Supporting Information

Coincident Modulation of Lattice and Electron Thermal Transport in MXene via Surface Functionalization

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Fig. S1 The convergence tests regarding the density of q-points to calculating the lattice thermal conductivity of Ti$_2$C MXene by ShengBTE.
Fig. S2 The convergence tests regarding the density of nearest neighbors to calculating the third order constants and thermal conductivities of Ti$_2$C MXene.
Fig. S3 The schematic views of the possible configurations for functionalized Ti$_2$C MXene. For Ti$_2$CO$_2$, Ti$_2$CF$_2$, and Ti$_2$C(OH)$_2$, the most energetic favorable configurations are all belong to type-(b).
Fig. S4 The calculated phonon group velocities of Ti$_2$CT$_2$ MXenes.
Fig. S5 The calculated specific heat of Ti$_2$CT$_2$ MXenes.
Fig. S6 The electron localization functions of pristine and functionalized Ti$_2$C MXenes.

It is well known that the Grüneisen parameter is in proportion to the anharmonicity (i.e., strength of scattering channels), which are closely related with the bond nature of materials (Nano Letter, 2016, 16, 3925-3935; Nanoscale, 2016, 8, 11306–11319). Hence, to better understand the influence of surface functionalization on the Grüneisen parameter of Ti$_2$C MXene, we have carried out further investigation through calculating the electron localization function (ELF) of pristine and functionalized MXenes (Fig. S6) in the revised manuscript. ELF is a pure ground-state and dimensionless property of material, which allows one to directly compare the bonding between different systems (Nature, 1994, 371, 683-686). It is clearly seen in Fig. S6a that Ti$_2$C is assembled mainly through the Ti–C bonds with densely localized one pair electrons from the Ti atoms on the surface. Generally, after surface functionalization as seen in Fig. S6b–d, these lone pair electrons disappear and there are strong covalent bonds between Ti and the surface groups. For O and F functionalized MXene, the Ti-C bonds
exhibits little change from the pristine ones, which interpret the comparable Grüneisen parameters of Ti$_2$C, Ti$_2$CO$_2$ and Ti$_2$CF$_2$ MXenes. While surface group OH not only enhances the Ti-C bonding in Ti$_2$C MXenes but also are bonded to the interlayer C atoms, leading to a more symmetric and localized electron distribution, which is indicative of the main reason for the less anharmonic bond and lower Grüneisen parameters of Ti$_2$C(OH)$_2$ MXene.
**Fig. S7** The calculated cumulative lattice thermal conductivity of Ti$_2$CT$_2$ MXenes as a function of the phonon mean free path.