Due to the increasing energy demand and public awareness of climate change and environmental problems, sustainable energy development has become one of the most strategic areas of research. In this work, a hybrid layered thermoelectric material is produced, which consists of the combination of poly(3,4-ethylenedioxythiophene) (PEDOT) and tin sulfide (SnS). The films are produced by the electrochemical deposition of SnS on the surface of a PEDOT electrode. The thermoelectric properties are optimized by controlling the doping level of SnS by adding Ag. As a consequence, the power factor is remarkably improved up to 58.6 μW m⁻¹ K⁻², which is more than two orders of magnitude higher than that of the undoped materials.

1. Introduction

Increasing energy demand is a central component of society, from feeding our energy-hungry appliances to powering our factories of the future. Recently, climate change, environmental concerns, UN sustainability goals, governmental emission targets and impending legislation have forced a rethink into how we source and store energy. It is clear that emerging energy harvesting systems can play a crucial role together with novel thermoelectric materials at the forefront of this new era of sustainable materials. These materials can harvest energy from waste heat, 90% of the world’s power is generated by heat engines of which more than two-thirds are lost as waste heat. Thermoelectric efficiency is determined by the power generated from the heat supplied to a device, and is described as follows:

\[
\phi_{\text{max}} = \frac{P_{\text{out}}}{Q_{\text{in}}} = \phi_C \frac{\sqrt{1+ZT_{av}} - 1}{\sqrt{1+ZT_{av}} + T_h / T_c} \tag{1}
\]

where \(Q_{\text{in}}\) is the heat that enters the device and \(P_{\text{out}}\) is power generated. \(\phi_C\) is the Carnot efficiency, \(T_h\), \(T_c\) and \(T_{av}\) are temperatures on the hot side, cold side, and the mean of the two. The \(ZT\) parameter is known as the dimensionless figure of merit:

\[
ZT = \frac{S^2 \sigma}{\kappa T} \tag{2}
\]

where \(S\) is the Seebeck coefficient, \(\sigma\) the electrical conductivity, \(\kappa\) the thermal conductivity, and \(T\) is the absolute temperature. \(ZT\) is used to compare the thermoelectric performance of materials where thermal conductivities differ. While the power factor \((PF = S^2 \sigma)\) compares the thermoelectric efficiency of materials with similar thermal conductivities.\(^{[1-7]}\) Currently, inorganic compounds such as Bi₂Te₃, PbTe, and SiGe dominate the thermoelectric market.\(^{[8-12]}\) However, the utilization of these compounds involves several disadvantages such as toxicity, scarcity of raw materials, high cost, and unsustainability. Therefore, there is enormous interest in finding alternatively sustainable, highly abundant, low-cost, and non-toxic materials. Organic semiconductors such as: conducting polymers, carbonaceous materials and nanocomposites offer an emerging alternative due to their advantageous properties such as availability, low thermal conductivity, ease of chemical modification, and large-scale production. Thermoelectric performance of conducting polymers has been increased by doping of PEDOT to enhance electrical conductivity achieving \(ZT\) values up to 0.2–0.4.\(^{[13]}\) Carbon nanostructures, in particular, carbon nanotubes (CNTs) have demonstrated excellent thermoelectric behavior in multilayer systems produced via
layer-by-layer (LbL) assembly, in particular materials based on polyaniline (PANI), double-walled carbon nanotubes (DWCNT) and graphene (1750 µW m⁻¹ K⁻¹), or PANI, DWCNT, poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS), and graphene (2710 µW m⁻¹ K⁻¹).⁴⁻¹⁵ Therefore, the development of hybrid layered materials offers an opportunity to produce highly efficient thermoelectric materials. One strategy to combine organic semiconductors with inorganic thermoelectric materials is utilizing electrochemical methods in which a thin layer of PEDOT can be used as a working electrode to produce layers of inorganic nanostructures.⁷

