Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supporting Information

3D-Printed Flexible Energy Harvesting Devices using Non-layered Two-Dimensional Tourmaline Natural Silicates

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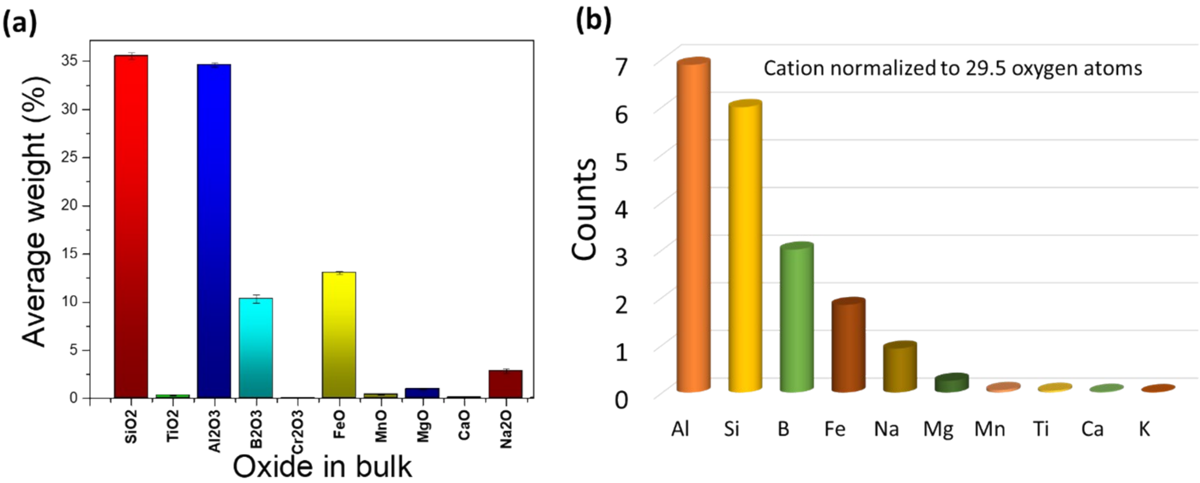

Fig. S1. EPMA study of bulk T-silicate showing (a) Weight % distribution of oxide compound contribution, and (b) Cations present normalized by 29.5 oxygen atoms.

Table S1: EPMA study of bulk T-silicate showing weight % distribution of oxide compound contributions.

Oxide	**Average (wt. %)**	**St Dev**
SiO_2	35.5	0.2
TiO_2	0.3	0.02
Al_2O_3	34.6	0.2
B_2O_3	10.3	0.4
Cr_2O_3	0.004	0.006
FeO	13.0	0.1
MnO	0.4	0.02
MgO	0.9	0.03
CaO	0.08	0.02
Na_2O	2.8	0.2
K_2O	0.04	0.01
F	0.08	0.07

Table S2: EPMA study of bulk T-silicate showing the number of cations present normalized by 29.5 oxygen atoms.

Cation normalized to 29.5 oxygen atoms	
Si	5.9
Ti	0.04
Al	6.8
B	3.0
Cr	0.001
Fe	1.8
Mn	0.05
Mg	0.2
Ca	0.01
Na	0.9
K	0.009
Anions	
F	0.04
OH	2.9

Table S3: Zeta potential series data of T-silicates in IPA.

Temperature °C	**Mean zeta potential mV**	**Distribution peak mV**	**Conductivity (mS/cm) x 10^{-4}**	**Electrophoretic mobility** (µm x cm/Vs)	**Processed runs**
30	-29.9	-31.1	5.99	-0.28	1000
30	-28.4	-10.4	5.94	-0.26	1000
30	-30.1	-12.4	5.82	-0.28	200
30	-30.6	-17.7	5.86	-0.28	140

