Supporting Information

WS_2 Nanotubes as a Functional Filler for Melt Mixing with Poly(lactic acid):Implications for Composites Manufacture

Eimear Magee[1], Fengzai Tang[1], Esra Ozdemir[1], Marc Walker[2], Tiziana Di Luccio[3], Julia A. Kornfield[3], Alla Zak[4], Reshef Tenne[5], Tony McNally[1]*

[1]International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, CV4 7AL, UK

[2]Department of Physics, University of Warwick, Coventry CV4 7AL, U.K.

[3]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

[4]Physics Department, Faculty of Sciences, Holon Institute of Technology - HIT, Holon 5810201, Israel

[5]Molecular Chemistry and Material Science, Weizmann Institute of Science, Rehovot 76100, Israel

*Corresponding Author: Tony McNally (t.mcnally@warwick.ac.uk)

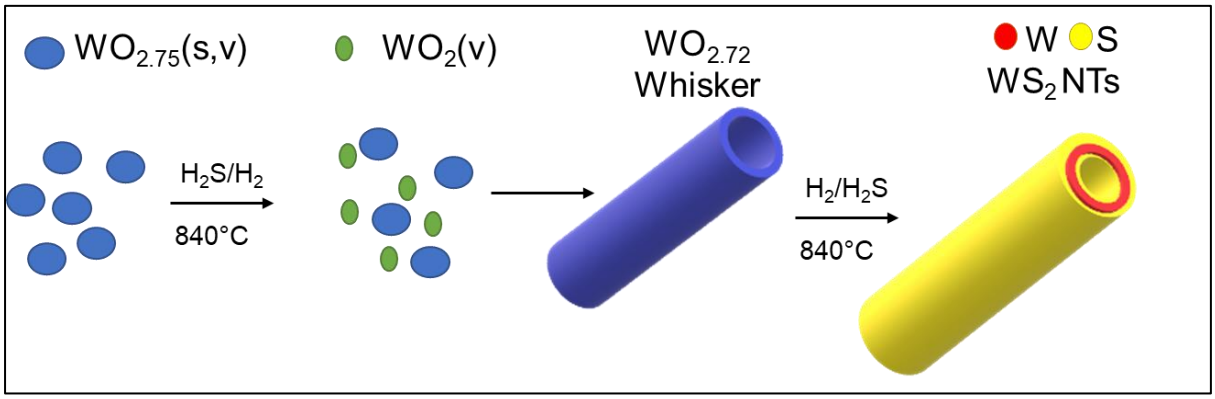

Figure S1. Schematic illustration of the synthesis of WS_2 NTs.

