

**THERMOELECTRIC PERFORMANCE OF  
ORGANIC-INORGANIC NANOCOMPOSITE  
FLEXIBLE FILMS**

**MANOJ SINGH**



**DEPARTMENT OF PHYSICS**

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**DECEMBER 2024**

©Indian Institute of Technology Delhi (IITD), New Delhi, 2024

# **THERMOELECTRIC PERFORMANCE OF ORGANIC-INORGANIC NANOCOMPOSITE FLEXIBLE FILMS**

*by*

**MANOJ SINGH**  
**Department of Physics**

**Submitted**

**in fulfillment of requirements of the degree of Doctor of Philosophy to the**



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**  
**DECEMBER 2024**

## **Dedication**

*I want to dedicate this thesis to my family.*

*You have been my constant source of inspiration, support, and encouragement throughout this journey. You have taught me the value of education, the joy of learning, and the importance of pursuing my dreams. You have sacrificed so much for me, and I can never thank you enough. You are the best gift I ever received, and I dedicate this thesis to you with all my love and gratitude.*

## Certificate

---

---

This is to certify that the thesis entitled “**Thermoelectric Performance of Organic-Inorganic Nanocomposite Flexible Films**”, being submitted by **Mr. Manoj Singh** to the **Department of Physics, Indian Institute of Technology Delhi** is worthy of consideration for the award of the degree of ‘**Doctor of Philosophy**’ and is a record of the original bonafide research work carried out by him under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which, in my opinion, has reached the requisite standard.

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

**Prof. Neeraj Khare**

Department of Physics

Indian Institute of Technology Delhi

Hauz Khas, New Delhi, 110016

India

## Acknowledgements

---

---

*I stand at the culmination of this incredible journey of pursuing my Ph.D., filled with deep gratitude and humility. I could not have completed this thesis without the unwavering support, guidance, and encouragement of numerous individuals who have enriched both my academic and personal life. This acknowledgment is not merely a formal requirement but a heartfelt opportunity to express my sincere gratitude to everyone who has supported me throughout this challenging yet fulfilling journey.*

*Foremost, I would like to express my profound gratitude to my thesis supervisor, Prof. Neeraj Khare, whose invaluable guidance, positive attitude, and constant encouragement have been a beacon of light throughout this journey. His unwavering faith in my abilities, even in times of doubt, has been a source of strength that propelled me forward. His insightful critiques and constructive feedback have played a pivotal role in shaping this thesis and have significantly contributed to my development as a researcher. His unwavering support throughout every phase of my Ph.D., from the initial conception to the completion of this thesis, has been invaluable to me. His mentorship has been a privilege, and I am eternally grateful for his contribution to my academic journey.*

*My heartfelt gratitude is extended to my research committee members, Prof. Sujeet Chaudhary, Prof. Brajesh Kumar Mani, and Prof. Vamsi Krishna Komarala. Their critical evaluation and constructive feedback at each phase of my research have been instrumental in refining my work. My profound gratitude is extended to Prof. Pankaj Srivastava, the Head of the Physics Department at IIT Delhi, for granting access to various research facilities.*

*I would like to extend my sincerest gratitude for the assistance and support of Nano Functional Oxides and Superconductivity lab (NFOSL) members Dr. Mohd. Faraz, Dr.*

*Deepanshu Sharma, Dr. Surbhi Sharma, Dr. Sunil Kumar, Dr. Huidrom Hemojit Singh, Dr. Mamta Dahiya, Dr. Dheeraj Kumar, Dr. Amish Kumar Gautam, Dr. Mohit Khosya, Mrs. Abhilasha Chouksey, Mr. Arun Mondal, Mr. Aman Sharma, Mr. Gaurav Kumar, Mr. Sandeep Kumar, Ms. Rajni Kandari, and Ms. Sarita Mittal. I express my sincere gratitude for their help, support, encouragement, and motivation. I am truly indebted to all of you.*

*I am very grateful to Prof. Sudhir Kumar for his unwavering encouragement and support, which have been invaluable to me. I also want to express my thanks to Dr. Durgesh Kumar Sharma for the guidance and insight he provided during crucial moments.*

*I wish to thank the Nanoscale Research Facility (NRF), Central Research Facility (CRF), and the dedicated technical staff of IIT Delhi for providing the necessary characterization facilities and technical assistance throughout my research. I am grateful for the financial support I received as a Junior Research Fellowship (JRF) and Senior Research Fellowship (SRF) from the Council of Scientific and Industrial Research (CSIR), India.*

*I am deeply grateful to my parents, Shri Lal Singh and Smt Meena Devi, my brothers, Mr. Jitendra Singh and Mr. Saroj Singh, and my sister-in-law, Mrs. Divya Singh, for their unwavering support and affection throughout my academic journey. Their belief in me has been a constant source of strength. I am also thankful to my niece, Atulya (Iti), whose joy and inspiration remind me of life's beauty.*

*Last but not least, I would like to express my sincere gratitude to my friends for their unwavering support and encouragement during this journey. Your support, laughter, and camaraderie have made this experience truly memorable. I am fortunate to have you all in my life.*

**Manoj Singh**

## Abstract

---

---

Utilizing renewable energy sources is critical in reducing our dependence on non-renewable energy resources. Renewable energy technologies such as solar, wind, biomass, hydro-power, mechanical energy, and thermal energy have emerged as promising alternatives. Thermoelectric generators (TEGs) can directly convert heat energy into electricity and vice versa. Thermoelectric generators find diverse applications, including converting waste thermal energy into additional electricity in power plants and factories, enhancing fuel efficiency in automobiles, serving as radioisotope thermoelectric generators (RTGs) in space probes, powering wearable microscale sensors, transmitters, and electronic devices by utilizing body heat. Conducting polymer-based flexible thermoelectric generators (f-TEGs) represents a promising avenue in energy harvesting. The present thesis focuses on enhancing the thermoelectric properties of freestanding conducting polymer films by incorporating nano-inorganic and carbon-based materials.

