Synthesis of hydrophilic carbon nanotubes via chemical vapor deposition using silicon oxide nanoparticles as seeds with potential biomedical applications

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The research presented in this paper explores the synthesis of hydrophilic carbon nanotubes using silicon oxide nanoparticles as seeds through chemical vapor deposition. The study demonstrates the successful production of uniform-sized carbon nanotubes, which is essential to control their properties in diverse applications. By employing silicon oxide nanoparticles as catalysts, the process yields carbon nanotubes with specific characteristics suitable for potential biomedical applications. The investigation also highlights the dispersion in the size of silicon oxide nanoparticles and its potential influence on their collective behavior, emphasizing the importance of this factor for future research endeavors. These findings contribute valuable insights to the field of carbon nanotubes, particularly in the context of biomedical applications, facilitating further advancements in this area.

Keywords: Carbon nanotubes; chemical vapor deposition; silicon oxide nanoparticles.

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1. Introduction

Carbon nanotubes (CNTs) have emerged as an exceptional class of nanostructures with unique physical, chemical, and mechanical properties [1]. These structures, which can be single-layered (single-walled carbon nanotubes, SWCNTs) or composed of multiple concentric layers (multi-walled carbon nanotubes, MWCNTs), exhibit a tubular architecture with carbon atoms arranged in a hexagonal lattice, imparting extraordinary properties at the nanoscale [2].

The synthesis and manipulation of carbon nanotubes have been the subject of intense study since their discovery in 1991 by Sumio Iijima [3]. The diversity of available synthesis methods, such as chemical vapor deposition (CVD) [4], arc discharge [5], laser ablation [6], and others, has enabled the production of nanotubes with different structures, sizes, and properties, thereby enhancing their versatility and applicability in various fields.

In the biomedical field, carbon nanotubes have attracted significant attention due to their unique combination of physical, chemical, and biological properties [7]. Their high surface area and ability to adsorb and transport biologically relevant molecules make them ideal candidates for biomedical applications [8]. Additionally, their biocompatibility and the possibility of functionalizing their surface to enhance affinity with specific biomolecules enable a wide range of medical applications [9].

Biomedical applications of carbon nanotubes range from drug delivery [10] to tissue engineering [11] and disease detection [12]. The ability of CNTs to act as drug delivery systems allows for controlled and targeted administration of therapeutic agents, which can increase treatment efficacy and reduce unwanted side effects [13]. Furthermore, their use in medical imaging techniques, such as magnetic resonance imaging [14] and positron emission tomography [15], has revolutionized early and accurate disease diagnosis.

2. Methodology/Experimental

The Stöber method, with some adaptations, was employed to synthesize silicon oxide nanoparticles [16]. A precursor solution was prepared by combining 7.5 ml of ethyl alcohol, 36.5 ml of deionized water, and ammonium hydroxide at a concentration of 0.38 M, with agitation maintained to facilitate the reaction. Subsequently, tetraethyl orthosilicate (TEOS) was added dropwise, in a quantity of 0.01 ml, with constant agitation. Upon completion of TEOS addition, the solution was left under agitation for one hour. At the end of this time, silicon oxide nanoparticles were obtained.

The carbon nanotube synthesis process via chemical vapor deposition was meticulously developed to ensure controlled and efficient production of high-quality carbon nanostructures [17-19]. Initially, silicon wafers underwent a standard RCA cleaning cycle, a crucial procedure to remove any surface contaminants that may affect the quality of the silicon oxide coating and, consequently, the subsequent formation of carbon nanotubes [20]. Subsequently, the wafers were exposed to a temperature of 1000°C to form a thermal silicon oxide layer with a thickness of approximately 100 nm, providing a suitable and uniform substrate for nanotube growth [21].

