Introduction

Carbon Nanohorns - CNH were first discovered in Japan in year 1998 by Prof. Iijima's team. Like Carbon Nanotubes, CNTs, they exhibit the same graphitic carbon structure. Single-walled nanohorns (SWNHs) are made of 2-20 nm wide and 25 to 150 nm long tubes which are closed at one end by a cone - the most appropriate shape comparison would be that of a nano-sized sewing thimble. The CNH aggregate to form agglomerates (secondary particles) of about 100 nm to some µm size. CNH are high purity products and can now be produced and supplied in industrial quantities by eenanoTech Ltd./ Japan and TIE GmbH/ Germany.

Structural features

Carbon Nanohorns (CNH) consist of 2-20 nm diameter, 30-150 nm long cone-shaped carbon structures. The sharpest cone-tip has exactly five pentagonal carbon rings.
Single-walled Nanohorns (SWCNH) were detected and described in the late 1990th in aggregated structures, where 3 types have been distinguished: (petal-like) dahlia-like, bud-like and seed-like. It seems that the seed-like type is quite rare, but it can be said that the type is influenced by the CNH synthesis parameters.
The first type has a structure in which the SWNHs are oriented like petals of dahlias (Fig. 1a and 1b), whereas the second type is composed in spherical round aggregates (Fig. 1c and 1d).

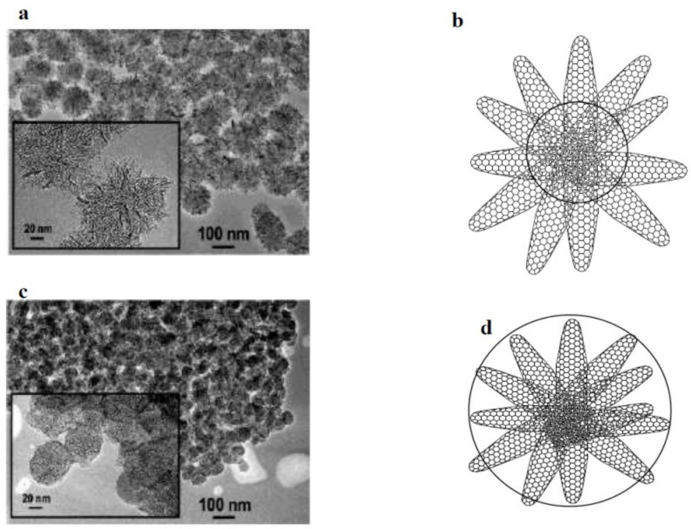
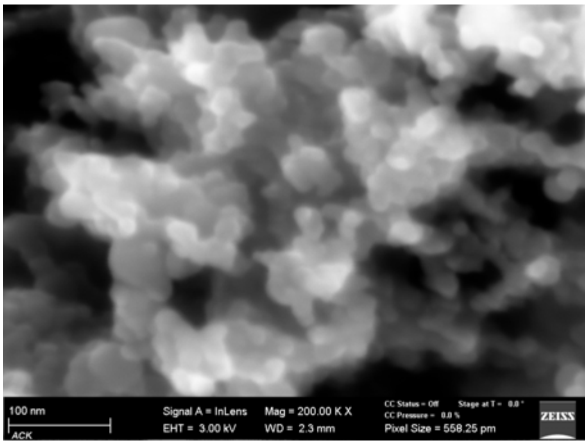


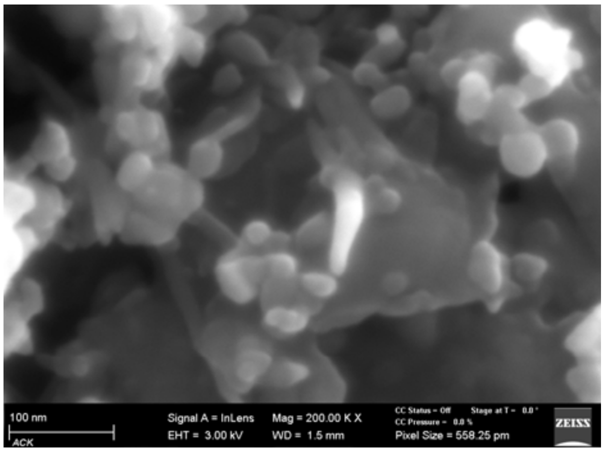
Figure 1: (a) TEM-photograph, (b) schematic representation of dahlia-like SWNH
(c) TEM-photograph, (d) schematic representation of bud-like SWNH [1]

