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Electric-Field-Assisted PECVD for Growth of High-Purity Horizontally Aligned Semiconducting Carbon Nanotube Arrays

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Semiconducting single-walled carbon nanotube (SWNT) horizontal arrays hold great promise for the development of next-generation, energy-efficient integrated circuits. While conventional chemical vapor deposition synthesis typically yields structurally diverse carbon nanotubes, achieving high-purity semiconducting SWNT horizontal arrays remains a major challenge. In this study, an electric-field-assisted plasma-enhanced chemical vapor deposition (PECVD) technique is introduced that enables the direct synthesis of high-purity semiconducting SWNT arrays. This method capitalizes on the inherent plasma sheath and the abundance of charged particles within the PECVD system to control charge accumulation on SWNTs. By inducing negative charge accumulation, the energy states of semiconducting nanotubes are effectively reduced, rendering them thermodynamically favored products, thereby enhancing semiconducting-tube purity in the resulting arrays. Additionally, the applied electric field modulates the growth kinetics of the SWNTs, ensuring efficient growth and high-density arrays. Utilizing this approach, semiconducting SWNT arrays are successfully synthesized with a purity of up to 96%. This electric-field-assisted PECVD technique represents a promising strategy for the controlled preparation of SWNTs, paving the way for advancements in carbon nanotube-based electronics.

can be classified into metallic SWNTs (m-SWNTs) and semiconducting SWNTs (s-SWNTs).^[2] Among them, s-SWNTs have attracted significant attention due to their excellent electrical properties and are considered ideal materials for fabricating high-performance, low-powerconsumption integrated circuits in the post-Moore era.^[3-4] Field-effect transistor (FET) fabricated from horizontally aligned s-SWNT arrays, which outperformed commercial silicon FETs with similar gate lengths, has been reported.^[5] SWNT-based integrated circuits have demonstrated significant advantages over silicon-based integrated circuits.^[6-8] However, the prevalent method for the preparation of s-SWNTs is solution separation, [9-12] which usually introduces numerous impurities that are hard to eliminate and damage s-SWNTs inevitably, degrading device performance. Moreover, this approach is cost-consuming and does not meet the requirements of green chemistry. On the other hand, direct synthesis of high-purity s-SWNT arrays through chemical vapor deposition (CVD),

1. Introduction

Single-walled carbon nanotubes (SWNTs) are one dimentional (1D) carbon nanomaterials with unique tubular structures.^[1] According to the differences in their band structures, SWNTs

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which possesses the advantages of higher crystallinity, less im-

purity, and better alignment, presents a significant problem. The structural similarities and diversity among SWNTs make the se-

lective growth of s-SWNTs a formidable challenge. The most used direct-growth method is selective etching of m-SWNTs, which is

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accomplished by employing oxidants or UV light.^[13–16] However, the uneven distribution and the uncontrollability of the etchants in the gas phase led to the over-etching of s-SWNTs or the retention of m-SWNTs, limiting the purity of s-SWNTs. Additionally, the etching process may diminish the density of s-SWNT arrays, adversely impacting the performance of devices.

The intrinsic difference between metallic and semiconducting SWNTs is reflected in their electronic structures. However, the etching method utilizes the chemical activity difference between the two types of SWNTs, which is related to a number of factors, such as the diameter, electrical properties, and crystallinity of the SWNTs. It is impossible to absolutely distinguish s-SWNTs from the mixture, leading to semiconducting purity commonly less than 95%. Therefore, utilizing the difference in their electronic structures is the key to the absolute distinction between the two types of SWNTs. Wang et al. found the growth process of SWNTs is accompanied by the transfer and accumulation of charge.^[17] The accumulation of charge changed the energy barriers for the chirality transformation between different SWNTs and induced the twist of chirality. Based on this, high-purity s-SWNT arrays were achieved by electrotwisting the helicity.^[18] Nevertheless, the application of this method necessitates the use of a strong alternating electric field of up to 200 000 V m⁻¹.

