Supporting Information

Enhanced thermoelectric properties of electrodeposited Cu-doped Te films

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A. The Seebeck coefficient measurements:

The schematic of the Seebeck measurement setup is shown in Figure S1. The Seebeck coefficient of all samples was evaluated in the in-plane configuration by establishing a temperature gradient (ΔT) along the length of the sample through commercially available Peltier modules at the two ends of the sample as shown in Figure S1.

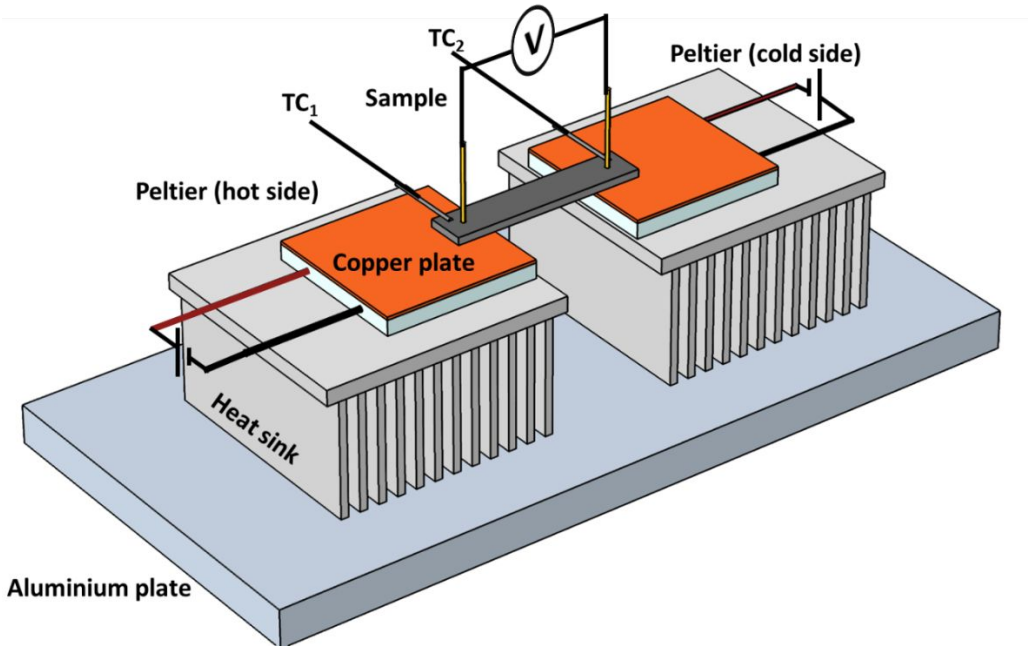


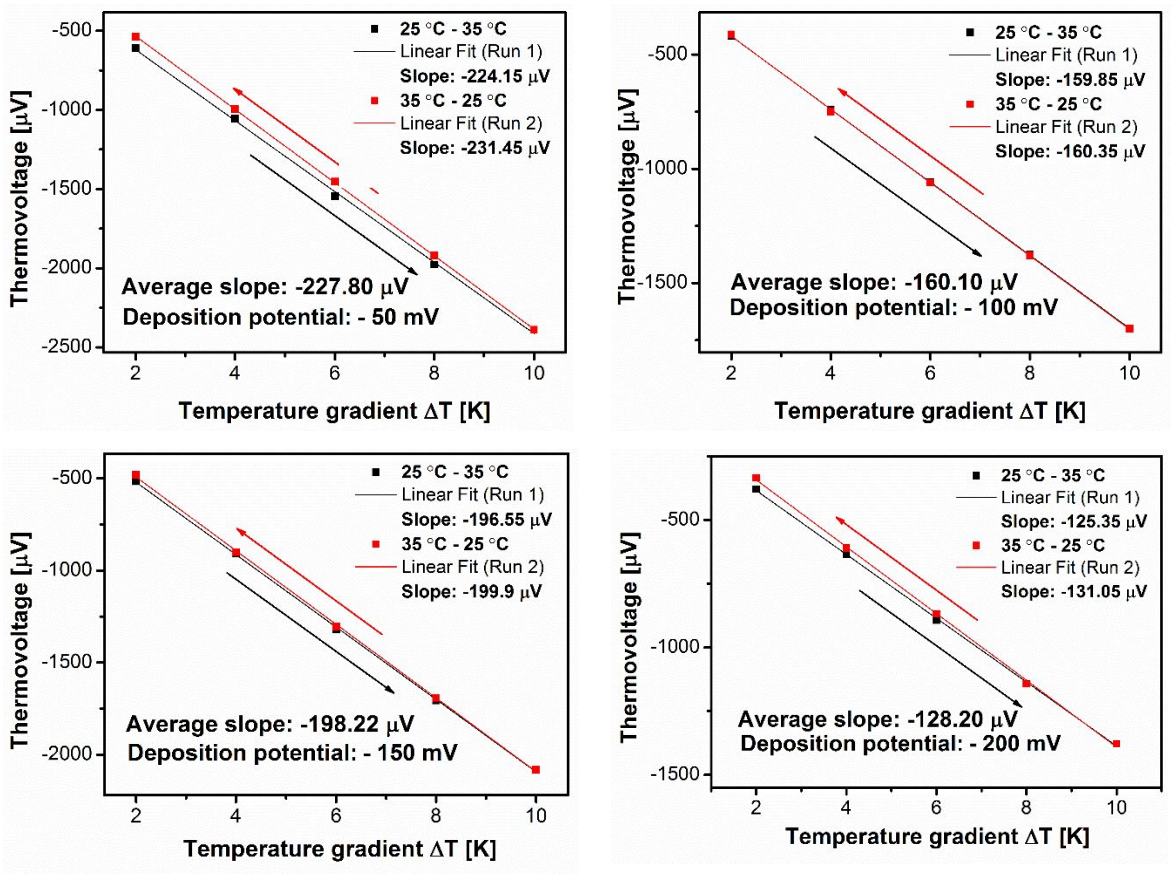
Figure S1: Schematic of the Seebeck coefficient measurement system of thin films.

Two separate thermocouples (Type K) situated at the ends of the sample recorded the temperatures (TC_1 and TC_2). The thermocouples were in direct contact with the sample ensuring minimal thermal losses. The temperature gradient between both the ends was measured using a thermocouple reader. The temperature of the cold was kept at a fixed temperature for e.g. at room temperature (298 K), and a temperature gradient of 2 to 10 K was created by increasing the temperature of the Peltier module on the hot side.

The sample was placed on the Peltier module and to ensure proper thermal contact of the sample with the Peltier modules, boron nitride-based commercial thermal interface materials was used between the sample and the Peltier module. The voltage readings were taken by a spring-loaded flat and spherical ended gold microprobes ensuring a good electrical contact with the thermoelectric film without cracking, stressing and damaging the films.