In order to perform work in this direction, first, freestanding, flexible films of the conducting polymer, polyaniline (PANI), are fabricated by using the drop-cast method. The non-conducting PANI emeraldine base form is doped with camphor sulfonic acid (CSA) to produce the conducting PANI emeraldine salt form. The thermoelectric properties of the pristine PANI films are observed to be notably low. In order to enhance its thermoelectric properties, different concentrations of graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) are introduced in the PANI matrix. The  $g\text{-C}_3\text{N}_4$  powder is synthesized employing the thermal polymerization technique, utilizing melamine as the precursor. Subsequently, nanocomposite films incorporating PANI with varying concentrations of  $g\text{-C}_3\text{N}_4$ , specifically, 0, 5, 10, and 20 wt%, are prepared. Remarkably, the thermoelectric performance of the resulting composite films improves after adding the  $g\text{-C}_3\text{N}_4$  nanosheets. The PANI composite film containing 20 wt% of

g-C<sub>3</sub>N<sub>4</sub> demonstrates an impressive threefold enhancement in the power factor, attributed to the improved value of the Seebeck coefficient ( $S$ ).

In the subsequent step, ternary nanocomposite films are synthesized by incorporating exfoliated g-C<sub>3</sub>N<sub>4</sub> and reduced graphene oxide (rGO) to enhance the thermoelectric properties of the PANI film. The mobility ( $\mu$ ) of charge carriers is enhanced, which can be attributed to the  $\pi - \pi$  interactions occurring between the PANI chains and the surfaces of g-C<sub>3</sub>N<sub>4</sub> and rGO. Furthermore, energy filtering of low-energy charge carriers at the interfaces leads to an improved Seebeck coefficient. Consequently, the ternary nanocomposite film, with 5 wt% g-C<sub>3</sub>N<sub>4</sub> and 5 wt% rGO exhibits a  $\sim 5$  times higher power factor and  $\sim 4.3$  times higher figure of merit ( $zT$ ) compared to the pristine PANI film.

Further, varied concentrations of two-dimensional tungsten disulfide (WS<sub>2</sub>) nanosheets and carbon nanotubes (CNTs) are incorporated in the PANI matrix to study their effects on the thermoelectric properties of the PANI film. The incorporation of WS<sub>2</sub> nanosheets leads to an enhanced Seebeck coefficient ascribed to the high Seebeck coefficient of the WS<sub>2</sub> nanosheets and the energy filtering effect at the PANI-WS<sub>2</sub> interfaces. However, the electrical conductivity ( $\sigma$ ) of the composite is reduced after incorporating WS<sub>2</sub> nanosheets. In order to compensate for the reduction in electrical conductivity, conducting CNTs are introduced in the composite. The PANI/WS<sub>2</sub>/CNT ternary composite with 20 wt% WS<sub>2</sub> and 5 wt% CNTs exhibits a  $\sim 13$  times higher power factor and a  $\sim 10$  times higher figure of merit ( $zT$ ) at 323 K in comparison to the pristine PANI film. These results demonstrate the potential of the PANI/WS<sub>2</sub>/CNT ternary composite as a promising candidate for thermoelectric applications. The simultaneous addition of high Seebeck coefficient filler (WS<sub>2</sub>) and highly conducting filler (CNT) in PANI film results in a PANI/WS<sub>2</sub>/CNT ternary nanocomposite film with better

properties at room temperature compared to previous works.

Lastly, a freestanding flexible film of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is prepared by the drop-cast method. The PEDOT:PSS is secondary doped with dimethyl sulfoxide (DMSO) to improve its electrical conductivity. However, the Seebeck coefficient of the doped PEDOT:PSS film remains low. In order to address this issue, exfoliated g-C<sub>3</sub>N<sub>4</sub> nanosheets are added to the PEDOT:PSS matrix at varying concentrations. PEDOT:PSS/g-C<sub>3</sub>N<sub>4</sub> composite film containing 10 wt% of the g-C<sub>3</sub>N<sub>4</sub> exhibits ~5 times higher Seebeck coefficient and ~11 times higher power factor at 313 K, as compared to the PEDOT:PSS film. However, the incorporation of the g-C<sub>3</sub>N<sub>4</sub> results in a decrease in electrical conductivity. Therefore, multiwalled carbon nanotubes (MWCNTs) are further incorporated as conducting filler in the PEDOT:PSS/g-C<sub>3</sub>N<sub>4</sub>(10 wt%) composite film to improve its electrical conductivity. The PEDOT:PSS composite film with 10 wt% g-C<sub>3</sub>N<sub>4</sub> and 10 wt% MWCNTs exhibits a ~20 times higher power factor as compared to the PEDOT:PSS film.