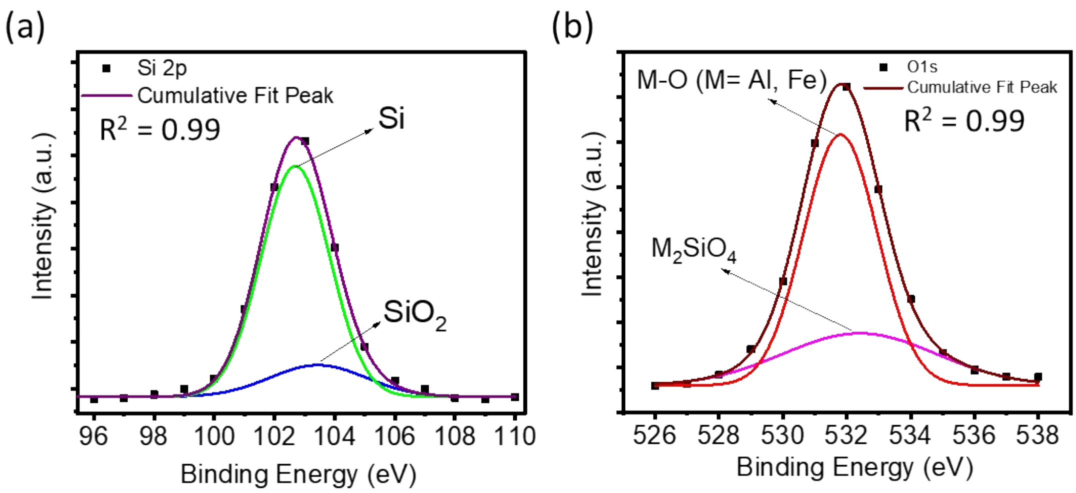

Fig. S2. Deconvoluted XPS spectra of (a) Si 2p and (b) O 1s spectra of 2D T-silicate.

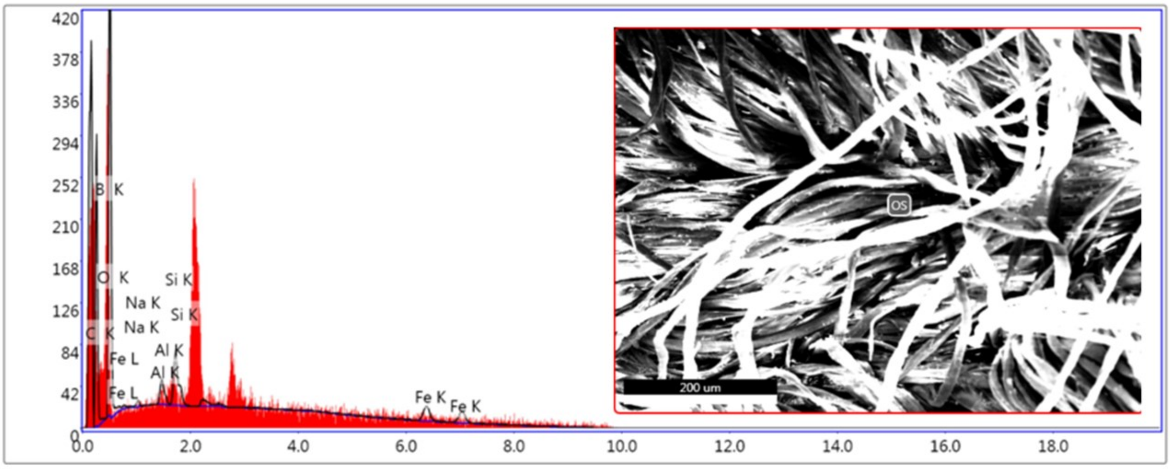

Fig. S3. EDS analysis of 2D T-silicate coated cotton fabric.

