Facile synthesis and characterization of Bi$_{13}$S$_{18}$I$_2$ films as a stable supercapacitor electrode material†

Keir Adams,‡a Alba Franco González,‡a John Mallows,aa Tianyue Li, a,b* John H. J. Thijssena,b and Neil Robertsonida,*a

Electrical double layer capacitors (EDLCs) featuring low-cost and solution-processable electrode materials have attracted significant research interest for their green and economical applications in energy harvesting and storage devices. Here, we demonstrate a novel synthetic route for films of an underexplored 3-D hexagonal bismuth chalcohalide, Bi$_{13}$S$_{18}$I$_2$, and investigate its potential as the active electrode material in EDLC-type supercapacitors. The synthetic procedure has been optimised and comprises the lowest annealing temperature (150 °C) and the shortest processing time (1 h) currently reported. When integrated in a symmetrical EDLC with an aqueous NaClO$_4$ electrolyte, the Bi$_{13}$S$_{18}$I$_2$-based device achieves a remarkable areal capacitance of 210.68 mF cm$^{-2}$ with 99.7% capacitance retention after 5000 cycles. Both the Bi$_{13}$S$_{18}$I$_2$ powder and thin-film electrodes have been characterized through XRD, XPS, Raman spectroscopy, and SEM. The superior stability, low-cost, and facile synthesis of Bi$_{13}$S$_{18}$I$_2$ proves its promising potential for supercapacitor applications.

Introduction

Demand for efficient, economic, and eco-friendly energy storage systems has grown dramatically in recent years for applications in electronic appliances, electric vehicles, and a smart and sustainable energy grid.1–4 Given the high production costs and environmental hazards of conventional energy storage technologies, researchers have focused on developing novel energy materials and optimising their performance in electronic devices.5–8 In particular, interest has grown in high-Z ns$^2$ cations with an electronic configuration of [Xe]6s$^2$5p$^{9,9,9,9}$ Among these main group cations, bismuth has attracted considerable attention because of its low-toxicity and structural-diversity.9,10 For example, bismuth-based perovskite-like materials have been well-studied in applications such as lead-free photovoltaic devices, radiation detectors, and supercapacitor electrodes.11–20 Among the inorganic bismuth-based materials, bismuth chalcogenides and chalcohalides have captured research interests for their manifold functionalities in photocatalysis,21–23 photovoltaics,24 and radiation detection.25,26 Bi$_2$O$_3$ and Bi$_2$S$_3$ have already proven their promising potential in photocatalytic water purification, thermoelectric systems, supercapacitors, and electrochemical sensors.21,27–29 Bi$_2$S$_3$ has also displayed remarkably varied crystal morphologies, including nanorods, nanobelts, and microflowers, which can be tuned for enhanced performance as the active electrode material in supercapacitors.30,31 Among the common Bi-based chalcohalides, BiI$_3$ and BiSeI have been studied as potential photovoltaic materials due to their n-type semiconducting properties and high absorption coefficients,32,33 while both theoretical and experimental studies have evaluated their promise in radiation detection. Still, despite BiI$_3$'s exhibition of strong photocurrent,34 such Bi-chalcohalides have yet to yield satisfactory photovoltaic performance in solar cells.35 Moreover, the fabrication of bismuth chalcogenides typically requires high annealing temperatures and laborious, multistep procedures, complicating research efforts and economic viability. To the best of our knowledge, no simple, one-step, solution-processing synthetic route has been reported.

