Dispersion and characterization of arc discharge single-walled carbon nanotubes-towards conducting transparent films

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**Publication Details**

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Abstract
This study addresses a combination of a well-developed and mild dispersion method and high-quality arc discharge single-walled carbon nanotubes (SWCNTs) as starting materials. Thus, we advance in fabrication of transparent, conducting films with extraordinary low material loss during SWCNT processing. The starting material was characterized by means of thermogravimetric analysis, high-resolution transmission electron microscopy and Raman spectroscopy. The quality of the starting material and produced dispersions was evaluated by ultraviolet and visible light absorption spectroscopy and Raman spectroscopy. A transparent conductive film was fabricated by drop-casting, whereas films were obtained with electrical to optical conductivity ratios (σDC/σOp) as high as 2.2, combined with a loss of nanotube material during processing well below 20 wt%. High pressure carbon monoxide conversion (HiPCO) SWCNTs, which are very well described in the literature, were used for comparison.

Keywords
towards, nanotubes, characterization, dispersion, arc, discharge, carbon, single, walled, films, transparent, conducting

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details
Dispersion and Characterization of Arc Discharge Single-walled Carbon Nanotubes – Towards Conducting Transparent Films

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Abstract: A huge scientific effort is spent on the research and development of transparent and conducting films consisting of single-walled carbon nanotubes. With various factors influencing the quality of nanotube films, there are some key challenges remaining for their production, i.e. the choice of high quality pristine material, the dispersion chemistry and the fabrication technique. This work addresses the first two of those by combination of a well developed and mild dispersion method with low material loss and high-quality arc discharge single-walled carbon nanotubes (SWCNTs) as starting material. High presssure carbon monooxide conversion (HiPCO) SWCNTs, which are very well described in literature, were used for comparison. The starting material was characterised by means of thermo gravimetric analysis,
high-resolving transmission electron spectroscopy and Raman spectroscopy. The quality of the produced dispersions was qualitatively evaluated by ultraviolet and visible light absorption spectroscopy and Raman spectroscopy. A transparent conductive film was fabricated by a simple technique in order to compare the two differently synthesised SWCNT materials. Films were obtained with electrical to optical conductivity ratios (\(\sigma_{DC}/\sigma_{Op}\)) as high as 2.2, combined with a loss of nanotube material during processing well below 20 wt%.

Keywords: carbon nanotubes, dispersion, transparent conducting film, electrical conductivity, optical conductivity.

SWCNTs have attracted huge scientific research efforts in the last two decades, since tubular structures of graphitic carbon were described by Iijima in 1991.\(^1\) The latter is due to their unique features both in terms of physical and chemical. In this context, the electronic properties as one-dimensional quantum conductors\(^2\) with ballistic charge transport even at room temperature stand out.\(^3\) Depending on their structure, SWCNTs may, however, show either metallic conductivity or semiconducting behavior, with a band gap that inversely scales with the SWCNT diameter.\(^3\)-\(^5\) Such peculiar properties, combined with the high transparency of thin SWCNT films, calls for this extraordinary material to be used in transparent, conducting thin films as, for example, electrode materials.\(^6\),\(^7\)

The current industry standard for transparent electrodes is indium tin oxide (ITO), whose use is associated with substantial disadvantages, which foster the idea to look for replacements. Quite importantly, high prices and the inherent brittleness of this material render ITO electrodes, on one hand, very expensive and, on the other hand, unsuitable for applications such as flexible electronics, \textit{etc.}\(^8\)-\(^11\) Myriad of attempts have been made to realize suitable substitutes for ITO. Most notable are efforts on metal nanowires, such as copper\(^8\) or silver,\(^9\) and on metal oxide frameworks.\(^12\),\(^13\) In parallel, a multitude of techniques and procedures have been explored to fabricate carbon-based nanostructured films. Mostly, SWCNT net-
works have been at the focal point, followed by graphene films grown on metal surfaces by chemical vapor deposition (CVD) and, finally, composite materials containing carbon nanotubes and graphene. None of the aforementioned led, however, to the needed breakthrough to be implemented as thin transparent, conducting electrodes owing to numerous drawbacks. One of these drawbacks is variation in quality of SWCNTs, even within different batches of the same synthesis process. The latter is certainly followed by the poor dispersability / solubility of SWCNTs in commonly used media. Here, the existence of SWCNT bundles leads to complications, especially in the context of dispersing and / or processing them.

The variations in SWCNT quality begin with the starting material. SWCNTs are generated in various purities, lengths, chiralities, diameters, and graphitization grades. While several methods have been developed to purify SWCNTs to remove by-products – amorphous carbon, fullerenes, and metal particles – properties of SWCNTs strongly depend on the synthetic methods. Of crucial importance for the control over quality are the synthesis parameters. Considering, for example, arc discharge synthesis, also the area of the reaction chamber from where SWCNTs are taken plays a role. In recent years, significant progress towards the synthesis of high quality SWCNTs with distinct properties has been made. Examples are the preferential growth of CVD grown SWCNTs featuring narrow diameter distributions, the CVD based growth of preferred metallic SWCNTs, and, last not least, the water-assisted CVD growth yielding highly graphitized materials. Still, arc discharge and laser ablation SWCNTs are of higher quality, that is, revealing higher degrees of graphitization than what is commonly found in CVD grown SWCNTs.