Considering charged systems, plasma-enhanced CVD (PECVD) is exactly that, a system filled with positive and negative charges. An early study also demonstrated a significant enhancement in the semiconducting purity of SWNTs synthesized via the PECVD method, although the underlying mechanism remained elusive.^[19] Therefore, if the charge state of the PECVD system can be specially designed and the SWNTs can be grown in this way, it is possible to control the electrical properties of the SWNTs from the nature of the electronic structure. Herein, we designed an electric-field-assisted PECVD system to directly synthesize high-purity s-SWNT arrays. The plasma sheath inherent to the PECVD system provides a negatively charged space on top of the insulating sapphire substrate,^[20] which induces SWNTs to accumulate negative charges and reduces the energy states of s-SWNTs and thermodynamically favors their growth. The application of a vertical electric field modulates the distribution of charged carbon fragments within the PECVD system, thereby enhancing the growth efficiency of s-SWNTs. As a result, we successfully achieved horizontally aligned s-SWNT arrays with an impressive purity of 96%. This electric-field-assisted method provides new ideas for structure control in the direct synthesis of s-SWNTs, and paves the way for the development of high-performance carbon-nanotube-based electronic devices.

2. Results and Discussion

The growth of SWNTs is accompanied by charge transfer and accumulation, and the charge accumulation state can significantly influence their structures.^[17,21] In a normal CVD system, the majority of particles are electrically neutral, with only a small fraction being positive or negative ions. In contrast, the PECVD system contains a significantly higher concentration of charged particles, such as free electrons and ions, compared to the normal CVD system. This plasma-rich environment and the unique sheath electric field inherent to the PECVD system enhance charge transfer and accumulation, thereby adding another control dimension over the SWNT structures. To further optimize this process, we proposed the use of an electric-field-assisted PECVD method, where the applied electric field can precisely manipulate the motion and distribution of charged particles, enabling the preparation of selectively structured s-SWNT arrays.

As illustrated in Figure 1a, the s-SWNT arrays were grown with a home-made electric-field-assisted radio frequency (RF, 13.56 MHz) PECVD system on sapphire substrates at 850 °C. The plasma discharge source, consisting of a copper coil wound around the outer wall of a 1-inch quartz tube, was placed at the upstream of the furnace. A specially designed quartz boat and graphite electrodes form an assisted electric field system, as shown in Figure S1 (Supporting Information). It is worth noting that two graphite foils are placed at the positions of the upper and lower electrodes in the quartz boat to ensure that a parallel plate electric field can be set up, as illustrated in Figure S1c-e (Supporting Information). A direct current (DC) power supply is connected to the graphite electrodes to establish the assisted electric field. The power supply is equipped with a remote communication port, which allows for programmatic control via computer software, as shown in Figure S1f (Supporting Information). CH₄ was used as a carbon source, and it can be decomposed effectively in plasma to provide high-activity charged carbon species and free electrons for the growth of s-SWNT arrays. Iron (Fe) was chosen as a catalyst for the growth of SWNT arrays. Conventional Fe and Fe₃C catalysts are unable to achieve structural control of SWNTs,^[22] making it essential to evaluate the performance of electric-field-assisted PECVD. Catalysts were loaded through ion implantation, and the substrate was then annealed at 1100 °C to reconstruct the surface structure. Before growth, hydrogen was introduced to the system to release the Fe element in the sapphire, leading to the formation of catalyst nanoparticles on the substrate surface.^[23] Subsequently, CH₄ and argon gas were introduced, and the assisted electric field was applied to initiate the growth process. Figure S2a (Supporting Information) shows the atomic force microscope (AFM) characterization results of the sapphire substrate surface after iron ion implantation, annealing, and reduction treatment. It is observed that the catalyst nanoparticles are uniformly distributed on the substrate surface without significant sintering or agglomeration. Figure S2b (Supporting Information) presents the size distribution statistics of the catalyst nanoparticles in Figure S2a (Supporting Information), with most nanoparticles being within 5 nm and an average size of ≈1.12 nm.