Electrical double-layer capacitors (EDLCs) are best known for their fast charge–discharge cycles, high power densities, long life cycles, and greater energy densities compared to conventional capacitors. However, EDLCs typically suffer from poorer energy densities compared to so-called pseudo-capacitors or conventional batteries that employ strong faradaic reactions to chemically store charge.36 Consequently, there has been a recent wave of research efforts directed toward advancing the energy densities of environmentally-benign, economical, and durable electrode materials for EDLC applications in order to enhance their commercial viability without sacrificing long-life...
cycle stability. In this respect, bismuth chalcogenides including Bi$_2$S$_3$ and Bi$_2$O$_3$ have been widely studied and applied as high-performing active electrode materials intended as supercapacitors, albeit typically with substantial faradaic mechanism.\textsuperscript{36} On the other hand, bismuth chalcohalides have often been overlooked as potential energy storage materials. In this study, a relatively unexplored bismuth chalcohalide material, Bi$_{13}$S$_{18}$I$_2$, has been synthesised from solution in a single and facile step. Traditionally, such materials are fabricated under high pressure and high temperature conditions requiring long reaction times.\textsuperscript{37–39} Using our easily synthesised Bi$_{13}$S$_{18}$I$_2$ as the active material in EDLC-type supercapacitors, we have achieved a device areal capacitance of 210.68 mF cm$^{-2}$, a specific capacitance of 6.58 F g$^{-1}$, and superior cycle stability with 99.7% capacitance retention even after 5000 cycles.

## Results and discussion

### Material characterization

#### Synthesis

Bi$_{13}$S$_{18}$I$_2$ was synthesised via thermal decomposition of a precursor solution containing bismuth xanthate (Bi(xt)$_3$), a sulfur-containing organobismuth material, and BiI$_3$. Bi(xt)$_3$ was synthesized from potassium xanthate and bismuth nitrate in a one-step reaction previously reported by Vigneshwaran and colleagues.\textsuperscript{40} A wide range of Bi(xt)$_3$ : BiI$_3$ ratios from 2 : 1 to 26 : 1 were tested and spin-coated on quartz glass, forming a thin film which was subsequently annealed at 150 $^\circ$C on a hot plate. The annealing temperature for the thin films was set slightly higher than the decomposition temperature of xanthate to ensure reaction completion (Scheme 1).

#### Structural and electronic characterization

The diffraction patterns obtained for thin films with 2 : 1, 10 : 1, and 18 : 1 ratios of the Bi(xt)$_3$ : BiI$_3$ precursor solution are recorded in Fig. 1. A crystallographic XRD pattern corresponding to Bi$_{13}$S$_{18}$I$_2$ was identified in each of the three spectra. The 2 : 1 ratio produces the pattern with the lowest peak intensity, attributed to the stoichiometric mismatch of the precursor solution. In contrast, using a 26 : 1 solution produced a thin film which was subsequently annealed at 150 $^\circ$C on a hot plate. The annealing temperature for the thin films was set slightly higher than the decomposition temperature of xanthate to ensure reaction completion (Scheme 1).

We also evaluated the effect of film thickness on the crystallographic patterns. The XRD for thin films comprised of 1, 3, and 5 layers are displayed in Fig. S3† and the characteristic Bi$_{13}$S$_{18}$I$_2$ pattern is most clearly identified with the samples containing 3 and 5 layers. Fig. 3 displays the SEM images of the as-prepared Bi$_{13}$S$_{18}$I$_2$. As the number of layers increases, the nano-particle crystals grow longer tube-like nano-rod structures approaching 250 nm in length. This suggests that increased surface area may be achieved by multiple-layer deposition of Bi$_{13}$S$_{18}$I$_2$ during the thin-film formation. We attempted to carry out BET isotherm determination of the surface area, however this is not possible on thin films of such small mass.

![Scheme 1](image1.png)

**Scheme 1** Synthesis of Bi$_{13}$S$_{18}$I$_2$ from different ratios (a : b) of a Bi(xt)$_3$ : BiI$_3$ precursor solution.

![Fig. 1](image2.png)

**Fig. 1** XRD for thin films synthesized from precursor solutions with (a) 2 : 1, (b) 10 : 1, and (c) 18 : 1 Bi(xt)$_3$ : BiI$_3$ ratios. The calculated XRD pattern of Bi$_{13}$S$_{18}$I$_2$.

