

# Efficient Chemical Modification of Carbon Nanotubes with Metallacarboranes

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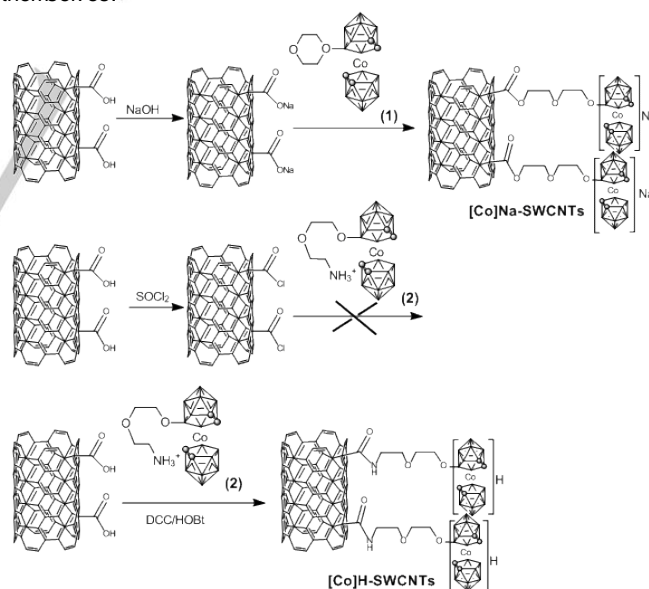
**Abstract:** As-produced single-walled carbon nanotubes (SWCNTs) tend to aggregate in bundles due to  $\pi-\pi$  interactions. Several approaches are nowadays available to debundle, at least partially, the nanotubes by surface modification via both covalent and non-covalent approaches. Herein we explore different strategies to afford an efficient covalent functionalization of SWCNTs with cobaltabisdicarbollide anions. Aberration corrected high-resolution transmission electron microscopy analysis reveals the presence of metallacarboranes along the walls of the SWCNTs. This new family of materials presents an outstanding water dispersibility which facilitates its processability for potential applications.

Preparation of boron-based hybrids is attracting an increased interest due to their applications in a wide range of fields such as materials science, nanotechnology and biomedicine.<sup>[1]</sup> One of the most used boron carriers are the ortho-carborane clusters and derivatives due to their high thermal and chemical stabilities along with their low toxicity in biological systems.<sup>[2]</sup> As a consequence, several strategies have been explored to prepare boron-containing materials using ortho-carborane derivatives. One approach is the functionalization of dendrimers to control the number of boron atoms and benefit from the combination of properties of the dendritic molecules.<sup>[3]</sup> Another strategy consists on grafting ortho-carborane clusters onto nanomaterials, including metal nanoparticles,<sup>[4]</sup> graphene<sup>[5]</sup> and carbon nanotubes. In this regard, encapsulation<sup>[6]</sup> and sidewall attachment of o-carborane clusters onto single-walled carbon nanotubes (SWCNTs) have been previously explored via covalent<sup>[7]</sup> and non-covalent functionalization.<sup>[8]</sup> These earlier works dealt with the use of closo-o-carborane, a neutral and hydrophobic cluster. It has recently been demonstrated that metallacarboranes, in special the cobaltabisdicarbollide or cosane,  $[3,3'\text{-Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ , have uncommon physico-chemical properties in water due to the self-assembling capacity,<sup>[9]</sup> inducing the formation of micelles and monolayer vesicles.<sup>[10]</sup> One evidence of the vesicles and micelles generation was the poor performance as electrolytes in the water electrolysis.<sup>[11]</sup>

On the other hand, carbon nanotubes (CNTs) can carry multiple moieties at high density because of their large specific surface area. Their unique properties make them suitable also for a wide range of areas such as energy, information, and biomedicine.<sup>[12]</sup> However, a major drawback of this family of

nanomaterials is that their applications are discouraged due to their tendency of agglomeration and their intrinsic hydrophobicity.<sup>[13]</sup> Many studies have been conducted with the purpose to increase the dispersibility of SWCNTs in water via covalent and non-covalent modifications.<sup>[14]</sup> In order to modulate their dispersibility in water we have combined the SWCNTs with the physical properties of metallacarboranes. This will afford a new family of carbon-based hybrids materials with better processability. In this work we report the chemical modification of SWCNTs by covalent functionalization of cobaltabisdicarbollide derivatives and their localization along the wall structure of the nanotubes.

