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Published in: Carbon

DOI: 10.1016/j.carbon.2024.119082

Published: 25/04/2024

Document Version Publisher's PDF, also known as Version of record

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Please cite the original version:

Khabushev, E. M., Krasnikov, D. V., Sainio, J., Novikov, I. V., Goldt, A. E., Fedotov, S. S., Kallio, T., & Nasibulin, A. G. (2024). High-temperature adsorption of nitrogen dioxide for stable, efficient, and scalable doping of carbon nanotubes. *Carbon*, *224*, Article 119082. https://doi.org/10.1016/j.carbon.2024.119082

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Contents lists available at ScienceDirect

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High-temperature adsorption of nitrogen dioxide for stable, efficient, and scalable doping of carbon nanotubes

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ARTICLE INFO

Keywords: Single-walled carbon nanotubes Adsorption doping Transparent conductive films Floating-catalyst Nitrogen oxides

ABSTRACT

This work is devoted to a novel efficient strategy for single-walled carbon nanotube doping employing heat treatment with nitrogen dioxide (NO₂). Unlike numerous reports of unstable NO₂ doping at room temperature, our method combines high efficiency and stability, enabled by its temperature-dependent adsorption on the nanotube surface. We reveal that doping stability increases with the treatment temperature reaching maxima at 300 °C avoiding any detrimental effect on nanotube structure and optical transmittance. As a result, we demonstrate doped carbon nanotube transparent conductive films exhibiting competitive performance (in respect to films treated with other dopants) with a less than 50% drop in conductive characteristics for over a year. Thermo-programmed desorption analysis and X-ray photoelectron spectroscopy confirm the preferential formation of long-living adsorbed nitrogen species, such as NO3-groups, as a result of high-temperature treatment. We believe the current work provides a basis for the robust and technologically efficient doping of singlewalled carbon nanotubes and related structures at industrial scales, as the developed method could be easily coupled with a continuous technology of carbon nano materials production.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are a class of onedimensional graphitic materials with exceptional physical properties, which could be produced in a large scale, and for this reason, getting huge attention [1-3]. The interest in SWCNTs is stirred up by numerous applications, especially those related to electronics [4-6]. Macroscopic assembles of SWCNTs, such as films, aerogels and fibers, possess outstanding mechanical stability and high electrical conductivity, making them excellent materials for transparent electronics, thermoelectric energy harvesting, and lightweight wires, amid a technology transition toward flexible and wearable applications [7–10].

Floating-catalyst (aerosol) chemical vapor deposition method (FCCVD) is a conventional approach for the direct preparation of SWCNT macrostructures offering continuous operation, excellent scalability, and resulting in a material of the highest performance [11]. One of the main advantages of FCCVD lies in avoiding additional wet purification procedures, which aggravate the fabrication process and cause material contamination by surfactants.

Since SWCNTs are usually produced as a mixture of metallic and semiconducting species, the conductive characteristics of nanotubebased networks are significantly affected by Schottky barriers formed at the intertube interface. Despite the continuous efforts on selective floating-catalyst synthesis of metallic SWCNTs and nanotube enlengthening, the current advances are still far from the desired performance [12]. Therefore, adsorption doping remains the principal technique for enhancing the conductive properties of SWCNT networks to the state comparable with commercially-used metal oxides [13]. Adsorption doping relies on a high sensitivity of nanotube electronic density to surrounding media and involves surface deposition of specific compounds, capable of shifting nanotube Fermi level up (n-type) or down (p-type). The Fermi level shift reduces the intertube contact resistance (lowers the Schottky barrier) and increases nanotube charge carrier density in general.

https://doi.org/10.1016/j.carbon.2024.119082

Received 17 December 2023; Received in revised form 24 March 2024; Accepted 25 March 2024 Available online 25 March 2024 0008-6223/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).