The next step involved further thermal treatment for 2 hours in an air environment at the same temperature of 1000°C, aiding in stabilizing the silicon oxide layer and

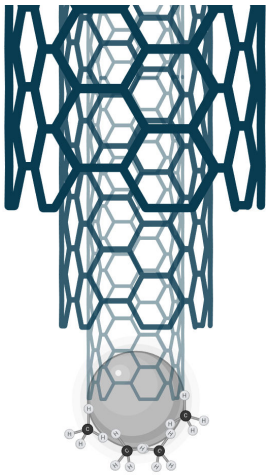

FIGURE 1. Process for the growth of MWCNT using SiO_2 nanoparticles.

promoting controlled nucleation of catalytic nanoparticles [21,22]. Once this stage was completed, silicon oxide nanoparticles with a thickness of around 2 nm were carefully deposited as catalysts using the spin coating technique. This precise deposition method ensured uniform distribution over the silicon wafer surface [24,25]. Figure 1 shows the suggested process for the growth of multi-walled carbon nanotubes (MWCNT) using SiO_2 nanoparticles as nucleation sites.

On the other hand, the CVD process began with a gradual heating cycle to 850°C, during which argon flowed to purge the system and remove moisture traces, essential for minimizing defects in carbon nanotubes [26,27]. Following the purging cycle, a thermal treatment was conducted at 850°C for 10 minutes to prepare the substrate for nanotube growth [28]. The temperature was then raised to 900°C over a short period to reach optimal growth conditions [29,30]. Once the desired temperature was attained, a mixture of argon with methane was introduced into the furnace, with a specific composition of 95% argon and 5% methane, serving as a carbon precursor for nanotube growth [31,32]. This process was carried out for 20 minutes, allowing carbon nanotubes to grow on the catalytic surface [33,34]. Finally, the furnace was cooled to room temperature to halt nanotube growth [21]. The entire process was conducted under controlled pressure of 0.02 MPa to maintain optimal reaction conditions [31]. This meticulous combination of steps ensured efficient and high-quality production of carbon nanotubes with potential applications in various fields, including biomedical [35,36]. Figure 2 presents a schematic diagram of the methodology employed in the synthesis of carbon nanotubes.

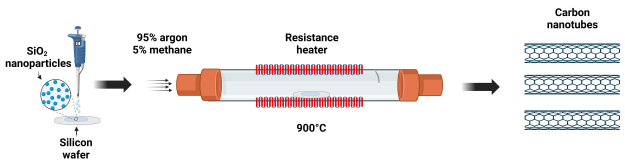

FIGURE 2. Schematic diagram of carbon nanotube synthesis.

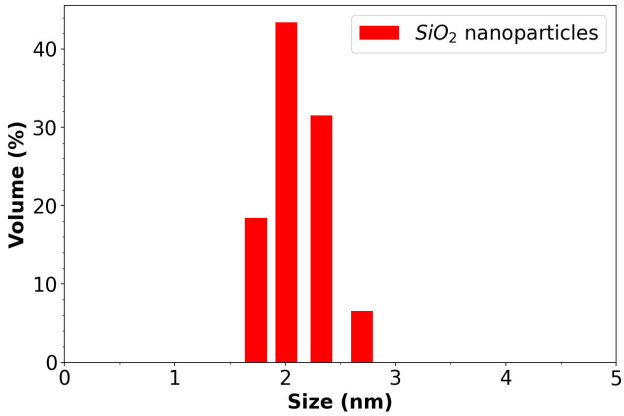

FIGURE 3. SiO_2 nanoparticles hydrodynamic diameter obtained by means of dynamic scatter light.

3. Results and discussion

3.1. Dynamic light scattering

Figure 3 provides a detailed look at the size distribution of SiO_2 nanoparticles, most of the nanoparticles are concentrated around an average diameter of 2 nanometers, suggesting a remarkable uniformity in the size of the particles. This uniformity is crucial for controlling the properties and behavior of nanoparticles in different applications.

However, a smaller number of nanoparticles with diameters that deviate from the average are also observed. This dispersion in size can be an important factor to consider when evaluating the collective behavior of nanoparticles and their potential for specific applications.

3.2. Infrared spectroscopy

Through the use of infrared spectroscopy (IR), the analysis of nanotubes has been conducted. In the IR spectrum of these nanotubes, a series of characteristic peaks is observed. Firstly, a peak located at approximately 3477 cm^{-1} (a) is distinguished, which is attributed to the O-H stretching vibration bond present in the sample. Next, another peak is identified around 2959 cm^{-1} (b), associated with asymmetric and symmetric C-H stretching. A third peak, situated around 1721 cm^{-1} (c), corresponds to the C=O double bond. Additionally, a peak is discerned at approximately 1375 cm^{-1} (d), due to the C-C bond stretching. Finally, an additional peak is recorded at around 1081 cm^{-1} (e), assigned to both the OH group and the C-O bond. The presence of these OH and C=O functional groups indeed confirms the hydrophilic nature of these CNTs, as these oxygen-containing groups can form hydrogen bonds with water molecules [37]. Figure 4 depicts the FTIR spectrum, wherein these characteristic peaks can be observed, aligning with those reported in previous scientific literature [38,39].

