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Polymer based Graphene /Titanium dioxide nanocomposite (GTNC): An Emerging and Efficient Thermoelectric Material

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Abstract: An ecofriendly procedure for synthesis of graphene-titanium dioxide nanocomposite (GTNC) has been developed by dispersing nano titanium dioxide (TiO_2) and graphene nano sheet (GNS) in ethanol via ultrasonication followed by microwave irradiation. Such nano hybrid was characterized by X-Ray Defraction (XRD), High Resolution Transmission Electron Microscopy (HRTEM), Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy. We have also demonstrated the synthesis of highly conductive composites like Poly(3,4-ethylenedioxythiophene) polystyrene sulphonate (PEDOT:PSS)-GTNC, Polyvinyl Acetate (PVAc)-GTNC, PEDOT:PSS-graphene, PVAc-graphene by ultrasonication followed by hot compaction towards their thermoelectric application. The fillers (Graphene, GTNC) concentration and polymer matrix were judiciously varied and optimized for the sake of high electrical conductivity and Seebeck coefficient which leads to higher power factor (PF). The PVAc based composite with a composition of PVAc (20%) and GTNC (80%) was found to be most promising material with an electrical conductivity of 2.6×10^4 S/m and Seebeck coefficient of -42 µV/K at room temperature (RT). As a result, the PF reaches to 47 $\mu W\ m^{-1}K^{-2}$ at RT which is approximately 37 times, 5 times and 3 times higher than PVAc-graphene based composite, PEDOT:PSS–GTNC based composite and PEDOT:PSS-graphene based composite respectively. The origin of the thermoelectric performance of GTNCcomposite is seems to be from the synergistic effect of graphene nano sheet and TiO_2 nanoparticle. The composite shows large power factor value without using any conducting polymer.

Keywords: Thermoelectric, GTNC, Nano composite, Polymer, Power factor.

1 Introduction

Thermoelectricity is an imminent area of research for alternative energy as it deals with smart materials which convert heat into electricity. Thermoelectric materials have gained great research interest as a source of green and clean energy that helps in harvesting of energy from waste heat. The ZT is the thermoelectric figure-of-merit, the temperature-averaged value of which determines the efficiency (ZT can be one or two, however efficiency of a heat engine is less than 100%), expressed as $ZT=S^2\sigma T/\kappa$, where Seebeck coefficient is denoted by 'S', electrical conductivity is expressed as σ, thermal conductivity is indicated by κ and T is absolute temperature[1] in Kelvin. It is known that some inorganic materials like Bi_2Te_3 nanowires, Ag-doped Cu_2Se and Cu_2Te, $AgSbSe_2$, lead bismuth telluride, Mg alloyed SnTe, $AgBiSe_2$, PbTe and Cu_xS, [2-10] display enhanced thermoelectric properties. Out of them, Bi_2Te_3 isfound to be the paramount room temperature thermoelectric material.[11-12]Other thanchalcogenides; Transition metal oxide ceramics like TiO_2[13] have fascinated more and more attention owing to their superior thermoelectric prospects and outstanding stability under high temperature. Because of high Seebeck coefficient and excellent thermal insulation property, TiO_2 might be considered as the prime candidate. Thurber et al.[14] has reported that large negative Seebeck coefficients from -1000 to -200000 μV/K have been observed at low temperature in rutile and Nb-doped rutile TiO_2. According to the expression of ZT, we can know that a high-ZT thermoelectric material need to simultaneously achieve high electrical conductivity (s), large Seebeck coefficient (S), and low thermal conductivity (k) in the same material. However, most oxides, including TiO_2, are known to be poor electrical conductivity.

Therefore, it has been an important issue of how to improve the electrical conductivity and maintain the Seebeck coefficient and thermal conductivity. In the past few decades, nanocomposites consisting of metal particles embedded in an insulating matrix have drawn great interest. For example, Xu et al.[15] prepared Al-doped TiO2 nanostructured materials to increase the electrical conductivity and achieved an enhanced ZT of 0.091; Liu et al.[16] reported that Ag-codoped TiO_2 nanostructured materials exhibit an enhanced ZT of 0.082 at 1073 K.

In addition, organic materials like conjugated polymers are also becoming potential materials due to their enhanced thermoelectric power factor and figure of merit.[17-18] Furthermore, their low thermal conductivity ($k = 0.1–0.5$ W m^{-1} K^{-1}),[19, 20] easy processibility, elasticity, non toxicity and cheaper cost as compared to chalcogenides and use in flexible electronics make them more advantageous. Several other advantages includes mechanical robustness for better durability, application as a thermoelectric paint over armor vehicle for stealth purpose and fabric of cloths using flexible thermoelectric materials for energy harvesting from body heat. It is very difficult to attain such applications using chalcogenide based thermoelectric materials.