Similar setups are well known and have been reported in the literature for near room temperature Seebeck coefficient measurement of the thermoelectric materials [1-3].

The thermovoltage was measured in the range of $\Delta T \rightarrow$ 2-10 K using a high impedance voltmeter. Two different runs of increasing and decreasing ΔT were performed to ensure the measurements obtained are stable and correct. In run-1 the ΔT was increased from 2 K to 10 K with an interval of 2 K for every thermovoltage measurement. The measured data were recorded only when both the temperature gradient and the thermovoltage depict stable value thereby minimizing the measurement errors. In run-2 the ΔT was decreased back from 10 K to 2 K. All the obtained thermovoltage data are plotted against ΔT. The thermovoltage dependence on the temperature gradient depicts a linear behaviour. The Seebeck coefficient is determined from the slope of the curve. The reported Seebeck coefficient in the manuscript is an average of the values calculated from run-1 and run-2.



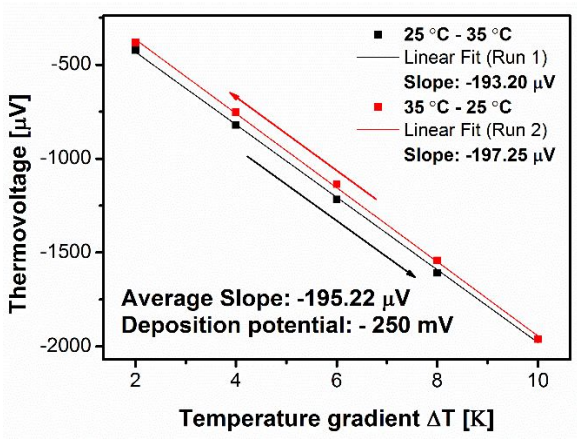


Figure S2: Measured thermovoltage data as a function of the temperature gradient ΔT. The slope of the curve corresponding to runs-1 and 2 is shown in the inset.

