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# Correlation between microstructure and surface chemistry of carbon nanofibers grown using different adhesive layers



Ishan Pande<sup>a</sup>, Sami Sainio<sup>b, c</sup>, Jani Sainio<sup>d</sup>, Ville Liljeström<sup>e</sup>, Hua Jiang<sup>d</sup>, Tomi Laurila<sup>a, f, \*</sup>

<sup>a</sup> Department of Electrical Engineering and Automation, School of Electrical Engineering, Aalto University, PO Box 13500, 00076 Aalto, Finland

<sup>b</sup> Microelectronics Research Unit, Faculty of Information Technology and Electrical Engineering University of Oulu, P.O. Box. 4500, 90570 Oulu, Finland

<sup>c</sup> Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, United States

<sup>d</sup> Department of Applied Physics, School of Science, Aalto University, PO Box 15100, 00076 Aalto, Finland

<sup>e</sup> Nanomicroscopy Center, OtaNano, Aalto University, FI-00076 Aalto, Finland

<sup>f</sup> Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, PO Box 16200, 00076 Aalto, Finland

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# ABSTRACT

Carbon nanofibers (CNFs) have applications in a wide range of technological and scientific fields. The connections between their micro- and macrostructure and observed performance are, however, currently lacking. This hinders the realization of their full potential. In this paper, we correlate the microstructure of CNFs grown on two types of substrates: (1) Si + 20 nm Ti + 20 nm Ni, and (2) Si + 80 nm Cr + 20 nm Ni, to their surface chemistry. We use transmission electron microscopy (TEM), supported by energy dispersive X-ray spectroscopy (EDS) and Xray diffraction (XRD) analysis, to describe the morphology and structure of CNFs as well as the underlying interfacial layers. Then, we study the similarities and differences in chemistry of these two types of CNFs using Xray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) and correlate them with the observed structural features of the fibers. Vertically aligned, tip-type fiber growth was observed on both substrates. TEM micrographs show that the CNFs grown on the Cr + Ni substrates have a slightly distorted herringbone-like structure, whereas fibers grown on the Ti + Ni substrates have relatively ill-defined structure with basal planes pointing outwards. Consequently, the latter possess a richer surface chemistry, which is apparent from the wider peaks and more spectral features observed during XAS and XPS measurements. This analysis provides us with some of the missing structure-chemistry connections, which can subsequently be expanded towards including correlations of these features with observed performance of the CNFs in different applications. Ultimately, this enables us to tailor features of the CNFs for specific target fields.

# 1. Introduction

Carbon nanofibers (CNFs) have attracted considerable attention in recent years due to their excellent physical and chemical properties. Their large surface area, wide potential windows and large electrical conductivity makes them especially suitable as electrodes for electrochemical sensing [1–4]. Moreover, CNFs have been reported to be suitable for a variety of other applications, including energy storage [5], gas storage [6], water purification [7], and catalysis [8].

Plasma enhanced chemical vapor deposition (PECVD) is a widely used technique for growing CNFs at relatively low temperatures. A PECVD growth process for CNFs usually requires a nanoscale catalyst metal layer (e.g. Ni, Fe, Co). An adhesive layer (e.g. Cr, Ti) is often deposited between the substrate material and the catalyst layer, to prevent interactions between the catalyst and substrate layers. The growth of CNFs occurs through the nucleation of the catalyst layer in the presence of a carbonaceous gas (e.g.  $C_2H_2$ ,  $C_2H_4$ ) as well as an etchant gas (e.g. NH<sub>3</sub> or H<sub>2</sub>), which are activated in a glow discharge. The microstructure and the macroscale morphology of CNFs depend upon the process parameters (e.g. temperature, chamber pressure, gas flow rates and plasma power), as well as the composition and thickness of the adhesive and catalyst layers [9–12].

