# NANOSTRUCTURED MATERIALS FOR THERMOELECTRIC DEVICES


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# NANOSTRUCTURED MATERIALS FOR THERMOELECTRIC DEVICES

**by**

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**Submitted**

**in fulfilment of the requirements of the degree of Doctor of Philosophy**

**to the**

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*Dedicated to my*

*Family and Teachers*

# Certificate

This is to certify that the thesis entitled **"Nanostructured Materials for Thermoelectric Devices"**, being submitted by **Mr. Amish Kumar Gautam** to the Department of Physics, Indian Institute of Technology Delhi, for the award of the degree of **"Doctor of Philosophy"**, is a record of the original bonafide research work carried out by him under my guidance and supervision. He has fulfilled the requirements for submitting this thesis, which in my opinion, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

NKhare 27/07/2022

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# Abstract

Energy demands are increasing daily due to the rapid growth of industrial production. Nonetheless, a lot of energy produced is lost as waste heat, necessitating the development of waste heat recovery systems. Thermoelectric materials are feasible to transform waste heat energy into electrical energy. In order to have a thermoelectric material with a large figure of merit (*zT*), the material must possess a larger value of Seebeck coefficient and electrical conductivity while at the same time should have a low value of total thermal conductivity. However, strong interdependency among these three parameters makes the task challenging. Nanosized materials are considered an effective method to overcome the challenges of interdependency among the *zT* parameters, improving the thermoelectric performance of a thermoelectric material. The present thesis focuses on synthesizing nanostructured thermoelectric material and fabricating the flexible thermoelectric device; the study is further explored to fabricate a hybrid device for harvesting multiple energies, i.e., mechanical and thermal energy, by utilizing triboelectric and thermoelectric hybrid effects. The thesis also focuses on the exploration and enhancement of thermoelectric properties of the 2D-$MoS_2$ material.

In order to carry out work in this direction, we have synthesized silver telluride ($Ag_2Te$) nanoparticles using the hydrothermal method and showed significant improvements in the thermoelectric properties compared to the bulk $Ag_2Te$ sample. $Ag_2Te$ nanoparticles showed the highest figure of merit (*zT*) of 1.37 at 373 K, which is the highest *zT* reported for this undoped material. This high *zT* in $Ag_2Te$ nanoparticles is mainly due to about ~ 2 times higher electrical conductivity (1967 S/cm) and subsequently ~ 2 times lower thermal conductivity (0.53 W/mK) as compared to the bulk $Ag_2Te$ sample.

To fabricate a flexible thermoelectric generator (*f*-TEG), we have utilized a vacuum filtration technique using a nylon membrane to prepare a flexible $Ag_2Te$-nylon composite film. Apart from having a higher Seebeck coefficient value (-135.5 μV/K) and simultaneous lower

thermal conductivity (0.29 W/mK), the developed composite film demonstrates good flexibility in the bending test by retaining about 87 % of the electrical conductivity even after 500 times bending. The film shows an enhanced power factor of about 450 μW/mK$^2$ and a $zT$ of about 0.48 at 313 K. A single *f*-TEG strip of the $Ag_2Te$-nylon film can generate a maximum power density ($PD_{max}$) of ~ 466 μW/cm$^2$ at a temperature difference ($\Delta T$) of ~ 36.8 K.

Further, to harvest multiple energy, we developed a multifunctional flexible $Ag_2Te$-nylon nanocomposite film that employs a unique approach to harvest mechanical and thermal energy by utilizing triboelectric and thermoelectric hybrid effects. In the flexible film, $Ag_2Te$ nanoparticles embedded in the nylon film act as a thermoelectric material, while the nylon membrane works as a triboelectric material. The flexible hybrid device can generate a power density of 58 μW/cm$^2$ through simple finger touch via the thermoelectric effect, whereas a power density of 23 nW/cm$^2$ can be generated via rubbing with fingertips due to the triboelectric effect. The fabrication concept is extended to fabricate the nanocomposite film of $Ag_2Te$ with polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) membranes. In the $Ag_2Te$-PVDF nanocomposite film, an output power density of 1 μW/cm$^2$ has been achieved while rubbing with fingertips. To explore the device's performance, capacitor charging was performed. The fabricated device in this study is the only one of its kind where a single material can harvest thermal and mechanical energy.