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Driven by the perspectives of SWCNT-based transparent conductive films (TCFs), adsorption doping research has been devoted to optimization of the so-called equivalent sheet resistance of the films (at 90% transmittance), being a quality factor for commercial TCF applications [14]. In particular, numerous works referred to the selection of efficient dopants and solvents [15–18], assessment of various deposition techniques [19–24], and analyzing the effect of SWCNT pretreatment to improve the efficiency of doping process. Recently, an extremely efficient doping strategy, realized by dip-coating of heat-treated SWCNT films into ethanol solution of chloroauric acid (HAuCl₄), was reported [25]. This approach resulted in one of the lowest reported equivalent sheet resistance values (31 Ω/\Box) and moderately high stability.

Despite chloroauric acid being an extremely efficient dopant for SWCNTs, it also exhibits several drawbacks. One of them is the deterioration of transmittance in the visible wavelength range, attributed to formation of gold nanoparticles, limiting overall performance. As the simultaneous control over transmittance and electrical conductivity of the films is the key step for achieving optimal performance [26], HAuCl₄-based techniques require precise tuning of the doping degree. It is worth mentioning that stability of doping with HAuCl₄ is still a matter of concern, even though it surpasses other common dopants such as strong acids, halogens, etc. For instance, one-week exposure of doped films to ambient might result in almost a two-fold increase in the equivalent sheet resistance. Recently, a feasible solution to the issue of doping stability, based on the implementation of non-volatile solid acids (e.g., phosphotungstic acid), was reported [27]. The approach enabled superior stability of the doped samples with only a 40% increase in the sheet resistance over a long time. However, the implementation of high-molecular compounds might constrain doping efficiency because of their limited diffusion into the specimen. In contrast, nitric acid (HNO₃) enables an extremely efficient doping of SWCNT, resulting in out-standing, but usually short-lasting, increase in conductivity of the films [28]. Summing up, the current advances in SWCNT doping are governed by the trade-off between efficiency and stability. Besides, the widely-used solid dopants require a conscious selection of solvents and deposition techniques to promote process robustness and scalability, increasing technology complexity and hindering the solvent-free fabrication of SWCNT-based (opto-)electrical components.

Here, we propose a novel method combining high doping efficiency, excellent stability, and technological effectiveness by employing a nitrogen dioxide (NO₂) adsorption at relatively high temperatures. One of the main advantages of this method is a pure gas-phase treatment of SWCNTs, enabling seamless coupling with the solvent-free fabrication of nanotube films and fibers, avoiding any liquid procedures. For instance, we demonstrate the technology can be integrated with the aerosol CVD in a tandem manner, unveiling excellent scalability for thin-film production. Despite NO₂ being an already-known dopant for SWCNTs, to our knowledge, this is the first-time demonstration of temperature-dependent doping with NO₂ enabling the fabrication of SWCNT transparent conductive films with both excellent performance and high stability at ambient conditions.

2. Experimental

2.1. Gases and reagents

Ferrocene (98% *Sigma Aldrich*), CO (4.0 purity *Linde Gas*), CO₂ (4.5 purity *MGPZ*), and NO₂ (2.5 purity *Linde Gas*) were used for the SWCNT synthesis and gas-phase doping. Chloroauric acid (HAuCl₄·3H₂O purity 99%, Sigma-Aldrich) and nitric acid (70% assay, Sigma-Aldrich) were used for solution-based doping of the films.

2.2. SWCNT synthesis

An aerosol CVD reactor employing Boudouard reaction on iron catalyst was used for SWCNT synthesis. The reactor was based on a tubular furnace (inner diameter of 72 mm and a heating length of 1 m). A mixture of CO, CO_2 and ferrocene vapor was introduced directly into reactor inlet at a fixed flow rate of 3 slpm using high-precision mass flow controllers (*Bronkhorst*). Additional CO flow, passing through a ferrocene saturator (held at a constant temperature of 28 °C) and diluted by pure CO thereafter, was injected into the reactor hot zone through a thin tube (4 mm diameter) at a fixed flow rate of 2 slpm. The resulting gas flow contained 0.6 ppm of ferrocene vapor, 0.59 vol% of CO₂, and CO (main gas), while the reactor temperature was fixed at 880 °C in order to guarantee an efficient synthesis of high-quality SWCNTs. A more detailed description of the reactor can be found elsewhere [29].