In this work, we have prepared layered hybrid films based on PEDOT and tin sulfide (SnS) utilizing electrochemical deposition. SnS has shown promising thermoelectric properties due to a remarkably low thermal conductivity and a high Seebeck coefficient up to 400 µV K⁻¹.⁴⁻¹⁵ In addition, SnS shows environmental benefits, because it is an abundant and non-toxic material lowering the cost compared to other inorganic materials (Te, Se, Bi).⁷ SnS in thermoelectric applications is typically synthesized using solid-state reactions at high temperatures (923 K) over a long period of time (days).⁸ However, in this work we report for the first time a quick and easy route to produce SnS films by electrochemical co-deposition in combination with a semiconductive electrode (PEDOT), enhancing the PF at room temperature compared to the state of the art synthesized via traditional solid-state reactions. In addition, we provide a complete understanding of the evolution of the thermoelectric properties based on structure/property relationships at varying temperature and dopant concentration (Ag) which has been analyzed via morphological and surface compositional changes. This work clearly establishes a new horizon for organic and hybrid thermoelectric materials allowing the manufacture of more efficient and sustainable thermoelectric devices.

2. Results and Discussion

The electropolymerization of PEDOT was carried out homogeneously on a PET-gold substrate, obtaining 100 nm thick blue colored films. PET confers flexible properties to the films while the film integrity remained after the gold removal step utilizing aqua regia.

During the electrochemical co-deposition of SnS (binary compound with an atomic ratio 1:1), the deposition potential of both elements is typically the same, $E_{\text{Sn}} = E_{\text{S}}$ with the following reactions occurring at the cathode:

\[
\begin{align*}
\text{Sn}^{2+} + 2e^- & \rightarrow \text{Sn}_{(s)} \quad (3) \\
\text{S}_2\text{O}_7^{2-} + 6\text{H}^+ + 4e^- & \rightarrow 2\text{S}_{(s)} + 3\text{H}_2\text{O} \quad (4) \\
\text{Sn}^{2+} + \text{S} + 2e^- & \rightarrow \text{SnS}_{(s)} \quad (5)
\end{align*}
\]

According to the Nernst equation, the equilibrium deposition potential of Sn and S can be expressed as follows:

\[
\begin{align*}
E_{(\text{Sn}^{2+}/\text{Sn}_{(s)})} &= E_{(\text{Sn}^{2+}/\text{Sn}_{(s)})}^0 - \frac{RT}{2F} \ln \frac{1}{(a_{\text{Sn}^{2+}})} \\
E_{(\text{S}_2\text{O}_7^{2-}/\text{S}_{(s)})} &= E_{(\text{S}_2\text{O}_7^{2-}/\text{S}_{(s)})}^0 - \frac{RT}{4F} \ln \frac{1}{(a_{\text{S}_2\text{O}_7^{2-}})(a_{\text{S}})}
\end{align*}
\]

where $E^{0}$ is the standard equilibrium potential and $a$ is the ionic activity of the ions in the bulk solution, which is related to their concentration. To establish the equilibrium potential between Sn and S, we studied different parameters such as ion concentration and pH, resulting in an optimum electrodeposition process of 10 mM of SnSO₄, 50 mM of Na₂S₂O₃ at a pH of 2.7. In addition, the temperature for the electrochemical deposition was varied from 30 to 50 °C in order to establish the optimum synthesis conditions.

Figure 1 shows the cyclic voltammetry results used to find the optimum potential for the electrodeposition of SnS:Ag on the PEDOT electrode. First, the potential was scanned in the cathodic direction, and as shown in Figure 1, the reduction of Sn²⁺ initiates at a potential of −0.39 V. Two peaks arise at −0.71 V and −0.92 V due to the active reduction of Sn²⁺. These ions react with the S, reduced from S₂O₇²⁻, to produce the SnS film.⁹⁻¹¹

Subsequently, chronoamperometry trials were performed at −0.71 V and −0.92 V for 7 h in a thermostatic bath at 30 °C using a PEDOT electrode. Results show that at −0.71 V there was no appreciable co-deposition and, therefore, −0.92 V was chosen as the fixed potential to perform chronoamperometric deposition of SnS.

