Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

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

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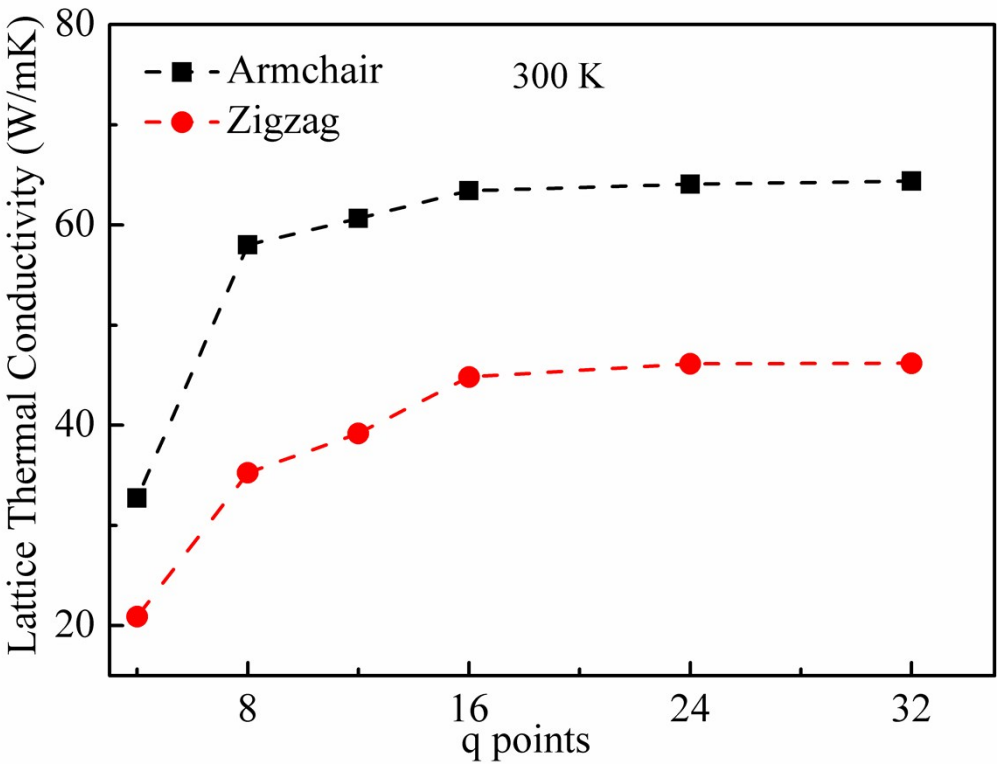

Fig. **S1** The convergence tests regarding the density of q-points to calculating the lattice thermal conductivity of Ti_2C MXene by ShengBTE.

