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Synthesis of carbon nano-materials by means of pulse modulated arc discharge in organic liquids

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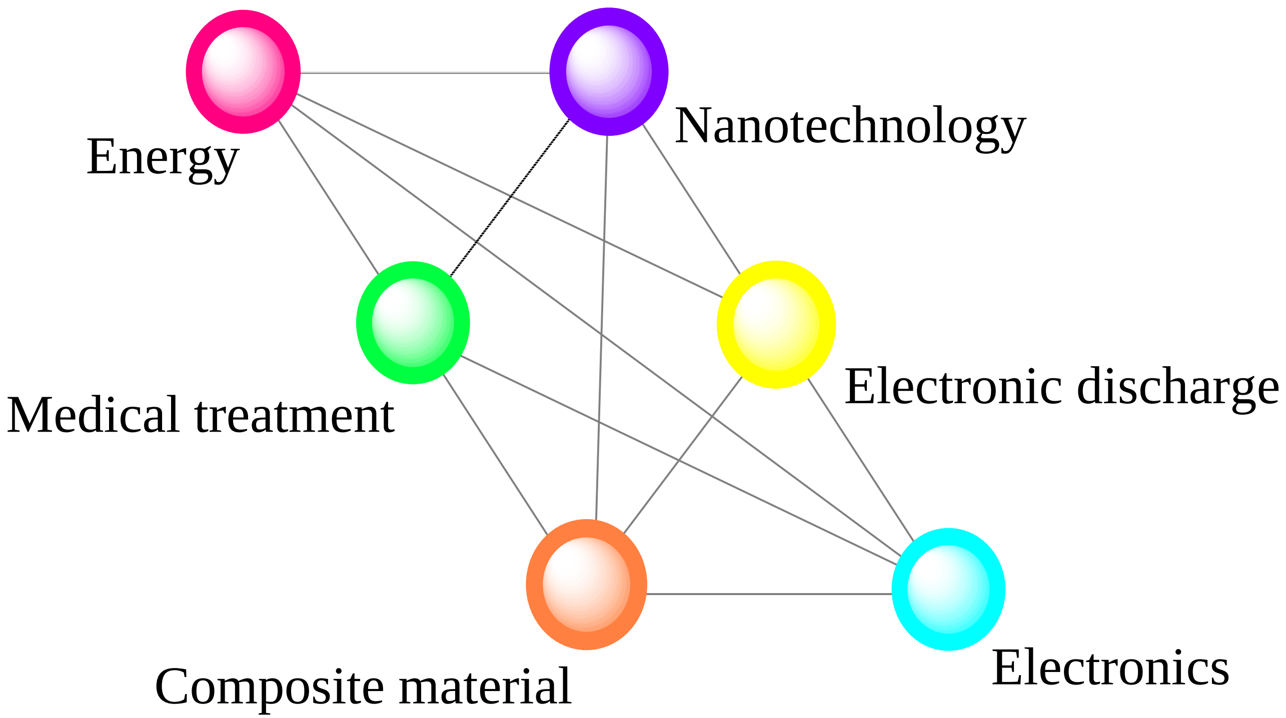
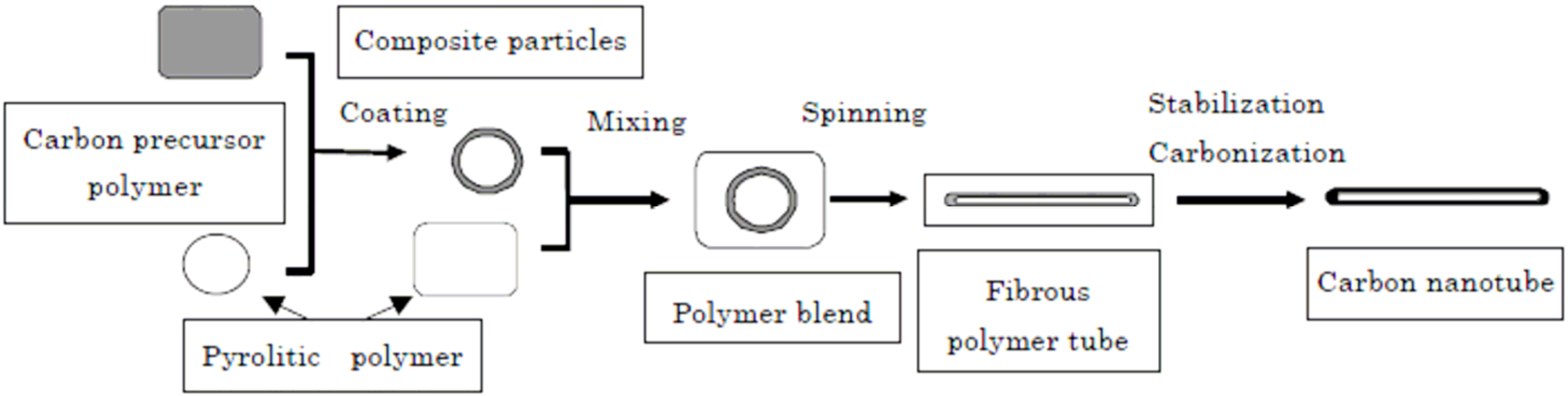
Introduction