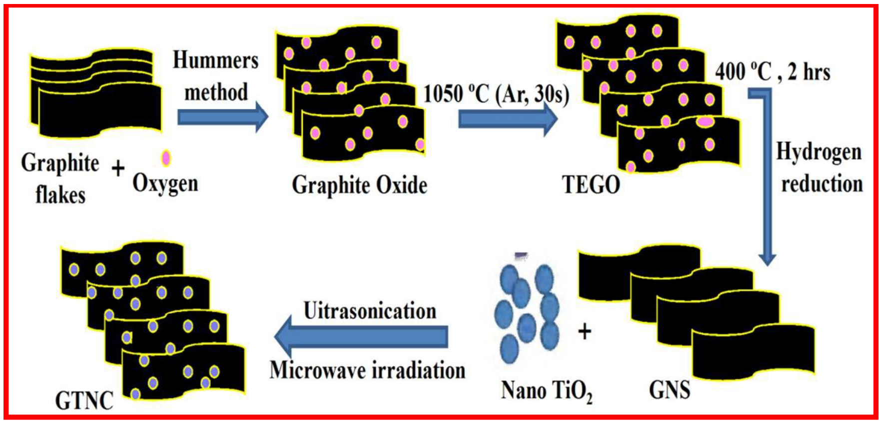
Doping the polymer[21-23] and blending with different conducting nano fillers[24-26] like graphenes[29-32] and CNT [27-28] are the two known mechanisms to achieve higher power factor ($S^2\sigma$) in polymer based composites. Effective research on the thermoelectric properties of these composites ended them competitive to chalcogenides. Nevertheless, their competence is still inferior.[34,37,38] Among numerous accessible polymers, 3,4-ethylenedioxythiophene: poly (styrenesulfonate) (PEDOT:PSS),[16,33] poly (3-hexylthiophene) (P3HT),[34] and polyaniline (PANI)[31, 35-37] are used frequently due to their intrinsic high electrical conductivity. It is possible to enhance the electrical properties of such polymers without affecting the mechanical flexibility and thermal conductivity.[38] Percolation law is mainly responsible for the enhancement of electrical conductivity in this case. According to this law, a drastic increase in electrical conductivity is possible after reaching to a percolation threshold.[39, 40]In our earlier report, we have already studied the efficiency of GINC (Graphene ironoxide nanocomposite) within polyvinyl acetate (PVAc) matrix.[41]

In the present study, we have attempted to demonstrate the simple preparation method of GTNC (scheme 1) and its thermoelectric application (scheme 2). The necessary raw chemical grades and instrumentation is described elaborately in supporting information (See S1 in ESI†). The characterization of structure, morphology and composition of the samples have been carried out by raman spectra, Fourier transform infrared spectroscopy (FTIR), Field emmission scanning electron microscope (FESEM), high resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (XRD). Further, an exhaustive study of thermoelectric properties of PEDOT:PSS and PVAc polymers with fillers like GTNC, graphene have been evaluated. Such materials could be engineered in a simple way to enhance thermoelectric properties ofsynthesized polymer nanocomposite in spite of high thermal conductivity. PEDOT: PSS is well known conducting polymer which has the ability to increase electrical conductivity and Seebeck coefficient and decrease thermal conductivity of the matrix. The other polymer PVAc was opted because of its good adhesive nature and binding capability with lower thermal conductivity. Such properties allow enhancing the filler loading and efficiency of thermoelectric material. Graphene was used as a substrate which also helps to increase the electrical conductivity drastically in the case of GTNC. The stacking nature of graphene sheet reduced drastically after nano titanium dioxide (TiO_2) adornment. Therefore, it reduces the tendency of transformation process from graphene to graphite.

