Supplementary Information

# Tuning Copper Sulfide Nanosheets by Cation Exchange Reactions to Realize Two-dimensional CZTS Dielectric Layers

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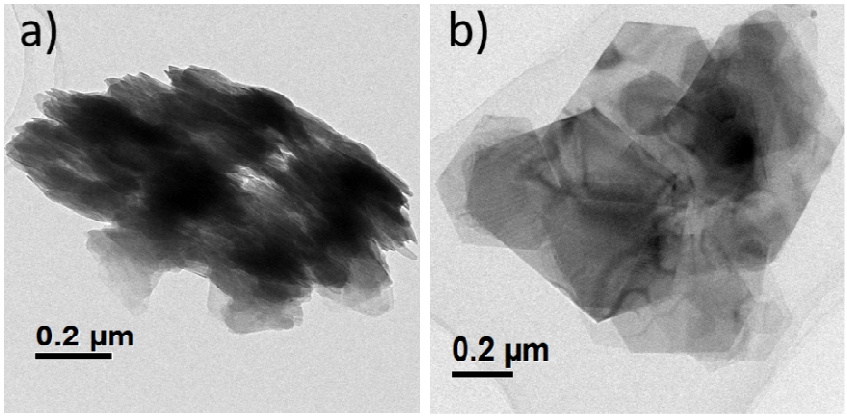



**Fig. S1** TEM images of $Cu_2S$ NSs synthesized at 240°C with annealing time of (a) 10 mins and (b) 60 mins.

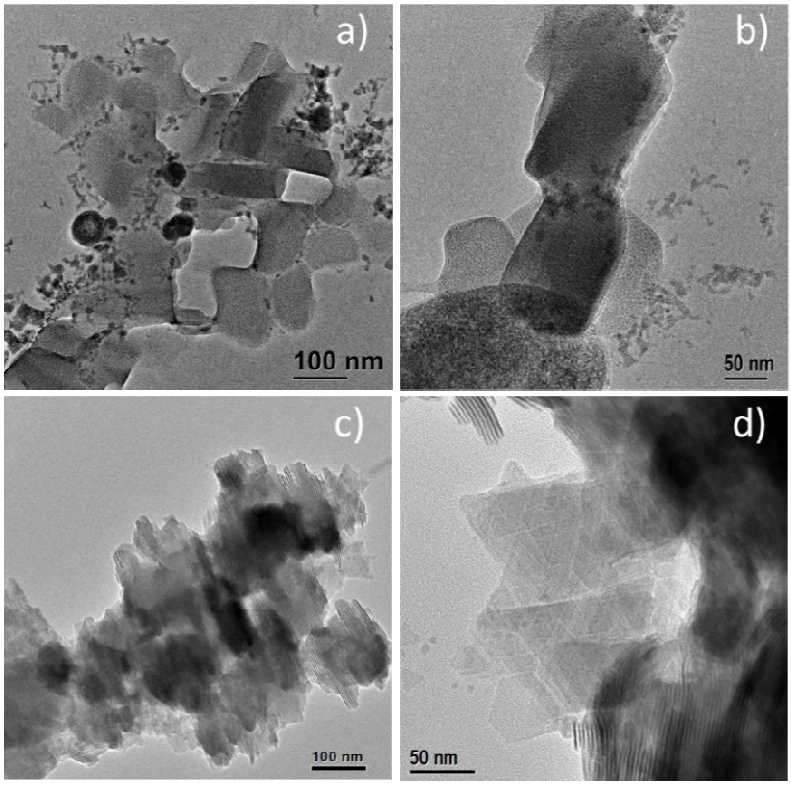



**Fig. S2** TEM images of $Cu_2S$ NCs synthesized at 240°C (a, b) without TOPO and (c, d) without oleic acid.

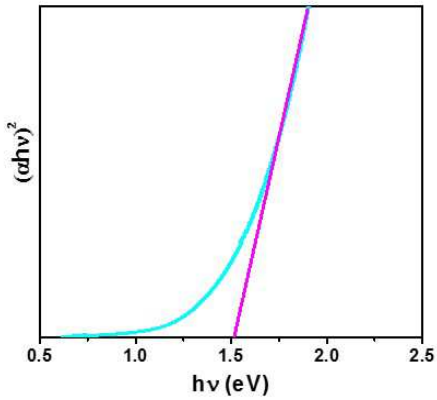



**Fig. S3** Tauc plot of CZTS NSs for the determination of band gap threshold of the synthesized NS. The band gap energy of CZTS NSs has been determined from the UV-vis spectrum to be 1.50 eV by extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), where $\alpha$ represents the absorption coefficient.