TGA-MS

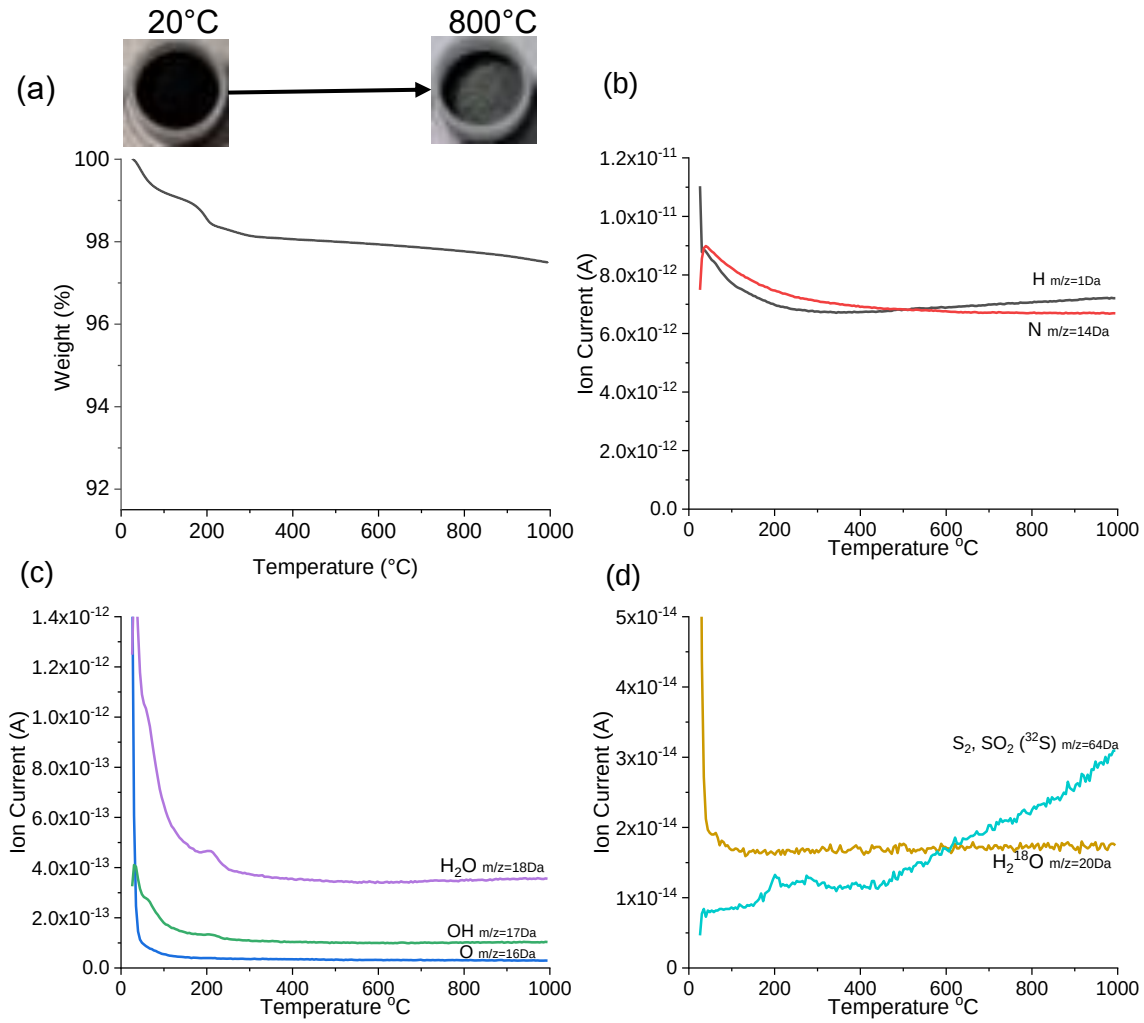

Figure S2. Thermal analysis of WS_2 NTs in an N_2 atmosphere, a) TGA and inset corresponding colour of WS_2 NTs and b) through d) TGA-MS analysis volatile elements detected.

Thermal analysis of WS_2 NTs in an N_2 atmosphere resulted in significantly different behaviour to that recorded in an air atmosphere in that there was no NT colour change observed after heating to 1000°C, see Figure S2 a), confirming there was no chemical reaction of the WS_2 NTs within the inert atmosphere. Additionally, TGA analysis (Figure S2 a)) shows the same small weight loss of 1.9% by 300°C, corresponding to possibly the loss of bound water vapour within the NT sample. However, only a further weight loss of 0.6% between 400-1000°C (2.5%

total) was obtained. TGA-MS correlates the mass loss to water vapour in the temperature region 0 -300°C, and from Figure S2 d) a very small amount ($3.1x10^{-10}$ SEM) of sulphur was detected, that eliminated from WS_2 when heated to 1000°C. WS_2 NTs have therefore shown to be stable within an inert atmosphere when heated up to temperatures of 1000°C showing no chemical reaction or significant change the chemical composition of the WS_2 NTs.

