Direct tuning of electrical properties in nano-structured Bi$_2$Se$_{0.3}$Te$_{2.7}$ by reversible electrochemical lithium reactions

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Lithium intercalation and de-intercalation processes have been used to fabricate bulk Bi$_2$Se$_{0.3}$Te$_{2.7}$ with internal nanostructures. The doped Li content can be precisely controlled through this method. It provides a chance to directly optimize electrical properties when preparing nano-structured materials, leading to the optimum carrier concentration for improved thermoelectric figure of merit.

Nano-structure designs provide an additional opportunity for further optimization of thermoelectric (TE) performance, which is evaluated by the dimensionless TE figure of merit ZT (ZT = $S^2T/k$), where $S$ is Seebeck coefficient, $\sigma$ is electrical conductivity, $T$ is absolute temperature, and $k$ is thermal conductivity. Either low dimensional structures like superlattices and nano-wire arrays, or internal nano-structures within three-dimensional bulk matrices such as nano-inclusions and nano-crystals could effectively decrease the lattice thermal conductivity ($k_L$), resulting in the enhancement of ZT in many types of TE materials, e.g., Bi$_2$Te$_3$, PbTe, SiGe, Skutterudites and even Si. Nevertheless, except for the reduced $k_L$, another aspect that should not be neglected to achieve optimum ZT values in nano-structured TE materials is the optimization of charge carrier concentration and electrical transport properties. In this communication, a novel three-step approach, involving a quick spark plasma sintering (SPS) technique and reversible electrochemical lithium intercalation and de-intercalation reactions, has been applied to prepare nano-structured Bi$_2$Se$_{0.3}$Te$_{2.7}$ TE material with well controlled carrier concentration, providing a direct opportunity to simultaneously optimize electrical and thermal properties during the synthesis of nano-structured TE materials.

Similar to Bi$_2$Te$_3$, Bi$_2$Se$_{0.3}$Te$_{2.7}$ has hexagonal structure, consisting of five layered lamellas (called quintuples) in the form of [Te$_{10}$(1), Se$_{10}$(1)]–Bi–[Te$_{10}$(2), Se$_{10}$(2)]–Bi–[Te$_{10}$(1), Se$_{10}$(1)]. Within each lamella, all the atoms are bonded covalently, but the neighboring quintuple layers are loosely held together by weak van der Waals bonds, which makes the intercalation of small atoms like lithium possible. Scheme 1 illustrates the fabrication method. It contains three steps. The first one is to intercalate Li into the van der Waals gap between the connected [Te$_{10}$(1), Se$_{10}$(1)]–[Te$_{10}$(2), Se$_{10}$(2)] layers of micro-sized Bi$_2$Se$_{0.3}$Te$_{2.7}$ powder using an electrochemical discharging process described in ref. 16 and ref. 22. In the second step, a reversed electrochemical lithium de-intercalation process was carried out by recharging the lithium cell using constant electrical currents to pull out a controlled amount of intercalated Li atoms from Bi$_2$Se$_{0.3}$Te$_{2.7}$. Finally, the obtained Bi$_2$Se$_{0.3}$Te$_{2.7}$ nano- and nano-scale composite scaled powders with a controlled residual lithium content were taken out of the cell, rinsed in acetone and sintered into bulk nano-structured material using spark sintering (SPS).

Fig. 1a shows the cyclic voltamogram of the reversed electrochemical lithium intercalation and de-intercalation reactions with Bi$_2$Se$_{0.3}$Te$_{2.7}$ (see the lithium intercalation and deintercalation curves in Fig. S1, ESI†). During the lithium intercalation and de-intercalation processes, the surface layer of original micro-scaled powder has been exfoliated into nano-scaled Bi$_2$Se$_{0.3}$Te$_{2.7}$ particles with scale around 10 nm (see more details in Fig. S2 and S3, ESI†). By following SPS,
Usually the intercalated Li atoms in Bi$_2$Se$_{0.3}$Te$_{2.7}$ donate their valence charges into the matrix crystal, which could be used to tune the carrier concentration and thereby electrical properties in these nano-structured Bi$_2$Se$_{0.3}$Te$_{2.7}$ samples. A sandwich-like nano/micro composite crystalline structure, in which nano-scaled grains sandwiched within the laminars of micro-scaled grains, has been obtained. Fig. 1b and c show its SEM image of fractured surface morphology both parallel and perpendicular to the SPS pressure (see XRD patterns along both directions in Fig. S4, ESI†). This structure could more effectively scatter lattice phonons. Significant decrease in $k_L$ has been achieved in both along and perpendicular to the sintering pressure directions, as shown in Fig. 1d (see more detailed thermal and electrical transportation properties in Fig. S5, ESI†).

