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Direct Correlation of MXene Surface Chemistry and Electronic Properties

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MXenes are a class of 2D materials with the chemical formula $M_{n+1}X_nT_x$ (M = transition metal element, X = C and/or N, and T = surface termination, e.g. –O, –OH, –F) with currently 20+ members and the potential for many more. Despite their recent discovery in 2011, MXenes have already demonstrated state-of-the-art performance in fields such as electromagnetic interference shielding, chemical sensing, and energy storage[1]. To a large extent, this exceptional performance is due to MXenes' high metallic conductivity. Methods to further improve conductivity, and thus performance, are a central objective of MXene research. A promising approach is through surface chemistry engineering; density functional theory has predicted a strong influence of surface terminations on MXene conductivity[2]. To date, such predications lack experimental validation. Here, we directly correlate MXene surface chemistry and electronic transport through novel microscopy techniques: direct-detection electron energy-loss spectroscopy[3] (EELS) and simultaneous *in situ* heating (up to 775 °C) and electric biasing. Our experiments uncover important chemistry-property relationships which advance our fundamental understanding of MXenes and provide clear guidelines for the optimization of MXene devices.

Three MXenes were studied: Ti_3C_2, Ti_3CN, and Mo_2TiC_2. The MXenes were spray cast[4] onto heating+biasing nanochips[5]. The basic sample morphology is shown in Fig. 1a-c. Heating and biasing experiments were performed with the DENSsolutions Lightning D9+ holder and a JEOL 2100F TEM. EELS experiments were performed with a GIF Quantum and Gatan K2 summit operated in electron counting mode[3].

The results for the Ti_3CNT_x sample are shown in Figure 1d-g. For this sample, the initial terminations are –O, –OH, and –F, and there is intercalation of H_2O. Theory predicts this MXene to be metallic[6], but to date, this has not been confirmed experimentally. In Fig. 2d, the post-annealing room temperature (RT) resistance is plotted versus the annealing temperature. Figure 2e shows the resistance versus temperature behavior observed during each annealing step. Clearly, annealing resulted in a reduction in sample resistance and a transition from semiconductor-like to metallic transport (as inferred from the sign of dR/dT). To understand these changes in electronic transport, we look to *in situ* EELS data. The O K edge (Fig. 2f) shows a large decrease in peak ii relative to peak i between RT and 400 °C, indicating loss of O which is not strongly bonded with Ti, i.e. the loss of intercalated H_2O. Thus the transition from semiconductor-like to metallic transport is attributed to the loss of intercalated H_2O. This finding confirms metallic conductivity in Ti_3CN and demonstrates that intercalated H_2O – present in all as-prepared MXenes – can induce semiconductor-like behavior in nominally metallic MXenes. At temperatures above 400 °C, the loss of H_2O is complete, and –F begins to desorb (Fig. 2g). Thus the decrease in resistance for annealing steps above 400 °C is attributed to the loss of –F terminations. This result is the first direct correlation of MXene termination and electronic properties and confirms predications that de-functionalization of Ti_3CNT_x increases conductivity. In addition to the described Ti_3CNT_x results, this talk will discuss the behavior of other MXenes and the effect of large organic intercalants.

We note that the use of direct-detection and electron counting was highly advantageous for this experiment. With the combined energy resolution/field-of-view offered by DD-EELS, we were able to simultaneously observe all relevant elements (C through F) while maintaining sufficient energy resolution to detect the onset of structural transitions, e.g. $Ti_3CNT_x \rightarrow TiO_2$. Additionally, the reduced sensor noise allowed extremely low electron doses to be used, which is important since MXenes are somewhat beam-sensitive[7].

In summary, we have utilized advanced *in situ* electron spectroscopy techniques to understand chemistry-property relationships in a rapidly emerging family of 2D materials, MXenes. Our results provide a critical first step in experimentally understanding and controlling MXene surface chemistry for applications ranging from chemical sensors to electromagnetic interference shielding[8].

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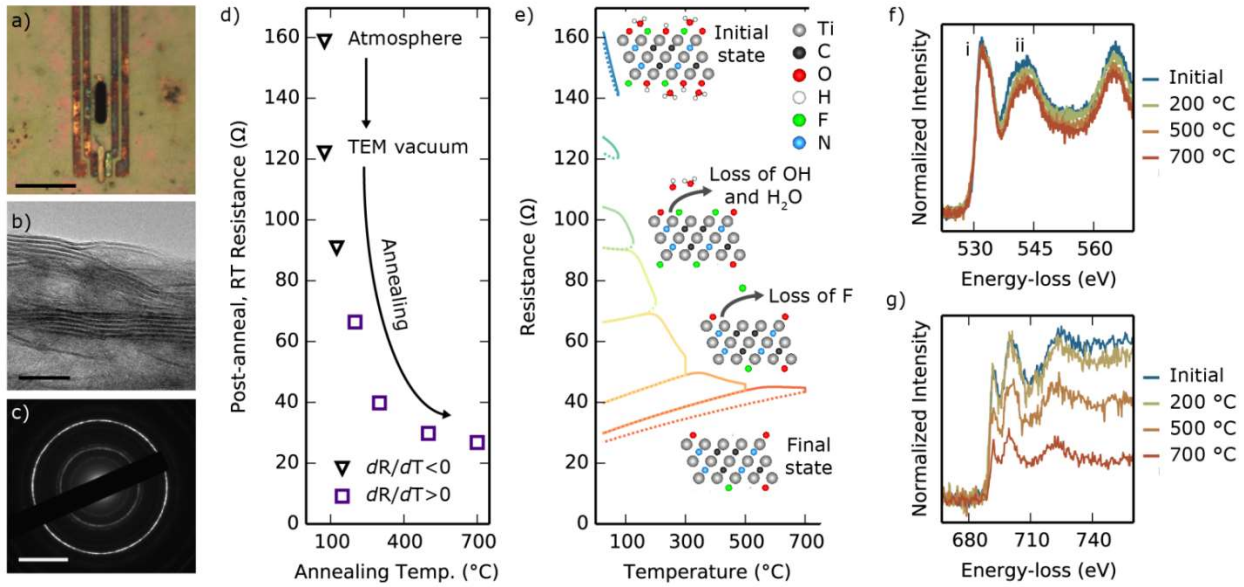

Figure 1. a) Optical image of a MXene film spray cast onto the *in situ* heating+biasing nanochip, scale bar = 30 µm. b) TEM image showing the layered structure of Ti_3CNT_x, scale bar = 10 nm. c) Electron diffraction taken after annealing at 700 °C demonstrating the sample is still MXene, scale bar = 5 nm^{-1}. d,e) Results from *in situ* heating and biasing within the TEM. Schematics show the changes in MXene intercalation and termination. f,g) *In situ* DD EELS of the O K and F K edges, respectively.

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