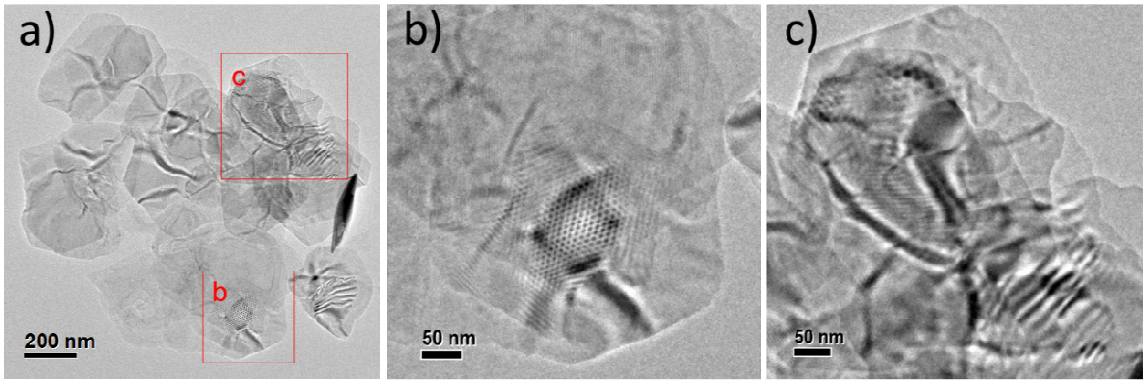



**Fig. S4** (a) TEM image of CZTS NSs. (b, c) Magnified areas of CZTS NSs showing Moiré pattern for the overlapped NSs with rotational offsets of the crystal lattice.

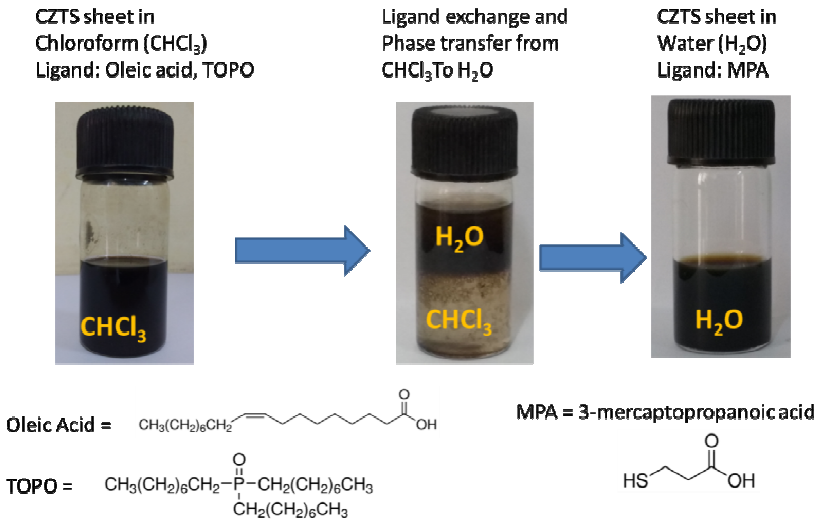



**Fig. S5** Photograph of colloidal solutions showing the ligand exchange and phase transfer process of CZTS NSs from chloroform to water.