XPS

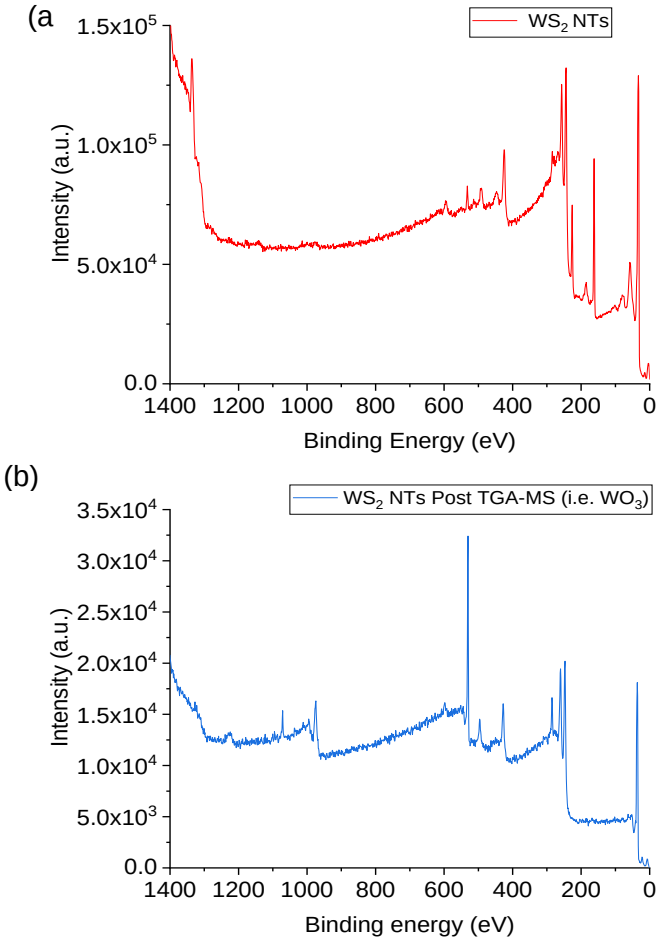

Figure S3. XPs Survey spectra of (a) WS_2 NTs, (b) WS_2 NTs post TGA-MS (i.e. WO_3)

Gel Permeation Chromatography (GPC)

The molecular weight distribution of the extruded pellets of the unfilled and WS_2 NT filled PLA was determined by GPC Analysis. Extruded pellets were dissolved in tetrahydrofuran (THF) in the ratio 5mg of pellets: 1ml THF, assisted by ultra-sonication at 40°C for 1hr. 1.5ml of each solution was pipetted into an Eppendorf tube and centrifuged for 15min at 10,000rpm. 1ml of solution was extracted via a syringe and injected into the GPC instrument through a 0.25µm filter for analysis. The weight average molecular weight (M_w) before and after melt extrusion of unfilled PLA (pellets) and composites of PLA and WS_2 NTs (up to 3wt% loading) were determined.