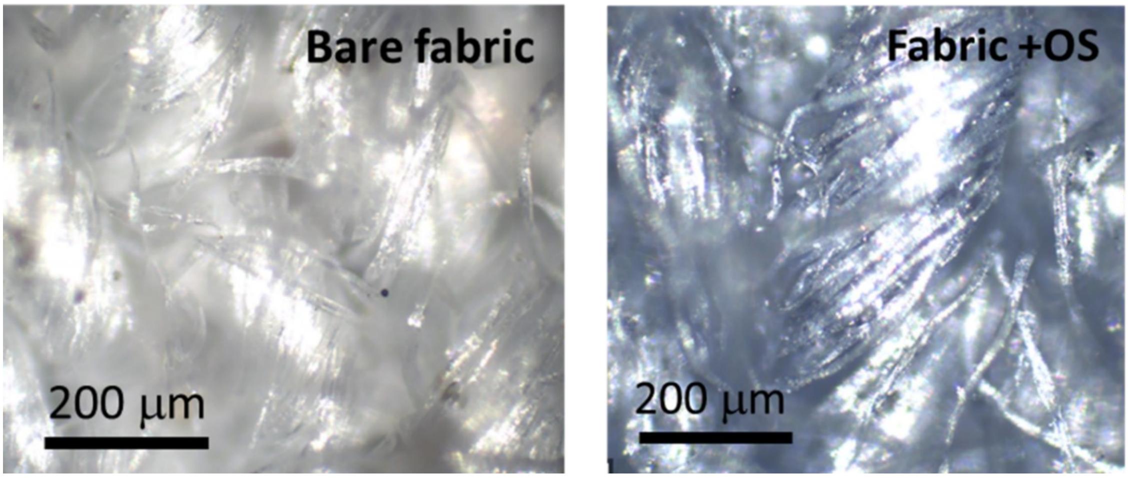

Fig. S4. Optical images of 2D T-silicate coated cotton fibers.

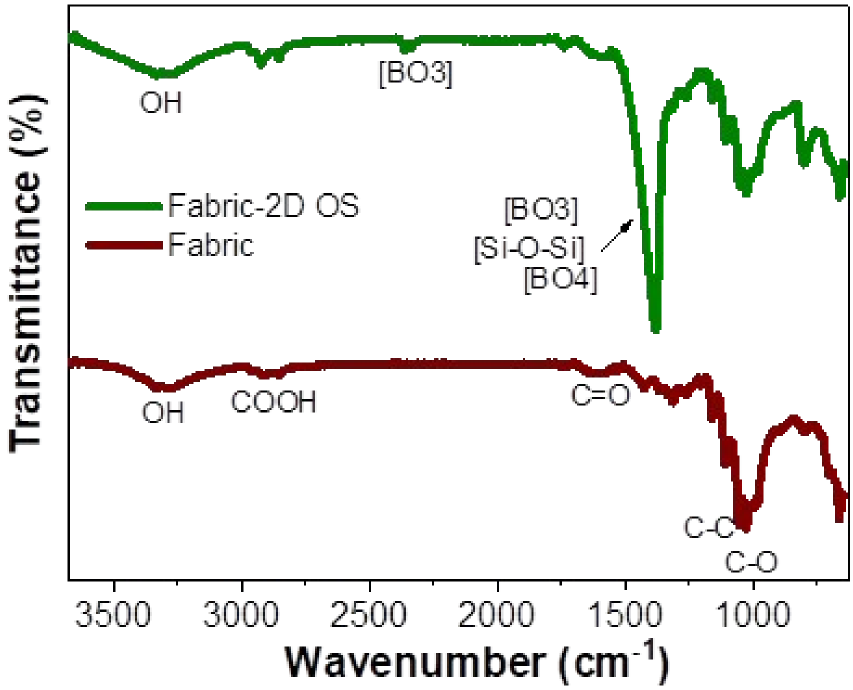

Fig. S5. FTIR comparative analysis of T-silicate coated cotton fabric and only fabric.