The poor dispersability / solubility and bundling of SWCNTs prompt to the needs of sophisticated dispersion chemistry. Please note that a high exfoliation grade is needed or, at least, is preferred for thin conducting films. Most commonly, SWCNTs are exfoliated by means of a surfactant based approach that yields stabilized SWCNT dispersions in either aqueous or organic media. Widely employed surfactants are sodium dodecylbenzene sulfonate
Typical organic solvents are, for instance, N-methyl-pyrrolidone (NMP) and N-cyclohexyl-pyrrolidone (CHP). Besides the surfactant and the solvent, which clearly govern the dispersion quality, the technical procedure spanning a wide variety of different parameters has also to be taken into account. As such, they have been demonstrated to influence the exfoliation grade. A rather successful method to obtain exfoliated SWCNTs includes several cycles of tip sonication, bath sonication, and centrifugation. The sonication steps are imperative to break up SWCNT bundles and to homogenize individualized SWCNTs and smaller bundles throughout the dispersion. Nevertheless, the sonication step needs careful adjustment to just provide the right amount of energy to individualize / disperse SWCNTs without damaging them, that is, shortening. As a complement, the centrifugation step serves to remove larger agglomerates, whose dispersions would be semistable and, in turn, would contaminate SWCNT thin films. Ultracentrifugation with G-values well over 40,000 is frequently used in the literature. Notably, the complexity of the aforementioned exfoliation technique is unsuitable with respect to upscaling due to substantial material loss.

What limits the applicability of SWCNTs for industrial use in, for example, electronic devices is after all not the fabrication of high-quality SWCNT devices but the technical demand and financial expenditures to take SWCNTs from scratch to the final product. Enormous efforts have been spent on synthesis, purification, and processing of SWCNTs. Nevertheless, the need for simple and cheap procedures, which ensures high device quality upon waste reduction and economic device fabrications, arises.

In the present work, we explore the relation between device quality and efficient processing by combination of a high quality starting material and advanced dispersion techniques under mild conditions. To this end, we focused in our work on arc discharge SWCNTs from Iljin Nanotech, which are well known for the effective production of transparent conducting films. Considering the factors that determine SWCNT dispersions – vide supra – our
choice went to a mild method developed by Bergin et al. that skips the ultracentrifugation. Based on previous experience, SDS, SDBS, and SC as well as CHP were chosen as surfactants and solvent, respectively. The key advantage of this method is a reduction of material waste during centrifugation, while affording a high dispersion quality as required for device productions. The latter is particularly advantageous, especially when using rather expensive SWCNTs such as arc discharge samples.

To shed first light onto the efficiency of our approach using high quality starting material, transparent conducting films were fabricated and characterized. To this end, we drop-casted our dispersions onto glass slides as a simple, reliable, and reproducible technique to evaluate their potential as transparent conductors, whereas the fabrication process has to be optimized in future work. This allows to correlate the characteristics of our films with benchmarks reported in the literature and to assess if our method is suitable as a simple and effective process.

To this date, most studies on dispersing SWCNTs are carried out with nanotubes synthesized by the HiPCO method. It seems conclusive that the overall dispersion might suffer from the lack of comparability if different SWCNTs, especially with different defect densities, are used. It is mainly the surface charge of SWCNTs that influences mutual interactions, that is, between SWCNT surfaces, surfactant, and solvent. All experiments were carried out with arc discharge as well as HiPCO SWCNTs to allow comparing the difference in dispersions and in device performance as a function of SWCNT materials. The starting materials were characterized by Raman spectroscopy, high-resolving transmission electron spectroscopy (HR-TEM), energy-dispersive X-ray spectroscopy (EDS), and thermogravimetric analysis (TGA). In addition, absorption spectroscopy (UV-Vis) and Raman spectroscopy were utilized to qualitatively determine the dispersion quality.

Results and Discussion
The properties of HiPCO SWCNTs are comprehensively described.\textsuperscript{4, 40, 41} In stark contrast, properties of arc discharge SWCNTs are barely documented in scientific publications at the moment. Here, we present a full-fledged investigation regarding the properties of Iljin arc discharge SWCNTs.

We performed thermogravimetric analyses under air to obtain first estimates on the purity of the starting material. This technique is particularly suited to reveal the graphitization grade of SWCNTs by comparing the maxima of the first derivatives and the amount of residual metal particles. Figure 1 shows the TGA of HiPCO SWCNTs, while the TGA of arc discharge SWCNTs are shown in Figure 2 as either received and after two subsequent purification steps.

