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Electronic Supporting information

Graphene /Titanium dioxide nanocomposite (GTNC): An Emerging, Ecofriendly and Efficient Thermoelectric Material

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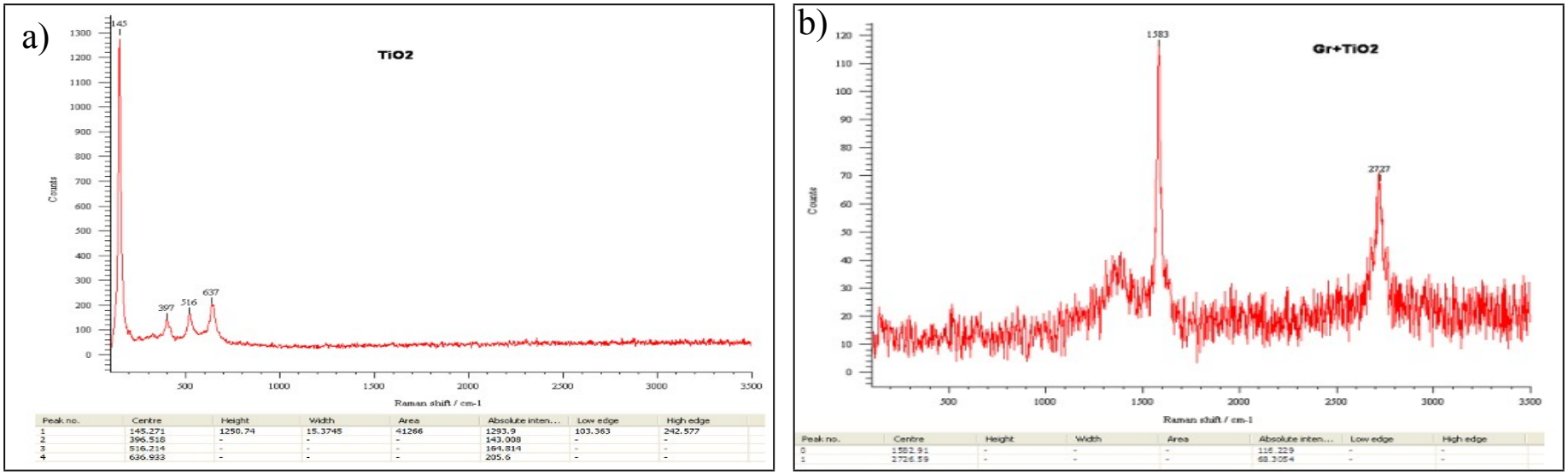


Figure S1: Raman traces of a) TiO2 nanoparticles. and b) Graphene-TiO_2 nano-composite The peak resembling D, G and 2D band of graphene are clearly visible.

