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CARBON NANOHORNS AND THEIR NANOCOMPOSITES: SYNTHESIS, PROPERTIES AND APPLICATIONS. A CONCISE REVIEW

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Abstract. *Single-walled carbon nanohorns (SWCNHs) are a kind of nanocarbon materials consist of horn-shaped sheath aggregate of graphene sheets. SWCNHs are generally synthesized with high yield by CO_2 laser ablation technique of graphite target without a metal catalyst. The SWCNHs reveal interesting properties such as high conductivity, high dispersibility, large specific surface area, etc. Nowadays, SWCNHs and their nanocomposites have been widely investigated for different applications such as energy management system (supercapacitor, photovoltaics, Li-Ion batteries, fuel cell), additive for improvement of electrical and mechanical properties of nanocomposites, electrochemical biosensing, gas adsorption and gas storage, catalyst support, medical (drug delivery system), gas sensing application and so on. The purpose of this paper is to review the recent research on single-walled carbon nanohorns and their nanocomposites including synthesis, properties, covalent and noncovalent functionalization and utilization.*

Keywords: Single-walled carbon nanohorns, laser ablation, functionalization, ethanol sensing, capacitor.

1. Introduction

Along with carbon nanotubes [1], fullerenes [2] and graphene [3, 4] a new nanocarbon material structure, the single walled nanohorns (SWCNHs), were discovered by Iijima in 1998 [5]. Harris, Tsang, Claridge and Green observed in 1994 very similar carbon - based molecular architecture [6]. SWNHs are conical carbon nanostructures constructed from a sp^2 carbon sheet of about 2-5 nm of diameter and 30 to 50 nm long (see Figure 1). Three different types of single-walled carbon nanohorns structure were observed: ‘dahlia-like’, ‘bud-like’ and ‘seed-like’ [7]. Synthesis of nanohorns by CO_2 laser ablation of graphite require no metal catalyst.

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Using this procedure, significant quantities of (SWCNHs) can be produced (approx. 1 kg/day). Thousands of these nanocones can associate to each other to form spherical clusters of 100 nm of diameter.

This structural feature was considered as a significant limitation in functionalization of individual carbon nanohorns. Fortunately, this drawback has recently been overcome by using a new strategy to separate these "dahlia-like" aggregates into individual nanohorns [8]. SWCNHs outstanding properties such as high conductivity, high dispersibility, large specific surface area. Carbon nanohorns are considered as a possible alternative to carbon nanotubes, and graphene, in different applications.

Fig. 1. The structure of a carbon nanohorn.

Currently, SWCNHs and their nanocomposites have been widely investigated for different applications such as design of supercapacitor, solar thermal collectors, photovoltaics, fuel and biofuel cells, biomedical engineering (anticancer drug delivery system), additive for improvement of electrical and mechanical properties of nanocomposites, electrochemical biosensing, gas adsorption, hydrogen and methane storage, catalyst support, photodynamic therapy, gas sensing application [9].

The aim of this concise review is to describe the progress research on single-walled carbon nanohorns and their nanocomposites including synthesis, properties, covalent and noncovalent functionalization and their utilization.

2. Synthesis of pristine carbon nanohorns

Different approaches to synthesize carbon nanohorns such as arc discharge and CO_2 laser ablation have already been reported. The morphology, size and purity of the SWCNHs are modified by varying the working parameters such as voltage, current, pressure, and temperature.

2.1 Arc discharge

One of the most versatile synthetic method of SWCNHs consist of a pulsed arc discharge between pure carbon rods in the atmospheric pressure of air and He and Ar with arcing period of 30 s. Using this synthesis, the purity of formed SWNHs is higher than 90%.

2.2 CO_2 laser ablation of graphite target

Recently, high-yield synthesis of SWCNHs by CO_2 laser ablation of graphite target without a catalyst was performed. A production rate of 1 kg/day single wall carbon nanohorns with high purity (about 95%) was achieved [10, 11]. Absence of catalyst during synthesis is an important advantage in mass- production of SWCNHs and allows formation of pure samples, without any other graphitic structures. CO_2 laser ablation system consists of three chambers, an exchange chamber (where is stores graphite rod), synthesis chamber, and collection chamber. The mean size of SWCNH particles is bigger than those prepared by the arc discharge method [12]. It has clearly been demonstrated that nature and pressure of the buffer gas used has a major impact in the level of purity and morphology of the synthesized SWCNHs. For instance, the SWCNH aggregates exhibit "bud-like'' morphology when He or N_2 were used, while 'dahlia-like' morphology in the case of Ar utilization [13, 14].

H. Wang *et al*. [15] reported on the novel and economical preparation method of single-walled carbon nanohorns (SWCNHs) based on arc discharge between two graphite electrodes submerged in liquid nitrogen. The synthesized spherical aggregates have size in the range of 50÷100 nm and consist of mixture of 'dahlia-like' and 'bud-like'. This synthetic procedure requires only liquid nitrogen and graphite electrodes as materials and direct current power supply and is a less expensive alternative for the preparation of single-walled carbon nanohorns. An identical preparation method can be used to synthesize nano-onions (deionized water is used in this case).

In the last years, other synthetic procedures for SWCNHs have also been developed such as welding arc torch in open air, arc in liquid method, cavity arc jet methods under open-air conditions, leading to various morphologies, sizes and level of purity [16-20].

3. Properties of carbon nanohorns

The distinctive conical structure of SWCNHs drastically influences the electronic properties of this nanocarbonic material. Theoretical calculations were used, and many models were developed to determine the electronic properties, stability and geometry of SWCNHs [21-23].

The electronic properties are strongly interrelated to the magnetic properties in SWCNHs. The magnetic properties of single-wall carbon nanohorns were investigated by static magnetic susceptibility measurements and electron spin resonance (ESR). Bandow et al demonstrated that the individual SWNHs had at least one unpaired electron spin.

Furthermore, the study indicates a value of the diamagnetic susceptibility as the same order of magnitude to those of different fullerenes such as C_{60} and C_{70}, but reveals a value smaller by an order of magnitude than that of randomly oriented graphite [24].

The electronic characteristics of "dahlia-SWCNHs" and oxidized SWCNHs were also investigated by adsorption of O_2 (an electron acceptor) and CO_2 (an electron donor). The increased electronic conductivity with adsorption of CO_2 reveals that "dahlia-SWCNHs" have n-type semiconducting behavior. Oxidized SWCNHs exhibit a pronounced electrical conductivity drop on CO_2 adsorption and almost no change on O_2 adsorption [25].

The Raman spectrum of pristine SWCNHs emphasizes different features from diamond-like amorphous carbon, nano-soot, graphite, glassy carbon. Two bands with almost equal scattering strengths were observed at 1341 cm^{-1} (‘‘D-band’’), and 1593 cm^{-1} (“G-band”) [26]. The increased intensity around the D-band of water soluble SWCNHs compared with pristine SWCNHs suggested the SWCNHs backbone which contains sp^3-hybridized carbon atoms [27, 28].