The properties of CNFs and other carbon-based nanomaterials, especially their electrochemical sensitivity and selectivity, are affected by their surface chemistry [4,13–17]. The surface chemistry of CNFs, in turn, depends on their microstructure [13]. It has been shown that the

E-mail address: tomi.laurila@aalto.fi (T. Laurila).

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<sup>\*</sup> Corresponding author at: Department of Electrical Engineering and Automation, School of Electrical Engineering, Aalto University, PO Box 13500, 00076 Aalto, Finland.

electrochemical properties of carbon-based nanomaterials are sensitive to small changes in their structural properties [18]. Therefore, in order to optimize the materials for a desired application, a thorough understanding of their surface chemistry is needed. Information about the types of functional groups, their relative abundance, as well as the chemical states of the different constituent elements, is therefore crucial for tailoring the properties of CNFs for specific applications. However, there is currently a lack of systematic studies linking the chemistry of CNFs to their observed structural properties. Thus, in this work, we describe the differences between the microstructure of two types of CNFs, and how these differences correlate with their surface chemistry.

We have synthesized CNFs on two types of substrates: (1) Si + 20 nm Ti + 20 nm Ni, and (2) Si + 80 nm Cr + 20 nm Ni (subsequently referred to as TiNi and CrNi, respectively) using a  $C_2H_2/NH_3$  PECVD process. Other process parameters were kept constant, so that the observed differences in microstructure and surface chemistry can be reasonably attributed to the differences between the adhesive layers. We present a detailed study of the microstructure of the fibers using transmission electron microscopy (TEM), supported by Energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) analysis. Then, we study the similarities and differences in the chemistry of these two types of CNFs using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS), and correlate them with observed microstructural differences.

# 2. Methods

p-type Silicon wafers (Siegert Wafers, Germany) were used as substrates for all the samples. First, the wafers were coated with adhesive and catalyst metal layers – 20 nm Ti followed by 20 nm Ni for TiNi-CNFs, and 80 nm Cr followed by 20 nm Ni for CrNi-CNFs. An electron beam evaporator (MASA IM-9912) was used for depositing the metal layers. The chamber pressure was approximately  $2 \times 10^{-7}$  mbar during evaporation. Subsequently, the wafers were cleaved into smaller pieces, measuring approximately 7 mm × 7 mm. Finally, CNF growth was carried out using a PECVD reactor (Aixtron Black Magic).

The PECVD process was carried out as follows: First, the chamber was pumped down to 0.1 mbar. Then, the chamber was heated to 400 °C with a ramp speed of approximately 250 °C per minute. When the temperature reached 395 °C, the chamber was injected with a 100 sccm NH<sub>3</sub> buffer. The ramp rate was then increased to 300 °C per minute and the chamber was heated up to 600 °C. When the temperature reached 575 °C, 230 W DC plasma was ignited. 30 sccm C<sub>2</sub>H<sub>2</sub> was simultaneously injected into the chamber, while the flow rate of NH<sub>3</sub> was increased to 125 sccm. These parameters were maintained for 10 min. The chamber pressure was approximately 3 mbar during the growth process.

TEM imaging was performed on a Jeol JEM 2200FS transmission electron microscope equipped with an X-ray energy dispersive spectrometer (EDS). Cross-sectional TEM samples were prepared by EAG Laboratories (USA) using a focused ion beam (FIB). Sputtered carbon was used as the filler material. The sample was coated locally at the cross-section site with two additional layers of carbon.