2 Methodology

2.1 Synthesis procedure

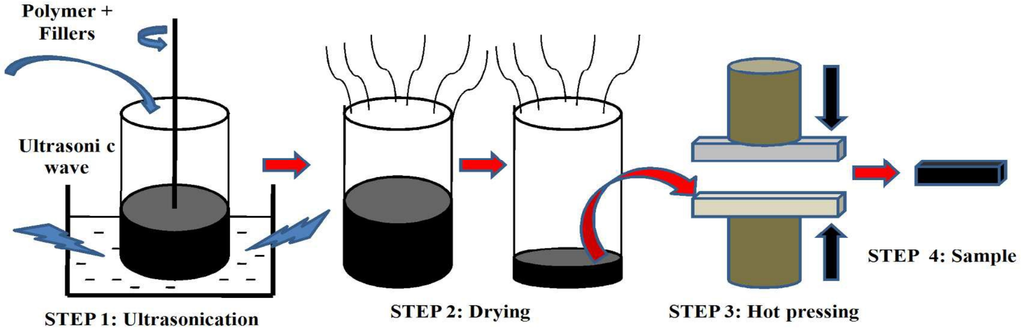
Myristic acid and titanium tetrachloride ($TiCl_4$) have been used for the synthesis of Anatase-TiO_2 nano-particles. To obtain highly crystalline TiO_2 (Scheme1), powder has been calcined at 500 °C. It has been observed that Broad X-ray diffraction (XRD) pattern showed all the prominent peaks for tetragonal crystal structure representing anatase-TiO_2 of as-prepared as well as calcined powder (See experimental section in ESI†). The graphene was prepared in three steps reported in the literature[42]. In the first step, graphite oxide was prepared from graphitic flakes by Hummers method. In the second step, thermally expanded graphene oxide (TEGO) was prepared by thermal expansion/exfoliation at 1050°C (Ar, 30s). Finally, GNS was obtained hydrogen reduction of TEGO at 400°C for 2 hr. For making GTNC, 50 mg graphene was first dispersed into absolute ethanol by ultrasonication for 40 min. After ultrasonication, nano titanium dioxide was added in to the graphene dispersion ultrasonication continued for 120 min. ultrasonication. After ultrasonication, the dispersed composite solution kept in ambient condition for drying. After evaporation of ethanol, GTNC was deposited on petri dish. The deposited nanocomposite placed into microwave reactor for 2 min for better exfoliation. After cooling, sample was collected in to sample vial. The synthesis of GTNC and its application is highlighted in Scheme-1).



Scheme 1: Schematic representation of synthesis of Graphene-Titanium dioxide nano composite (GTNC)

2.2 Synthesis of thermoelectric polymer nanocomposite

For the preparation of polymer nanocomposites, both fillers (i.e. graphene and GTNC) with PVAc water dispersion were spread ultrasonically for 30 min at 35 kHz. Mechanical stirring was continued for 4 hours at 250 rpm after ultrasonication. Casting was carried out in an aluminum tray after completion of dispersion process. For the purpose of complete drying, the sample was placed in a vacuum oven at 105°C for 4 hrs. The dried sample was subjected to hot pressing at 120°C with 5 min preheating time and 3 min compression (Pressure 10 T approx). Following above mentioned methodology, polymer nanocomposite sheets were prepared and subjected to the measurement of thermoelectric properties. In case of PEDOT:PSS based nanocomposite, above methodology has been followed except drying and molding. Here, drying and hot molding have been carried out at 60˚C. Other condition remain unchanged (Scheme 2)



Scheme 2: Synthesis and application of thermoelectric polymer nanocomposite

2.3 Charecterization

a. GTNC characterization

Using ultrasonication bath (35 kHz, Kudos), sonication was performed. Microwave irradiation has been carried out by a microwave reactor (Make: Raga). High Resolution Transmission Electron Microscopy (HRTEM images) characterization was carried out by TACHNAI F-30, FEI with 300 kV Field Emission Gun (FEG). For surface pictures, Field Emission Scanning Electron Microscopy (FESEM) was carried out with Quanta 200, FEI. Nano TiO_2, graphene and GTNC were well dispersed in methanol after ultrasonication process. Such dispersed sample was placed on TEM grid. The evaporation of solvent was performed with oven for drying. The data of Fourier Transform Infrared Spectroscopy (FTIR) was collected by Nicolet 5700, Thermoscientific. Corresponding Raman traces and mapping were measured by Invia reflex micro Raman, Renishaw.

