Supplementary Information

Electrodeposition of crystalline HgTe from a non-aqueous plating bath

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Solubility and compatibility studies
A compatibility test of [N\textsubscript{4}Bu\textsubscript{4}]\textsubscript{2}HgCl\textsubscript{4} and [N\textsubscript{4}Bu\textsubscript{4}]\textsubscript{2}[TeCl\textsubscript{6}] with supporting electrolyte [N\textsubscript{4}Bu\textsubscript{4}]Cl was carried out by comparing the \textsuperscript{199}Hg (I = \frac{1}{2}, N.A. 16.8\%, reference \(\delta = 0\) HgMe\textsubscript{2}) (Figure S1) and \textsuperscript{125}Te (I =1\slash 2, N.A. 7\%, reference \(\delta = 0\) TeMe\textsubscript{2}) (Figure S2) NMR spectra of the individual compounds and the combined reagents in dichloromethane.

No changes in the \textsuperscript{199}Hg or \textsuperscript{125}Te NMR spectra were observed when the individual reagents were mixed with a 10-fold excess of supporting electrolyte [N\textsubscript{4}Bu\textsubscript{4}]Cl, or when the Hg(II) salt was combined with the [N\textsubscript{4}Bu\textsubscript{4}]\textsubscript{2}[TeCl\textsubscript{6}] in a 1:1 molar ratio. Similarly, no changes were observed when the two reagents were combined together with a 10-fold excess of [N\textsubscript{4}Bu\textsubscript{4}]Cl. These experiments indicate that the mixture is chemically stable on the NMR timescale and suggest they might be suitable for the electrochemical studies.

Figure S1. \textsuperscript{199}Hg NMR spectrum of [N\textsubscript{4}Bu\textsubscript{4}]\textsubscript{2}[HgCl\textsubscript{4}] (CH\textsubscript{2}Cl\textsubscript{2}/CD\textsubscript{2}Cl\textsubscript{2}, 293 K).

Figure S2. \textsuperscript{125}Te NMR spectrum of [N\textsubscript{4}Bu\textsubscript{4}]\textsubscript{2}[TeCl\textsubscript{6}] (CH\textsubscript{2}Cl\textsubscript{2}/CD\textsubscript{2}Cl\textsubscript{2}, 293 K).
Electrochemical set-up

Photographs of the custom-built Faraday cage, and electrochemical cell used are shown in Figure S3. The cell is set within a small Faraday cage which allows for low-noise electrochemical measurements inside the acrylic glove box (Figure S3 a). The cell consisted of a < 10 mL glass container with a custom-made lid which ensures precise placement of the working, counter and reference electrodes (Figure S3 b). The working electrodes were 200 nm thin-film platinum sputtered with AJA Orion sputtering system in DC mode onto a Si wafer and cut into 20 mm x 10 mm chips (< 2 Ω resistivity measured from the exposed working electrode area to the end of the BVT connector). The working electrode area (5 mm diameter) is defined by enclosing the chip in a front seal holder (designed in-house) which provides a CH₂Cl₂ compatible seal to the front of the chip (Figure S3 c). The chip is placed onto a carrier and pushed against an O-ring (silicone/VMQ or Viton) surrounding the front opening by tightening a sealing screw in the back of the holder. A second O-ring (Viton) inlaid in the screw head provides the seal to the back. The working electrode is connected to the potentiostat via a modified chip electrode connector (BVT Technologies, a.s.).

A Pt:Ir disc (90 : 10 %, 10 mm diameter) was used as the counter electrode. The counter electrode is placed parallel to the working electrode at a distance of 9.25 mm. A custom-made Ag/AgCl reference electrode immersed in 0.1 mol dm⁻³ [NⁿBu₄]Cl in CH₂Cl₂ is used as the reference electrode and is placed near the working and counter electrodes.