Research tends to be focussed on dahlia-type CNH, because they can be produced in larger quantities in high quality and different applications were predicted, such as methane storage, hydrogen-deuterium separation, fuel-cells, synthesis of hydrogen from methane and water vapour, capacitors and pharmaceutical therapy.

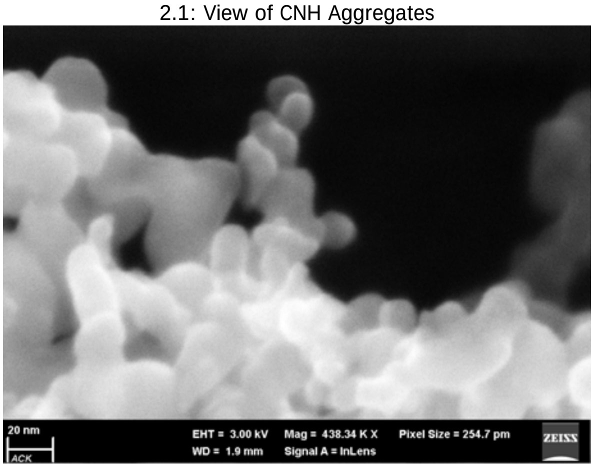
The dahlia-type aggregates are spherical structures as shown in Fig. 1 a. Individual cone angles are about 20°, which implies pentagonal carbon rings as tubule termination structure. The diameters of the individual tubules are about 2 nm at the closed end and larger at the open end.



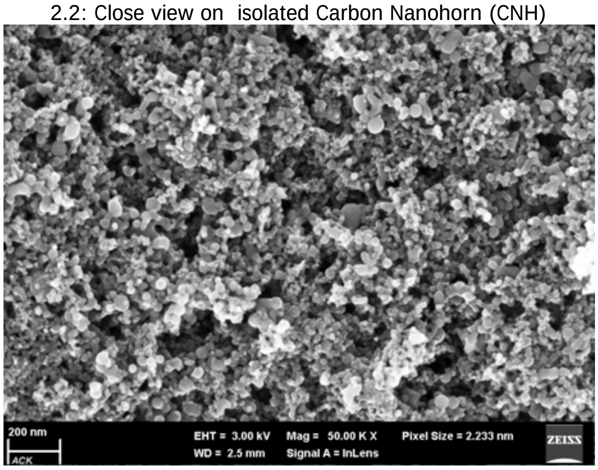
2.1: View of CNH Aggregates



2.2: Close view on isolated Carbon Nanohorn (CNH)