Grazing incidence X-ray diffraction (GI-XRD) from the samples was measured using a Rigaku SmartLab X-ray diffractometer with a rotating anode source. The X-ray beam was monochromatized by the incident side Ge-220 double-bounce monochromator with a 5.0° incident side soller slit. The used wavelength was the copper K- $\alpha_1$  wavelength ( $\lambda =$ 1.541 Å). The intensity was collected using a 2D hybrid pixel detector used in 1D mode. Slit settings during XRD measurements were - Length limiting slit: 2.0 mm, incident slit: 1.0 mm, receiving slit 1: 12 mm, receiving slit 2: 20.1 mm. Slit settings during GI-XRD and other 2 $\theta$ measurements were - Length limiting slit: 2.0 mm, incident slit: adjusted according to the x-ray beam footprint at each  $\omega$ , receiving slit 1: 6 mm, receiving slit 2: 10.1 mm. Slit settings during XRR measurements were: Length limiting slit: 2.0 mm, incident slit: 0.04 mm, receiving slit 1: 0.15 mm, receiving slit 2: 0.15 mm. The detector was set on X-ray fluorescence reduction mode in all experiments and an additional antiair scatter slit was installed between the sample and receiving slit 1. No background or other corrections are applied to the data. The data were analyzed using Vesta (Version 3.4.0) and Match (Version 3.14) softwares.

X-ray photoelectron spectroscopy (XPS) was carried out with a Kratos Axis Ultra spectrometer with monochromated Al K<sub>α</sub>-radiation, a pass energy of 40 eV, an X-ray power of 75 W and an analysis area of approximately 700 µm × 300 µm. The binding energy scale is based on instrument calibration and no additional binding energy correction has been applied. The elemental composition was determined from peak areas of high-resolution core level spectra after Shirley background subtraction using equipment specific sensitivity factors. Peak fitting was done using Gaussian-Lorentzian peaks (GL (30) line shape in CasaXPS) with the positions of the peaks fixed to within  $\pm 0.1$  eV of given binding energies. For sp<sup>2</sup> carbon an asymmetric line shape was used in CasaXPS [19]. The full widths at half-maximum (FWHMs) of the peaks were restricted to be equal within a fit with the exception of sp<sup>2</sup> carbon and N-oxide peaks.

Soft X-ray absorption spectroscopy (XAS) measurements were performed on the 33- pole wiggler beamline 10-1 at Stanford Synchrotron Radiation Lightsource (SSRL) using 55° incidence angle (magic angle) of X-rays. A resolution of ~200 meV was achieved with a spherical grating monochromator which was operated using  $40 \times 40 \,\mu\text{m}$  slits. X-ray beam spot size was approximately  $1 \times 1 \text{ mm}^2$  with total flux in order of  $10^{11}$ photons/s. The following edges were measured: C 1s, N 1s, O 1s, Ti 2p, Cr 2p and Ni 2p. The X-ray energy ranges for the C 1s, N 1s, Ti 2p, O 1s, Cr 2p and Ni 2p edges were 260-340 eV, 380-480 eV, 450-490 eV, 520-560 eV, 570-610 eV, and 840-890 eV, respectively. A Keithley picoammeter was used for amplifying the drain current to collect all the data in total electron yield (TEY) mode, where the incoming flux was measured using a nickel grid coated with Au sputtered film. Here, a reference sample was used for energy calibration of the data prior to the data analysis. Beamline energy calibration is based on matching the Ni L3 in 2nd order at 426.35 eV prior to measurement for low energy samples (up to O1 s) and Ni L3 at 852.7 eV for high energy samples (above O1 s). The C 1s spectra were confirmed to match their energy calibration by observing the core exciton signature at 291.65 eV [26-28] after the reference sample energy alignment.

The presented C 1s spectra is normalized, while the other spectra are shown as absolute intensities. All of the spectra with a single line are averages of three different location from the sample surface. Furthermore, all the data treatment (background subtraction and energy correction) was done using IGOR Pro v. 8.02 software.