X- Ray Diffractometer D8 advance, Bruker with Cu Kα source has been used for collecting the X-Ray diffraction traces in the measurement angle range 2θ=2-90° with a scan rate 2° min^{-1}.

b. Seebeck coefficient measurement: A 30mm × 6 mm × 1 mm pieces[43] of the polymer nanocomposite film was sliced and positioned on a thermal insulating fibre glass in order to measure the thermopower as a function of temperature. A piece of copper (drainage of heat) makes a contact with the Peltier cooling module at one end of the sample with a thermally conductive epoxy (electrically insulating 2763 Stycast), while a Peltier heater was positioned at the other end. The voltage drop and temperature gradient along the film was measured with thermocouples which are arranged in series (Electrical insulation was maintained for the sample with 2763 Stycast) with two copper wires. To make sure that the thermal gradient and the voltage drop were being measured at the same place, two small Cu films were attached to the PVAc-GTNC film with thermally/electrically conducting silver epoxy (Dupont 4929N). The voltage wires and the thermocouple were attached to these Cu films. Keithley 2182A nanovoltmeter has been used to monitor the thermoelectric voltages with respect to temperature difference. The base temperature was altered with Peltier cooling module. The determination of thermoelectric power was considered by two independent means: i. By fitting the linear V vs ΔT response to a heating pulse and ii. After reaching a steady state through an applied current to the heater. The observed deviation between both the methods and different experimentation was constantly found to be less than 5%.

c. Electrical resistivity measurements: Delta mode four probe method was employed to measure electrical resistivity due to high electrical conductive nature of the composite. The least possible current was sourced (100mA) by Keithley 6220 and voltage was scrutinized with a Keithley 2182A nanovoltmeter. To avoid heating of the sample at low temperature, the smallest possible current was used. Polymer nanocomposite sample with a dimension of 8mm × 3mm × 1mm have been prepared and subjected to measurement of electrical conductivity (†S-3 in ESI).

3 Resultsanddiscussion

3.1 Analysis

To examine the quality of graphene sheet before and after nanocomposite formation by above mentioned techniques, Raman Spectroscopywas performed. The most distinct Raman traces are G band 1575 cm^{-1} corresponds to in plane vibration of sp^2 carbon and D band at 1310 cm^{-1} corresponds to defect. 2D band which is generated due to a two phonon double resonance process has been observed at 2727.4 cm^{-1}. The presence of a small amount of defects on graphene flakes can be realized by the lower intensity D band. The I(D)/I(G) of the graphene-titanium dioxide composite increased by 1.5 times (0.7) with respect to pure graphene (0.497). Several defects with sp^2 domain were formed during nanocomposite preparation. Fig.1 corresponds to the Raman traces of nano TiO_2 and GTNC (See **Figure 1**).

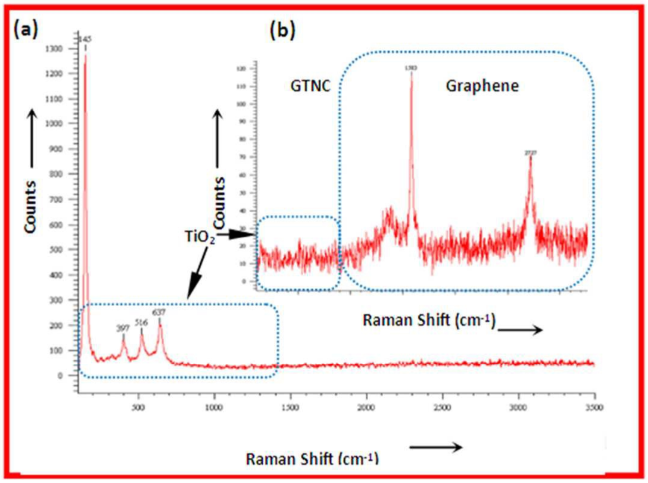


Fig. 1 (a) represents the Raman traces of nano TiO_2 and (b) represents GTNC (Gr-TiO_2 composite)

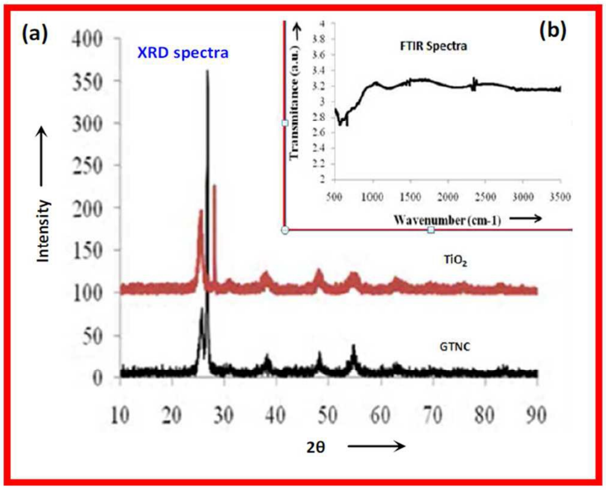


Fig.2: XRD profiles of nano TiO_2, GTNC (Graphene-TiO_2 composite). FTIR traces of graphene are shown in the inset (b).