2.3. Post-treatment reactor

A part of the gas flow from the output of the synthesis reactor was mixed with NO_2 and introduced into the second tubular furnace (diameter of 44 mm and a heating length of 1 m) for post-treatment (similar to the approach reported earlier [30]). SWCNTs were subsequently collected by filtration of the gas flow using nitrocellulose filters (*Merck, Millipore*) with a help of a membrane pump at a fixed flow rate of 4 slpm (secured using a needle valve). The flow rate of the corrosive NO_2 gas was controlled using a rotameter. During the experiments, the set temperature of the hot zone varied in the range from 24 to 400 °C.

2.4. Solution-based doping of SWCNT films

To compare the efficiency of NO_2 doping with other well-established dopants the 30 mM chloroauric acid solution in ethanol and 70% nitric acid essay was drop-casted on the pristine films (produced at the same synthesis conditions) and dried afterward in air.

2.5. Thin film characterization

To verify the efficiency of SWCNT doping and evaluate the performance of produced transparent conductive films, the samples were analyzed using four-probe conductivity (sheet resistance) measurements, optical absorption and Raman spectroscopies. Sheet resistance of the film was measured by a Jandel RM3000 tool. The measurements were repeated at least five times and then averaged. PerkinElmer UV–vis–NIR dual-beam spectrophotometer Lambda 1050 was employed to measure optical absorption spectra of the samples in the range from 250 to 2500 nm. The equivalent sheet resistance was calculated based on film optical density (absorbance) at the wavelength of 550 nm and measured sheet resistance values as follows:

$$R_{90} = -R_S \bullet \frac{A_{550}}{\log_{10}(0.9)}$$

Raman measurements were carried out using a DXRxi Raman Imaging microscope equipped with \times 100 long-focus objective and 532 nm laser. To minimize the effect of sample exposure with laser light, the lowest available excitation power of 0.1 mW was employed. The signal was continuously collected and averaged until a high signal-to-noise ratio (>300) was obtained.

2.6. Infrared spectroscopy

Middle infrared spectra of the samples treated with NO_2 were studied using a vacuum FTIR spectrophotometer Bruker Vertex 70 V. For this, a free-standing SWCNT membrane were developed to avoid substrate contribution.

2.7. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra spectrometer with monochromated Al K α -radiation, a pass energy of 40 eV, an X-ray power of 75 W, and an analysis area of

approximately 700 × 300 μ m². The binding energy scale is based on instrument calibration and no additional binding energy correction has been applied. The elemental composition was estimated based on peak areas of high-resolution core level spectra (C, N, O) after Shirley background subtraction considering the equipment-specific sensitivity factors. The peak decomposition was done in CasaXPS Software with Lorentzian Asymmetric line shape (LA(1.2, 2.5, 5)) for sp² carbon peak and Gaussian-Lorentzian line shapes (GL (30)) for the others [31]. The peak positions were fixed within ±0.1 eV of previously reported binding energies, while the full widths at half-maximum were set to be equal for within every core level with the exception for sp² carbon (0.4–0.5 eV) and π - π * satellite (2.4–2.7 eV).

2.8. Thermal analysis

Before the thermal analysis, SWCNT samples were placed in a tubular furnace and treated with NO_2 at different temperatures. The asprepared samples were studied with a simultaneous thermal analyzer Netzsch F3 STA-449 combined with a mass spectrometer Netzsch QMS 403 D Aëolos. The thermal analysis was performed under a constant Ar flow of 100 ml/min and 10 K/min heating rate, without preliminary evacuation of the sample chamber.

3. Results and discussion

3.1. Temperature-dependent doping of nanotube films with NO₂

For continuous gas phase growth and doping of SWCNTs, we developed a set-up consisting of a two-stage (tandem) sequential aerosol reactor (Fig. 1). This apparatus allowed us to separately synthesize SWCNTs at a high temperature (880 °C) in CO/CO₂ atmosphere and further add NO₂ to the gas mixture for treatment at lower temperature (25–400 °C). Reaction conditions used in this work results in no selectivity in SWCNT electronic structure (metallicity), and the anticipated fractions of metallic nanotubes is 1/3 [30]. Adjusting the NO₂ flow rate (NO₂ concentration x_{NO2} was varied in range of 0–50 vol%) and temperature at the second reactor stage we could tune the treatment (doping) conditions.