Figure 1b presents typical scanning electron microscope (SEM) characterization results of the SWNT arrays grown on the sapphire substrates. It is evident that the SWNT arrays prepared by the electric-field-assisted PECVD method exhibit excellent alignment and high array density. Figure 1c shows the AFM characterization results of the SWNT arrays, revealing a local density of ≈ 12 tubes μm^{-1} . More SEM and AFM characterization results of SWNT arrays grown on different zones are shown in Figure S3 (Supporting Information). The regional inhomogeneity in array density primarily stems from the non-uniformity of the substrate surface morphology and growth gas flow.^[13] Transmission electron microscopy (TEM) characterization indicates that the carbon nanotubes are single-walled, as shown in Figure 1d. The inset

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Figure 1. Synthesis and characterization of s-SWNT arrays. a) Schematic illustration of synthesizing s-SWNT arrays via an electric-field-assisted PECVD method. b) An SEM image of the s-SWNT arrays grown on a sapphire substrate. c) An AFM image of the s-SWNT arrays grown on a sapphire substrate. d) A TEM image and corresponding FFT patterns of SWNTs on a holey SiN_x TEM grid. e) Raman spectra of the as-grown s-SWNT arrays.

displays the Fast Fourier Transform (FFT) result of the region corresponding to the SWNT on the right, revealing distinct 1D structural characteristics. Raman spectroscopy was further used to characterize the SWNT arrays grown on the sapphire substrate, as depicted in Figure 1e. Under 532 nm laser excitation, the prepared SWNT arrays exhibited prominent G-band peaks and radial breathing mode (RBM) peaks, with a relatively small D band (\approx 1370 cm⁻¹), indicating that the SWNT arrays have few defects and high crystalline quality.

The control of length and morphology during the preparation of SWNT arrays via the CVD method poses a significant challenge, particularly in complex systems such as the PECVD system. In the absence of an assisted electric field, SWNTs synthesized by PECVD typically exhibit shorter lengths and poor alignment, as illustrated in Figure 2a. This phenomenon is often attributed to an insufficient supply of carbon fragments during the growth process in low-pressure systems. In conventional CVD systems, this issue can generally be mitigated by increasing the carbon source supply. However, in PECVD systems, the carbon source undergoes highly efficient decomposition, which means that even a small amount of introduced carbon source can generate a significant concentration of carbon fragments. Due to the limited precision of gas flow controllers, it is challenging to finely control the carbon source supply. Increasing the carbon source supply, even slightly, can lead to a rapid and uncontrollable rise in the concentration of carbon fragments. This excessive concentration of carbon fragments can overwhelm the catalyst, leading to catalyst poisoning and deactivation, thereby hindering the growth of SWNTs. To address this issue, the application of an assisted electric field offers a promising solution. Since the PECVD system contains a substantial amount of charged carbon fragments, an electric field can be utilized to regulate their concentration and distribution within the reaction system. We systematically regulated the strength of the applied electric field from -250 to +600 V and found that the applied forward electric field (direction: downward perpendicular to the growth substrate) could effectively regulate the carbon debris concentration on the substrate surface (Figure S4, Supporting Information; Figure 2a–f). The stronger the applied forward electric field, the higher the effective carbon fragment concentration on the substrate surface.

Due to the complexity of the PECVD reaction system, it is essential to detect and analyze the active species produced in the system in order to understand the reaction mechanism. Methane, the simplest hydrocarbon, typically undergoes spontaneous ionization at high temperatures. This is due to the electronegativity difference between carbon and hydrogen, producing H⁺ and CH₃^{-.[17]} However, the ionization behavior differs significantly in the plasma environment. While a small fraction of methane molecules ionize spontaneously at high temperatures, the majority are ionized by high-energy electrons and argon ions accelerated by the radiofrequency electric field, generating free electrons and carbon cations such as CH₄⁺. These cations further decompose into CH₃⁺, CH₂⁺, CH⁺, and H⁺, releasing additional electrons. CH+ may also react with other CH_x^+ species to form $C_2H_y^+$.^[24] Additionally, a minor fraction of methane undergoes homolytic cleavage, producing carbon and hydrogen radicals.^[25] In the plasma, high-energy electrons collide with other ions, molecules, and free radicals, which can excite some particles. When these excited high-energy particles return to their original energy levels, luminescence occurs. Therefore, the plasma luminescence contains characteristic