![Figure 1](image-url) a) Cyclic voltammetry simulating the conditions for the electrodeposition, using PEDOT as the working electrode and b) inset of the pics in the cyclic voltammetry.
Figure 2a shows the typical cauliflower morphology of PEDOT obtained by electrodeposition.\textsuperscript{[1,4]} Once SnS is deposited on the PEDOT layer, it is homogeneously distributed on the electrode surface generating a granular morphology. However, as the amount of Ag in the solution increases, it is possible to observe hexagonal structures, SnS strands and small aggregates of silver appear (Figure 2e,f). The composition of the SnS strands has been determined utilizing energy dispersive spectroscopy (EDS) microanalysis mapping in a HRSTEM (see Figure S10, Supporting Information). The formation of hexagonal crystals at high concentrations of silver (0.25%) is explained through the formation of the Ag$_8$SnS$_6$ phase.\textsuperscript{[22]}

When the synthesis temperature increases, the hexagonal morphology of SnS is less predominant and mainly SnS threads are observed as shown in Figure 3.\textsuperscript{[23]}

XPS (Figure S3, Supporting Information) shows the presence of multiple elements, including carbon and gold, which were attributed to carbon-based contaminants from the atmosphere and traces of gold that were not completely removed by the aqua regia, respectively. The high-resolution XPS spectra of S 2p, Sn 3d and Ag 3d for PEDOT, undoped and Ag-doped SnS films are shown in Figure 4. In addition, Figure 4d shows a schematic of the relative positions of the core levels S 2p, Sn 3d and Ag 3d and the differences in binding energies. The spectrum of the S 2p for the PEDOT films shows the characteristic peaks of thiol groups and thiophene rings of the polymeric chain \textsuperscript{[24]} and the peaks of sulphone and sulfate due to the over oxidation of PEDOT. For the films with undoped PEDOT/SnS and Ag-doped PEDOT/SnS, the spectra show a binding energy of 161.28 eV which corresponds to the energy of S$^{2–}$–Sn$^{2+}$ state confirming the presence of the SnS phase,\textsuperscript{[25,26]} and the presence of silver is evidenced by a peak at 162.44 eV related to the energy of S$^{2–}$–Ag$^+$ which indicates that silver is bonded to sulfur atoms.\textsuperscript{[27]} These peaks have an energy difference of 1.16 eV which is in agreement with the oxidation state of S$^{2–}$.\textsuperscript{[28,29]} In addition, other peaks appear due to impurities of the starting reagents. The magnified XPS spectra of Sn 3d exhibited two signals at 486.64 eV and 495.04 eV, which correspond to the Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ energy levels of Sn atoms, respectively. The binding energy between Sn 3d$_{5/2}$ and
Sn 3d_5/2 is 8.40 eV, indicating the normal state of Sn^{2+} in the film. Therefore, the peaks Sn 3d_5/2 and S 2p_3/2 are related to Sn^{2+} and S^{2–} in SnS and the binding energy between them is 324.2 eV (see diagram Figure 4d) indicating the formation of a SnS phase.\(^{[25,30]}\) Finally, the high-resolution XPS spectra of Ag 3d in the films show two signals at 368.21 eV and 374.22 eV which correspond to Ag 3d_5/2 and Ag 3d_3/2, respectively, and the binding energy between them is 6.01 eV, indicating the presence of silver nanoparticles in the film.\(^{[26–28]}\) Furthermore, the high-resolution XPS spectrum at various silver concentrations (see Figure S6, Supporting Information), highlights how the 3d_5/2 Ag peak becomes wider and moves towards lower binding energies, confirming the formation of the Ag_{x}SnS_{6} phase, which presents a regular polygonal morphology as observed in the SEM images (Figure 3f).\(^{[22]}\) In summary, the magnified XPS spectrum confirms the synthesis of silver-doped tin sulfide on a PEDOT:ClO₄ layer, thereby obtaining a hybrid layered material by electrochemical co-deposition.

