Supporting Information

Chemical Modification of Carbon Nanomaterials (SWCNTs, DWCNTs, MWCNTs and SWCNHs) with Diphenyl Dichalcogenides

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Materials and Methods.

Solvents and chemicals were purchased from Aldrich and were used as received.

Pristine SWCNTs were obtained from Carbon Nanotechnologies Inc. (HiPco® Single-Wall Carbon Nanotubes, lot number R0513).

Pristine DWCNTs were purchased from Nanocyl (lot number: NC2100, DWCNT 90 % Carbon purity).

The pristine MWCNTs used in this study are commercially available and were purchased from Nanostructured & Amorphous Materials (1229YJ 95 %, outer diameter 20–30 nm).

Pristine SWCNHs were produced by Carbonium s.r.l., Padova (Italy) by direct graphite evaporation in Ar flow, according to a patented method 1,2 and used without purification.

Characterization.

<u>Thermogravimetric analyses</u> (TGA) were performed using a *TA Instruments TGA Q500* with a ramp of 10 °C/min under N_2 from 100 to 800 °C.

<u>Raman spectra</u> were acquired with a *Renishaw* instrument, model *InVia reflex* equipped with 532, 633, and 785 nm lasers. After acquisition, the spectra were normalized with respect to the G-band and then the area of the D and G peaks were calculated.

<u>X-ray photoelectron spectroscopy (XPS)</u> analyses were performed with a *VGMicrotech ESCA 3000Multilab*, equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatized Al K α source (1486.6 eV) run at 14 kV and 15 mA. The analyzer was operated in the constant analyzer energy (CAE) mode. For the individual peak energy regions, a pass energy of 20 eV set across the hemispheres was used. Survey spectra were measured at 50 eV pass energy. The sample powders were analyzed as pellets, mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10⁻⁸ torr during data collection. The constant charging of the samples was removed by referencing all the energies to the C1s set at 284.4 eV, on the main C1s peak of SWCNTs. The invariance of the peak shapes and widths at the beginning and at the end of the analyses ensured absence of differential charging. Analyses of the peaks were performed with the software provided by VG, based on non-linear least squares fitting program using a weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood.^{3, 4} Atomic concentrations were calculated from peak intensity using the sensitivity factors provided with the software. The binding energy values are quoted with a precision of ± 0.15 eV and the atomic percentage with a precision of $\pm 10\%$.

<u>UV/Vis/nIR spectra</u> were obtained with a *Cary 5000* spectrophotometer using a 10 mm path length quartz cuvettes. The functionalized SWCNTs materials were redispersed in *N*-methyl-2-pyrrolidone (NMP) or methanol (where mentioned) (1mg/ml) by ultrasonication for 30 min. Spectra were taken from the supernatant after mild centrifugation (10 krpm, 10 min, *Hettich EBA 21*) in order to remove coarse aggregates.⁵ SWCNTs concentration was evaluated as 1 mg/ml of carbonaceous material.

Fourier Transform-InfraRed (FT-IR) spectra have been recorded in KBr on a *Perkin Elmer 2000* spectrometer.

<u>Transmission Electron Microscopy</u> (TEM) images were acquired using a *Philips EM 208* microscope, with accelerating voltage of 100 kV. Samples were prepared by sonication for 10 min and dropwise addition (8 μ L) of the sample onto a carbon coated 200 mesh Ni grid (*EM Sciences*, Gibbstown, NJ) followed by solvent evaporation under vacuum.



Figure S1. TGA of *p*-SWCNTs and *f*-SWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Weight losses have been calculated in the 250-700°C range and *p*-SWCNTs weight loss has been subtracted to the *f*-SWCNTs one. To be noticed, the slope of *f*-SWCNTs functionalized with (PhSe)₂ and (PhTe)₂ appear different from the profile of the (PhS)₂.



Figure S2. Insight of the D- and G-bands region from the recorded Raman spectra ($\lambda_{exc} = 532$ nm) of *p*-SWCNTs and of *f*-SWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Normalization of the peaks was performed taking in account the intensity of the G-band peak.



Figure S3. RBM region from the recorded Raman spectra ($\lambda_{exc} = 532$ nm) of *p*-SWCNTs and *f*-SWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Normalization of the peaks was performed taking in account the intensity of the peak localized at 186 cm⁻¹ in order to avoid the effect of nanotubes individualization over peaks intensity.



Figure S4. Insight of the D- and G-bands region from the recorded Raman spectra ($\lambda_{exc} = 633$ nm) of *p*-SWCNTs and *f*-SWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Normalization of the peaks was performed taking in account the intensity of the G-band peak.



Figure S5. RBM region from the recorded Raman spectra ($\lambda_{exc} = 633$ nm) of *p*-SWCNTs and *f*-SWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Normalization of the peaks was performed taking in account the intensity of the peak localized at 257 cm⁻¹ in order to avoid the effect of nanotubes individualization over peaks intensity.

