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## ***Carbon Nanohorn: The Promising Drug Delivery System: A Concise Review***

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### ***Abstract***

*The current review paper provides an overview of our recent achievements in the field of CNHs, along with a summary of several significant properties and applications. Carbon nanoforms are conical horn-shaped nanostructures composed of sp<sup>2</sup> carbon atoms. Carbon Nano horns have gained significant attention in the field of nanomaterials due to their versatility, high purity, ability to modulate chemical, physical and electronic properties and potential applications. The properties of Carbon nanohorn include a high surface area, excellent mechanical strength, good electrical and thermal conductivity, thermal diffusivity and porosity. These properties make carbon nanohorns suitable for various applications such as gas storage media, support for the catalyst, in energy applications, transporters in the pharmaceutical delivery system, Adsorption, Magnetic Resonance Analysis, in gas sensing, in photodynamic therapy, in electrochemistry, in fuel cells, bio sensing application, as a photo electrochemical and photovoltaic cells. In recent years, there has been extensive research on carbon nanohorns and their applications. This review article focuses on overview of the properties and applications of carbon nanohorns. It covers various topics including the physical properties and applications of carbon nanohorns in different fields.*

***Keywords:*** *Carbon nanohorn, properties, applications, thermal conductivity.*

## INTRODUCTION

Iijima discovered a novel nanocarbon material structure in 1998 called single walled nanohorns (SWCNHs), in addition to carbon nanotubes, graphene, and fullerenes<sup>2</sup>. As a novel and promising material for a wide range of technical and biological applications, carbon nanohorns (CNHs), a new carbon allotrope within the family of elongated carbon nanotubes, have been introduced. CNHs were first produced in significant quantities in 1999 using CO<sub>2</sub> laser ablation of a graphite target at room temperature under Ar, with a high purity (95%) and yield (75%).<sup>4</sup> Carbon nanohorns (CNHs) are single-walled carbon nanostructures that resemble horns and have diameters ranging from 3 to 25 nm and lengths ranging from 20 to 150 nm. It could have one wall, two walls, or even multiple walls.<sup>1</sup> The SWCNHs consist of minuscule graphene sheets that are coiled into horn-shaped cones with typical diameters of 2.5 nm, lengths of 40–50 nm, and cone angles of nearly 20°.<sup>7</sup> During synthesis, the nanohorns form ball-shaped aggregates with diameters ranging from 80 to 100 nm; however, aggregates with much smaller sizes (about 50 nm) have also been described.

The closed cages of sp<sup>2</sup> -bonded carbon atoms, called carbon nanohorns (CNHs) or nano cones, are usually 2–5 nm in diameter and 40–50 nm in length. Because of their closed cage structure, they can be thought of as a high-aspect ratio subset of fullerenes, though they can also be opened via oxidation to increase their surface area and give access to their interior cavity.<sup>6</sup> They may be cylindrical graphitic carbon tubes and have a black tint. They are shaped like a horn, a little like thimble sewing, and they are useful for a lot of things. Since they may provide an open channel for gas and a layer for conduction with a large surface area.

It has been demonstrated that the nature and pressure of the buffer gas employed in the significantly influences the product's purity and shape; for example, using Ar results in aggregates that resemble dahlias, while using He creates aggregates that resemble buds. Crucially, the primary benefit of the as-produced carbon nanotubes over the metal-contaminated ones is thought to be the complete lack of any transition metal impurities in them.

Pentagons, hexagons, and heptagons are the structural building blocks of nanohorns, and this mix of structural patterns and forms produces a rich and diverse chemistry.

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One significant benefit of carbon nanotubes (CNHs) over metal-contaminated ones is the complete lack of any transition metal impurities in them. More purifying techniques have been described, notwithstanding the great purity of the as-grown CNHs.

