Facile Synthesis and Characterization of Bi$_{12}$S$_{18}$I$_2$ Films as a Stable Supercapacitor Electrode Material

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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$_2$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$_x$ electrolyte, the Bi$_2$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$_2$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$_2$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.1–3 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.4–8 In particular, interest has grown in high-Z ns$^2$ cations with an electronic configuration of [Xe]6S$^5$Sp$^0$.9,10 Among these main group cations, bismuth has attracted considerable attention because of its low-toxicity and structural-diversity.11,12 For example, bismuth-based perovskite-like materials have been well-studied in applications such as lead-free photovoltaic devices, radiation detectors, and supercapacitor electrodes.19–20 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 chalcogenides, Bi$_2$I$_3$ and Bi$_2$Se$_3$ 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 Bi$_2$I$_3$’s exhibition of strong photocurrent,34 such Bi-chalcohalides have yet to yield satisfactory photovoltaic performance in solar cells.32 Moreover, the fabrication of bismuth chalcohalides 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 pseudocapacitors or conventional batteries that employ strong Faradaic reactions to chemically store charge.35 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

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Electronic Supplementary Information (ESI) available: [XRD spectra of different layers, SEM images, Raman, and IR spectra of electrode after cycles; Bode plot, Frequency vs. Z“ and Nyquist plot before and after 5000 cycles]. See DOI: 10.1039/x000000x
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Results and Discussion

Material Characterization

Synthesis

\(\text{Bi}_3\text{S}_2\text{I}_2\) was synthesised via thermal decomposition of a precursor solution containing bismuth xanthate (\(\text{Bi}(\text{xt})_3\)), a sulfur-containing organobismuth material, and \(\text{BiI}_3\). \(\text{Bi}(\text{xt})_3\) was synthesized from potassium xanthate and bismuth nitrate. A wide range of \(\text{Bi}(\text{xt})_3:\text{BiI}_3\) 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°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.

\[
\begin{align*}
\text{a Bi} & \text{ (xt)} + \text{b BiI}_3 \xrightarrow{150 \text{C}} \text{Bi}_3\text{S}_2\text{I}_2 + \text{CS}_2 \uparrow + \text{CO} \uparrow + \text{CO}_2 \uparrow
\end{align*}
\]

Scheme 1. Synthesis of \(\text{Bi}_3\text{S}_2\text{I}_2\) from different ratios (a:b) of a \(\text{Bi}(\text{xt})_3:\text{BiI}_3\) precursor solution.

Structural and Electronic Characterization

The diffraction patterns obtained for thin films with 2:1, 10:1, and 18:1 ratios of the \(\text{Bi}(\text{xt})_3:\text{BiI}_3\) precursor solution are recorded in Figure 1. A crystallographic XRD pattern corresponding to \(\text{Bi}_3\text{S}_2\text{I}_2\) 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 with XRD (Figure S2) displaying both \(\text{Bi}_3\text{S}_2\text{I}_2\) and \(\text{Bi}_3\text{S}_3\) crystal peaks, suggesting that the sulfur concentration of the precursor solution was too high. Under these considerations, a 18:1 \(\text{Bi}(\text{xt})_3:\text{BiI}_3\) ratio was ultimately selected for further syntheses and characterization of the thin films. We note that \(\text{Bi}_3\text{S}_2\text{I}_2\) has been previously reported as \([\text{Bi}]:\text{BiI}_3]_2[\text{BiI}_3]_{18}^{38}\) and \(\text{Bi}_3\text{S}_2\text{I}_2]_{18}^{38}\) prompting Groom and colleagues to reconsider the crystal structure and propose the formula \(\text{Bi}_3\text{S}_2\text{I}_2]\) which we adopt in our study. \(\text{Bi}_3\text{S}_2\text{I}_2\) contains \(\text{BiI}_3]\) dimers, which justifies the close proximity of the bismuth cations positioned at the origin of the unit cell (Figure 2).

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 Figure S3 and the characteristic \(\text{Bi}_3\text{S}_2\text{I}_2\) pattern is most clearly identified with the samples containing 3 and 5 layers. Figure 3 displays the SEM images of the as-prepared \(\text{Bi}_3\text{S}_2\text{I}_2\). As the number of layers increases, the nano-particle crystals grow longer tubule-like nano-rod structures approaching 250 nm in length. This suggests that increased surface area may be achieved by multiple-layer deposition of \(\text{Bi}_3\text{S}_2\text{I}_2\) 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.