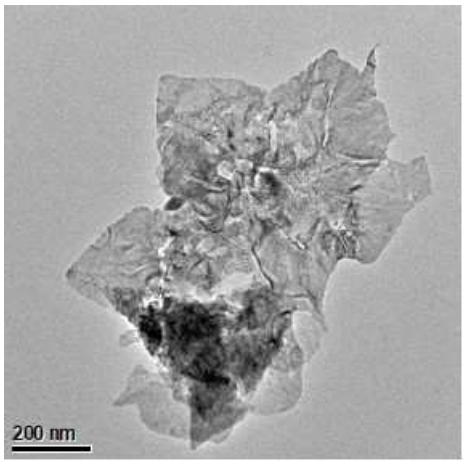



**Fig. S6** TEM image of CZTS NSs after ligand exchange.

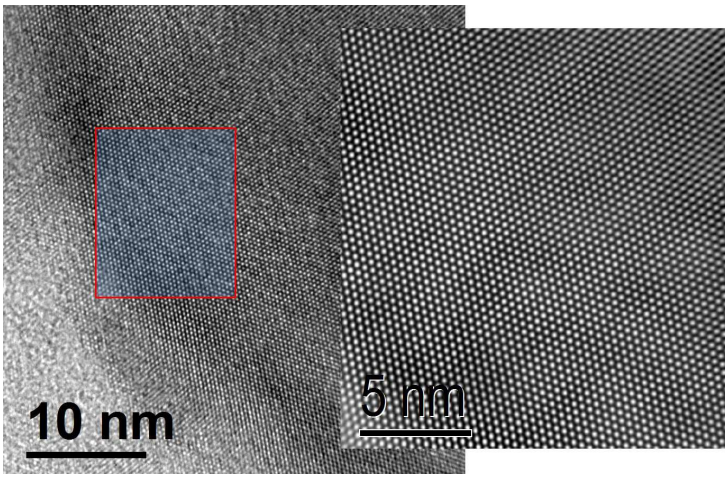



**Fig. S7** HRTEM image of a single CZTS NS showing the well resolved atoms indicating the single crystalline nature of the NS.

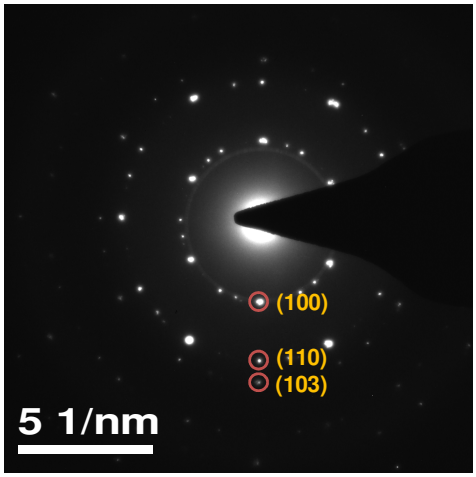



**Fig. S8** SAED pattern of the CZTS NSs, which is showing the diffraction spot corresponding to reflection of different planes of wurtzite crystal structure.

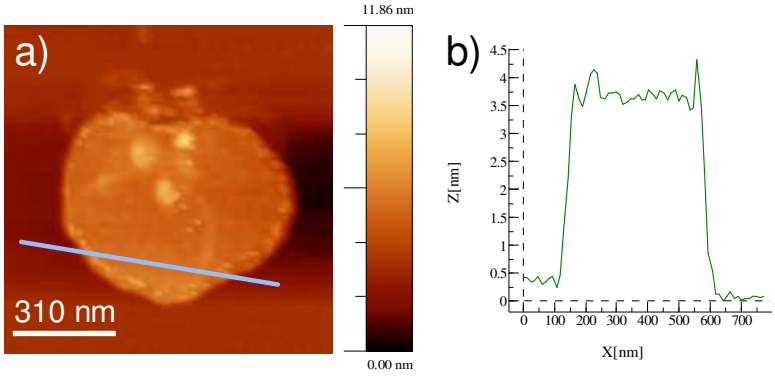



**Fig. S9** (a) Tapping mode AFM image of the ligand exchange CZTS nanosheets. (b) Height profiles obtained from the AFM image along the cyan line.