Firstly, we evaluated the effect of NO₂ concentration (hereafter x_{NO2}) and treatment temperature on the transparent conductive properties of produced films. As expected NO₂ treatment results in a drastic decrease in the film sheet resistance reaching an 8-fold drop at the maximum (compared to pristine samples with $R_{90} \approx 1 \text{ k}\Omega/\Box$; Fig. 2a). Surprisingly, analyzing the effect of NO₂ content in the temperature range from 25 to 300 °C, we found similar patterns of sheet resistance change, initially showing a substantial decline followed by a plateau at high x_{NO2} . However, due to technical limitations of the developed NO₂ supply system, we could not investigate the doping effect at low concentrations, which might strongly depend on temperature. We observed a deviation from the above-mentioned concentration dependence at 400 °C with R₉₀ increasing $x_{NO2} > 10$ vol%. This effect could be associated with a strong NO2 oxidation effect at higher temperatures resulting in defect formation in the SWCNT structure. This fact is supported by Raman measurements, showing an upward trend for the I_D/I_G value at high concentrations (Fig. 2c). Furthermore, at temperatures below 300 °C changes in defectiveness (I_D/I_G) are comparable with deviation along the sample, thus, indicating limited chemical interaction of SWCNT with NO₂ at those conditions.

Our results indicate that samples treated at different temperature actually reach similar doping degree (sheet resistance drop). As adsorption is usually more favorable at lower temperatures one could find this finding counterintuitive. However, the observation could be explained by the fact that at output of the second tubular furnace the mixture of SWCNT aerosol and NO₂ reaches room temperature, smoothing the difference in doping degree between the samples.

According to film absorption spectra (Fig. 2b) the increase in NO2



Fig. 1. Sketch of the experimental tandem set-up for SWCNT synthesis and subsequent gas-phase treatment of produced material with nitrogen dioxide. (A colour version of this figure can be viewed online.)

concentration enhances the doping degree as it is underpinned by a gradual disappearance of S_{11} , S_{22} , and M_{11} peaks, associated with van Hove singularities in the SWCNT electronic structure. Besides, Raman spectroscopy reveals a monotonic redshift of G and 2D modes with x_{NO2} increase, corresponding to p-type doping of SWCNTs (Fig. 2d). Despite, the G peak shift of 7 cm⁻¹ indicating a moderate doping efficiency [23], the developed method results in a high resistance drop and does not increase optical absorption in the visible wavelength range (inherent to doping by metal-containing compounds), suggesting that the doping procedure is efficient. Interestingly, FTIR shows only a shift in the Drude peak which presumably overlaps with the signal from NO₂-induced vibrations (Fig. S1).

At first glance, the treatment temperature has a rather limited effect on the doping process as it is displayed by the comparable drop in equivalent sheet resistance of the films. However, analyzing the film resistance change over time we found a significant variation in the doping stability of the samples treated at different temperature (Fig. 3). Thus, samples doped at 25 °C (room temperature) have a much higher rate of resistance increase (lower doping stability) compared to the samples treated at elevated temperature. This fact is also supported by online FTIR measurements, showing rapid changes in film IR specter (attributed to dedoping) in a vacuum after NO₂ treatment at room temperature and more long-lasting effect after high temperature treatment (Fig. S2). In favt, the data shows a clear trend in doping stability, gradually increasing with a treatment temperature rise to 300 °C.



Fig. 2. (a, c) R_{90} and I_D/I_G of films treated at different temperatures and NO_2 content. Shaded area in (c) corresponds to 25% deviation from I_D/I_G of pristine nanotubes. (b, d) Evolution of film optical absorption spectra and G/2D Raman peak positions with NO_2 concentration at a treatment temperature of 300 °C. Optical spectra of the pristine film indicates bimodal diameter distribution of constituent SWCNTs. (A colour version of this figure can be viewed online.)