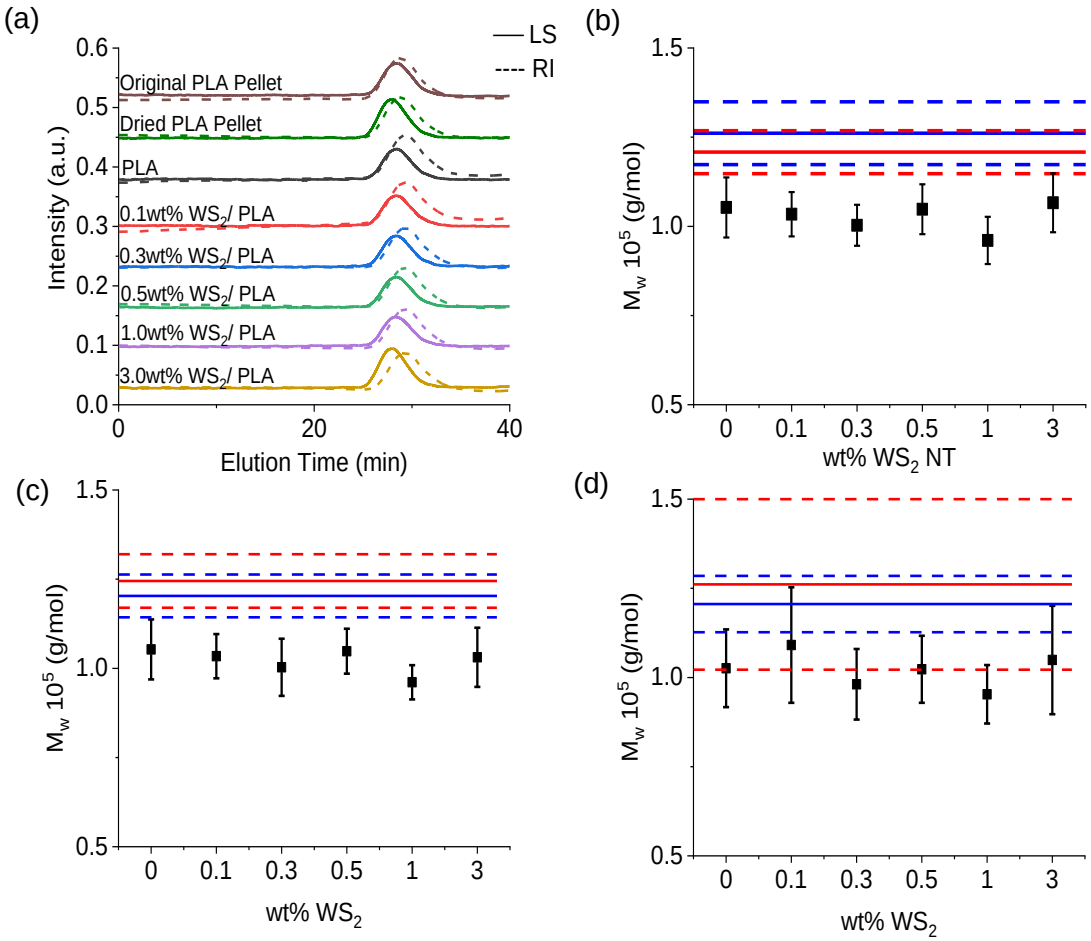

Figure S4. a) GPC curves from light scattering (LS) (solid lines) and the refractive index (RI) (dashed lines) detectors. Measured molecular weight (M_w) of PLA with corresponding uncertainties, b) first measurement, c) second measurement and d) averaged results. Solid blue and red horizontal lines represent the M_w of PLA pellets and dried PLA pellets (before extrusion) respectively, and corresponding dashed lines represent associated uncertainties. Square markers identify the measured M_w of unfilled PLA and composites of PLA and WS_2 NTs as a function of WS_2 NT filler loading after extrusion and uncertainties with associated error bars.

Tensile Testing

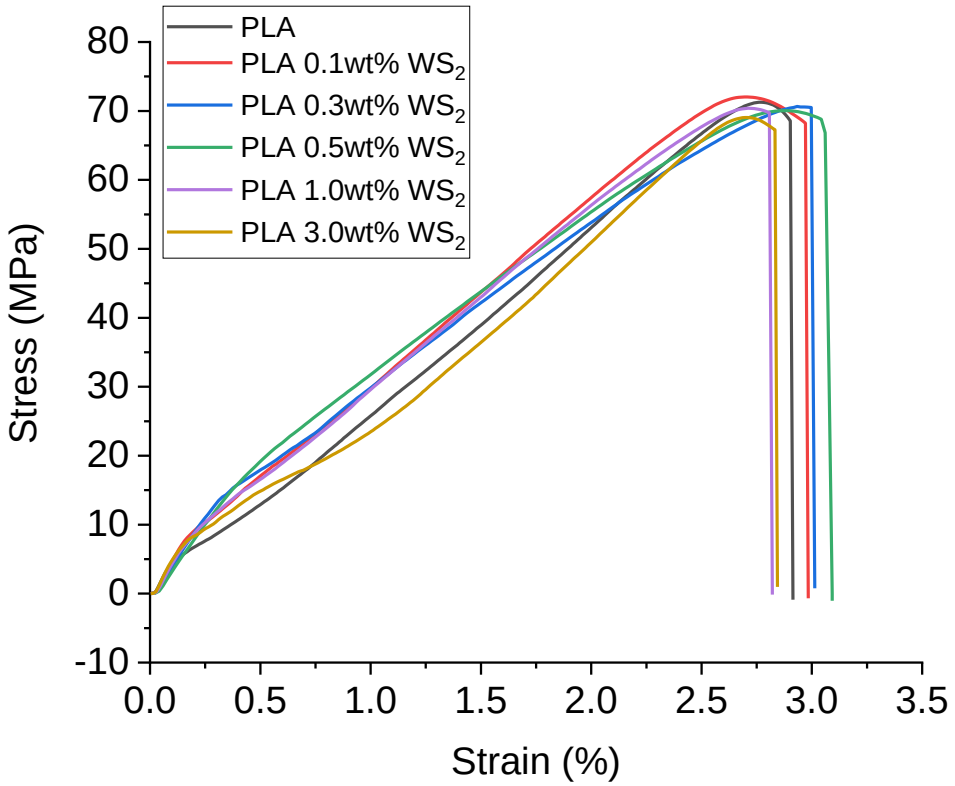

Figure S5. Representative stress-strain curves for neat PLA and composites of PLA and WS_2 NTs. The results for each specimen represent the average value of seven test samples. Dog bone samples were cut from thin (0.5mm) films obtained by pressing at 200 bar each composite in a mould in a Colin hot press ((P 200 PM) at 190 °C for 3 min and then cooled to room temperature at 10 °C/min. The tensile tests were performed using a Shimadzu Autograph AGS-X series instrument with Trapezium X software, specimen gauge length of 26 mm, thickness and width of 0.5mm–0.53 mm. A 10 kN load cell was used with a stroke speed of 5 mm/min from 0 – 0.25% strain according to ISO 527.

