1. Introduction

A single-walled carbon nanotube (SWCNT) can be conceptually regarded as a seamless cylinder rolled up from a piece of graphene sheet, and its geometrical structure is defined by a pair of integers, \((n, m)\), namely the chirality.\(^1\) Numerous theoretical\(^2\) and experimental\(^3,4\) studies have shown that the electronic structure of an SWCNT is determined by its chirality, or equivalently, its diameter and chiral angle. As-grown nanotube samples are always a mixture of both metallic and semiconducting SWCNTs,\(^5\) which poses a drawback in their applications.\(^6–9\) Direct selective growth\(^10–20\) and post-growth separation\(^21–25\) techniques have been developed in recent years in an attempt to select SWCNTs with a given chirality. These methods are based on the different stabilities and chemical reactivities of SWCNTs with different geometrical structures.\(^26\) Theoretical studies have touched this fundamental question, aiming to compare the energy and chemical reactivity differences among individual SWCNTs.\(^27–31\) However, it is rather challenging to investigate the chirality-dependent intrinsic stability and reactivity of individual SWCNTs experimentally. Previous experiments\(^21,32,33\) were only carried out on SWCNT bundles or SWCNTs supported on substrates or dispersed in solvents, where the interactions among SWCNTs inside a bundle,\(^34\) on a substrate,\(^35\) or in the solution alter the properties of SWCNTs. Meanwhile, the purification process\(^32,33\) generally introduces defects in SWCNTs. For example, acid treatment is commonly used to
purify raw nanotubes, while such processes may cause surface functionalization of nanotubes with oxygenated functional groups\textsuperscript{[36,37]} and destroy nanotube structure.\textsuperscript{[38]} On the other hand, sonication involved in many purification methods can create vacancy-type defects in nanotubes, disrupt their tubular structure, and even cut them.\textsuperscript{[22–24,39]} This further hinders the investigation of the intrinsic properties of SWCNTs. Moreover, optical methods like Raman, optical absorption, and photoluminescence spectroscopy are usually used to characterize the chirality of SWCNTs.\textsuperscript{[10–12,20,22–25,32,33,40,41]} These methods are not unambiguous for charactering the chiralities of large diameter SWCNTs and the nanotube environment may have an effect on their chirality assignment.

Here, we devised a novel and robust approach to solve the above problems and to study the chirality-dependent intrinsic reactivity nanotubes. We used as grown high quality, individual suspended SWCNTs to exclude the influence from nanotube bundles and substrates on their properties, and the nanobeam electron diffraction (ED) technique ensures a precise characterization of nanotube chirality. Our results show that the reaction of SWCNTs to O\textsubscript{2} sensitively depends on their diameters, metallicity, and particularly, chiral angles, which is in well agreement with the first-principles calculations.

2. Results and Discussion

High-quality SWCNTs grown using a floating catalyst (aerosol) chemical vapor deposition (CVD) method\textsuperscript{[42,43]} were directly collected on Si\textsubscript{3}N\textsubscript{4} transmission electron microscopy (TEM) grids (see Experimental Section). Figure 1a presents a typical TEM image of as-grown SWCNTs inside a hole on a Si\textsubscript{3}N\textsubscript{4} TEM grid, where the nanotubes form a dense network. Raman spectroscopic study (Figure 1b) shows the presence of radial breathing modes (RBMs) located at 100 cm\textsuperscript{-1} to 300 cm\textsuperscript{-1}, indicating a relatively broad diameter distribution, as the diameters of SWCNTs are determined by their RBM frequencies.\textsuperscript{[44–47]} Furthermore, a low defect-related D-band to tangential G-band intensity ratio of $\sim$0.03 indicates the very high quality of the as-grown nanotubes.\textsuperscript{[20,47]} Detailed high-resolution TEM (HRTEM) studies reveal that most of the products are high quality SWCNTs, which are clean and straight with suspended segments having lengths of $\sim$50–200 nm (Figure 1c,d).

We characterized the chiralities of individual suspended SWCNTs using ED\textsuperscript{[48]} (see Experimental Section) and simultaneously recorded their position on the grid inside TEM (Supplementary Figure S1). Afterwards, these SWCNTs underwent oxidation treatment in air at 400 °C for 30 min and were characterized by TEM again to examine whether they had reacted. The samples then underwent repeated treatments under more harsh conditions, followed by subsequent TEM examinations. By a series of such oxidation treatments, recording, and characterization, we constructed a chirality-dependent reaction sequence for SWCNTs.