Three different strategies have been investigated to covalently functionalize SWCNTs with cobaltabisdicarbollide anions (Co), as outlined in Scheme 1. Steam purified SWCNTs were treated with nitric acid to introduce oxygen bearing functionalities in their structure, mainly carboxylic acid groups (COOH-SWCNTs). The steam purification was performed, prior to the nitric acid treatment, to remove amorphous carbon from the as-received SWCNTs.<sup>[15]</sup> The reaction of amorphous carbon with nitric acid would result in the formation of oxidation debris that is known to hinder the sidewall functionalization of the SWCNTs themselves.<sup>[16]</sup>



**Scheme 1.** Synthetic strategies to functionalize SWCNTs with  $[3,3\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  anions.

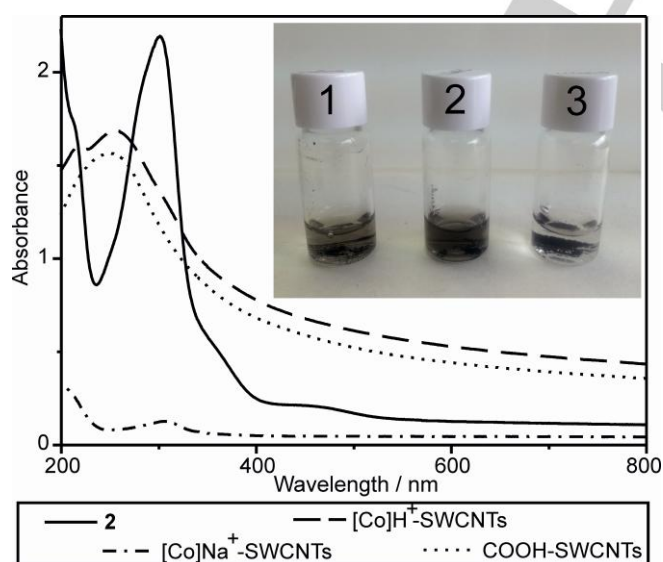
The first route that was explored to attach the metallacarboranes involved the *in situ* ring-opening of metallacarborane **1**<sup>[17]</sup> by reaction with preactivated COONa-SWCNTs in anhydrous DME, resulting in the immobilization of cobaltabisdicarbollide anions as sodium salts ( $[\text{Co}]\text{Na-SWCNTs}$ ) (see S.I.). For the second strategy, in order to

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control the ring-opening step, the dioxane ring was opened to obtain metallacarborane **2**<sup>[18]</sup> before the reaction with preactivated COCl-SWCNTs. However, this approach was unsuccessful, due to the instability of **2** in the presence of SOCl<sub>2</sub>. As an alternative, **2** was reacted with preactivated COOH-SWCNTs with DCC/HOBt, resulting in the functionalization of SWCNTs with the protonated salts ([Co]H-SWCNTs (see S.I.)). The presence of the cobaltabisdicarbollide anions in the samples was further confirmed by thermogravimetric analysis (TGA) in air and X-ray Photoelectron Spectroscopy (XPS). As it can be seen in the TGA curves (Figure S2) the metallacarborane-functionalized SWCNTs start to oxidize at lower temperatures than the purified sample confirming the presence of organic moieties. Furthermore after the complete combustion of the sample at 900 °C, the inorganic solid residue was higher in the metallacarborane-modified samples (9.1 wt.% for [Co]H-SWCNTs; 12.8 wt.% for [Co]Na-SWCNTs) than in the purified SWCNTs (2 wt.%). At this temperature all the carbon from the SWCNTs and organic moieties have been completely oxidized and thus removed from the samples. Therefore, the solid residue corresponds to iron oxide (from the oxidation of the iron catalyst employed for the growth of the SWCNTs) and to the oxidized metallacarborane clusters. Taking into account that Na has a higher atomic weight than H, a similar degree of loading of boron clusters can be inferred from the present analysis. Next, XPS measurements were performed to confirm the integrity of the metallacarborane cluster after being anchored onto the SWCNTs. The presence of both B and Co could be already detected in the general survey scan of the prepared hybrids. Analysis of the high resolution XPS spectra over the B 1s and Co 2p regions indicates a B to Co ratio of about 20:1 in both samples (Figures S3-S4 and Table S1). This value is in agreement with the stoichiometry of the employed cobaltabisdicarbollide anion, confirming that the cluster has been well preserved during the whole functionalization process.