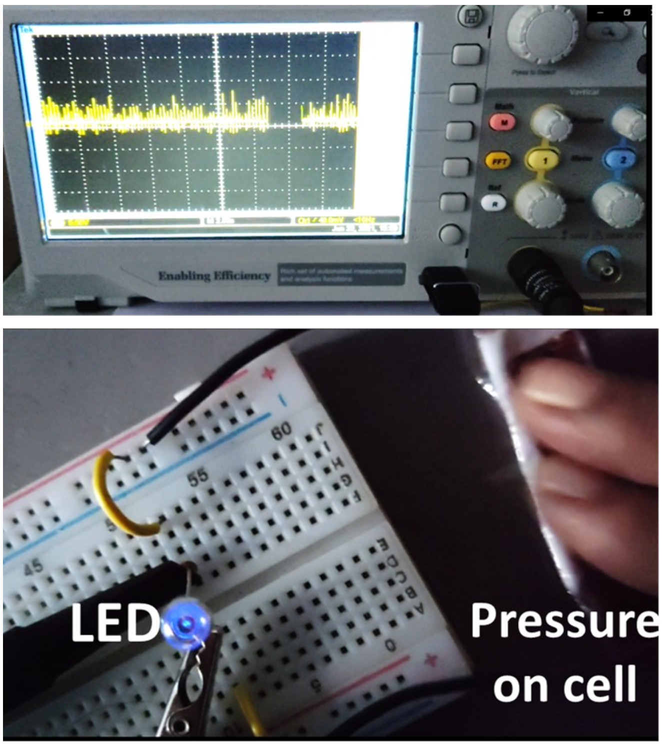

Fig. S6. Tapping of T-silicate-fabric device real-time response image showing glow of a blue LED.

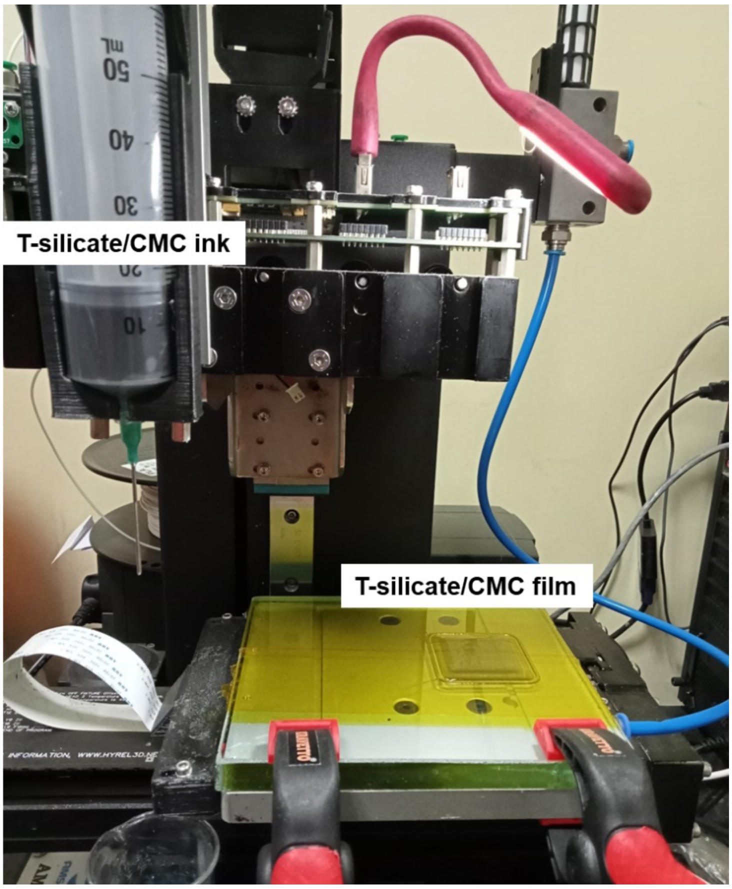

Fig. S7. Digital image of the 3D printer (*Hyrel*) with T-silicate/CMC ink in the syringe and freshly printed film on the print bed.