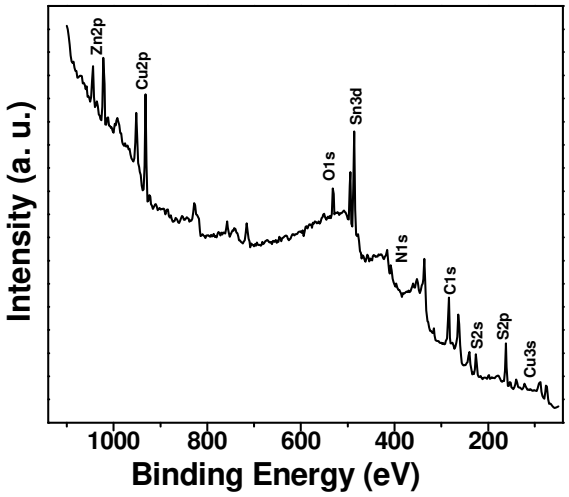



**Fig. S10** X-ray photoelectron survey spectrum of the CZTS NSs showing the different constituent elements present within the NSs.

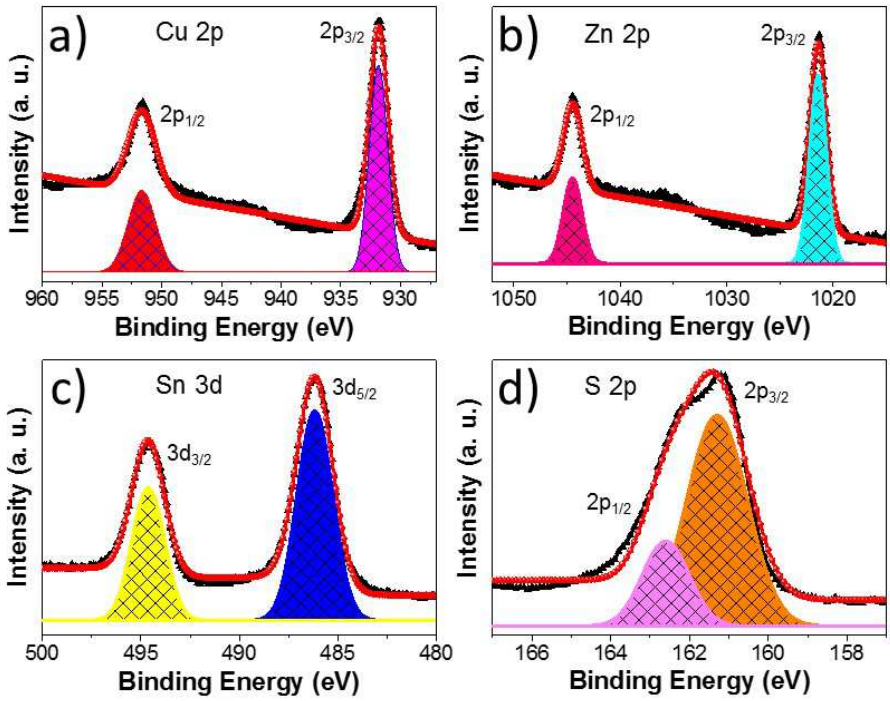
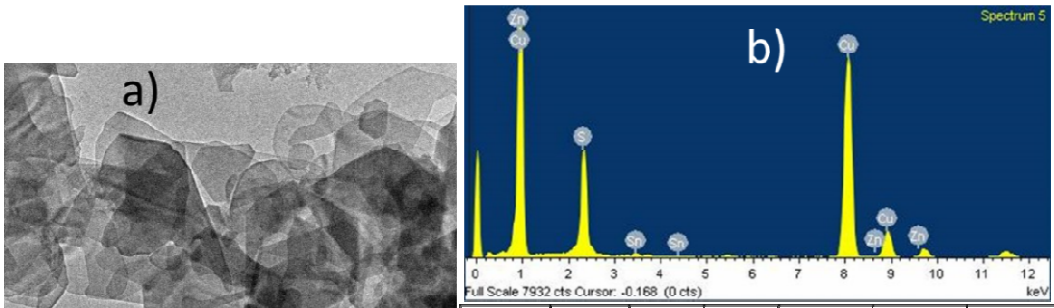