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Figure 2. The impact of assisted electric fields on the growth of SWNT arrays. a) An SEM image of the SWNT arrays grown without an applied electric field. b-f) SEM images of SWNT arrays grown under the application of a forward electric field with a strength of b) 100 V cm⁻¹, c) 200 V cm⁻¹, d) 250 V cm⁻¹, e) 300 V cm⁻¹. f) 600 V cm⁻¹. g) In situ OES characterization of reactive species in the PECVD reaction system. h) Schematic representation of the influence zones of the applied electric field and the sheath electric field.

information of various components. By detecting the plasma luminescence with in situ optical emission spectroscopy (OES), the active species existing in the reaction system can be analyzed. Figure 2g shows the signature spectral lines of active species in this PECVD reaction system detected in situ by OES. The main spectral lines in the 690-800 nm region (red light and nearinfrared region) are attributed to Ar, originating from its 4p-4s transition. The spectral lines at 656.24, 486.37, and 434.04 nm correspond to the characteristic peaks of H_{α} , H_{β} , and H_{γ} , respectively. Several spectral lines near 420 nm are attributed to H₂. The characteristic spectral lines at 388.4 and 516.4 nm correspond to the peaks of CH and C₂, respectively.^[26] These results indicate that methane can be fully dissociated. Since the spectral lines of CH₃ are not within the detection range of OES, they cannot be detected. CH₂ is also difficult to detect because of its short fluorescence lifetime,^[27] which easily decomposes to produce CH and H. However, as CH₃ and CH₂ are the necessary pathways for the dissociation of CH_4 into CH and C_2 , there must be a certain amount of CH₃ and CH₂ in this system. The OES characterization results proved that Ar, H₂, and CH₄ were all fully dissociated in the system, generating a large number of active carbon fragments, argon ions, and hydrogen ions. Argon is introduced to function as a carrier gas and an auxiliary cracking gas, thereby enhancing the completeness of methane decomposition. Meanwhile, hydrogen is introduced to supply additional reducing species, ensuring the preservation of a suitable growth environment. As illustrated in Figure S5 (Supporting Information), upon the introduction of argon, a significant enhancement in the characteristic peaks corresponding to carbon fragments was observed (Figure S6, Supporting Information). Further, the introduction of hydrogen can regulate the concentration of carbon fragments and provide a reducing atmosphere (Figure S7, Supporting Information).

The characterization results of OES confirmed the presence of these carbon and hydrogen fragments, although their charge states remain undetermined. Therefore, we further utilized the constructed electric-field-assisted PECVD reaction system to investigate the charge states of carbon ions by applying electric fields in different directions. Without an assisted electric field and under low plasma power, the plasma glow was confined to the vicinity of the tube furnace center. However, upon applying an electric field, the plasma glow extended along the graphite electrode rods beyond the furnace chamber, reaching the T-junction region, as illustrated in Figure S9 (Supporting Information). Notably, the plasma glow was not uniformly distributed around the electrodes but preferentially adsorbed near the negatively charged electrode. Reversing the electric field direction shifted the adsorption position accordingly. This behavior aligns with charge interaction principles, as cations accumulate near the negative electrode. The emission spectrum of carbon ions (388.4 nm, violet light) further supports the conclusion that the carbon ions generated in the system are predominantly carbon cations, consistent with prior studies.^[28]

A plasma sheath electric field develops at the surface of an insulating sapphire substrate upon plasma immersion. The plasma sheath electric field is generated due to the significant mass difference between electrons and cations, which results in a disparity in their velocities accelerated by the radiofrequency electric field and leads to charge separation within a thin region of several hundred micrometers above the substrate surface.^[29] The electric field is directed perpendicularly downward from the substrate. This sheath electric field can be conceptualized as consisting of a cation sheath and an electron region. The electron region is located at the substrate surface, while the cation sheath lies above the electron region. Beyond the cation sheath is the quasineutral plasma region.^[20] In the absence of the assisted electric field, the local concentration of carbon fragments near the substrate surface is limited. However, under an externally applied electric field with a direction perpendicular to the substrate and oriented downward, the plasma sheath will expand according to Child-Langmuir law and significantly enhancing ion flux density and ion energy.^[30] The resulting high-energy ion bombardment promotes dissociation of carbon-containing precursors via collisional fragmentation, thereby increasing reactive carbon cations density near the substrate and accelerating SWNT growth, as shown in Figure 2h.