### 3. Results and discussion

Vertically aligned CNFs were grown on both types of substrates. CrNi-CNFs appear to have a clear herringbone structure (Fig. 1E). On the other hand, TiNi-CNFs do not have a well-defined structure. There appears to be a "spine" that resembles a stacked-cup or bamboo structure, which is surrounded by graphene sheets that are aligned at acute angles with respect to the fiber axis (i.e. the direction perpendicular to the substrate's surface) (Fig. 1B). We refer the readers to a review article by Melechko et al. [10] for definitions of different types of CNF structure (herringbone, bamboo) and growth modes (tip-type, base-type). From the higher magnification images (Fig. 2), we see that the graphene sheets are aligned more towards the vertical direction in TiNi-CNFs. Moreover, TiNi-CNFs appear to have a less ordered structure than CrNi-CNFs - they appear to consist of graphene sheets that are relatively misaligned with each other, as shown by the red lines in Fig. 2. Moreover, from Fig. 2, we see that in CrNi-CNFs, the graphene sheets terminate at the surface in such a way that the edge planes are exposed at the sidewalls. On the other hand, in TiNi-CNFs, the sidewalls consist mostly of basal planes.

Tip-type growth mode occurred on both substrates. In Fig. 1A and D,



**Fig. 1.** TEM micrographs of CNFs. TiNi-CNF overview (A). TiNi-CNF microstructure (B). Interface between fiber and TiNi substrate (C). CrNi-CNF overview (D). CrNi-CNF microstructure (E). Interface between fiber and CrNi substrate (F). Interfacial layers are marked in (C) and (F) with yellow text. The yellow arrow in (C) indicates the interface between Ti and Ni<sub>1-x</sub>Si<sub>x</sub> layers. A detailed description of the interfaces is provided in our previous work [20].

we can see that the tips of both types of CNFs are nearly identical. A high magnification micrograph of the tips is provided in Fig. S2. The tips are elongated in the downwards direction (with respect to the fibers axis) and surrounded by graphene sheets on all surfaces except at the top. The tips consist of almost pure Ni; EDS scans (Fig. S2) do not show significant amounts of Cr or Ti at the tips.

Microstructure of the fiber-substrate interfaces has been described in detail elsewhere [20]. Briefly: In case of CrNi-CNFs, the interface consists of Cr with dissolved graphite and/or chromium carbides (Fig. 1F). In case of TiNi-CNFs, there are two distinct regions – an intermediate reaction layer at the Ti/Si interface that contains significant amounts of Ni, as well as a Ti region with dissolved C and/or Ti<sub>x</sub>C<sub>y</sub> (Fig. 1C).

GI-XRD (Grazing incidence XRD) diffractograms (Fig. 3) provide further evidence for the description of the microstructure that we have provided above. Diffraction peaks are expected to be caused by the tip nanoparticles and by the top interfacial layer that is below the CNF layer. The carbon nanofiber layer should absorb and diffract weakly, hence it is assumed not to contribute significantly to the diffractograms. In addition, we have provided GI-XRD profiles of the samples at two stages of the growth process - (1) pristine substrate, and (2) substrate ramped up to 575 °C - in Fig. S1. Thus, Fig. S1 shows the evolution of the phases at different stages of the growth process. GI-XRD patterns of both types of CNFs contain strong peaks at  $2\theta \approx 44, 51, 77$  and  $93^{\circ}$ . These match reasonably well with both elemental Ni and Ni<sub>x</sub>Si<sub>y</sub>. Since a silicide layer exists below the TiNi-CNFs [20], we can reasonably assign these peaks to Ni<sub>x</sub>Si<sub>y</sub> in this case. Moreover, the population density of fibers is rather low in case of TiNi-CNFs, therefore we can expect to get more signal from the underlying layer. In case of CrNi-CNFs, it is reasonable to assign these peaks to Ni because of (1) higher population density of fibers, and consequently, Ni tip particles, and (2) lack of evidence of formation of silicides from the TEM/EDS measurements. Notable differences in the two diffractograms arise due to the different adhesive layers.  $Cr_xC_y$  peaks are observed in CrNi-CNFs, while Ti<sub>x</sub>C<sub>y</sub> peaks are observed in TiNi-CNFs. It should be noted that NTi (osbornite) has a similar profile as Ti<sub>x</sub>C<sub>y</sub>. Owing party to this, they exhibit complete solid solubility at a wide temperature range [21,22].