Figure 2 presents a TEM image sequence illustrating the evolution of an individual suspended SWCNT after being treated at temperatures of 400 °C, 450 °C, 470 °C, and 490 °C. The original SWCNT is shown in Figure 2a (indicated by a solid arrow). Figure 2b shows the ED pattern of this SWCNT, which presents a set of parallel diffracted layer lines in addition to the bright spot at the centre. An ED pattern analysis revealed that the chirality of this SWCNT is (11, 10).\textsuperscript{[48]} The sample then underwent oxidation treatment at 400 °C, and Figure 2c clearly shows that this nanotube did not react. The situation was the same for 450 °C (Figure 2d) and 470 °C (Figure 2e). However, after treatment at 490 °C, this SWCNT disappeared, as indicated by the dotted arrow in Figure 2f. Note that we did not observe any significant changes in the surrounding nanotube network, as evident from the figures. Figure 2a,c–f exclude any effects of the underlay support on the disappearance of this (11, 10) SWCNT. Consequently, the disappearance of this (11, 10) SWCNT at 490 °C is attributed...
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Figure 2. Sequential images illustrate the evolution of an SWCNT sample after air treatment at different temperatures. (a) A TEM image of a pristine SWCNT. (b) A nanobeam ED pattern of the SWCNT suggesting a chirality of (11, 10). (c–f) TEM images of the same SWCNT after air treatment for 30 min at 400 °C (g), 450 °C (d), 470 °C (e), and 490 °C (f). The solid arrows in images (a,c–e) indicate the SWCNT, while the dotted arrow in image (f) indicates the disappearance of this SWCNT.

Figure 3 shows chirality maps of reacted and unreacted SWCNTs for the four reaction temperatures. In each map, unreacted SWCNTs are marked with green hexagons while the reacted SWCNTs are colored in blue (400 °C, Figure 3a), dark brown (450 °C, Figure 3b), red (470 °C, Figure 3c), and orange (490 °C, Figure 3d). As shown in Figure 3a and the Supporting Information Table 1, only two SWCNTs, i.e., (11, 2) and (12, 1), reacted after the treatment at 400 °C. Interestingly, the (11, 3) SWCNT, which possesses a diameter and a chiral angle slightly larger than the (12, 1) SWCNT, survives the treatment. We remark that both (11, 3) and (12, 1) SWCNTs are semiconducting nanotubes. The above results indicate that even SWCNTs with similar geometrical structures and the same electronic properties, they exhibit distinctly different reactivity in air. The smallest SWCNT observed in this study, a (7, 6) nanotube, did not react during 400 °C treatment, despite it having a smaller diameter than the (11, 2) and (12, 1) SWCNTs. It is noted that a (7, 6) SWCNT has a chiral angle of 27.5°, much higher than that of the (11, 2) and (12, 1) SWCNTs with chiral angles of 8.2° and 4.0°, respectively. Furthermore, the (19, 3) SWCNT, which possess a small chiral angle of 7.2°, but a large diameter of 1.62 nm, remained unreacted. Overall, the above results indicate that the reactivity of SWCNTs does not depend solely on a single structural parameter, but more on the interplay of both their diameters and chiral angles.

By increasing the treatment temperature up to 450 °C, nine more SWCNTs reacted, among which two (11, 3) SWCNTs reacted simultaneously (Figure 3b and Supporting Information Table 2). These nanotubes possess diameters in the range of 1.04–1.34 nm, which are much smaller than most of the unreacted SWCNTs in Figure 3b, e.g., the (19, 3) and (26, 4) SWCNTs. This fact indicates that small diameter SWCNTs possess an intrinsically higher reactivity in air. Once again we observed that some small-diameter SWCNTs like (7, 6), (9, 7), (9, 8), (10, 8), and (11, 7) remain unreacted after 450 °C treatment. These nanotubes share a common feature of large chiral angles. This observation is in good agreement with the 400 °C reaction case, suggesting that high chiral angles imbue SWCNTs with high stability against the air treatment. However, it is worth noting that the metallic (10, 7) nanotube reacted at 450 °C, even though it has a similar diameter and chiral angle compared to the semiconducting (9, 7), (9, 8), (10, 8), and (11, 7) nanotubes mentioned above (Figure 3b). This result suggests that metallic SWCNTs intrinsically possess higher reactivity than their semiconducting counterparts with similar diameters and chiral angles.