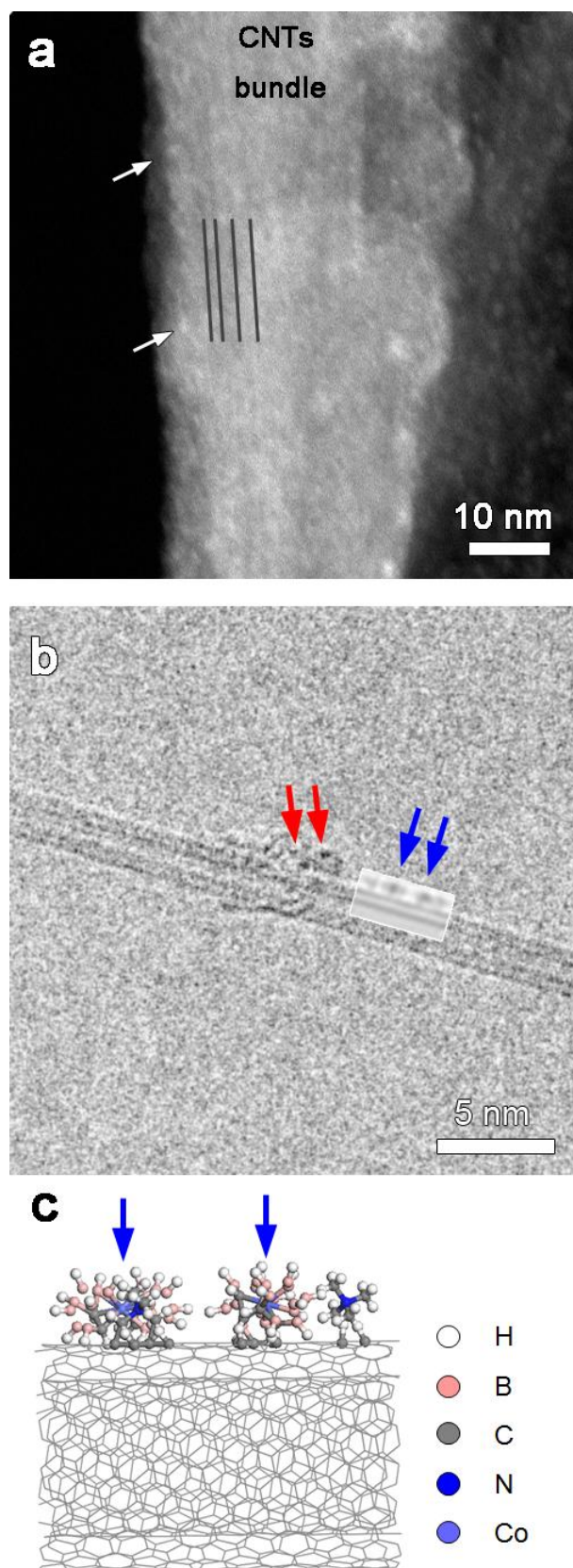


**Figure 1.** UV-Vis spectra of oxidized SWCNTs, **2**, COOH-SWCNTs, [Co]H-SWCNTs and [Co]Na-SWCNTs. Inset picture: 1 mg/ml dispersions in water of COOH-SWCNTs (vial 1), [Co]H-SWCNTs (vial 2), [Co]Na-SWCNTs (vial 3).

As mentioned, a major obstacle for the use of CNTs in the biomedical field is their lack of dispersibility in aqueous media.

