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Single walled Carbon Nanohorns: A Review on Synthesis, Properties and Applications

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ABSTRACT

Since after the discovery of the Fullerene(C_{60}), the family of carbon nanostructures has been gradually extended. Single-walled carbon nanohorns(SWCNHs) are integrated in this family for the first time in 1999 revealed by Sumio lijima et al. and Harris et al. and are closely related to single-wall carbon nanotubes. The remarkable features of SWCNs are their synthesis in nonexistence of catalyst which makes them high purity materials and the high surface area which leads to the outstanding electronic and magnetic properties including microporosity. On the basis of structure SWCNHs are categorized into three types 'dahlia-like', 'bud-like' and 'seed-like'. SWCNHs are generally synthesized by CO_2 laser ablation and Arc discharge methods. Without any doubt, SWCNHs offers great potential in diverse applications such as, gas storage, adsorption, catalyst support, drug delivery system, magnetic resonance analysis, electrochemical & bio-sensing application, photovoltaic & photo electrochemical cells, photodynamic therapy, fuel cells and other fields of material science which are still being researched heavily. This review summarizes the synthesis, properties and applications of SWCNHs in the field of technology and medicines.

Keywords: SWCNHs, Fullerenes, Microporosity, Biosensors, Magnetic-Resonance.

I. INTRODUCTION

Last few years have witnessed the innovation, progress and large scale manufacture of novel materials lie within the nanometer range. Such novel materials consist of organic and inorganic matter. Single-walled carbon nanohorns (SWCNHs) are one of them[1]. SWCNHs are horn-shaped single-walled tubules of graphene sheets having diameter about 2-5 nm, length about 40-50 nm and ended by a five-pentagon conical cap with a cone opening angle of ~ 20^o (fig.1). CNHs increase in diameter as their length increases, because as length increases so does the base of then ancone[2,3,4]. About 2000 of SWCNHs accumulate to form the collective structure having an average diameter of 80-100 nm. Similar to SWCNTs, SWCNHs are composed of single graphene. SWCNHs are closed tubes and their specific area increase by opening holes through which various molecules can pierce inside SWCNHs[5]. Three different types of single-walled carbon nanohorns have been observed.

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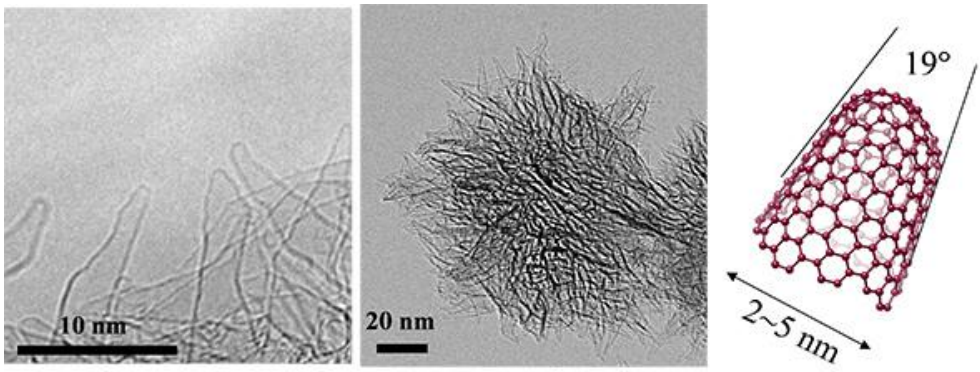

Figure 1: SWCNHs

- Dahlia like
- Bud like
- Seed like

In first type, the SWCNHs turn out from the aggregate surface while in second and third types they appear to grow inside the particle itself. 95% of the SWCNHs take 'dahlia like' morphology when Ar was used in synthesis, but 70-80% yield of 'bud like' SWCNHs were shaped when He or N_2 were used[6,7]. The size and purity of the SWCNHs can be altered by varying parameters like temperature, pressure, voltage and current.