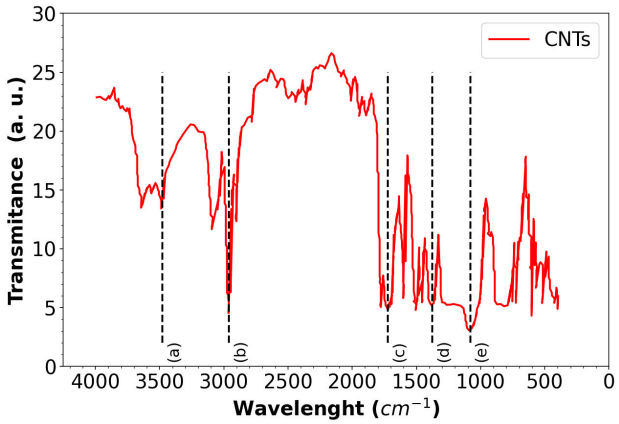

FIGURE 4. Infrared spectrum of the carbon nanotubes.

3.3. Scanning electron microscopy

Characterizing carbon nanotubes using scanning electron microscopy (SEM) plays a fundamental role in understanding and evaluating the morphological properties of these nanostructures. SEM enables sample observation at a microscopic scale with high resolution, allowing for detailed visualization of the surface topography of the nanotubes. Additionally, SEM provides information on the size, shape, distribution, and alignment of the nanotubes, crucial aspects for comprehending their structure and physical properties.

Figure 5 presents a scanning electron microscopy image of CNTs. The image was acquired at an accelerating voltage of 30.0 kV and a magnification of 22,000x.

Figure 6 displays a high-resolution SEM image of carbon nanotubes. The image was acquired at an accelerating voltage of 30.0 kV and a magnification of 45,000x, providing a detailed view of the individual CNTs and their precise starting and termination points.

The diameter distribution of the synthesized CNTs is presented in Fig. 7 as a histogram. The data, obtained from the analysis of 400 individual CNTs using Scanning Electron

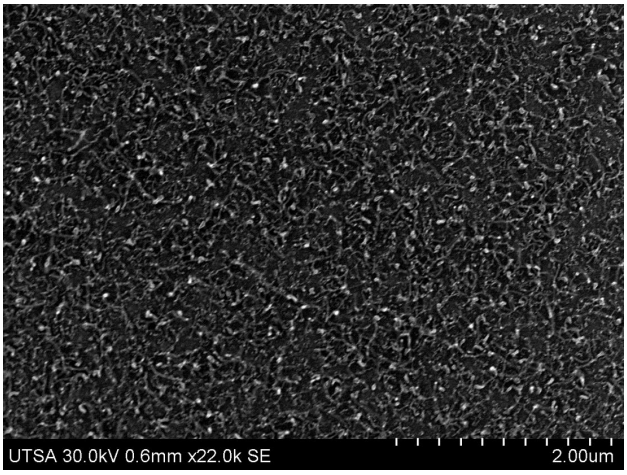

FIGURE 5. SEM image of CNTs at 22,000x magnification.

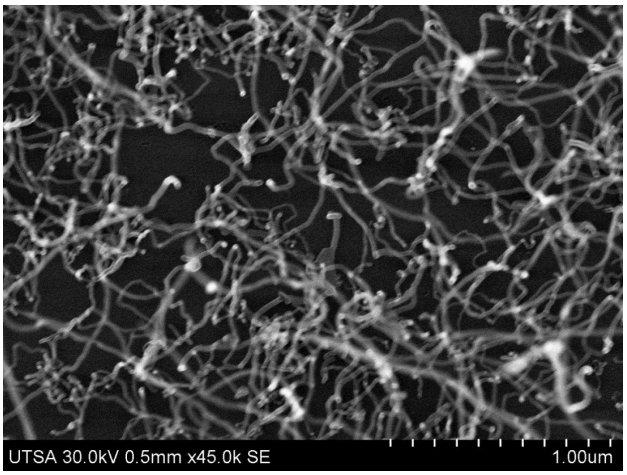

FIGURE 6. SEM image of CNTs at 45,000x magnification.