The dispersibility of the functionalized SWCNTs was assessed in water by UV-Vis spectroscopy. Aqueous dispersions of both samples of metallacarborane-functionalized SWCNTs were freshly prepared (1 mg/mL), and the resulting UV-Vis spectra, along with that of metallacarborane **2** are presented in Figure 1. As a control experiment, a 1 mg/mL dispersion of COOH-SWCNTs in water was prepared, and the resulting UV-Vis spectrum is also included in the Figure for comparison. COOH-SWCNTs were chosen since it is well established that the chemical oxidation of SWCNTs in strong oxidizing acids leads to highly water-dispersible nanotubes.<sup>[19]</sup> The absorption value at  $\lambda = 500$  nm was employed to assess the relative degree of dispersion in the samples.<sup>[20]</sup> For ease of comparison, the absorbance of COOH-SWCNTs at 500 nm was set as 100 %. The higher dispersibility was achieved with [Co]H-SWCNTs (117 %), confirming an efficient functionalization of the material and highlighting the role that the metallacarborane clusters play in the properties of the hybrids. However, despite that the amount of clusters present in [Co]Na-SWCNTs is similar to that of [Co]H-SWCNTs, the former presented a much lower degree of dispersibility in water (8 %). This indicates that the employed counterion is crucial in defining the properties and potential applications of the functionalized SWCNTs. Additional information can also be extracted from the observed absorption bands. Metallacarborane **2** presents a well defined band centered at 300 nm and a visible band (present as a shoulder) at 213 nm. The UV-Vis spectrum of [Co]H-SWCNTs still presents two bands, one at 217 nm, indicating the presence of the cobaltabisdicarbollide anion and a second broad band at 256 nm, which is shifted with respect to the band present in the COOH-SWCNTs; confirming the anchoring of the metallacarboranes onto the SWCNTs. It is worth noticing that even after three months, the dispersions of [Co]H-SWCNTs and COOH-SWCNTs were still stable (Figure S5).

The performed analysis so far relies on bulk techniques that confirm the presence of cobaltabisdicarbollide anions in the samples and their link via covalent bonds. Nevertheless, these techniques can not discern between a cluster anchored onto a SWCNT and a cluster covalently bonded to any other carbon impurity that might be present in the samples (such as graphitic particles or fullerenes, side products from the synthesis of SWCNTs). Direct evidence of metallacarborane clusters anchored onto the sidewalls of the SWCNTs was obtained using high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) of [Co]H-SWCNTs. Figure 2a presents a HAADF-STEM image of a bundle of CNTs (indicated by assistive lines) where dots of bright contrast can be seen along the CNTs walls (as indicated by white arrows). The contrast of HAADF-STEM images (also called Z-contrast images) scales approximately with the atomic number. Therefore, heavy elements will appear brighter than light elements and the bright dots observed in the image can be attributed to Co atoms from the metallacarboranes covering the walls of the SWCNTs. The samples were also investigated by HRTEM. In the image presented in Figure 2b, an individual carbon nanotube (in this case a double-walled CNT) can be observed containing several aggregates on top of its walls. Dark contrast is noticed in the aggregates as indicated by red arrows, and is assumed to be contributed by Co atoms in the metallacarboranes. Therefore, image simulation is performed using the similar hybrid model of [Co]H-DWCNT as demonstrated in Fig.2c. Under the same imaging condition as in



**Figure 2.** STEM and HRTEM analysis of the material a) Dark field STEM image of  $[\text{Co}]\text{H}^+$ -SWCNTs. b) HRTEM of a carborane cluster attached to the wall of a DWCNT with the corresponding simulation (inset) and model (c).

the microscope, the simulated image shows darker contrast for Co atoms (indicated by blue arrows) and lighter for its agglomerates, as presented in Fig.2c. The good agreement between the experimental HRTEM image and the simulated image indicates that the observed aggregates on top of the DWCNT are very likely to be  $[\text{Co}]\text{H}$ , further confirming the successful anchoring of carboranes onto the CNTs.

In summary, we have performed a new anionic boron-enriched CNT-based nanocarrier that exhibit an outstanding dispersibility in water. For this purpose, several strategies to achieve an efficient covalently functionalisation of SWCNTs with cobaltabisdicarbollide derivatives have been investigated. Complementary techniques have been employed to confirm the covalent anchoring of the clusters and to determine the composition of the modified nanotubes. Notably, the visualization of the metallocarboranes along the tubular structure of the SWCNTs was achieved using aberration-corrected HRTEM and STEM imaging, providing direct evidences of the anchoring of the anionic boron clusters. The degree of dispersibility of the hybrids in water is found to be highly dependent on the counterion of the metallocarboranes. Whereas  $\text{Na}^+$  leads to hybrids with poor water dispersibility, a high dispersibility, superior to that of nitric acid oxidized SWCNTs, has been achieved when employing  $\text{H}^+$  as the counterion. In conclusion, the combination of cobaltabisdicarbollide anions with carbon nanostructures leads to a new hybrid that may be used as high boron content nanocarriers.