In the case of HiPCO SWCNTs, the entire mass loss stretched from 300 to 500°C featuring a maximum of the derivative at 443°C. Notably, the graphitization grade of HiPCO SWCNTs tends to be relatively low and the defect density is relatively high. From the latter, a poor thermal stability and a burn-off peak evolve under air at rather low temperatures compared to well graphitized SWCNTs. The defect density does, however, not necessarily scale linearly with the burn-off temperature. For example, a small change in defect density may result in a significantly higher or lower derivative maximum.\textsuperscript{42} The residue left after annealing to around 500°C is 14.7 wt\%, which was identified in good accordance with the product data sheet\textsuperscript{41} as iron catalyst in EDS measurements (see SI, Figure S 1).

From the TGA of the arc discharge SWCNTs a different picture about the sample quality is concluded. We expected that the burn-off temperature is markedly higher than in HiPCO SWCNTs due to higher graphitization grade. Roughly 60 wt\% of the sample lived up to these expectations with a derivative maximum at 730°C (Figure 2). As such, we believe that our batch of arc discharge SWCNT consist of high-quality, well graphitized SWCNTs with a high thermal stability that is rarely reported on in the literature. However, circa 30 wt\% start to burn off at around 400°C. In other words, one third of the pristine arc discharge SWCNTs purchased from Iljin Nanotech is poorer graphitized material – either in the form of CNTs with
lower quality or carbon shells around the remaining catalyst particles.\textsuperscript{43} Amorphous carbon should burn off at temperatures below $400^\circ\text{C}$,\textsuperscript{42} leading to the hypothesis that the shoulder in the TGA stems from some form of graphitized carbon. The full width half maximum (FWHM) is also larger than in HiPCO SWCNTs. This seems to be intuitive taking into account that the reaction environment is more uniform during thermal CVD growth than in an arc discharge reactor.

In the context of producing high-quality electronic devices, the existence of one third of low-quality material is, of course, far from being satisfactory. To further purify the Iljin SWCNTs, several 100 mg of the starting material were annealed under air stream at $400^\circ\text{C}$ for three days. These conditions were carefully chosen based on the TGA of the untreated material and a study from Jeong \textit{et al.}\textsuperscript{44} On the one hand, the poorly graphitized material starts to burn off at roughly $370^\circ\text{C}$ while, on the other hand, oxidation of high quality SWCNTs does not set in at these temperatures.

After annealing, the shoulder vanished in line with the expectation. The overall weight of the annealed tubes was, however, reduced by one third and the TGA featured one uniform peak in the first derivative with a maximum around $690^\circ\text{C}$. The catalyst residue was with 11.7 wt\% higher than in the measurements with the starting material with a value of 7.76 wt\%. The nature of the catalyst was again revealed by EDS (see Figure S 2) and was found to be a mixture from iron, cobalt and nickel. It is worth mentioning that the slight weight increase, which sets in in all of the TGA spectra above $800^\circ\text{C}$, relates to the formation of metal oxides. Overall, the metal oxidation is more pronounced for arc discharge catalysts, which contain cobalt and nickel, than what is seen for iron catalyst only HiPCO tubes. This effect is, however, weaker upon preannealing SWCNTs owing to the partial oxidation during the three day treatment. The higher content of oxidized catalyst particles in the annealed sample also explains the slightly lower peak temperature due to heating effects located at the metal oxide particles accelerating the oxidation of the surrounding SWCNTs.\textsuperscript{42}
Next, the second purification step was meant to remove metallic impurities. A number of fairly successful methods have been established, including high temperatures, reflux, and treatment with concentrated acids.\textsuperscript{21} Regardless of the aforementioned, we opted for a method as mild as possible to successfully remove metal particles from the SWCNT material. In particular, the preannealed SWCNTs were therefore added to 2 M hydrochloric acid and stirred at 60°C for one week. The outcome of this treatment is indicated in the TGA plots. Now, the residue is found to be as low as 0.63 wt% and the peak maximum is noted at 738°C. On the downside, a small shoulder is discernable between 550 and 650°C. The latter indicates that some SWCNTs have been damaged during the acid treatment as the TGA of the annealed SWCNTs lack this feature. We attribute this effect to be more than compensated by the purity of the SWCNTs in respect to metal particles. It is worth mentioning that the small peak around 300°C relates to the presence of incorporated HCl. Taking the aforementioned into concert, we reach the conclusion that a satisfying SWCNT quality with respect to purity was reached after two mild purification steps.

For further characterization, the materials were analysed by means of UV-Vis/NIR spectroscopy and Raman spectroscopy. This was meant to shed light onto the average diameter and chirality distribution. Typically, the diameter of HiPCO SWCNTs range from 0.8 to 1.2 nm,\textsuperscript{41} whereas the diameter of Iljin SWCNTs is between 1.2 and 1.8 nm with a mean diameter of 1.6 nm. For Iljin SWCNTs, the diameters are derived from STM and AFM assays with surfactant-stabilized SWCNTs in aqueous media.\textsuperscript{45} One obvious question arises if the surfactants tend to contribute to the overall diameters.