It is also worth noting that the diffraction from the thin layers is weak and the diffraction peaks are broad as the crystal width is small and high-resolution XRD settings are not applicable for GI-XRD scans, since they would decrease the signal further. Furthermore, the diffraction peaks can shift less than the full width at half maximum (FWHM), especially if residual stresses exist or if the phase is not pure (i.e., if there is deformation). Another challenge is that in our multicomponent system, the different crystal phases might have diffraction peaks that



**Fig. 2.** High magnification TEM micrographs of CrNi-CNF (A, C) and TiNi-CNF (B, D). The yellow rectangles in (A) and (B) indicate the sections of the figures which are shown in (C) and (D), respectively. The brightness and contrast were adjusted in (C) and (D) to clearly show the graphene sheets. Graphene sheets close to the fiber edge are traced with white lines, while graphene sheets that are further inside the fiber are traced with red lines. The yellow arrows in (C) and (D) indicate the direction of the fiber's axis.

overlap. The elements that are present (Ni, Ti, Cr, C, Si) can form alloys with a range of compositions as well as intermediate compounds, such that their crystal structures are very similar. Also a single set of elements can form multiple crystal phases. Moreover, there likely exist metastable phases in our system owing to the short annealing times.

For highly textured or epitaxial films, it is possible that diffraction peaks are not observed if Bragg conditions are not valid. Hence, it is possible that a crystal phase does not cause diffraction due to the chosen geometry. It is important to note that our measurements can confirm that a specific crystal structure is present in the system, but crystal structures cannot be perfectly excluded. Thus, our analysis is more or less qualitative and intended to complement the HRTEM analyses presented above.

There are notable differences between the growth behaviour and macroscale geometry of the fibers grown on the two types of substrates. These have been described in detail elsewhere [20]. Briefly - the higher solubility of carbon into Cr, in comparison to Ti, results in a smaller rate of growth of CrNi-CNFs. In other words, the fibers reach a smaller average height in the same amount of time when grown on CrNi

substrates. Moreover, the population density (i.e., number of fibers per unit area) is smaller in TiNi-CNFs because a considerable part of the available Ni reacts with Si to form silicide, which reduces the amount of Ni available for CNF nucleation.

To connect the structural features discussed above with the chemical properties of the CNFs we carried out a detailed spectroscopy analysis utilizing XAS and XPS as discussed next.

Fig. 4 shows the C 1s, N 1s, O 1s, Ti 2p, Cr 2p and Ni 2p XAS spectra of both types of CNFs. Energy alignment for the C1s spectra in XAS was done using a reference sample along the beam path and recording C1s signature from that reference, then fitting a peak to this signature and aligning them all to the same energy. Then this energy was shifted so that the most reliable C1s signature, the exciton, at 291.65 eV was at its signature energy. Highly oriented pyrolytic graphite (HOPG) was measured along with the samples to record the exciton calibration data. The sp<sup>2</sup>  $\pi^*$  signature is lower in energy than the same signature for graphite or HOPG, which is expected as these fibers are less ordered and have more amorphous material in them, than pure graphite or HOPG [23].



Fig. 3. GI-XRD profile of CrNi- and TiNi-CNFs. The measurements were performed at incident angle ( $\omega$ ) = 0.3<sup>0</sup>. The probable phases, according to TEM/EDS analysis, have been marked for each peak.

Based on earlier work [23,24], the order of appearance for the C1s functional groups is Aldehyde, Ketone, Amide. The energy ranges provided in [24] do not support the claim that the 287.03 eV peak/shoulder would be ketone. This would indicate that (see [23]) the feature could be from C—H. If we take this avenue of thought, we could then expect the 289.21 eV peak to be C-OH. This leaves the 287.83 and 288.2 eV peaks. These features can be solved as we see nitrogen present in the samples (see XPS discussion below and Table S1). Based on earlier literature [24], the energy matches amide-like groups, however as the fabrication temperature is 600 °C, the formation of amide-like groups is limited (see [25]). Further, work by Schiros et al. [26] shows that pyridinic, graphitic and nitrilic N groups have similar N 1s XAS signature as our materials and the main intensity that they observe at C 1s is below 288.8 eV. It is therefore expected that the abovementioned features arise from pyridinic (and possibly graphitic/nitrilic) groups.