Lastly, to explore the thermoelectrics of 2D materials, we have chosen molybdenum disulfide ($MoS_2$), a transition metal dichalcogenide (TMDC). $MoS_2$ nanosheets have been prepared using the refluxing method. The low electrical conductivity of $MoS_2$ is improved by making its nanocomposite with reduced graphene oxide (RGO). The higher value of electrical conductivity and a simultaneous decrease in thermal conductivity results in enhanced $zT$ in the nanocomposite sample.

# सारांश

औद्योगिक उत्पादन की तीव्र वृद्धि के कारण ऊर्जा की मांग प्रतिदिन बढ़ रही है। अभी उत्पादित ऊर्जा का एक बड़ा हिस्सा अपशिष्ट ताप के रूप में नष्ट हो जाता है, जिससे अपशिष्ट ताप पुनर्प्राप्ति प्रणालियों के विकास की आवश्यकता है। थर्मोइलेक्ट्रिक मटेरियल अपशिष्ट ताप ऊर्जा को विद्युत ऊर्जा में बदलने की छमता रखता है। थर्मोइलेक्ट्रिक मटेरियल में उच्च फिगर ऑफ़ मेरिट(zT) होने के लिए, मटेरियल में सीबेक गुणांक और विद्युत चालकता अधिक होनी चाहिए, जबकि साथ ही कुल थर्मल चालकता को कम मूल्य होना चाहिए। इन तीन मापदंडों के बीच मजबूत परस्पर निर्भरता के कारण उच्च zT को प्राप्त करना अत्यंत चुनौतीपूर्ण है। zT मापदंडों के बीच परस्पर निर्भरता की चुनौतियों को दूर करने के लिए और थर्मोइलेक्ट्रिक मटेरियल के थर्मोइलेक्ट्रिक प्रदर्शन में सुधार करने में, नैनोसाइज्ड मटेरियल को एक प्रभावी तरीका माना जाता है। वर्तमान थीसिस नैनोसंरचित थर्मोइलेक्ट्रिक मटेरियल को संश्लेषित करने और फ्लेक्सिबल थर्मोइलेक्ट्रिक डिवाइस के निर्माण पर केंद्रित है; अध्ययन को आगे अन्वेषण करते हुए ट्राइबोइलेक्ट्रिक और थर्मोइलेक्ट्रिक हाइब्रिड प्रभावों का उपयोग करके, कई ऊर्जाओं, यानी यांत्रिक और थर्मल ऊर्जा की हार्वेस्टिंग के लिए एक हाइब्रिड डिवाइस बनाया गया है। इस थीसिस में 2D-$MoS_2$ मटेरियल के थर्मोइलेक्ट्रिक गुणों की खोज और वृद्धि पर भी कार्य किया गया है।

इस दिशा में काम करने के लिए, हमने हाइड्रोथर्मल विधि का उपयोग करके सिल्वर टेल्यूराइड ($Ag_2Te$) नैनोपार्टिकल्स को संश्लेषित किया है और बल्क $Ag_2Te$ सैंपल की तुलना में थर्मोइलेक्ट्रिक गुणों में महत्वपूर्ण सुधार दिखाया है। $Ag_2Te$ नैनोपार्टिकल्स ने 373 K पर 1.37 का फिगर ऑफ़ मेरिट (zT) दिखाया, जो इस अनोपेड मटेरियल के लिए रिपोर्ट किया गया उच्चतम zT है। $Ag_2Te$ नैनोपार्टिकल्स में यह उच्च zT मुख्य रूप से बल्क $Ag_2Te$ सैंपल की तुलना में लगभग ~ 2 गुना अधिक विद्युत चालकता (1967 S/cm) और साथ में ~ 2 गुना कम तापीय चालकता (0.53 W/mK) के कारण है।