II. SYNTHESIS OF SINGLE WALLED CARBON NAOHORNS

There is no use of metal catalysts during manufacture which leads to high production rate with high yield of SWCNHs. SWCNHs can be synthesized by two different techniques i.e. CO_2 laser ablation method and Arc discharge method.

2.1 CO_2 Laser Ablation Method

CO_2 laser ablation technique is used to produce initially SWCNHs at room temperature under Ar atmosphere at a high rate with a high yield of about 75%[8] and high purity of about 95%[9]. CO_2 laser ablation generator is composed of a high power laser source having wavelength 10.6μm, 5kW of power, 10 nm of beam diameter and pulse width varies from 10ms for uninterrupted illumination. Metal catalysts introduced during the fabrication of SWCNHs are usually removed by strong acids[10]. Meanwhile, a graphite rod in the middle of chamber rotates constantly and advances along the axis so that a new surface could be exposed to the laser beam vertical to the rod and hence SWCNHs are produced[11](fig.2). Sometimes the strong acids may spoil the graphitic structure and can cause loss of carbon materials. Therefore pure samples of SWCNHs are available more easily rather than SWCNTs which favors the study of properties and applications of SWCNHs.

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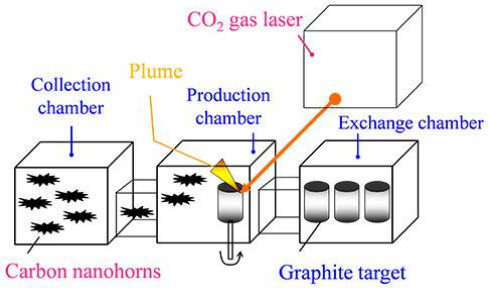

Figure 2: CO_2 Laser Ablation Method

2.2. Arc Discharge Method

SWCNHs can also be prepared by using simple pulsed arc discharge between pure carbon rods in the atmospheric pressure of air and He and Ar with arcing period of 30s. The arc current is set at 100A and voltage between the electrodes is 15-30V(fig.3). Before the ignition of arc, carbon rod is preheated up to 1000^0C to improve the quality of SWCNHs. Hence arc dust is collected on the surface of chamber and characterized. Purity of SWCNHs obtained by this method is more than 90%. The mean size of SWCNH formed is about 50nm, which is smaller than those produced by CO_2 laser method[12].

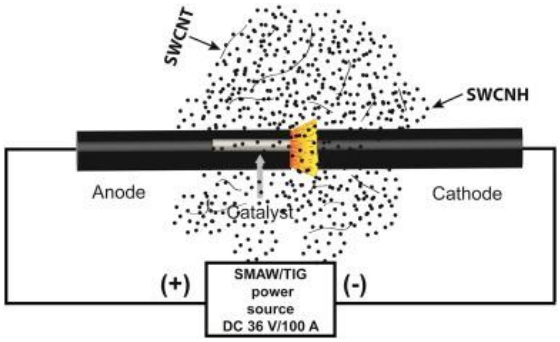

Figure 3: Arc discharge Method

III. PROPERTIES OF SINGLE-WALLED CARBON- NANOHORNS

3.1. Porosity

X-ray diffraction showed that the interhorn-wall distance for SWCNHs was 0.4nm, greater than the interlayer spacing of graphite i.e. 0.335nm[13]. Therefore SWCNH aggregates contain both properties microporosity and mesoporosity[14]. SWCNHs have two groups of pores: the inter-nanohorn pores and intra-nanohorn pores[15]. As SWCNHs are closed with a surface area of about $300m^2g^{-1}$ however having windows which can be opened to make the internal pores accessible[16]. The number and size of these nanowindows can be controlled by oxidation at different temperatures[17]. Soon after it was discovered that oxidation in a low oxygen concentration(21% in air) might results in hole opening, avoiding c-dust[18]. The oxidation and compression of SWCNHs could stimulate a

marked increase in microporosity and production of mesopores[19]. Acids can also be used for pore opening for example Dahlia-like SWCNHs when treated in H_2SO_4 or H_2O_2/H_2SO_4 mixture[20] or HNO_3[21,22] followed by heat treatment resulting in improved microporosity. Thus highly ultramicroporus SWCNH assemblies were successfully prepared. These ultramicroporus SWCNH assemblies showed superior storage capacity of supercritical CH_4[23].