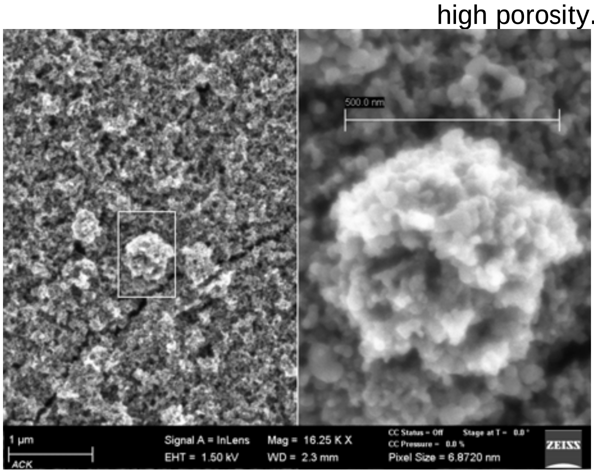


2.3 High resolution picture of Type A CNH powder

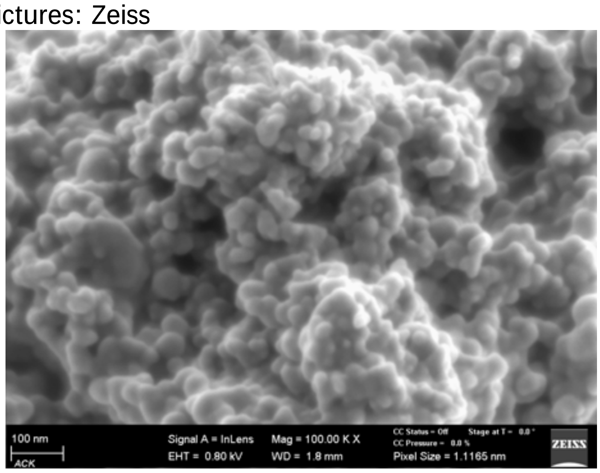


2.4 CNH-layer on bucky paper.

Figures 2a: Thanks to their shape, the CNH-Aggregates create a specific surface structure and a very high porosity. Pictures: Zeiss



2.5 Typical spherical CNH-aggregate



2.6 CNH aggregates (Type B) in varnish matrix.

Figures 2b: Thanks to their shape, the CNH-Aggregates create a specific surface structure and a very high porosity. Pictures: Zeiss

CNH are stable, strong and hard materials. As single walled carbon nanostructures they have strong mechanical strength, good electrical and thermal conductivity at nano-scale. The very strong Van-der-Waals forces between the CNH result in a spontaneous three-dimensional arrangement into spherical aggregates. In difference to Carbon NanoTubes (CNT) the CNH structures are predominantly single walled due to the geometrical constraints of the cones and build larger (typically between 200 nm and several µm) nano-structured aggregates of spheroid shape.

The available CNH are of high purity, the absence of metals (no catalysts such as Co, Fe or other metals are used for their synthesis which is mostly the case for the synthesis of other carbon nanomaterials). The purity of CNH (no metals) has the advantage that their cytotoxicity is negligible.

The surface morphology tending probably for a minimum of Van-der-Waals interactions between the individual aggregates may contribute to the much higher stability of CNH-suspensions.

The health risk related to carbon nanoparticles is currently controversially discussed. Due to the aggregation of CNH to spherical structures they tend not to build stable aerosols (Stoke's Law) and can be dispersed both in non-polar solvents or in pure water without tensides so that they can be handled without formation of dust.