The electric field direction determines the charge state of migrating ions. Within a forward electric field strength range of 0-250 V cm⁻¹, the density and length of SWNT arrays increased significantly with increasing positive field strength, as shown in Figure 2a–d. At 250 V cm⁻¹, the average length of SWNTs is approximately a few hundred micrometers. However, exceeding this threshold led to excessive carbon cation concentrations near the substrate, causing catalyst poisoning and deactivation, which reduced SWNT lengths. Additionally,

amorphous carbon deposits formed on the sapphire substrate, degrading SWNT arrays alignment, as illustrated in Figure 2e. At +600 V cm⁻¹, the substrate was entirely covered by amorphous carbon, and no SWNT was observed, as shown in Figure 2f. These results indicate that the carbon fragment concentration near the substrate increases with electric field strength, but an optimal window exists for SWNT growth. Below this window, insufficient carbon supply limits growth, while excessive concentrations lead to catalyst deactivation and amorphous carbon deposition. Thus, the optimal electric field strength for SWNT array growth is +250 V cm⁻¹. An optimal electric field strength exists for SWNT growth because it balances the carbon fragment concentration near the substrate. Below this threshold, insufficient carbon supply limits growth, while above this threshold, excessive concentrations lead to catalyst deactivation and amorphous carbon deposition. If a reverse electric field was applied, the density of SWNT arrays decreased compared to the case without an electric field, as shown in Figure S4 (Supporting Information). While SWNT lengths slightly increased at -250 V cm^{-1} , we hypothesize that a thin electron-repelling sheath may form due to the electrode's potential exceeding the plasma potential, which can impede carbon and hydrogen cations transport to the substrate, reducing their concentrations.^[30] Meanwhile, the presence of a small fraction of carbon anions, likely originating from spontaneous methane ionization, which migrate toward the substrate under the negative field, results in slightly increased SWNT lengths. The reduced SWNT array density may result from decreased hydrogen ion concentrations, increasing catalyst poisoning. In contrast, a forward electric field (+250 V) significantly enhanced both the density and length of SWNT arrays, as more carbon cations were driven toward the substrate, increasing carbon fragment concentrations and improving catalyst efficiency.

To validate the efficacy of the electric-field-assisted PECVD method in synthesizing high-purity s-SWNT arrays, the semiconducting purity of SWNT arrays grown under +250 V cm⁻¹ electric field was systematically characterized using multi-wavelength resonant Raman spectroscopy^[31–32] using laser excitations at 488, 532, and 633 nm. The RBM peaks were analyzed to determine the chiralities of the SWNTs by correlating the excitation energies with the Kataura plot. Based on the chiralities, the electrical properties of the SWNTs were determined, enabling a statistical evaluation of the s-SWNT purity within the horizontal arrays. Figure 3a-c display the Raman line-mapping spectra of the SWNT arrays synthesized by the electric-field-assisted PECVD method, while Figure S9 (Supporting Information) shows the corresponding Raman spectra with a wider wavenumber range. As shown in Table S1 (Supporting Information) and Figure 3d, under 633 nm laser excitation, 150 SWNTs exhibited RBM peaks, of which 12 were metallic and 138 were semiconducting. Under 532 nm excitation, 236 SWNTs showed RBM peaks, with 4 metallic and 232 semiconducting. Under 488 nm excitation, 197 SWNTs displayed RBM peaks, including 8 metallic and 189 semiconducting. In total, 583 SWNTs were analyzed, with 559 being semiconducting, corresponding to a semiconducting purity of 96%. And a representative G-band region Raman spectrum of the SWNTs grown by the electric-field-assisted PECVD method is shown in Figure 3e. The spectrum exhibits a distinct splitting of the G peak into G^+ (1591 cm⁻¹) and G^- (\approx 1570 cm⁻¹) peaks