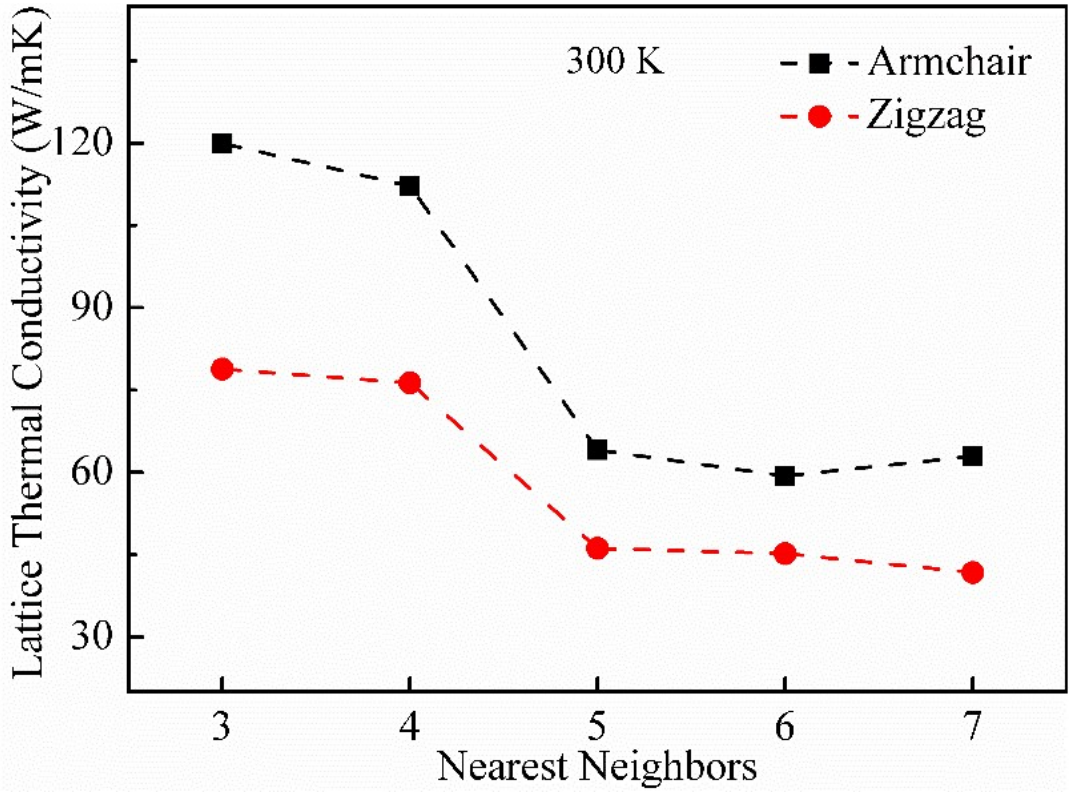

Fig. **S2** The convergence tests regarding the density of nearest neighbors to calculating the third order constants and thermal conductivities of Ti_2C MXene.

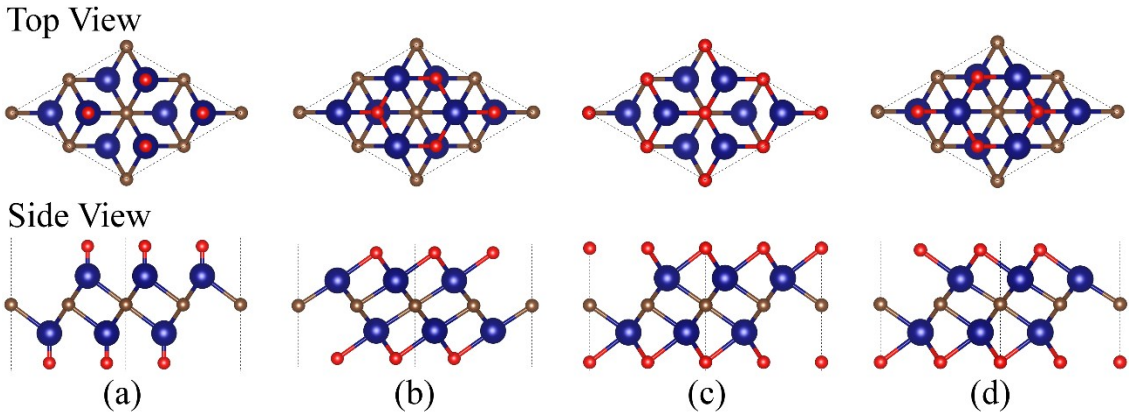

Fig. **S3** The schematic views of the possible configurations for functionalized Ti_2C MXene. For Ti_2CO_2, Ti_2CF_2, and $Ti_2C(OH)_2$, the most energetic favorable configurations are all belong to type-(b).