In light of the aforementioned, we conducted a HR-TEM study with particular emphasis on evaluating the SWCNT morphology and deriving their mean diameters. While SWCNTs are generally bundled, which are discernable in TEM, single individual SWCNTs are sometimes seen to stick out the bundles. Figure 3 shows typical TEM images taken for Iljin SWCNTs. In line with the expectation, bundles, metal particles as catalyst residue, and the some individual
SWCNTs are visualized. The metal particles tend to be embedded within carbon shells, which relates to the overall SWCNT growth. In addition, the presence of empty carbon shells correlates with the initial purity featuring a metal content of under 8 wt% as arc discharge reactors are usually loaded with a higher catalyst to carbon ratio. The encapsulated metal particles and empty carbon shells are a first indication for the existence of carbonic impurities within SWCNT samples. Notably, the latter burn off at far lower temperatures than the average high quality SWCNTs. It seems, however, to be unlikely that these carbonic impurities contribute much to the overall weight – *vide supra*.

More important is the SWCNT characterization with respect to their mean diameter. In order to gain first insights, we analyzed the diameter of 14 different SWCNTs yielding an average diameter of 1.59 nm and diameters that reach from 1.4 to 1.8 nm. This diameter distribution is plausible, when comparing it with the study by Nirmalraj *et al.*, apart from the fact that we found no evidence for diameters as small as 1.2 nm.

With the diameters in hands – HiPCO by data sheet and Iljin SWCNTs by HR-TEM measurements – we interpreted the UV-Vis/NIR and Raman spectra. To this end, the calculated correlation between SWCNT diameters and energy gaps, well known as the Kataura Plot, is crucial. On one hand, it enables assigning the observed peaks either to semiconducting or to metallic transitions. On the other hand, it enables determining what kind of SWCNTs are resonant at certain Raman laser lines and, in turn, deriving an estimate about the chirality distribution of the SWCNT samples from the Raman radial breathing mode (RBM).

The UV-Vis/NIR spectra of three different HiPCO SWCNT dispersions, which were diluted by a factor of ten, are shown in Figure 4. Obviously, each of the three different conditions, that is, SDS in water, SC in water, and CHP, is capable of successfully dispersing HiPCO SWCNTs. The spectra imply, especially the good resolution of the van Hove singularities, a fairly high exfoliation of the HiPCO SWCNTs within the dispersions. Additionally, the absorption peaks are clearly correlated to the nature of the electronic transition by referring to
the SWCNT diameter – please compare to the Kataura Plot.\textsuperscript{46} The $S_{11}$ transitions dominate the range between 900 and 1350 nm, while the $S_{22}$ transitions are seen to evolve between 500 and 850 nm. Finally, the $M_{11}$ transitions are located between 400 and 650 nm. All of the latter are in good accordance with a diameter distribution from 0.8 to 1.2 nm. It is worth mentioning that the $M_{11}$ transitions overlap partially with the $S_{22}$ transitions due to the small SWCNT diameters.

Notably, the organic dispersions feature broader peaks than the surfactant-stabilized aqueous dispersions. Especially the absorption peaks in the 950 to 1200 nm range are appreciably better resolved in the spectra taken for the SDS and SC dispersions. It has to be noted that the aqueous dispersions were prepared well above the critical micelle concentration (CMC)\textsuperscript{28} to obtain the best exfoliation possible. Still, with CHP to act as a surfactant and a solvent at concentrations high enough to physisorb at the SWCNT’ surface, we anticipated better resolved van Hove singularities. Especially the red-shifted $S_{11}$ transitions between 900 and 1350 nm indicate larger mean bundle sizes than what is the case for the aqueous dispersions.\textsuperscript{35} This might be surprising at first glance considering the high maximum HiPICO SWCNT concentration of 3.5 mg/ml that has been reported by Bergin \textit{et al.} in CHP.\textsuperscript{29} A possible explanation for the poorer exfoliation grade relates to the higher viscosity of CHP\textsuperscript{47} relative to the surfactant solutions.\textsuperscript{48} As such, the removal of SWCNT aggregates and larger SWCNT bundles using the same centrifugation parameters is less efficient. The viscosity effect might also influence the sonication process with respect to the dynamics of solvent molecules physisorbing at the individual SWCNTs surface.