The C 1s spectra can be interpreted to show that CrNi-CNFs have lessrich O/N chemistry with C than the TiNi-CNFs do, since the intensities before and after the 287.83–288.2 eV areas (Fig. 5) have less intensity. This is also supported by the O 1 s XAS (Fig. 4B), since the 530–534 eV area is wider on the Ti spectra. The difference between the intensity of Ni 2p spectra (Fig. 4D) can be explained by the lower amount of fibers in the Ti based samples. Since the absolute counts are increased, we can reasonably assume that there are more fibers on the affected beam spot, since the beam measures approximately 200 um  $\times$  800 um. Moreover, the relative amount of higher oxides of Ni is increased on the TiNi-CNF compared to the CrNi-CNF.

Fig. 6 shows the XPS spectra of C 1s, O 1s, Ni 2p and N 1s regions for both types of CNFs. Spectra for other elements and atomic concentrations are provided in the Supporting Information (Fig. S3 and Table S1). The samples were measured in a tilted geometry with a  $60^{\circ}$  angle between the analyzer and the surface normal to reduce the contribution of the substrate signal to the spectra.

Fig. 6A shows the C 1s regions of the samples. As can be seen from the figure, the C 1s spectra for the two samples grown on different substrates are very similar. They exhibit a main asymmetric peak at 284.5 eV which can be related to  $sp^2$  carbon. At binding energies 285–289 eV there are additional contributions from other types of carbon and carbon-oxygen and carbon-nitrogen bonding [27–29]. The spectrum has been fitted with five additional components corresponding to:  $sp^3$  carbon (285.1 eV), which can include contributions from  $sp^2$  C–N bonds; C–O–C and/or C–OH (286.3 eV), which can include contributions from

sp<sup>3</sup> C–N bonds; C=O (287.5 eV), O–C=O and/or N-C=O (288.7 eV) and a p–p\* shake up transition (290.9 eV). However, because of the complexity and high number of possible components this peak fitting should be considered somewhat qualitative. The concentrations of the different components derived from peak fitting are given in Table S1.

Fig. 6B shows the O 1s spectra for the two samples, which show small differences. The rather broad O 1s peak has been fitted with three components corresponding to metal-oxygen (O-M) bonds (530.3 eV), O=C bonds (531.8 eV) and O-C and/or OH-C bonds (533.2 eV) [27]. The concentrations of the different components derived from peak fitting are given in Table S1. The peak for metal-oxygen bonds could arise from oxidized nickel in the CNF layer or from the substrate. Some titanium in mainly oxide form is observed for TiNi-CNF in the measurements but for CrNi-CNF no chromium was found (see Fig. S3 and Table S1). The metal-oxygen peak is larger for CNFs grown on TiNi-substrate compared to CrNi-substrate which can be explained by the smaller population density of CNFs on the TiNi-substrate which will amplify the substrate signal. Thus, the higher amount of metal-oxygen bonds observed on TiNi-CNF can be attributed to titanium oxide from the substrate.

The Ni 2p spectra are shown in Fig. 6C. Both types of CNFs show a prominent  $2p_{3/2}$  Ni peak at a binding energy of 852.5 eV. Both the position and shape of the Ni 2p peak indicate a metallic state [30]. The smaller  $2p_{3/2}$  peaks observed at ~856 eV and ~858 eV are most likely related to some hydroxide form [31]. The nickel chemical states appear to be quite similar for both CNF types. This finding is in line with TEM and EDS measurements: the CNF tips consisting of nickel are similar and only the ends are open. Thus it is expected that nickel is mostly protected from oxidation by the graphene sheets.