![Fig. 2](image3.png)

**Fig. 2** Crystallographic packing diagram of Bi$_{13}$S$_{18}$I$_2$ unit cell bismuth: magenta; iodine: purple; sulfur: yellow. The disordered bismuth is shown in grey/magenta with an occupancy factor of 0.25.
Fig. 4 depicts the X-ray photoelectron spectra (XPS) of an 18 : 1 thin film on FTO-coated glass with a mesoporous TiO2 layer, and Table 1 tabulates the observed experimental atomic percentages of specific bismuth, iodine, and sulfur in the film. The values agree closely with the theoretical atomic composition of Bi13S18I2. Diffuse reflectance measurements were also conducted to obtain the optical band gap of Bi13S18I2 in its solid state. An indirect energy gap ($E_{\text{gind}}$) of 0.75 eV and a direct energy gap ($E_{\text{gdir}}$) of 0.91 eV were estimated, which compare well with the literature values in Table S1.† Furthermore, we performed cyclic voltammetry (CV) measurements on a thin film sample spin-coated on FTO as the working electrode to evaluate the electrochemical behaviour of Bi13S18I2. The cyclic voltammograms in Fig. S4† represent an average of 5 cycles at a sweep velocity of 0.1 V s$^{-1}$. The full CV scans indicate that Bi13S18I2 undergoes irreversible redox processes, and the ionization potential (IP) can be estimated using the oxidation potential $E_{\text{ox}}$ against the Ag/AgCl electrode (4.4 ± 0.1 eV below vacuum-level).42 The electronic band gap of solid-state Bi13S18I2 is estimated to be 0.99 V for the sample sweep at 0.1 V s$^{-1}$, calculated from the difference in $E_{\text{pa}}$ and $E_{\text{pc}}$ values and consistent with diffuse reflectance (Fig. 5).

**Supercapacitor studies**

**Electrode preparation.** The performance of Bi13S18I2 as the active electrode material in an EDLC-type symmetric supercapacitor was evaluated using cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS). The Bi13S18I2-based electrodes were fabricated with a facile, single-step, and solution-processable procedure. An 18 : 1 mixture of Bi(x,t)3 and BiI3 was combined with activated charcoal and polytetrafluoroethylene (PTFE) powder and dispersed in DMF in sufficient relative amounts to form a 85 : 10 : 5 weight ratio of Bi13S18I2 : charcoal : PTFE upon subsequent thermal decomposition of the Bi(x,t).3 This heterogeneous solution was then drop-cast on 1 cm$^2$ sections of carbon cloth and heated at 150 °C to achieve a high mass loading of approximately 8–10 mg cm$^{-2}$ on each electrode. Although the Bi13S18I2 constitutes the primary active material for the supercapacitor electrodes, the activated charcoal and

<table>
<thead>
<tr>
<th>Element/orbital</th>
<th>At% Total</th>
<th>At% in Bi13S18I2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi/4f 3</td>
<td>18.16</td>
<td>39.39</td>
</tr>
<tr>
<td>Bi/4d 5</td>
<td>20.36</td>
<td></td>
</tr>
<tr>
<td>I/3d 3</td>
<td>3.81</td>
<td>7.97</td>
</tr>
<tr>
<td>I/3d 5</td>
<td>4.16</td>
<td>6.06</td>
</tr>
<tr>
<td>5/2s</td>
<td>53.42</td>
<td>54.55</td>
</tr>
</tbody>
</table>
PTFE are added for enhanced electrical conductivity and mechanical stability respectively of the overall layer. The powder XRD pattern of as-prepared Bi$_{13}$S$_{18}$I$_2$ electrode is shown in Fig. 6, and the crystallite size of Bi$_{13}$S$_{18}$I$_2$ is calculated to be around 5 nm according to the Scherrer equation. The SEM images of the as-prepared electrodes show good coverage of the underlying carbon cloth with the activated Bi$_{13}$S$_{18}$I$_2$ material, with rod-shaped Bi$_{13}$S$_{18}$I$_2$ layering on top of the carbon cloth as well as binding directly to the carbon fibres (Fig. 7b). A thin (25 μm) microporous membrane (Celgard 3501) previously soaked in a saturated NaClO$_4$ (aq.) electrolytic solution was sandwiched between two of these as-coated electrodes, and the entire set-up was assembled in a standard capacitor test cell (ECC-std, EL-CELL GmbH) for tight packing and ease of measurement (Fig. 7a).