Fig. 3. Time-stability comparison of SWCNT films treated with 10 vol% of NO_2 at different temperatures and samples doped with nitric and chloroauric acids. Here R_0 and R(t) denotes sheet resistance of as-doped samples and the one measured at a certain time (t) after doping, correspondingly. (A colour version of this figure can be viewed online.)

Similar conclusion could be derived from Raman measurements after heat treatment in nitrogen atmosphere (Fig. S3). Overall, most of the samples exhibit quite a similar "dedoping pattern", with a drastic increase in resistivity for the first few days after treatment (1.4–3.6-fold increase in the first 10 days), slowly reaching a plateau below the pristine level afterward. The only exception is the room temperature sample sustaining steady dedoping for a long period until reaching almost a pristine state.

It is worth mentioning that after one month, samples treated at 300 °C exhibit a resistance increase of less than 50% without further change for almost a year. The achieved stability of samples treated by "hot" NO₂ appears to be a good result itself, which could be highlighted by comparison with common p-type dopants such as nitric (HNO₃) and

chloroauric (HAuCl₄) acids. For performance comparison, we deposited the dopant solutions on the films collected from the same synthesis process employing the drop-casting technique reported previously. Indeed, in 2 months, samples doped with HNO₃ and HAuCl₄ show a 160% and 60% resistance increase, correspondingly, compared to 40% for NO₂-doped samples. For all the tested dopants, the absolute values of R₉₀ were comparable. Thus, employing the same SWCNTs providing film equivalent sheet resistance of *ca* 700 Ω/\Box in a pristine state, we obtain R₉₀ values of 59 Ω/\Box , 61 Ω/\Box , and 73 Ω/\Box after NO₂, HAuCl₄, and HNO₃ doping, correspondingly. It is worth mentioning that evaluation of doping stability for the different samples was carried out at the same conditions, as we stored the films in room with a temperature of 21 °C and relative humidity of 40%. We also briefly addressed the effect of temperature and humidity (see Fig. S4) on doping stability indicating a key role of these two parameters in dedoping mechanism. A more detailed analysis of stability in respect to ambient parameter changes would be a great interest to get more mechanistic insights. However, that kind of research is out of the scope of the current study.

3.2. Mechanism of NO₂ adsorption on single-walled carbon nanotubes

The remarkably slow increase in resistance for samples treated with "hot" NO2 indicates high stability of dopant groups on the surface of SWCNTs. In general, the treatment temperature could affect the thermodynamics and kinetics of a gas adsorption process. Previously, adsorption and reactions of nitrogen oxides on carbon surface have been thoroughly investigated for soot particles, driven by research on exhaust fumes forming during fuel combustion [32,33]. Later, more research on NO2 interaction with carbon nanomaterials (motivated by sensor applications), including SWCNTs and graphene, came out [34-38]. Overall, two types of NO2 chemical interaction with carbon are known. At low temperatures, adsorption is believed to be the dominant process, while elevated temperatures result in the commencement of redox reactions with formation of gaseous products (such as NO, CO and CO₂). Despite, from the theoretical side, adsorption of a single NO₂ molecule on a pure SWCNT surface is believed to have a weak physisorptive nature, thischanges for real SWCNT networks possessing reactive defect-sites on the nanotube surface and forming bundles and/or nanotube junctions, which might enable the co-adsorption of several molecules.