XRD (X-Ray Diffraction) was proven as useful tool for the investigation of the structural characteristics of pristine SWCNHs. While the interlayer distance of graphite is 0.335 nm, the van der Waals distance of the aggregated SWNHs was calculated as being around 0.4 nm [29].

Individual SWNHs are closed, so the adsorption sites of SWCNHs are located only on the outer surface. When pristine SWNHs are oxidized, the sheaths of the nanohorns are opened and the inside spaces become accessible (holey-SWCNHs).

A different type of molecules such as metal compounds, gases, drug, fullerene, etc. can be trapped in the inside space of SWCNHs and can be released again [30-33].

The SWCNHs can be dispersed in ethanol and other organic solvents more easily than carbon black and/or carbon nanotubes. Due to their hydrophobicity, the pristine SWCNHs did not disperse at all in water [34].

The holey-SWCNHs can be dispersed in water and organic solvents such as ethanol and isopropyl alcohol.

SWCNHs and/or holey-SWCNHs exhibit high conductivity, high dispersibility and high specific surface.

4. Functionalization of carbon nanohorns

Different strategies of SWCNHs functionalization were attempted to modulate their physical and chemical properties or to generate supramolecular aggregates with intriguing properties. There are two major approaches:

- Covalent attachment of organic fragments either to the open conical ends or to the sidewalls of the nanohorns [35, 36];

- Non-covalent interactions based on electrostatic interactions or π–π stacking interactions between SWCNHs and aromatic organic molecules (such as pyrene and derivatives) [37, 38].

4.1 Noncovalent functionalization of SWCNHs

Noncovalent functionalization of SWCNHs has the advantage to preserve π-conjugated system of SWCNHs. Thus, ionic porphyrins such as tetracationic water-soluble porphyrin (H_2P^{4+}) [39] or anionic porphyrin (H_2P^{2-}) [40] were immobilized onto the backbone of SWCNHs (in the latter case noncovalent functionalization is mediated by positively charged pyrene units - Py^+).

Recently, a water soluble colloid nanohybrid was generated through the noncovalent functionalization of SWCNHs using a amphiphilic poly[sodium (2-sulfamate-3-carboxylate) isoprene-b-styrene] block polyelectrolyte [41].

The hydrophobic polymeric unit is immobilized on the carbon nanohorn surface through hydrophobic interactions, while the polyelectrolyte block stabilizes the synthesized hybrid nanoaggregate through electrosteric interactions.

4.2 Covalent functionalization of SWCNHs

Covalent functionalization of carbon nanohorns both to sidewalls and to the open conical ends allows to tune the molecular architecture of SWCNHs to obtain nanocarbonic materials with desirable properties. Furthermore, solubility in water or in organic solvents can be significantly improved by covalent functionalization.

For instance, holes in carbon nanohorns walls can be opened through light-assisted oxidation in the presence of hydrogen peroxide with generation of a lot of carboxylic groups at the hole edges. Besides increased solubility, oxidized carbon nanohorns can react with protein such as BSA [42].

By oxidizing with concentrated nitric acid, Agresti *et al* [43] synthesized carbon nanohorns with increased hydrophilicity and dispersibility in polar solvents. SEM microscopy, XPS, and thermogravimetric analysis were used for investigation of surface damage and oxidation level.

A large number of pyrrolidine units fused to C–C bonds at the side-walls of SWCNHs were grafted through 1,3 -dipolar cycloaddition [35].

Amines can react with pristine SWCNHs sidewalls through nucleophilic addition [9]. Functionalization of SWCNHs can be performed through amidation of the oxidized carbon nanohorns [9]. All these types of functionalizations are depicted in Figure 2.

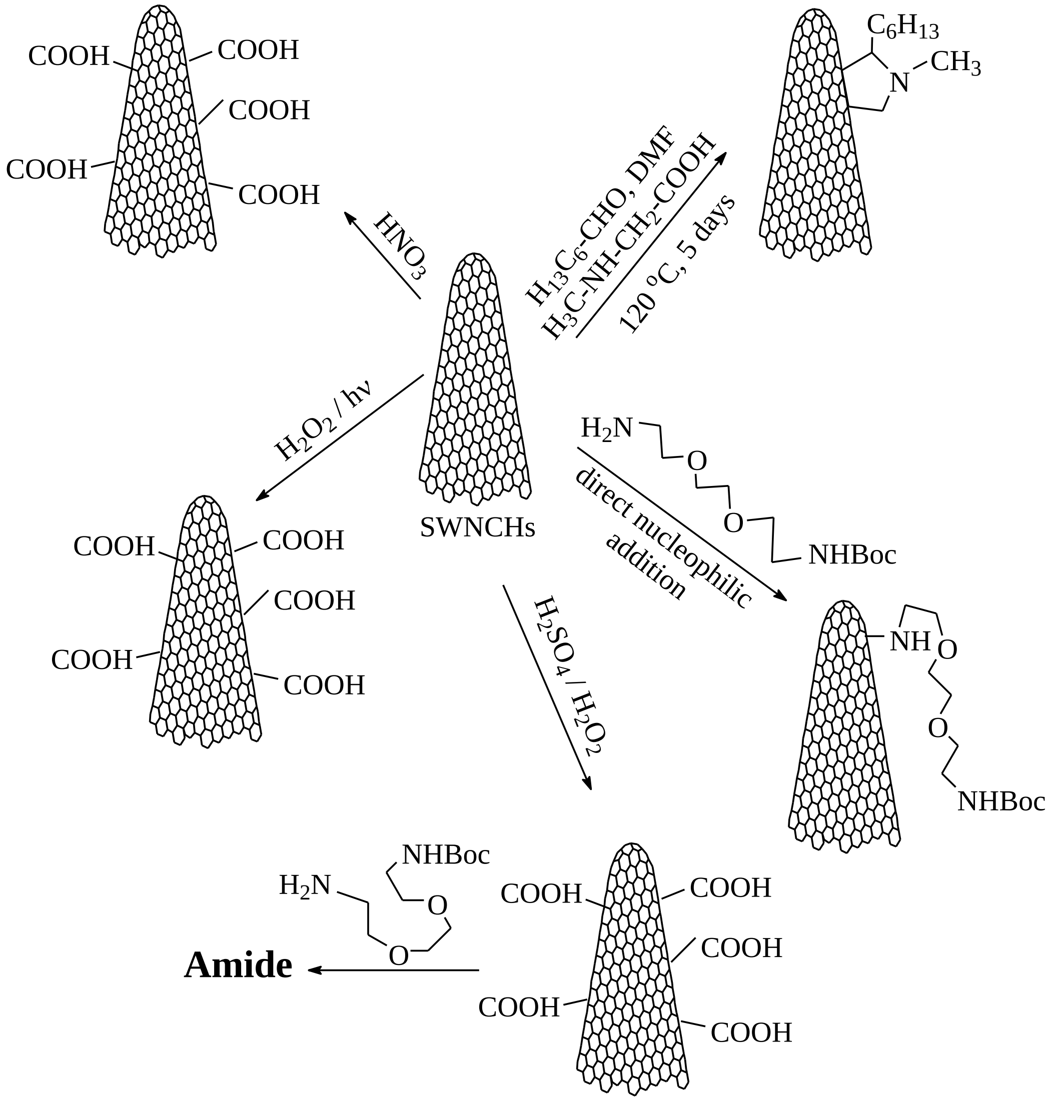

Fig. 2. Different types of covalent functionalization of SWCNHS.