X-Ray diffraction scan for the samples of TiO_2 nanoparticles synthesized by sol-gel method showed somewhat crystalline nature with 2θ peaks lie at 25.25 (101), 37.8 (004), 47.9 (200), 53.59 (105) and 62.36 (204). The broad peak at $2\theta = 25.8$ ° in the GTNC indicates a randomly pucking of graphene sheets and corresponds to (002) plane of graphite.Fig. 2a represents XRD profiles of nano TiO_2 and GTNC. Information regarding the presence of organics in the product was not observed in FTIR spectrum (Fig. 2b) of the GTNC. However, it has been confirmed that pure graphene is present in the sample as peaks for graphene oxide are missing.Field emission scanning electron microscopy (FESEM) profiles (see Fig. 3) describes continuous dispersion of TiO_2 nano particle over graphene nano sheet. It has been observed that uniform decoration of nano TiO_2 over the graphene sheet.To inspect the quality of nano titanium dioxide decoration on the graphene layer, high resolution transmission electron microscope (HRTEM) has been used. The results confirms nano level size of titanium dioxide and graphene (Fig. 4). Here we can see the clear picture of graphene sheets. Titanium dioxide nano particles were placed over the graphene sheet suggesting the formation of nano composite (Fig.4b).

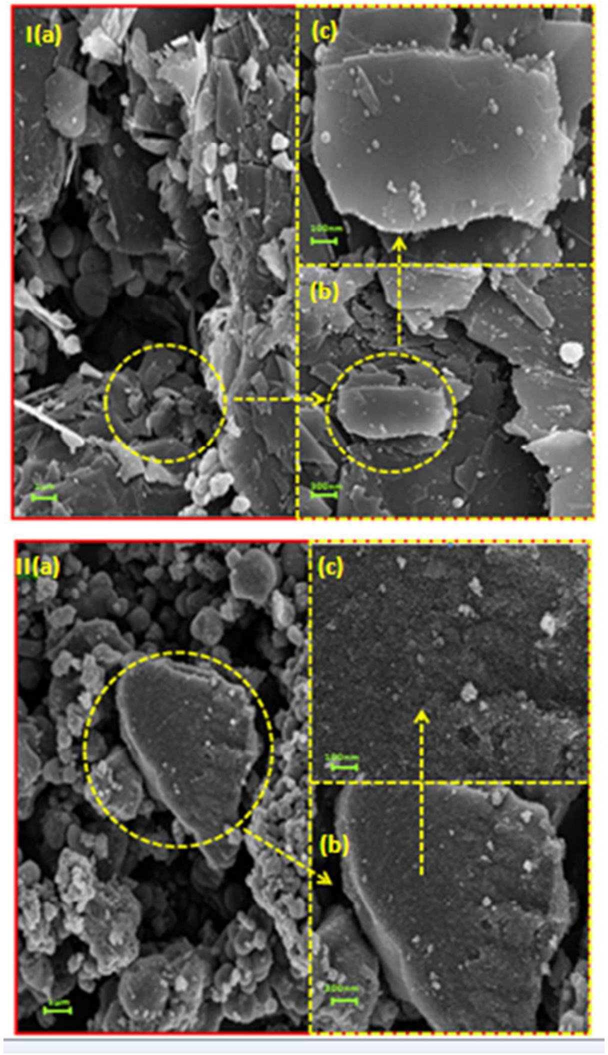


Fig. 3FESEM traces GTNC (I a, b and c) and nano TiO_2(II a, b and c) at different magnification [see also Figure S-2 in ESI]