3.2. Electronic Properties

The unique conical structure of SWCNHs reveals excellent electronic properties. It has been investigated that the conical endcaps contain five pentagons in the hexagonal arrangement[24]. Berber et al. found a net electron transfer to the pentagonal sites of the SWCNHs tips by simulated scanning tunneling microscopy(STM). The local density of electronic states the tip changes according to shapes of the SWCNHs[25]. Further Kolesnikov et al. investigated the effects of pentagonal defects on the electronic properties of SWCNHs within the continuum gauge field-theory model. The increased electronic conductivity with adsorption of CO_2 shows that dahlia-SWCNHs are n-type semiconductors and SWCNHs can be transformed into p-type semiconductors after oxidation treatment. The initial drop is due to transfer of electrons from CO_2 to ox-SWCNH annihilates holes which reduces the conductivity, while in later there is increase due to further electron transfer from CO_2 after compensation of hole carriers. Hence addition of CO_2 decreases the electronic conductivity of SWCNHs[2,26].

3.3. Magnetic Properties

Magnetic properties are closely interrelated to electronic properties. Two electronic systems were discovered for dahlia-like SWCNHs in one electron spin resonance (ESR). The first one has an exceptional temperature-activated paramagnetic susceptibility due to 2D graphene like structure at the surface of dahlia-like. The second is due to the chaotic graphitic like interior of dahlia that consist of crushed nanohorns and touching graphene sheets. Hence the susceptibility, composed of localized spins and conduction electrons, is increasing with decreasing temperature until 17K. While below 17K there is a huge suppression of the paramagnetic susceptibility that implies an antiferromagnetic correlation between localized electrons. Also a typical SWCNH consisting of ~1000 carbon atoms with ~ 40nm of length and ~2nm of diameter has at least one unpaired electron spin that may derivate from the electronic structure of the nanohorns tips. It is recommended that the unusual small diamagnetic susceptibility observed for SWCNHs is due to the termination of expected large diamagnetism by Van Vleck paramagnetism[27].

IV. APPLICATIONS OF SINGLE WALLED CARBON NANOHORNS

4.1. Gas storage media

High purity and definite morphology make SWCNHs novel candidates for gas storage like methane and fluorine, as gas molecules can be stored in both cylindrical inner nanospace and interstitial channels. Adsorption of hydrogen on SWCNHs had been investigated experimentally which illustrate that there are two physical adsorption sites on interstitial and internal spaces of SWCNH assemblies. As the temperature decreases hydrogen adsorption density

increases[28]. According to simulations, the hydrogen isotopes are quickly adsorbed in the cone part of SWCNH with a strong potential field. As pressure decreases the difference between amounts of H_2 and D_2 adsorbed increases.

4.2. Adsorption

Noble gases can be adsorbed on SWCNHs like xenon. The adsorption plots of xenon showed that the ability of SWCNHs to adsorb the molecules is greater than that of planar graphite[29]. Experiments demonstrate the presence of interstitial channels between SWCNHs which allowed the Xe gas atoms to penetrate while these channels are too small to allow for Xe penetration[30]. Specific surface area and highest binding energy for SWCNHs indicate their highly desirable properties as an adsorbent.

4.3. Catalyst support

As nanohorns consists of large surface area and the catalyst at molecular level can be integrated into nanotubes in huge amount and simultaneously can be released in necessary rate at particular time. Hence reduction in the frequency and amount of catalyst accumulation can be achieved by using CNHs[31].