![Figure S3. Photographs of the custom-built electrochemical setup: Faraday cage with external banana sockets for connecting the working (WE), counter (CE) and reference (RE) electrodes and the potentiostat ground (GND) (a), cell and cell lid with electrodes in situ (b) and disassembled front seal holder with chip carrier, WE chip and sealing screw used for defining the working electrode area (c) The distance between the WE and the CE in b is 9.25 mm.](image-url)
Reproducibility of voltammetric response of HgTe plating bath

Figure S4. Comparison of CVs recorded on different days in plating baths containing 5 x 10^{-3} mol dm^{-3} each of [N\text{Bu}_4][HgCl_4] and [N\text{Bu}_4][TeCl_6] in 0.1 mol dm^{-3} [N\text{Bu}_4]Cl. A Pt thin film (A = 0.196 cm^2) working, a 10 mm diameter Pt : Ir (90 : 10 %) disc counter and an Ag/AgCl (0.1 mol dm^{-3} [N\text{Bu}_4]Cl) reference electrode were used. The scan origins at 0.5 V are indicated by the leftwards arrows with the bar. Further arrows are included to indicate the scan directions. The highlighted boxes (I – VI) indicate different regions of the voltammograms and the limits of the boxes are identical for both panels.
Deposit morphology
SEM (Figure S5) and optical (Figure S6) images of full HgTe deposits (5 mm circular area) of the series of samples shown in Figure 3 in the main manuscript.

Figure S5. SEM images of the full deposition areas of the samples presented in Figure 3. The samples were deposited from 5x10^{-3} mol dm^{-3} each of [N\textsubscript{Bu\textsubscript{4}}\textsubscript{2}][HgCl\textsubscript{4}] and [N\textsubscript{Bu\textsubscript{4}}\textsubscript{2}][TeCl\textsubscript{6}] in 0.1 mol dm^{-3} [N\textsubscript{Bu\textsubscript{4}}]Cl in CH\textsubscript{2}Cl\textsubscript{2} at the deposition potentials indicated in the figure panels. Pt thin film working electrodes, a Pt:Ir disc (90 : 10 %, 10 mm diameter) counter electrode and an Ag/AgCl (0.1 mol dm^{-3} [N\textsubscript{Bu\textsubscript{4}}]Cl in CH\textsubscript{2}Cl\textsubscript{2}) reference electrode were used. The scale bars represent 1 mm.
Figure S6. Photographs of samples presented in Figure S5 and Figure 3. The bottom edge of the photographed chips was at the bottom end of the front seal reactor during deposition. The deposit is the central dark or dark and yellow region. This is surrounded by a mark caused by the O-ring seal which defined the deposition area. The images show that the -0.25 V (a) and -0.5 V (b) samples are relatively thin but uniform. The -0.75 V (c) and -1.0 V (d) films are the most uniform. There is clear evidence of delamination of the films deposited at more negative potentials (e – g). In addition the sample deposited at -2.0 V (h) has a significantly different color. This is presumably due to the onset of the electrochemical breakdown of the supporting electrolyte. The graph paper squares in the background measure 1 x 1 mm². The diameter of the electrodeposited area was approximately 5 mm.
Figure S7. Representative 3D AFM plots of the surface morphology measured in the middle of HgTe samples deposited at -0.5 V, -1 V and -1.25 V discussed in the main manuscript. The samples were deposited from a plating bath containing $5 \times 10^{-3}$ mol dm$^{-3}$ each of [N$^\text{Bu}_4$]$_2$[HgCl$_4$] and [N$^\text{Bu}_4$]$_2$[TeCl$_6$] in 0.1 mol dm$^{-3}$ [N$^\text{Bu}_4$]Cl in CH$_2$Cl$_2$. The deposition potentials are provided in the figure panels. The AFM images were acquired using the standard conditions described in the experimental section of the main text.
Crystallographic characterization of HgTe deposits on Pt

XRD measurements were performed on range of samples as shown in Figure S8. All HgTe films show similar features. The XRD peaks for HgTe get narrower as the deposition potential increases from -1.75 V to -0.25 V and the Pt 220 peak becomes weaker as the films become thicker.

Figure S8. XRD patterns from a series of electrodeposited samples produced on Pt thin film electrodes using a plating bath containing 5 $\times$ 10$^{-3}$ mol dm$^{-3}$ each of [N$^n$Bu$_4$][HgCl$_4$] and [N$^n$Bu$_4$][TeCl$_6$] in 0.1 mol dm$^{-3}$ [N$^n$Bu$_4$]Cl in CH$_2$Cl$_2$ at the indicated deposition potentials. All of the features observed are due to crystalline HgTe, Pt or the underlying silicon. As can be seen clearly by eye, the HgTe 111 peak is significantly narrower for the films obtained at less negative deposition potentials. As discussed in the main text this is associated with the development of larger crystallites due to the decreased growth and nucleation rates at these potentials.
Acceleration voltage effect on EDX composition analysis

In order to choose an appropriate electron beam acceleration voltage and sample thickness for the EDX composition analysis a series of HgTe samples were electrodeposited onto Pt electrodes under exactly the same conditions: at -1.75 V from a plating bath containing $5 \times 10^{-3}$ mol dm$^{-3}$ each of $[\text{NnBu}_4][\text{HgCl}_4]$ and $[\text{NnBu}_4][\text{TeCl}_6]$ in 0.1 mol dm$^{-3}$ $[\text{NnBu}_4]\text{Cl}$ in CH$_2$Cl$_2$, for different deposition times (3600 s, 1800 s and 300 s) leading to different sample thicknesses.