Figure 3. Characterization of semiconducting-SWNT purity in the arrays fabricated via the electric-field-assisted PECVD method. a–c) Raman line mapping spectra of SWNT arrays in the RBM region with excitation lasers of a) 633 nm, b) 532 nm, c) 488 nm (S: s-SWNTs; M: m-SWNTs). d) Semiconducting-SWNT purity results obtained by statistical analysis of RBM peaks. e) Typical G-band region of the Raman spectra for the SWNTs. f) A typical transfer curve of an FET based on the SWNT arrays. Inset is the corresponding SEM image of the device.

with both symmetric Lorentzian line shapes, which are features of s-SWNTs. The RBM peak positions were also utilized to estimate the diameter distribution of the SWNTs. For all three excitation wavelengths, the majority of RBM peaks were observed in the range of 120–200 cm⁻¹, indicating that the diameters of the synthesized SWNTs predominantly ranged from 1.2 to 2.1 nm.

To further evaluate the electrical properties of the synthesized s-SWNT arrays, bottom-gated field-effect transistors (FETs) were fabricated, and their transfer characteristics were measured. Key performance metrics, including the on/off current ratio (I_{on}/I_{off}) and on-state current, were analyzed. Figure 3f shows the typical transfer characteristics, with red and blue curves representing linear and logarithmic scales, respectively. The source-drain bias was fixed at -0.1 V, while the gate voltage (V_{CS}) was swept from -30 to 30 V. The inset displays a SEM image of the corresponding FET device. The s-SWNT FETs exhibited an on/off ratio of $\approx 10^2$ and an on-state current of 3.4 μ A (channel length $\approx 2 \mu$ m), demonstrating good electrical performance and high purity of the synthesized s-SWNTs. It should be noted that residual polymer introduced during the transfer process may lead to contact resistance between the SWNTs and electrodes, potentially affecting the measured electrical performances.

To investigate the growth mechanism of s-SWNTs, we characterized the catalyst template for SWNT growth using HRTEM, as shown in Figure S10 (Supporting Information). The grown SWNT arrays were transferred onto a 10 nm porous silicon nitride microgrid using PMMA-assisted transfer and characterized by TEM, as shown in Figure S10a (Supporting Information). The catalyst nanoparticles exhibited lattice fringes with a spacing of 2.0 Å, consistent with the (2 0 1) plane spacing of Fe₃C. Figure S10b (Supporting Information) displays the FFT result corresponding to the catalyst nanoparticle region. By analyzing the diffraction spots and matching them with the lattice spacing, the diffraction pattern was identified to be consistent with the [0 1 0] zone axis of Fe₃C. Figure S10c (Supporting Information) shows the theoretically simulated atomic arrangement of the crystal plane, which matches the atomic arrangement of the corresponding plane in Figure S10a (Supporting Information). Based on the TEM and FFT analysis, it is concluded that the catalyst nanoparticles consist of Fe₃C, which likely formed through the carbonization of iron nanoparticles during the growth process.

Normal Fe or Fe₃C catalysts cannot achieve structural control of SWNTs during the growth process, therefore, the high selectivity can only be attributed to the unique growth environment of the PECVD system. Since the catalysts are located on the substrate surface and the nanometer-diameter SWNTs grow along the substrate surface, they remain within the electron-rich region of the sheath electric field throughout the growth process.^[20] Consequently, the high concentration of free electrons in this region continuously collides with the catalysts and SWNTs, causing them to accumulate negative charges. This is one of the most significant differences between the charged PECVD system and conventional thermal CVD systems. Using density functional theory (DFT), we theoretically calculated the energy variations of SWNTs with different chiralities during electron accumulation

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Figure 4. Mechanism analysis of s-SWNT growth via the electric-field-assisted PECVD method. a) Theoretical calculation results of energy changes for different SWNTs upon negative charge accumulation. b) Different charge accumulation behaviors of m-SWNTs and s-SWNTs and energy change diagram of SWNTs under negative- charged environment. c) Schematic illustration of the enrichment mechanism of s-SWNTs grown in the sheath electric field.