Nitrogen was also observed in the samples with atomic concentrations 6.3-8.1 atomic-%. At the CNF growth temperature used in this work nitrogen doping could be expected. The nitrogen 1s spectra are shown in Fig. 6D. They show two main peaks, which can be assigned to pyridinic-N (398.5 eV) and graphitic-N (400.8 eV) [28,32]. In the fit, a peak for N-oxides (ca. 402-403 eV) has been included. In the N 1 s spectrum of TiNi-CNF also a peak at ~396.6 eV is required to explain the spectra. The low binding energy is indicative of a nitride, which could be forming with e.g. Ti or Si [33]. Typically, also pyrrolic nitrogen would be considered (around 400.1 eV), but such a component was not needed in the fitting to explain the spectra. Many other possible nitrogen-carbon bonding configurations also exist with binding energies around 399–400 eV, such as amine, amide and cyano groups but these have not been considered either for the same reason. The concentrations of the different components derived from peak fitting are given in Table S1. Again, the two CNF samples appear rather similar, but the nitrogen doping level in the TiNi-CNF sample is found to be somewhat higher, especially if we consider that in that sample also signal from the substrate is observed.

How do the XAS and XPS spectra correlate with each other and with the microstructure of CNFs? The TEM micrographs (Fig. 2) show the sidewalls of the TiNi-CNFs comprise mostly of basal graphene planes, whereas in case of CrNi-CNFs, the edge planes of graphene sheets point outwards. Edge planes are considered to be more reactive than basal planes [34–36]. Thus, we can reasonably assume that CrNi-CNFs will form specific attachments with a few functional groups that are energetically most favorable. On the other hand, the TiNi-CNFs, owing to their relatively disordered structure and exposed basal planes, are likely to adsorb and/or form nonspecific attachments with a larger variety of functional groups. The TiNi-CNF surface is also likely to contain a fair amount of defects, for example step defects on basal planes, which are expected to allow richer bonding with O and N [37,38].

The C 1s, O 1s and N 1s XAS spectra of TiNi-CNFs are broader than the corresponding spectra of CrNi-CNFs. The valley between 286 and 291 eV in the C 1s spectra of TiNi-CNFs (Fig. 5) also has broader features and more shoulders and peaks, likewise indicating richer surface chemistry. The O 1 s XAS spectrum of TiNi-CNFs is wider especially



Fig. 4. XAS spectra of TiNi- and CrNi-CNFs. C 1s (A), O 1s (B), N 1s (C), Ni 2p (D), Cr 2p (E) and Ti2p (F) regions.

between 529 and 534 eV, which further supports the findings from the C 1s spectra. Furthermore, the N 1s XAS spectrum of TiNi-CNFs also shows broader spectral features starting at 395.3 eV.

It should be noted that neither of the CNFs have the distinctive exciton peak at 291.65 eV, which is observed for highly ordered materials such as pristine single-walled carbon nanotubes (SWCNTs) and highly oriented pyrolytic graphite (HOPG). This clearly indicates a lack of long range order, and we can reasonably assume that the observed sidewall structures in the TEM micrographs cannot be "damage free".

We observe a larger intensity of Ni 2p signal for CrNi-CNFs (Fig. 4D). This is likely due to the larger population density of fibers [20]. On the other hand, the O 1s and N 1s XAS spectra of TiNi-CNFs have larger intensities than the corresponding CrNi-CNF spectra. Since O 1s and N 1s XAS spectra show the absolute intensities, it follows that the amount of O and N is higher in TiNi-CNFs, despite their smaller population density. It should be noted that the previous statement assumes that the scanning beam does not significantly probe the substrate layer, i.e., the measurements are confined to the fibers.