**Fig. S11** High-resolution XPS spectra of (a) Cu, (b) Zn (c) Sn, and (d) S of CZTS NSs.

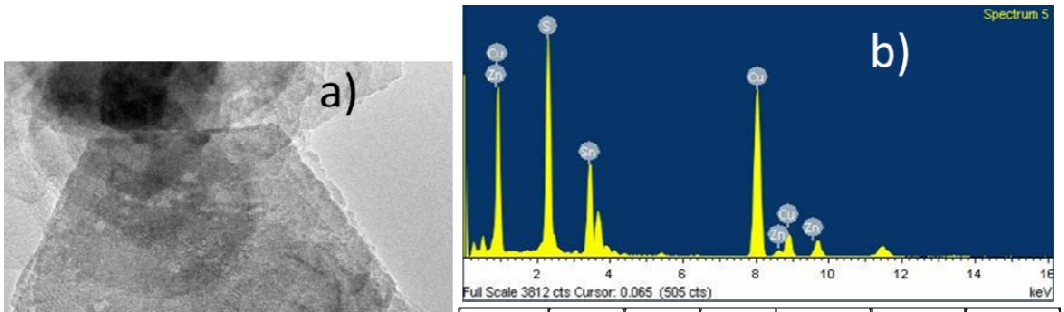



| Element | Peak Area | Area Sigma | k factor | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|---|---|
| S K | 22205 | 319 | 0.940 | 19.54 | 0.25 | 32.67 |
| Cu K | 61983 | 396 | 1.366 | 79.29 | 0.31 | 66.88 |
| Zn K | -147 | 90 | 1.434 | -0.20 | 0.12 | -0.16 |
| Sn L | 803 | 124 | 1.818 | 1.37 | 0.21 | 0.62 |
| Totals | | | | 100.00 | | |

**Fig. S12** (a) The TEM image and (b) EDS spectrum and elemental analysis of Tin doped $Cu_2S$ NSs synthesized via one pot synthesis (following the $Cu_2S$ NSs preparation procedure) using the 2:1:1 mole ratio of Cu(I)/Zn(II)/Sn(IV).

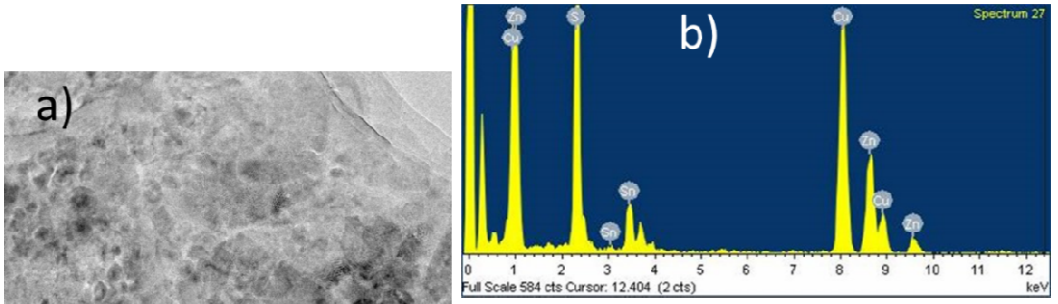
**Table S1** Amount of precursors used for the cation exchange reaction and the final composition of the ions in the NSs.

| $Cu_2S$ NSs (mmole) | Zn(OAc) (mmole) | $ZnCl_2$ (mmole) | $Zn(acac)_2$ (mmole) | $SnCl_4$ (mmole) | $SnCl_2(acac)_2$ (mmole) | Zn:Sn used | Ligands used | TEM grid used | S:Cu:Zn:Sn from TEM-EDS |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 0.25 | -- | -- | 0.25 | -- | 1:1 | 0.5mL DDT | Au | 44 : 37 : 1 : 18 |
| 0.5 | -- | 0.25 | -- | 0.25 | -- | 1:1 | 0.5mL DDT | Cu | 35 : 56 : 0.33 : 8 |
| 0.5 | -- | 1.5 | -- | 0.25 | -- | 6:1 | 1mL DDT | Cu | 39 : 42 : 3 : 16 |
| 0.5 | -- | 0.0625 | -- | -- | 0.25 | 1:4 | 0.5mL OLA | Cu | 25 : 56 : 18 : 3 |
| 0.5 | -- | 0.05 | -- | -- | 0.3 | 1:6 | 0.5mL OLA | Au | 43 : 36 : 15 : 7 |
| 0.5 | -- | -- | 0.03 | -- | 0.3 | 1:10 | 0.5mL OLA | Au | 49 : 32 : 10 : 9 |
| 0.5 | -- | -- | 0.03 | -- | 0.322 | 1:10.7 | 0.5mL OLA | Au | 49 : 32 : 11 : 9 |
| 0.5 | -- | -- | 0.04 | -- | 0.4 | 1:10 | 0.5mL OLA | Au | 49 : 27 : 11 : 12 |




