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CARBON NANOTUBE-BASED SUPERHYDROPHOBIC COATINGS

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Abstract: *This study focuses on the development of superhydrophobic coatings based on carbon nanotubes (CNTs), which exhibit unique structural and physicochemical properties. The research includes film materials with both aligned and non-aligned CNT structures prepared by various deposition techniques, such as chemical vapor deposition (CVD), spray coating, dip coating, and electrospinning. The primary objective is to analyze current strategies for fabricating CNT-based superhydrophobic surfaces, identify key parameters influencing the water-repellent performance, and evaluate the scalability and environmental compatibility of these approaches. The main finding highlights the effectiveness of both aligned and randomly distributed CNT films in achieving the Cassie-Baxter wetting regime, with contact angles exceeding 150° and low sliding angles. The study demonstrates that functionalization with hydrophobic groups, combination of CNTs with other nanomaterials, and optimized deposition parameters can significantly enhance surface hydrophobicity while extending the functionality of the coatings. These improvements include mechanical durability, self-cleaning ability, anti-icing behavior, and antifouling performance. The results underscore the potential of CNT-based superhydrophobic coatings for practical applications in fields such as energy, construction, transportation, and biomedical engineering.*

Key words*: Superhydrophobicity, Carbon Nanotubes (CNTs), Coatings, Surface Roughness, Low Surface Energy, Anti-icing, Self-cleaning, Anti-fouling, Water-Repellent*

Superhydrophobicity is a remarkable property that describes the extreme water repellency of certain surfaces. It is quantitatively measured by the contact angle

(CA), which is the angle formed between the tangent to the liquid droplet and the surface at the contact point. Surfaces with contact angles greater than 150° are classified as superhydrophobic, exhibiting not only high contact angles but also low sliding angles (SA), typically less than 10°, allowing water droplets to roll off easily. This behavior is a result of a synergistic combination of high surface roughness and low surface energy, which reduces the liquid-solid contact area and minimizes adhesion forces between the surface and the liquid. Superhydrophobicity has gained considerable interest due to its potential applications in various fields, including self-cleaning materials, anti-fouling coatings, anti-icing technologies, and water-repellent fabrics [1-5]. The principles underlying superhydrophobicity have been extensively studied, with most attention focusing on the Cassie-Baxter wetting model. This model describes the situation where the liquid rests on top of the surface roughness, creating a composite interface of air and solid. In this state, the liquid droplet is supported by the surface topography, which significantly reduces the contact area between the liquid and the solid, thereby minimizing adhesive forces and promoting droplet mobility.

Nature has often been the inspiration for creating artificial superhydrophobic surfaces, particularly the lotus leaf (Nelumbo nucifera), as shown in the Figure 1, which exhibits excellent water-repellent properties due to its unique micro- and nanoscale surface structure combined with hydrophobic wax-like coatings [6, 7]. The creation of synthetic superhydrophobic surfaces typically involves the design of hierarchical micro- and nanostructures, often combined with the modification of surface chemistry to reduce the surface energy. This can be achieved through various means, including the deposition of hydrophobic molecules or the incorporation of hydrophobic polymers into the material matrix. Among the various materials explored for superhydrophobic coatings, carbon nanotubes (CNTs) have emerged as a particularly promising candidate due to their unique structural, mechanical, and chemical properties. CNTs are cylindrical structures composed of rolled-up graphene sheets, which possess extraordinary strength, electrical conductivity, and large surface areas. These properties make CNTs highly suitable for the creation of superhydrophobic surfaces, as they provide the necessary nanoscale roughness that is critical for achieving the Cassie-Baxter wetting state. CNTs are highly tunable, both in terms of their surface chemistry and their ability to form networks or composite structures, which further enhances their potential for superhydrophobic applications. The high aspect ratio and large surface area of CNTs contribute to the formation of intricate micro- and nanoscale textures that can significantly enhance the water-repellent properties of a surface. When CNTs are incorporated into coatings, they can facilitate the formation of a hierarchical roughness that not only increases the surface area but also aids in the retention of air within the surface structure, thus promoting the Cassie-Baxter state.