Figure 5 shows the UV-Vis/NIR spectra for Iljin SWCNTs dispersed in CHP as well as dispersions of SDBS and SC – diluted by a factor of ten. The larger tube diameter shifts the electronic transitions to lower energies with $S_{22}$ transitions between 850 and 1150 nm, $M_{11}$ transitions between 600 and 800 nm, and $S_{33}$ transitions between 400 and 600 nm. With the different transition types not overlapping due to the tube diameters, the energy gaps feature smaller
The latter results in a poor resolution of the van Hove singularities, namely the $S_{22}$ and the $M_{11}$ transitions. However, this trend is not due to a poorer exfoliation, but must stem from smaller energetic differences between the individual absorption peaks. Figure 6 shows the spectrum for CHP extended into the NIR region. Due to the fact that surfactant solutions feature strong absorption bands in this region of the spectrum, it was impossible to detect any features in the corresponding spectra. CHP also shows a strong absorption between 1600 and 1800 nm (see SI, Figure S 3). This leads to strong noise in the absorption spectrum at these wavelengths. Opening the aperture slit of the spectrometer to maximum avoids, on one hand, this problem, but results, on the other hand, in poorer wavelength resolution including slight shifts of the peaks – compare the red graph in Figure 6. Still, the $S_{11}$ transitions of Iljin SWCNTs are discernable in the range between 1500 and 2000 nm, which is – to the best of our knowledge – the first time that a noise free detection of $S_{11}$ transitions in this particular diameter range.

The three dispersions give rise to similar behavior even at comparable concentrations. It renders, of course, extremely difficult to estimate absolute concentrations considering the fact that Iljin SWCNTs differ in type relative to HiPCO SWCNTs. And, as such, they behave differently and feature different absorption coefficients. In high concentration experiments this exerts strong impact. In particular, a concentration of 1.0 mg/ml HiPCO SWCNTs was stable in CHP, while dispersions with the same initial concentration of Iljin SWCNTs precipitated after centrifugation. Here, the resulting supernatant has a concentration of roughly 0.2-0.3 mg/ml. This, in turn, is less than one tenth of the maximum concentration of HiPCO SWCNTs in CHP. A higher defect density in HiPCO SWCNTs leads to higher charged surfaces and, per se, to stronger interactions with the surfactants or solvent molecules. In other words, these higher defected SWCNTs interact better with CHP than less defected and better graphitized Iljin SWCNTs. No doubt, further investigations are necessary, especially to quan-
tify the aforementioned effects and to fully adapt our mild dispersion method, which was developed for dispersing HiPCO SWCNTs, to Iljin arc discharge SWCNTs.

Next, absorption spectra were recorded prior and after centrifugation to provide an overview about the material loss of Iljin SWCNTs upon dispersion. Figure 7 shows the resulting differences in absorptions. Comparing the absorption at prominent peaks, that is, 464, 683, 965, and 1007 nm, yields values for the absorption of the centrifuged dispersions in the range of 88 to 98% of the initial absorptions. This data needs to be considered with owing to the fact that the absorption coefficients slightly differ prior and after centrifugation. In other words, the mass loss is underestimated. The exact mass loss detection renders difficult, but is, nevertheless, far below 20 wt%.

When turning to Raman analysis of HiPCO SWCNTs and Iljin SWCNTs, the corresponding spectra – excited by a 633 nm laser – are shown in Figure 8 and Figure 9. Typical Raman features including RBMs as well as D-, G-, G’, and M-bands and are all noted. In addition, iTOLA second order modes are detected. The earlier four are most characteristic for different SWCNTs and as used to gain insights into the nature of SWCNTs such as chirality distribution, exfoliation grade, and defect density. For example, the chirality distribution is derivable from the RBMs at different excitation energies. The exfoliation grade, on the contrary, evolves as a function of the RBM resolution. Finally, an estimate of the defect density is typically made from the ratio of G- to D-band and / or of G’- to G-band.

The Raman spectrum of HiPCO SWCNTs – using an excitation energy of 1.96 eV (633 nm) – confirms the presence of semiconducting species as it is anticipated from the Kataura Plot. From the typical line shapes of the G- and the M-band as well as the iTOLA second order mode we conclude that different chiralities are resonantly enhanced at 633 nm and these consists of semiconducting SWCNTs. In the RBM area, clearly resolved features evolve between 150 and 300 cm\(^{-1}\). This is due to the facts that 633 nm excites a relatively large diameter variance and that a good exfoliation grade is realized. The D to G ratio is, however, rather large,
with similar peak maxima of the D- and G-bands – a finding that is in sound agreement with the high defect density disclosed by the TGA.

The interpretation of the Iljin SWCNT Raman spectra is rather than straightforward. A closer look at the Kataura Plot shows that there are two electronically different types of SWCNTs, which are in resonance at the 633 nm excitation. Specifically, metallic SWCNTs, with diameters between 1.2 and 1.4 nm feature their M_{11} transitions in this energy range, and semiconducting SWCNTs, whose diameter reach from 1.6 to 1.8 nm give rise to S_{33} transitions at around 1.96 eV. As a matter of fact, the observed spectrum is most likely to be a superposition of Raman features stemming from metallic and semiconducting SWCNTs. It is important to keep this fact in mind as it is helpful for the interpretation of some experimental observations, which seem, at the first glance, to be contradictive.