## सार

गैर-नवीकरणीय संसाधनों पर हमारी निर्भरता को कम करने के लिए नवीकरणीय ऊर्जा स्रोतों का उपयोग महत्वपूर्ण है। सौर, पवन, बायोमास, पनबिजली, यांत्रिक ऊर्जा और तापीय ऊर्जा जैसी नवीकरणीय ऊर्जा प्रौद्योगिकियाँ आशाजनक विकल्प के रूप में उभरी हैं। वर्तमान ऊर्जा मांगों को पूरा करने के लिए नवीकरणीय स्रोतों से ऊर्जा का दोहन करना अनिवार्य है। तापविद्युतीय जनित्र (टीईजी), ऊष्मा ऊर्जा को बिजली में और इसके विपरीत बिजली को ऊष्मा ऊर्जा में परिवर्तित करते हैं। तापविद्युतीय जनित्र विविध अनुप्रयोगों में उपयोग किए जाते हैं, जिनमें बिजली संयंत्रों और कारखानों में अपशिष्ट तापीय ऊर्जा को अतिरिक्त बिजली में परिवर्तित करना, मोटर-वाहनों में ईंधन दक्षता बढ़ाना, अंतरिक्ष जांच में विकिरण-समस्थानिक तापविद्युतीय जनित्र (आरटीजी) के रूप में कार्य करना, मानव शरीर की ऊष्मा का उपयोग करके पहनने योग्य सूक्ष्म सेंसर, ट्रांसमीटर और इलेक्ट्रॉनिक उपकरणों को शक्ति प्रदान करना शामिल है। चालक बहुलकों पर आधारित लचीले तापविद्युतीय जनित्र (एफ-टीईजी) का संचालन ऊर्जा संचयन में एक आशाजनक अवसर का प्रतिनिधित्व करता है। वर्तमान थीसिस नैनो-अकार्बनिक और कार्बन-आधारित पदार्थों को शामिल करके चालक बहुलकों की स्वतंत्र फिल्मों के तापविद्युतीय गुणों को बढ़ाने पर केंद्रित है।

इस दिशा में कार्य करने के लिए, सबसे पहले, चालक बहुलक, पॉलीएनिलिन (PANI) की स्वतंत्र, लचीली फिल्मों को बूँद-निक्षेपण विधि का उपयोग करके संश्लेषित किया गया। गैर-चालक PANI एमराल्डाइन क्षार रूप को, चालक PANI एमराल्डाइन लवण रूप में परिवर्तन के लिए, कैम्फर सल्फोनिक अम्ल (CSA) के साथ डोप किया गया। मूल PANI फिल्मों के तापविद्युतीय गुण उल्लेखनीय रूप से कम पाए गए। इसके तापविद्युतीय गुणों को बढ़ाने के लिए, PANI आव्यूह में ग्रेफाइटिक कार्बन नाइट्राइड ( $g-C_3N_4$ ) की विभिन्न सांद्रताएं समावेशित की गयी हैं।  $g-C_3N_4$  पाउडर को ऊष्मीय बहुलकीकरण तकनीक का उपयोग करके संश्लेषित किया गया, जिसमें पूर्ववर्ती के रूप में मेलामाइन का उपयोग किया गया है। इसके बाद,  $g-C_3N_4$  की विभिन्न सांद्रताओं, विशेष रूप से 0, 5, 10, और 20 wt% के साथ PANI में समावेशित करते हुए नैनोसम्मिश्रण फिल्में संश्लेषित की गयी। उल्लेखनीय रूप से, परिणामी नैनोसम्मिश्रण फिल्मों का तापविद्युतीय प्रदर्शन  $g-C_3N_4$  नैनोशीट को जोड़ने के बाद बेहतर हो गया। 20 wt%  $g-C_3N_4$  युक्त PANI नैनोसम्मिश्रण फिल्म, ऊर्जा घटक में प्रभावशाली तीन गुना वृद्धि दर्शाती है, जिसका श्रेय सीबेक गुणांक ( $S$ ) के बेहतर मूल्य को जाता है।

अगले चरण में, PANI फिल्म के तापविद्युतीय गुणों को बढ़ाने के लिए अपशल्कित g-C<sub>3</sub>N<sub>4</sub> और अपचयित ग्रेफीन ऑक्साइड (rGO) को सम्मिलित करके त्रिक नैनोसम्मिश्रण फिल्मों को संश्लेषित किया गया है। आवेश वाहकों की गतिशीलता ( $\mu$ ) बढ़ गयी, जिसका श्रेय PANI श्रृंखलाओं और g-C<sub>3</sub>N<sub>4</sub> और rGO की सतहों के बीच होने वाली  $\pi - \pi$  अंतःक्रियाओं को दिया जा सकता है। इसके अलावा, अंतराफलक पर कम ऊर्जा वाले चार्ज वाहकों की ऊर्जा छनन से सीबेक गुणांक में सुधार हुआ। परिणामस्वरूप, 5 wt% g-C<sub>3</sub>N<sub>4</sub> और 5 wt% rGO वाली त्रिगुण नैनोसम्मिश्रण फिल्म, मूल PANI फिल्म की तुलना में  $\sim 5$  गुना अधिक ऊर्जा घटक और  $\sim 4.3$  गुना अधिक फ़िगर ऑफ़ मेरिट ( $zT$ ) प्रदर्शित किया।