फ्लेक्सिबल थर्मोइलेक्ट्रिक जनरेटर (f-TEG) को बनाने के लिए, नायलॉन मेम्ब्रेन का उपयोग करके, वैक्यूम फिल्ट्रेशन तकनीक से एक फ्लेक्सिबल $Ag_2Te$-नायलॉन कम्पोजिट फिल्म तैयार किया गया है। उच्च सीबेक

गुणांक मान (-135.5 μV/K) और कम तापीय चालकता (0.29 W/mK) होने के अलावा, विकसित कम्पोजिट फिल्म 500 बार मोड़ने के बाद भी लगभग 87% विद्युत चालकता बनाए बनाये रखती है जो बहुत ही अच्छी फ्लेक्सिबिलिटी प्रदर्शित करता है। यह फिल्म 313 K पर बढ़ा हुआ लगभग 450 $\mu W/mK^2$ पावर फैक्टर और लगभग 0.48 का zT दिखाती है। $Ag_2Te$-नायलॉन फिल्म की एक सिंगल *f*-TEG स्ट्रिप ~ 36.8 K के तापमान अंतर (ΔT) पर ~ 466 $\mu W/cm^2$ का अधिकतम पावर डेंसिटी (PDmax) उत्पन्न कर सकती है।

इसके अलावा, कई ऊर्जा का उत्पादन करने के लिए, हमने एक बहुक्रियाशील फ्लेक्सिबल $Ag_2Te$-नायलॉन नैनोकम्पोजिट फिल्म विकसित की है जो ट्राइबोइलेक्ट्रिक और थर्मोइलेक्ट्रिक हाइब्रिड प्रभावों का उपयोग करके यांत्रिक और तापीय ऊर्जा के लिए एक अद्वितीय दृष्टिकोण का उपयोग करती है। फ्लेक्सिबल फिल्म में, नायलॉन फिल्म में समाहित $Ag_2Te$ नैनोपार्टिकल्स थर्मोइलेक्ट्रिक मटेरियल के रूप में कार्य करते हैं, जबकि नायलॉन मेम्ब्रेन ट्राइबोइलेक्ट्रिक सामग्री के रूप में काम करती है। फ्लेक्सिबल हाइब्रिड डिवाइस थर्मोइलेक्ट्रिक प्रभाव के माध्यम से साधारण फिंगर टच से 58 $\mu W/cm^2$ की पावर डेंसिटी उत्पन्न कर सकती है, जबकि ट्राइबोइलेक्ट्रिक प्रभाव के कारण 23 $nW/cm^2$ की पावर डेंसिटी उंगलियों से रगड़कर उत्पन्न की जा सकती है। निर्माण अवधारणा को बढ़ाने के लिए पॉलीटेट्राफ्लोरोएथिलीन (PTFE) और पॉलीविनाइलिडीन फ्लोराइड (PVDF) मेमब्रेन्स के साथ $Ag_2Te$ की नैनोकम्पोजिट फिल्म भी बनायीं गयी है। $Ag_2Te$-PVDF नैनोकम्पोजिट फिल्म में, उँगलियों से रगड़ते हुए 1 $\mu W/cm^2$ का पावर डेंसिटी प्राप्त किया गया है। डिवाइस के प्रदर्शन का पता लगाने के लिए, कैपेसिटर चार्जिंग का प्रदर्शन किया गया। इस अध्ययन में बनायीं गई डिवाइस अपनी तरह की इकलौती ऐसी डिवाइस है जहां एक ही मटेरियल से तापीय और यांत्रिक ऊर्जा प्राप्त की जा सकती है।

अंत में, 2D मैटेरियल्स के थर्मोइलेक्ट्रिक्स का पता लगाने के लिए, हमने मोलिब्डेनम डाइसल्फ़ाइड ($MoS_2$), एक ट्रांजीशन मेटल डाइक्लोजेनाइड (TMDC) को चुना है। $MoS_2$ नैनोशीट को रिफ्लक्स विधि का उपयोग करके तैयार किया गया है। रेडूस ग्राफीन ऑक्साइड (RGO) के साथ इसके नैनोकम्पोजिट बनाकर $MoS_2$ की कम विद्युत चालकता में सुधार पाया गया है। विद्युत चालकता का उच्च मूल्य और तापीय चालकता में एक साथ कमी के परिणामस्वरूप नैनोकम्पोजिट सैंपल में zT बढ़ा हुआ पाया गया है।