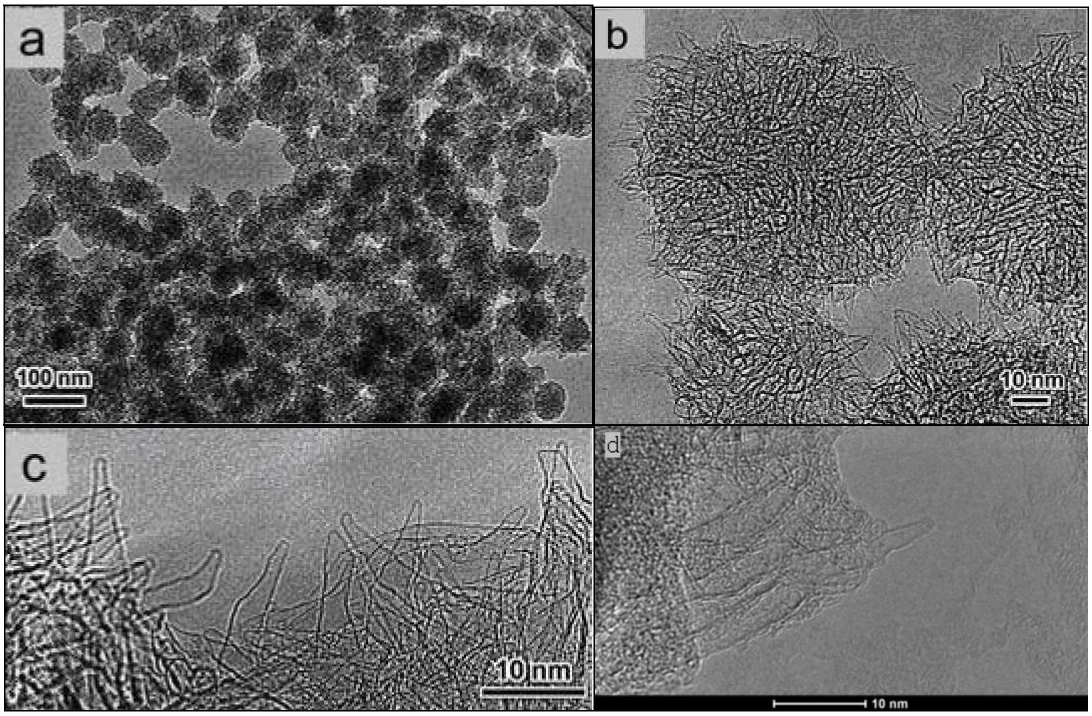


Figure 3: TEM-photographs of SWNHs in various magnifications
a-c from literature [1], d from own production [17].

Availability and properties of CNH

Together with eenanoTech Ltd. (Japan) and TIE GmbH (Germany), Plejades GmbH (Germany) is able to provide CNH in several forms, which can be adjusted to customer requirements.

Several characterisation tests and application research were performed with our CNH by German and International institutions [17][18][23][24][28]