Figure 4 depicts the X-ray photoelectron spectra (XPS) of an 18:1 thin film on FTO-coated glass with a mesoporous TiO\(_2\) 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 \(\text{Bi}_3\text{S}_2\text{I}_2\). Diffuse
reflectance measurements were also conducted to obtain the optical band gap of Bi$_{13}$S$_{18}$I$_2$ in its solid state. An indirect energy gap (E$_{g\text{ind}}$) of 0.75 eV and a direct energy gap (E$_{g\text{dir}}$) 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 Bi$_{13}$S$_{18}$I$_2$. The cyclic voltammograms in Figure S4 represent an average of 5 cycles at a sweep velocity of 0.1 V/s. The full CV scans indicate that Bi$_{13}$S$_{18}$I$_2$ 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). The electronic band gap of solid-state Bi$_{13}$S$_{18}$I$_2$ is estimated to be 0.99 V for the sample sweep at 0.1 V/s, calculated from the difference in E$^\text{pa}$ and E$^\text{pc}$ values and consistent with diffuse reflectance.

Table 1. Atomic percentages of elements present in thin film shown by XPS compared with theoretical values in Bi$_{13}$S$_{18}$I$_2$

<table>
<thead>
<tr>
<th>Element/Orbital</th>
<th>At. %</th>
<th>Total At. % in Bi$<em>{13}$S$</em>{18}$I$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi / 4d 3</td>
<td>18.16</td>
<td>38.52 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 6.06</td>
</tr>
<tr>
<td>I / 3d 5</td>
<td>4.16</td>
<td></td>
</tr>
<tr>
<td>S / 2s</td>
<td>53.42</td>
<td>54.55</td>
</tr>
</tbody>
</table>

Figure 3. SEM images for (a) one, (b) three, and (c) five layers of Bi$_{13}$S$_{18}$I$_2$ on conductive FTO glass substrate.

Figure 4. High resolution X-ray photoelectron spectrum of Bi 4f, S 2p (a), I 3d (b) for a thin Bi$_{13}$S$_{18}$I$_2$ film. Specific peaks are labelled with their corresponding electronic orbitals.
Supercapacitor Studies

Electrode Preparation

The performance of Bi$_2$S$_3$I$_2$ 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 Bi$_2$S$_3$I$_2$-based electrodes were fabricated with a facile, single-step, and solution-processable procedure. An 18:1 mixture of Bi(xt)$_3$ and Bi$_3$ 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 Bi$_2$S$_3$I$_2$ : charcoal : PTFE upon subsequent thermal decomposition of the Bi(xt)$_3$. 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 Bi$_2$S$_3$I$_2$ constitutes the primary active material for the supercapacitor electrodes, the activated charcoal and PTFE are added for enhanced electrical conductivity and mechanical stability respectively of the overall layer. The powder XRD pattern of as-prepared Bi$_2$S$_3$I$_2$ electrode is shown in Figure 6, and the crystallite size of Bi$_2$S$_3$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$_2$S$_3$I$_2$ material, with rod-shaped Bi$_2$S$_3$I$_2$ layering on top of the carbon cloth as well as binding directly to the carbon fibres (Figure 7b). A thin (25µm) 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 (EC-standard, EL-CELL GmbH) for tight packing and ease of measurement (Figure 7a).

Cyclic Voltaometry and Galvanostatic Charge-Discharge Tests

The predominant charge storage mechanism of the Bi$_2$S$_3$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$^{-1}$ (Figure 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 supercapacitators, 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:

$$C_{\text{areal}} = \frac{\iota}{\Delta V} \times \frac{i}{dV/dt} \times A$$

$$C_{\text{specific}} = \frac{\iota}{\Delta V} \times \frac{i}{dV/dt} \times m$$

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$_2$S$_3$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$^{-2}$ (Figure 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$_2$S$_3$I$_2$ supercapacitor. The areal and specific capacitances were also calculated from the slope of the discharge curves in their linear regimes according to:

$$C_{\text{areal}} = \frac{\iota}{\Delta V} \times \frac{i}{dV/dt} \times A$$

$$C_{\text{specific}} = \frac{\iota}{\Delta V} \times \frac{i}{dV/dt} \times m$$

Figure 5. Tauc plots for the estimation of direct (a) and indirect (b) band gaps of Bi$_2$S$_3$I$_2$. Schematic diagram of the energy levels of Bi$_2$S$_3$I$_2$, estimated from electrochemistry measurements.
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\(^{-2}\). Pious and colleagues previously integrated (CH\(_3\)NH\(_2\))\(_2\)Bi\(_4\)I\(_{16}\) in a similar symmetric EDLC device and reported an electrode areal capacitance of 5.5 mF cm\(^{-2}\). Since our supercapacitor device employs two symmetrical electrodes in series, the electrode capacitance is equal to twice the device capacitance, or 210.68 mF cm\(^{-2}\) for our best trial at the lowest tested current density. The energy density and power density calculated from CV and Galvanostatic charge-discharge measurements are summarized in Table S2, and the energy density can be potentially increased by operating in a larger potential window. Control experiments were carried out showing that the capacitance arises from Bi\(_{13}\)S\(_{18}\)I\(_2\) rather than the carbon cloth substrate or additives (Figure S5, Table S3). In addition, an electrode prepared from Bi\(_{13}\)S\(_{18}\)I\(_2\) powder suspension was also tested, showing only about 1/10 capacitance compared to solution-processed Bi\(_{13}\)S\(_{18}\)I\(_2\) electrode (Figure S6, Table S4). This is caused by inferior surface area of the active material Bi\(_{13}\)S\(_{18}\)I\(_2\) in powder form as shown in the SEM images (Figure S7).

The long-term cycle stability of the Bi\(_{13}\)S\(_{18}\)I\(_2\) electrodes was evaluated by performing 5000 sequential galvanostatic charge-discharge cycles at the high current density of 2 mA cm\(^{-2}\) (Figure 7e). Even after 5000 cycles, the device retains 99.7% of its initial capacitance, demonstrating the electrodes’ remarkable stability under intense electrical conditions. Moreover, SEM images of electrodes after undergoing the 5000 cycles indicate that the surface coverage of the carbon fibres with the activated Bi\(_{13}\)S\(_{18}\)I\(_2\) remained largely the same after cycling (Figure S8). We note however that limited information can be gleaned from the SEM images, as the electrodes become heavily coated and obscured with crystallized NaClO\(_4\) after use in the supercapacitor device. Still, the FTIR and Raman spectra of the electrodes after cycling display the same vibrational peaks as those of the non-tested electrodes with no significant shifts in the peak wavelengths or Raman shifts (Figure S9), indicating that the Bi\(_{13}\)S\(_{18}\)I\(_2\) material underwent no systematic chemical degradation during the 5000 cycles. The drastically reduced intensity of the Raman spectrum for the cycled-electrodes is likely due to the thick NaClO\(_4\) coating concealing the active layer. Finally, XRD was utilized to evaluate the crystal structural integrity of Bi\(_{13}\)S\(_{18}\)I\(_2\) over the 5000 cycles. Figure 6 compares the electrodes’ XRD pattern both before and after the 5000 cycles with the XRD peaks calculated for the pure Bi\(_{13}\)S\(_{18}\)I\(_2\) powder. Although the intensity of Bi\(_{13}\)S\(_{18}\)I\(_2\)’s XRD peaks also drop after cycling, the persistent peaks near 24\(^\circ\), 28.5\(^\circ\), 30\(^\circ\), and 32\(^\circ\) demonstrate that the Bi\(_{13}\)S\(_{18}\)I\(_2\) largely retains its crystal morphology throughout the electrochemical cycling. The extra, sharp peaks are attributed to crystalline NaClO\(_4\) and exposed carbon cloth fibres.