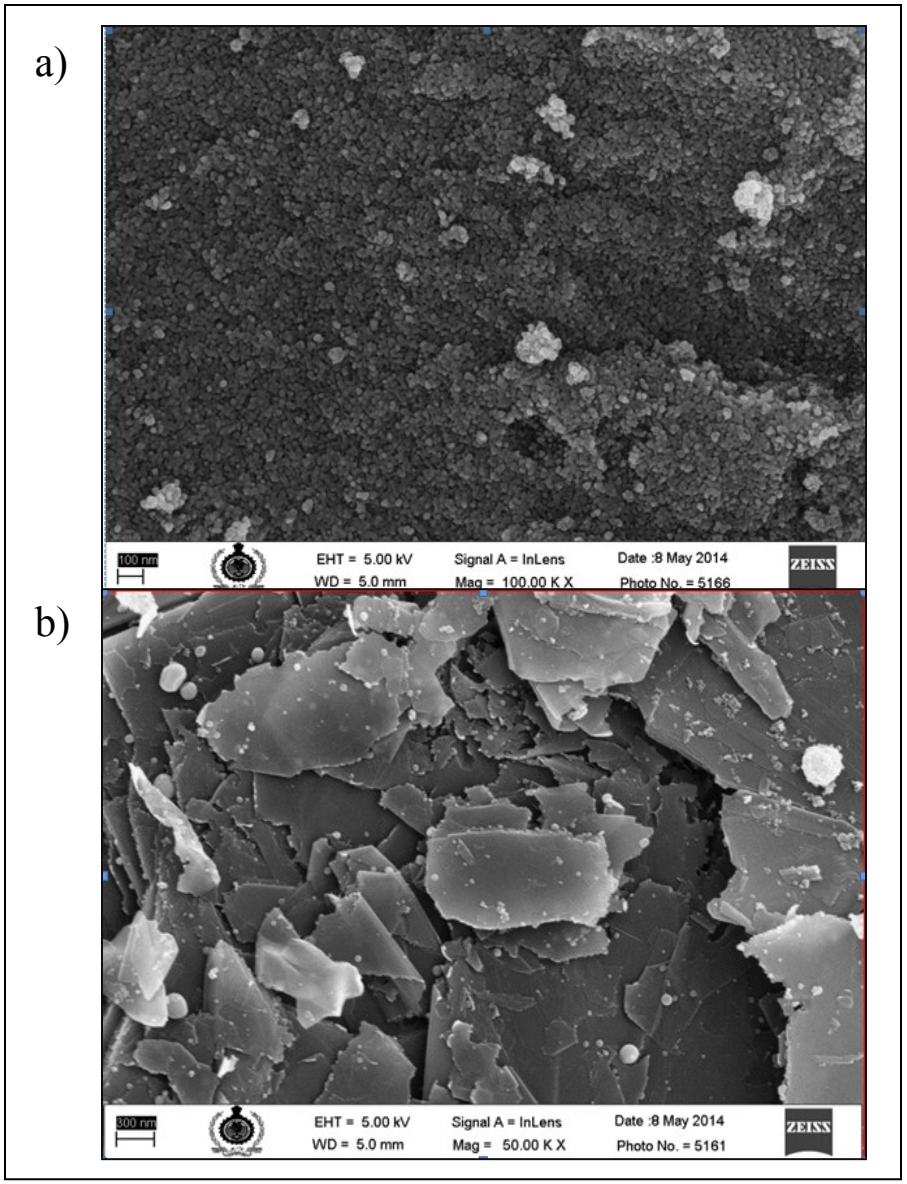


Figure S2: Additional FE-SEM images of a) TiO_2 nanoparticles and b) Graphene-TiO_2 nano-composites.

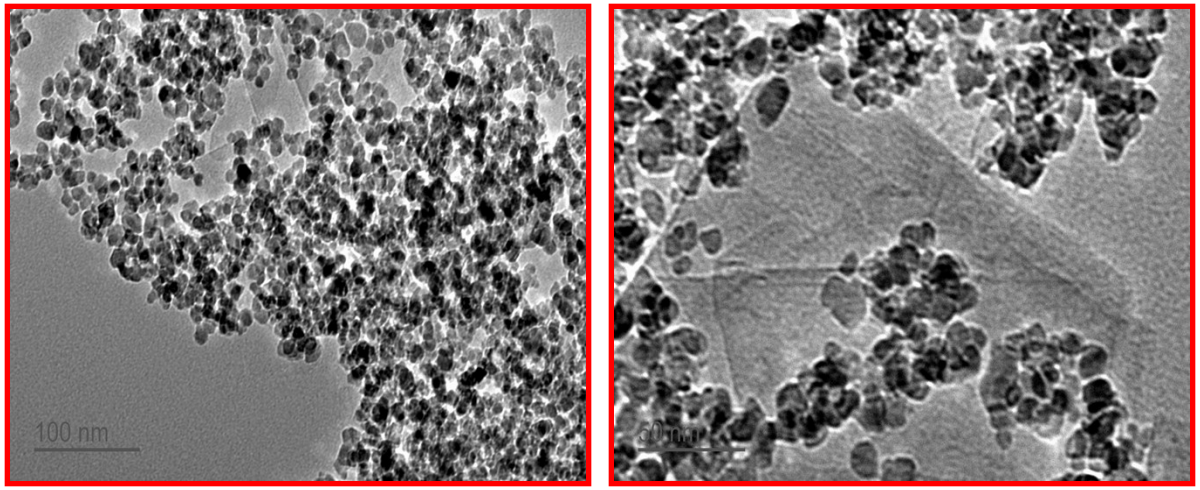


Figure S3: Additional HR-TEM images of Graphene-TiO_2 nano-composites.