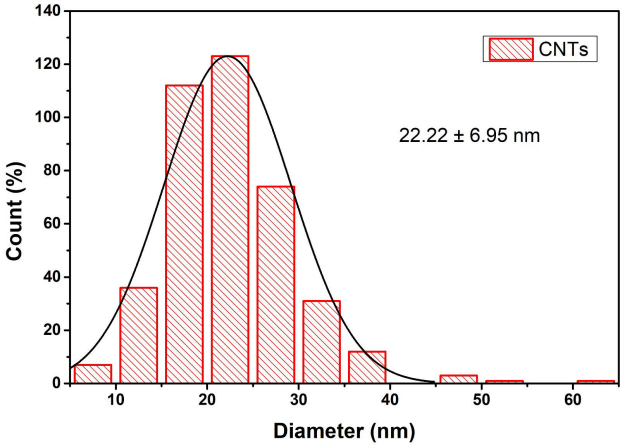

FIGURE 7. Diameter distribution of the synthesized CNTs.

Microscope (Fig. 6), shows a relatively narrow distribution, centered around a mean diameter of 22.22 ± 6.95 nm. This observed mean diameter is notably larger than the 2 nm diameter of the silicon oxide nanoparticles used as nucleation points. The significant difference between the CNT diameters and the nucleation particle size strongly suggests that the synthesized CNTs are multi-walled carbon nanotubes. The larger diameter can be attributed to the concentric arrangement of multiple graphene layers, which is characteristic of MWCNTs. The growth process likely involves the initial formation of a single-walled nanotube around the 2 nm silica nanoparticle, followed by the subsequent addition of multiple concentric graphene layers, resulting in the observed larger diameters. Additionally, the variation in diameters seen in the histogram could indicate differences in the number of walls among the synthesized nanotubes, with thicker nanotubes potentially possessing more concentric graphene layers.

3.4. Contact Angle

The surface characterization of materials, including their hydrophobicity or hydrophilicity, is fundamental to understand-

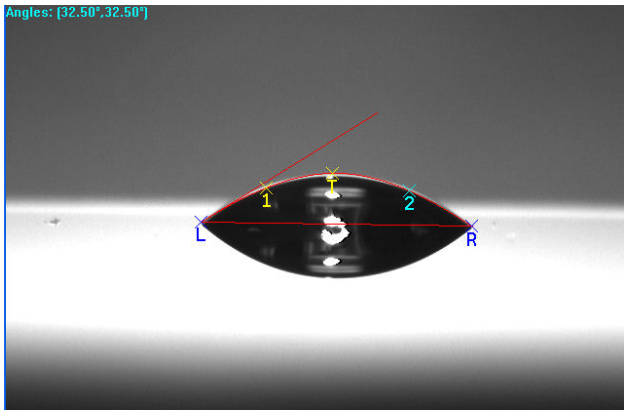

FIGURE 8. Contact angle of an unmodified silicon wafer.

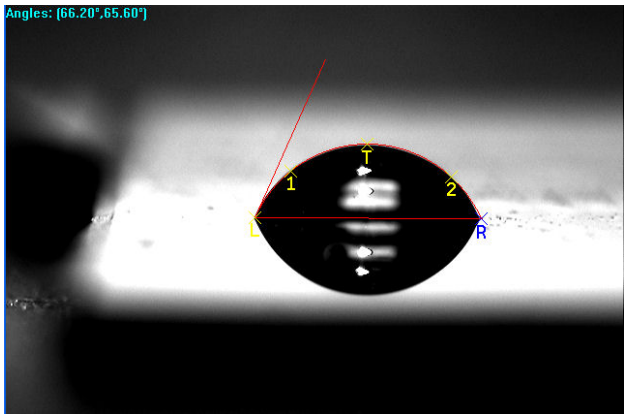

FIGURE 9. Contact angle of a silicon wafer with thermally grown silicon oxide.