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\(^{41}\) 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. \(^{44}\)

**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. Figure 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 (Figure 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 R₁ in the equivalent circuit, representing the combined resistance due to the aqueous NaClO₄ 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, R₁ 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 Q₁ and resistor R₂, which are fitted in parallel to represent the two possible behaviours of the electrolyte during the charging and discharging of the supercapacitor. At higher frequencies or shorter charging times, the electrolytic ions have insufficient time to penetrate the surface of the Bi₃S₃I₈ electrodes, instead forming an electrostatic capacitive layer at the surface of the electrodes highlighted in Figure 7a. This electrostatic capacitor is modelled with a constant phase element Q₁ with an ideality factor of 0.80, signifying an imperfect capacitor, and a relatively limited Y₀ of 22.8 μ(F s⁻¹ 0.20) 1.25. Y₀ is the numerical value of admittance at ω=1 rad/s, 43 and Q₁ − Y₀ is given by the Frequency Response Analyser EIS software as:

\[ Z = \frac{1}{(Y₀/\omega)^n} \]

where Z is the complex impedance, \( j = \sqrt{-1} \), \( \omega \) is the angular frequency, and \( n \) is the ideality factor. Q₁ − Y₀ can be crudely approximated as the capacitance of the CPE with units of Farads, but such false-equivalence has been strongly criticized.45 Instead, we report Y₀ with its proper units of \((F s^{n-1})^{1/n}\) to avoid confusion, but note that at high \( n \) (\( n = 1 \)), the approximation \( Y₀ = C \) becomes increasingly valid. The non-ideality of Q₁ is attributed to surface roughness and uneven coverage of the carbon cloth with the activated Bi₃S₃I₈ layer, which is apparent in the SEM images of the coated electrodes (Figure 7b). At moderate frequencies, however, the ions penetrate the electrodes’ active layer, introducing R₂ with a calculated value of 16.8 Ω, representing the charge transfer resistance and the bulk resistance of the active material and electrode pores. In series with R₂ is a Warburg impedance element W, a characteristic feature of a Randles circuit that simulates the charge transport and mass diffusion of the electrolyte into the activated electrodes at mid to low frequencies. The fitted Warburg impedance gives a so-called Warburg coefficient

\[ \sigma = \frac{1}{\sqrt{2} Y₀} \]

with W − Y₀ giving the admittance of the impedance at an angular frequency of 1 rad/s. Our simulated W gives W − Y₀ = 0.45 Ω⁻¹ s¹/². A simple Randles circuit without the addition of Q₂ will produce linear behaviour with a 45° angle with respect to the Z’ axis, characteristic of the Warburg diffusion element. The Nyquist plot for our experimental data, however, displays linear behaviour with a much steeper angle approaching 81.8°. To model this increased slope, we add a second constant phase element Q₂ in series with R₂ and W with an ideality factor \( n = 0.95 \) and Y₀ = 71 m(F s⁻¹ 0.05) 1.05. The high n value suggests that Q₂ acts very nearly as an ideal capacitor, and the Q₂ − Y₀ 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 Bi₃S₃I₈ layer.

<table>
<thead>
<tr>
<th>Circuit Element</th>
<th>Value Before Cycles</th>
<th>Value After Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>0.89 Ω</td>
<td>0.81 Ω</td>
</tr>
<tr>
<td>Q₁ − n</td>
<td>0.80</td>
<td>0.85</td>
</tr>
<tr>
<td>Q₁ − Y₀</td>
<td>22.8 μ(F s⁻¹ 0.20) 1.25</td>
<td>13.0 μ(F s⁻¹ 0.15) 1.18</td>
</tr>
<tr>
<td>R₂</td>
<td>16.8 Ω</td>
<td>19.0 Ω</td>
</tr>
<tr>
<td>W</td>
<td>0.45 Ω⁻¹ s¹/²</td>
<td>0.45 Ω⁻¹ s¹/²</td>
</tr>
<tr>
<td>Q₂ − n</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>Q₂ − Y₀</td>
<td>71.0 m(F s⁻¹ 0.05) 1.05</td>
<td>70.0 m(F s⁻¹ 0.05) 1.05</td>
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</table>

