





**Table S1** Structural parameters of Reitveld refined XRD patterns of  $\text{TiSe}_{2-x}$  samples. ( $x$ ,  $y$  and  $z$  denote the fractional coordinates).

| Sample | Elements | $x$   | $y$   | $z$      | $a=b$    | $c$      | $c/a$    |
|--------|----------|-------|-------|----------|----------|----------|----------|
| CP_850 | Ti       | 0     | 0     | 0        | 3.541(2) | 6.009(4) | 1.697(2) |
|        | Se       | 0.333 | 0.666 | 0.257(2) |          |          |          |
| HP_650 | Ti       | 0     | 0     | 0        | 3.537(2) | 6.006(5) | 1.698(2) |
|        | Se       | 0.333 | 0.666 | 0.258(2) |          |          |          |
| HP_750 | Ti       | 0     | 0     | 0        | 3.534(6) | 6.003(1) | 1.699(3) |
|        | Se       | 0.333 | 0.666 | 0.251(3) |          |          |          |
| HP_850 | Ti       | 0     | 0     | 0        | 3.533(5) | 6.003(6) | 1.699(4) |
|        | Se       | 0.333 | 0.666 | 0.251(3) |          |          |          |

## II. X-ray photoelectron spectroscopy analysis

The x-ray photoelectron spectroscopy (XPS) data for all the  $\text{TiSe}_{2-x}$  samples has been recorded using Mg  $K\alpha$  (1253.6 eV) x-ray source. The energy calibration was made against the C 1s peak. Figure S2(a) and S2(b) shows the XPS spectra for all the samples corresponding to Ti and Se.

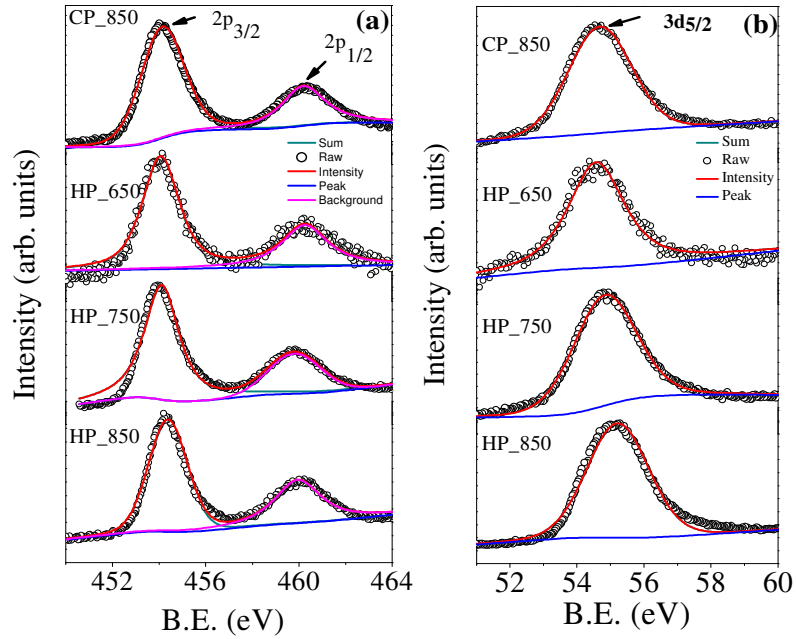


Fig. S2 Fitted XPS spectrum of samples (a) CP\_850 and (b) HP\_850.

The observed peaks in Ti at binding energy (BE) of 455.8 eV and 461.7 eV corresponds to the Ti  $2p_{3/2}$  and  $2p_{1/2}$ . Observed slight shift of 1.8 eV towards higher binding energy side with respect to pure Ti (454 eV for  $2p_{3/2}$ ) is due to the Ti-Se bond formation. The analyses of Ti and Se XPS spectra indicate that the BE position of Ti  $2p_{3/2}$  peak in CP\_850 and HP\_850 samples are at 455.7 and 455.3 eV, respectively. This shift in BE of Ti from 455.7 eV to 455.3 eV is attributed to the increased Se deficiency in the sample. The XPS spectra corresponding to Se  $3d_{5/2}$  exhibits peak at BE of 54.8 eV which correspond to the selenide. In case of Ti or Se oxide formation the BE energy should shift to 458.8 eV ( $TiO_2$ ) with respect to Ti and between 58.9 eV to 59.8 eV (SeO) with respect to Se. In present study, the observed BE of Ti and Se does not give any signature of the oxide formation.