The resulting Raman spectra show several interesting trends that should be rationalized on the presence of metallic and semiconducting SWCNTs. First of all, the RBMs are shifted to lower wavenumbers relative to what has been seen for HiPCO SWCNTs, namely between 140 and 220 cm\(^{-1}\), and are less well resolved. The aforementioned is due to larger SWCNT diameters, which lower their vibration energies, and to a smaller diameter variance that are in resonance at 633 nm which leads to more tubes with a different chirality around a certain diameter and thus to more RBM modes in the same range of vibration energy.\(^{46}\)

The peak at around 150 cm\(^{-1}\) is assigned to semiconducting SWCNTs with a diameter in the range from 1.6 to 1.8 nm and the peak at around 170 cm\(^{-1}\) including its shoulders is assigned to metallic SWCNTs with smaller diameters, that is, from 1.2 to 1.4 nm. It might occur that the peak around 150 cm\(^{-1}\) is rather unusual for semiconducting SWCNTs in terms of intensity and peak shape relative to the other features. A like rationale implies the fact that the RBM intensity varies markedly between metallic and semiconducting SWCNTs\(^{49}\) and that the mixture gives rise to a lower variances in RBM vibration energies at larger diameters than at smaller diameters.
Even more striking is the G-band, which appears to be split into four peaks. The nature of this feature proves to be even more complicated to explain. In general, the G-band consists of several overlapping peaks, including coupled vibration modes besides the G\(^+\)- and the G\(^-\)-bands. Additionally, the G-mode frequency and the line shape differ rather strongly for semiconducting and metallic SWCNTs.\(^{49-51}\) As we are dealing with Iljin SWCNTs that are resonantly enhanced at 633 nm, the assumption of a mixed semiconducting / metallic resonance is again valid. Bearing this in mind, the two peaks at 1548 and 1563 cm\(^{-1}\) represent the G\(^-\)-band of metallic and semiconducting SWCNTs, respectively, while the two peaks at 1584 and 1592 cm\(^{-1}\) relate to the G\(^+\)-band.\(^{50}\) The D- to G-band ratio is remarkably small and the G\(^-\)- to G-band ratio is much higher than seen for HiPCO SWCNTs – *vide supra*. From the latter we conclude that the Iljin SWCNTs are low in defects, which is in good accordance with the TGA results.

Nevertheless, an important question about the tip sonication induced SWCNT damage remains. Figure 10 shows Raman spectra of Iljin SWCNTs that were recorded for pristine and untreated material as well as a dried film of a CHP dispersion at two different excitation wavelengths. Please note that the intensity has been adjusted to the G-bands of both spectra. The comparison discloses after dispersion a slight increase of the D-band intensity and a slight decrease of the G\(^-\)-band intensity all relative to the G-band. After all, dispersions of pretreated SWCNTs are indeed more defected than the corresponding starting materials. However, the overall differences should be regarded as small at the larger scale, especially considering the subsequent treatment with concentrated nitric acid during film production.

Finally, we turned out to correlate optical transparency with film conductivity to evaluate the potential of SWCNT films as transparent conductors. SWCNT films were fabricated by a simple drop-casting method. Subsequently, the drop-casted films were doped by immersion into concentrated nitric acid. The transparency in the visible light region and the sheet re-
sistance were measured by UV-Vis absorption spectroscopy and four-point probe resistivity measurements, respectively.

It turned out that the transparency varied strongly using the same method. The only variable in these experiments was the coverage area on the glass substrates. With the overall variance in hand, we screened the film performance throughout a transparency range at 550 nm from 65 to 86%. The uniformity of the fabricated films lags behind alternative deposition methods, such as filtering. This effect was taken into account by measuring the sheet resistance at ten different locations throughout the entire film and determining statistical errors. Figure 11 shows the correlation of the sheet resistance with the transparency at 550 nm. We calculated the ratio $\sigma_{DC}/\sigma_{Op}$, which is a widely used figure of merit,\textsuperscript{16} to be 2.1 to 2.2 for films produced with Iljin SWCNTs which is an order of magnitude higher than the values we found for HiPCO SWCNT films deposited with the same method. This is, of course, an unsatisfying value in the context of high performance applications. Recently, a new benchmark implies a factor that is 30 times.\textsuperscript{38} Nevertheless, values of 2.1 to 2.2 are in the order of magnitude to become interesting for applications that rely on cheap and reliable transparent conductors.

**Conclusions**

A comprehensive study was carried out to evaluate and compare the properties of HiPCO and Iljin SWCNTs in terms of quality of the starting materials and of dispersions for the production of transparent conducting films. Characterization was done by means of thermogravimetric analysis, high resolution transmission electron microscopy, visible and infrared light absorption spectroscopy, and Raman spectroscopy. This widely spread set of spectroscopic techniques shed light onto the characteristics and the behavior of different SWCNTs on two accounts. On one hand, it considers a certain point of view or a certain stage of production, as it is quite common in the literature. On the other hand, it reflects the entire procedure, beginning with the starting material and ending with the deposited films.
It was found that the chosen SWCNTs, namely arc discharged SWCNTs from Iljin Nanotech, featured a much higher quality of the starting material than the cheaper and widely used HiPCO SWCNTs. However, the necessity evolved to purify even this material in order to meet high quality requirements. We showed that this material was able to form transparent conducting films with performances resulting in a figure of merit, which is by a factor of 10 higher than HiPCO SWCNT films produced by the same procedure.