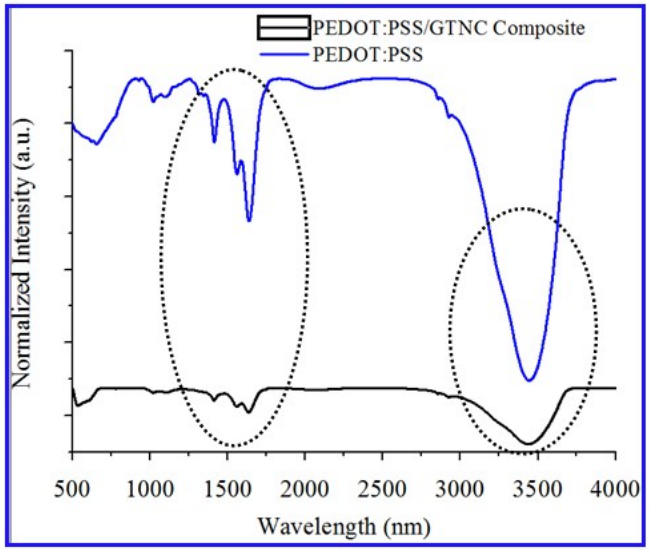


Figure S4: FTIR spectra of PEDOT:PSS and PEDOT:PSS/GTNC composite.

Experimental:

Chemicals: Graphitic flakes (Reinste nano ventures), ethanol (absolute, AR, Merck), Graphite powder, H_2SO_4, $NaNO_3$, NaOH, H_2O_2 (30%), $K_3Fe(CN)_6$ and $KMnO_4$ were purchased from Sigma-Aldrich. All the chemicals were of analytical reagent grades and used as received, without further purifications. The aqueous solutions were prepared in Milli-Q water (18 MΩ cm-1), For the synthesis of TiO2 nanoparticles. myristic acid (Loba chemicals, India), titanium tetrachloride (Sigma Aldrich) were purchased commercially and used without further purification. PVAc (Pidilite industries), PEDOT:PSS (Sigma Aldrich)

Instruments: Sonication was conducted by using ultrasonication bath (35 kHz, Kudos). Microwave irradiation was carried out by a microwave reactor (Raga) FESEM was carried out with Quanta 200, FEI. High resolution transmission microscopy (HRTEM images) characterization was conducted by TACHNAI F-30, FEI with 300 kV field emission gun (FEG). For TEM ananlysis, the samples were first re-dispersed in methanol with ultrasonication. A small drop of re-dispersion was placed on TEM grid and the solvent was evaporated by oven drying. Fourier Transform Infrared Spectroscopy (FTIR) was performed on Nicolet 5700, Thermoscientific. Raman traces were measured by Invia refelex micro raman, Renishaw. X-Ray Diffraction was performed on X- Ray Defractometer, D8 advance, Bruker with Cu Kα source at measurement angle range 2θ=2-90º with a scan rate 2º/ min. Differential Scanning Calorimetry (DSC) curves were collected from DSC-7, Perkin Elmer. Thermo gavimetric analysis (TGA) was conducted by Metter Toledo, Model-TGA/SDTA851. Finally, STA, Mechanical properties was performed using Nasa CEC 71, CAL-VAL,

Synthesis of nano Titanium dioxide: TiO_2 nanoparticles were synthesized by following a reported method[1]. TiO_2 nanoparticles were prepared by sol–gel method *via* hydrolysis of titanium tetrachloride by deionised water. $TiCl_4$ (3 mL) was diluted with deionised water and it was mixed with myristic acid (MA) to obtain a ratio of 1:0.1 ($TiCl_4$: MA). The suspension thus formed was heated on a water bath for about 30 min at about 100°C which resulted in a fine white precipitate. The precipitate was dried completely at 100°C and was calcined at 500 °C for 2 h. The calcined product was directly used for futher experiments

Detail procedure for thermoelectric properties measurement

The electrical conductivity of our samples was measured with four probe instrument (using Delta mode techniques by coupling Keithley 6220 as current source and Keithley 2182A as nano voltmeter, and labview software). The deial procedure is as follows. Electrical conductivity(σ) is the reciprocal of electrical resistivity(ρ). Electyrical resistivity has been calculated from resistance by following equation

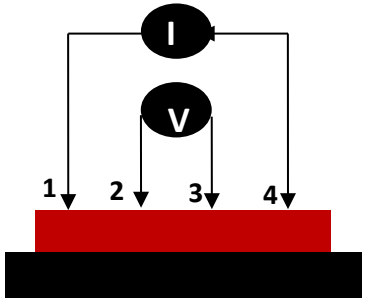
$$\rho = (V/l) / (I/wt)$$

where, V is the voltage, l is the spacing of the probe tips, *w* is the width, t is the thickness and I is the current

The electrical conductivity (σ) can be expreseed as; $\sigma = 1/\rho$

Four probe measurement of electrical conductivity is shown in the figure. Though two contact points is necessary for applying current (I) and measuring voltage (V) of the material. But, four probe method eliminate any contact resistance, electrical noise which

are the main error during electrical resistivity measurement. The thickness of the sample has been measured by degital screw gauge.