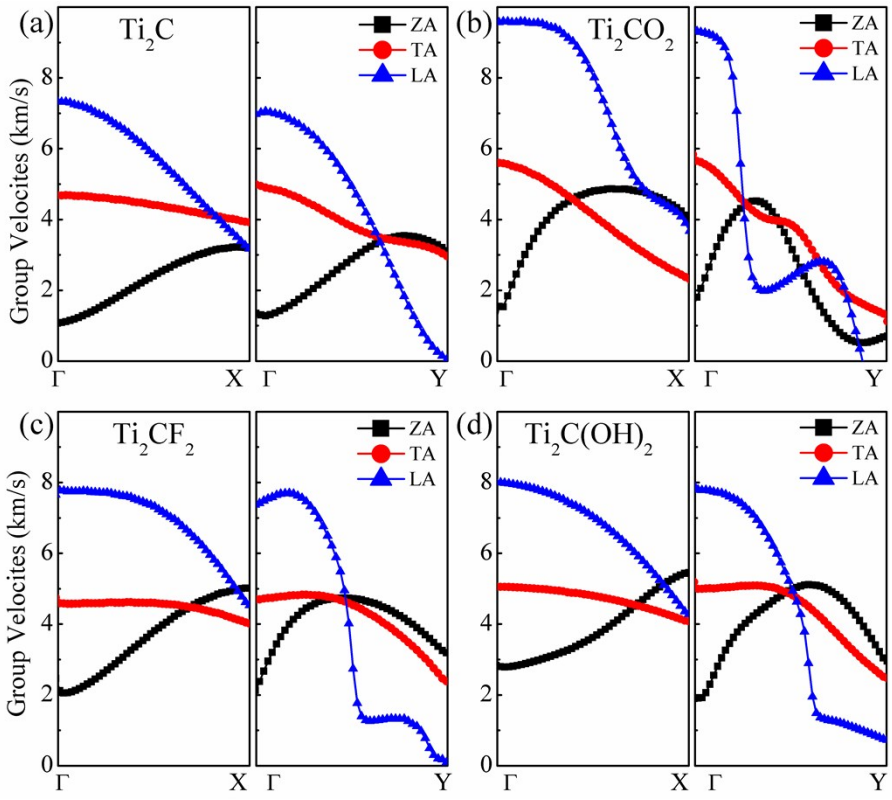

Fig. S4 The calculated phonon group velocities of Ti_2CT_2 MXenes.

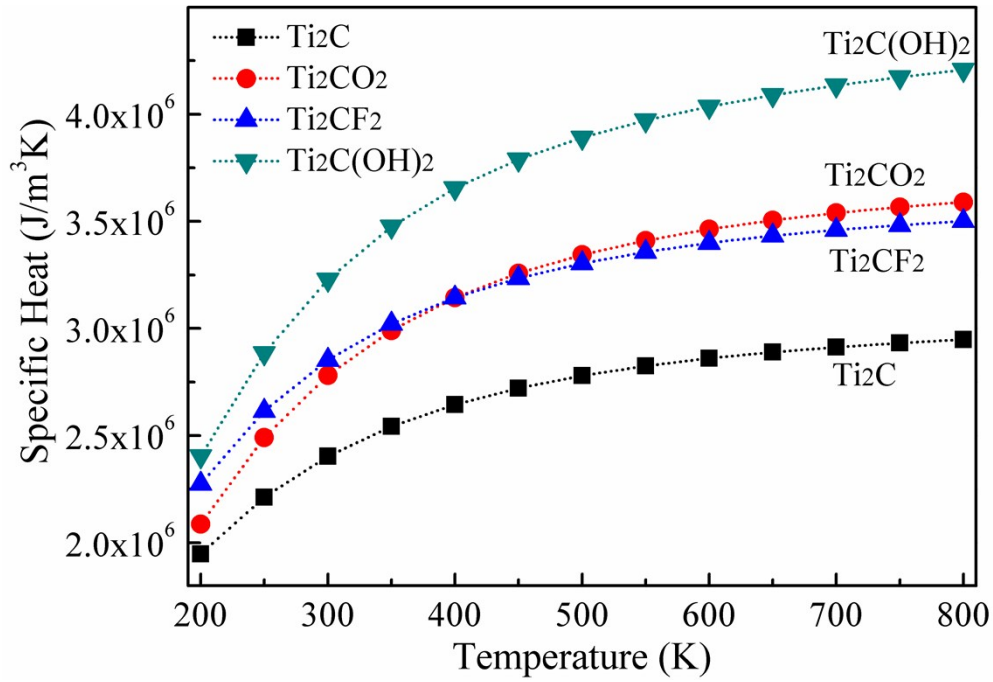

Fig. S5 The calculated specific heat of Ti_2CT_2 MXenes.