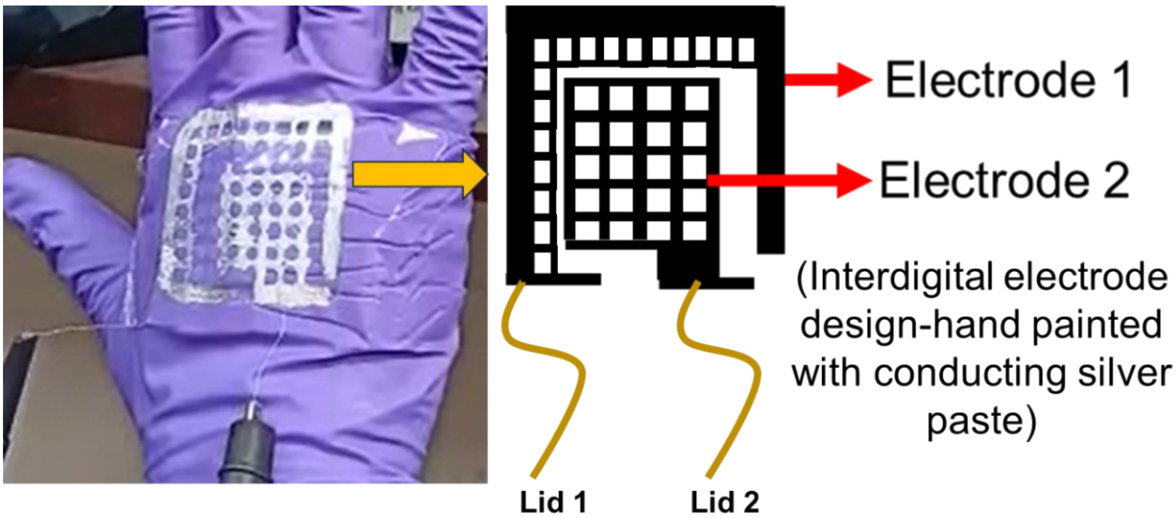

Fig. S8. Digital image of mesh film CMC-TS device mounted on the glove during measurement, the schematic at right shows the electrode design.