processes. The results in Figure 4a demonstrate that the energy of SWNTs progressively decreases with increasing electron accumulation. Owing to the distinct structural characteristics of m-SWNTs and s-SWNTs, their charge accumulation behaviors differ significantly. Upon the formation of a cap structure by the catalyst, the chirality of the SWNT is determined. Given the metallic nature of m-SWNTs, electrons are readily conducted along them, thereby impeding the accumulation of negative charge.^[33] Conversely, s-SWNTs exhibit a propensity for negative charge accumulation in the beginning, which is attributable to the semiconducting nature of the s-SWNTs and the energy barriers between the s-SWNT and the catalyst nanoparticle.^[34] Therefore, a notable energy difference exists between negatively charged s-SWNTs and the m-SWNT, as depicted in Figure 4b. The energy of s-SWNTs undergoes a significant reduction concomitant with the increase in negative charge accumulation, rendering the energy state of s-SWNTs markedly lower than that of m-SWNTs, according to the DFT calculations. This results in a thermodynamic advantage in the growth of s-SWNTs,^[35] as illustrated in Figure 4c. Ultimately, this negatively charged atmosphere promotes the preferential growth of s-SWNTs, resulting in their enrichment.

3. Conclusion

In summary, we developed an electric-field-assisted PECVD method for the direct synthesis of high-purity semiconducting s-SWNT horizontal arrays with good alignment and density. The method leverages the unique charged environment of the PECVD system to control the charge accumulation on SWNTs. The energy reduction of semiconducting SWNTs through negative charge accumulation creates a thermodynamically favored growth pathway over metallic SWNTs. The plasma sheath electric field and the applied electric field work synergistically to optimize the distribution of charged carbon fragments, enhancing the growth efficiency and purity of s-SWNT arrays. The synthesized s-SWNT arrays achieved an impressive purity of 96%. If the energy gap between metallic and semiconducting SWNTs can be further enlarged, there is potential for higher purity. This work provides new ideas and an additional dimension of control for the structural-controllable synthesis of SWNTs, and paves the way for the development of high-performance carbon nanotubebased electronic devices.

4. Experimental Section

Preparation of Catalysts by the lon Implantation Method: A-plane sapphire substrates (single-side polished, surface roughness < 5 Å, miscut angle < 0.5°) purchased from Hefei Kejing Materials Technology Co., China, were used as substrates for growing SWNT arrays. The Fe ion implantation was conducted at room temperature (RT) by employing a FAD-MEVVA ion implanter at Peking University. The ion fluence was set as 1×10^{15} ions cm⁻². And the ion energy was set as 20 keV. After ion implantation, the sapphire substrates were sent into a muffle furnace and annealed at 1100 °C in air for 8 h to repair the radiation damage of the substrate surface.

Synthesis of SWNT Arrays via Electric-Field-Assisted PECVD Method: The treated sapphire substrate was then placed on the specially designed quartz boat and positioned in the reaction chamber, 6 cm from the furnace center and adjacent to the plasma generator side. Two electrodes ADVANCED SCIENCE NEWS ______ www.advancedsciencenews.com

were connected to the positive and negative terminals of a DC power supply, with the initial voltage set to 0 V. The reaction protocol was initiated by heating the furnace to 850 °C with a heating rate of 20 °C min⁻¹ in an air atmosphere. The chamber was then purged with 300 sccm of Ar for 5 min to remove residual air, followed by a reduction step with 300 sccm of H₂ for 10 min. After reduction, the vacuum system was activated, and the gas flow rates were adjusted to 30 sccm of Ar and 15 sccm of H₂. Simultaneously, 3 sccm of CH₄ was introduced into the chamber. Next, the PECVD system power was set at 15 W. Once the pressure stabilized, the plasma generation system was activated. After achieving a stable glow discharge, the voltage was adjusted to apply an assisted electric field, and the growth process was carried out for 15 min. Upon completion of the growth process, the DC power supply, plasma generation system, and vacuum system were sequentially turned off. The flow of CH₄ and H₂ was terminated, and the system was allowed to cool naturally to room temperature in an argon flow. All gas flows into the reactor were controlled with mass flow controllers (MFCs).

General Characterization: SEM images were obtained on a Hitachi S4800 SEM operated at 1.0 and 10 kV. Raman spectra of SWNT arrays were collected by Jovin Yvon–Horiba LabRam systems with 488, 532, and 633 nm excitation lasers. AFM images were obtained using a Dimension Icon microscope (Bruker). OES characterization results were collected by AvaSpec-DESKTOP-EVO-USB3 Four-Channel Spectrometer (Avantes).

