Supporting Information

Thermoelectric properties of bismuth telluride thin films electrodeposited from a non-aqueous solution.

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Section 1: Cyclic voltammetry

Prior to electrodeposition, cyclic voltammetry in an electrolyte containing 2.25 mM $[N^nBu_4][BiCl_4]$ and 3mM $[N^nBu_4]2[TeCl_6]$ was performed to investigate the deposition of bismuth telluride. Figure 1 shows three consecutive cycles for $[N^nBu_4][BiCl_4]$ and $[N^nBu_4]_2[TeCl_6]$ in 0.1M $[N^nBu_4]Cl$ supporting electrolyte at a glass carbon (GC) working electrode. Scanning negatively inthe first scan (black curve) two reduction peaks are observed at -0.75 and -1.4 V. Thefirst peak at -0.75 V was attributed to the underpotential deposition of Bi onto alreadydeposited Te in our previous work. The charge under the reduction peaks was

calculated to be 3.3mC. On the return scan there is a large oxidation peak starting fromca.-0.2 C and the second oxidation peak at 0.7 V. The charge calculated for oxidative stripping peakis 1.4 mC, which is 42% of the reduction charge value indicating that the deposited Bi_2Te_3 is not completely oxidised. On the second and third scan (red and blue curve,respectively), the two reduction peaks are noticeable as well. The first peaks at -0.75V vs. Ag/AgCl corresponds to the same position as in the first scan, however the reduction current is larger. The second peak at -1.3 V vs. Ag/AgCl is shifted towardsmore positive potential in comparison to the first scan. This change in voltammetry for the second and third scan is due to the modified electrode surface as the materialis not fully oxidised after the first scan resulting in facilitated deposition onto already deposited material. The oxidative stripping for the second and third scan is very similar to the first scan in both potential and current.

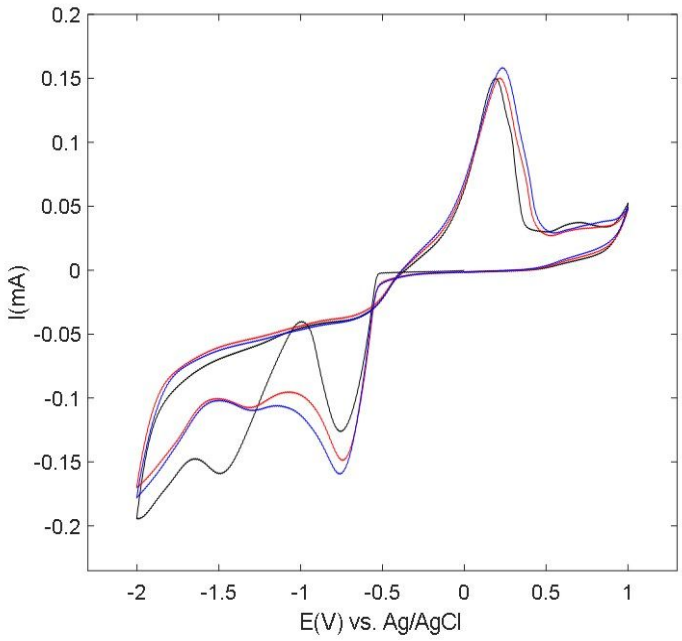

Figure S1:Three consecutive CVs for the reduction of 2.25 mM $[N^nBu_4][BiCl_4]$, 3 mM $[N^nBu_4]_2[TeCl_6]$ in CH_2Cl_2 solution containing 0.1 M $[N^nBu_4]Cl$ supporting electrolyte on a 3 mm diameter GC electrode. The scan rate is 50 mV s^{-1}. Black: 1st scan, red: 2nd scan, blue: 3 rd scan.

Section 2. Image of a substrate with the electrodeposited bismuth telluride film on 7×11 mm area of working electrode (black). The film covers completely the area of working electrode.

Figure S2. Image of the film electrodeposited by pulsed electrodeposition (t_{on}=5s, t_{off}=10 s) at -1 V vs. Ag/AgCl, with -1.3 C of the passed charge.

Section 3. Thickness of the electrodeposited bismuth telluride thin film was controlled by the passed charge, and calculated using Faraday's law:

$$Q = n\,z\,F = \frac{\rho\,A\,l\,z\,F}{M}$$

Where Q is the charge (C), n is the amount of substance (mol), ρ is bismuth telluride powder density (7.74 g cm^{-3}), l is the film's thickness (μm), A is the working electrode area (7 mm × 11 mm), z is number of exchanged electrons (18 electrons), and M is bismuth telluride molar mass (800.76 g mol^{-1}).

Table S1. Nominal thicknesses of bismuth telluride thin films electrodeposited by different methods calculated from the passed charge.

Method	Potential vs. Ag/AgCl / V	Charge / C	Thickness / µm
Potentiostatic	E_{dep}=-1.0	-1.3	1.00
Potentiostatic	E_{dep}=-0.8	-1.3	1.00
Potentiostatic	E_{dep}=-0.6	-1.3	1.00
Pulsed	E_{dep}=-1.0	-1.2	0.95
Pulsed	E_{dep}=-0.8	-1.8	1.40
Pulsed	E_{dep}=-0.6	-2.3	1.80
Potentiostatic with nucleation pulse	E_{dep}=-0.6 , E_{nuc}=-1.4	-1.3	1.00
Potentiostatic with nucleation pulse	E_{dep}=-0.6 , E_{nuc}=-1.0	-1.3	1.00
Pulsed with nucleation pulse	E_{dep}=-0.6 , E_{nuc}=-1.4	-1.8	1.40
Pulsed with nucleation pulse	E_{dep}=-0.6 , E_{nuc}=-1.0	-0.6	0.50