Cyclic voltammetry and galvanostatic charge–discharge tests. The predominant charge storage mechanism of the Bi$_{13}$S$_{18}$I$_2$-based supercapacitor was investigated through cyclic voltammetry (CV) scans and galvanostatic charge–discharge cycles. The CV tests were performed in a voltage window ranging from 0.0 V to 0.6 V, with scan rates varying from 500 mV s$^{-1}$ to 10 mV s$^{-1}$ (Fig. 7c). No oxidation or reduction peaks were observed in this window, with the lowest 10 mV s$^{-1}$ scan rate displaying a rounded-rectangular shape indicative of a predominantly non-faradaic charge storage mechanism. We note that the potential values recorded for this two-electrode device are different from the three-electrode CV measurement above, where a separate reference electrode was used. For the two-electrode measurements we carried out on the supercapacitor device, we restricted the scans to a range where we saw no faradaic peaks to ensure we are only probing EDLC-type capacitance behaviour. The non-symmetry of the CV curves at the higher scan rates are attributed to leakage current during the ultra-fast charging process and should not be attributed to a faradaic process. Such non-faradaic behaviour is characteristic of electric double layer capacitors, in contrast with so-called pseudocapacitors or supercapacitors, which rely on strong faradaic reactions to store charge. The areal and specific capacitances of the assembled supercapacitor device were calculated from the CV curves according to the following equations:

\[
C_{\text{areal}} = \frac{F}{\text{cm}^2} = \frac{\int V_i dV}{\Delta V \times s \times A}
\]

\[
C_{\text{specific}} = \frac{F}{g} = \frac{\int V_i dV}{\Delta V \times s \times m}
\]

where $\Delta V$ is the voltage window of the negative (cathodic) current (V), $s$ is the constant scan rate (V s$^{-1}$), $A$ is the average geometric area of the two electrodes (cm$^2$), and $m$ is the combined mass of the active material on both electrodes (g). The device’s areal and specific capacitances as calculated from
the CV curves spread from 53.65 mF cm\(^{-2}\) to 6.70 mF cm\(^{-2}\) and from 3.35 F g\(^{-1}\) to 0.42 F g\(^{-1}\) for scan rates increasing from 0.01 V s\(^{-1}\) to 0.5 V s\(^{-1}\). The decrease in capacitance with increasing scan rate is a common feature of EDLCs and is caused by the different time regimes of charge transport and ion diffusion for the varying scan rates. At lower scan rates, electrolytic ions have sufficient time to diffuse into the pores of the Bi\(_{13}S_{18}I_2\) active layer, increasing the charge accumulation and thus the capacitance. At higher scan rates, charge accumulation is confined to the surface of the electrodes, decreasing the electrodes' capacitances.

The galvanostatic charge–discharge measurements were similarly carried out over a 0.0–0.6 V window, with current densities varying from 2.0 mA cm\(^{-2}\) to 0.1 mA cm\(^{-2}\) (Fig. 7d). The charge–discharge curves are largely symmetric and the discharge curve displays remarkable linearity following an initial \(iR\) drop even at the lowest current densities, corroborating the non-faradaic, EDLC behaviour of the Bi\(_{13}S_{18}I_2\) supercapacitor. The areal and specific capacitances were also calculated from the slope of the discharge curves in their linear regimes according to:
where \( i \) is the constant current (A), \( \frac{dV}{dt} \) is the slope of the discharge curve taken in the voltage range 0.0–0.1 V for consistency, and \( m \) and \( A \) retain their previously defined meanings. The device’s areal and specific capacitances derived from the galvanostatic charge–discharge curves ranged from 105.34 mF cm\(^{-2}\) to 57.83 mF cm\(^{-2}\) and from 6.58 F g\(^{-1}\) to 3.61 F g\(^{-1}\) for current densities increasing from 0.1 mA cm\(^{-2}\) to 2 mA cm\(^{-2}\).