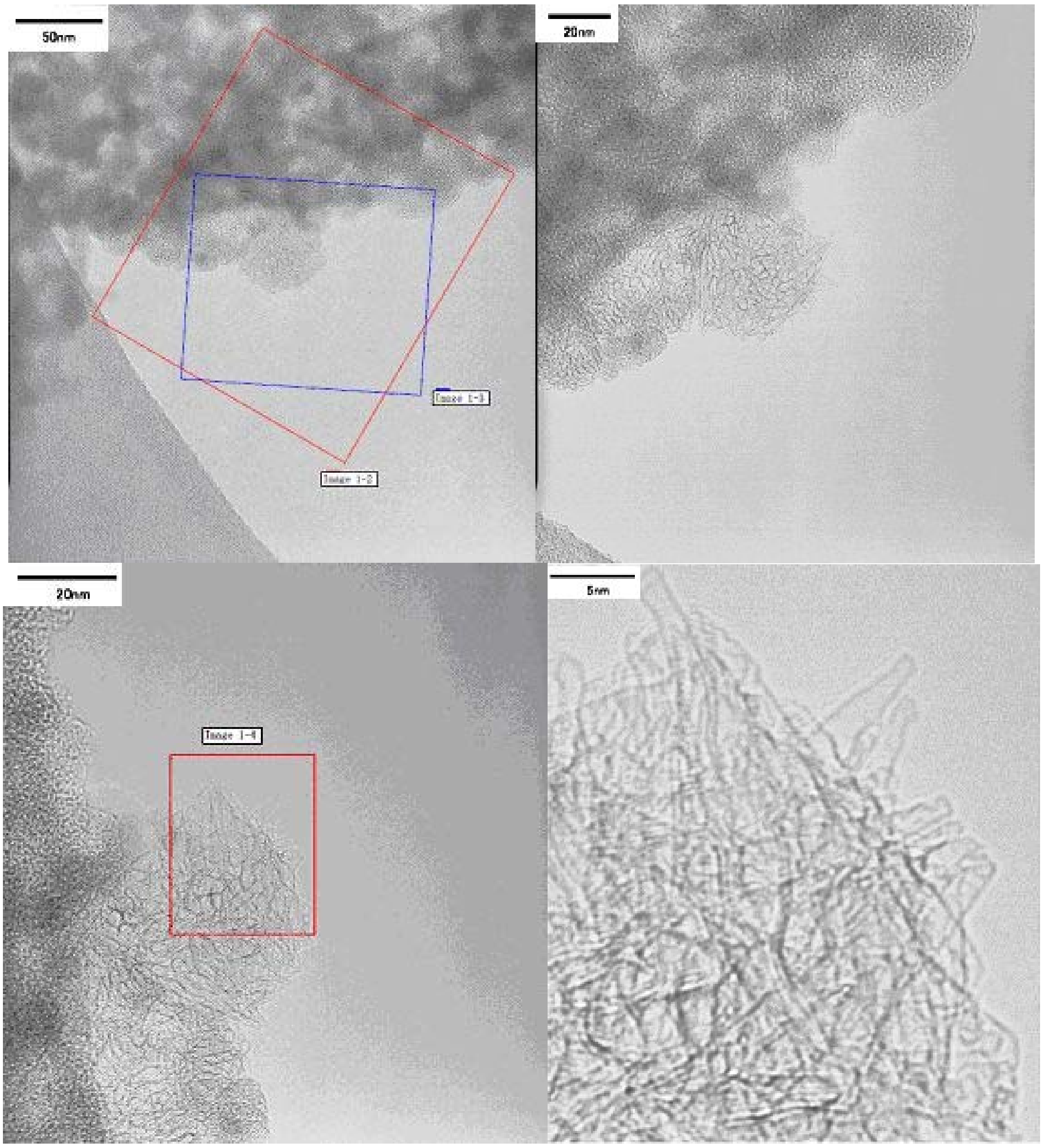


Figure 4: TEM-photographs (various magnifications) of CNH from own production (eenanoTech 2010, [23])

Raman spectrometry is a standard method to assess the quality of nano-structured carbon particles. Results obtained on our CNH (see Fig. 5) reveal the high quality of the material. As there is no shift in the Raman spectrum after thermal treatment under Argon (Fig. 6) [17], a very high purity can be assumed.

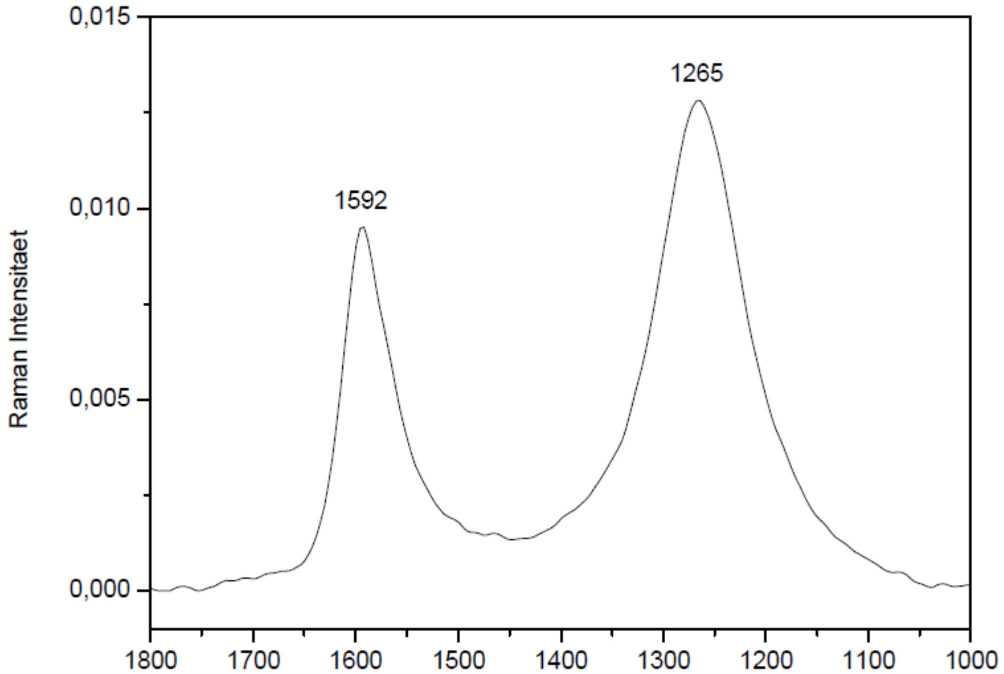


Figure 5: Raman spectrum [17]