## Acknowledgements

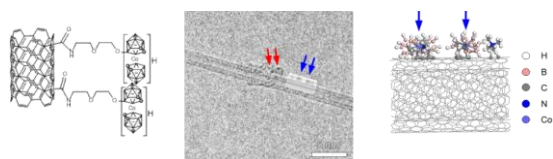
The research leading to these results has received financial support from MINECO (MAT2014-53500-R; CTQ2013-44670-R), Generalitat de Catalunya (2014/SGR/149), and from the European Commission under the FP7 ITN Marie-Curie Network programme RADDEL (grant agreement 290023), the Integrated Infrastructure Initiative N. 262348 European Soft Matter Infrastructure (ESMI) and the European Research Council ERC Grant No 246791- COUNTATOMS. AGC thanks to CSIC for the JAE-DOC grant.

**Keywords:** boron hybrids, carbon nanotubes, metallocarborane, carborane, HRTEM

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Single-walled carbon nanotubes have been covalently modified with cobaltabisdicarbollide anions. High resolution transmission electron microscopy reveals localization of the clusters along the walls of the carbon nanotubes. The resulting hybrids present an outstanding water dispersibility.

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**Efficient Chemical Modification of Carbon Nanotubes with Metallacarboranes**



a)

b)

c)

### **Scheme 1. Functionalization of SWCNTs with metallacarborane clusters**

#### Methodology A:

COOH-SWCNTs were activated following literature methods.<sup>9</sup> Briefly, COOH-SWCNTs (15 mg) were mixed with a solution of 10 M NaOH in water (10 mL) for 5h at 90 °C. The mixture was filtered through a 0.2 µm polycarbonate membrane and thoroughly washed with water. Then, the collected COONa-SWCNTs were dried under vacuum at 60°C to remove the traces of water. Afterwards, the flask was purged with bubbling argon and vacuum for 3 times to remove any traces of oxygen and a solution of **1** (22 mg) in anhydrous DME (5 mL) was added drop wise. The mixture was then stirred at room temperature for 72h. The solvent was removed and the final [Co]Na-SWCNTs were washed with EtOH, filtered through the polycarbonate membrane, washed with MeOH and dried.

#### Methodology B:

COOH-SWCNTs were activated following literature methods.<sup>10</sup> Briefly, acid treated SWCNTs (15 mg) were heated at 65 °C in thionyl chloride (5 mL) for 24h. After this time the solvent was removed under vacuum and a solution of **2** (46.3 mg) in dried DMF (5 mL) was added to the thionyl chloride treated SWCNTs. After 96h, the mixture was cooled at room temperature and 10 mL of MeOH was added. The product was filtered through the polycarbonate membrane, washed with MeOH and dried.

### Methodology C:

COOH-SWCNTs were activated following literature methods.<sup>10</sup> Briefly, COOH-SWCNTs (15 mg) were preactivated with DCC/HOBt (20.6 mg/13.5 mg) in dried DMF (5 mL). After 45 min, a solution of **2** (24 mg) in dried DMF (3 mL) was added. The mixture was then stirred at room temperature for 72h. After this time, the solvent was removed under vacuum and 10 mL of MeOH was added. The final mixture was filtered through the polycarbonate membrane, washed with MeOH and dried to get the final functionalized [Co]H-SWCNTs.

### Instrumentation:

#### Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded in the transmission mode with a Perkin Elmer Spectrum One spectrometer at 4 cm<sup>-1</sup> resolution by co-adding 10 scans. Thin films of carborane-SWCNT hybrids were prepared on top of a ZnSe disk (2 mm thickness) by drop-drying sample dispersions on 2-propanol onto the preheated substrate at 80 °C.<sup>11</sup>

#### Thermogravimetric Analysis (TGA)

TGA analyses were performed under flowing air at a heating rate of 10°C/min up to 950°C (Jupiter<sup>®</sup>, Netzsch Instrument, Germany).

