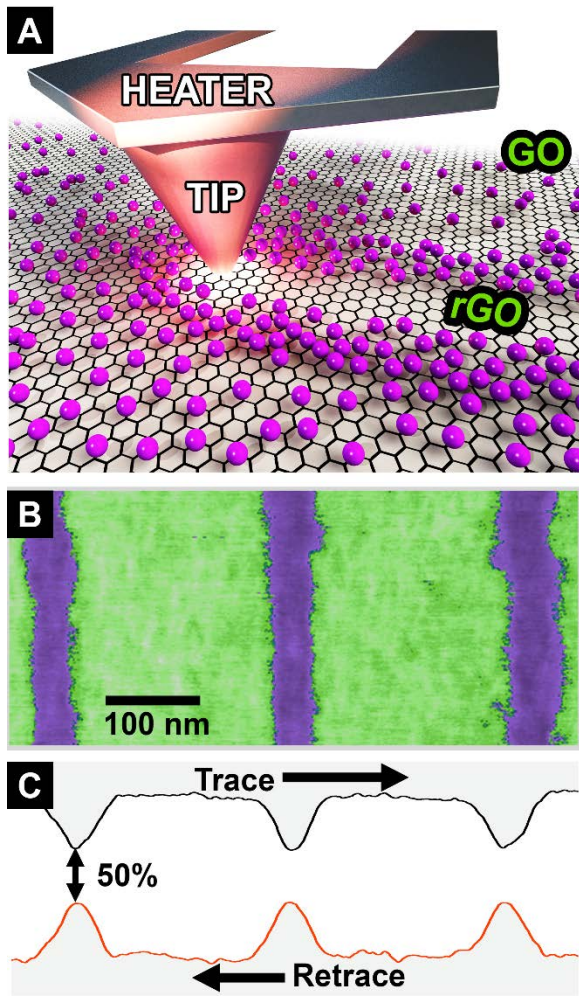


Figure 1: (a) Illustration of the reduction process, where heat and pressure locally remove oxygen groups. (b) friction force image of reduced linescans. (c) friction drop of 50% due to oxygen group removal.

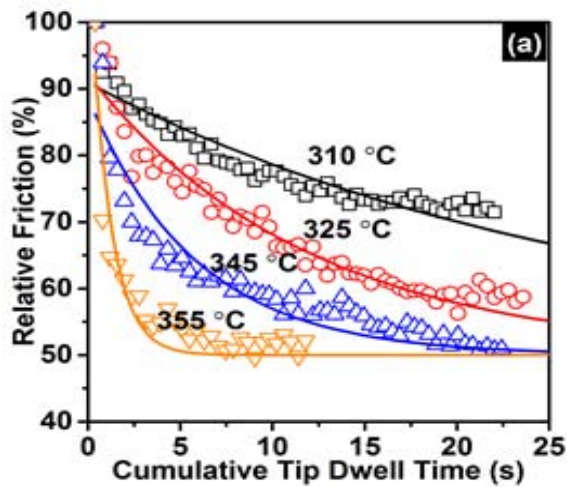


Figure 2: Relative friction drop as a function of tip dwell time for various tip temperatures.

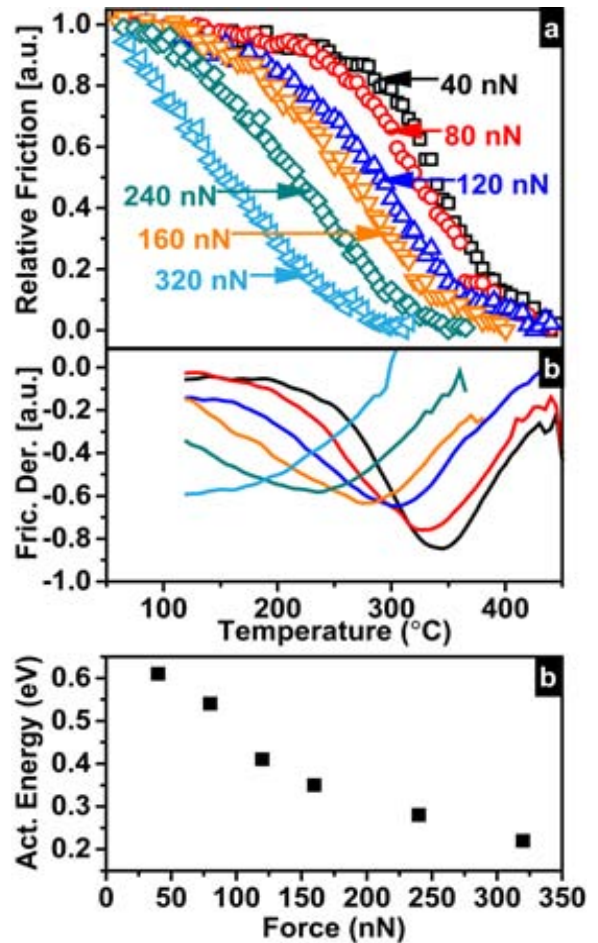


Figure 3: (a) Relative friction drop as a function of tip force while linearly ramping the tip temperature from 50 - 450 °C. (b) Normalized derivative of the friction drop curves, showing a shift in maximum removal to lower temperatures for higher forces. (c) Measured activation energy as a function of tip load, showing a linear reduction with increasing load.

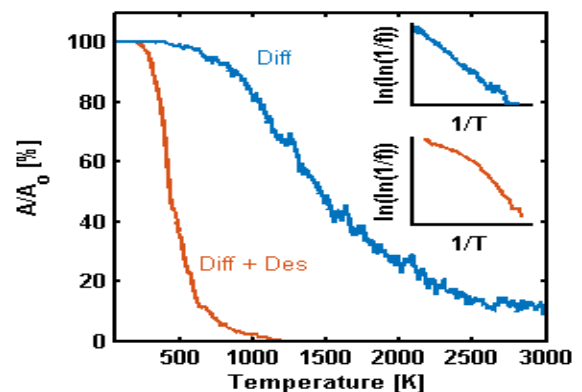


Figure 4: Monte Carlo simulation showing the removal of atoms underneath the tip for both thermally driven diffusion only and diffusion + desorption. Insets show that the diffusion reaction is 1st order, in agreement with experimental data.