Recently, Rubio *et al* [44] developed covalent functionalization of SWCNHs through the addition of diazonium salts in water and 1,3-dipolar cycloaddition of azomethine ylides by microwave activation. Organic molecules such as amines, thiols, alcohols, different types of porphyrin and pyrene derivatives was attached through the opening of SWCNHs conical ends [45-47].

Voiry *et al* [48] investigated dismantling and individualization of SWCNHs by their reductive dissolution with potassium naphtalenide. The reduced carbon nanohorns are soluble in different solvents such as dimethylsulfoxide, benzonitrile, dimethylformamide, acetone, acetonitrile and N-methylpirrolidone. Furthermore, reduced CNHs can be reoxidized in the presence of dried air or can react with different alkyl or aryl iodide (as depicted in Figure 3).

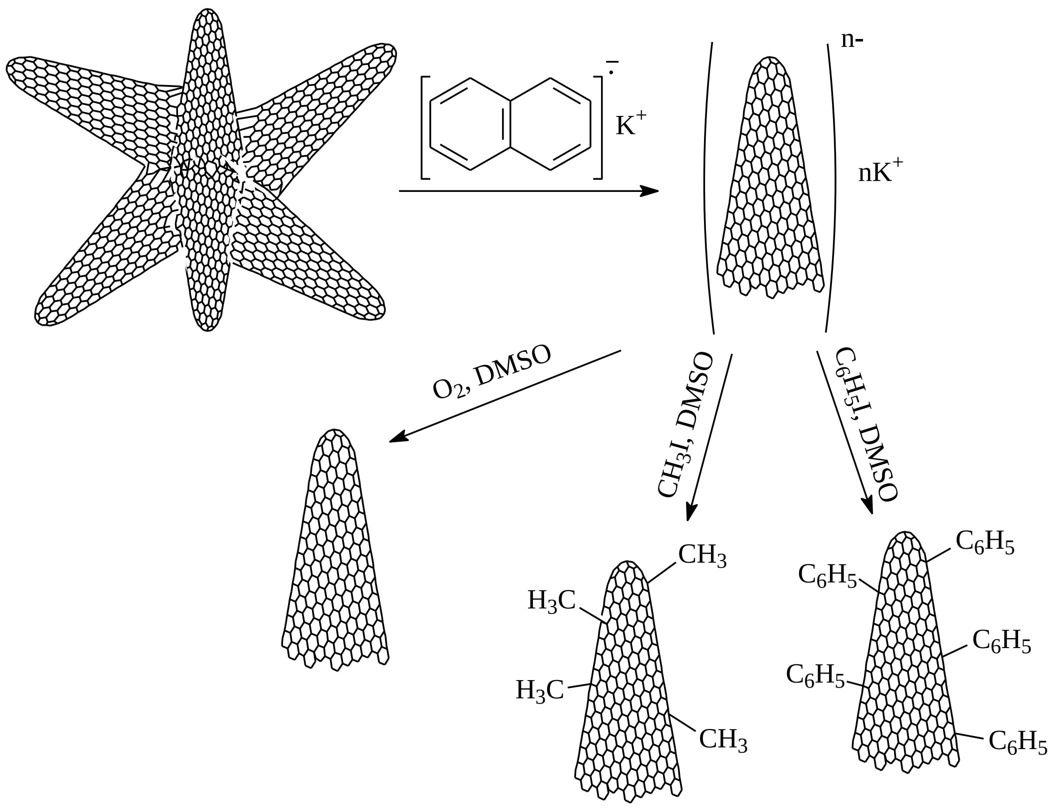

Fig. 3. Reductive dismantling of carbon nanohorns, reoxidation and covalent functionalization of the reduced carbon nanohorns.

5. Applications of carbon nanohorns

Recently, SWCNHs have attracted a great deal of attention for various applications due to their outstanding features:

- versatile synthetic methods;
- available in high purity, no metal catalyst is involved in their synthesis;
- the chemical, physical, and electronic properties of SWCNHs can be modulated by covalent and noncovalent functionalization in order to obtain novel materials with desirable properties for appropriate applications;

- large surface area (from 400 m^2/g from carbon nanohorns - as grown to 1400 m^2/g for oxidized carbon nanohorns) [49, 50].
- the facile processability of single wall carbon nanohorns in water and various organic solvents affords generation of films with different morphology, porosity, and texture [51-52]

5.1 Carbon nanohorns as gas storage media

Due to their cylindrical structure and interstitial sites, SWCNHs and holey-SWCNHs are promising materials for storage of gases such as hydrogen, methane and fluorine [31, 53 - 55].

Murata *et al* found that the dispersion of lanthanide nitrate in the compressed SWCNHs (0.1 mmol/g SWCNHs) improve the methane adsorbtion through charge transfer effects [56]. Sano *et al* demonstrated that the amount of H_2 absorbed by single-walled carbon nanohorns containing Pd–Ni alloy nanoparticles (Pd–Ni/SWCNHs) was larger than the combined absorption contributed by Pd–Ni alloy and SWCNHs [57].

5.2 Applications of carbon nanohorns in pharmacy and medicine

Due to its low cytotoxicity and cylindrical structure, holey-SWCNHs were proven as an effective carrier material for drug delivery system [58].

Ajima *et al* [59] demonstrated that oxidized single-wall carbon nanohorns incorporate cisplatin, a well- known anticancer agent. The drug is released in aqueous environments from the carbonaceous tubules of oxidized single-wall carbon nanohorns, being effective in human lung cancer cells.

Murakami *et al* [60] investigated the ability of as-grown SWCNHs and ox - SWCNHs to act as carriers for dexamethasone, one of the most used antiinflammatory glucocorticoid.

After trapping, dexamethasone- oxidized single-wall carbon nanohorns complex slowly release the drug in cell cultural medium.

Oxidized single-walled carbon nanohorns were used as carriers for prednisolone, an anti-inflammatory glucocorticoid drug.

Nakamura *et al* [61] showed that the quantity of the adsorbed is strongly correlated to the numbers and sized of holes on the ox-SWNHs.

In order to increase their solubility in water, polyethylene glycol is sometimes grafted on the hydrophobic surface of SWCNHs [62].

Other biomedical applications of carbon nanohorns and their derivatives include magnetic resonance analysis and photodynamic therapy [63, 64].

5.3 Carbon nanohorns in energy applications

Due to its high electron, heat and phonon transport, high surface area, high nanoporosity, carbon nanohorns has found various applications in the field of energy conversion.