The reaction tendency observed at 400 °C and 450 °C also appeared at 470 °C and 490 °C. As shown in Figure 3c and in Supporting Information Table 3, several nanotubes with diameters in the range of 0.88–1.43 nm reacted after 470 °C treatment. These nanotubes either possess relatively smaller diameters or smaller chiral angles than the unreacted ones. The reaction of a very small diameter (7, 6) SWCNT at such a high temperature further demonstrates the importance of chiral angles on the reactivity of nanotubes. After further treatment at 490 °C (Figure 3d and Supporting Information Table 4), we observed four remaining SWCNTs with chiralities of (14, 13), (15, 13), (16, 14), and (23, 16). As expected, they all share the common features of large diameter, high chiral angle, and are semiconducting. Therefore, starting from samples containing individual and suspended SWCNTs, one can increase the concentration of SWCNTs with such characteristics by simply heating them in air. We noted that the intensity ratios of D bands to G bands do not change significantly after each treatment (Supporting Information Figure S2), suggesting the unreacted nanotubes keep high quality. The preferential reaction of small diameter SWCNTs is also confirmed by Raman spectra (Supporting Information Figure S2). However, the in-depth chirality-dependent reaction behavior cannot be extracted from Raman spectra owing to its inaccuracy for chirality assignment for large SWCNTs.

Figure 4a shows SWCNTs that reacted at different temperatures in a single chirality map. This suggests a clear trend of the reaction towards SWCNTs with larger diameter and higher chiral angle as the reaction temperature increased from 400 °C to 490 °C (indicated by the red arrow). Note that this trend is applicable to both semiconducting and metallic SWCNTs, as presented in Figure 4b,c.
The primary reaction taking place during air treatment is the oxidation of SWCNTs by O$_2$ molecules. Therefore, the above results suggest a preferential oxidation of small SWCNTs, which is in line with previous experiments addressing the chemical reactivity of SWCNTs.[21,32,40] This is attributed to large curvature inducing high strain in small SWCNTs, which arises from misalignment of π-orbitals.[26] The metallicity-dependent oxidation is also in agreement with previous studies[21,40] where the higher reactivity of metallic SWCNTs originates from delocalized electronic states near the Fermi level. Nevertheless, our results reveal that the metallicity-dependent reactivity trend is applicable only to SWCNTs with similar diameters to each other, and large diameter metallic SWCNTs are more stable than small diameter semiconducting ones. For example, large diameter metallic SWCNTs (19, 10) and (21, 6) left even many small diameter semiconducting SWCNTs reacted at 470 °C treatment (Figure 3c).

The most intriguing finding here is the chiral-angle-dependent reactivity of individual SWCNTs, which was rarely observed previously. As shown in Figure 4b,c, SWCNTs with higher chiral angles are less reactive and thermodynamically more stable than those with small chiral angles, providing they have similar diameters and the same metallicity. This differs from another study[32] where a larger oxidation rate of SWCNTs with high chiral angles was observed than for those with small chiral angles. In solution phase reaction of nanotubes, the redox potential is typically used to describe the reaction process.[49–51] However, previous studies show that the redox potential of SWCNTs does not scale with their chiral angles.[51] Therefore, it is clear that the gas phase reaction trend we observed here is not governed by the redox properties of nanotubes. Our detailed HRTEM examinations show partial destruction of SWCNT sidewalls under air treatment (Supporting Information Figures S3 and S4), which is similar to a very recent study based on in situ environmental TEM observations of the oxidation of multi-walled CNTs.[52] As the typical lengths of SWCNTs range from a few microns to tens of microns in our sample,[42,43] we speculate that the oxidation of the SWCNTs takes place at SWCNT sidewalls in the monitored segments, although oxidation from the ends cannot be excluded.