The high capacitance performance is attributed to a combination of reasons. Firstly, the X-ray structure of Bi\(_{13}\)S\(_{18}\)I\(_2\) indicates the presence of both Bi(III) and Bi(II) ions. This illustrates an ability of the Bi centre to accommodate varying charge which may explain the capacitance mechanism and would be of great interest to investigate further. The significance of Bi\(^{2+}\) is supported by the calculated band structure that was previously reported and showed the lowest unoccupied states to be predominantly derived from the Bi\(^{2+}\) centres along with contributions from the immediately-adjacent Bi\(^{3+}\) and sulfur ions. As would be expected, the highest occupied states were predominantly iodide in character. Both the valence band and conduction band showed notable dispersion, at least along some directions, pointing towards an ability to delocalise and hence accommodate the added charge. Secondly, enhanced active material coverage and homogeneity have been achieved from a new solution-deposition method, which should facilitate the electrolyte diffusion into the pores. This process is also favourable for large scale solution-based manufacturing, and using flexible carbon fibre as substrate provides the possibility for roll-to-roll production methods. Finally, pH neutral NaClO\(_4\) aqueous solution was used as the electrolyte, which has proven to be economic, eco-friendly and electrochemically superior with a wide potential window.

**Electrochemical impedance spectroscopy.** Electrochemical impedance spectroscopy (EIS) was performed to characterize the physical and electrochemical processes of the Bi\(_{13}\)S\(_{18}\)I\(_2\) supercapacitor in response to AC current at varying frequencies. All of the EIS measurements were conducted with a baseline potential of 0 V and an AC amplitude of 10 mV at frequencies ranging from 150 kHz to 0.1 Hz. Fig. 7f displays the imaginary (out-of-phase) impedance versus the real (in-phase) impedance of the Bi\(_{13}\)S\(_{18}\)I\(_2\) supercapacitor in a Nyquist plot prior to the 5000 galvanostatic charge–discharge cycles. From the Nyquist plot and the Bode plot (Fig. S10†), a modified Randles equivalent circuit was fitted and shown as an inset in the Nyquist plot to analyse the resistive and capacitive elements in the supercapacitor.

The Nyquist plot shows typical EDLC-type behaviour with a semi-circle in the high-frequency regime and a linear branch in the low-frequency region. The intercept of the high-frequency end of the semi-circle with the real \(Z’\) axis gives the value of \(R_1\) in the equivalent circuit, representing the combined resistance due to the aqueous NaClO\(_4\) electrolyte and the resistance in the current collectors, often referred to as equivalent series resistance (ESR). Since all charge migration during the charge–discharge process occurs through the electrolyte, \(R_1\) is fitted in series with the other circuit elements and found to have a value of 0.89 Ω (Table 2). The curvature and diameter of the semi-circle are simulated with constant phase element \(Q_1\) and resistor \(R_2\), which are fitted in parallel to represent the two
Table 2  Electrochemical impedance spectroscopy equivalent circuit elements, for Bi13S18I2 supercapacitor both before and after 5000 cycles

<table>
<thead>
<tr>
<th>Circuit element</th>
<th>Value before cycles</th>
<th>Value after cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>0.89 Ω</td>
<td>0.81 Ω</td>
</tr>
<tr>
<td>$Q_1 - n$</td>
<td>0.80</td>
<td>0.85</td>
</tr>
<tr>
<td>$Q_3 - Y_0$</td>
<td>22.8 μ(F s$^{-0.20}$)</td>
<td>13.0 μ(F s$^{-0.15}$)</td>
</tr>
<tr>
<td>$R_2$</td>
<td>16.8 Ω</td>
<td>19.0 Ω</td>
</tr>
<tr>
<td>$W - Y_0$</td>
<td>0.45 Ω$^{-1}$ s$^{1/2}$</td>
<td>0.45 Ω$^{-1}$ s$^{1/2}$</td>
</tr>
<tr>
<td>$Q_2 - n$</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>$Q_3 - Y_0$</td>
<td>71.0 m(F s$^{-0.05}$)</td>
<td>70.0 m(F s$^{-0.05}$)</td>
</tr>
</tbody>
</table>

Table 2 continued

Element $Q_3$ in series with $R_2$ and $W$ with an ideality factor $n = 0.95$ and $Y_0 = 71$ m(F s$^{-0.05}$)$^{1.05}$. The high $n$ value suggests that $Q_3$ acts very nearly as an ideal capacitor, and the $Q_3 - Y_0$ closely matches the measured device capacitances derived from the CV and galvanostatic charge-discharge curves at lower scan rates or currents. We attribute this second, low-frequency regime capacitance to strong electrostatic charge storage once the electrolytic ions fully diffuse into the pores of the active Bi$_{13}$S$_{18}$I$_2$ layer.