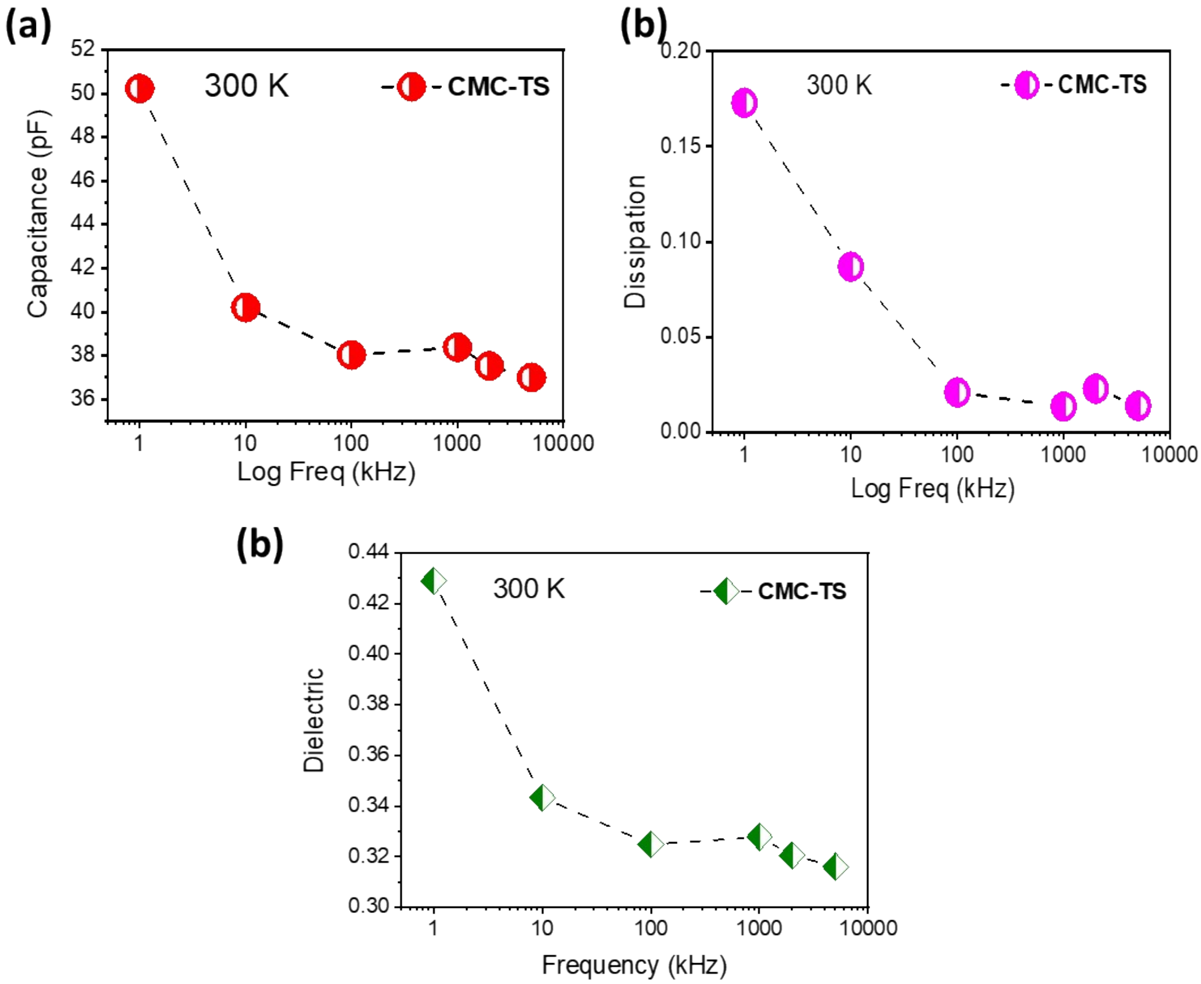

Fig. S9. (a) Capacitance at room temperature for T-silicate-CMC device at variable frequency. (b) Dissipation graph of the fabricated device from T-silicate-CMC, and (c) The dielectric constant value of the device as a function of the frequency.

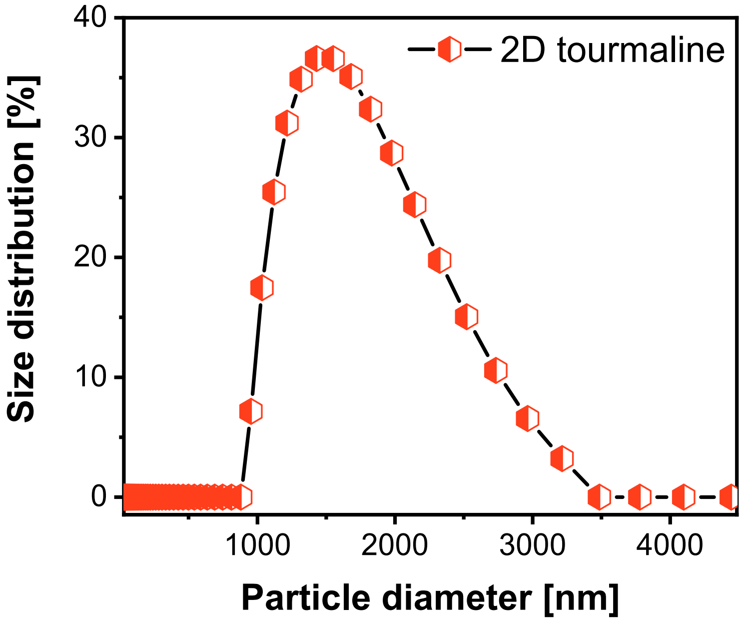

Fig. S10. Size distribution graph of particle diameter of exfoliated tourmaline obtained with particle size analyzer.