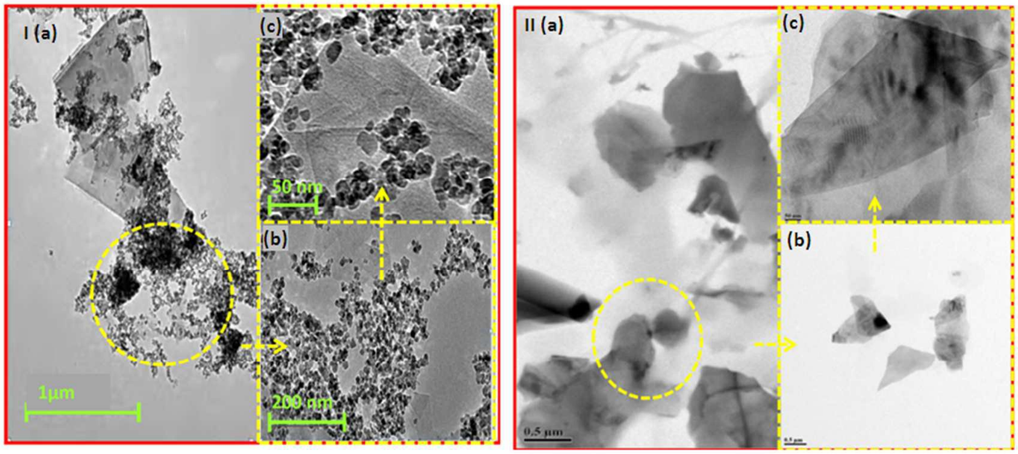


Fig.4HR-TEM image graphene-titanium dioxide nanocomposite (I a b and c) and graphene (II a, b and c). (See also supporting information Figure S-3 in ESI†).

3.2. Thermoelectric application of GTNC in different polymer matrix

Seebeck coefficient/thermopower, electrical conductivity and power factor are the three main parameters of thermoelectric properties. Thermopower and electrical conductivity were measured and hence power factor (PF) was calculated from these values. Electrical conductivity, Seebeck coefficient and power factor as a function of filler concentration at room temperature (300K) for non conducting polymer matrix PVAc are shown in Fig. 5a–5c. Similarly, electrical conductivity, Seebeck coefficient and power factor as a function of filler concentration at room temperature (300K) for conducting polymer matrix like PEDOT:PSS were shown in Figures 5d–f.

The Fig. 5a–c indicates the enhancement of all the three properties, i.e. electrical conductivity, Seebeck coefficient and power factor at a filler concentration level of 80-90 wt % in PVAc matrix. Fig. 5d–f suggests the increase in electrical conductivity and power factor with filler concentration in PEDOT:PSS matrix (reaches to maximum at 80% wt. filler) but decrease in Seebeck coefficient to certain level then increases. Moreover, we have processed several composition like CP-1 to CP-6 (detail composition is given in table S-5, ESI). Fig. 6 represents comparative bar diagram of (a) electricatical conductivity (b) Seebeck coefficient and (c) power factor of different compositions from CP-1 to CP-6. It has been observed that CP-1 i.e. PVAc (20%) and GTNC(80%) shows maximum power factor i.e. 46.54 μW $m^{-1}K^{-2}$ with high Seebeck coefficient and moderate electrical conductivitywhich is higher than the thermoelectric material based on other composition. The detail data sheet has been given in table S-1 to S-4 in ESI.

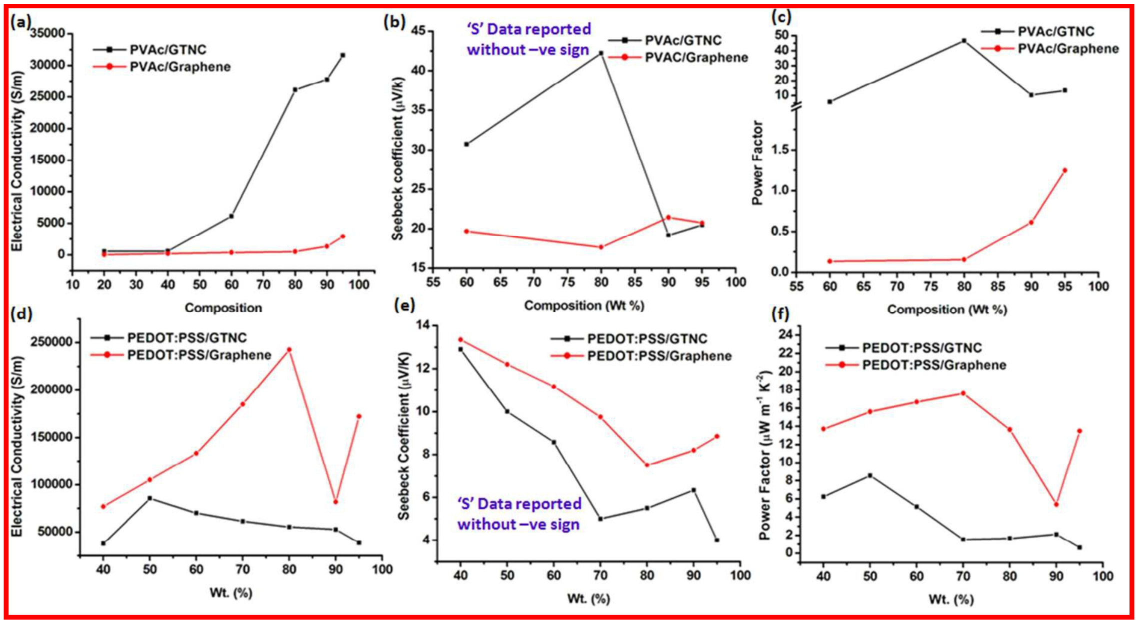


Fig. 5 (a) electrical conductivity, (b) seebeck coefficient and (c) power factor with different filler concentration for PVAc based composite. (d) electrical conductivity, (e) seebeck coefficient and (f) power factor with different filler concentration for PEDOT:PSS based composite.