EIS was also used to characterize the stability of the Bi$_{13}$S$_{18}$I$_2$ supercapacitor after the 5000 charge–discharge cycles. Fig. S11† compares the experimental Nyquist plot for the same Bi$_{13}$S$_{18}$I$_2$ supercapacitor before and after the cycle stability test was performed. While the low-frequency behaviour remained largely the same after cycling, $R_1$ decreased slightly from 0.89 Ω to 0.81 Ω, $Q_1 - Y_0$ decreased from 22.8 μ(F s$^{-0.20}$) to 13.0 μ(F s$^{-0.15}$), and $R_2$ increased from 16.8 Ω to 19.0 Ω. The slight decrease in the electrolyte resistance $R_1$ is likely due to surface film and electrolyte conditioning after multiple cycles, while the simultaneous decrease in $Q_1 - Y_0$ and increase in $R_2$ may be due to mechanical wear, decreased surface area of the active layer, and trapped ions inside the surface pores of the electrodes. The largely unchanged low-frequency behaviour, however, proves the long-term electrochemical stability of the Bi$_{13}$S$_{18}$I$_2$ active layer, as long-term pore penetration and ion diffusion does not significantly affect the low-frequency diffusion and capacitive elements.

Conclusions

We have demonstrated the first facile, low-temperature, and solution-processing synthesis of both powder and thin-film samples of a relatively-unexplored bismuth chalcohalide material, Bi$_{13}$S$_{18}$I$_2$. The optimal ratio for the Bi(x)I$_3$ and BiI$_3$ precursors has been studied and established, and the crystal structure of deposited thin films match the theoretical pattern calculated by powder XRD measurements. The elemental composition of Bi$_{13}$S$_{18}$I$_2$ has been verified by XPS, and the direct and indirect band gap values (0.68 eV and 0.92 eV, respectively) are characterized via diffuse reflectance measurements. The energy level diagram for Bi$_{13}$S$_{18}$I$_2$ has been estimated based on electrochemistry techniques, using solid state Bi$_{13}$S$_{18}$I$_2$ on FTO as the working electrode. In an extensive supercapacitor device study, Bi$_{13}$S$_{18}$I$_2$ has been employed as the active material in an EDLC device, and a simple and economical electrode fabrication process has been demonstrated. Optimization of the active material deposition via solution-processing methodology and choice of electrolyte solution have together enhanced the EDLC performance. Utilizing a high mass loading (7–8 mg cm$^{-2}$) of active material and saturated aqueous sodium perchlorate as the electrolyte, we have achieved a non-faradaic EDLC with a superior areal capacitance of 210.68 mF cm$^{-2}$ and an excellent 99.7% capacitance retention over 5000 charge–discharge cycles. The EDLC mechanism is supported by the lack of any redox peaks in the cyclic voltammogram and a largely linear galvanostatic discharge curve, suggesting the capacitance derives from the transfer of delocalised electrons, a mechanism which is also consistent with the reported band structure. For the
first time, we have proven that Bi₁₃S₁₈I₂-based electrodes can be fabricated from solution and integrated in low-cost, commercially-viable supercapacitors featuring promising energy storage capabilities and excellent long-term cycle stability.