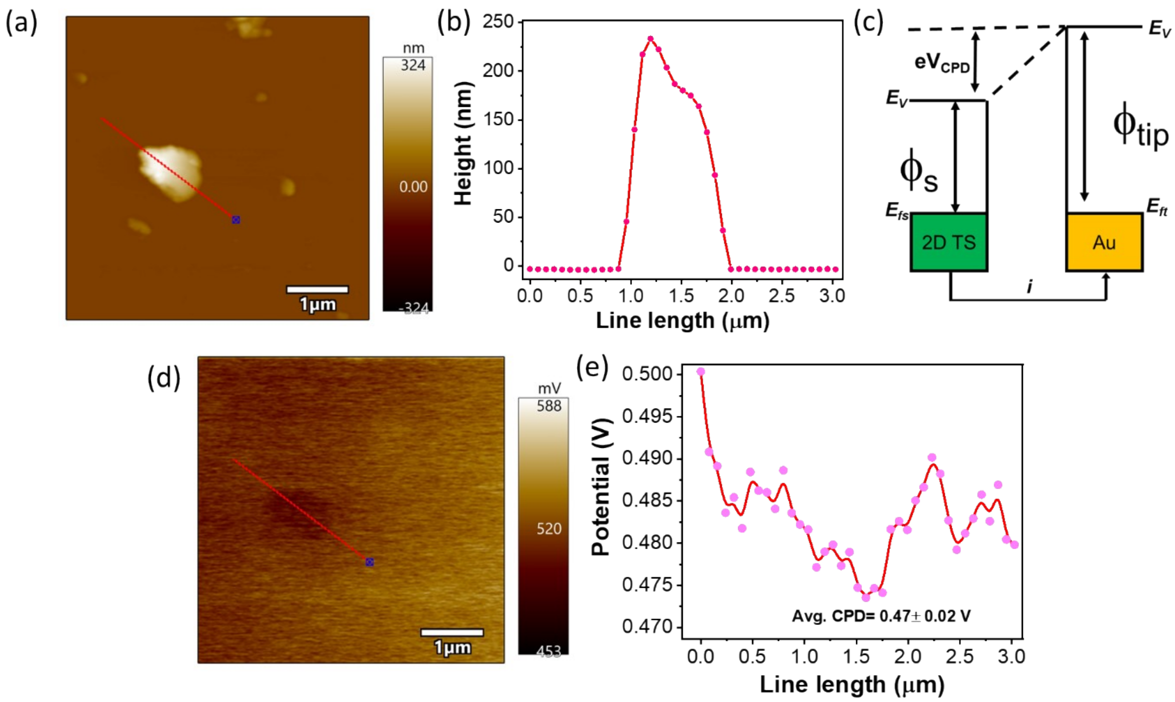

Fig. S11. KPFM obtained (a-b) height profile image and graph of marked T-silicate particle, (c) schematic of KPFM-based electronic bands between tip and sample. (d) potential image and (e) potential graph showing CPD value.

The work function is a property of materials that determines how easily electrons can be emitted from them. A lower work function means electrons can move between energy bands more easily. **Figure S11(a-b)** shows the data taken with KPFM to observe the work function of the material. During the experiments, the surface potential could not be measured for thinner sheets due to resolution issues. Therefore, a thicker particle/ agglomerated particle was used to measure the work function. **Figure S11(e)** shows the measured contact potential difference (CPD) of sample ~0.47V. Subtracting this from the tip work function (~6.6V), we get the work function of the sample to be ~6.2V. Fermi level alignment is introduced by electrical contact between the tip and the sample via current flow i, which causes an offset in the vacuum levels Ev and the contact potential difference V_{CPD} (shown schematically in **Figure S11(c)**). A work function greater than 6 volts indicates a relatively high energy barrier for electron emission. This is due to the high dielectric nature of the silicate, which makes the flow of electrons difficult. In the context of piezoelectric/flexoelectric materials, the work function can affect the charge distribution and polarization of the material in response to mechanical stress. The work function of this type of material may be lowered after applying mechanical stress.

Table S4: comparison of theoretical piezoelectric constant of different nanomaterials including this work

Material	Formula	Theoretical piezoelectric constant (pm/V or pC/N)	Reference
PVDF	$(CH_2CF_2)n$	$d_{31} = 28$	S1
Zinc oxide	ZnO	$d_{33} = 12$	S1
Barium titanate (single crystalline)	$BaTiO_3$	$d_{15} = 587$	S1
Barium titanate (polycrystalline)	$BaTiO_3$	$d_{15} = 270$	S1
Quartz	SiO_2	$d_{11} = 2.3$	S1
2D Tourmaline	$Na(Fe^{2+}{}_2Al)_{\Sigma=3}Al_6(Si_6O_{18})(BO_3)_3(OH)_3O$	$d_{11} = 2.0$	This work

Supporting References

[S1] N. SC, Abrahams; N, *Concise encyclopedia of advanced ceramic materials*, 1991.