Table S1. Tensile mechanical properties of composites of PLA and WS_2 NTs.

PLA (wt% WS_2 NTs)	**Young's Modulus GPa**	**Maximum tensile stress MPa**	**Elongation at break %**	**Tensile toughness* Jm^{-3}**
0	3.28 ± 0.09	72.12 ± 0.84	2.9 ± 0.32	146.55 ± 5.44
0.1	2.77 ± 0.19	72.11 ± 0.83	2.98 ± 0.34	167.82 ± 6.15
0.3	2.90 ± 0.28	71.86 ± 1.98	3.02 ± 0.46	131.87 ± 10.63
0.5	2.44 ± 0.27	70.22 ± 1.20	3.08 ± 0.40	143.85 ± 12.55
1.0	2.84 ± 0.12	70.06 ± 2.52	2.78 ± 0.40	107.28 ± 11.78
3.0	3.12 ± 0.20	68.46 ± 1.19	2.82 ± 0.30	104.90 ± 14.48

*The significant decrease in AR and limited interfacial interaction between the NTs and PLA results in a decrease in mechanical properties, particular tensile toughness. It is likely that less severe mixing is required to avoid breakage of the NTs combined with functionalisation of the NTs to promote favourable interactions with PLA. Both are required to provide a mechanism for effective stress transfer at the interface between composite components.

STEM-EDS

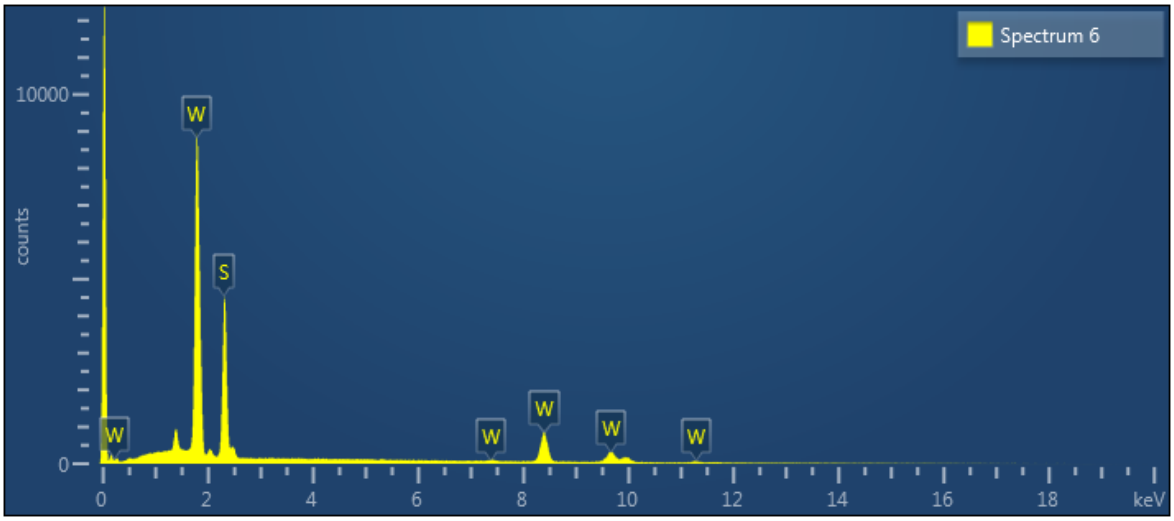

Figure S6. Representative EDS spectrum of the WS_2 NTs.

Table S2. Atomic percentage (at%) for WS2 NTs determined from STEM-EDS spectrum

Spectrum 6				
Element	**Line Type**	**Weight %**	**Weight % Sigma**	**Atomic %**
S	K series	30.37	0.36	71.44
W	L series	69.63	0.36	28.56
Total		100.00		100.00