| Element | Peak Area | Area Sigma | k factor | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|---|---|
| S K | 20822 | 285 | 0.940 | 23.71 | 0.31 | 44.00 |
| Cu K | 24030 | 252 | 1.366 | 39.77 | 0.38 | 37.24 |
| Zn K | 641 | 85 | 1.434 | 1.11 | 0.15 | 1.01 |
| Sn L | 16075 | 284 | 1.818 | 35.41 | 0.45 | 17.75 |
| Totals | | | | 100.00 | | |

**Fig. S13** (a) The TEM image and (b) EDS spectrum and elemental analysis of CZTS NSs synthesized by cation exchange of $Cu_2S$ NSs with equal amounts (moles) of Zn and Sn in the presence of DDT.




| Element | Peak Area | Area Sigma | k factor | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|---|---|
| S K | 4713 | 131 | 0.940 | 25.35 | 0.65 | 42.70 |
| Cu K | 5370 | 121 | 1.366 | 41.98 | 0.80 | 35.69 |
| Zn K | 2214 | 88 | 1.434 | 18.17 | 0.65 | 15.01 |
| Sn L | 1393 | 90 | 1.818 | 14.50 | 0.83 | 6.60 |
| Totals | | | | 100.00 | | |

**Fig. S14** (a) The TEM image and (b) EDS spectrum and elemental analysis of CZTS NSs synthesized by cation exchange of $Cu_2S$ NSs in the presence of oleylamine.

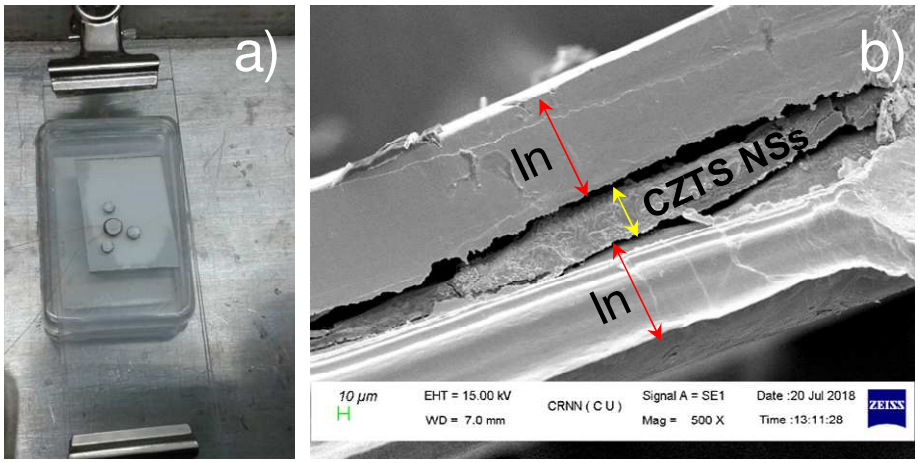



**Fig. S15** (a) Device picture and (b) the cross-sectional SEM image of In-CZTS NSs-In dielectric device, showing ~50 µm thick CZTS layer between two Indium (In) plate.