It is essential for the ability to industrially produce thin conducting films for application as transparent electrodes that the production process is cheap, scalable, and straightforward. SWCNT films are thereby predestinated especially for the use in flexible devices.\textsuperscript{52} We demonstrated that the combination of high quality SWCNTs with an optimized dispersion procedure is applicable towards the production of transparent conducting films of high quality. The key advantage inherent to our method is the extremely low material loss, which is usually the major drawback coming along with most other dispersion methods. If this mild method is adapted to disperse high quality starting material, the film performance will improve significantly compared to low quality nanotubes. Still lagging behind this year’s benchmark,\textsuperscript{38} our approach provides a sound basis for further developments, that is, more sophisticated film deposition methods, well developed doping procedures, and starting materials of even higher quality. The effective processing in terms of amount of starting materials that remains usable for the final application provides optimum preconditions for an industrially worthwhile production of transparent conducting films for – at this stage of the development – at least for low performance applications, such as e-paper.

\textbf{Materials and Methods}

Arc discharge synthesized SWCNTs were purchased from Iljin Nanotech Co., LTD (batch number A-100125-1) and HiPCO SWCNTs were purchased from Carbon Nanotechnology, Inc. (batch number P0341). The HiPCO nanotubes were used as purchased. Purification of the
arc discharge SWCNTs was conducted in two subsequent steps. In the first step, the SWCNTs were annealed in an air stream at 400°C for three days. The second step was a treatment with 2 M hydrochloric acid at 60°C for one week. SDS, SDBS and CHP were purchased from Sigma-Aldrich, SC was purchased from Fisher Scientific GmbH and used as received. Millipore water (18.2 MΩ cm at 25°C) was used for the aqueous solvent systems.

Raman spectroscopy (using Horiba Jobin Yvon spectrometers with different laser lines: 532 nm and 633 nm) and TGA (TA instruments TGA Q500, under air, flow rate 90 ml/min, temperature ramp 5°C/min) were performed with both the pristine and purified SWCNT material. For the HR-TEM measurements (Jeol JEM-2200FS), pristine SWCNTs were deposited onto hollow carbon TEM grids with aid of a scalpel blade. This, indeed, destroyed the hollow carbon at some parts of the grid, but provided the possibility of depositing SWCNTs without getting in contact with any solvents. The measurements were conducted in areas with an intact carbon film.

The nanotubes were dispersed by a slightly modified method developed by Bergin et al.32 Stock solutions of SDS, SDBS, and SC in Millipore water with a concentration of 10 mg/ml, which is well above the CMC of 2.0-2.9 mg/ml, 0.73 mg/ml and 4-6.5 mg/ml, respectively, were prepared by dissolution of the surfactant and stirring for half an hour. 1.0 mg of either HiPCO or arc discharge SWCNTs were carefully weighed into glass vials and 10 ml of a surfactant stock solution or CHP were added. If the SWCNT weight slightly differed from that value, more or less solvent was added in order to adjust the SWCNT initial concentration to $c_i = 0.1$ mg/ml. The solvent-SWCNT mixture was then sonicated with a pulsed tip sonicator for 15 minutes (pulse duration: 1.0 s on / 1.0 s off, power: 500 W, amplitude: 40%), followed by one hour of bath sonication and an additional subsequent tip sonication step using identical parameters as before. During tip sonication, the dispersion was cooled by an ice bath to avoid overheating. This technique is believed to only break SWCNT bundle and to avoid further damage to SWCNTs.32 After sonication, the dispersion was mildly centrifuged for 90 min
to remove agglomerates. The supernatant was carefully transferred into a clean vial after centrifugation and stored under ambient conditions.

UV-Vis and near infrared (UV-Vis/NIR) absorption spectra were recorded using a Shimadzu UV-3600 spectrometer. The dispersions were diluted by a factor of ten to reduce absorption saturation. Raman spectra of the processed SWCNTs were recorded on dried droplets of undiluted dispersions. Direct measurements of the wet dispersions proved to be difficult, because the laser spot did not stay in focus due to dynamic effects of the liquid. The Raman spectra were generally recorded using a 300 mm$^{-1}$ grating. The RBM areas were typically recorded with a better resolution (1800 mm$^{-1}$ grating). For calibration purposes, the 520.7 cm$^{-1}$ line of SiO$_2$ was used.