इसके अलावा, दो-आयामी टंगस्टन डाइसल्फ़ाइड (WS<sub>2</sub>) नैनोशीट और कार्बन नैनोट्यूब (CNTs) की विभिन्न सांद्रताओं को PANI आव्यूह में समावेशित किया गया ताकि PANI फिल्म के तापविद्युतीय गुणों पर उनके प्रभावों का अध्ययन किया जा सके। WS<sub>2</sub> नैनोशीट के समावेशन से सीबेक गुणांक में वृद्धि हुयी, जो WS<sub>2</sub> नैनोशीट के उच्च सीबेक गुणांक और PANI-WS<sub>2</sub> अंतराफलक पर ऊर्जा छनन प्रभाव के कारण हुआ। हालाँकि, WS<sub>2</sub> नैनोशीट के समावेशन के बाद सम्मिश्रण की विद्युत चालकता ( $\sigma$ ) कम हो गयी। विद्युत चालकता में कमी की भरपाई के लिए, सम्मिश्रण में चालक CNTs को शामिल किया गया। 20 wt% WS<sub>2</sub> और 5 wt% CNTs के साथ PANI/WS<sub>2</sub>/CNT त्रिक सम्मिश्रण, मूल PANI फिल्म की तुलना में 323 K पर लगभग 13 गुना अधिक ऊर्जा घटक और लगभग 10 गुना अधिक फ़िगर ऑफ़ मेरिट ( $zT$ ) प्रदर्शित करता है। ये परिणाम तापविद्युतीय अनुप्रयोगों के लिए एक आशाजनक उम्मीदवार के रूप में PANI/WS<sub>2</sub>/CNT त्रिक सम्मिश्रण की क्षमता को प्रदर्शित करते हैं। PANI फिल्म में उच्च सीबेक गुणांक पूरक (WS<sub>2</sub>) और अत्यधिक चालक पूरक (CNT) को एक साथ सम्मिलित करने से PANI/WS<sub>2</sub>/CNT त्रिक नैनोसम्मिश्रण फिल्म बनी, जिसके तापविद्युतीय गुण कमरे के तापमान पर पिछले कार्यों की तुलना में बेहतर हैं।

अंततः, बूँद-निक्षेपण विधि द्वारा पॉली(3,4-एथिलीनडाइऑक्सीथियोफ़ीन) पॉलीस्टाइरीन सल्फोनेट (PEDOT:PSS) की एक स्वतंत्र लचीली फिल्म तैयार की गयी। PEDOT:PSS को इसकी विद्युत चालकता में सुधार करने के लिए डाइमिथाइल सल्फ़ोक्साइड (DMSO) के साथ द्वितीयक रूप से डोप किया गया। हालाँकि, डोप किए गए PEDOT:PSS फिल्म का सीबेक गुणांक कम रहता है। इस समस्या को हल करने के लिए, अलग-अलग

सांद्रता में PEDOT:PSS आव्यूह में अपशुक्ति  $g-C_3N_4$  नैनोशीट को सम्मिलित किया गया। PEDOT:PSS/ $g-C_3N_4$  सम्मिश्रण फिल्म जिसमें  $g-C_3N_4$  का 10 wt% होता है, PEDOT:PSS फिल्म की तुलना में 313 K पर  $\sim 5$  गुना अधिक सीबेक गुणांक और  $\sim 11$  गुना अधिक ऊर्जा घटक प्रदर्शित किया। हालांकि,  $g-C_3N_4$  के समावेश से विद्युत चालकता में कमी आती है। इसलिए, PEDOT:PSS/ $g-C_3N_4$ (10 wt%) सम्मिश्रण फिल्म में इसकी विद्युत चालकता को बेहतर बनाने के लिए बहु-दीवार कार्बन नैनोट्यूब (MWCNTs) को चालक पूरक के रूप में शामिल किया गया। 10 wt%  $g-C_3N_4$  और 10 wt% MWCNTs वाली PEDOT:PSS नैनोसम्मिश्रण फिल्म, PEDOT:PSS फिल्म की तुलना में लगभग 20 गुना अधिक ऊर्जा घटक प्रदर्शित किया।

# Contents

<b>Certificate</b>	<b>i</b>
<b>Acknowledgements</b>	<b>ii</b>
<b>Abstract</b>	<b>iv</b>
<b>Saar</b>	<b>vii</b>
<b>Contents</b>	<b>xv</b>
<b>List of Figures</b>	<b>xix</b>
<b>List of Tables</b>	<b>xx</b>
<b>Nomenclature</b>	<b>xxi</b>
<b>1 Introduction</b>	<b>1</b>
1.1 Overview . . . . .	1
1.2 Brief Overview of Thermoelectric Phenomenon . . . . .	2
1.2.1 Seebeck Effect . . . . .	2
1.2.2 Peltier Effect . . . . .	3
1.2.3 Thomson Effect . . . . .	4
1.3 Thermoelectric Generators . . . . .	5
1.3.1 Conversion Efficiency . . . . .	6
1.3.2 Figure of Merit . . . . .	8
1.3.3 Transport Parameters and Coupling Relationships . . . . .	8
1.3.3.1 Carrier Concentration . . . . .	9
1.3.3.2 Effective Mass . . . . .	10