Thus, SWCNHS and their derivatives can be used in:

- **Catalyst support or catalyst in design of fuel cells**. A large number of studies regarding deposition of Pt or metal alloys catalyst on SWCNHs used in fuel cells have been reported [65, 66]. Moreover, N-doped SWCNHs (synthesized from SWCNHs and urea at 800°C) was found to be more efficient than Pt in proton exchange membrane fuel cells [67].
- **Design and construction of solar thermal collector** [68].
- **Design and construction of dye-sensitized solar cells.** Different light absorbers such as porphyrin functionalized SWCNHs (SWCNHs-H_2P), SWCNHs-Zn porphyrin supramolecular assembly (SWCNHs - ZnP) were used in design of dye-sensitized solar cells (DSCs) with satisfactory results [69]. Furthermore, SWCNHS were used as counter electrode [70].
- **Construction of recheargeable batteries.** SWCNHs composite have been used as anode materials in Li-Ion and *Li-S* rechargeable batteries [71,72].
- **Construction of supercapacitors**. Oxidized SWCNHs, SWCNH-polymer composite, SWCNH-SWCNT, SWCNH-graphene (as electrodes, thin film, etc.) were used in design and construction of supercapacitors [73, 74].

5.4 Carbon nanohorns in gas sensing

Sano et al fabricated chemiresistive gas sensor for ammonia and ozone detection at room temperature using a single-walled carbon nanohorns (SWCNHs) as sensing layer.

It was demonstrated that the electrical resistance of the SWCNHs film decreases with adsorption of O_3, while the adsorption of NH_3 increases the resistance of carbonaceous sensing layer [75].

A novel chemiresistive ethanol sensor based on CuO/oxidized carbon nanohorns as sensing layer was recently proposed [76].

The ethanol sensor includes a dielectric substrate such as quartz, electrodes (made up of gold or platinum) and the sensing layer.

Electrodes can be linear, planar (as in Figure 4) or can have interdigitated configuration (show in Figure 5).

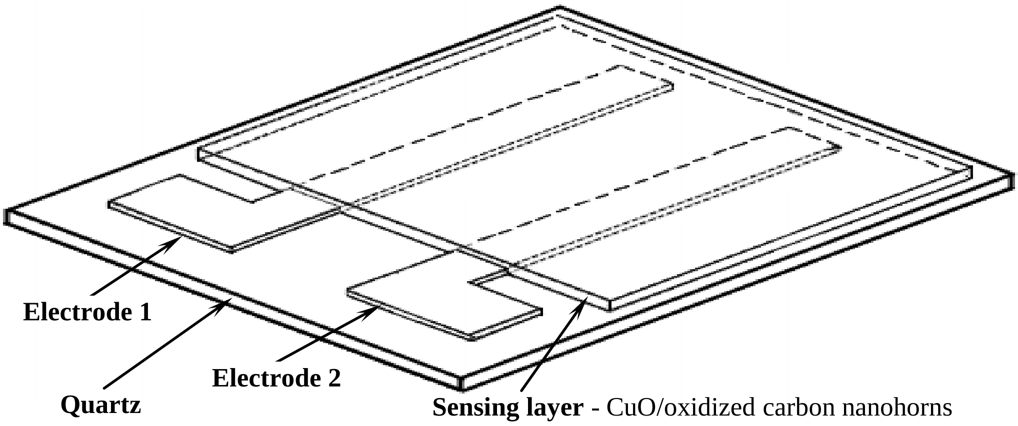

Fig. 4. The structure of the sensors with linear electrodes.

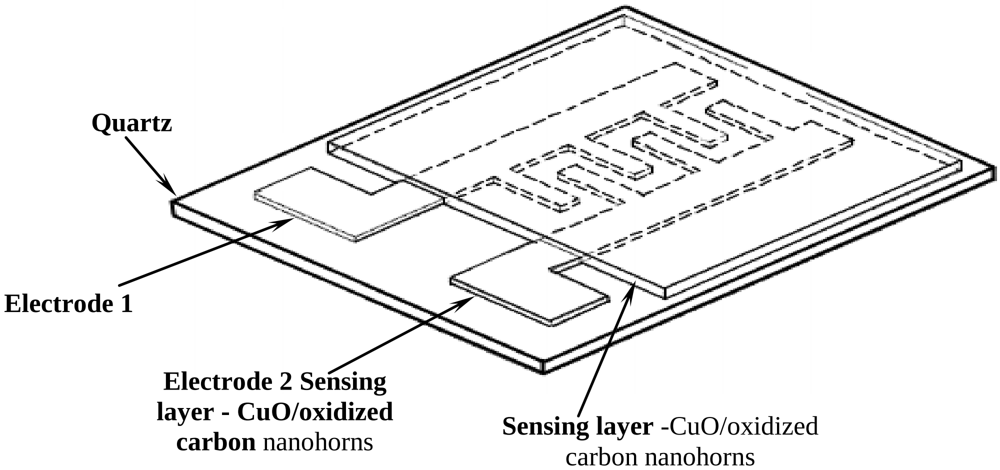

Fig. 5. The structure of the sensor with interdigitated electrodes.

The sensing layer was synthesized through sol gel method using, alternatively, poly(2 ethyl- 2- oxazoline), depicted in Figure 6, and polyethylene glycol, shown in Figure 7, as stabilizing agents.

The detailed processes are depicted in Figures 8 and 9.

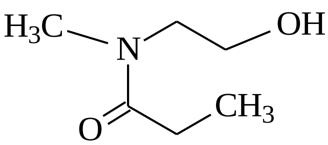

Fig. 6. The structure of a poly(2-etil-2-oxazoline).

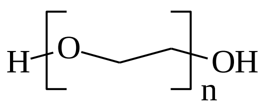

Fig. 7. The structure of polyethylene glycol.