Schematic diagram of the four probe instrument used probe head set up in these experiments contained four gold contacts with equal spacing.

Table S1: Thermoelectric properties of PVAc/GTNC composite with concentrations.

Sr. No	Composition	Electrical conductivity (σ) S/m (20°C)	Seebeck coefficient (*S*), µV/k,	Power Factor(PF) $\mu W\ m^{-1}K^{-2}$
1.	PVAc (80%)+GTNC (20%)	538	--[a]	--[a]
2.	PVAc (60%)+GTNC (40%)	564.3	-- [a]	-- [a]
3.	PVAc (40%)+GTNC (60%)	6157	-30.71	5.806
4.	PVAc (20%)+GTNC (80%)	26096	-42.23	46.54
5.	PVAc (10%)+GTNC (90%)	27777	-19.18	10.21
6.	PVAc (5%)+GTNC (95%)	31605	-20.48	13.26

Table S2: Thermoelectric properties of PVAc/Graphene composite with concentrations.

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Sr. No	Composition	Electrical conductivity (σ) S/m (20°C)	Seebeck coefficient (*S*), µV/k	Power Factor(PF) $\mu W\ m^{-1}K^{-2}$
1.	PVAc (80%) + Graphene(20%)	21.47	--	--
2.	PVAc (60%) + Graphene (40%)	186.48	--	--
3.	PVAc (40%) + Graphene (60%)	346.32	-19.69	0.134
4.	PVAc (20%) + Graphene (80%)	484.84	-17.64	0.154
5.	PVAc (10%) + Graphene (90%)	1333.33	-21.44	0.612
6.	PVAc (5%) + Graphene (95%)	2898.55	-20.73	1.245

Table S3: Thermoelectric properties of PEDOT:PSS/GTNC composite with concentrations.

Sr. No	Composition	Electrical conductivity (σ) S/m (20°C)	Seebeck coefficient (*S*), µV/k	Power Factor(PF) µW $m^{-1}K^{-2}$
1.	PEDOT:PSS (60%) + GTNC(40%)	37514	-12.9	6.24
2.	PEDOT:PSS (50%) + GTNC(50%)	85530	-10.0	8.55
3.	PEDOT:PSS (40%) + GTNC (60%)	69930	-8.58	5.14
4.	PEDOT:PSS (30%) + GTNC (70%)	61236	-5.0	1.53
5.	PEDOT:PSS (20%) + GTNC (80%)	55634	-5.4	1.62
6.	PEDOT:PSS (10%) + GTNC (90%)	52671.5	-6.33	2.11
7.	PEDOT:PSS (5%) + GTNC (95%)	38461.5	-4.00	0.61

Table S4: Thermoelectric properties of PEDOT:PSS/GTNC composite with concentrations.

Sr. No	Composition	Electrical conductivity (σ) S/m (20°C)	Seebeck coefficient (*S*), µV/k	Power Factor(PF) µW $m^{-1}K^{-2}$
1.	PEDOT:PSS (60%) + Graphene (40%)	76987	-13.34	13.7
2.	PEDOT:PSS (50%) + Graphene (50%)	105067	-12.2	15.6
3.	PEDOT:PSS (40%) + Graphene (60%)	133333	-11.17	16.65
4.	PEDOT:PSS (30%) + Graphene (70%)	185125	-9.75	17.6
5.	PEDOT:PSS (20%) + Graphene (80%)	242541	-7.5	13.64
6.	PEDOT:PSS (10%) + Graphene (90%)	81726	-8.2	5.4
7.	PEDOT:PSS (5%) + Graphene (95%)	172057	-8.85	13.48

Table S5: Thermoelectric properties of PEDOT:PSS/GTNC composite with concentration

