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Transmission Electron Microscopy of Two-Dimensional MXene Sheets

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Graphene is a two-dimensional (2d) material and possesses a number of interetsing bulk properties due to quantum confinement effects [1]. Since its discovery, in the last decade, the world has witnessed an exponential growth in research on developing new 2d materials. It is because these materials perform better than their bulk counterparts for various applications including electronics and energy-storage [2]. MXene is a generic name for a large family of 2d transition metal carbides, nitrides and carbonitrides. MXenes are synthesized by etching the Group A metal from its parent MAX (Ti_3AlC_2) phase [3]. It has been shown that MXene can be applied as anode material for lithium ion baterry (LIB) due to its two-dimensional nature which provides gallery spacing for Li^+ ion shuttling during charge/discharge process [4]. The as-prepared MXene shows reasonable charge storage performance and excellent cyclic stablity. However, hydrogen peroxide (H_2O_2) treatment of MXene results in the formation of titanium oxide (TiO_2) phase on its surface and consequently doubled the charge storage capacity Mxene sheets [5]. These excellent properties of MXene are linked with its atomic scale structural properties and hence it is essential to charcterize it with a technique, e.g. transmission electron microscopy (TEM), capable of providing information at atomic scale spatial resolutions. This is why, in this paper, we present a study which is on the TEM-characterization of both as-prepared and partially-oxidized MXene sheets.

MXene sheets included in this study were synthesized by treating Ti_2AlC powder with hydroflouric acid (HF) and while the partially-oxidized MXene sheets were prepared by oxidizing as-prepared sheets with H_2O_2 solution at room temperature [5]. A TEM of model Titan 80-300 ST from FEI Company (Hillsboro, OR) was utilized to carry out the analysis of samples. The microscope was also equipped with GIF Tridiem 863™ to perform energy-filtered TEM (EFTEM) and electron energy-loss spectroscopy (EELS) anlayses of samples. EFTEM allowed generating the elemental maps of Ti, C, and O elements and while EELS enabled to apply "white lines" analysis on the Ti-L23 edge of Ti element. It in fact provided the ratios of Ti-L3 to Ti-L2 peaks which are linked to the valence states of Ti in these samples [6].

TEM anlaysis of MXene sheets, shown in Figure 1A, revealed that the sheets were produced in large and unifrom sizes. Corresponding selected area electron diffratcion (SAED) pattern and high-resolution TEM (HRTEM) image of these sheets, given in Figure 1B-C, were free of noise and can be attributed to superier structural packing of MXene sheets. Similalry, the side-view image in Figure 1D also revealed a high quality of MXene sheets along (0010) planes. Zero-loss EFTEM image of partially-oxidized MXene is presented in Figure 2 A and qualitatively speaking the darker regions therein can be attributed to the presence of partially oxidized regions. Indeed it was confirmed by the elemental mapping of Ti, C, and O elements as evidenced by a composite image in Figure 2C. The core-loss EELS spectrum of partially

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oxidized MXene sheet (Figure 2B) not only showed the presence of Ti, C, and O elements but it also revealed the existence of Fluorine (F) in the samples. The incorporation of F, basically, took place during the treatment of MAX with HF and it generally functionalizes the surface. Finally the ratios of Ti-L3 to Ti-L2 for samples were determined from the Ti-L23 energy-loss edge and the obtained results are shown in Figure 2D. It showed a steady decrease in the ratio with increasing O concentraion which can be attributed to the decrease in Ti^{+3} (or increase in Ti^{+4} fraction) fraction with increasing O contents.

In summary, the provided results demonstrate that a structural analysis of 2d MXene sheets with a TEM can be acomplished successfuly. It is capable of not only providing the atomic scale information on the structure of sheets but also allows the determination of structure-property relationship for those sheets. Hence, in conclusion, a comprehensive TEM anlaysis of 2d materials is essential before using them for energy-related applciations.

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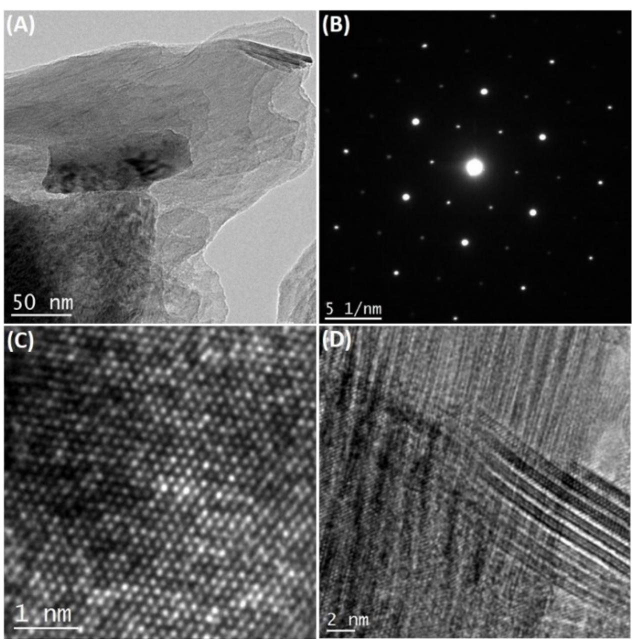

Figure 1

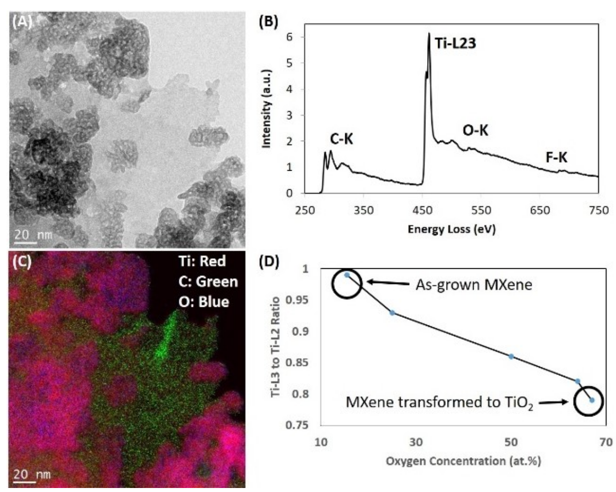

Figure 2

Figure 1: TEM analysis of MXene layers. (A): BF-TEM image of flake in plan-view orientation. (B): Corresponding SAED pattern showing the hexagonal symmetry for the structure of MXene. (C): HRTEM image from the flake shown in (A). (D): Side-view HRTEM image from a flake.
Figure 2: EFTEM analysis of partially oxidized MXene layers. (A): BF-TEM image of a flake in plan-view orientation. (B): The corresponding background removed EELS spectrum acquired from a region of flake shown in (A). (C): RGB Composite map of Ti, C, and O elements. (D): Ti-L3 to Ti-L2 ratios as a function of oxygen concentration.

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