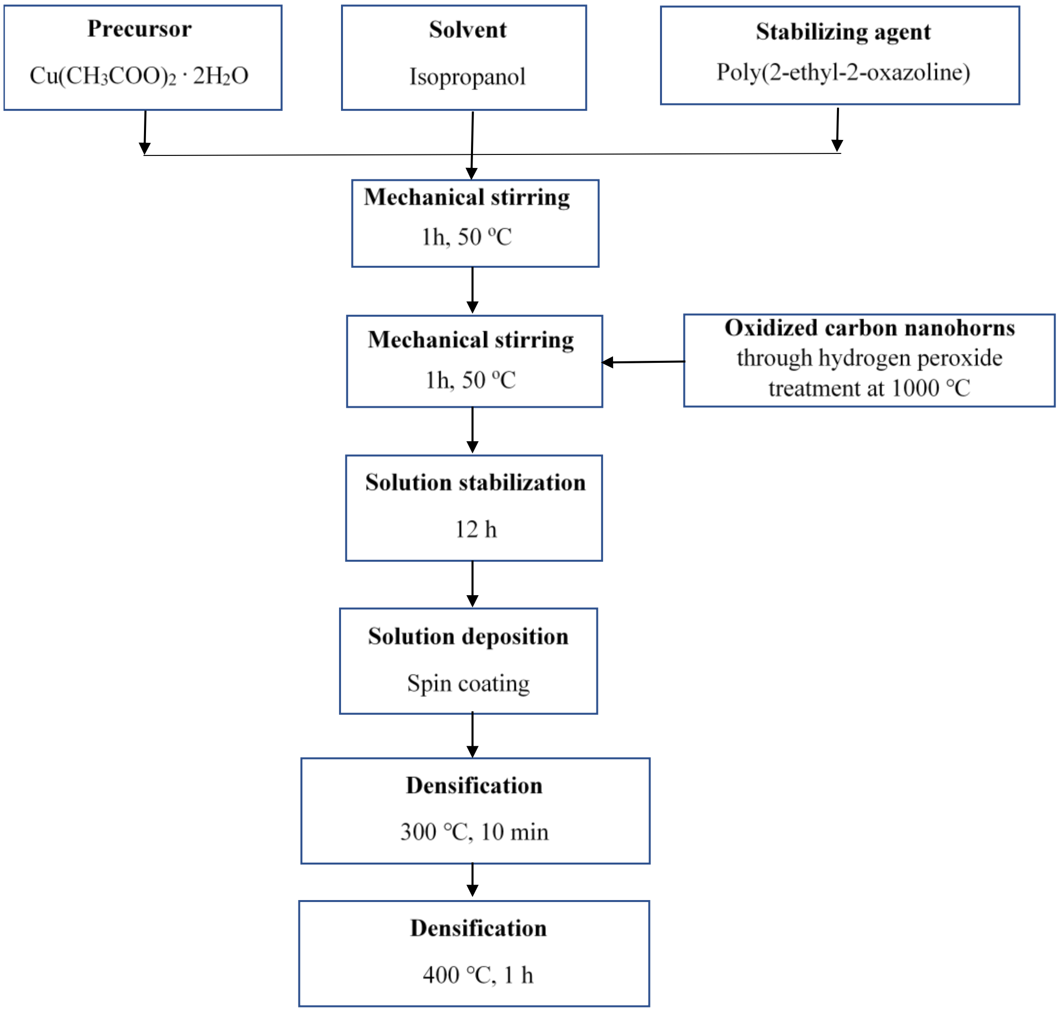

Fig. 8. Synthesis of CuO/ oxidized carbon nanohorns - based sensing layer using poly(2 ethyl- 2- oxazoline) as stabilizing agent.

A novel chemiresistive ethanol sensor, using TiO_2/La_2O_3 /oxidized carbon nanohorns as sensing layer, was introduced by Serban *et al*. [77].

The proposed sensor consists of a dielectric substrate such as glass, electrodes (aluminum, copper, chromium, etc.) and the ethanol-sensing layer obtained by drop casting and/or spin coating method.

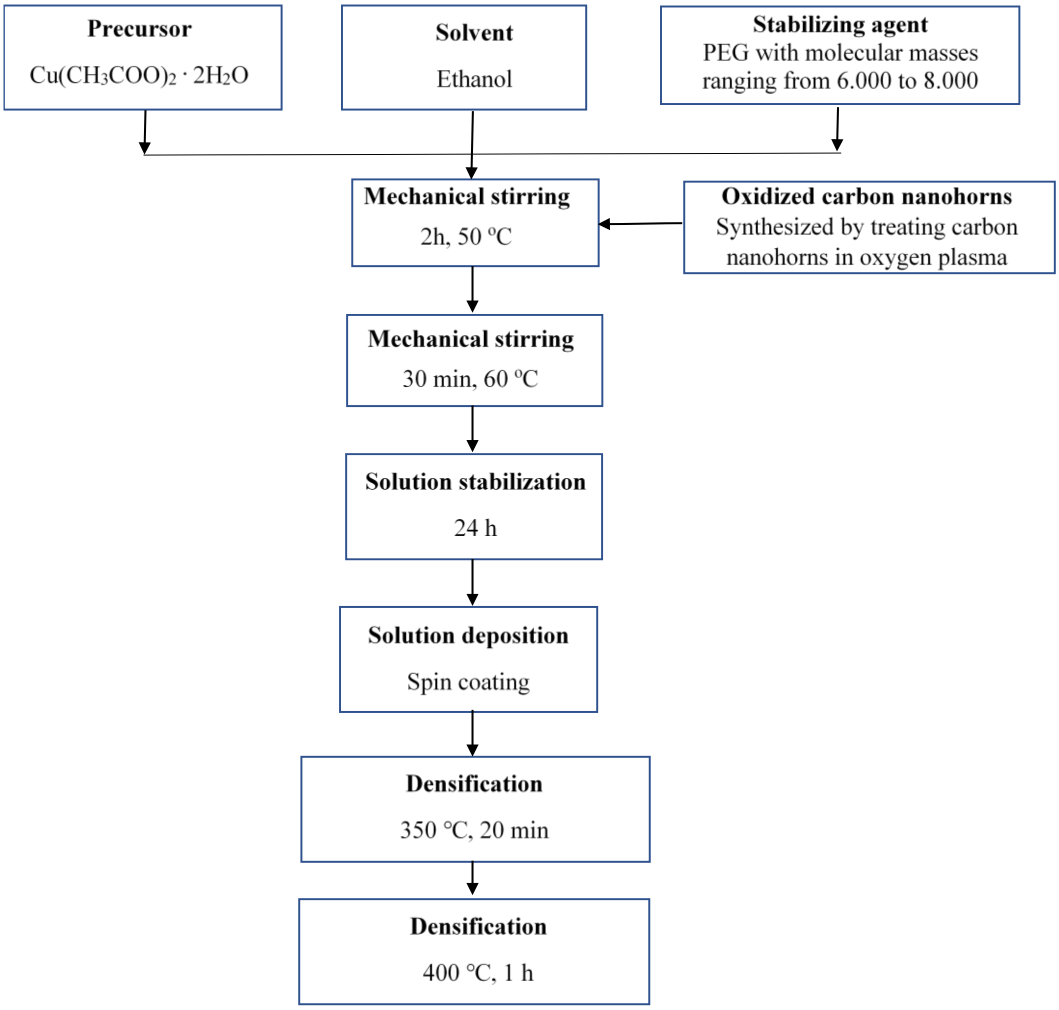

Fig. 9. Synthesis of CuO/ oxidized carbon nanohorns - based sensing layer using poly(2 ethyl- 2- oxazoline) as stabilizing agent.

Synthesis of oxidized nanohorns is achieved by two different methods, using oxygen plasma treatment and oxidation of H_2O_2 to 100^{o}C, respectively, of pristine carbon nanotubes.

The synchronous use of La_2O_3 and oxidized carbon nanotubes, along with TiO_2, deposited on a dielectric substrate, gives the sensor some significant advantages: improved mechanical properties and sensitivity of the touch layer, increased surface area of the sensitive layer, detection over a wide temperature range – up to 400^{o}C), rapid response to variation in ethanol concentration, selectivity, thermal stability up to 400^{o}C, low weight.

The synthesis of sensing layers is depicted in Figures 10 and 11.