In search for underlying processes responsible for the observed changes in doping stability with temperature, we referred to thermoprogrammed desorption analysis, employing thermogravimetric analyzer coupled with mass spectroscopy (TGA-MS). Fig. 4 illustrates the results of the TGA-MS for pristine SWCNTs and the samples treated with NO₂ at different temperatures. Overall, treated samples lose up to 21% percent of their mass during the constant heating to 600 °C with a ramp rate of 5 °C/min compared to only 6% percent change for pristine nanotubes, indicating a high amount of surface species on treated samples. Their presence is manifested in DTG curves in the form of pronounced peaks at different temperatures mostly in the region below 300 °C. The peak right-shift trend with NO2 treatment temperature increase is clearly noticed. The MS analysis of the outflow of the TG chamber enables the association of DTG peaks with gaseous products of a certain mass-to-charge ratio (m/e). In Fig. 4 we presented only signals of high interest for m/e = 30, 44, and 46, corresponding to the main components of NO/NO₂, CO₂, and NO₂ ionization spectra, respectively. MS signals for other m/e values might be found in the Supporting information (Fig. S5). The data reveals a clear shift of the NO₂ desorption temperature with the increase of treatment temperature, highlighted by a gradual change of the m/e = 46 signal peak position from 100 °C to 210 °C. However, the thermal degasification of SWCNTs is not limited to NO₂ desorption only. We observed a similar effect for m/e = 30 signal, but with a relatively different peak width and shape compared to m/e =46 signal. In fact, m/e = 30 signals exhibit longer high-temperature tails and a similar pattern to the DTG curve (at least in the region below 400 °C). We attribute it to the presence of NO surface species formed during the treatment and/or NO2 reduction reaction taking place on the surface sites. This fact is also supported by the m/e = 44 signal profile, corresponding to CO₂, with characteristic peaks similar to m/e = 30curve, indicating carbon oxidation by NO₂.

Nevertheless, the TGA-MS directly confirms the higher stability of adsorbed nitrogen species on the SWCNT surface for samples treated with at high temperatures, resulting in a more durable doping (discussed in the previous section). However, it does not provide enough evidence for the nature of the high stability of adsorbed species which might lie in distinct surface-associated forms of nitrogen appearing at different temperatures as well as in higher penetration of NO₂ into the nanotube bundle structure at elevated temperatures resulting in a slower



Fig. 4. Thermal analysis of SWCNTs treated with 10 vol% of NO₂ at different temperatures. (A colour version of this figure can be viewed online.)

desorption.

To find the origin of highly-stable nitrogen forms, we carried out XPS analysis, which is a well-established tool for probing the chemical state of surface species. However, as the measurements were carried out in a high vacuum, we could consider only strongly bounded surface species being detected, while the rest desorbed during the evacuation. The nitrogen content estimation from the survey analysis (if recalculated to NO₂ mass) is lower compared to the mass loss in terms of TGA-MS

Table 1

Atomic concentrations of the pristine and treated SWCNT samples obtained using XPS analysis. Si signal originates from a thin layer of silicon dioxide on the used substrates.

Sample	C, at.%	N, at.%	O, at.%	Si, at.%	Fe, at.%
pristine	91.2	<0.2	5.7	2.5	0.3
25 °C	91.5	1.4	6.4	0.5	0.2
100 °C	91.5	1.5	6.4	0.4	0.2
200 °C	91.6	1.5	6.3	0.4	0.2
300 °C	88.3	2.2	8.8	0.5	0.2

analysis (Table 1). Overall, we observed a minor change in the nitrogen atomic concentration from 1.4 at.% at room temperature to 1.5 at.% at 200 °C, followed by a noticeable increase in nitrogen content to 2.2 at.% for the sample treated at 300 °C. All the samples had carbon as the major component (roughly 90%) with its concentration slightly decreasing at higher treatment temperatures. The significant amount of oxygen detected in samples might come from the Si/SiO₂ substrate, as the thin SWCNT films are non-continuous porous material (network). Thus, the O/Si atomic ratio in the pristine sample is close to two, corresponding to mainly SiO₂ contribution, meaning pristine SWCNTs contain insignificant amount of oxygen groups. Nevertheless, we can assume that the treated samples have a detectable content of oxygen groups associated with carbon oxidation. The SWCNTs also contain barely detectable iron catalyst impurities at the level of 0.2-0.3 at.%. We should acknowledge that the XPS analysis may be influenced by the presence of iron, covered with a graphitic shell, which could potentially react with NO₂. Nonetheless, our developed treatment approach leverages the aerosol-phase material in its as-produced state, and we believe that conducting a study on it is more representative rather than on purified material.