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# Nomenclature

## Symbols

| | |
|---|---|
| $S$ | Seebeck coefficient |
| $\Delta V$ | Electromotive force |
| $I$ | Current |
| $J$ | Current density |
| $\Delta T$ | Temperature gradient |
| $k$ | Thermal conductivity |
| $\eta$ | Thermoelectric efficiency |
| $l$ | Length |
| $A$ | Area |
| $Q$ | Heat |
| $T_h$ | Hot end temperature |
| $T_c$ | Cold end temperature |
| $R/R_l$ | External load resistance |
| $r/R_i$ | Internal resistance |
| $\sigma$ | Electrical conductivity |
| $V_{oc}$ | Open circuit voltage |
| $W$ | Power |
| $P_{max}$ | Maximum output power |
| $\bar{T}$ | Average temperature |
| $\eta_{max}$ | Maximum efficiency of thermoelectric generator |
| $\eta_c$ | Carnot efficiency |
| $k_e/k_{electronic}$ | Electronic thermal conductivity |
| $k_l/k_{lattice}$ | Lattice thermal conductivity |
| $\rho$ | Electrical resistivity |
| $E$ | Electric field |
| $\alpha$ | Temperature coefficient of resistivity |
| $E_g$ | Band gap |
| $n$ | Carrier concentration |

| | |
|---|---|
| $\mu$ | Carrier mobility |
| $V$ | Electric potential |
| $E_F$ | Fermi energy |
| $m^*$ | Effective mass |
| $L$ | Lorentz number |
| $\mu_w$ | Weighted mobility |
| $m_e$ | Electronic mass |
| $\mu_H$ | Hall mobility |
| $S^2\sigma$ | Power factor |
| $k_B$ | Boltzmann constant |
| $\Delta\chi$ | Electronegativity difference |
| $m_I^*$ | Inertial or conductive effective mass |
| $d_{hkl}$ | Interplanar spacing |
| $\theta$ | Diffraction angle |
| $V_{cd}$ | Contact surface potential difference |
| $\phi$ | Work function |
| $e$ | Electronic charge |
| $D_c$ | Average crystallite size |
| $E_b$ | Energy barrier at the interface |

## Abbreviations

| | |
|---|---|
| TEG | Thermoelectric generators |
| $zT$ | Material figure of merit |
| *f*-TEG | Flexible thermoelectric generator |
| RTEG | Radioisotope thermoelectric generator |
| DC | Direct current |
| DOS | Density of states |
| $zT_{average}$ | Average figure of merit |
| TMDC | Transition metal dichalcogenide |
| $Ag_2Te$ | Silver telluride |
| $MoS_2$ | Molybdenum disulfide |

| | |
|---|---|
| GO | Graphene oxide |
| RGO | Reduced graphene oxide |
| XRD | X-ray diffraction |
| SEM | Scanning electron microscopy |
| EDX | Energy dispersive X-ray spectroscopy |
| TEM | Transmission electron microscopy |
| AFM | Atomic force microscopy |
| KPFM | Kelvin probe force microscopy |
| Au | Gold |
| Ag | Silver |
| JCPDS | Joint Committee on Powder Diffraction Data |
| $LaB_6$ | Lanthanum Hexaboride |
| HOPG | Highly oriented pyrolytic graphite |
| RTD | Resistance temperature detector |
| TPS | Transient plane source |
| PD | Power density |
| $PD_{max}$ | Maximum power density |
| Te | Tellurium |
| NaOH | Sodium hydroxide |
| $NaBH_4$ | Sodium borohydride |
| DI | Deionized |
| $AgNO_3$ | Silver nitrate |
| PTFE | Polytetrafluoroethylene |
| PVDF | Polyvinylidene fluoride |
| CC | Cubic centimeter |
| TENG | Triboelectric nanogenerator |
| $(NH_4)_6Mo_7O_{24}.4H_2O$ | Ammonium heptamolybdate tetrahydrate |
| HCl | Hydrochloric acid |