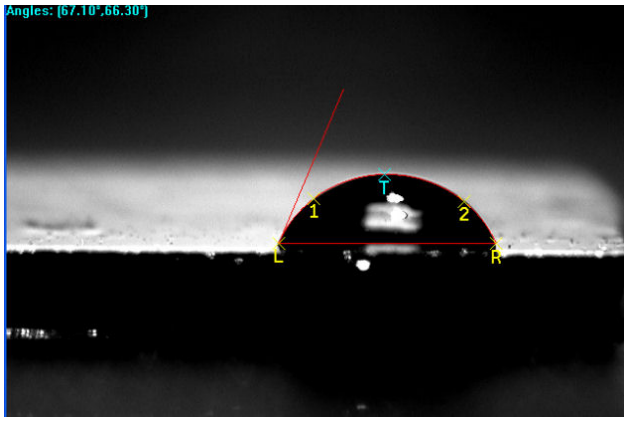

FIGURE 10. Contact angle of a silicon wafer with thermally grown silicon oxide and a deposition of silicon oxide nanoparticles as a catalyst.

ing their behavior in various applications [40]. In the case of carbon nanotubes, this property can influence their dispersion, functionalization, biocompatibility, and other relevant properties [41,42].

In this study, the contact angle measurement technique was used to determine the hydrophobicity/hydrophilicity of CNTs. The technique involves depositing a drop of deionized water on the surface of the material and measuring the angle formed between the drop and the surface.

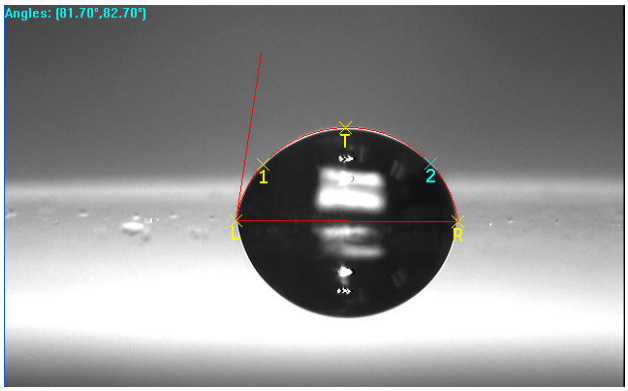

FIGURE 11. Contact angle of a silicon wafer with carbon nanotubes.

Angle less than 90°: indicates a hydrophilic surface (that attracts water). Angle greater than 90°: indicates a hydrophobic surface (that repels water) [43].

In Fig. 8, the presence of a water droplet on the unmodified silicon wafer is depicted, exhibiting average contact angle values of 32.50° and 32.50°.

In Fig. 9, the water droplet on the silicon wafer with thermally grown silicon oxide is shown, yielding average angle values of 66.20° and 65.60°.

In Fig. 10, the water droplet on the silicon wafer with thermally grown silicon oxide and a deposition of silicon oxide nanoparticles as a catalyst can be seen, with average angle values of 67.10° and 66.30°.

In Fig. 11, the water droplet on the silicon wafer coated with carbon nanotubes is clearly visible, demonstrating average contact angle values of 81.70° and 82.70°. These values indicate that the carbon nanotubes are hydrophilic.

4. Conclusions

The successful synthesis of carbon nanotubes with high uniformity in size is a pivotal achievement in nanomaterials engineering. This uniformity is essential for controlling the physical and chemical properties of the nanotubes, which can significantly enhance their functionality in various applications, particularly in biomedical fields.

The use of silicon oxide nanoparticles as catalysts in the chemical vapor deposition process has proven effective in producing carbon nanotubes with specific characteristics. This reinforces the potential of this technique for creating nanotubes tailored for biomedical applications, such as drug delivery systems and biosensors.

The research indicates that the size and dispersion of silicon oxide nanoparticles play a crucial role in the growth and behavior of carbon nanotubes. Understanding these factors can lead to improved synthesis methods and better control over the properties of the resulting nanotubes, which is vital for their application in advanced technologies.

Overall, the research contributes valuable insights into the synthesis of carbon nanotubes and their potential applications, particularly in the biomedical sector. The ability to design nanotubes with specific attributes, such as hydrophilicity and uniform size, can significantly impact their effectiveness in practical applications, paving the way for further innovations in this field.

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