Thermal conductivity is found to be 2.9 W/mK and hence, ZT approaches to 0.0048 for CP-1 composite. Such results are more promising than our earlier finding regarding PVAc-GINC composite. In GTNC, nano TiO_2 is decorated over 2D graphene sheet and its presence helps to destroy thermally conducted network but allow electrical network to remain intact.[57]The incorporation of GTNC as conducting filler not only decouples σ and S, but also enhances both the parameters concurrently. Such enhancement of Seebeck coefficient is marginal with respect to electrical conductivity in case of PVAc-GTNC composite. Important fact of reducing the thermal conductivity of the matrix in thermoelectric field can be achieved by thermal insulating nature of the PVAc. According to the listed reference (see Table 1) PVAc composite shows PF value upto 12. By addition of PEDOT: PSS , values increases to more than 30. In our previous work[41], we have reported PF value 32.9 μW $m^{-1}K^{-2}$ and corresponding ZT is 0.0031 for PVAc-GINC composite. In our present study, we have achieved PF value upto 47 and corresponding ZT is 0.0048 at RT. To the best of our knowledge, no one has reported such interesting feature in the literature till now.

Mechanism of enhancement of thermoelectric properties:

The most difficult part of thermoelectric properties is the interconnection of Seebeck coefficient, electrical conductivity and thermal conductivity with each other. If one property is enhanced, other property will also be increased. Graphene as such is not a very good thermoelectric material because of high thermal conductivity but it's electrical conductivity is very high which helps to be a efficient TE material by some means. In the present study, nano TiO_2 particles are placed between the graphene sheets during processing. As a result, decreases the stacking nature of the graphene as well as it helps in decreasing it's thermal conductivity. Hence, electrical conductivity and thermal conductivity decouples and increase power factor value. To justify the novelty of the present work, a comparative summary of the latest results based on PVAc matrix (see Table 1) and other composites of inorganic and organic materials have been highlighted in S-6 in ESI.

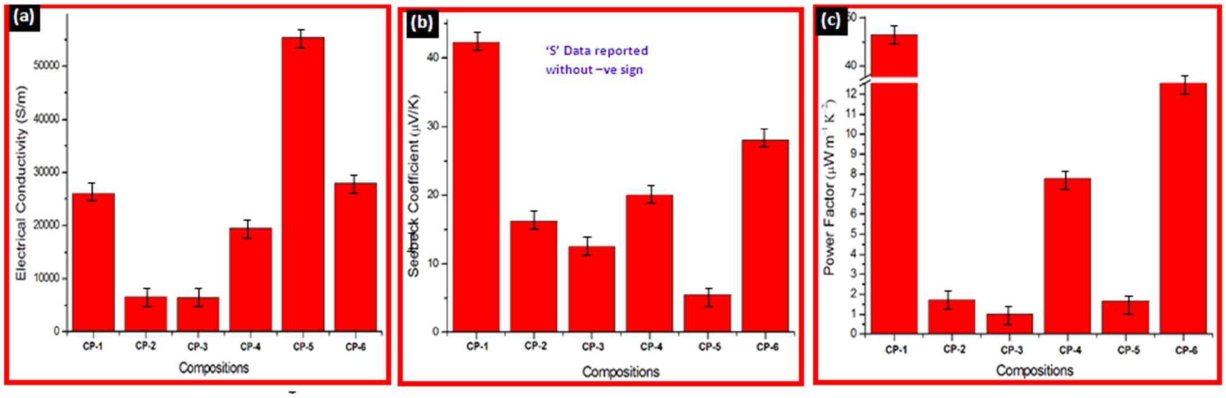


Fig.6(a) Electrical conductivity (b) Seebeck coefficient (c) power factor as a function of filler concentration at room temperature (300K) **CP-1:** PVAc (20%), GTNC(80%), **CP-2:** PVAc (15%), PEDOT:PSS (5%), GTNC (80%), **CP-3:** PVAc (10%), PEDOT:PSS (10%), GTNC (80%)**CP-4:** PVAc (5%), PEDOT:PSS (15%), GTNC (80%),**CP-5:**PEDOT: PSS (20%), GTNC (80%), **CP-6:** PEDOT sheet.