EIS was also used to characterize the stability of the Bi₃S₃I₈ supercapacitor after the 5000 charge-discharge cycles. Figure S11 compares the experimental Nyquist plot for the same Bi₃S₃I₈ supercapacitor before and after the cycle stability test was performed. While the low-frequency behaviour remained largely the same after cycling, R₁ decreased slightly from 0.89 Ω to 0.81 Ω, Q₁ − Y₀ decreased from 22.8 μ(F s⁻¹ 0.20) 1.25 to 13 μ(F s⁻¹ 0.15) 1.18, and R₂ increased from 16.8 Ω to 19.0 Ω. The slight decrease in the electrolyte resistance R₁ is likely due to surface film and electrolyte conditioning after multiple cycles, while the simultaneous decrease in Q₁ − Y₀ and increase in R₂ 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 Bi₃S₃I₈ active layer, as long-term pore penetration and ion diffusion does not significantly affect the low-frequency diffusion and capacitive elements.
Figure 7. a) Schematic diagram of the EDLC in our study. b) SEM image of an as-prepared Bi$_{13}$S$_{18}$I$_2$ electrode on carbon cloth. c) Cyclic voltammograms of the Bi$_{13}$S$_{18}$I$_2$-based EDLC at varying scan rates. d) Galvanostatic charge–discharge curves of the Bi$_{13}$S$_{18}$I$_2$-based EDLC. e) Capacitance retention of the Bi$_{13}$S$_{18}$I$_2$-based EDLC over 5000 cycles. (f) Experimental (black) and simulated (red) Nyquist plots, with equivalent circuit inserted.

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$I_y$)$_3$ 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 $\text{Bi}_2\text{S}_3\text{I}_2$ on FTO as the working electrode. In an extensive supercapacitor device study, $\text{Bi}_2\text{S}_3\text{I}_2$ 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 $\text{Bi}_2\text{S}_3\text{I}_2$-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 (Acrôs 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 (III) 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%), tetrabutylammonium 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). $^1$H NMR spectra were recorded in deuterated acetone for potassium xanthate and bismuth xanthate on a 500 MHz Bruker AV III (Avs500) at a constant temperature of 300 K. The chemical shifts are reported in ppm using SiMe$_4$ 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 Oding using a Zeiss (SIGMA HD VP) Field Emission-SEM. Diffuse reflectance measurements for powder and thin film samples of $\text{Bi}_2\text{S}_3\text{I}_2$ were recorded on a Jasco (V-670) spectrophotometer with SpectraManager software. The powder sample was prepared by mixing thin film material with a barium sulphite ($\text{BaSO}_4$) matrix in a 5:95 weight ratio. The Kubelka-Munk function was used to analyse the diffuse reflectance data, and Tauc plots were constructed to obtain the optical $E_g$ for direct and indirect transitions. Cyclic voltammetry measurements were performed using a three-electrode cell with the spin-coated $\text{Bi}_2\text{S}_3\text{I}_2$ on FTO-coated glass on top of a mesoporous TiO$_2$ layer as the working electrode. The sample was placed in dichloromethane, using tetrabutylammonium hexafluorophosphate (0.3 M) as the supporting electrolyte, platinum as a counter electrode, and a Ag/AgCl reference electrode. The cyclic voltammetry was recorded in an Autolab (Type III) potentiostat at linear scan rates of 0.5 V s$^{-1}$, 0.2 V s$^{-1}$, and 0.1 V s$^{-1}$. The samples were cycled 5 times at each sweep speed and the average obtained, with degassing of the solvent under N$_2$ before each measurement. The redox process of the ferrocenium/ferrocene couple was recorded to be used as the internal standard. The FT-IR spectra were recorded using Perkin Elmer FT-IR Spectrum 65 range from 400 to 4000 cm$^{-1}$, with resolution of 4 cm$^{-1}$. Raman spectra were acquired from a Renishaw InVia Raman Microscope with the excitation laser wavelength of 785 nm, with a spectral resolution of roughly 1 cm$^{-1}$.

**EDLC Studies**

The precursor solution of $\text{Bi}_2\text{S}_3\text{I}_2$ was made by mixing BiI$_3$ and Bi(II) 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 $\text{Bi}_2\text{S}_3\text{I}_2$: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 cm$^2$ 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 $\text{Bi}_2\text{S}_3\text{I}_2$ 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 $\text{Bi}_2\text{S}_3\text{I}_2$ layer was loaded onto two carbon cloths (dimensions: 10.2 mm x 10.9 mm, 9.8 mm x 10 mm). For the 5000 cycles and EIS testing, a total of 14.7 mg was loaded onto two carbon cloths (dimensions: 11.3 mm x 11.0 mm, 10.7 mm x 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 (GEPES) and Frequency Response Analyser (FRA) software. The equivalent circuit modelling was carried out with the FRA software. The control experiments with electrodes deposited from Bi$_2$S$_3$O$_3$ suspension were achieved by dispersing Bi$_2$S$_3$O$_3$; 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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Notes and References

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