Fixing the intercalated Li amount in the first step, the actual residual Li content (marked as $x$) in Li$_x$Bi$_2$Se$_{0.3}$Te$_{2.7}$ could be well controlled by the de-intercalation process during the second step. Fig. 2a shows the relationship between measured actual $x$ value (by ICP-OES) and the nominal lithium de-intercalation amount (recharging current $\times$ recharging time). The actual residual lithium amount shows a decreasing trend with the increasing nominal deintercalation lithium amount. Usually the intercalated Li atoms in Bi$_2$Se$_{0.3}$Te$_{2.7}$ donate their valence charges into the matrix crystal, which could be used to tune the carrier concentration and thereby electrical properties in these nano-structured Bi$_2$Se$_{0.3}$Te$_{2.7}$ samples.

The measured room temperature carrier concentration is shown in Fig. 2a. An unusual non-monotonic trend is observed when changing the Li content, while it should monotonically increase if only the effect of intercalated Li is accounted. Table 1 further compares the carrier concentration and carrier mobilities of Li$_x$Bi$_2$Se$_{0.3}$Te$_{2.7}$ samples with various residual lithium contents at 300 K. This abnormal behavior of carrier concentration variation could be explained by a readjustment of Bi–Te (or Se) anti-site defect concentration, which also affects the carrier concentration in bismuth chalcogenide compounds. Our original Bi$_2$Se$_{0.3}$Te$_{2.7}$ sample shows that the dominated carriers are electrons due to the deficient Se or Te atoms in the lattice. The intercalated Li atoms in Bi$_2$Se$_{0.3}$Te$_{2.7}$ are believed to more easily bond with Se atoms because of their highest electronegativity value among elements Bi, Se, and Te. In order to accept more Li atoms during electrochemical reactions, the amount of Se defects is reduced in the mixed nano- and micro-powders, leading to the lowered electron concentration. The Se defects are reduced quickly and finally saturated when increasing the intercalated Li atoms. The measured electron concentrations are thereby dominated by the Li content, leading to a continually enhanced electron concentration (see Fig. 2a and Table 1).

Two opposite mechanisms to adjust the carrier concentration are at play here: intercalated Li atoms donating electrons, and reduced density of Se defects generating holes. Combining the above two effects, we can directly optimize both electrical and thermal properties in nano-structured Bi$_2$Se$_{0.3}$Te$_{2.7}$. Fig. 2b shows the data of $\sigma$ and $S$ at 300 K.

<table>
<thead>
<tr>
<th>$x$ Value in Li$<em>x$Bi$<em>2$Se$</em>{0.3}$Te$</em>{2.7}$</th>
<th>Carrier concentration ($10^{19}$ cm$^{-3}$)</th>
<th>Carrier mobility (cm$^2$ V$^{-1}$ S$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>0 (Orig.)</td>
<td>6.52</td>
<td>195</td>
</tr>
<tr>
<td>0.09</td>
<td>3.47</td>
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<tr>
<td>0.11</td>
<td>2.78</td>
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<tr>
<td>0.18</td>
<td>3.62</td>
<td>166</td>
</tr>
<tr>
<td>0.30</td>
<td>6.26</td>
<td>155</td>
</tr>
</tbody>
</table>

Fig. 1 (a) Cyclic voltammogram of reversible lithium reactions with Bi$_2$Se$_{0.3}$Te$_{2.7}$ (with scanning speed of 50 mV s$^{-1}$, and scope of 1 V–3 V). (b), (c) SEM images of fractured surface morphologies both parallel (b) and perpendicular (c) to SPS pressure in nano-micro-composite crystalline bulk Li$_{0.11}$Bi$_2$Se$_{0.3}$Te$_{2.7}$ (the insets show morphologies of the nano-scaled grains with larger magnification). (d) Lattice thermal conductivity of as-fabricated nano/micro composite crystalline Li$_{0.11}$Bi$_2$Se$_{0.3}$Te$_{2.7}$ (NM) in directions both perpendicular ($\perp$) and parallel ($\parallel$) to SPS pressure, compared with Bi$_2$Se$_{0.3}$Te$_{2.7}$ samples SPSed using pristine micro-powders under same conditions (M).

Fig. 2 (a) Carrier concentrations as a function of Li content at 300 K, together with the relationship between residual Li content ($x$) measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) in nano-structured Bi$_2$Se$_{0.3}$Te$_{2.7}$ and nominal de-intercalation lithium amount (fixing intercalation lithium amount as 25 mAh g$^{-1}$); (b) Seebeck coefficient and electrical conductivity as a function of Li content at 300 K.

Table 1 Hall measurement for Li$_x$Bi$_2$Se$_{0.3}$Te$_{2.7}$ fabricated through lithium intercalation/deintercalation reactions at 300 K.
Similar to electron concentration, $S$ (or $\sigma$) initially increases (or decreases) in magnitude when $x$ values are from 0.05 to 0.15. When $x$ is larger than 0.15, absolute $S$ (or $\sigma$) gradually decreases (or increases). For $x$ around 0.15, the lowest carrier concentration and electrical conductivity, and the highest absolute $S$ are obtained; leading to an enhancement of the maximum $ZT$ of more than 20% (see Fig. S5, ESI†).

In summary, a new three-step approach, based on reversible electrochemical lithium reactions, has been demonstrated to fabricate bulk $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ with internal nanostructure. The doped Li content can be well controlled to realize optimum carrier concentration for electrical properties and TE performance.

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Notes and references