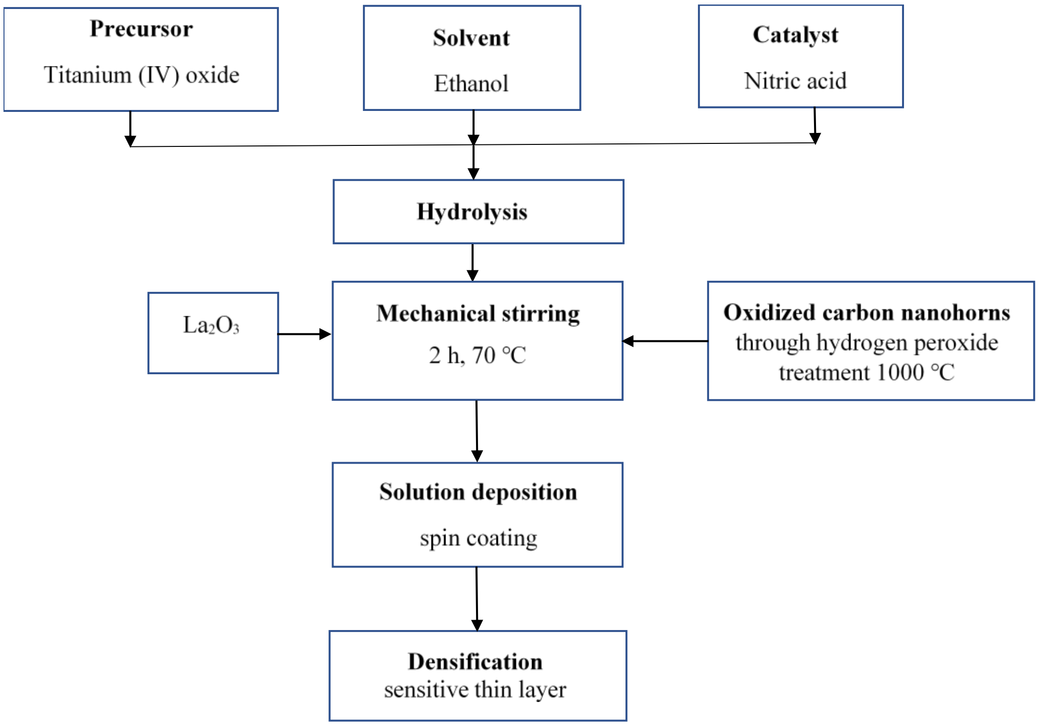

Fig. 10. Synthesis of TiO_2 / La_2O_3 /oxidized carbon nanohorns sensing layer.

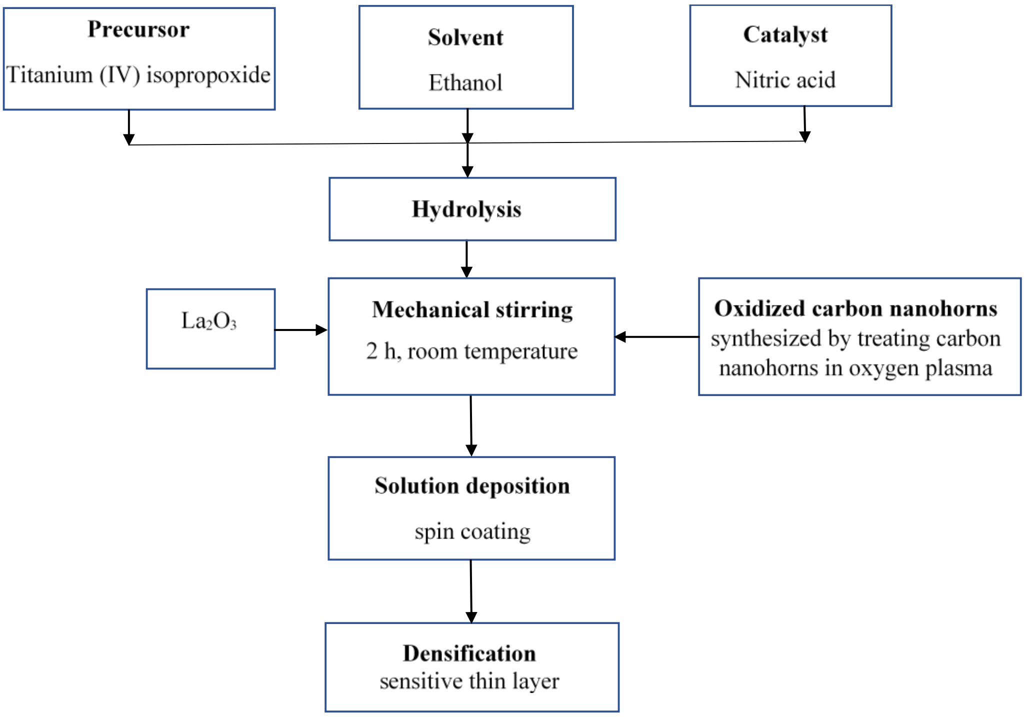

Fig. 11. Synthesis of TiO_2 / La_2O_3 /oxidized carbon nanohorns sensing layer.

Sm_2O_3/ oxidized carbon nanohorns Gd_2O_3/ oxidized carbon nanohorns, In_2O_3/ oxidized carbon nanohorns are other options to detect ethanol at room temperature using a chemiresistive sensors [78].

6. Conclusions

Single-walled carbon nanohorns (SWCNHs) are a type of of carbonaceous material consist of horn-shaped sheath aggregate of graphene sheets. SWCNHs differ significantly from carbon nanotubes in that they have long cone-shaped tips with cone angles of about 20°. SWCNHs are generally synthesized in high yield by CO_2 laser ablation technique of graphite target without a metal catalyst. The chemical, physical, and electronic properties of SWCNHs can be tuned by covalent and noncovalent functionalization in order to synthesize novel derivatives with desirable properties for appropiate applications.

The SWCNHs reveal interesting properties such as high conductivity, high dispersibility, large specific surface area, high nanoporosity, etc. Nowadays, SWCNHs and their nanocomposites have been widely investigated for different applications such as energy management system (supercapacitors, dye- sensitized solar cells, Li-S recheargeable batteries, fuel cells), additive for improvement of electrical and mechanical properties of nanocomposites, electrochemical biosensing, gas adsorption and gas storage, medical (drug delivery system, magnetic resonance analysis and photodynamic therapy), gas sensing application and so on.

SWCNHs and novel SWCNH-based hybrid materials offer significant opportunities to basic science and nanotechnology.

R E F E R E N C E S

[1] S. Iijima, and T. Ichihashi, *Single-shell carbon nanotubes of 1-nm diameter*, Nature, **363 (6430),** 603 (**1993**).

[2] H. W Kroto, *The stability of the fullerenes Cn, with n= 24, 28, 32, 36, 50, 60 and 70,* Nature, **329 (6139),** 529 (**1987**).

[3] Nair *et al*, *Fine structure constant defines visual transparency of graphene*, Science, **320 (5881),** 1308-1308, (2008).

[4] X. Li *et al*, Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science*, **324 (5932),** 1312-1314, (**2009**).

