Structural characterization of MXene and its heterostructures with TEM, X-ray scattering, and simulation

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Two-dimensional (2D) transition metal carbides and nitrides (MXenes) with metallic conductivity, rich surface chemistry, and layered structure, suggest uncommonly broad combination of important functionalities amongst two-dimensional materials. For a comprehensive understanding of the structure-property relationship of MXenes, the quantitive structural characterization methods from atomic scale to mesoscopic scale are becoming extremely important. Transmission electron microscopy (TEM) is a powerful tool for acquiring detailed structural information about MXenes, such as crystal structure, mapping chemical composition, morphologies, etc. However, it is difficult to use TEM as a statistical analysis tool, which means the measurement bias coming from the objectively selected area can hardly be removed. On the other hand, the X-ray scattering methods, including small- and wide-angle X-ray scattering (SAXS/WAXS), are widely used tools for statistical structural analysis from sub-nanometers to hundreds of nanometers. The combination of TEM and SAXS/WAXS has been proven to be an efficient method for comprehensive structure investigation in the study of many low-dimensional nanomaterials. However, for MXene, the relevant research is still sparse. In our work, we have combined electron microscopy and X-ray scattering to study the structures of $Ti_3C_2T_x$ MXene stacking and its heterostructure with layered double hydroxides (LDH) at different length scales. From the cross-sectional TEM, we found a mesoscopic porous structure in the MXene stackings, which is caused by the 2D flake stacking deficiency. Then we employed SAXS/WAXS for statistical analysis of the porous size distribution and morphologies, as well as the anisotropic alignment degree of the 2D flakes. The results from electron microscopy and X-ray scattering show good coherency, proving the efficiency and wide applicability of our combining methods. For the study of MXene-LDH heterostructures, the combination of electron microscopy, X-ray scattering (diffraction), and various simulation methods also provides useful structural information. Specifically, we found a decreased crystalline domain size of LDH growth on MXenes. By comparing the TEM and X-ray diffraction results, we also found the changing texture of LDH, where the preferred growth direction was altered in the heterostructure. The simulation based on our experimental results indicates the various surface chemistry of MXenes may affect the growth of LDH. With this combination

method, we have proposed new a guided growth mechanism of LDH on MXene surface. We further demonstrate the high performance of the MXene stacking and MXene-LDH heterostructure with desirable structures in electromagnetic shielding and electrocatalysis respectively, where a better understanding of the structure-property relationship can facilitate further material design.

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