The XPS results are mostly consistent with the information gained from the XAS analyses. The high resolution C 1s showing  $sp^3$  carbon

(285.1 eV), which can include contributions from sp<sup>2</sup> C–N bonds; C–O–C and/or C–OH (286.3 eV), which can include contributions from sp<sup>3</sup> C–N bonds; C=O (287.5 eV), O–C=O and/or N-C=O (288.7 eV) and a p–p\* shake up transition (290.9 eV) must, however, be taken only as tentative. This is especially true for the carboxylic group of which presence is indicated by XPS, which is not seen in XAS. As this is one of the most distinctive and stable peaks in C1s XAS spectrum [23], its absence from the XAS spectra indicates that some other groups, most likely pyridinic (and possibly graphitic/nitrilic) groups, are in fact largely responsible for that feature. The O 1s spectra shows that there is a much larger contribution from the metal-oxygen bonds in the TiNi-CNFs than in the case of CrNi-CNFs as expected based on the very high solubility of oxygen into Ti.

Hence, as a summary we can state that the TiNi-CNFs, which have a relatively disordered structure and whose sidewalls comprise mostly of basal planes, provide adsorption sites for a relatively larger variety of functional groups. This is clearly seen in both XAS and XPS analyses as wider peaks and in more spectral features. The presence of nitrogen in addition to carbon and oxygen complicates the interpretation of the high resolution spectra and more detailed further analysis will require the use



Fig. 5. C 1s XAS spectra of TiNi- and CrNi-CNFs, highlighting the valley between 286 and 291 eV.

of recently developed computational methods [39-41].

# 4. Conclusions

In this work, we have investigated the microstructure and surface chemistry of CNFs grown on CrNi and TiNi substrates. Vertically aligned, tip-grown CNFs were observed on both substrates. Despite the identical process conditions and catalyst layers, there were notable differences between the microstructure of the two types of fibers, which are expected to arise due to the different adhesive layers (Cr or Ti). CrNi-CNFs had a slightly distorted herringbone structure, while TiNi-CNFs had a somewhat ill-defined structure consisting of a bamboo-like "spine", surrounded by graphene that are relatively misaligned. Edge planes are exposed at the sidewalls of CrNi-CNFs, while basal planes are exposed in case of TiNi-CNFs. Moreover, TiNi-CNFs had a smaller population density because a considerable part of the available Ni reacts with Si to form silicide, which reduces the amount of Ni available for CNF nucleation. to study the differences in surface chemistry between the two types of CNFs and correlate that with the structural differences seen with TEM. Neither of the CNFs have the distinctive exciton peak at 291.65 eV that is observed in highly ordered materials, indicating a lack of long range order in both types of CNFs consistent with the TEM. However, the C 1s, O 1s and N 1s XAS and XPS spectra of TiNi-CNFs had clearly broader peaks and more spectral features, indicating a richer surface chemistry, which is expected to arise from their more defective microstructure. Moreover, the larger intensity of Ni 2p spectra of CrNi-CNFs was correlated to their larger population density. In conclusion, we have shown that (1) the microstructure of CNFs is strongly affected by the adhesive layer metallurgy, and (2) these structural changes have observable effects on the surface chemistry. Finally, this work provides a foundation for tailoring the features of CNFs for electroanalytical chemistry, which we have described in a separate work [42].

#### CRediT authorship contribution statement

We conducted a detailed spectroscopic analysis, using XAS and XPS,

Ishan Pande: Conceptualization, Investigation, Resources,



Fig. 6. X-ray photoelectron spectra of CNF samples: C 1s region (A), O 1s region (B), Ni 2p region (B) and N 1s region (D) (peak fitted components are explained in the main text).

Visualization, Writing- Original draft preparation, Writing- Reviewing and Editing. **Sami Sainio**: Investigation, Visualization, Writing- Original draft preparation, Writing- Reviewing and Editing. **Jani Sainio**: Investigation, Visualization, Writing- Original draft preparation, Writing-Reviewing and Editing. **Ville Liljeström**: Investigation, Writing- Original draft preparation. **Hua Jiang**: Investigation, Writing- Reviewing and Editing. **Tomi Laurila**: Conceptualization, Methodology, Writing-Original draft preparation, Writing- Reviewing and Editing, Resources, Funding acquisition, Supervision.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

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