[5] S. Iijima *et al*, *Nano-aggregates of single-walled graphitic carbon nano-horns*, Chemical Physics Letters, **309 3-4**, 165-170, (**1999**).

[6] P.J.F. Harris et al, *High-resolution electron microscopy studies of a microporous carbon*, J Chem Soc, Faraday Trans. **90 (18)**, pp. 2799–2802, (**1994**).

[7] S.Zhu and G. Xu, *Single-walled carbon nanohorns and their applications, Nanoscale*, **2 (12)**, 2538-2549, (**2010**).

[8] N. Karousis et al, *Structure, properties, functionalization, and applications of carbon nanohorns,* Chemical reviews, **116 (8)**, 4850-4883 (**2016**).

[9] C T. Cioffi, *Functionalization and application of carbon nanohorns and carbon onions*, PhD thesis (**2008**). https://www.openstarts.units.it/handle/10077/2614

[10] T. Azami et al, *Large-scale production of single-wall carbon nanohorns with high purity*, The Journal of Physical Chemistry C, **112 (5),** 1330-1334, (**2008**).

[11] S. Iijima et al, Nano-aggregates of single-walled graphitic carbon nano-horns. *Chemical Physics Letters* **309.3-4**, 165-170, (**1999**).

[12] T. Yamaguchi et al, *Synthesis of carbon nanohorn particles by simple pulsed arc discharge ignited between pre-heated carbon rods*". Chem. Phys. Lett. **389**: 181–185, (**2004**).

[13] D. Kasuya et al, *J. Phys. Chem. B*, 2002, **106**, 4947–4751, (**2002**).

[14] T. Azami et al, *Carbon*, 2007, **45**, 1364–1369, (**2007**).

[15]. H. Wang et al, *Large-scale synthesis of single-walled carbon nanohorns by submerged arc*, Nanotechnology, **15(5)**, 546, (**2004**).

[16] M. Ikeda et al, Preparation of carbon nanohorn aggregates by cavity arc jet in open air, *Japanese journal of applied physics*, **41(7B),** L852, (**2002**).

[17] H. Takikawa et al, *Phys. B*, **323**, 277–279, (**2002**).

[18] T. Yamaguchi, *Chem. Phys. Lett.*, 2004, **389**, 181–185, (**2004**).

[19] N. Sano et al *Carbon*, 2004, **42**, 686–688, (**2004**).

[20] N. Sano, *J. Phys. D: Appl. Phys.*, 2004, **37**, L17–L20, (**2004**).

[21] S.Gara *et al*, Electronic properties of carbon nanohorns studied by ESR, Phys. Rev. B. **62 (24):** 17115–17119, (**2000**).

[22]. S. Berber *et al*, *Electronic and Structural Properties of Carbon Nano-horns*, Phys. Rev. B. **64 (4):** R229, (**2008**).

[23] D.V *et al*, *Electronic Structure of Carbon Nanohorns near the Fermi Level*. JETP Lett. **79 (11):** 532–536, (**2004**).

[24] S. Bandow *et al*, *Unique magnetism observed in single-wall carbon nanohorns*, Applied Physics A, **73(3),** 281-285, (**2001**).

[25] K. Urita *et al*, *Effects of gas adsorption on the electrical conductivity of single-wall carbon nanohorns,* Nano letters, **6(7),** 1325-1328, (**2006**).

[26] S. Bandow *et al*, *Evidence for anomalously small charge transfer in doped single-wall carbon nanohorn aggregates with Li, K and Br*, Appl. Phys. A: Mater. Sci. Process., **71**, 561–564, (2000).

[27] S Utsumi *et al*, *Direct evidence on C− C single bonding in single-wall carbon nanohorn aggregates*, Phys.Chem. C **111**, 5572, (**2007**).

[28] D. Kumar *et al*, *Investigation of pristine and functionalized single- walled carbon nanohorns for phosphor applications*, Digest Journal of Nanomaterials and biostructures, **9(4),** 1713-1727, (**2014**).

[29] S. Bandow *et al, Interlayer spacing anomaly of single-wall carbon nanohorn aggregate,* Chem. Phys. Lett., 2000, **321**, 514–519 , (**2000**).

[30] E. Bekyarova *et al*, *Single-wall nanostructured carbon for methane storage*, J. Phys. Chem. B, **107,** 4681, (**2003**).

[31] Y. Hattori *et al*, *Direct thermal fluorination of single wall carbon nanohorns*, J. Phys. Chem. B, **108,** 9614, (**2004**).

[32] T. Murakami *et al*, *Solubilization of single-wall carbon nanohorns using a PEG-doxorubicin conjugate*, Mol Pharm. **3**, 407–414, (**2006**).

[33] J. X. Xu et al, *Single wall carbon nanohorn as a drug carrier for controlled release,* Chem. Phys. Lett. **461 (4–6):** 189–192, (**2008**).

[34] https://www.sigmaaldrich.com/technical-documents/articles/technology-spotlights/single-walled-carbon-nanohorns.html

[35] N. Tagmatarchis *et al*, *Functionalization of Carbon Nanohorns with Azomethine Ylides: Towards Solubility Enhancement and Electron-Transfer Processes*, Small, **2**, 490, (**2006**).

[36] C. Cioffi *et al*, *Functionalisation of carbon nanohorns*, Chem. Commun. **2129**, (**2006**)

[37] G. Pagona *et al*, Cone-end functionalization of carbon nanohorns, Chem. Mater. **2006**, **18**, 3918, (2006)

[38] I. D. Petsalakis *et al*, *Unbalanced strain-directed functionalization of carbon nanohorns: A theoretical investigation based on complementary methods*, Chem. Phys. Lett. **429**, 194, (**2006**).

[39] G. Pagona *et al*, *Electronic interplay on illuminated aqueous carbon nanohorn− porphyrin ensembles*. J. Phys. Chem. *B*, **110**, 20729–20732, (**2006**).

[40] G. Pagona *et al*, *Aqueous carbon nanohorn–pyrene–porphyrin nanoensembles: controlling charge-transfer interactions*, Diamond Relat. Mater. **16**, 1150–1153, (**2007**).

[41] G. Mountrichas *et al*, *Solubilization of carbon nanohorns by block polyelectrolyte wrapping and templated formation of gold nanoparticles*, J. Phys. Chem. C, **113**, 5444–5449, (**2009**).

[42] M. Zhang et al, *Light-assisted oxidation of single-wall carbon nanohorns for abundant creation of oxygenated groups that enable chemical modifications with proteins to enhance biocompatibility*, ACS Nano, **1(4),** 265-272, (**2007**).

[43] F. Agresti *et al*, *Surface oxidation of Single Wall Carbon Nanohorns for the production of surfactant free water-based colloids,* Journal of colloid and interface science, **514**, 528-533, (**2018**).

[44] N. Rubio *et al*, *Efficient functionalization of carbon nanohorns via microwave irradiation,* Journal of Materials Chemistry, **19(25),** 4407-4413, (**2009**).