The thermovoltage measured for samples deposited using different deposition potentials have been plotted against the ΔT. The slope of the curves corresponding to runs-1 &2 has been calculated and shown in Figure S2. The plot depicts a linear behaviour over the measured temperature gradient. The sample with the optimized Seebeck coefficient was re-measured after eight months. It exhibits the same Seebeck coefficient for the films within the measurement errors thereby indicating that the thermoelectric properties of Cu-dope Te thin films are reproducible and stable as a function of time.

B. Stability of Thermoelectric Film:

Re-measured the Seebeck coefficient of our films eight months after the film deposition. The film was stored in the normal atmosphere for eight months. The behaviour of the thermovoltage against the temperature gradient is shown in Figure S3. The average Seebeck coefficient for the optimized sample deposited at -50 mV deposition potential has been re-measured and the obtained value (-236.97 μV/K) is in excellent agreement with the previous value (-227.8 μV/K) within the error of the measurements indicating the stability of thin film under room temperature.

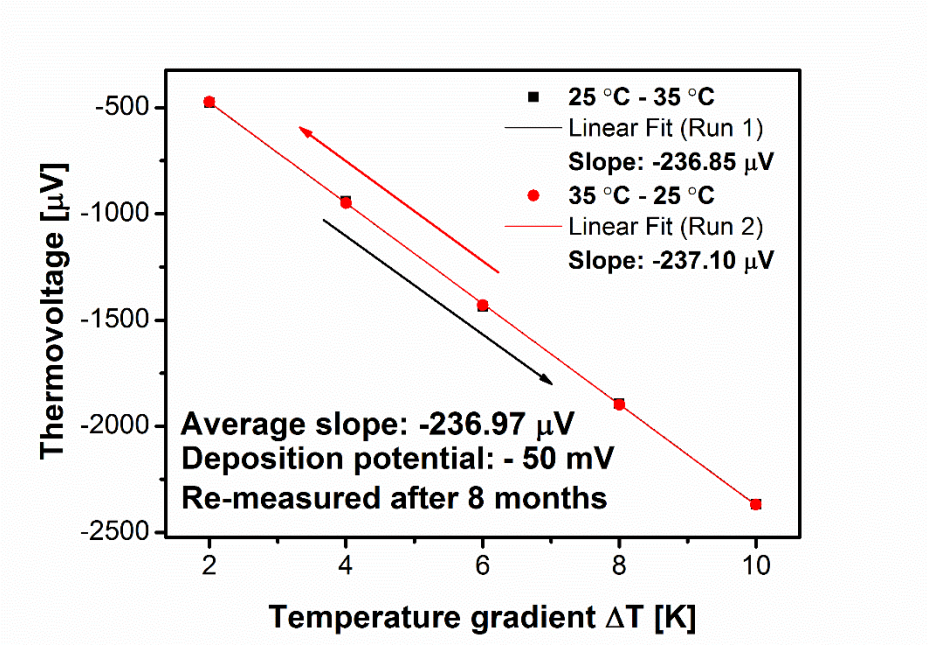


Figure S3: Re-measured thermovoltage of the sample deposited at -50 mV and plotted against temperature gradient (ΔT), eight months after the deposition.

C. Roughness measurements

AFM characterization has been performed on -50 mV and -200 mV deposited samples, which exhibited the maximum and minimum power factor, respectively. The measurements were performed on the sample using contact mode at the room temperature in the ambient atmosphere. The scan area for the roughness measurements was 10×10 μm^2. Scans were performed on different places on the sample surface. The data were processed by using Nanoscope analysis software.

The RMS roughness, along with the sample details, is tabulated in Table 1 and the 2-d and 3-D images of the AFM measurements are shown in Figure S4. This information has also been included in the supporting information document.