Figure 5 shows the results of the thermoelectric measurements for the samples prepared with different quantities of Ag. A substantial increase of the conductivity is observed with the addition of Ag due to the fact that Ag ions act as charge compensators in the SnS lattice increasing the hole carrier concentration.\(^{[26,33,34]}\) The electrical conductivity of PEDOT (80 S cm⁻¹, Figure S7, Supporting Information) decreased with the addition of the SnS layer due to the fact that non-doped SnS typically shows low values of electrical conductivity (10⁻⁴ S cm⁻¹) at room temperature.\(^{[16]}\) This supports the hypothesis that the SnS layer dominates the electric transport of the final material. Therefore, when Ag is added during the electrodeposition of SnS over a PEDOT substrate, SnS is doped according to the reaction proposed by Kanatzidis et al.:\(^{[16]}\)

\[
\text{Ag} + \text{S} \rightarrow \text{Ag}_{x}\text{SnS}_{6} + x\text{S}^{2–} + \text{h} \cdot.
\]

Thus, the enhancement of the electrical conductivity with the addition of Ag is attributed to the generation of holes (h ·) during the doping process (Equation (8)).

In addition, the change in the morphology, observed in the SEM images may contribute to an improvement in the electric transport in samples. The SnS grain boundaries are thinner and consequently, the scattering of charge carriers is reduced leading to an increase in their mobility.\(^{[26]}\) Also, the presence of SnS nano-strands may improve carrier mobility and consequently the electrical conductivity. Figure 5a clearly shows the effect of the Ag doping on the Seebeck coefficient increasing values to 69 µV K⁻¹ when the Ag-dopant concentration in the solution is 0.15%. Without Ag doping, the Seebeck coefficient values are in the order of 30 µV K⁻¹ which indicates that the Seebeck coefficient is mainly governed by the PEDOT layer since PEDOT in a reduced state presents Seebeck values around 33 µV K⁻¹ (Figure S7, Supporting Information). Typically, SnS shows high Seebeck coefficient values, around 400 µV K⁻¹, which is enhanced with the addition of low amounts of Ag (≥300 µV K⁻¹), then the Seebeck coefficient decreases to values of 300 µV K⁻¹ at higher amounts of Ag due to the increase of the carrier concentration.\(^{[16]}\) This trend is also observed in this study for the samples based on PEDOT:SnS doped with Ag, being the maximum value of Seebeck coefficient
reached 0.15%. This is explained by the increment of the Ag concentration in the SnS lattice which can modify the Fermi level energy owing to the heavy-mass band contribution. However, the values of the Seebeck coefficient reached for the samples PEDOT:SnS is not as high as SnS bulk due to the presence of the PEDOT layer. As the PF depends on the conductivity and the Seebeck coefficient, the best results were obtained for the samples with an optimized quantity of Ag in the hybrid material (0.15%). The highest PF obtained reached a value of 58.6 µW m⁻¹ K⁻², a better value than that of SnS doped with silver obtained by solid-state reactions, at 300 K. ZT can be estimated by taking into account the thermal conductivity values of the raw materials previously published, being 0.2–0.4 W m⁻¹ K⁻¹ for PEDOT and 0.8–1.4 W m⁻¹ K⁻¹ for SnS (Ag doped). Thus these materials could reach a ZT in the range of 0.01–0.05. These results evidenced that hybrid materials synthesized by electrochemical methods can contribute to the improvement of the thermoelectric efficiency in organic and inorganic materials without the need for extreme synthesis conditions. In addition, the thermoelectric efficiency of this material is quite high in terms of the power factor so this material would be an interesting alternative to the classical Bi, Pb and Te based materials that are toxic, low in abundance, and listed as critical raw materials (Bismuth).

Figures 5c,d,e show the thermoelectric properties as a function of the temperature of the synthesis. The results show a large decrease in the conductivity. This could be attributed to the different morphologies of the samples induced by the temperature. The formation of SnS:Ag wires produce a high degree of heterogeneity of the SnS coating increasing the grain boundary scattering of charge carriers. Furthermore, an increase in temperature could induce phase changes and consequently reduce the electrical conductivity. It could also increase the silver content within the SnS structure, forming Ag-related alternative phases. In addition, a decrease in the Seebeck coefficient is observed as a function of the temperature of synthesis.