It is possible to create extremely pure carbon nanohorns in either a suspended or dispersed form. In order to develop materials for use in refrigerators, heat exchangers, solar panels, fuel cells, composites, and bio composites, researchers are now working in a number of sectors, including biosensors, MEMS, nano electronics, NEMS, bio nanoparticles, and different carbon-based nanostructured particles.<sup>6</sup> They can be utilized in both polymer electrolyte fuel cells (PEFC) and proton exchange membranes (PEM).<sup>1</sup>

One of the most intriguing properties of carbon nanohorns is their high surface area and porosity, which make them excellent candidates for adsorption and storage of gases and small molecules. Additionally, their biocompatibility and ability to easily penetrate cell membranes open up possibilities for targeted drug delivery and biomedical imaging applications. Furthermore, the horn-like structure of carbon nanohorns allows for enhanced mechanical strength and conductivity, making them promising candidates for use in composites and electronics.<sup>12</sup>

Applications for carbon nanohorns can be found in a wide range of fields, including biofuels, solar panels, displays of different electronic devices, microscopes, lubricants, sensors, cancer detection, sports equipment, air conditioners, and freezers. Additionally, an area of bioscience also uses carbon nanohorns.<sup>1</sup>

### **Properties**

A number of appealing characteristics of carbon nanohorns like high specific surface area, superior mechanical strength, chemical stability, outstanding electrical and thermal conductivity, and biocompatibility etc make them very appealing for various uses. Because of their large specific surface area, carbon nanohorns may interact with molecules more readily, which makes them useful for gas adsorption and storage, among other uses.<sup>1</sup>

CNH's unique conical structure has a significant impact on this nanocarbonic material's electrical characteristics. The electronic characteristics, stability, and shape of SWCNHs were ascertained by means of theoretical computations and the development of several models.<sup>2</sup>

Properties that are common to CNH on the nanoscale include high specific surface, great mechanical strength, and superior electrical and thermal conductivity. With respect to materials science, CNH exhibits tremendous promise as a foundation material, functional filler, or coating due to its physical features. Properties of thermoplastics, thermo sets, elastomers, and metallic and ceramic sintering materials have been shown to be improved in industrial applications.<sup>6</sup> Carbon nanotubes (CNTs) have a greater diameter, which contributes to their about 6250 W/m K thermal conductivity. In contrast, the front-apex passage of nano horns tapers and the passage is smaller and fashioned like a barrel. The molecules can move freely because of their bigger diameter. Since their transverse section is shaped like a "dogbone" by the smaller nanotube sections and bigger diameter, nano horns are more conductive than carbon nanotubes.

One interesting characteristic of CNHs is their porosity, which allows them to hold onto things by adsorption. Essentially, when CNHs partially oxidize, they create nano windows on their skeleton, which allow direct access to their internal pores. A heat treatment in an oxidative or acidic environment can readily produce holes in virgin CNHs. <sup>80-83</sup> Certain holes (i.e., sidewalls vs. tips) close more slowly than tips, and holes smaller than 0.9 nm shut more quickly. These factors determine whether the process is occasionally thermally reversible.<sup>6</sup> In SWCNHs, there is a high correlation between the electrical and magnetic properties. Static magnetic susceptibility tests and electron spin resonance (ESR) were used to examine the magnetic characteristics of single-wall carbon nanohorns. It was shown by Bandow et al. that each individual SWNH included at least one unpaired electron spin.<sup>2</sup>Aggregates made of SWCNH have both mesoporosity and microporosity. The inter- and intra-nanohorn pores are the two types of pores found in SWCNHs. SWCNHs have a surface area of approximately and are close 300m<sup>2</sup>g<sup>-1</sup>d, however they include windows that can be opened to allow access to the internal pores. Oxidation at varying temperatures can regulate the quantity and dimensions of these nano windows. Soon after, it was found that hole opening may occur from oxidation at low oxygen concentrations (as low as 21% in air), preventing the formation of C-dust. SWCNHs' oxidation and compression may cause a noticeable rise in microporosity and mesopore formation.

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Additionally, the study finds that the diamagnetic susceptibility of C60 and C70, two distinct fullerenes, has a value that is the same order of magnitude as theirs, but that of randomly oriented graphite is an order of magnitude smaller.

An analysis of the porosity development of budlike CNHs with increasing O<sub>2</sub> oxidation temperature has also been conducted. Subsequently, it was proposed that oxidation, using a slow temperature increase of 1°C/min or less in air, could result in hole opening, avoiding C-dust contamination that occurs when fast temperature increase is used. An analysis of H<sub>2</sub>O adsorption in ox CNH suggested that oxygen-containing functional groups, such as carboxyl (COOH), hydroxyl (OH), carbonyl (CO), etc., exist at the defect sites of the holes.<sup>4</sup>