[45] G. Pagona *et al*, *Covalent functionalization of carbon nanohorns with porphyrins: nanohybrid formation and photoinduced electron and energy transfer*. Adv. Funct. Mater., **17**, 1705–1711, (**2007**).

[46] G. Pagona *et al*, *Characterization and photoelectrochemical properties of nanostructured thin film composed of carbon nanohorns covalently functionalized with porphyrins*, J. Phys. Chem. *C*, **112**, 15735–15741, (**2008**).

[47] A. S. D. Sandanayaka *et al, Photoinduced electron-transfer processes of carbon nanohorns with covalently linked pyrene chromophores: charge-separation and electron-migration systems.*, J. Mater. Chem., **17**, 2540–2546, (**2007**).

[48] D. Voiry *et al*, *Reductive dismantling and functionalization of carbon nanohorns*, Chemical Communications, *51*(24), 5017-5019, (2015).

[49] https://www.sigmaaldrich.com/catalog/product/aldrich/804118?lang=en&region=RO

[50] https://www.sigmaaldrich.com/catalog/product/aldrich/804126?lang=en&region=RO

[51] S. Y Zhu *et al, Simultaneous voltammetric determination of dihydroxybenzene isomers at single-walled carbon nanohorn modified glassy carbon electrode*, Sens. Actuators B **198**, 388–394, (**2014**).

[52] S.Y Zhu *et al*, *Electrochemical behavior and voltammetric determination of l-tryptophan and l-tyrosine using a glassy carbon electrode modified with single-walled carbon nanohorns*. Microchim. Acta **2014**, *181*, 445–451, (**2014**).

[53] S. Utsumi *et al*, Porosity and Adsorption Properties of Single-Wall Carbon Nanoborn, *Novel Carbon Adsorbents*, 1st ed.; Tascón, J.M.D., Ed.; Elsevier: Kidlington, Oxford, UK, Chapter 13; pp. 401–433, (**2012**).

[54] G. Chen *et al*, *Theoretical investigation of hydrogen storage ability of a carbon nanohorn*, Comput. Mater. Sci., *49*, S378–S382, (**2010**).

[55] C. Pagura *et al*, *Large Scale and Low Cost Production of Pristine and Oxidized Single Wall Carbon Nanohorns as Material for Hydrogen Storage*, Nanosci. Nanotechnol. Lett., *4*, 160–164, (**2012**).

[56] K. Murata *et al*, *The Use of Charge Transfer to Enhance the Methane-Storage Capacity of Single-Walled, Nanostructured Carbon*., Adv. Mater., **16**, 1520–1522, (**2004**).

[57] N. Sano *et al*, *Hydrogen Storage in Porous Single-Walled Carbon Nanohorns Dispersed with Pd-Ni Alloy Nanoparticles.* J. Phys. Chem. C, **118,** 3402–3408, (2014).

[58] J. Xu *et al*, *Single wall carbon nanohorn as a drug carrier for controlled release*. Chem Phys Lett., **461**:189–192, (**2008**).

[59] K. Ajima, *et al*, *Enhancement of in vivo anticancer effects of cisplatin by incorporation inside single-wall carbon nanohorns, Mol. Pharm.* **2005**, *2*, 475, (**2005**).

[60] T. Murakami *et al*, *Drug-loaded carbon nanohorns: adsorption and release of dexamethasone in vitro,* Mol. Pharm., **1,** 399, (**2004**).

[61] M. Nakamura *et al*, *Single-walled carbon nanohorns as drug carriers: adsorption of prednisolone and anti-inflammatory effects on arthritis*, Nanotechnology, **22**:465102, (**2011**).

[62] S. Matsumura *et al*, *Prevention of Carbon Nanohorn Agglomeration Using a Conjugate Composed of Comb-Shaped Polyethylene Glycol and a Peptide Aptamer,* Molecular Pharmaceutics, **6 (2):** 441–447, (**2009**).

[63] B.P Jiang *et al*, *One-step preparation of a water-soluble carbon nanohorn/phthalocyanine hybrid for dual-modality photothermal and photodynamic therapy*, ACS applied materials & interfaces, **6(20),** 18008-18017, (**2014**).

[64] J. Miyawaki *et al*, *Synthesis of ultrafine* Gd_2O_3 *nanoparticles inside single-wall carbon nanohorns.* The Journal of Physical Chemistry B, **110(11),** 5179-5181, (**2006**).

[65] T. Yoshitake *et al. Preparation of fine platinum catalyst supported on single-wall carbon nanohorns for fuel cell application*. *Phys. B*, **323,** 124–126, (**2002**).

[66] N. Sano *et al*, *One-step synthesis of Pt-supported carbon nanohorns for fuel cell electrode by arc plasma in liquid nitrogen.* Mater. Chem. Phys., **99,** 447–450, (**2006**).

[67] G. Ciric-Marjanovic *et al*, *One-dimensional nitrogen-containing carbon nanostructures*. Prog. Mater. Sci., **69,** 61–182, (**2015**).

[68] E. Sani *et al*, *Carbon nanohorns-based nanofluids as direct sunlight absorbers*, Opt. Express, **18,** 5179–5187, (**2010**).

[69] M. Vizuete *et al*, *A Carbon Nanohorn-Porphyrin Supramolecular Assembly for Photoinduced Electron-Transfer Processes.* Chem. A, **16,** 10752–10763, (**2010**).

[70]. R. Cruz *et al*, *Use of single-wall carbon nanohorns as counter electrodes in dye-sensitized solar cells*. Int. J. Energy Res., **37,** 1498–1508., (**2013**).

[71] Y. Zhao *et al*, *A nanocomposite of* SnO_2 *and single-walled carbon nanohorns as a long life and high capacity anode material for lithium ion batteries*, RSC Adv., *1*, 852–856, (**2011**).

[72] W. Wu *et al*, Single-walled carbon nanohorns with unique horn-shaped structures as a scaffold for lithium-sulfur batteries. *RSC Adv.*, *4*, 28636–28639, (**2014**).

[73] C.M Yang *et al*, *Nanowindow-regulated specific capacitance of supercapacitor electrodes of single-wall carbon nanohorns*. J. Am. Chem. Soc., *129*, 20–21, (**2007**).

[74] S. Maiti *et al*, *Polyaniline integrated carbon nanohorn: A superior electrode materials for advanced energy storage*, Express Polym. Lett. , *8*, 895–907, (**2014**).

[75] N Sano *et al*, *Gas sensor using single-wall carbon nanohorns,* Advanced power technology, **18(4)**, p 455-466, (**2007**).

[76] B. Serban *et al*, *Strat senzitiv pentru senzor de etanol si procedeu de obtinere a acestuia*, Patent Application, OSIM, Romania, A/00228, 28.03.**2018**.

[77] B. Serban *et al*, *Senzor chemirezistiv de etanol*, Patent Application, OSIM, Romania, A/00232, 28.03 **2018**.

[78] B. Serban *et al*, *Senzor de etanol si procedeu de obtinere a acestuia*, Patent Application, OSIM, Romania, A/00233, 28.03 **2018**.