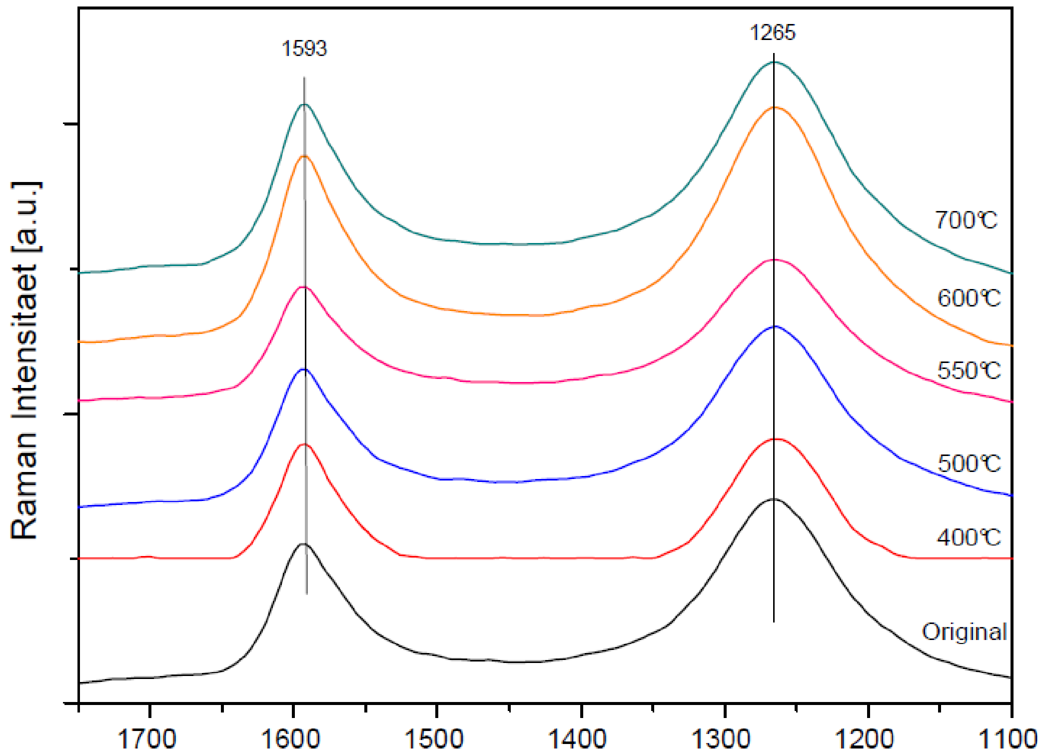


Figure 6: Raman spectrum after thermal treatment under Argon atmosphere [17]

CNH are commonly available as powder (of CNH aggregates, as described above).

A new type of CNH has been developed: the CNH are suspended without any additives in a water-based paste – called Type F - for foam (relative high mass-percentage is about 8 % upwards). Through dewatering of this foam, we can also produce a CNH-paste with residual 10 - 20 % H_2O content – internally called Type W (for “wet”) which has the consistency of a humidified powder. With regard to health and safety, both types have incontestable advantages (for instance no release of flammable, explosive vapours of non-polar solvents or nanoparticles in powder form in the atmosphere), but there is little experience available about their usability in industrial processes.

We are producing the following CNH types:

- CNH Type A: powder, very pure > 99,5 %, extremely fine fraction, (air screened finest fraction)
- CNH Type B: powder, very pure > 99,5 %, very fine fraction, (unscreened)
- CNH Type F, „Foam“: paste made of pure CNH-clusters in water, ca. 8 % CNH Type B
- CNH Type W: CNH Type B humidified with H_2O, water content 10-20 %

Other types/processing can be prepared according to customer’s specifications (for instance as suspension in solvents or doped with Pt).