When compared to SWCNTs, the chemistry of CNHs is largely controlled by its high purity because in the latter, reactions take place on associated amorphous and  $\pi$ -stacked polyaromatic impurities that are present from growth or oxidation, 92–94, whereas the chemistry of graphene is heavily dependent on edge sites 95 and metallic impurities<sup>6</sup>. Since the  $\pi$  and  $\sigma$  orbitals have a curvature that causes assimilation, carbon nanotubes (CNT) have a higher thermal diffusivity than carbon nanotubes (CNH). The  $\pi$ -orbital imbalance caused by an additional curvature is associated with this vulnerability. For 2, 3, and 4-pentagon cones, CNH contains two subcategories that are spitted against each other based on vector length. By adding or removing neighbouring carbon atoms, these subcategories can be redesigned. Because of its non-stable nano cone helicity and the potential for choral and archrival nano cones, CNH has a higher thermal diffusivity than other carbon nano-structured materials.

Electronic characteristics and magnetic properties are strongly connected. In one electron spin resonance (ESR), two electronic systems for dahlia-like SWCNHs were found. The first one's surface of dahlia-like material has a 2D grapheme-like structure that gives it an extraordinary temperature-activated paramagnetic susceptibility. The second is because the inside of dahlia is made up of interacting graphene sheets and crushed nanohorns, resembling

a graphitic environment. Because of this, the susceptibility—which is made up of conduction electrons and localized spins—increases when the temperature drops up to 17 K. There is a significant reduction in paramagnetic susceptibility below 17K, which suggests an antiferromagnetic link between localized electrons.<sup>13</sup> Different features from graphite, glassy carbon, nano-soot, and diamond-like amorphous carbon are visible in the Raman spectrum of pristine SWCNHs. There were two bands at 1593 and 1341  $\text{cm}^{-1}$  with about identical scattering intensities. The distinctive conical structure of SWCNHs significantly affects this material's electrical characteristics.<sup>7</sup>

The simulations of carbon nano horn's density structure reveal a contagious deviation in the nano cone with acute strobilus, implying graphene and larger nano tubes. The inculcation of oxygen atoms to graphene is endothermic, ensuring 2+2 cyclic fullerene inclusion. Covalent radical inclusion improves apex reactivity and regional enzymatic reactivity due to pyramidal exaggeration of covalent carbon  $\text{sp}^2$  bonding. CNH has higher corrosion resistance than other nano particles.

It is possible to deliver the holey-SWCNHs in organic solvents like ethanol and isopropyl alcohol as well as water. High specific surface area, high dispersibility, and high conductivity are displayed by SWCNHs and/or holey-SWCNHs.<sup>2</sup>

### **Application**

SWCNHs are gaining attention due to their versatile synthetic methods, high purity, and ability to modulate chemical, physical, and electronic properties through covalent and non-covalent functionalization. They have a large surface area and can be easily processed in water and various organic solvents, resulting in films with varying morphology, porosity, and texture. Following are various applications of carbon nanohorn:

#### **Carbon nanohorns as gas storage media**

Gas storage media is one of the main uses for carbon nanohorns. The potential application of carbon nanohorns in gas storage, specifically for hydrogen and methane, has been thoroughly investigated. Because of their large surface area, porosity, and adjustable pore size, carbon nanohorns are advantageous in various applications because they enhance storage efficiency and boost gas adsorption capacity.<sup>1</sup> Moreover, the interwoven tubular network of carbon

nanohorns distinctive structure offers improved gas diffusion paths, facilitating the effective storage and release of gases. For gas storage medium in a variety of industries, such as fuel cells, transportation, and energy storage, carbon nanohorns are therefore a potential option.<sup>8</sup> The interstitial sites and cylindrical structure of SWCNHs and holey-SWCNHs make them ideal materials for the storage of gases like fluorine, methane, and hydrogen. According to Murata et al., charge transfer effects help the lanthanide nitrate dispersion in compressed SWCNHs (0.1 mmol/g SWCNHs) enhance methane adsorption. The amount of H<sub>2</sub> absorbed by carbon nanohorns containing Pd–Ni alloy nanoparticles (Pd–Ni/SWCNHs) was shown by Sano et al. to be more than the total absorption provided by Pd–Ni alloy and SWCNHs combined.<sup>2</sup>

### Support for the catalyst

Due to the vast surface area of nanohorns, a significant amount of molecular catalyst can be incorporated into nanotubes and simultaneously released at the required rate at a certain time. Therefore, employing CNHs can result in a decrease in both the frequency and volume of catalyst accumulation.<sup>13</sup>