#### X-ray Photoelectron Spectroscopy

XPS were acquired with a Kratos AXIS ultra DLD spectrometer with an Al K $\alpha$  X ray font and a power of 120 W. Samples were measured as dry powder. Survey-scan was conducted with a Pass Energy of 160 eV and high resolution scans at a Pass Energy of 20 eV. Hybrid-slot lens mode was employed, with an area of analysis of 700 x 300 microns. The XPS data was acquired at the Laboratorio de Microscopias Avanzadas (LMA)-Instituto de Nanociencia de Aragón (INA) in Spain

#### Electron Microscopy

HAADF-STEM and HRTEM images were acquired using an FEI Titan 80-300 cubed microscope fitted with an aberration-corrector for the imaging lens and another for the probe-forming lens, as well as a monochromator, operated at 80kV. The monochromator was excited to provide an energy resolution of approximately 0.3eV. The Cs value was tuned to below 10 $\mu$ m. Image simulation of HRTEM images was performed using JEMS (<http://cimewww.epfl.ch/people/stadelmann/jemsWebSite/jems.html>).

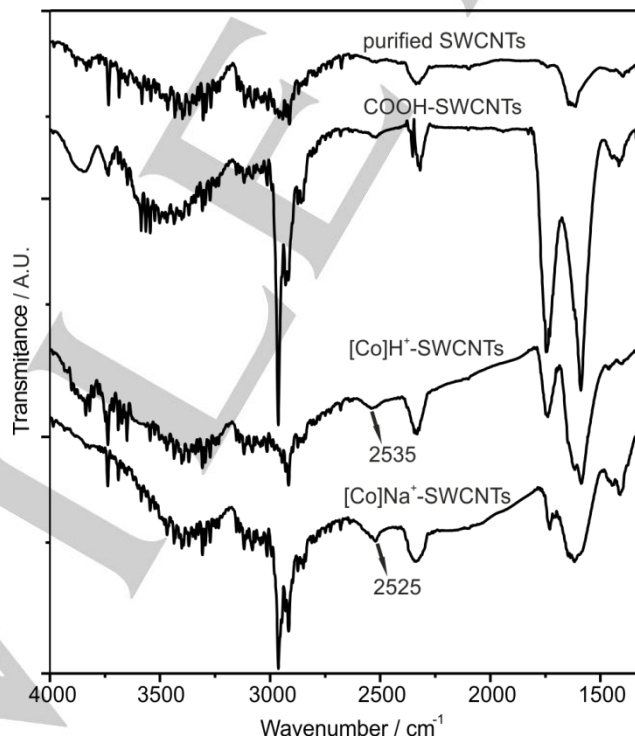


STEM and HRTEM samples were prepared by dispersing a small amount of powder in absolute ethanol and sonicated in an ultrasonic power bath. Afterwards, the dispersion was drop dried onto a lacey carbon TEM grid.

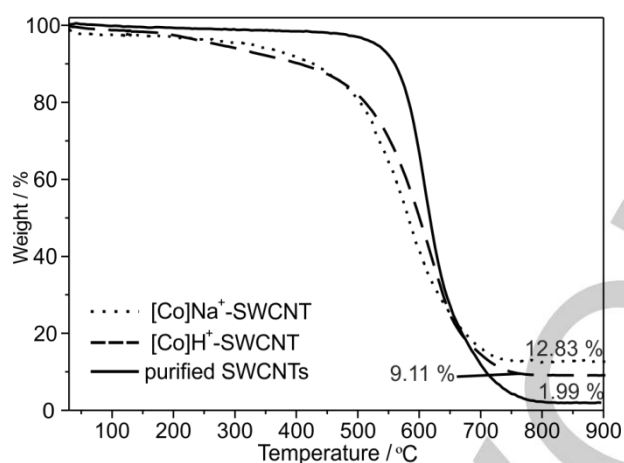
#### Ultraviolet-Visible spectroscopy

The dispersions of the hybrids were characterized using a Cary 5 Varian UV/Vis/NIR spectrophotometer, operating between 200-800 nm.