In order to gain microscopic insight into the oxidation process and assess the relative reactivity of different structure SWCNTs with O$_2$, we carried out extensive first-principles calculations within the framework of density-functional theory (DFT, see Experimental Section). In agreement with previous calculations,[53] we found that there is a potential
barrier of $\sim 1$ eV for an O$_2$ molecule to chemisorb on an SWCNT surface by cyclo-addition (Figure 5, C). Once the O$_2$ molecule is chemisorbed, it easily splits into two close oxygen adatoms in an epoxy (or bridge, Figure 5, B) configuration. The factor that governs the stability of the SWCNTs is the formation of the first vacancy by evolving a CO$_2$ molecule, which requires energy input. When the first vacancy is created, the process of oxidation becomes exothermic. The energetics of the process depends on the diameter and chirality of the SWCNTs. The reactivity of the SWCNTs naturally decreases with diameter, so that in our calculations we focus mainly on the intriguing dependence of the reactivity on chirality. Four different SWCNTs with roughly the same diameter were studied (Figure 5 and Table 1). In perfect agreement with the experimental results, our simulations indicated that SWCNTs with higher chiral angles are more stable than those with smaller ones. This is associated with the energies of the bridge configurations, as in armchair SWCNTs (the highest chiral angle) there are C–C bonds (parallel to the y axis, Figure 5) perpendicular to the nanotube axis (parallel to the x axis) in a three-dimensional space. This makes it easier for an oxygen adatom in the bridge configuration to break up the underlying C–C bond, thus lowering the total energy of the system. The situation is opposite in zigzag SWCNTs, while chiral ones fall in between. As seen from Figure 5, the energy required to create the first single vacancy and CO$_2$ molecule, $E_{\text{etch}}$, is simply the difference between the energies of the final (SV) and the B states plus a barrier energy ($E_{\text{bend}}$) of $\sim 0.5$ eV, which is associated with the bending of the angle between the C–O bonds in the CO$_2$ molecule when it approaches the vacancy (Supporting Information Figure S5). We stress that for any thermally activated
process (diffusion, chemical reactions, etc.), the reaction rate of the process is exponentially related to the energetic of the process. Consequently, even a small difference in initial and final energies can lead to considerable changes in reaction rates. Further close inspection reveals that the etching process proceeds through an intermediate (M) state where two oxygen atoms are bonded to the carbon atom to be removed. For clarity, only the carbon atoms in front of the SWCNTs are shown.

### 3. Conclusion

In summary, we experimentally investigated the intrinsic reactivity of individual suspended SWCNTs with known chiralities and have constructed a map illustrating a chirality-dependent reactivity of SWCNTs. The reactivity of SWCNTs to $O_2$ is intricately related to their diameters, metallicity, and more intriguingly, chiral angles. The chirality-dependent reactivity of SWCNTs is further verified based on first principles calculations of the chirality-dependent vacancy formation energies of SWCNTs with different geometrical structures. Our work demonstrates that oxidation in air can be used to selectively obtain large diameter and high chiral angle semiconducting SWCNTs, which provides an effective approach towards controlling the chirality of SWCNTs. Moreover, the unique tracking method developed in this study is versatile, robust, and can be applied to investigate the structure-dependent reactions and properties of other materials and systems.

### 4. Experimental Section

**SWCNT Synthesis:** SWCNTs were synthesized in a vertical CVD furnace at 880 °C using CO as carbon source and ferrocene as catalyst precursor.[42,43] A ceramic tube with an internal diameter of 22 mm and a length of 550 mm was used as the reaction chamber. Ferrocene powder was filled in a cartridge maintained at room temperature. A CO flow (300 cm$^3$/min) was passed through the ferrocene and was then introduced directly into the high-temperature zone of the reactor through a water-cooled probe inserted 65 mm deep into the reactor. An additional CO flow (100 cm$^3$/min) was introduced directly into the reactor for the growth of SWCNTs.

The as-grown SWCNTs were floating in the gas phase inside the chamber and directly collected with silicon wafers, carbon TEM grids, and Si$_3$N$_4$ TEM grids (DuraSiN meshes, Protochips Inc.,...
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USA) at the outlet of the furnace with the assistance of nitrocellulose membrane filters (Millipore Corp., USA). The collection time varied from 10 min to 60 min to obtain samples with optimal density and abundant individual and suspended SWCNTs. The samples were then put above an ethanol tank for 10 min to firmly attach the SWCNTs on the substrate surface.