### Carbon nanohorns in energy application

Carbon nanohorns have found several uses in the field of energy conversion because of their high surface area, high nano porosity, and high electron, heat, and phonon transmission. SWCNHs and its derivatives have applications in:

- **Catalyst in the fuel cell architecture or catalyst support:** Numerous investigations on the catalyst deposition of Pt or metal alloys on SWCNHs used in fuel cells have been published. Also, in proton exchange membrane fuel cells, N-doped SWCNHs—which are made by combining SWCNHs with urea at 800°C—were discovered to be more effective than Pt.
- **A method of creating dye-sensitized solar cells:** The design of dye-sensitized solar cells (DSCs) produced good results when various light absorbers, such as porphyrin functionalized SWCNHs (SWCNHs-H<sub>2</sub>P) and SWCNHs-Zn porphyrin supramolecular assembly (SWCNHs - ZnP), were employed. SWCNHs were also used as a counter electrode.<sup>14</sup>

- **Designing rechargeable batteries:** Li-Ion and Li-S rechargeable batteries have utilized SWCNHs composite as their anode material.
- **Supercapacitors Using SWCNHs:** The great power density and extended cycle life of supercapacitors make them highly desirable. They could find use in a variety of industries, including portable electronics, hybrid electric cars, and other applications involving the storage of renewable energy. The application of supercapacitors could effectively address the issues of lead acid battery pollution and urban pollution while reducing reliance on foreign oil imports and oil consumption.<sup>14</sup>

### **Transporters in the pharmaceutical delivery system**

SWCNHs are prospective drug delivery system carriers due to their large surface areas and many horn interstices. It is also possible for oxSWCNHs to absorb and release the well-known anti-cancer drug cisplatin (CDDP). The growth of human lung cancer cells was found to be effectively stopped by the released CDDP, despite the decreased discharge rate of CDDP from oxSWCNHs in PBS and culture media.<sup>13</sup>

### **Adsorption**

Noble gases, such as xenon, were adsorbed onto SWCNHs and exhibited a greater capacity to permeate interstitial channels in comparison to planar graphite. Also adsorbed onto SWCNHs and oxidized SWCNHs (oxSWCNHs) was benzoene. There were three SWCNH sites where adsorption took place; the two sites that were the second deepest away from the points and convex sections and the energetically deepest inside the walls. Moreover, liquid ethanol was efficiently adsorbed on SWCNHs. Clusters formed in the interstitial and internal nanospaces of SWCNHs during the investigation of water adsorption. It was discovered that the adsorption of tetracyano-p-quinodimethane (TCNQ) onto SWCNHs was more successful than that of hSWCNHs; this is probably because high-temperature oxygen treatments produce holes and flaws.

### **Magnetic Resonance Analysis**

If an MRI agent was affixed to SWCNHs, magnetic resonance imaging (MRI) may be utilized to assess toxicological risks in the living body. On oxSWCNHs, ultrafine Gd<sub>2</sub>O<sub>3</sub> nanoparticles functioned as a positive magnetic resonance agent. Even at a low concentration

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of Gd<sub>2</sub>O<sub>3</sub>-oxSWCNHs, a bright, sharp image was still visible. Another useful agent for MRI is super paramagnetic magnetite nanoparticles.<sup>13</sup>

### **Carbon nanohorn in gas sensing**

Using single-walled carbon nanohorns (SWCNHs) as the sensing layer, Sano et al. created a chemiresistive gas sensor for the room temperature detection of ozone and ammonia. Gas sensor uses the ability of charge transfer between gas molecules and nanomaterials to identify NH<sub>3</sub> and O<sub>3</sub>. Adsorption of NH<sub>3</sub> led to a rise in the electric resistance of the SWNH film; however, this tendency was reversed when O<sub>3</sub> was present.<sup>16</sup>

### **Carbon nanohorn in photodynamic therapy**

Holey-SWCNHs, a carbonaceous tube material, are potential photodynamic treatment candidates due to their ability to absorb near-infrared light, allowing photo hyperthermia (PHT) to eradicate malignancies. Zinc phthalocyanine (ZnPc) and protein bovine serum albumin (BSA) were used to create a double PDT and PHT cancer phototherapy system with a single laser. The system demonstrated phototherapy's effectiveness in both vivo and in vitro settings.<sup>17</sup>