Sr. No	Composition	Electrical conductivity (σ) S/m (20°C)	Seebeck coefficient (*S*), µV/k	Power Factor(PF) µW $m^{-1}K^{-2}$
CP-1	PVAc (20%)+GTNC (80%)	26096	-42.23	46.54
CP-2	PVAc (15%)+ PEDOT:PSS (5%) +GTNC (80%)	6555	-16.21	1.72
CP-3	PVAc (10%)+ PEDOT:PSS (10%) +GTNC (80%)	6405	-12.5	1.01
CP-4	PVAc (5%)+ PEDOT:PSS (15%) +GTNC (80%)	19503	-20.0	7.80
CP-5	PEDOT:PSS (20%) + GTNC (80%)	55634	-5.4	1.62
CP-6	PEDOT:PSS sheet	27972	-28	21.93

Table S6: Summary of thermoelectric properties of the best composite of inorganic and organic materials.

Thermoelectric materials	σ, S/m	*S*, µV/k	κ, W/mK	Calculated PF ($S^2\sigma$), µW $m^{-1}K^2$
PANi + SWCNT composites with different SWCNT [2]	10-125 (RT)	11-40 (RT)	0.5-1 (RT)	0.5-5 (300K)
PANi+ unoxidized SWCNT [3]	5.30×10^4	33		0.6
PANi+ HCL+ MWCNT(40%) [4]	1.71×10^3	10	--	0.17
PANI+CNT (15.8%) [5]	6.1×10^3	29	0.4-0.5	PF=5
CNT+graphite+polylactic acid [6]	4.123×10^3	17	5.5	ZT=7.2×10^{-5} at RT
P3HT+MWCNT (30%) [7]	11	11.3 at 493K	--	--
P3HT+MWCNT (5%) [8]	1.31×10^{-1}	131	--	--

P3HT+SWCNT (81%) P3HT+$FeCl_3$+ SWCNT (42-81%) P3HT+$FeCl_3$+ MWCNT (10-40%) P3HT+$FeCl_3$+ MWCNT (50%) [9]	1.8×10^4 1.1×10^5 8×10^3 1×10^3	32 29 29 12	0.13 -- -- 0.16	18 95 6 0.2
PEDOT:PSS+CNT(35%) [10]	4×10^4	--	0.2-0.4	ZT=0.02
PEDOT:PSS+ SWCNT(20-95%) [11]	6×10^4-3.6×10^5	15-28	0.56	42-95
Nafion +MWCNT (10-50%) [12]	0-8	20-26	--	0.5
Nafion +FWCNT (10 -50%) [6]	0-13	17-24	--	0-1
Nafion +SWCNT (10-50%) [6]	0-1	25-30	--	0.1-0.2
Graphene [13]	10^6	5000	--	ZT= 0.006 at 300K
Thermoelectric materials	**σ, S/m**	***S*, μV/k**	**κ,** W/mK	**Calculated PF ($S^2\sigma$),** μW $m^{-1}K^2$
PANi/Graphene composite [14] PANi Graphene **Pallet :** PANi :Graphene:: 4:1 to 1:1 **Film** PANi :Graphene:: 4:1 to 1:1	 10^3 2×10^4 1.4×10^3-5×10^3 20-700	 14 15 20-30 27-41	 -- -- -- --	 0.2 8 0.7-5.6 0.04-1.2
PANi + HCL +Graphene (50%) [15]	123	34	3.3	14
PANi+GNP (In situ polymerization with protonation ratio- 0.2) Neat PANi Neat GNP PANi/GNP (50mM, as made) PANi/GNP (50mM, reprotonated) [16]	 150 2×10^4 5900 1.74×10^4	 7 5 33 19	 0.6 74 13 15	ZT (300K)= 3.68×10^{-6} 3.04×10^{-6} 1.51×10^{-4} 1.26×10^{-4}
PANI + 30% Graphene (*In-situ* polymerization) [17]	5×10^3 at 323K	12	--	ZT= 1.95×10^{-3} at 453 K

PANI at 420K PANI + 5-30% Graphene [18]	500 700-4.0×10^3	13 28-32	-- --	0.1 0.4-2.6
PANI+$HClO_4$+Graphite (50 wt.%) [19]	1.2×10^4	19	1.2	1.2
PEDOT:PSS+GNP(2-3%) PEDOT:PSS + GN (1-4%) [20]	74-3170	44.75-165.8	0.14-0.30	
PEDOT:PSS/Graphene (1-5%) [21]	52800-63700	21.750-26.778	--	PF= 26.444-45.677

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