Figure S6. Insight of the D- and G-bands region from the recorded Raman spectra ($\lambda_{exc} = 785$ nm) of *p*-SWCNTs and *f*-SWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Normalization of the peaks was performed taking in account the intensity of the G-band peak.

Figure S7. RBM region from the recorded Raman spectra ($\lambda_{exc} = 785$ nm) of *p*-SWCNTs and *f*-SWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Normalization of the peaks was performed taking in account the intensity of the peak localized at 266 cm⁻¹ in order to avoid the effect of nanotubes individualization over peaks intensity.

	C1s (eV)	O1s (eV)	Heteroatom	O/C	X/C
			(X)		
p-SWCNTs	284.4 (66%)	532.4 (100%)		0.03	
	286.1 (13%)				
	287.4 (6%)				
	290.3 (15%)				
(PhS)-SWCNTs	284.4 (61%)	530.4 (24%)	169.1	0.14	0.01
	285.5 (35%)	532.3 (76%)			
	286.9 (4%)				
(PhSe)-	284.4 (67%)	530.2 (29%)	53.4 (39%)	0.04	0.005
SWCNTs	285.7 (22%)	532.6 (71%)	55.7 (47%)		
	286.9 (5%)		58.4 (14%)		
	289.9 (6%)				
(PhTe)-	284.4 (95%)	530.3 (28%)	573.3 (7%)	0.04	0.005
SWCNTs	285.7 (5%)	533.5 (72%)	575.9 (93%)		

 Table S1. XPS binding energy (eV) and atomic ratio of f-SWCNTs functionalized with diphenyl dichalcogenides

Figure S8. IR spectra of *p*-SWCNTs and *f*-SWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂.

Figure S9. TEM image of *f*-SWCNTs functionalized with $(PhS)_2$ (scale bar = 500 nm).

Figure S10. TEM image of *f*-SWCNTs functionalized with $(PhSe)_2$ (scale bar = 500 nm).

Figure S11. TEM image of *f*-SWCNTs functionalized with $(PhTe)_2$ (scale bar = 500 nm).

Figure S12. ESP charge distribution charts generated for *f*-SWCNTs functionalized with (PhS)₂; color intensity ranges from red (negative residual charge) to black (no residual charge) to green (positive residual charge).

Figure S13. ESP charge distribution charts generated for f-SWCNTs functionalized with (PhSe)₂; color intensity range is defined as for Figure S12.

- **Figure S14**. ESP charge distribution charts generated for *f*-SWCNTs functionalized with (PhTe)₂; color intensity range is defined as for Figure S12.
- **Table S2**. ESP charge medium values of the chalcogen and sp³-C atoms involved in the functionalization of SWCNTs.

	pristine (7,3) SWCNTs	(PhS) ₂ funct. (7,3) SWCNTs	(PhSe) $_2$ funct. (7,3) SWCNTs	(PhTe) ₂ funct. (7,3) SWCNTs
sp ³ -C atom	-	0,570	0,619	0,336
chalcogen atom	-	-0,320	-0,191	0,038

Table S3. Graphic representation of the HOMO-1, HOMO, LUMO and LUMO+1 orbitals from the models produced for *f*-SWCNTs functionalized with the different diphenyl dichalcogenides.

	pristine	$(PhS)_2$ funct.	$(PhSe)_2$ funct.	(PhTe) ₂ funct.	
	(7,3) SWCNTs	(7,3) SWCNTs	(7,3) SWCNTs	(7,3) SWCNTs	
НОМО-1	-4,633 eV	-4,633 eV	-4,604 eV	-4,560 eV	
НОМО	-4,487 eV	-4,426 eV	-4,391 eV	-4,377 eV	
LUMO	-2,978 eV	-3,106 eV	-3,068 eV	-3,169 eV	
LUMO+1	-2,849 eV	-2,887 eV	-2,878 eV	-2,919 eV	

Table S4. Energy values of the HOMO-1, HOMO, LUMO and LUMO+1 orbitals from the models produced for *f*-SWCNTs functionalized with the different diphenyl dichalcogenides.