### **Carbon nanohorn in electrochemistry**

SWCNHs are utilized as electrode materials in electrochemical processes because they don't contain any metals. Concentrated hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was measured amperometrically using the first SWCNH paste electrode. For the purpose of creating free-standing electrodes for electrochemical applications, direct growth of SWCNHs on carbon microfibre substrates has been developed. Because of their unique physical characteristics and porous structure, SWCNHs are also regarded as innovative materials for supercapacitors.<sup>13</sup>

### **Fuel cell**

SWCNHs can be utilized as a catalyst support material in fuel cells. Adsorbed nanoparticles on the SWCNH surface must be consistent for the application. Because there are many large particular surfaces as well as faulty or interstitial sites between SWCNH sheaths, the catalyst sizes are about 2 nm, smaller than those supported on ordinary carbon black. When

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employing SWCNH electrodes supported by catalysts, the fuel cell's current density was higher than when using carbon black supported by catalysts.<sup>13</sup>

### **Biosensing application**

SWCNHs are suitable for biosensing investigations and are devoid of metals. They were employed in the production of myoglobin, hydrogen peroxide biosensor, and glucose biosensors. Myoglobin's activity and affordability make it an attractive component for hydrogen peroxide biosensors. Ascorbic acid, dopamine, and uric acid can all be measured simultaneously with SWCNHs.<sup>11</sup>

### **CNHs as photo electrochemical and photovoltaic cells**

High purity metal-free SWCNHs can be used into novel photoactive hybrid materials. They provide an outstanding platform for photovoltaics and optoelectronic energy conversion devices. A unique SWCNHs-COO-Cu II type metallo-nanocomplex was produced. When the -COOH at the conical terminals of SWCNHs was coordinated with copper (II) terpyridine. One electron is reduced by the nanohorns and one electron is immediately oxidized by the Cu II type unit when an electron is moved from the singlet excited state of Cu II type to SWCNHs as a result of photoexcitation.<sup>13</sup>

### **CNHs in cancer treatment**

A high surface area to volume ratio and customizable physicochemical qualities have made carbon nanohorns promising for use in cancer therapy. CNHs are appropriate for use in medicine because of their little toxicity in vivo. To safely employ them in cancer treatment, their biocompatibility is essential.

### **Anticancer medications are transportable by CNHs**

- CNH surfaces bind to medicines that are loaded.
- Drugs are shielded by CNHs from premature release while in circulation.
- CNHs facilitate localized therapy by releasing the medication at the tumour location.<sup>10</sup>

The anticancer drug cisplatin, which was gradually released from the oxidized SWNHs in aqueous settings, could be trapped by these structures. The development of human lung cancer cells was effectively stopped by the released cisplatin, but the oxidized SWNHs did

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not have the same impact. This suggests that cisplatin-incorporated oxidized SWNHs might be a useful drug delivery method.<sup>15</sup>

### **Field emission**

The release of electrons caused by an electric field is known as field emission. Creating high-volume, low-cost production techniques is a major obstacle to field emission optimization. There is no need for additional purification when synthesizing huge amounts of carbon nanohorns. These thin films long-term stability, low turn-on field, and pointed horn-like features provide them good field emission characteristics. However, because of distinct structure and high resistivity, nanohorns can tolerate current densities higher by at least two orders of magnitude, but nanotubes can only withstand densities higher by at least two orders of magnitude. Consequently, in field emission applications where high current densities are not required, nanohorns may present an appealing substitute.<sup>18</sup>

### **CONCLUSION**

Carbon nanohorns, also known as CNHs, are a fascinating family of nanocarbon materials that have gained attention recently. These horn-shaped aggregates of graphene sheets are appealing for a variety of applications due to their unique characteristics. The field of SWCNHs is still in its infancy despite ongoing efforts and research. Due to their distinct structures, large surface area, and micro porosity, SWNHs are becoming a material of significant potential for gas adsorption, drug delivery, biosensing, gas storage, and catalyst support in fuel cells. Carbon nanohorns are members of the family of carbon nanocones. There are a lot of potential uses for nanotechnology and biotechnology, but as solubility of functionalized CNHs is accomplished, basic problems with CNH synthesis and manipulation appear to be resolved.

While CNHs provide fundamental science and nanotechnology with great prospects, they also represent severe obstacles for further research in these areas. It will be necessary to prepare and research novel and inventive SWCNH-based hybrid materials for future use. This will be an even more active field of study because of the adaptability and commercialization of CNHs.

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