Transfer of s-SWNT Arrays and Catalysts onto SiN, Grid for TEM Characterization: A poly (methyl methacrylate) (PMMA) solution (950K, 4 wt.%, from Allresist GmbH, Germany) was spin-coated onto the sapphire substrate with as-grown s-SWNT arrays and then baked at 180 °C for 10 min until a thin film encapsulating the s-SWNT arrays formed. The PMMA/s-SWNT arrays film was exfoliated from the sapphire surface by immersing in KOH aqueous solution (1 mol I⁻¹, 70 °C) for 20 min. The PMMA/ s-SWNT array film would be detached from the substrate due to the sapphire being etched by KOH. The film was transferred and floated onto deionized water several times to remove residuals left by the etchant. Afterward, the PMMA/ s-SWNT arrays film was attached to a holey silicon nitride (SiN_x) TEM grid (from Norcada Inc., Canada) for TEM characterization. The sample was then dried on the hotplate at 60 °C. Finally, the sample was immersed in acetone for 8 h to remove PMMA. TEM imaging was conducted on a FEI Tecnai G2 F20 fitted with a probe and image aberration correctors under an accelerating voltage of 200 kV.

Electrical Characterization of s-SWNT Arrays: Pre-synthesized s-SWNT arrays on sapphire substrates were transferred to SiO₂/Si substrate by the PMMA wet transfer technique. Then, using a scanning electron microscope (Regulus 8220), the position and orientation of s-SWNT arrays deposited on SiO₂/Si substrate were recorded. The fabrication of FET devices based on s-SWNT arrays proceeded through the following steps: 1) A thin poly (methyl methacrylate) (PMMA, \approx 260 nm thick) was spun at 2 000 rpm onto the 300 nm SiO₂/Si substrate. 2) The geometry of FET devices was patterned into the PMMA resist via electron beam lithography (Vistec EBPG 5000plus ES). 3) The exposed PMMA was developed with 1: 3 MIBK: IPA solution at 21 °C. 4) Using the electron beam evaporation (DE400), the Ti/Au (5 nm/60 nm) film was deposited on the samples, followed by lift-off in hot acetone. Electrical characterizations of s-SWNT arrays were performed using a semiconductor device analyzer B1500A coupled with a probe station at room temperature and under atmospheric conditions.

Computational Details: All the calculations were performed in the framework of the density functional theory with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package (VASP).^[36] The generalized gradient approximation proposed by Perdew–Burke–Ernzerhof was selected for the exchange-correlation potential.^[37] The van der Waals interaction was described by the DFT-D3 approach.^[38] The cut-off energy for the plane wave was set to 400 eV. The energy criterion was set to 10^{-5} eV in the iterative solution of the Kohn–Sham equation. A vacuum layer of 15 Å was added perpendicular to the sheet to avoid artificial interaction between periodic images. The Brillouin zone integration was performed using a 2 × 2 × 1 k-mesh with a Monkhorst-Pack sampling scheme.^[39] All the structures were relaxed until the residual forces on the atoms had declined to less than 0.02 eV Å⁻¹.

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The system energy of charge-doped CNT was calculated using VASP, with the input parameter NELECT controlling the electron number in the system. Other VASP settings can be found in the Experimental Section. The energy change due to charge doping is calculated as:

$$\Delta E(\rho) = E(\rho) + E(0) - \rho \times \varepsilon_{ref}$$
(1)

where ρ is the doping charge, ε_{ref} is the reference energy level, $E(\rho)$ and E(0) are the DFT energies of charge-doped CNT and the neutral CNT, respectively. Since CH₄ is used as a carbon source, and CH_x has a relatively high LUMO level (CH₄: +0.43 eV; CH₃: -2.1 eV; CH₂: -2.5 eV), it is reasonable to take $\varepsilon_{ref} = -2$ V. It is noted that since ε_{ref} is a constant value for all CNTs, the relative stability of different CNTs is independent of the exact value of ε_{ref} .

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electrical field, PECVD, plasma sheath, semiconducting carbon nanotube

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