In order to investigate the material reliability under mechanical stress, we have monitored the change of sheet resistance of the film, PEDOT/SnS:Ag 0.15% synthesized at 30 °C, after bending with various bending radius and through multiple bending cycles. Figure 6a indicates that there were no significant changes (less than 5%) in the sheet resistance bending the film with different radius. For the durability test, the film was repeatedly bent up to 3000 cycles with a bending radius of 20 mm. The film also shows a stable sheet resistance, decreasing around 10% after 3000 bending cycles. Under bending, the mechanical stress is mostly concentrated on the PET substrate, which is well-coated with PEDOT, and this helps to keep the electrical conductivity nearly constant under the mechanical stress. However, the layer of SnS:Ag is not flexible and after 1800 bindings it starts to crack and, therefore, the sheet resistance decreases at a higher rate. These results show a tremendous potential for room temperature thermoelectric applications since SnS and PEDOT are combined with a low-cost, easy and scalable synthetic route to develop hybrid films.
PEDOT:ClO$_4$ were obtained by electrodeposition on a polyethylene substrate in a three-electrode system equipped with a microfocused monochromatic X-ray source (1486.58 eV). The morphology of the films is influenced by the addition of Ag and the temperature of their synthesis. Structural analysis indicates the presence of Ag$_8$SnS$_6$ which is shown to negatively influence the thermoelectric properties of the films. Electrical conductivity increases as a function of Ag content while the Seebeck coefficient is optimum at an Ag concentration of 0.15% in the electrochemical solution. The maximum power factor observed is 58.6 $\mu$W m$^{-1}$ K$^{-2}$, achieved at 0.15% Ag. These values represent a clear improvement in the efficiency of hybrid organic thermoelectric materials based on sustainable raw materials compared to the state of the art. In addition, PEDOT/SnS:Ag films have high flexibility due to the PET substrate allowing 1800 bending cycles with a radius of 20 mm with little influence on electrical resistance. Overall, the results obtained in this work show the enormous potential of these layered materials in thermoelectric applications where flexible materials are required.

3. Conclusion

Sustainable thermoelectric materials that can allow the efficient conversion of waste heat from areas as diverse as heat engines to biological processes are of growing social, environmental, and commercial importance. Here, hybrid layered thin films of PEDOT/SnS doped with Ag were successfully synthesized utilizing electrochemical co-deposition. The morphology of the films is influenced by the addition of Ag and the temperature of their synthesis. Structural analysis indicates the presence of Ag$_8$SnS$_6$ which is shown to negatively influence the thermoelectric properties of the films. Electrical conductivity increases as a function of Ag content while the Seebeck coefficient is optimum at an Ag concentration of 0.15% in the electrochemical solution. The maximum power factor observed is 58.6 $\mu$W m$^{-1}$ K$^{-2}$, achieved at 0.15% Ag. These values represent a clear improvement in the efficiency of hybrid organic thermoelectric materials based on sustainable raw materials compared to the state of the art. In addition, PEDOT/SnS:Ag films have high flexibility due to the PET substrate allowing 1800 bending cycles with a radius of 20 mm with little influence on electrical resistance. Overall, the results obtained in this work show the enormous potential of these layered materials in thermoelectric applications where flexible materials are required.

4. Experimental Section

3,4-Ethénylenedioxytiophene (EDOT, 97%) and lithium perchlorate (LiClO$_4$) were purchased from Alfa Aesar, tin (II) sulfate (SnSO$_4$, 97%) and sodium thiosulfate (Na$_2$S$_2$O$_3$, 99%) were purchased from Acros Organics, silver nitrate (AgNO$_3$, ≥99%) was obtained from Sigma-Aldrich and, acetonitrile and sulfuric acid (95%) were purchased from VWR Chemicals. All the chemicals were used as received and no further modification or purification was carried out.

**Electrodeposition of Poly(3,4-ethénylenedioxytiophene):** Thin films of PEDOT:ClO$_4$ were obtained by electrodeposition on a polyethylene terephthalate (PET) substrate as follows. First, a gold layer was deposited on the PET substrate by evaporation in a vacuum chamber (Univex 300 evaporation system) at a pressure of $10^{-5}$ mbar. The gold films were about 40 nm. Once the PET substrates were coated with gold, the electrochemical deposition of PEDOT:ClO$_4$ was carried out on said substrate in a three-electrode cell with a 0.01 m EDOT solution, and 0.1 m LiClO$_4$ applying a current of 3 mA for 30 s. The working electrode was the PET-gold substrate, the reference electrode was the Ag/AgCl one, and the counter electrode was made of steel. The electrochemical deposition was performed in an IVIUM n-stat potentiostat. Finally, the gold layer was removed using aqua regia (a mixture of nitric acid and hydrochloric acid, in a molar ratio of 1:3), which is capable of dissolving gold while maintaining the properties of the conductive polymer.