Characteristics of the produced CNH:

- CNH dimensions: Length: 5 nm - 150 nm,
  Typical diameter 2 nm - 20 nm
  Purity > 99 %
- CNH-Agglomerates:

  Cauliflower-like substructure up to several 100 nm Diameter of agglomerates is up to some µm
  Frequent structures: Seed-like and dahlia-like

Bulk Density (dry):	ca. 35 g/l
Pore Volume:	ca. 1,1 cm^3/g
Pore Diameter:	ca. 12 nm
Specific surface:	>200 m^2/g (200-235 m^2/g)
Hydrogen storage capacity:	ca. 0,057 % (wt. H_2 / CNH)

These features prove that this is an interesting material for industrial applications.

Research status / ongoing experiments / Possible fields of application

Tests for various possible applications have already been launched and/or are currently under scrutiny among the partners, with first results available:

- Tribological characteristics (high friction and hardness of the CNH) [19][21]
- CNH-reinforced plastics (among others thermoplastics) – Use of the hardness and thermal conductivity of the CNH for upgrade of plastics [22]
- CNH-metal sintering alloys – Application of the hardness properties by low density metals for production of low abrasive light metal sinter alloys [20]
- CNH-reinforced CNT-Bucky Papers – Application of the hardness properties of CNH for mechanical reinforcement of thin CNT-Bucky-Papers [18][21]
- Melioration of organic lubricants [5]
- Observation of increased electrical conductivity in bucky papers by application of higher voltage [26]
- Testing of Hydrogen storage capacity [28]

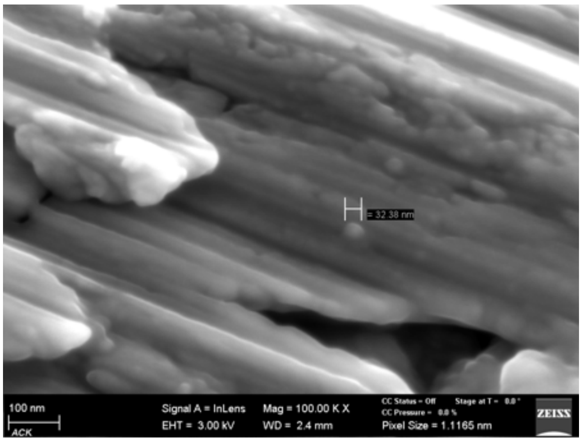


Figure 7: High resolution picture of a AlSi12 sinter alloy with 0,1% CNH
(FEM – picture with Zeiss ULTRA System)

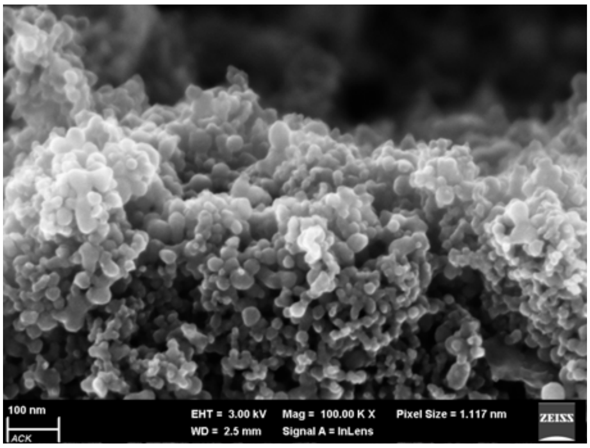


Figure 8: High resolution picture of the surface of a CNH-CNT bucky paper.
(FEM picture with Zeiss MERLIN System)

In addition, a series of concrete pre-concepts are being developed on the following topics:

- CNH / ceramic composites (with Fraunhofer-IPA)
- AGeNT R&D contract for CNH-reinforced thermoplastics (with LNP) was awarded in May 2011
- CNH-reinforced lacquers (internal research, with LNP)
- CNH-sinter (100 % CNH, with eenanoTech)
- CNH-Al-metal sinter (97 % Al + 3 % CNH, through eenanoTech)
- CNH-zeolite sinter (97 % zeolite + 3 % CNH, through eenanoTech)
- Disaggregation of CNH aggregates into isolated CNH (through eenanoTech)
- Electrical conductivity of CNH structures (through eenanoTech)