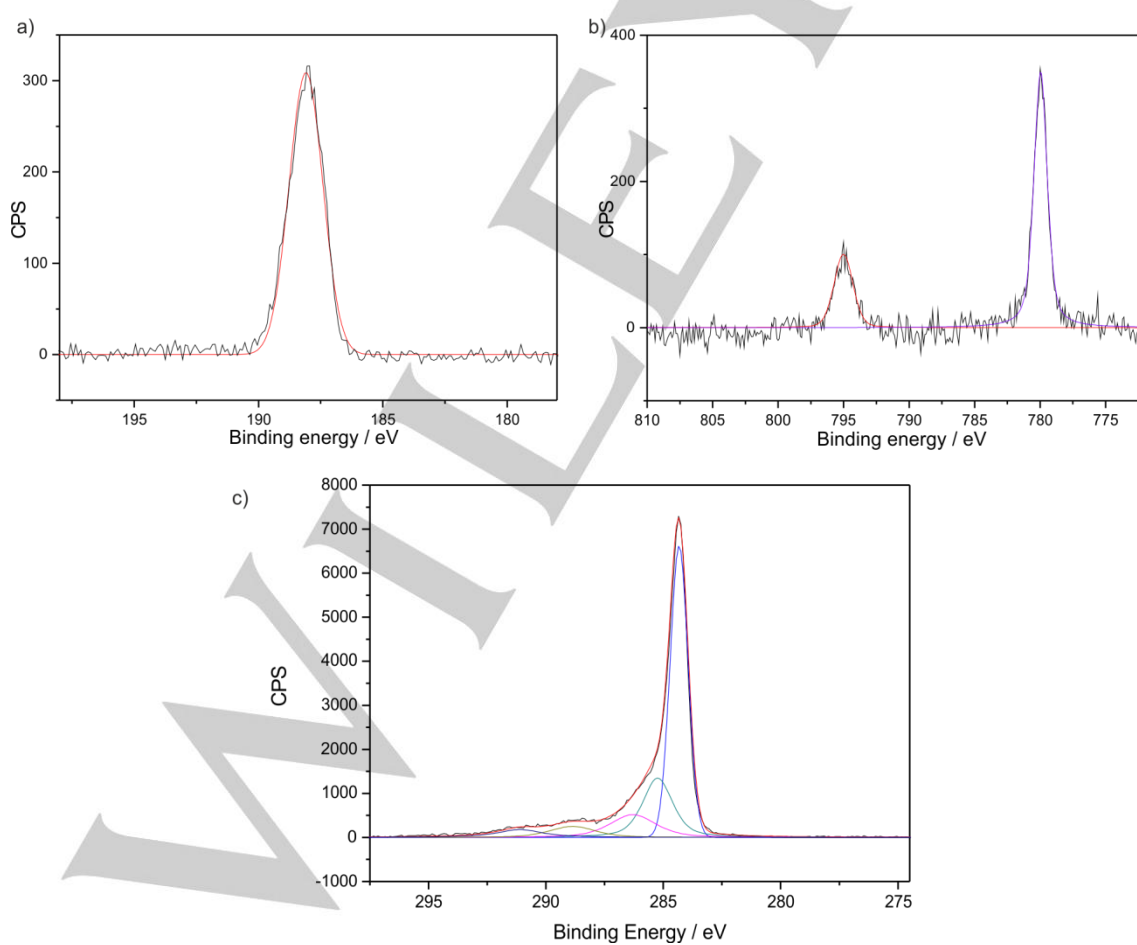
#### Supplementary Figures



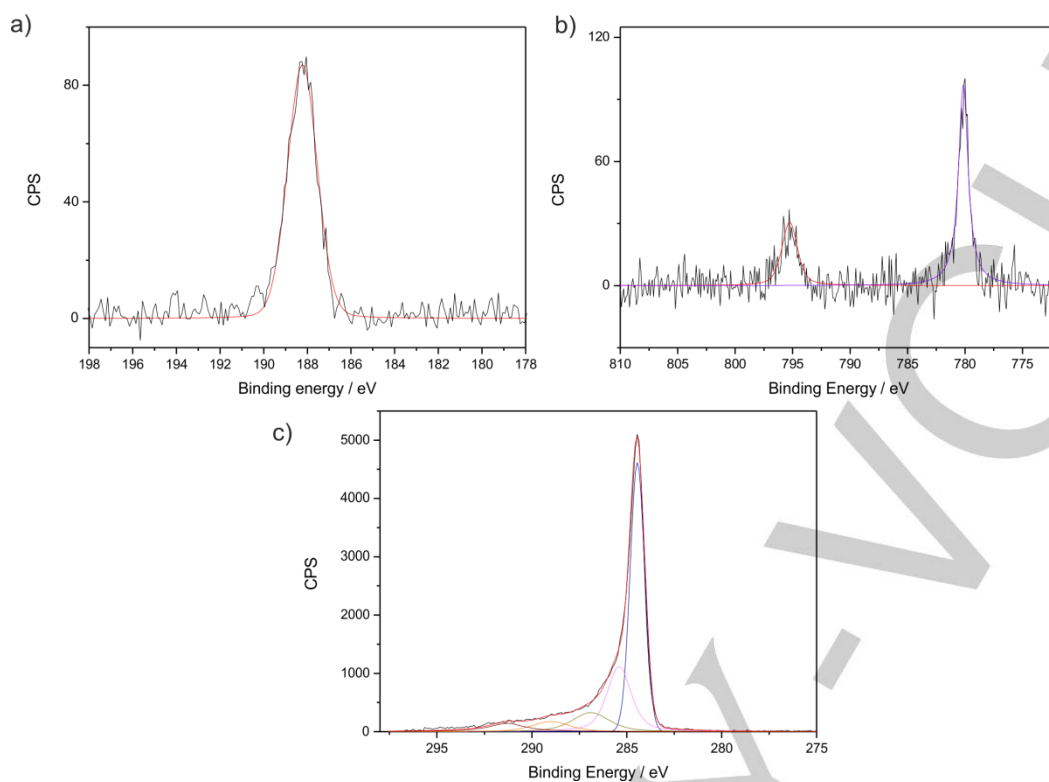
**Figure S1.** FT-IR spectra of purified SWCNTs, COOH-SWCNTs, [Co]Na-SWCNTs and [Co]H-SWCNTs.



**Figure S2.** TGA curves of purified SWCNTs, [Co]H-SWCNTs and [Co]Na-SWCNTs.



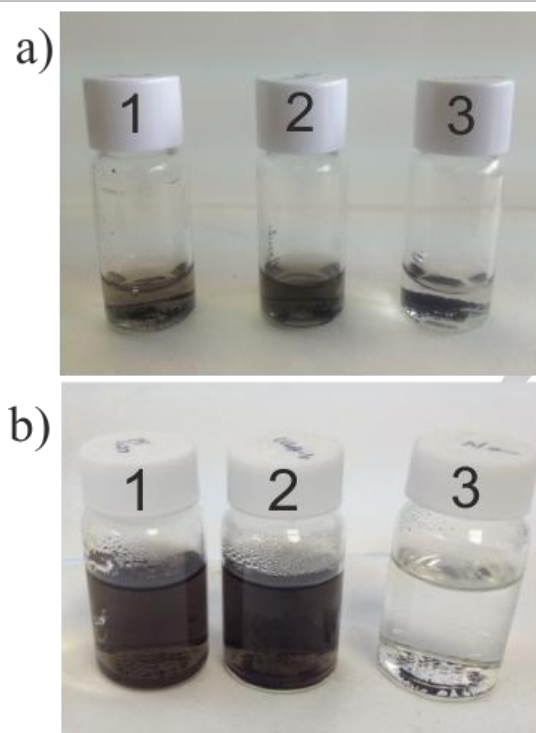
**Figure S3.** XPS spectra of [Co]Na-SWCNTs of (a) B1s, (b) Co 2p and (c) C1s



**Figure S4.** XPS spectra of [Co]H-SWCNTs of (a) B 1s, (b) Co 2p and (c) C 1s

**Table S1:** B:Co atomic ratio determined by integration over the high resolution B 1s and the Co 2p<sub>3/2</sub> regions in the XPS spectra.

Element	Atomic ratio	
	[Co] H-SWCNTs	[Co] Na-SWCNTs
<b>B</b>	20	19
<b>Co</b>	1	1



**Figure S5:** 1 mg/ml dispersions of 1- COOH-SWCNTs, 2- [Co]H-SWCNTs, 3- [Co]Na-SWCNTs a) in fresh solutions and b) after 3 months of its preparation.

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