# NANOCARBON MATERIALS

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Nanocarbons are among the most promising materials developed last years. Nanocarbon materials include fullerenes, nanotubes (NT), nanofibers (NF), nanodiamond, onions, and various hybrid forms and 3-dimensional structures based on these. Several years ago these materials were available in milligram-scale quantities. Now many of them are produced by tones per year.

TMSpetsmash Ltd. research team has developed some new kinds of nanocarbon materials and processes for their production.

Now we have created pilot installation for CVD production of multiwall carbon nanotubes (MWNT) from ethylene in industrial scale. MWNT produced by this process have average diameter 12-20 nm, surface area near 200-400 $m^2/g$, mass content of minerals 6-20% for non-purified NT and <1% for purified NT.

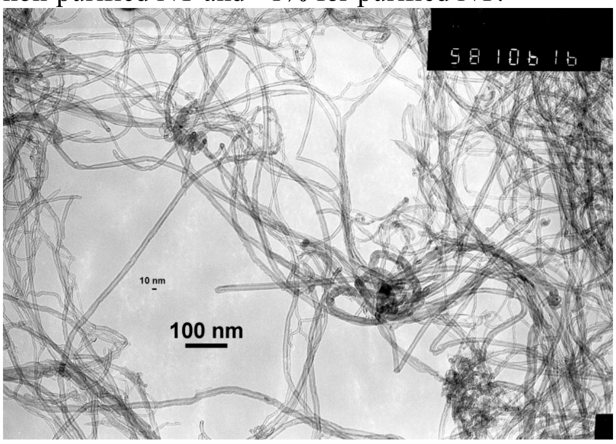


Fig. 1. MWNT by CVD from ethylene

MWNT are produced in form of black powder with bulk density of 15-40 $g/dm^3$. Experiments carried out by us have shown that low bulk density NT samples are preferable for application in composite materials. So, we tried to produce MWNT with the bulk density as low as possible. This was achieved by use of co-precipitated Fe-Mo/$Al_3O_3$ catalysts containing aerosil as a pseudo-liquid diluent of growing nanotubes [1, 2].

For different electrochemical applications such as batteries, supercapacitors, fuel elements porous carbon nanomaterials are used. We have obtained porous carbon nanofibers by CVD method from acetylene with use of new (Fe,Co)-C-$SiO_2$ catalysts obtained by mechanochemical method [3, 4].

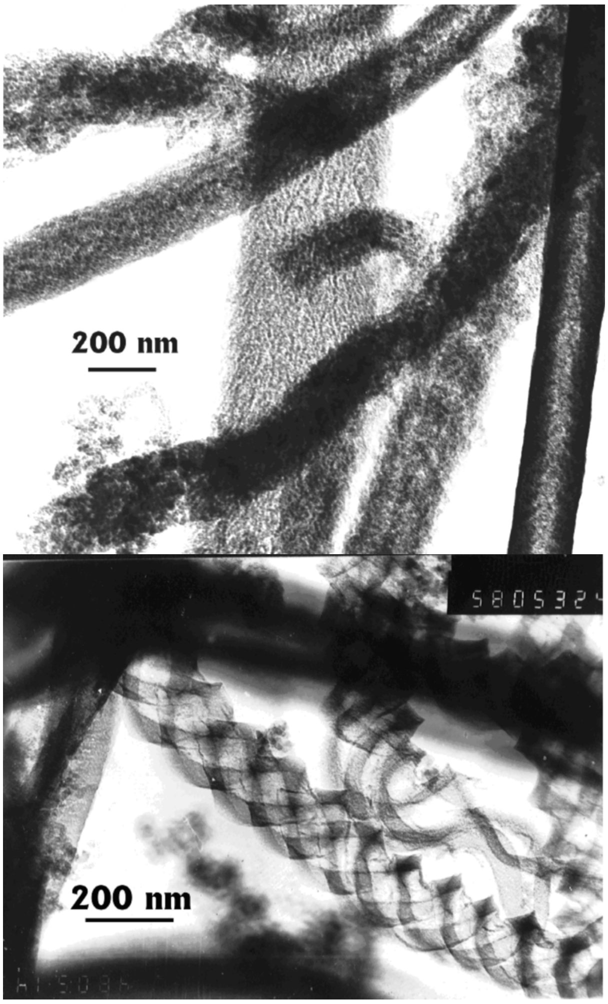


Fig. 2, 3. Porous carbon nanofibers from acetylene

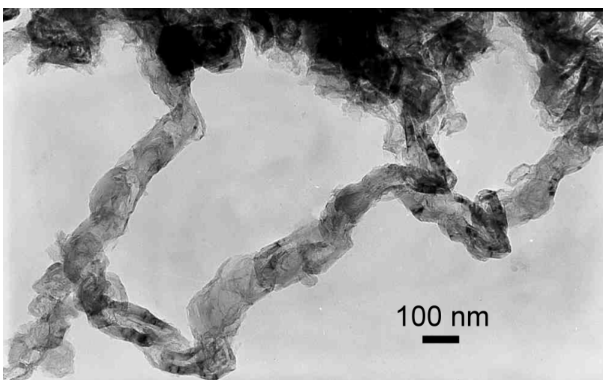


Fig. 4. High surface area activated CNF (4000 $m^2/g$).