- Textile coating tests (with Japanese Industry - through eenanoTech)
- Paper coating tests, coated rice paper (through eenanoTech)
- Capacitor tests (with Nagoya Institute of Technology (National University) and Cambridge University (coordinated through eenanoTech) [11]
- CNH characteristics for improvement of performances of Zn-film batteries (various research institutions in Japan and the UK, through eenanoTech, [12]
- CNH properties for hydrogen storage (with TU Chemnitz, [28])
- CNH plastic composites: New approach in compounding with nanomaterials (with TU Chemnitz)
- Duroplasts tempered with CNH (with TU Chemnitz)
- CNH Press tests on various materials (with LNP, [29])
- CNH-filler in rubber (through eenanoTech, [32])

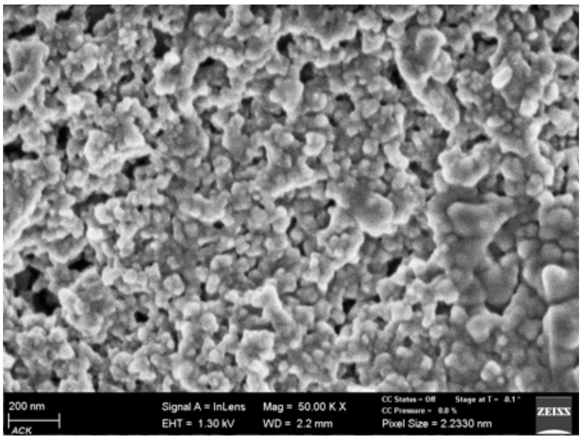


Figure 9: Result of a press test made with Type B CNH on a PEEK surface
(FEM – picture with Zeiss ULTRA System)

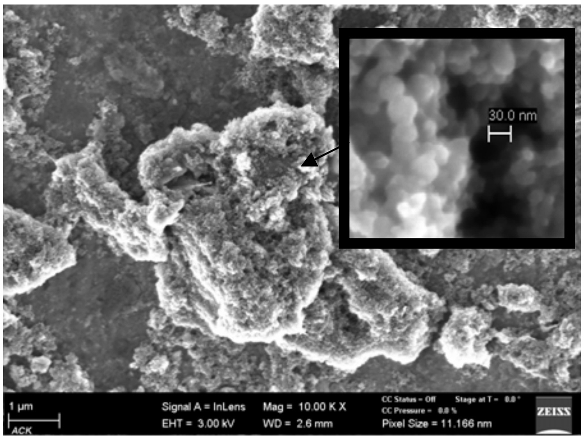


Figure 10: Result of a press test made with Type B CNH on a Aluminum surface
(FEM – picture with Zeiss ULTRA System,)

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   b. On BuckyPapers
   c. On Friction tests
   d. On Sinter tests
   e. On pressure tests
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Authors: Dr. Norbert Molitor, Dr. Tsuzuki Kitamura, Cécile Javelle
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Contact in Europe:
TIE GmbH
Attn. Dr. Norbert Molitor
Managing Director

Feldstrasse 5
D 64347 Griesheim / GERMANY

Tel.: +49 6155 8234 40
Mobile:+49 179 229 5272
E-mail: norbertmolitor@pleja.de

Contact in Japan:
Environment Energy Nanotech Research Institute Co., Ltd.
Attn. Dr. Tsuzuki Kitamura

5263-5 Aizome, Ikeda-cho
Kitaazumi-gun, Nagano 399-8602, Japan

Mobile:+81 90 7032-5374
E-mail: t-kitamura@eenanotech.co.jp

Subsidiary Lower Saxony:
TIE GmbH Niederlassung Niedersachsen, Prieche 7, D-37154 Northeim/Germany