SWCNT Oxidation Treatment and Characterization. The SWCNTs on Si₃N₄ TEM grids were first treated in air at 300 °C for 1h in a horizontal CVD furnace to remove absorbed gas molecules and amorphous carbon and to expose a clean surface. Afterwards, the grid was inserted into a TEM chamber (JEOL 2200FS, double Cs-corrected TEM operated at a low electron accelerating voltage of 80 kV, Japan) for TEM imaging and nanobeam ED analysis. We started from holes close to a corner with a special marker (Supplementary Figure S1) and moved the grid parallel so as to monitor SWCNTs in many holes inside the grid. In each hole, we chose only those clean, individual, suspended, and straight SWCNTs so as to exclude the influence of catalyst particles, adjacent nanotubes, and substrates. Therefore, we believe that possible concurrent reactions, e.g., metal particles catalyzed carbon reactions, should not play important roles. Moreover, to get a reliable ED analysis on the chirality of SWCNTs, the suspended segments of the SWCNTs typically possessed a length of ~50–200 nm. We set this criterion based on the consideration that a length shorter than 50 nm is not enough to get high-quality ED patterns, while longer than 200 nm may lead to the bending of SWCNTs, which both may produce uncertainty for chirality analysis. The positions and ED patterns of the same nanotube were recorded simultaneously. By switching to other holes in the grid, we monitored a large number of SWCNTs for statistical analysis. Afterwards, the grid was carefully taken out from the TEM chamber and underwent ~400 °C air treatment for 30 min and then inserted into the TEM again. Guided by the marker on the grid, we could accurately move to the same holes that were recorded in previous experiments to examine whether the previously recorded SWCNTs remained or were reacted after the ~400 °C treatment. The same procedure was applied to the SWCNTs after air treatment at ~450 °C, 470 °C, and 490 °C for 30 min. After each reaction, we recorded and analyzed a few more SWCNTs to expand the number of SWCNTs for statistical analysis. We remark that for some SWCNTs, they disappeared after treatment at one specific temperature, accompanying with the destroying of the underlying nanotube mattress. For such cases with significant change of SWCNT environment, we only concluded that the SWCNTs were not reacted prior to this specific temperature, but not discussed their reactivity at this or even higher temperatures to avoid any uncertainty. It is worth noting that the TEM grids we used are made of Si₃N₄ membrane deposited on the top of Si framework. Both Si and Si₃N₄ are materials with very low volumetric thermal expansion coefficients of ~10⁻⁶/K. A temperature change from room temperature to 490 °C (the highest temperature in this study) will only lead to a volume change of ~10⁻⁶–10⁻⁴, which would not cause any significant structural deformity to the grids. The electron beam density was established to be 10¹⁵–10¹⁹ e⁻/cm²s during TEM and ED characterization, which is rather safe and does not introduce noticeable structural defects in SWCNTs (Supporting Information Figures S6, S7, and S8).

We used an intrinsic layer distance method for chirality analysis of individual SWCNTs from their ED patterns, based on the following equations:

\[
\begin{align*}
n &= \frac{\pi}{\sqrt{3}t} \left( \frac{4d_2}{3} - \frac{d_3}{3} \right) \quad (1) \\
m &= \frac{\pi}{\sqrt{3}t} \left( \frac{4d_4}{3} - \frac{d_5}{3} \right) \quad (2) \\
\theta &= \tan \left( \frac{1}{\sqrt{3}} \left( \frac{4d_2}{3} - \frac{d_3}{3} - 1 \right) \right) \quad (3)
\end{align*}
\]

where \(d_2\) and \(d_3\) are the layer-line distances between the equatorial line and the second and third layer line for the first-order hexagons in the ED pattern of SWCNTs, and \(t\) is the period of the equatorial line oscillations. The chirality assignments were also cross-checked by using other available layer line combinations, e.g., \(d_2\) and \(d_4\) or \(d_3\) and \(d_5\), where \(d_5\) is the distance between the equatorial line and the sixth line for the second-order hexagons in the ED patterns of SWCNTs.

Raman spectra (LabRAM, Horiba Yvon, France) were collected on SWCNTs on Si wafers and Si₃N₄ TEM grids using a 633 nm He-Ne laser with a laser spot size of ~1 μm in a back-scattering configuration.

Theoretical Calculations. The first-principles simulations were performed using spin-polarized DFT as implemented in the plane-wave-basis-set Vienna ab initio simulation package. Projector augmented wave potentials were used to describe the core electrons, and the generalized gradient approximation to describe the exchange and correlation. The kinetic energy cutoff for the plane waves was set to 400 eV, and all the nanotube structures consisting of 80–152 atoms were relaxed until atomic forces were below 0.01 eV/Å. The same accuracy was achieved with regard to the number of k-points in the one-dimensional Brillouin zone (up to 8 k-points). The length of the supercell along the nanotube axis varies from 9.8 to 18.6 Å depending on the nanotube chirality, and the periodic images of the nanotubes in the transverse direction are separated by 12 Å of vacuum. Nudged elastic band calculations with 10 images between the initial and final configurations were carried out to find the energy barriers.

Supporting information

Supporting Information is available from the Wiley Online Library or from the author.

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