The C1s region of XPS spectra shows a strong asymmetric sp²-carbon line for all the samples (Fig. 5a). A steady redshift of the sp² peak position from 284.6 eV for the pristine sample, to 284.2 eV for the sample treated at 300 °C indicates the charge transfer from SWCNTs (doping) [39]. At the same time, a slight increase in the high-energy tail intensity, attributed to carbon oxidation and the presence of oxygen-containing functional groups (such as C–O, C=O, etc.) is observed. Though, their contribution to the resulting spectra is limited to a few percent that is supported by ~90% carbon content in all the samples. As most of the

oxygen signal is coming from the substrate, the O1s region spectra are dominated by Si–O/O–SiO components (Fig. 5b). Though, a rise in the intensity of the high energy part of the spectra, observed for treated samples, indicates the presence of NO_x groups associated to the carbon nanotube surface [40].

The analysis of the N1s core level revealed the presence of nitrogen forms with different stoichiometry on the surface of treated SWCNTs (Fig. 5c-g). Considering the previously reported XPS results for NO₂ adsorption on SWCNT surface at low temperatures (150-200 K) [41,42] as well as ones for adsorption on metal oxides surface [43], we assumed five distinct spectral components with the following binding energies: 407.1, 405.9, 403.3, 401.1, and 399.5 eV. The component with the highest energy is believed to be associated with the NO_3^- functional group, corresponding to the highest oxidation state of nitrogen (+5). The peak at 405.9 eV could be associated with NO2 stabilized on the carbon surface and/or NO_3^{2-} functional group with the +4 oxidation state. The components at 403.3 and 401.1 eV presumably correspond to NO in dimerized (N_2O_2) and surface-stabilized (NO^-) forms, correspondingly. The low energy peak, observed mostly in the sample treated at 300 °C and associated with a near-zero nitrogen oxidation state, might be related to nitrogen incorporation in the SWCNT lattice in a pyrrolic form [44]. The appearance of pyrollic nitrogen forms is expected as increase in treatment temperature promotes NO₂ reactivity with carbon, and these forms are stable in the temperature range below 900 °C [45].

SWCNTs treated at different temperatures show quite similar N1s core level patterns with two strong components at 405.9 and 401.1 eV, correspondingly, that is consistent with previously reported results for metallicity-sorted SWCNTs at 100 K [42]. A minor change in peak



Fig. 5. XPS analysis of SWCNTs treated with NO₂ at different temperatures: evolution of C1s (a) and O1s (b) regions, deconvolution of N1s region (c)–(g). Vertical grey lines and corresponding top tick labels in subplots a and b indicate possible bonds present in the samples. (A colour version of this figure can be viewed online.)

distribution is observed for samples treated in the range from 25 to 200 °C limited to a slight decrease of the 401.1 eV component intensity and an increase in 407.1 eV component intensity (Table 2). In contrast, SWCNTs treated at 300 °C exhibit a drastic rise of 407.1 and 399.5 eV components, associated with the NO_3^- and nitrogen incorporation, correspondingly, as well as a decrease of the NO⁻ (401.1 eV) contribution and a slight redshift of NO_2 (405.9 eV) component. The appearance of the strong high energy component at 407.1 eV stands in favor of higher doping stability of samples treated at 300 °C, as NO₃⁻ is believed to be one of the most long-living species on nanotube surface [46,47]. One of the probable ways of its formation is via the following surface reaction: $2NO_2 \rightarrow NO_3 + NO$ [48] and the temperature of 300 °C might be sufficient to overcome its energy barrier. In this case, the accompanying decrease of the NO⁻ component in XPS might seem to be an unexpected result. Though, further evolution of NO⁻ via the reaction with NO₂ and/or desorption is still possible and could explain this inconsistency. In fact, the redshift of second high energy component (405.9 eV) might also indicate an appearance of NO_3^{2-} species as a result of surface reaction.

