

## METHOD FOR SYNTHESIS OF HELICAL CARBON NANOTUBES

Schur D.V., Savenko A.F., Bogolepov V.A., Kaverina S.N., Zaginaichenko S.Yu.,  
Zolotarenko A.D., Pishuk V.K.

Institute for Problems of Materials Science of NAS of Ukraine, lab. # 67,  
3, Krzhizhanovsky str., Kiev, 03142 Ukraine

### Introduction

Carbon microfibers observed in many products produced for the last 5-6- decades attract attention due to the discovery of fullerene. The single-wall nanotube is thought to be a graphene sheet rolled up in the tube. However, the nanotube (NT) may be a fullerene elongated in the tube. Both approaches are correct. There are many disputable moments in this field of knowledge.

The search of new, more effective methods for nanotube synthesis makes scientists perform hundreds of experiments. It is difficult to list all the current methods which applied to produce this product. However, the problem on the large-scale controlled synthesis of carbon NTs is still unsolved. In this report we represent the experiment that allowed preparation of helical multi-wall NTs 30-60 nm in diameter.

### Experimental

The pyrolytic apparatus designed in laboratory 67 in Institute for Problems of Material Science of National Academy of Sciences of Ukraine, was used to synthesize nanostructural carbon by catalytic pyrolysis.

Acetylene and toluene vapor were used as sources for carbon. The process was carried out in the quartz reactor on Ni-Cu catalysts in the nitrogen flow.

Electron microscopic investigations of the products were performed on a transmission microscope.

### Results and discussion

In the temperature range of 600-1200 °C carbon NTs and fibers were synthesized both from acetylene and toluene vapor. In the course of NTs synthesis from toluene vapor at 880 °C the dark-brown condensate forms in the more cooled part of the reactor.

When acetylene passes through the reactor, this liquid reacts with the gas phase and turns into fume. The fume is collected by the liquid seal.

Electron microscopy of the product collected revealed (see Fig.) that helical nanofibers 30-60 nm in diameter formed in the given experimental conditions. The spirals have different configurations, they can be straight (Fig.a,d), interweave (Fig.a,e), form Y-like shapes (Fig.e,f).

There exist two variants in formation of such nanostructures. The straight NT twists under mechanical loading and elastic bending. The second way consists in the spiral formation during NT growth. It may be possible due to alternating the pair defects, pentagon-heptagon, on the hexagonal lattice. Pentagon will induce the positive curvature, and heptagon - the negative one. Each pair of defects may twist the tube at 0-36° angles [1-23].

It is difficult to conclude about the mechanism of NT formation observing the photographs. However,

we consider that the tubular spirals formed in the course of NTs growth. The organic compound produced by toluene pyrolysis and admixed into acetylene has a stronger effect on formation of the helical shape than turbulent movement of the product-containing gas mixture and its quick quenching in the liquid seal.

The main feature of the product prepared is the fact that none of the tubular spirals is fixed by one of its ends on the catalyst and does not have catalytic particles on its ends what contradicts the concepts about the mechanism of NTs growth.

### Conclusions

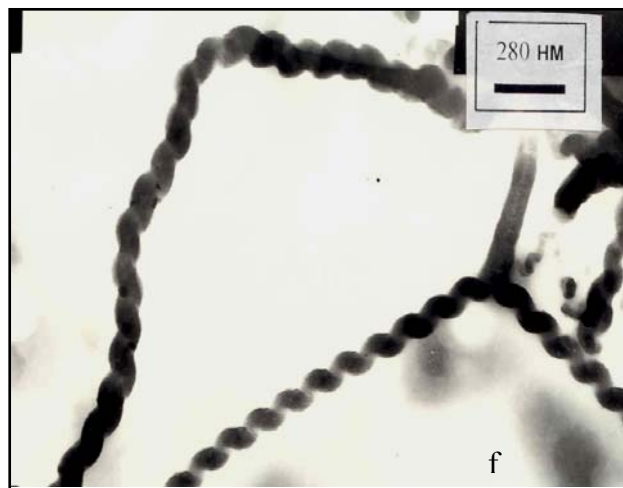
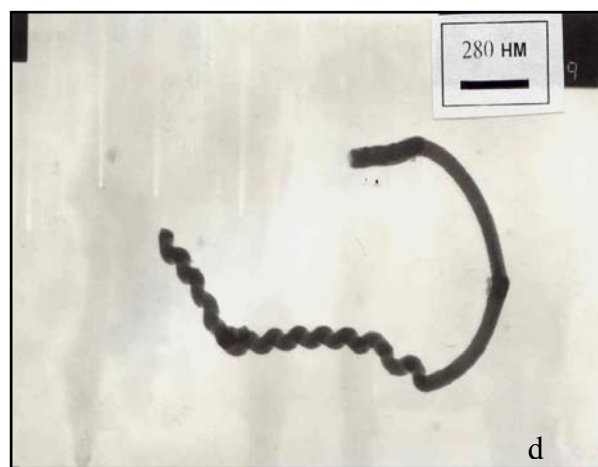
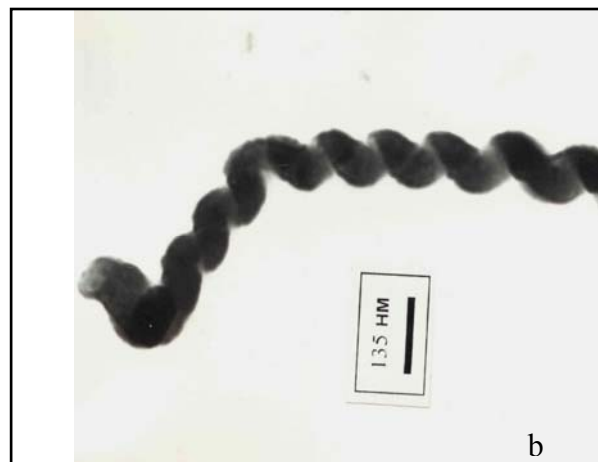
Method for preparation of helical nanotubes 30-60 nm in diameter has been proposed.