After characterization of the different dispersions, transparent conducting films were fabricated by a simple technique. A droplet of 0.5 ml SWCNT dispersion in CHP, obtained as described above, was deposited onto a clean glass slide. Prior to the deposition, the glass slides were degreased by sonication in fairy liquid solution for 30 minutes, followed by bath sonication in acetone for 30 minutes. The air dried slides were then terminated by immersion into a 10 wt% solution of trimethylsilyl chloride (from Sigma-Aldrich) in Millipore water and a lacing of hydrochloric acid over night to improve wettability in regard to the solvent CHP. The slides were rinsed with Millipore water and air dried. The dispersion droplet was then deposited onto the slides on a hotplate at around 110 to 120°C to dry off the solvent. The drying temperature is important as CHP has a high boiling point above 150°C but decomposes already below that temperature. The dried SWCNT films were then immersed into 12 M nitric acid for 30 minutes to improve the film conductivity. The prepared SWCNT films were characterized by UV-Vis spectroscopy in transmission mode and four-point probe sheet resistance measurements (Jandel in-line four point probe). The sheet resistance was determined at ten different spots within the films, which had around one square centimeter in size, and averaged with a statistical error.
Acknowledgement

We gratefully acknowledge R. Jalili and R. Schäfer for their contributions to this work. We furthermore thank the groups of P. Müller (Department of Physics, University of Erlangen), K. Meyer (Chair of Inorganic Chemistry II, University of Erlangen and A. Hirsch (Institute of Advanced Materials and Processes, Fürth, Germany) for technical support. The HR-TEM measurements were performed by D. Mitchell at the Australian Microscopy & Microanalysis Research Facility (University of Sydney). The work was funded by an Australian Research Council Program grant (DP0877348) and by the DAAD by the ISAP program (50 7300 75).

Supporting Information Available: EDS on the residue of the TGA for determination of the catalyst material, typical greyscale profile of HR-TEM for the determination of the tube diameter and UV-Vis absorption spectrum of the organic dispersant CHP. This material is available free of charge via the Internet at http://pubs.acs.org.

References


43. However, one third of the overall mass seems to be too high to only represent carbon shells around 7.76 wt% of metal particles. Note that the molecular weight of the metal particles is five times as high as that of carbon. This would mean that the stoichiometry would be at least C20 : M1


48. The viscosity of CHP is roughly by a factor of ten higher than the viscosity of water.


Figure 1: TGA of pristine HiPCO SWCNTs. The continuous graph depicts the relative weight in percent; the dotted line represents its first derivative.
Figure 2: TGA of Iljin SWCNTs – as received / pristine (black), annealed (blue), and acid-treated (red). The continuous graphs depict the relative weight in percent; the dotted lines represent their first derivative.
Figure 3: HR-TEM images of pristine Iljin SWCNTs with magnifications of 8k, 50k, 100k and 300k, recorded using an acceleration voltage of 300 kV.
**Figure 4:** UV-Vis/NIR spectra of pristine HiPCO SWCNT dispersions.
Figure 5: UV-Vis/NIR spectra of pristine Iljin SWCNT dispersions.
Figure 6: UV-Vis/NIR spectrum of a Iljin SWCNTs dispersion in CHP.
Figure 7: UV-Vis spectra of Iljin SWCNT dispersions with different initial concentrations before and after centrifugation.
Figure 8: Raman spectra of HiPCO SWCNTs – excitation energy of 1.96 eV.
**Figure 9:** Raman spectra of Iljin SWCNTs – excitation energy of 1.96 eV.
Figure 10: Raman spectra of Iljin SWCNTs before and after dispersion – excitation energies of 2.33 eV (left) and 1.96 eV (right).
Figure 11: Correlation of transparency and sheet resistance of the Iljin SWCNT films.

Supporting Information

EDS was performed on the residue of the TGA. Figure S1 shows the elemental composition of the residue of both Iljin and HiPCO SWCNTs. It has to be mentioned that the oxygen content has to be contributed to oxidation of the metallic catalyst particles during the TGA under air. These two measurements allow an estimate of the average catalyst composition due to the macroscopic amount of material used in the TGA (several milligrams). The catalyst of HiPCO SWCNTs only consists of iron – in good accordance to the product data sheet – whereas the spectrum for Iljin SWCNTs reveals cobalt, nickel and iron as catalyst. The EDS of individual catalyst particles in HR-TEM measurements revealed that the ratio of these metals varies throughout the particles, which might be ascribed to the use of milled metal particles instead of a homogeneous alloy. We furthermore detected individual silica particles within the pristine material from Iljin which can be contributed to a chromatographic purification step using a silica loaded column.

Figure 2 shows the absorption spectrum of the pure organic solvent CHP (air as reference), featuring a strong absorbance peaking at 4.5 in the range of 1650 cm\(^{-1}\) to 1800 cm\(^{-1}\). It becomes obvious that the light intensity for recording nanotube spectra is very poor in this range ac-
According to the Lambert-Beer law, leading to extreme statistical noise in determining the quotient $I/I_0$ (compare Figure 6).

Figure S1: EDX spectrum of the TGA residue of (a) HiPCO SWCNTs and (b) the arc discharge SWCNTs.
Figure S2: UV-Vis/NIR spectrum of pure CHP.