1.3.3.3	Thermal Conductivity . . . . .	10
1.4	Thermoelectric Materials and Recent Developments . . . . .	11
1.4.1	Inorganic Thermoelectric Materials . . . . .	12
1.4.1.1	Chalcogenides . . . . .	12
1.4.1.2	Skutterudites . . . . .	13
1.4.1.3	Half-Heusler Alloys . . . . .	13
1.4.1.4	Clathrates . . . . .	14
1.4.1.5	Silicides . . . . .	14
1.4.1.6	Zintl Phases . . . . .	14
1.4.2	Organic Thermoelectric Materials/Conducting Polymers . . . . .	15
1.4.2.1	Mechanism of Charge Transport in Conducting Polymers . . . . .	21
1.4.2.2	Doping of Conducting Polymers . . . . .	23
1.5	Approaches to Optimize the Thermoelectric Properties of Conducting Polymers . . . . .	25
1.5.1	Doping . . . . .	25
1.5.2	Secondary Doping . . . . .	26
1.5.3	Post Treatment . . . . .	26
1.5.4	Energy Filtering Effect . . . . .	27
1.5.5	Organic-Inorganic Composites . . . . .	27
1.5.6	Conducting Polymer-Carbon Based Materials Composites . . . . .	28
1.6	Motivation of the Present Work . . . . .	28
1.7	Objectives of the Thesis . . . . .	29
1.7.1	Organisation of the Thesis . . . . .	30
1.7.1.1	Chapter 1: Introduction . . . . .	30
1.7.1.2	Chapter 2: Experimental Methods and Characterization Techniques . . . . .	30
1.7.1.3	Chapter 3: Fabrication of PANI/g-C <sub>3</sub> N <sub>4</sub> Composite Flexible Films With Improved Thermoelectric Properties . . . . .	31

1.7.1.4	Chapter 4: Freestanding PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO composite Flexible Films for Improved Thermoelectric Properties . . . .	31
1.7.1.5	Chapter 5: PANI Film Incorporated with The Liquid Phase Exfoliated WS <sub>2</sub> Nanosheets and CNTs for Enhanced Thermoelectric Properties . . . . .	32
1.7.1.6	Chapter 6: PEDOT:PSS Film Incorporated with g-C <sub>3</sub> N <sub>4</sub> Nanosheets and MWCNTs for Enhanced Thermoelectric Properties . . . . .	33
1.7.1.7	Chapter 7: Conclusions and Future Scope . . . . .	33
	References . . . . .	34
<b>2</b>	<b>Experimental Methods and Characterization Techniques</b>	<b>39</b>
2.1	Introduction . . . . .	39
2.2	Synthesis of Nanomaterials . . . . .	39
2.2.1	Thermal Polymerization Method . . . . .	39
2.2.2	Liquid Phase Exfoliation Method . . . . .	40
2.3	Nanocomposite Film Deposition . . . . .	41
2.3.1	Drop-Cast Method . . . . .	41
2.4	Characterization Techniques . . . . .	41
2.4.1	X-Ray Diffraction . . . . .	41
2.4.2	Scanning Electron Microscopy . . . . .	44
2.4.3	Energy Dispersive X-Ray Spectroscopy . . . . .	45
2.4.4	Raman Spectroscopy . . . . .	46
2.4.5	Fourier Transform Infrared Spectroscopy . . . . .	48
2.4.6	Atomic Force Microscopy . . . . .	49
2.4.7	Kelvin Probe Force Microscopy . . . . .	51
2.5	Thermoelectric Measurements . . . . .	52
2.5.1	Seebeck Coefficient Measurement . . . . .	52
2.5.2	Electrical Conductivity Measurement . . . . .	53

2.5.3	Thermal Conductivity Measurement . . . . .	54
	References . . . . .	56
<b>3</b>	<b>Fabrication of PANI/g-C<sub>3</sub>N<sub>4</sub> Composite Flexible Films With Improved Thermoelectric Properties</b>	<b>57</b>
3.1	Introduction . . . . .	57
3.2	Experimental Section . . . . .	59
3.2.1	Preparation of Conducting PANI . . . . .	59
3.2.2	Synthesis of Graphitic Carbon Nitride (g-C <sub>3</sub> N <sub>4</sub> ) Nanosheets . . . . .	59
3.2.3	Preparation of PANI/g-C <sub>3</sub> N <sub>4</sub> Nanocomposite Films . . . . .	59
3.3	Results and Discussion . . . . .	61
3.3.1	Structural Analysis . . . . .	61
3.3.2	Morphological Study and Cross-Sectional SEM . . . . .	62
3.3.3	FTIR Analysis . . . . .	63
3.3.4	Raman Analysis . . . . .	64
3.3.5	Thermoelectric Properties . . . . .	66
3.4	Conclusions . . . . .	68
	References . . . . .	69
<b>4</b>	<b>Freestanding PANI/g-C<sub>3</sub>N<sub>4</sub>/rGO composite Flexible Films for Improved Thermoelectric Properties</b>	<b>73</b>
4.1	Introduction . . . . .	73
4.2	Experimental Section . . . . .	75
4.2.1	Preparation of Conducting PANI . . . . .	75
4.2.2	Preparation of g-C <sub>3</sub> N <sub>4</sub> Nanosheets . . . . .	75
4.2.3	Synthesis of Reduced Graphene Oxide . . . . .	75
4.2.4	Preparation of PANI and PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO Nanocomposite Films . . .	76
4.3	Results and Discussion . . . . .	76

