In situ surface termination modification of 2D Ti_3C_2 MXene in an environmental TEM

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Two-dimensional (2D) materials exhibit a high surface area per volume, and are excellent candidates for energy storage, [1] photocatalysis, [2] and electromagnetic interference shielding (EMI) applications among others. [3] MXenes (M= transition metal, X= C and/ or N) constitute a large family of 2D materials that exhibit a rich and attractive chemistry because of the transition metal surfaces. These materials have attracted significant attention primarily because of their electrochemical properties. [4] MXenes are formed from a nanolaminated parent MAX phase (e.g. Ti_3AlC_2). In the MAX phase, a single atom thick A layer (e.g. Al) separates sheets of MX. A chemical etching process results in removal of this layer and results in the formation of the 2D MXene sheets. However, the emerging MXene is subject to the adsorption of (surface) terminating groups (T_x) on the transition metal surfaces originating from the etchant. As an example, the archetype MAX phase Ti_3AlC_2 transforms into $Ti_3C_2T_x$ MXene after hydrofluoric acid treatment. The surface groups (O and F with small amounts of OH) are functionalizing the MXene, [5] and influence its properties. The surface groups are identified as disordered after etching, however, after a high temperature (~700 °C) treatment in vacuum, F adatoms desorb together with OH leaving the surface covered predominantly by O in minimum energy positions. [6] The ability to control the surface groups is critical for MXene property engineering. Presently, no means of substituting the native surface termination exist other than modification of the O, OH and F contents.

In the present contribution, we have investigated the limits for modification and tailoring of the surface functionalization of Ti_3C_2. This was conducted by exposing single or few layer $Ti_3C_2T_x$ to a range of environments in an aberration corrected environmental transmission electron microscopy (ETEM). The structural evolution of $Ti_3C_2T_x$ was followed through a range of gas environments at pressures ranging from 10^{-6} mbar to 10 mbar and in a temperature range from room temperature to 750 °C. High-resolution ETEM, electron diffraction (ED), electron energy-loss spectroscopy (EELS) and residual gas analysis (RGA) was employed to observe structure and chemistry of Ti_3C_2 the single sheets, but more importantly to investigate the potential for manipulation of the surface functional groups.

In conclusion, we demonstrate the capability to manipulate the surface groups on Ti_3C_2 MXene by environmental processing. The results pave way for an entirely new direction in the property tuning of new 2D materials.

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