Summing up, the XPS analysis of the SWCNTs treated with NO₂ revealed the presence of strongly bonded nitrogen compounds on the nanotube surface. The abrupt increase in nitrogen content accompanied by the rise of NO_3^- component intensity at a treatment temperature of 300 °C, highlights the importance of elevated temperatures for the formation of long-living nitrogen species. We suggest SWCNT treatment with NO₂ at elevated temperatures helps to overcome the energy barrier for surface reaction, leading to the formation of long-living NO_3^- species, which benefits the stability of doping effect.

The XPS measurements conducted in this study have an exploratory purpose, aiming to elucidate the prolonged doping effect observed. A more precise and systematic examination of purified samples, including their evolution over time, should have a high importance in analysing the underlying processes of NO₂ interaction with SWCNTs and uncovering the dedoping mechanism. This part falls outside of the scope of the current study.

4. Conclusion

To conclude, we report overcoming a stability-efficiencytransparency trade-off for nanotube doping by means of a new and robust SWCNT doping procedure, combining high efficiency and stability, employing gas-phase heat treatment of SWCNTs in a NO2-containing atmosphere. This is enabled by the discovery of the temperaturedependent nature of NO₂-adsorption on carbon nanotubes, caused by changes in nitrogen surface species appearing as a results of surface reaction. Thus, we found the doping stability to increase with the treatment temperature, reaching maxima at 300 °C. Thermoprogrammed desorption (TGA-MS) analysis carried out on the treated samples supports higher stability of surface nitrogen species forming at higher temperatures, while XPS data indicates that NO3 groups (prevailing at high treatment temperatures) might be responsible for the prominent stability of the doping. The optimal temperature of 300 °C corresponds to the boundary, where formation of long-living surface species is promoted without noticeable SWCNT oxidation.

The developed method allows us to fabricate SWCNT-based transparent conductive films with comparable performance (sheet resistance) to that achieved with the HAuCl₄ dopant but showing less than 50% resistance increase after almost one-year storage at ambient conditions. The gas-phase NO₂ treatment also has no detrimental effect on optical properties of the films (e.g., transmittance decrease, haze) unlike other techniques.

We would like to emphasize the technological efficiency of the current approach, as it perfectly stacks with the floating-catalyst CVD method, enabling fast, continuous, and scalable synthesis of SWCNTs with subsequent doping in the aerosol phase. The process might be Table 2

Peak deconvolution of N1s XPS region for SWCNT samples treated with NO2.

Sample	Component content, %					
	NO_3^-	NO_2, NO_3^{2-}	N_2O_2	NO^-	Pyrrolic N	
25°C	11.0	51.5	3.6	28.1	5.8	
100°C	11.5	53.2	3.2	26.8	5.2	
200° C	13.6	50.6	4.8	24.7	6.3	
300° C	28.2	48.5	3.5	9.1	10.7	

organized in closed-loop way, so the NO₂ is separated from exhaust gases by cryogenic distillation and reused further, drastically reducing not only cost but also environmental impact of the technology, as there is no liquid or solid waste. Current approach also shows perspectives for capturing and utilization of dangerous exhaust gas. For this reason, we believe our findings might be of high interest for the industrial-scale and sustainable production of nanotube/graphene based transparent conductors.

CRediT authorship contribution statement

Eldar M. Khabushev: Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. Dmitry V. Krasnikov: Methodology, Conceptualization. Jani Sainio: Writing – review & editing, Investigation. Ilya V. Novikov: Investigation. Anastasia E. Goldt: Investigation. Stanislav S. Fedotov: Investigation. Tanja Kallio: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. Albert G. Nasibulin: Validation, Resources, Funding acquisition, Data curation, Conceptualization.

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.

Acknowledgement

Research Council of Finland (the Profi 5 project) is thanked for the funding. D.V.K. and A.G.N acknowledge Russian Science Foundation grant No. 22-13-00436. We acknowledge the provision of facilities and technical support by Aalto University at OtaNano - Nanomicroscopy Center (Aalto-NMC), RAMI and Bioeconomy infrastructures.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2024.119082.

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