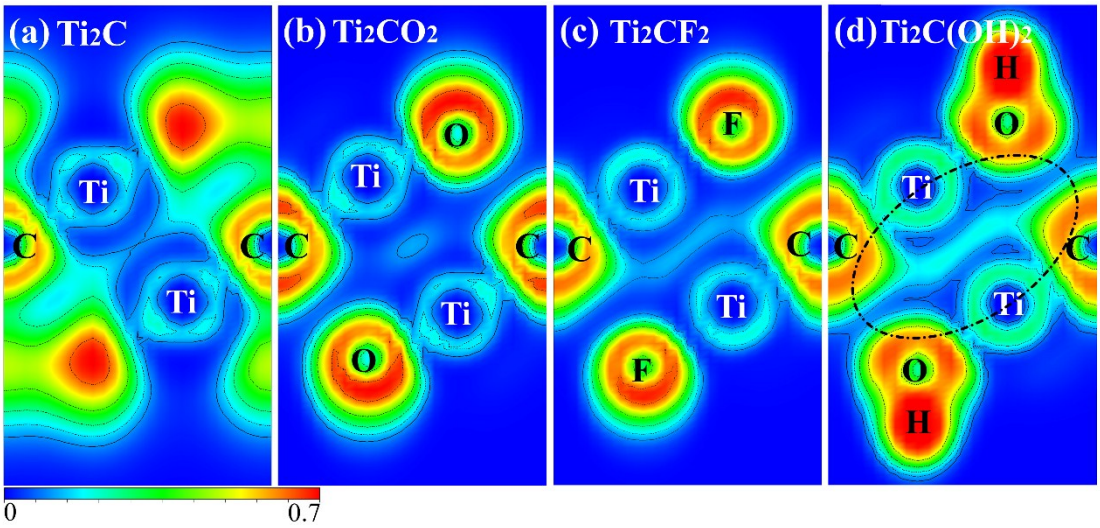

Fig. **S6** The electron localization functions of pristine and functionalized Ti_2C MXenes.

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_2C 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_2C 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_2C, Ti_2CO_2 and Ti_2CF_2 MXenes. While surface group OH not only enhances the Ti-C bonding in Ti_2C 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 $Ti_2C(OH)_2$ MXene.

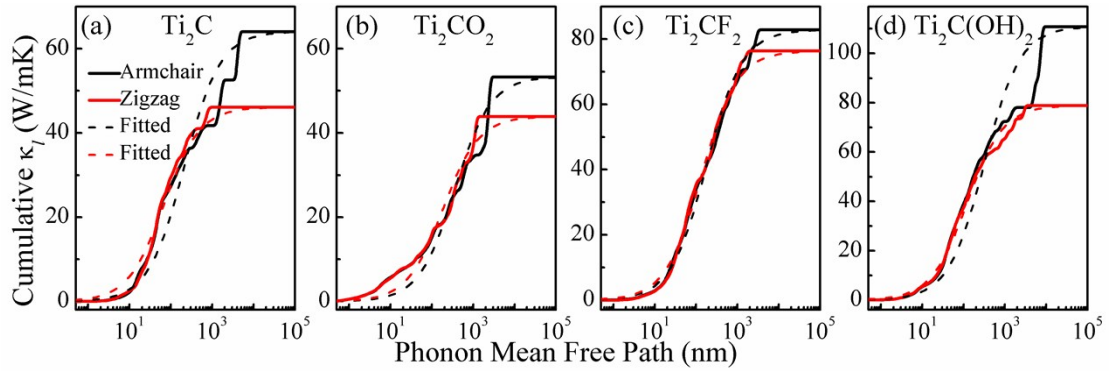

Fig. S7 The calculated cumulative lattice thermal conductivity of Ti_2CT_2 MXenes as a function of the phonon mean free path.