**Electrodeposition of SnS:Ag:** The electrodeposition of SnS:Ag films was performed on a PEDOT substrate previously prepared. The films were electrodoped from a solution of 10 mm SnSO$_4$ and 50 mm Na$_2$S$_2$O$_3$ at a voltage of −0.92 V versus an Ag/AgCl reference electrode, for 7 h at a pH of 2.7. The steel electrode was used as a counter electrode. The concentration of AgNO$_3$ was changed in the different films to get the optimum conditions for the doping of SnS films. The percentages of silver in the films are proportional to the moles of sulfur in the solution. The electrochemical deposition process was carried out in an IVIUM n-stat potentiostat.

**Characterization Techniques:** Cyclic voltammetry studies were used to determine the reduction potential of the reaction. The cyclic voltammetry studies we carried out utilizing the same electrodeposition conditions, using a film of PEDOT as a working electrode, a steel electrode as a counter electrode, and an Ag/AgCl electrode as a reference electrode. The solution was also composed of 10 mm SnSO$_4$ and 50 mm Na$_2$S$_2$O$_3$. The potential range was varied from 0 to −1.5 V with a scanning rate of 10 mV s$^{-1}$. Surface morphological characteristics of the final films were evaluated using scanning electron microscopy (Hitachi S-4800) with an acceleration voltage of 10 kV. The samples were coated with Au-Pd in a sputtering system prior to the observation. In addition, microanalysis studies were carried out with a Hitachi S-4800 scanning electron microscope using an RX Bruker as backscattered electron X-rays. Thermoelectric properties of the films were evaluated by measuring the electrical conductivity through the Van der Pauw method using a Keithley 2400 current source and measuring the Seebeck coefficient as the relationship between electrical potential and the temperature difference using an Agilent 34401A digital multimeter and a Lakeshore 340 temperature controller, respectively (see supporting information for details about the thermoelectric measurements). The binding energies of various electronic states in the films were evaluated using an X-ray photoelectron spectroscopy (XPS, Kratos AXIS ULTRA spectrometer) system equipped with a microfocused (20 mA, 15 kV) monochromatic Al-Kα X-ray source (1486.58 eV).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

electrodeposition, flexible materials, hybrid thermoelectrics, PEDOT, tin sulfide