**Experimental**

**Materials**
All reagents were obtained from commercial suppliers (Acrós Organics, Sigma Aldrich, Fluka) and used as received, unless otherwise stated. Solvents used were of analytical grade (Sigma Aldrich, Fisher Scientific, VWR Chemicals, and Cambridge Isotope Laboratories). The following compounds and solvents were used in this experiment: bismuth(m) nitrate pentahydrate (98%), potassium xanthate (96%), bismuth iodide (99%), hydrochloric acid (37%), n,n-dimethylformamide (99.8%), dimethyl sulfoxide (>99%), deuterated acetone (99.9%), barium sulfide (99%), dichloromethane (>99.8%), ferrocene (98%), tetra-Butylammonium hexafluorophosphate (98%), activated charcoal, PTFE powder (particle size < 1 μm), butanol, and ethanol were purchased from Sigma-Aldrich. Titania paste was obtained from Greatcell Solar (18NRT-Active Opaque). ¹H NMR spectra were recorded in deuterated acetone for potassium hydrochloric acid (37%), potassium xanthate (96%), bismuth iodide (99%), sulfur dimethyl sulfoxide (>99%), deuterated acetone (99.9%), barium sulfide (99%), dichloromethane (>99.8%), ferrocene (98%), tetra-Butylammonium hexafluorophosphate (98%), activated charcoal, and PTFE powder. The chemical shifts are reported in ppm using SiMe₄ as the reference.

**Material characterizations**

Powder X-ray diffraction (PXRD) was performed on a Bruker (D8 Advance) diffractometer with monochromatic Cu-Kα radiation and wavelength of 1.5406 Å. The measurements were performed at room temperature over a 2-theta scattering angle of 5–60°, with increments of 0.1° on the 2-theta scale.

X-ray photoelectron spectra were acquired in a Thermo Scientific (VG Sigma Probe) XPS spectrometer using monochromatic Al-Kα as the source of X-rays. Scanning electron microscopy was performed by Gylen Odling using a Zeiss (SIGMA 0.1 V s⁻¹) at a constant temperature of 300 K. The chemical shifts are reported in ppm using SiMe₄ as the reference.

**EDLC studies**

The precursor solution of Bi₁₃S₁₈I₂ was made by mixing BiI₃ and Bi(III) in a molar ratio of 1:18 together with activated charcoal powder and PTFE powder in 1 mL DMF as the solvent to make a final Bi₁₃S₁₈I₂ : charcoal : PTFE mixture with a weight ratio of 85:10:5 (total mass: 565.7 mg). The resulting suspended solution was sonicated until homogenized, and around 200 μL was drop-coated onto 1 cm² of conductive carbon cloth (ELAT, NuVant Systems Inc.) substrate. Absorbing tissue was placed underneath the carbon cloth to absorb excess solution in order to maximize surface coverage and film homogeneity of the carbon cloth while reducing the mass loading of the active Bi₁₃S₁₈I₂ layer. The coated electrodes were then annealed at 150 °C for 1 h on a hotplate. The dimension of carbon cloth was measured under an optical microscope, and the mass of active material was determined by subtracting the mass of carbon cloth (density: 13 mg cm⁻², shown on the product manual) from the total mass of the dried electrode (estimated error: ±0.4 mg based on multiple repeat measurements). For the cyclic voltammetry and galvanostatic charge-discharge tests, a total of 16.0 mg of the activated Bi₁₃S₁₈I₂ layer was loaded onto two carbon cloths (dimensions: 10.2 mm × 10.9 mm, 9.8 mm × 10.9 mm). For the 5000 cycles and EIS testing, a total of 14.7 mg was loaded onto two carbon cloths (dimensions: 11.3 mm × 11.0 mm, 10.7 mm × 10.7 mm). When assembling the EDLC, two coated electrodes were separated by a thin polymer separator (Celgard 3501) pre-soaked in a saturated sodium perchlorate aqueous electrolyte solution and then sandwiched in a symmetrically assembled capacitor test cell (EC-std, EL-CELL GmbH). Electrochemical measurements were carried out by connecting the test cell in a two-electrode configuration to an Autolab potentiostat with FRA2 module using General Purpose Electrochemical System (GPES) and Frequency Response Analyzer (FRA) software. The equivalent circuit modelling was carried out with the FRA software. The control experiments with electrodes deposited from Bi₁₃S₁₈I₂ suspension were achieved by dispersing Bi₁₃S₁₈I₂ : charcoal : PTFE mixture in 1 mL ethanol, with same weight ratio and a total mass of 529.3 mg.

**Conflicts of interest**

The authors state there are no conflicts to declare.

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