4.4. Carriers in drug delivery system

The extensive surface areas and multitudes of horn interstices of SWCNHs make them as promising carriers in drug delivery systems. The well known anti cancer agent cisplatin (CDDP) can also be incorporated into and released from oxSWCNHs[32]. It was found that discharge rate of CDDP from oxSWCNHs in PBS and culture medium was slower but the released CDDP was efficient in terminating the growth of human lung cancer cells.

4.5. Magnetic resonance analysis

Magnetic resonance imaging(MRI) could be used to analyze toxicological hazards in the living body if an MRI agent was attached to SWCNHs[33]. Ultrafine Gd_2O_3 nanoparticles on oxSWCNHs worked as positive MR agent. A sharp bright image was observed still at a low concentration of Gd_2O_3-oxSWCNHs. Super paramagnetic magnetite nanoparticles are also effective agent for MRI.

4.6. Electrochemical applications

As SWCNHs are metal free consequently they are used as electrode materials in electrochemical applications. First SWCNH paste electrode was used for amperometric determination of concentrated hydrogen peroxide(H_2O_2)[34]. Direct growth of SWCNHs on carbon microfiber substrates had been developed for fabrication of free-standing electrodes for electrochemical applications[35]. SWCNHs are also considered as novel material for supercapacitors due to their porous structure and novel physical properties.

4.7. Biosensing applications

SWCNHs can be directly used as biosensor as they are metal free. For the first time they were used to fabricate glucose biosensor by encapsulating glucose oxidase in the Nafion-SWCNHs compound. Such biosensor possessed high sensitivity, low detection limit and good selectivity which offer superior conductivity for electron transfer[36].

4.8. SWCNHs as photovoltaic and photoelectrochemical cells

The metal free SWCNHs with high purity can be used in new photoactive hybrid materials. They constitute an exceptional platform for energy conversion systems to photovoltaics and optoelectronics. When copper (II) terpyridine was coordinated with the –COOH at conical terminals of SWCNHs, a novel SWCNHs-COO-Cu^{II}typ metallo-nanocomplex produced[37]. An electron transferred from the singlet excited state of Cu^{II}typ to SWCNHs due to photo excitation results in one electron reduction of nanohorns with immediate one electron oxidation of the Cu^{II}typ unit.

4.9 Photodynamic therapy

SWCNHs are expected as candidate materials for the photodynamic therapy. These tubules absorb light in the near infrared region and hence annihilate the tumors by photo hyperthermia(PHT) effect. A double photodynamic therapy (PDT) and PHT cancer phototherapy system using a single laser and zinc phthalocyanine (ZnPc) and protein bovine serum albumin (BSA)-supported holey-SWCNHs was fabricated[38]. In this system, ZnPc was the PDT agent, holey-SWCNH was the PHT agent and the BSA improved biocompatibility. The phototherapy effect was confirmed in vitro and in vivo.

4.10 Fuel cell

SWCNHs can be used as a support materials of the catalysts of fuel cells[39,40]. The application requires consistent nanoparticles adsorbed on the SWCNH surface. The catalyst sizes to be about 2 nm, smaller than that supported on the conventional carbon black because there are not only large specific surfaces but also a lot of defective sites or interstitial sites between SWCNH sheaths. The current density of the fuel cell using the catalyst-supported SWCNH electrode was superior than that of catalyst supported carbon black[39].

V. CONCLUSION

Unique structures and high surface area make SWCNHs useful in various applications. Even though the continuous efforts and researches on SWCNHs, the field is still in infancy. Size of holes on SWCNHs can be controlled by changing temperature. Opening and closing of holes make them usable in adsorption, drug carrier and storage. The low toxicities and in vivo anticancer effect oxSWCNHs can be potentially used for clinical purposes. SWCNHs are hypothetically wonderful electrode materials due to defect sites and high purity. SWCNHs present significant

opportunities to nanotechnology which pretense a great challenge for future applications. The flexibility and commercialization will make SWCNHs more dynamic research area.

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