4.3.1	Structural Analysis . . . . .	76
4.3.2	Morphological Study . . . . .	77
4.3.3	Cross-Sectional SEM and Elemental Analysis . . . . .	78
4.3.4	FTIR Analysis . . . . .	80
4.3.5	Raman Analysis . . . . .	81
4.3.6	Thermoelectric Properties . . . . .	82
4.4	Conclusions . . . . .	87
	References . . . . .	89
<b>5</b>	<b>PANI Film Incorporated with The Liquid Phase Exfoliated WS<sub>2</sub> Nanosheets and CNTs for Enhanced Thermoelectric Properties</b>	<b>92</b>
5.1	Introduction . . . . .	92
5.2	Experimental Section . . . . .	94
5.2.1	Exfoliation of WS <sub>2</sub> Nanosheets . . . . .	94
5.2.2	Preparation of Carbon Nanotubes . . . . .	95
5.2.3	Synthesis of PANI Emeraldine Salt . . . . .	95
5.2.4	Preparation of PANI/WS <sub>2</sub> /CNT Nanocomposite Film . . . . .	95
5.3	Results and Discussion . . . . .	96
5.3.1	Structural Analysis . . . . .	96
5.3.2	Morphological Study . . . . .	97
5.3.3	Cross-Sectional SEM and Elemental Analysis . . . . .	98
5.3.4	FTIR Analysis . . . . .	100
5.3.5	Raman Analysis . . . . .	101
5.3.6	Thermoelectric Properties . . . . .	102
5.4	Conclusions . . . . .	111
	References . . . . .	112
<b>6</b>	<b>PEDOT:PSS Film Incorporated with g-C<sub>3</sub>N<sub>4</sub> Nanosheets and MWCNTs for</b>	

<b>Enhanced Thermoelectric Properties</b>	<b>116</b>
6.1 Introduction . . . . .	116
6.2 Experimental Section . . . . .	117
6.2.1 Synthesis of g-C <sub>3</sub> N <sub>4</sub> Nanosheets . . . . .	117
6.2.2 Synthesis of PEDOT:PSS Nanocomposite . . . . .	118
6.3 Results and Discussion . . . . .	119
6.3.1 Structural Analysis . . . . .	119
6.3.2 Morphological Study . . . . .	120
6.3.3 Raman Analysis . . . . .	120
6.3.4 Thermoelectric Properties . . . . .	122
6.4 Conclusions . . . . .	128
References . . . . .	130
<b>7 Conclusions and Future Scope</b>	<b>133</b>
7.1 Conclusions of the Thesis . . . . .	133
7.1.1 Thermoelectric Properties of PANI/g-C <sub>3</sub> N <sub>4</sub> nanocomposite . . . . .	134
7.1.2 PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO Ternary Nanocomposite Film: Influence of g-C <sub>3</sub> N <sub>4</sub> and rGO on Thermoelectric Properties of PANI. . . . .	135
7.1.3 Thermoelectric Properties of PANI/WS <sub>2</sub> /CNT nanocomposite . . . . .	135
7.1.4 PEDOT:PSS/g-C <sub>3</sub> N <sub>4</sub> /CNT Ternary Nanocomposite Film . . . . .	136
7.2 Future Scope of the Thesis . . . . .	137
<b>List of Publications</b>	<b>140</b>
<b>Author's Biodata</b>	<b>142</b>

# List of Figures

1.1	A schematic depiction of various sources of waste heat energy . . . . .	1
1.2	Schematic representation of the Seebeck effect in <i>n</i> -type and <i>p</i> -type conductor .	3
1.3	Schematic representation of the Peltier effect in a conducting bar . . . . .	4
1.4	Schematic of a thermoelectric generator device and a close-up view of a single thermoelectric element . . . . .	5
1.5	A thermoelectric element delivering power to a load resistance $R_L$ . . . . .	6
1.6	Variation of the Seebeck coefficient ( $\alpha$ ), electrical conductivity ( $\sigma$ ), thermal conductivity ( $\kappa$ ), power factor ( $S^2\sigma$ ), and figure of merit ( $zT$ ) with carrier concentration ( $n$ ) . . . . .	10
1.7	Schematic showing the molecular structure of typical conducting polymers . .	16
1.8	Schematic showing how the band structure changes as the number of polymer units increases . . . . .	22
1.9	Schematic showing formation of polarons, bipolarons, and solitons . . . . .	23
2.1	(a) Schematic diagram showing the basic principle of X-ray diffraction. (b) Schematic representation of experimental setup of the XRD measurement system	42
2.2	Rigaku Ultima IV X-ray diffractometer . . . . .	43
2.3	Schematic illustration displaying the working of the scanning electron microscope	45
2.4	Schematic diagram of light-molecule interaction, three types of scattering processes can occur . . . . .	46
2.5	Schematic diagram displaying the working of Raman spectrometer based on Horiba LabRAM HR Evolution . . . . .	47
2.6	Schematic diagram displaying the working of a typical Fourier transform infrared (FTIR) spectrometer . . . . .	48
2.7	Schematic diagram describing the working of a typical atomic force microscope (AFM) . . . . .	50
2.8	The energy-level diagram of sample and tip with different wavefunctions. (a) The sample and tip before electrical contact, (b) Fermi level alignment after electrical contact between the sample and the tip, and (c) DC bias voltage $V_{DC}$ applied to compensate the $V_{CPD}$ . . . . .	51