Table 1: Roughness measurements on the Cu doped Te electrodeposited thermoelectric films

Sample	**Deposition potential**	**RMS roughness**
Cu doped Te films	-50 mV	6.50 nm
Cu doped Te films	-200 mV	4.96 nm

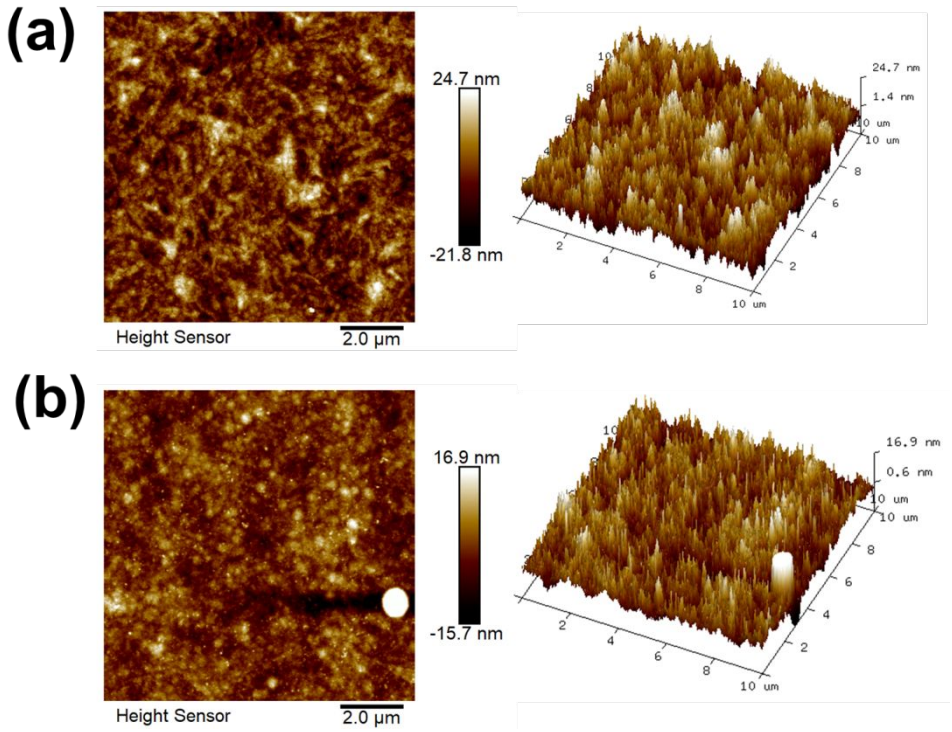
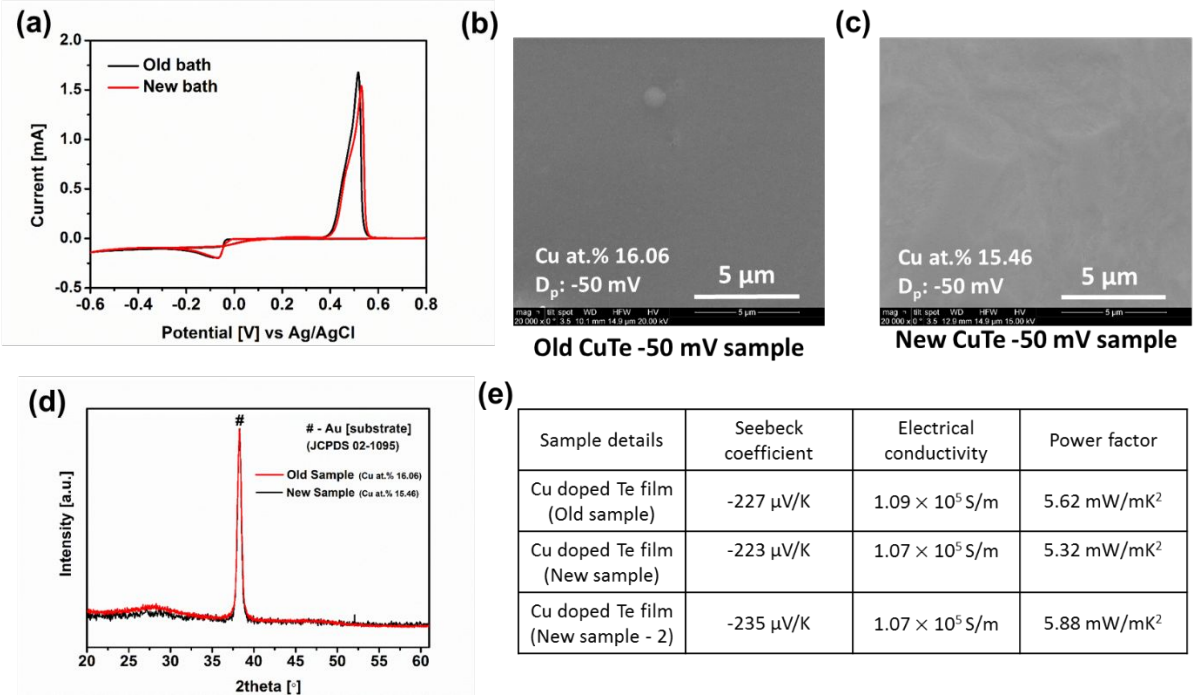