Table 1: Comparative summary of the latest results based on PVAc matrix

Sample	**σ, S/m**	***S*, μV/k**	**κ,** W/mK	**Calculated PF (*$S^2\sigma$*)** μW $m^{-1}K^{-2}$
PVAc +CNT (20%) [Ref. 45]	4800 (300K)	40-50 (300K)	0.18-0.34 at 300K	PF= 7.8-12
PVAc+SWCNT (40%) [Ref. 46]	900	40	0.25	PF= 1.44
PVAc+SWCNT (3wt.%) + GA [Ref: 47]	22-49	39-42	0.22-0.25	PF=0.033
PVAc+Au+ CNT [Ref. 48]	10^5	---	Unaffected	Unaffected
PVAc+ DOC + MWCNT (7-12%)	32-63	5-10	0.13-0.17	PF= 0.34-0.50
PVAc+ TCPP+ MWCNT (7-12%)	10-100	22-26	0.14	PF= 0.079-0.34
PVAc+ DOC + DWCNT (7-12%)	--	50-70	0.15	PF=0.045- 0.096
PVAc+ TCPP + DWCNT (7-12%) [Ref. 49]	--	70-82	0.155-0.16	PF= 0-0.2
PVAc+ polyethyleneimine (10 wt. %) +CNT with 99% purity (20 wt. %) + SDBS (20-60 wt. %),	420-1250	-66- -75	--	PF= 1.9- 7.0
PVAc+ CNT with 99% purity (20 wt.%)+ SDBS(20 wt. %) + PEI (0-40 wt. %),	320-430	-65- -80	--	PF= 1.3- 2.7
PVAc+ CNT with 99% purity (20 wt. %) + SDBS (40 wt. %)+ PEI (0-40 wt%), Composition IX [Ref. 50]	440-920	-110 - 110	--	PF= 5- 11
PVAc+ Au deposited CNT (0-20 wt. %) +PEDOT: PSS (15% vol. Replacement by Au) [Ref. 48]	6×10^5	2.5	--	PF= 3.75
PEDOT:PSS+ PVAc + CNT(35-75%) [Ref. 44]	5×10^4 - 1.35×10^5	19-34	0.2-0.4	PF=30-110
Previous work (reference) [Ref. 41]				
PVAc + GINC (80 wt. %)	2.18×10^4	39	3.21	PF= 33, ZT=0.0031
PVAc + Graphene (95%)	2.89×10^3	21	-	PF= 1.2
Present work				PF= 47
PVAc+ GTNC(80 wt. %)	2.6×10^4 S/m	-42	2.9	ZT= 0.0048

4 Conclusions

In summary, we have presented an ecofriendly procedure for synthesis of graphene-titanium dioxide nanocomposite (GTNC) by dispersing nano titanium dioxide (TiO_2) and graphene nano sheet (GNS) in ethanol via ultrasonication followed by microwave irradiation. In this hybrid construction, TiO_2 nanoparticles are interconnected with flexible graphene sheet forming a electrical conductive network. Such nano hybrid was characterized by XRD, HRTEM, FTIR and Raman spectroscopy. We have also demonstrated the synthesis of highly conductive composites like PEDOT:PSS-GTNC, PVAc-GTNC, PEDOT:PSS-graphene, PVAc-graphene by ultrasonication followed by hot compaction towards their thermoelectric application. The concentration of Graphene, GTNC and polymer matrix were judiciously varied in the mixture and optimized for the sake of high electrical conductivity and Seebeck coefficient which leads to higher power factor (PF). The PVAc based composite with a composition of PVAc (20%) and GTNC (80%) was found to be most promising material with an electrical conductivity of 2.6×10^4 S/m and Seebeck coefficient of -42 μV/K. As a result, the PF reaches to 47 $\mu W\ m^{-1}K^{-2}$ which is approximately 37 times higher than PVAc- graphene based composite and five times higher than PEDOT:PSS based composite. The improvement of thermoelectric performance of GTNCcomposite originates from the synergistic effect of graphene nanosheet and TiO_2 nanoparticle. This PF value is found to be maximized, ever reported in the absence of conducting polymer

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Supporting Information

Raman spectra, additional FESEM images, additional HRTEM images, Details of raw materials, instrumentation, nano TiO_2 synthesis, detail procedure for thermoelectric properties measurement,tabulated data,summary ofthermoelectric properties of the best composite of inorganic and organic materials are given.

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