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[1] M. Culebras, C. M. Gómez, A. Cantarero, J. Mater. Chem. A 2014, 2, 10109.
[2] M. Culebras, C. M. Gómez, A. Cantarero, Materials 2014, 7, 6701.
[3] M. Culebras, B. Uriol, C. M. Gómez, A. Cantarero, Phys. Chem. Chem. Phys. 2015, 17, 15140.
[4] M. Culebras, M. M. de Lima, Jr., C. Gómez, A. Cantarero, J. Appl. Poly. Sci. 2017, 134, 43927.
[5] J. Gao, C. Liu, L. Miao, X. Wang, C. Li, R. Huang, Y. Chen, S. Tanemura, Synth. Met. 2015, 210, 342.
[6] H. Shi, C. Liu, J. Xu, H. Song, B. Lu, F. Jiang, W. Zhou, G. Zhang, Q. Jiang, ACS Appl. Mater. Interfaces 2013, 5, 12811.
[7] M. Culebras, A. M. Igual-Muñoz, C. Rodríguez-Fernández, M. I. Gómez-Gómez, C. Gómez, A. Cantarero, ACS Appl. Mater. Interfaces 2017, 9, 20826.
[8] J. P. Heremans, V. Jovovic, E. S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, G. J. Snyder, Science 2008, 321, 554.
[9] O. Caballero-Calero, P. Díaz-Chao, B. Abad, C. V. Manzano, M. D. Ynsa, J. J. Romero, M. M. Rojo, M. S. Martín-González, Electrochim. Acta 2014, 123, 117.
[10] G. Carotenuto, C. L. Hison, F. Capezzuto, M. Palomba, P. Perlo, P. Conte, J. Nanopart. Res. 2008, 11, 1729.
[11] T. C. Harman, P. J. Taylor, M. P. Walsh, B. E. LaForge, Science 2002, 297, 2229.
[12] X. W. Wang, H. Lee, Y. C. Lan, G. H. Zhu, G. Joshi, D. Z. Wang, J. Yang, A. J. Muto, M. Y. Tang, J. Klatsky, S. Song, M. S. Dresselhaus, G. Chen, Z. F. Ren, Appl. Phys. Lett. 2008, 93, 193121.
[13] M. Culebras, K. Choi, C. Cho, Micromachines 2018, 9, 638.
[14] C. Cho, B. Stevens, J.-H. Hsu, R. Bureau, D. A. Hagen, O. Regev, C. Yu, J. C. Grunlan, Adv. Mater. 2015, 27, 2996.
[15] C. Cho, K. L. Wallace, P. Tzeng, J.-H. Hsu, C. Yu, J. C. Grunlan, Adv. Energy Mater. 2016, 6, 1502168.
[16] Q. Tan, L.-D. Zhao, J.-F. Li, C.-F. Wu, T.-R. Wei, Z.-B. Xing, M. G. Kanatzidis, J. Mater. Chem. A 2014, 2, 17302.
[17] E. A. Cerwenka, W. C. Cooper, Arch. Environ. Health Int. J. 1961, 3, 189.
[18] B. Zhou, S. Li, W. Li, J. Li, X. Zhang, S. Lin, Z. Chen, Y. Pei, ACS Appl. Mater. Interfaces 2017, 9, 34033.
[19] H. W. Do, Y. H. Kwon, H. K. Cho, J. Mater. Sci. Mater. Electron. Vol. 2015, 26, 8609.
[20] S. Cheng, Y. Chen, C. Huang, G. Chen, Thin Solid Films 2006, 500, 96.
[21] H. Kafashan, F. Jamali-Sheini, R. Ebrahimi-Kahrizsangi, R. Yousefi, Int. J. Miner. Metall. Mater. 2016, 23, 348.
[22] C. An, K. Tang, G. Shen, C. Wang, L. Huang, Y. Qian, Mater. Res. Bull. 2003, 38, 823.
[23] H. Hu, B. Yang, J. Zeng, Y. Qian, Mater. Chem. Phys. 2004, 86, 233.
[24] M. A. Khan, S. P. Armes, C. Perruchot, H. Ouamara, M. M. Chehimi, S. J. Greaves, J. F. Watts, Langmuir 2000, 16, 4171.
[25] V. R. Minnam Reddy, S. Gedi, C. Park, R. W. Miles, R. R. Ramakrishna, Curr. Appl. Phys. 2015, 15, 588.
[26] S. Gedi, V. R. Minnam Reddy, T. R. Reddy Kotte, S. H. Kim, C. W. Jeon, Ceram. Int. 2016, 42, 19027.
[27] Y. Jiang, Z. Yang, P. Zhang, H. Jin, Y. Ding, RSC Adv. 2018, 8, 13408.
[28] C. Behera, S. P. Ghosh, J. P. Kar, S. L. Samal, New J. Chem. 2020, 44, 11684.
[29] B. K. Rajwar, S. K. Sharma, Mater. Res. Express 2019, 6, 2, 075524.
[30] H. Peisert, T. Chassé, P. Streubel, A. Meisel, R. Szargan, J. Electron. Spectrosc. Relat. Phenom. 1994, 68, 321.
[31] M. Devika, R. NK, K. Ramesh, G. KR, G. ESR, R. KTR, Bull. Mater. Sci. 2019, 42, 1223.
[32] M. Culebras, K. Choi, C. Cho, J. Electron. Spectrosc. Relat. Phenom. 1994, 68, 321.
[33] M. M. Kamel, M. M. Ibrahim, J. Solid State Electrochem. 2011, 15, 683.
[34] A. Supee, Y. Tanaka, M. Ichimura, Mater. Sci. Semicond. Process. 2015, 38, 290.