Surface area of as-obtained CNF materials is nearly 300-500 $m^2/g$. Effective surface area for some of these materials (measured by argon desorption method) increases up to nearly 4000 $m^2/g$ and in some experiments even to 6000 $m^2/g$ after activation with melted KOH.

In spite of physical vagueness of such high surface area values these materials are interesting for electrochemical and hydrogen storing applications. One can suppose that slit-like pores exist in these materials. Activated CNF were investigated as a hydrogen adsorbing electrode materials instead of metal hydrides [5].

Along with improving of CNT/CNF production technology new methods of nanocarbon materials obtaining are of interest besides of widely used arc-discharge and CVD techniques. One of promising ones is solid-state reaction method. We have investigated a new nanocarbon-producing system, $CaC_2$-S [6]. When reacted with sulfur vapor at 400-600$^o$C or in burning mode, calcium carbide powder gives nanotubes together with other carbon nanoparticles:

$CaC_2 + S \rightarrow CaS + 2C$

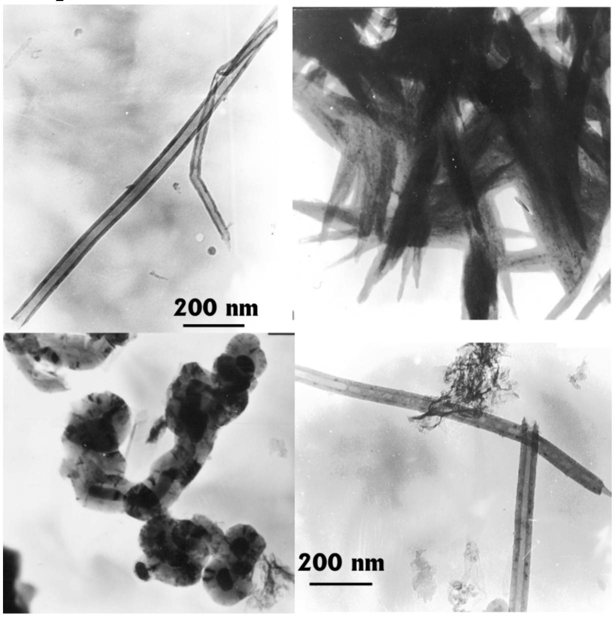


Fig. 4. Carbon nanoparticles from $CaC_2$-S reaction

This reaction gives high yield of carbon (44-80%) and can be easily scaled. Purifying of the raw material includes treatment of it with sodium carbonate solution with following treatment with acid. Surface area of nanocarbons obtained was 64-500 $m^2/g$, specific electric resistance of powder 0.02-0.07 Ohm.cm.

As is known structure and properties of CNT and CNF obtained by CVD method in great extent depends on catalyst used in this process. Even for catalysts of the same composition, for instance, well-known $Fe_2O_3$-$MoO_3$/$Al_2O_3$ system, the properties and yield of nanocarbon materials strongly depends on the catalyst preparation method.

We have investigated different methods of obtaining catalysts for CNT/CNF CVD production from ethylene and acetylene. These methods use co-precipitation, “appearing reagent”, redox, sol-gel and mechanochemical techniques. Good results were obtained with $Fe_2O_3$-$MoO_3$/$Al_2O_3$ co-precipitated with use of urea as a reagent slowly evolving ammonia. Both 2-valent and 3-valent iron salts can be used for coprecipitation. The catalysts so obtained are effective for CNT growth from ethylene. However these catalysts are much less effective for CNT/CNF growth from acetylene.

Highly effective iron-containing catalysts for synthesis of porous CNF from acetylene were obtained by mechanochemical method [3, 4]. It was found that carbonization of iron-containing organic precursors in oxygen-free atmosphere greatly increases catalytic activity in CNF growth process. On contrary, similar treatment of catalyst precursors greatly decreases catalytic activity in CNT growth process from ethylene. It may be that porous CNF growth process from acetylene is initiated by free-radical centers on carbon clusters adjacent with iron particles.

On the other hand, it is possible that CNT growth from ethylene is promoted by Broensted acid centers which can appear on $MoO_3$/$Al_2O_3$ after reduction of it with hydrogen. This centers can initiate dehydrocyclization of ethylene by mechanism similar to transformations of hydrocarbons on bi-functional solid acid catalysts.

**References**

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