2.9	Schematic diagram describing the temperature-dependent Seebeck coefficient measurement setup . . . . .	53
2.10	Photograph of Hot Disk (TPS 2200) and a schematic diagram depicting the thermal conductivity measurement set-up . . . . .	54
3.1	Schematic for the (a) synthesis of g-C <sub>3</sub> N <sub>4</sub> , and (b) fabrication of PANI/g-C <sub>3</sub> N <sub>4</sub> composite film . . . . .	60
3.2	XRD patterns of (a) PANI, (b) PANI/g-C <sub>3</sub> N <sub>4</sub> (5 wt%), (c) PANI/g-C <sub>3</sub> N <sub>4</sub> (10 wt%), (d) PANI/g-C <sub>3</sub> N <sub>4</sub> (20 wt%) films, and (e) g-C <sub>3</sub> N <sub>4</sub> . . . . .	61
3.3	SEM images of (a) PANI film, (b) g-C <sub>3</sub> N <sub>4</sub> , (c) PANI/g-C <sub>3</sub> N <sub>4</sub> (20 wt%) films, and (d) cross-sectional SEM image of PANI/g-C <sub>3</sub> N <sub>4</sub> (10 wt%) sample . . . . .	62
3.4	FTIR spectra of (a) PANI, (b) PANI/g-C <sub>3</sub> N <sub>4</sub> (5 wt%), (c) PANI/g-C <sub>3</sub> N <sub>4</sub> (10 wt%), (d) PANI/g-C <sub>3</sub> N <sub>4</sub> (20 wt%) films, and (e) g-C <sub>3</sub> N <sub>4</sub> . . . . .	64
3.5	Raman spectra of (a) PANI, (b) PANI/g-C <sub>3</sub> N <sub>4</sub> (5 wt%), (c) PANI/g-C <sub>3</sub> N <sub>4</sub> (10 wt%), (d) PANI/g-C <sub>3</sub> N <sub>4</sub> (20 wt%), and (e) g-C <sub>3</sub> N <sub>4</sub> samples . . . . .	65
3.6	The temperature dependence of (a) Seebeck coefficient ( <i>S</i> ), (b) Electrical conductivity ( $\sigma$ ), and (c) Power factor ( <i>PF</i> ) of PANI, PANI/g-C <sub>3</sub> N <sub>4</sub> (5 wt%), PANI/g-C <sub>3</sub> N <sub>4</sub> (10 wt%), and PANI/g-C <sub>3</sub> N <sub>4</sub> (20 wt%) samples . . . . .	67
4.1	Schematic representation of the fabrication procedure of PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO nanocomposite film . . . . .	76
4.2	X-Ray diffraction patterns of PANI, PANI/g-C <sub>3</sub> N <sub>4</sub> , PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO, rGO, and g-C <sub>3</sub> N <sub>4</sub> samples . . . . .	77
4.3	FESEM images of (a) g-C <sub>3</sub> N <sub>4</sub> , (b) rGO, (c) PANI, and (d) PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO nanocomposite films . . . . .	78
4.4	(a-c) Cross-sectional SEM of PANI, PANI/g-C <sub>3</sub> N <sub>4</sub> , and PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO films. (d) SEM image and corresponding elemental maps of (e) Carbon (C), (f) Oxygen (O), (g) Nitrogen (N), and (h) Sulphur (S) and (i) overlay image of PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO composite film . . . . .	79
4.5	(a) FTIR spectra, and (b) Raman spectra of PANI, PANI/g-C <sub>3</sub> N <sub>4</sub> , PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO, rGO, and g-C <sub>3</sub> N <sub>4</sub> samples . . . . .	80
4.6	Variations of (a) Seebeck coefficient, (b) Electrical conductivity, and (c) Weighted mobility ( $\mu_w$ ) with temperature of PANI, PANI/g-C <sub>3</sub> N <sub>4</sub> , and PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO nanocomposite films . . . . .	82
4.7	(a) Variation of power factor ( <i>PF</i> ) with temperature, (b) figure of merit ( <i>zT</i> ) for PANI, PANI/g-C <sub>3</sub> N <sub>4</sub> , and PANI/g-C <sub>3</sub> N <sub>4</sub> /rGO composite films . . . . .	86