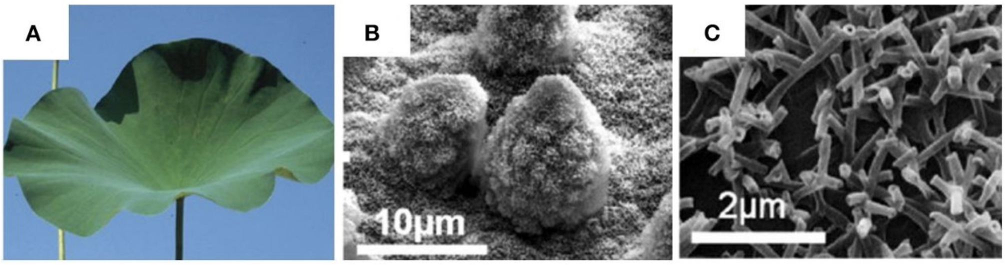

Fig. 1. Digital images and scanning electron microscopy (SEM) images of different natural species that display hydrophobic properties [8]: (A–C) Nelumbo nucifera (lotus)

A variety of techniques have been developed to integrate CNTs into superhydrophobic coatings, each with its advantages and limitations. Chemical vapor deposition (CVD) is one of the most widely used methods for directly growing CNTs onto substrates, offering precise control over the alignment and density of CNTs [9-11]. However, CVD is often limited by the scalability and cost-effectiveness of the process. Alternatively, solution-based techniques, such as electrospinning, dip-coating, and spray-coating, offer more versatile and cost-efficient alternatives for large-scale production. These methods enable the incorporation of CNTs into polymer matrices or the formation of CNT-based composite coatings, enhancing not only the water-repellent behavior but also the mechanical durability and environmental stability of the coatings. Hybrid coatings that combine CNTs with other nanomaterials, such as silica nanoparticles, graphene oxide, or metal oxide nanoparticles, have also demonstrated enhanced performance, including improved anti-fouling, anti-corrosion, and self-healing properties.

Aligned carbon nanotube (CNT) films particularly those fabricated as vertically aligned CNT forests (VACNTs) or anisotropic CNT films (ACNTs), have shown significant promise in the development of superhydrophobic surfaces due to their unique structural characteristics and the high aspect ratio of individual nanotubes. These films provide a platform for achieving superior water-repellent properties by combining micro/nanoscale surface roughness with low surface energy materials. Various strategies have been developed to enhance the superhydrophobic performance of CNT-based films, including functionalization with fluorocarbon compounds, the introduction of hierarchical structures, and the deposition of additional coatings to improve surface stability and durability. Lau et al. [12] were among the pioneers in fabricating superhydrophobic CNT forests by modifying vertically aligned CNTs (VACNTs) with a polytetrafluoroethylene (PTFE) coating using the chemical vapor deposition (CVD) method, the SEM images of the surfaces as shown in the Figure 2. The resultant surface exhibited outstanding water repellency, with advancing and receding contact angles (CAs) of 170° and 160°, respectively.

Non-aligned CNT films present a versatile and scalable approach to creating superhydrophobic surfaces, leveraging the inherent properties of carbon nanotubes without the complex alignment procedures required for VACNTs or ACNT films. These films are typically fabricated through techniques like spray coating, dip-coating, spin coating, or electrospinning, wherein CNTs are either randomly dispersed on a substrate or incorporated within a matrix material, often a polymer [13, 14]. The key to achieving superhydrophobicity with non-aligned CNT films lies in creating sufficient surface roughness and maintaining a low surface energy. The random arrangement of CNTs inherently provides a degree of nanoscale roughness. This can be further enhanced by controlling the concentration of CNTs in the coating solution, the deposition parameters, and the post-treatment processes. Moreover, the choice of matrix material plays a crucial role. Polymers with intrinsically low surface energies, such as fluoropolymers, or those that can be easily modified to reduce surface energy, are commonly employed [15]. Non-aligned CNT films are typically created using spray coating, dip-coating, spin coating, or electrospinning to randomly disperse CNTs (often with a polymer binder) onto a substrate, followed by surface modification techniques like fluorination, alkylation, or plasma treatment to lower surface energy and enhance superhydrophobic properties. Xu et al. [14] demonstrated

