Advanced Layered Carbides (MXenes): Tailored Synthesis, Mechanistic Insights, Properties, and Their Applications in Sensing and Energy

ABSTRACT

The escalating global energy demand and the urgent need to mitigate environmental pollution necessitate advanced multifunctional materials for both energy storage and gas sensing. Two-dimensional (2D) MXenes, a family of transition metal carbides, nitrides, and carbonitrides, exhibit high metallic conductivity (~10,000 S cm^{-1} for $Ti_3C_2T_x$), hydrophilicity, tunable interlayer spacing, and diverse surface terminations (–O, –OH, –F, –Cl, –Br, –I). Despite over fifty experimentally realized MXenes, conventional hydrofluoric acid (HF) etching and high-temperature molten salt synthesis remain limited by fluorine contamination, slow kinetics, and safety concerns.

This work systematically explores synthesis–structure–property–function relationships in MXenes to optimize performance in chemiresistive gas sensing and electrochemical energy storage. Various etching strategies, including direct HF, in-situ HF (LiF/HCl, NH_4F/HCl), Lewis acidic molten salts ($ZnCl_2$), were employed. NH_4^+-intercalated $Ti_3C_2T_x$ (N–$Ti_3C_2T_x$) achieved a work function of 3.8 eV, NO_2 sensitivity of 5.02% at 5 ppm, ultralow detection limit of 7 ppb, and signal-to-noise ratio of 1673.3. HF/HCl-derived $Ti_3C_2T_x$ with mixed halides (FCl-$Ti_3C_2T_x$) exhibited broad gas versatility, responding to NO, N_2O, NH_3, and CO. Extending beyond $Ti_3C_2T_x$, this work explored M_2CT_x MXenes (M = Ti, V, Nb, Mo) synthesized via selective etching and tetramethylammonium hydroxide (TMAOH) delamination revealed that TMA^+ intercalation enhanced interlayer swelling in Ti_2CT_x, V_2CT_x, and Nb_2CT_x, yielding NO_2 responses of ~660% at 50 ppm for Ti_2CT_x with a detection limit <1 ppm. Mo_2CT_x displayed superior CO selectivity (−3.2% at 50 ppm), demonstrating the decisive role of transition metal identity and surface functionalization.

Furthermore, it introduces a carbon-enabled microwave synthesis (CEMS) approach as an ultrafast, environmentally benign route to engineer MXene surface chemistry. Microwave-driven

dielectric heating combined with carbon additives (such as graphene, CNTs, carbon black) and Lewis acidic molten salt (LAMS) enables solvent-free, five-minute etching of MAX phases under ambient conditions, producing halogen-terminated MXenes (Cl, Br, I). Br-terminated $Ti_3C_2T_x$ achieved NO_2 response of 51.7% at 5 ppm with detection limit of 50 ppb, outperforming Cl- (38.1%), I- (37.0%), and F- (~2.4%) analogues. Sensors exhibited fast response/recovery times (159/381 s), high selectivity against interferents, and stability over 30 days. Parallel electrochemical energy studies revealed that, CEMS synthesized Cu-$Ti_3C_2T_x$ electrodes demonstrated pseudocapacitive Li-ion storage with 220 mAh g^{-1} at 0.1 A g^{-1}, 65% retention at 1 A g^{-1}, and 99.9% capacity retention over 100 cycles, surpassing HF-derived MXenes (~175 mAh g^{-1}). Besides, MXene-derived sodium titanium phosphate/carbon nanohybrids in combination with ether-based electrolyte delivered 150 mAh g^{-1} at −40 °C (0.1 C), ~110 mAh g^{-1} at 0.5 C, with excellent long-term stability, highlighting suitability for ultralow-temperature operation.

Collectively, this work establishes etching-driven surface engineering as a cornerstone for MXene functionalization. By correlating structural design, interlayer chemistry, and surface terminations with functional outcomes, it demonstrates MXenes' transformative dual functionality in gas sensing and energy storage, providing a roadmap for next-generation clean energy and environmental monitoring materials.

Keywords: *MXenes; Surface Chemistry; Gas Sensing; Energy Storage; Carbon-enabled Microwave Synthesis.*