Further investigations will help to refine the technology for the purposeful synthesis of nanotubes which have a helical shape with the certain diameter and the pitch.

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## МЕТОД СИНТЕЗА СПИРАЛЕПОДОБНЫХ УГЛЕРОДНЫХ НАНОТРУБОК

Щур Д.В., Савенко А.Ф., Боголепов В.А., Каверина С.Н., Загинайченко С.Ю.,  
Золотаренко А.Д., Пишук В.К.

Институт проблем материаловедения НАН Украины, лаборатория № 67  
ул. Кржижановского 3, Киев, 03142 Украина

### Введение

Углеродные микроволокна которые, наблюдали во многих продуктах, получаемых в течение последних 5-6 десятилетий, привлекли к себе внимание в связи с открытием фуллерена. Считается, что одностенная нанотрубка – это свернутый в трубу графеновый лист. Однако можно сказать, что нанотрубка (НТ) – это вытянутый в трубу фуллерен. И то и другое будет правильно. И таких спорных моментов в этой области знания очень много.

Поиски новых более эффективных методов синтеза нанотрубок заставляют ученых проделывать сотни экспериментов. Все методы, которыми сегодня получают этот продукт трудно перечислить. Однако вопрос о крупномасштабном контролируемом синтезе углеродных НТ остается нерешенным. В настоящей работе описывается эксперимент, позволивший получить спиралеподобные многослойные нанотрубки диаметром 30-60 нм.

### Экспериментальная часть

Для синтеза наноструктурного углерода методом каталитического пиролиза использовали пиролитическую установку, изготовленную в лаб. № 67 ИПМ НАН Украины.

В качестве источников углерода использовали ацетилен и пары толуола. Процесс проводили в кварцевом реакторе на Ni-Cu катализаторах в потоке азота.

Электронномикроскопические исследования продуктов проводили на просвечивающем микроскопе.

### Результаты и обсуждение

В диапазоне температур 600-1200<sup>0</sup>С были синтезированы углеродные нанотрубки и волокна как из ацетилена, так и из паров толуола. В ходе синтеза НТ из паров толуола при 880<sup>0</sup>С в более охлажденной части реактора образуется темно-коричневый конденсат.

При пропускании через реактор ацетилена эта жидкость реагирует с газовой фазой, превращаясь в дым. Дым улавливался жидкостным затвором.

Электронная микроскопия уловленного затвором продукта показала (см. рисунок), что в данных экспериментальных условиях

образуются спиралевидные нановолокна диаметром 30-60 нм. Спирали имеют различную конфигурацию, могут переходить в прямые (рис. а и г), переплетаться (рис. а и д), образовывать "у" подобные формы (рис. д и е).

Существует два варианта образования подобного рода наноструктур. Скручивание под воздействием механической нагрузки и при упругом изгибе прямой нанотрубки. Второй способ предполагает формирование спирали во время роста НТ. Это может быть возможным благодаря чередованию парных дефектов пятиугольник-семиугольник в гексагональной решетке. Пятиугольник будет вызывать положительную кривизну, а семиугольник – отрицательную. Каждая пара дефектов может скручивать трубку под углами 0 - 36<sup>0</sup> [1].

При рассмотрении фотографий нанотрубок трудно сделать заключение о механизме их формирования. Однако мы склонны считать, что трубчатые спирали формировались в ходе роста НТ. В большей степени на формирование спиралеподобной формы влияло подмешивание в ацетилен органического соединения, полученного пиролизом толуола, а в меньшей степени - турбулентное движение продуктосодержащей газовой смеси и ее быстрое закаливание в жидкостном затворе.

Основной особенностью полученного продукта является тот факт, что ни одна из полученных трубчатых спиралей не закреплена на катализаторе одним из концов и не имеет на концах каталитических частиц, что противоречит имеющимся представлениям о механизме роста НТ.

### Выводы

Предложен метод получения спиралеподобных нанотрубок диаметром 30-60 нм.

Дальнейшие исследования помогут отработать технологию целенаправленного синтеза нанотрубок, имеющих спиральную форму с определенным диаметром и шагом.

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