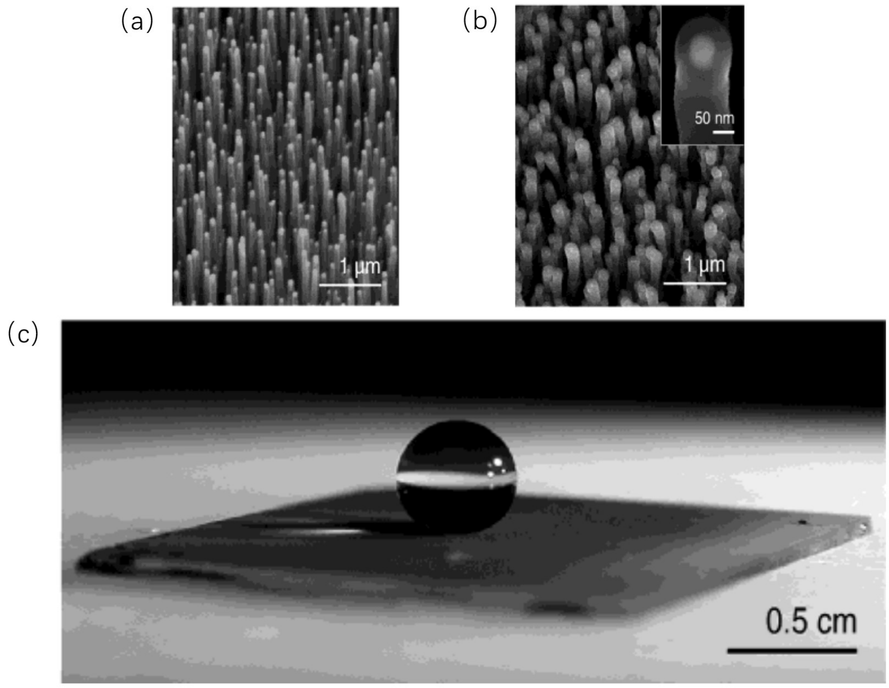

Fig. 2. SEM images of carbon nanotube forests [12]: a – As-grown forest prepared by PECVD with nanotube diameter of 50 nm and a height of 2 μm; b – PTFE-coated forest after HFCVD treatment; c – an essentially spherical water droplet suspended on the PTFE-coated forest

a significant advancement in the fabrication of superhydrophobic surfaces using a simple method involving non-aligned, alkyl-modified multi-wall carbon nanotubes (MWCNTs), as shown in Figure 3. The left column presents low magnification images, the right column shows high magnification, and the inset displays the highest magnification. And the shapes of water droplets on the films surfaces correspond to contact angles of 155°, 163°, and 159°, respectively. The resulting films exhibited excellent water repellency, with contact angles (CA) exceeding 150° and sliding angles below 5°. Notably, these impressive properties were achieved without the need for spatially aligned nanotube structures, demonstrating that double-structured roughness and reduced surface energy from grafted alkyl chains are sufficient. Films prepared from chloroform suspensions, showed a maximum CA of 163°. The work underscores the scalability and industrial potential of this approach, offering a cost-effective solution for producing superhydrophobic surfaces with applications in anti-contamination and water-repellent coatings. This research not only simplifies the production process but also expands the practical usability of advanced materials.