	C1s	O1s	Heteroatom (A)	O/C	A/C
n-DWCNTs	284 4 (80%)	530.0 (31%)	_	0.02	_
	286 2 (12%)	532, 5 (69%)		0.02	
	289.6 (8%)	002.0 (0) (0)			
Ph-S-DWCNTs	284.4 (79%)	532.0 (85%)	163.7 (39%)	0.03	0.004
	286.0 (10%)	534.5 (15%)	168.2 (61%)		
	287.9 (5%)				
	290.4 (6%)				
Ph-Se-DWCNTs	284.4 (83%)	532.1 (100%)	n.d.	0.02	n.d.
	286.2 (12%)				
	288.7 (5%)				
Ph-Te-DWCNTs	284.4 (90%)	530.2 (19%)	573.5 (9%)	0.04	0.007
	285.8 (10%)	531.8 (81%)	575.9 (91%)		
<i>p</i> -MWCNTs	284.4 (74%)	532.6 (3.7)	-	0.01	-
	285.7 (14%)				
	286.9 (6%)				
	290.0 (6%)				
Ph-S-MWCNTs	284.4 (82%)	532.1 (100%)	n.d.	0.01	n.d.
	285.4 (15%)				
	286.7 (3%)	522 4 (100g)	1	0.02	1
Ph-Se-MWCNTs	284.4 (77%)	532.4 (100%)	n.d.	0.02	n.d.
	285.7(19%)				
	280.9(5%)				
Ph-To-MWCNTs	290.0(170)	530 3 (50%)	573 2 (5%)	0.04	0.02
	285 7 (16%)	530.3(39%) 532 1 (41%)	576.0 (95%)	0.04	0.02
n-SWCNHs	284 4 (70%)	532.4 (100)%	-	0.01	_
	285.4 (27 %)	552.1 (100)/0		0.01	
	286.7 (3%)				
Ph-S-SWCNHs	284.4 (94%)	532.0 (100%)	163.9 (55%)	0.05	0.003
	286.0 (5%)	· · · ·	168.7 (45%)		
	287.5 (1%)				
Ph-Se-SWCNHs	284.4 (75%)	529.6 (3%)	n.d.	0.03	n.d.
	285.7 (22%)	532.3 (97%)			
	287.3 (2%)				
Ph-Te-SWCNHs	284.4 (75%)	532.2 (100%)	576.0 (100%)	0.03	0.002
	285.6 (19%)				
	286.7 (6%)				

Table S5. XPS binding energy (eV) and atomic ratio of *f*-DWCNT, *f*-MWCNT and *f*-SWCNHsfunctionalized with diphenyl dichalcogenides.

Figure S15. TGA of *p*-DWCNTs and *f*-DWCNTs functionalized with $(PhS)_2$, $(PhSe)_2$ and $(PhTe)_2$. Weight losses have been calculated in the 250-600°C range and *p*-DWCNTs weight loss has been subtracted to the *f*-DWCNTs ones.

Figure S16. Insight of the D- and G-bands region from the recorded Raman spectra ($\lambda_{exc} = 532$ nm) of *p*-DWCNTs and of *f*-DWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Normalization of the peaks was performed taking in account the intensity of the G- band peak.

Figure S17. IR spectra of *p*-DWCNTs and of *f*-DWCNTs functionalized with $(PhS)_2$, $(PhSe)_2$ and $(PhTe)_2$.

Figure S18. TEM image of *f*-DWCNTs functionalized with $(PhS)_2$ (scale bar = 1000 nm).

Figure S19. TGA of *p*-MWCNTs and of *f*-MWCNTs functionalized with $(PhS)_2$ $(PhS)_2$, $(PhSe)_2$ and $(PhTe)_2$. Weight losses have been calculated in the 250-600°C range and *p*-MWCNTs weight loss has been subtracted to the *f*-MWCNTs one.

Figure S20. Insight of the D- and G-bands region from the recorded Raman spectra ($\lambda_{exc} = 532$ nm) of *p*-MWCNTs and of *f*-MWCNTs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Normalization of the peaks was performed taking in account the intensity of the G- band peak.

Figure S21. IR spectra of *p*-MWCNTs and of *f*-MWCNTs functionalized with $(PhS)_2$, $(PhSe)_2$ and $(PhTe)_2$.

Figure S22. TEM image of f-MWCNTs functionalized with (PhS)₂ (scale bar = 1000 nm).

Figure S23. TGA of *p*-SWCNHs and of *f*-SWCNHs functionalized with $(PhS)_2$, $(PhSe)_2$ and $(PhTe)_2$. Weight losses have been calculated in the 250-600°C range and *p*-SWCNHs weight loss has been subtracted to the *f*-SWCNHs one.

Figure S24. Insight of the D- and G-bands region from the recorded Raman spectra ($\lambda_{exc} = 532 \text{ nm}$) of *p*-SWCNHs and *f*-SWCNHs functionalized with (PhS)₂, (PhSe)₂ and (PhTe)₂. Normalization of the peaks was performed taking in account the intensity of the G- band peak.

Figure S25. TEM image of *f*-SWCNHs functionalized with $(PhS)_2$ (scale bar = 100 nm).

Figure S26. Column a) C1s core of the corresponding *f*-CNFs with (PhSe)₂ (red line) and column b) Se3d high-resolution XPS spectra.

Figure S27. Column a) C1s core of the corresponding f-CNFs with (Ph-Te)₂ (red line) and column b) Te3d high-resolution XPS spectra.

References:

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