5.1	Schematic for (a) liquid phase exfoliation of bulk WS <sub>2</sub> to WS <sub>2</sub> nanosheets, and (b) the synthesis procedure of PANI/WS <sub>2</sub> /CNT nanocomposite film . . . . .	94
5.2	XRD patterns of CNTs, exfoliated WS <sub>2</sub> , PANI, PANI/WS <sub>2</sub> , and PANI/WS <sub>2</sub> /CNT nanocomposite films . . . . .	96
5.3	FESEM images of (a) WS <sub>2</sub> nanosheets, (b) carbon nanotubes, (c) PANI, (d) PANI/WS <sub>2</sub> , and (e) PANI/WS <sub>2</sub> /CNT nanocomposite films . . . . .	98
5.4	SEM images of cross-sections of (a) PANI, (b) PANI/WS <sub>2</sub> , and (c) PANI/WS <sub>2</sub> /CNT nanocomposite films. (d) SEM image of PANI/WS <sub>2</sub> /CNT nanocomposite film and corresponding EDX elemental mapping images of (e) carbon (C), (f) tungsten (W), (g) sulfur (S), and (h) mixed image of carbon (C), tungsten (W), and sulfur (S) . . . . .	99
5.5	(a) FTIR, and (b) Raman spectra of the PANI, PANI/WS <sub>2</sub> , and PANI/WS <sub>2</sub> /CNT nanocomposite films . . . . .	100
5.6	Variation with temperature of the (a) Seebeck coefficient ( $S$ ), (b) electrical conductivity ( $\sigma$ ), and (c) weighted mobility ( $\mu_w$ ) for PANI, PANI/WS <sub>2</sub> , and PANI/v/CNT nanocomposite films . . . . .	102
5.7	The surface topography, surface potential, and potential distribution of (a-c) PANI, (d-f) PANI/WS <sub>2</sub> , and (g-i) PANI/WS <sub>2</sub> /CNT samples, respectively . . . . .	105
5.8	(a) Temperature-dependent power factor ( $S^2\sigma$ ) and (b) the figure of merit ( $zT$ ) at room temperature for PANI, PANI/WS <sub>2</sub> , and PANI/WS <sub>2</sub> /CNT samples . . . . .	107
5.9	(a) The ratio of electrical conductivity after and before bending cycles at room temperature for the PANI/WS <sub>2</sub> /CNT nanocomposite films as a function of bending cycles, (b) Variation of open circuit voltage ( $V_{OC}$ ) with temperature difference at hot and cold ends ( $\Delta T$ ), (c) variation of output power with load resistance ( $R_L$ ), and (d) the variation of output voltage and output power with output current at 40 K of the fabricated eight-leg thermoelectric module . . . . .	109
6.1	Schematic diagram for the synthesis of the flexible films of the PEDOT:PSS and its composite with g-C <sub>3</sub> N <sub>4</sub> and CNTs . . . . .	118
6.2	XRD patterns of PEDOT:PSS, P/gCN10, P/gCN10/CNT10, CNT, and gCN samples . . . . .	120
6.3	FESEM images of (a) PEDOT:PSS film, (b) gCN, (c) CNT, and (d) P/gCN10/CNT10 film . . . . .	121
6.4	Raman spectra of PEDOT:PSS, P/gCN10, P/gCN10/CNT10, CNT, and gCN samples . . . . .	122
6.5	Temperature dependence of the (a) Seebeck coefficient ( $S$ ), (b) electrical conductivity ( $\sigma$ ), and (c) power factor ( $PF$ ) for the PEDOT:PSS, P/gCN10, and P/gCN10/CNT10 films . . . . .	123

6.6 Arrangement of contacts for the Hall effect measurement. . . . . 124

# List of Tables

1.1	A summary of the thermoelectric properties of commonly used conducting polymers for thermoelectric application . . . . .	17
3.1	Comparison table showing the thermoelectric performance of selected composites that are based on PANI . . . . .	68
4.1	Comparison of the thermoelectric performance of earlier published work on PANI composites with the present work . . . . .	87
5.1	Comparison of thermoelectric properties of PANI-based composite films . . . .	108
6.1	A comparison of the thermoelectric properties at room temperature for PEDOT:PSS based composites . . . . .	127

# Nomenclature

## List of Abbreviations

<i>BF<sub>4</sub></i>	Tetrafluoroborate
<i>CSA</i>	Camphorsulfonic Acid
<i>DBSA</i>	Dodecylbenzenesulfonic Acid
<i>DCA</i>	Dicyanamide
<i>DMSO</i>	Dimethyl Sulfoxide
<i>EG</i>	Ethylene Glycol
<i>EMIM</i>	1-ethyl-3-methylimidazolium
<i>F<sub>4</sub>TCNQ</i>	2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane
<i>FTIR</i>	Fourier Transformed Infrared Spectroscopy
<i>FTS</i>	(tridecafluoro-1,1,2,2,-tetrahydrooctyl)-trichlorosilane
<i>HCl</i>	Hydrochloric Acid
<i>NAP</i>	1,5-naphthalenedisulfonic acid
<i>NaSIPA</i>	5-sulfoisophtalic acid sodium salt
<i>NMP</i>	N-Methyl-2-pyrrolidone
<i>P3HT</i>	Poly(3-hexylthiophene)
<i>PANI</i>	Polyaniline
<i>PEDOT : PSS</i>	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
<i>PF<sub>6</sub></i>	Hexafluorophosphate
<i>PPpTS</i>	p-toluene sulphonate
<i>PPy</i>	Polypyrrole
<i>rGO</i>	Reduced Graphene Oxide
<i>SEM</i>	Scanning Electron Microscopy/Microscope
<i>TCB</i>	Tetracyanoborate
<i>TEG</i>	Thermoelectric Generator
<i>XRD</i>	X-Ray Diffraction

**List of Symbols**

$\beta$	Thomson Coefficient
$\eta$	Efficiency
$\kappa$	Thermal Conductivity
$\kappa_e$	Electronic Thermal Conductivity
$\kappa_L$	Lattice Thermal Conductivity
$\lambda$	Wavelength
$\mu$	Mobility
$\mu_w$	Weighted Mobility
$\phi$	Work Function
$\pi$	Peltier Coefficient
$\sigma$	Electrical Conductivity
$\theta$	Diffraction Angle
$c$	Speed of light in a vacuum
$e$	Electrical Charge
$E_F$	Fermi Level
$E_g$	Band Gap
$h$	Plank's Constant
$i$	Electrical Current
$J$	Current Density
$k_B$	Boltzmann Constant
$L$	Lorentz Factor
$m^*$	Effective Mass of the Charge Carrier
$m_e$	Electron Mass
$n$	Carrier Concentration
$q$	Heat Energy
$R$	Resistance
$R_L$	Load Resistance

$S$	Seebeck Coefficient
$S^2\sigma$	Power Factor
$T$	Absolute Temperature
$V_{CPD}$	Contact Potential Difference
$zT$	Figure of Merit