SEM EDX measurements were performed on the three HgTe samples using the same conditions and three different acceleration voltages; 10, 20 and 30 keV. The EDX spectra (Figure S9) show peaks for Hg, Te and Pt with trace peaks associated with O and C. The fraction of the reported EDX composition due to HgTe as a function of the acceleration voltage and deposition charge is shown in Figure S10. As expected, the importance of the Pt substrate in the EDX composition decreases with increasing deposition time and decreasing acceleration voltage with more than 60% of the EDX signal associated with HgTe at 20 keV for samples produced with a deposition time of more than 1800 s. As shown in Figure S11 we observe a clear trend of increasing Hg content in the films with increasing acceleration voltage in all samples. The strength of the trend is much greater for the lower deposition time/thinner samples. Interestingly at 20 keV the reported composition is fairly independent of sample thickness.

Based upon these results the bulk of our EDX characterization data was taken at 10 keV and 20 keV acceleration voltages on samples with deposition times greater than 600 s. Indeed, most samples discussed herein were deposited using a cutoff charge of -0.8 C cm$^{-2}$, to account for variations in the deposition rate. Having two acceleration voltages allows us to check for any thin sample effects. Where these are present the 20 keV results are likely to be the most accurate.
Figure S9. SEM-EDX composition of HgTe films electrodeposited at -1.75 V as a function of the deposition time and acceleration voltage.
Figure S10. Percentage of SEM-EDX signal from HgTe films electrodeposited at -1.75 V due to Hg and Te as a function of deposition time/sample thickness and acceleration voltage.

Figure S11. The Hg to Te ratio determined by SEM: EDX for HgTe thin films electrodeposited at -1.75 V from plating baths containing 5 x 10^{-3} mol dm^{-3} each of [N\text{Bu}_4][HgCl_4] and [N\text{Bu}_4][TeCl_6] in 0.1 mol dm^{-3} [N\text{Bu}_4]Cl in CH_2Cl_2 as a function of acceleration voltage and deposition time/sample thickness.
SEM-EDX on TiN substrates

In order to check the wider applicability of the new HgTe electrodeposition method a small number of samples were prepared using sputtered TiN electrodes. The SEM imaging and SEM-EDX characterization of these samples are presented here. The SEM images (Figure S12 a) showed the presence of films with comparable texture to the films produced on Pt. The SEM-EDX spectra measured on the samples showed Hg, Te, Ti, N and Si with traces of O and C in line with the Pt deposited samples. The thinner deposits investigated on the TiN substrates (approximately 200 nm, assuming 100 % Faradaic efficiency) led to reduction in the Hg and Te EDX signals relative to the substrate signals (Figure S12 b). The EDX results report the composition of the HgTe to be between 48 and 49.5% Hg. This is well within the range reported for thinner HgTe films deposited on Pt and these films are likely to be stoichiometric.

Figure S12. (a – d) SEM SE images of HgTe electrodeposited on TiN substrates at a range of deposition potentials from plating baths containing $5 \times 10^{-3}$ mol dm$^{-3}$ each of [N$^4$Bu$4$][HgCl$_4$] and [N$^4$Bu$4$][TeCl$_6$] in 0.1 mol dm$^{-3}$ [N$^4$Bu$4$]Cl in CH$_2$Cl$_2$. (e) The percentage of the composition determined from EDX signal due to HgTe for the same samples, (f) the percentage of the Hg and Te EDX signal due to Hg for the same samples measured with an acceleration voltage of 10 keV. The equivalent result for the bulk calibration samples is also shown.
XRD on TiN substrates

Figure S13. (a – e) Glancing incidence X-ray diffractograms for series of films electrodeposited onto TiN substrates. The measured peaks can all be associated with the sputtered TiN, underlying silicon substrate or crystalline HgTe. As with the films deposited onto Pt the films deposited at more positive potentials produce significantly narrower XRD peaks. (f) Crystallite size determined using Halder-Wagner approach from diffractograms.