Figure S4: 2-D and 3-D AFM image of Cu doped Te film deposited at (a) -50mV and (b) -200 mV deposition potential for 1-hour duration respectively.

D. Reproducibility of Cu doper Te films

Figure S5 demonstrates and compares the structural and the thermoelectric properties of the old -50 mV deposited sample (which also tend to show maximum power factor) with the recently deposited film using a freshly prepared electrolytic bath. Figure S5 (a) compares the cyclic voltammograms (CV) of the old and the new electrolytic baths prepared at different times. Both the electrolytic baths recorded a similar CV with the same maximum cathodic and anodic peak position. The CV's were recorded on the standard gold electrode and both the CV tend to show the similar reduction peak currents. The film was deposited at -50 mV for 1 hour. The microstructure of the deposited film is depicted in Figure S5 (b) and (c). Figure S5 (b) exhibits the micrograph of old Cu-doped Te films, which shows no specific microstructure. Similar microstructure features has been observed for the recent deposited thin films, as shown in Figure S5 (c). The Cu at.% of both the deposited materials are given as the inset. It can be observed that the Cu at.% measured using EDS are almost the same taking into account the instrumental error. Figure S5 (d) shows the XRD diffractograms of the old and the recent deposited film. Both the deposited materials exhibit single crystalline peak arising from the Au seed layer on which the materials has been electrodeposited. A hump can be observed signifying the amorphous nature of the Cu-doped Te films. It should be noted that no other peak corresponding to Cu, Te or CuTe were recorded in the diffractogram. The intensity has been normalised to compare both the diffractograms. It can be seen

from Figure S5 (d), both patterns tend to superimpose each other indicating an amorphous nature of both the electrodeposited Cu-doped Te films. Finally, the thermoelectric properties were evaluated for the recently sample. Multiple samples were prepared and measured for the Seebeck coefficient and the electrical conductivity. Out of which the sample with the maximum calculated power factor and the minimum power factor have been reported in the Table as shown in Figure S5 (e). The reported Seebeck coefficient and the corresponding electrical conductivity of the sample deposited at -50 mV for 1 hour in the main manuscript is -227 µV/K and 1.09×10^5 S/m, which constitutes to a calculated power factor of 5.62 mW/mK^2. The electrical conductivity values of the recent prepared samples are almost the same compared to the old samples as shown in the Table S5 (e). The Seebeck coefficient of the new samples are -223 µV/K and -235 µV/K, which individually constitutes a calculated power factor of 5.32 mW/mK^2 and 5.88 mW/mK^2, respectively. The reported power factor of the old sample falls in between these values and within the error of the measurement of the individual parameters.



(e)

Sample details	Seebeck coefficient	Electrical conductivity	Power factor
Cu doped Te film (Old sample)	-227 µV/K	1.09×10^5 S/m	5.62 mW/mK^2
Cu doped Te film (New sample)	-223 µV/K	1.07×10^5 S/m	5.32 mW/mK^2
Cu doped Te film (New sample - 2)	-235 µV/K	1.07×10^5 S/m	5.88 mW/mK^2

Figure S5: (a) Cyclic voltammogram of old and the new electrolytic baths prepared and scanned at 10 mV s^{-1} (b) SEM image of old sample deposited at -50 mV for 1-hour duration along with its Cu at. %, (c) SEM image of new sample deposited at -50 mV for 1-hour duration along with its Cu at. %, (d) XRD diffractograms of old and new -50 mV deposited samples and (e) comparison of the Seebeck coefficient, electrical conductivity along with the calculated power factor of old and the new deposited films.

References:

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3. Iwanaga, S.; Toberer, E. S.; LaLonde, A.; Snyder, G. J., A high temperature apparatus for measurement of the Seebeck coefficient. *Review of Scientific Instruments* **2011,** *82* (6), 063905.