**Table S2** A comparison of dielectric properties of established dielectric materials with 2D NCs of CZTS.

| Composition | $\varepsilon'$ | D or tan(δ) (100 kHz) at 300 K | $TC_{\varepsilon'}$( ppm/K) 100 kHz at 300 K |
|---|---|---|---|
| $TiO_2$ [S1] | 110 | 0.015 | (-)750 |
| $SiO_2$ [S1] | 3.7 | 0.0015 | - |
| $CaTiO_3$ [S1] | 130 | 0.11 | (-)1600 |
| $SrTiO_3$ [S1] | 285 | 0.006 | (-)2400 |
| MgO [S1] | 10 | 0.001 | (+)190 |
| $MgTiO_3$ [S1] | 16 | 0.02 | (+)100 |
| $Al_2O_3$ [S1] | 10 | 0.002 | (+)120 |
| $BaTi_4O_9$ [S2] | 37 | 0.0015 | (-)110 |
| $Ta_2O_5$ [S3] | 35 | 0.006 | (+)600 |
| $Bi_2Zn_{1/3}Nb_{2/3}O_7$ [S2][S4] | 80 | 0.001 | (+)150 |
| $HfO_2$ [S5] | 26 | 0.1 | (+)300 to (+) 600 |
| $Ho_2CuTiO_6$ [S6] | 53 | 0.005 | (-)64 |
| PbS [S7] | 13 | 0.0012 | (+) 51 |
| CZTS | 6.1 | 0.03 | 600 |

**Table S3** Fitted results of impedance parameters at different temperatures.

| Temperature (K) | $R_1$(Ohm) | $CPE_1$ (F) | $CPE_1$-($\alpha_1$) | $R_2$(+) | $CPE_2$ (F) | $CPE_2$-($\alpha_2$) |
|---|---|---|---|---|---|---|
| **280.095** | 2.289E+09 | 6.244E-12 | 1 | 9.992E+07 | 1.994E-10 | 0.87968 |
| **290.065** | 1.469E+09 | 7.260E-12 | 1 | 2.573E+07 | 5.272E-11 | 0.93947 |
| **300.035** | 7.794E+08 | 8.419E-12 | 0.9886 | 1.570E+07 | 3.426E-11 | 0.97592 |
| **310.095** | 3.942E+08 | 8.808E-12 | 1 | 1.596E+07 | 2.678E-11 | 0.96032 |
| **320.14** | 2.304E+08 | 1.011E-11 | 0.99739 | 1.419E+07 | 2.141E-11 | 0.96561 |
| **330.21** | 1.476E+08 | 1.167E-11 | 0.99307 | 1.280E+07 | 1.845E-11 | 0.96909 |
| **340.535** | 1.012E+08 | 1.307E-11 | 0.98571 | 1.001E+07 | 1.719E-11 | 0.97355 |
| **350.23** | 7.449E+07 | 1.435E-11 | 0.97947 | 8.308E+06 | 1.652E-11 | 0.9758 |

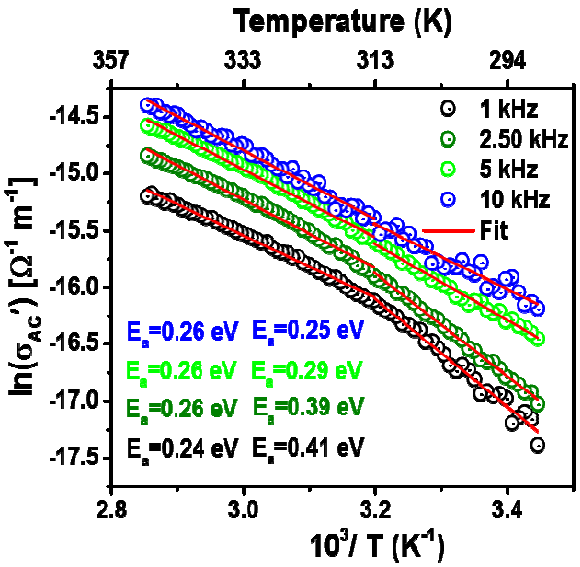



**Fig. S16** AC conductivity ($\sigma'_{AC}$) versus reciprocal of temperature (1/T) plots at different frequencies suggests that the activation energy decreases both at lower and higher temperatures with increasing frequencies.

References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