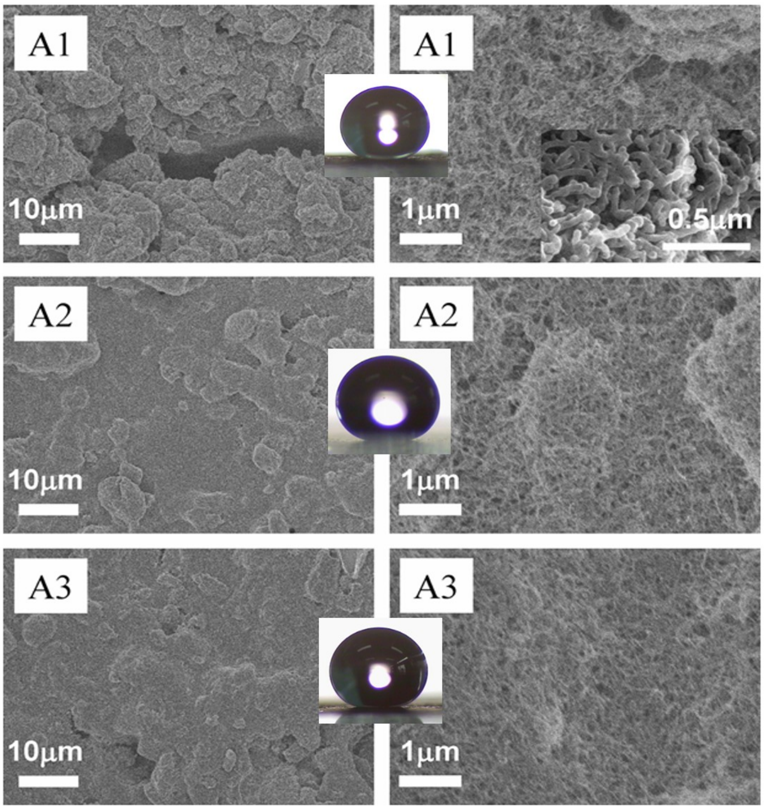

Fig. 3. SEM micrographs of the surfaces of MWCNT ($COOC_{18}H_{37}$)$_n$ films, prepared from suspensions of water (A1), chloroform (A2), and dimethylbenzene (A3) [14].

CONCLUSIONS

CNT-based superhydrophobic coatings offer diverse applications across industries, leveraging their ability to repel water. In anti-icing technologies, they minimize ice formation on surfaces like aircraft wings and wind turbines. For self-cleaning materials, these coatings facilitate easy removal of dirt and dust from building facades and solar panels via rainwater. As anti-fouling coatings, they prevent organism accumulation on ship hulls, reducing drag. Water-repellent fabrics benefit from these coatings, enhancing comfort and functionality in apparel, while biomedical applications utilize them to prevent bacterial adhesion on devices, minimizing infection risks. Future research in CNT-based superhydrophobic coatings will likely focus on integrating CNTs with advanced materials like graphene, silica, or metal oxides to enhance performance and create multifunctional coatings. Simultaneously, efforts will be directed towards developing sustainable and environmentally friendly fabrication techniques, emphasizing green solvents, reduced energy consumption, and minimized waste. Addressing scalability and durability challenges remains critical, driving innovation in CNT dispersion, coating stability through crosslinking or hybridization, and the creation of self-healing materials for widespread adoption. CNT-based superhydrophobic coatings represent a promising area of research with significant potential for various applications. While challenges remain, ongoing advancements in fabrication techniques, material integration, and durability enhancement are poised to make these coatings more viable for commercial use, contributing to innovations in self-cleaning surfaces, anti-icing technologies, and beyond.

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СУПЕРГІДРОФОБНІ ПОКРИТТЯ НА ОСНОВІ ВУГЛЕЦЕВИХ НАНОТРУБОК

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Анотація: Це дослідження зосереджено на розробці супергідрофобних покриттів на основі вуглецевих нанотрубок (ВНТ), які демонструють унікальні структурні та фізико-хімічні властивості. Дослідження охоплюють плівкові матеріали як з вирівняними, так і з невирівняними структурами ВНТ, виготовлені різними методами осадження, такими як хімічне осадження з парової фази (CVD), напилення, нанесення покриття зануренням і електроспінінг. Основна мета — проаналізувати поточні стратегії виготовлення супергідрофобних поверхонь на основі ВНТ, визначити ключові параметри, що впливають на водовідштовхувальні властивості, і оцінити масштабованість і екологічну сумісність цих підходів. Основний висновок підкреслює ефективність як вирівняних, так і випадково розподілених плівок CNT у досягненні режиму змочування Кессі-Бакстера з контактними кутами понад 150° і низькими кутами ковзання. Дослідження демонструє, що функціоналізація гідрофобними групами, поєднання ВНТ з іншими наноматеріалами та оптимізовані параметри осадження можуть значно підвищити гідрофобність поверхні, розширюючи функціональність покриттів. Ці покращення включають механічну довговічність, здатність до самоочищення, захист від зледеніння та ефективність захисту від обростання. Результати підкреслюють потенціал супергідрофобних покриттів на основі УНТ для практичного застосування в таких сферах, як енергетика, будівництво, транспорт і біомедична інженерія.

Ключові слова: супергідрофобність, вуглецеві нанотрубки (ВНТ), покриття, шорсткість поверхні, низька поверхнева енергія, захист від зледеніння, самоочищення, захист від обростання, водовідштовхувальний засіб