carbon nano structure

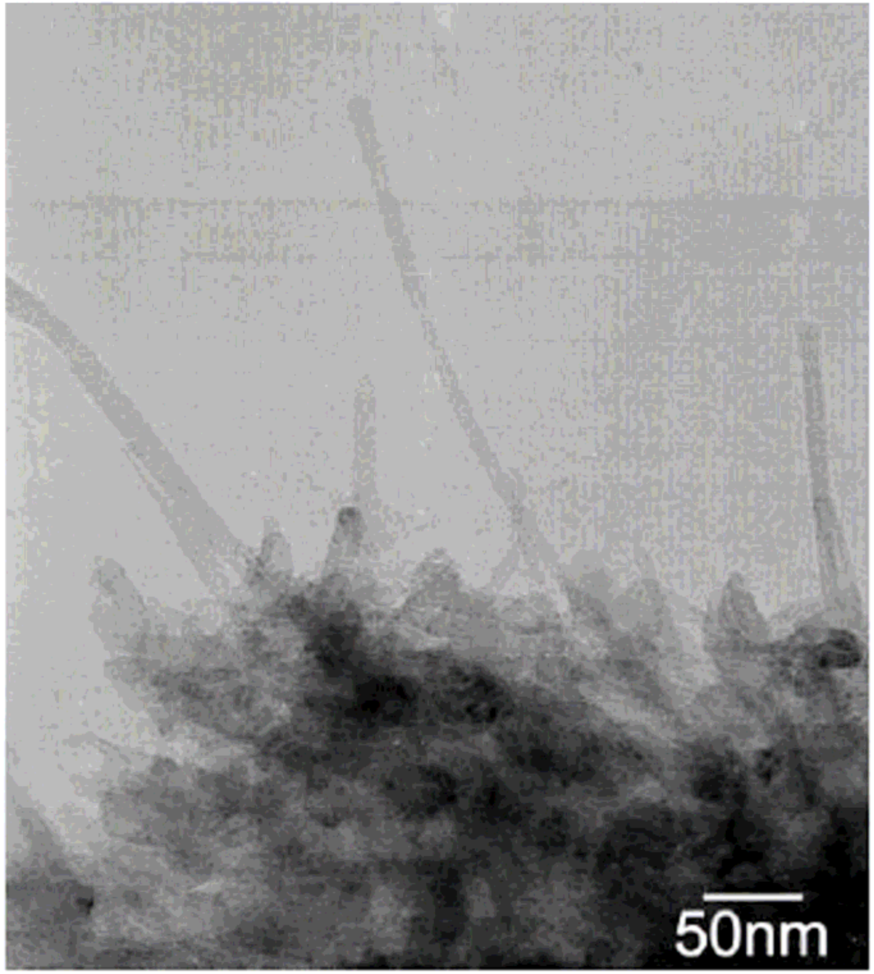
The carbon material of a nanometer order

【Carbon Nanotube(CNT)】





A schematic procedure of polymer-blend method for carbon nanotube preparation



TEM micrograph of carbon nanotubes obtained from CS2

Introduction（2）

Synthesis of CNTs

Arc discharge

Laser ablation

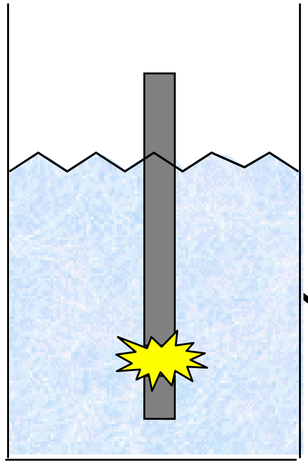
CVD

disadvantage

- **Large-size equipments**
- **High running costs**

"arc in liquid" methods

The technique of causing electric discharge between graphite electrodes in liquid



liquid nitrogen or deionized water

A carbon nanostructure can be prepared with being highly dispersed in a liquid.

M. Ishigami, Cumings J., Zettl A., Chen S. Chem. Phys. Lett. 2000, 319, 457.

N. Sano, Weng H., Chhowalla M., Alexandrou I., Amratunga G. A. J., Nature 2001, 414, 506.

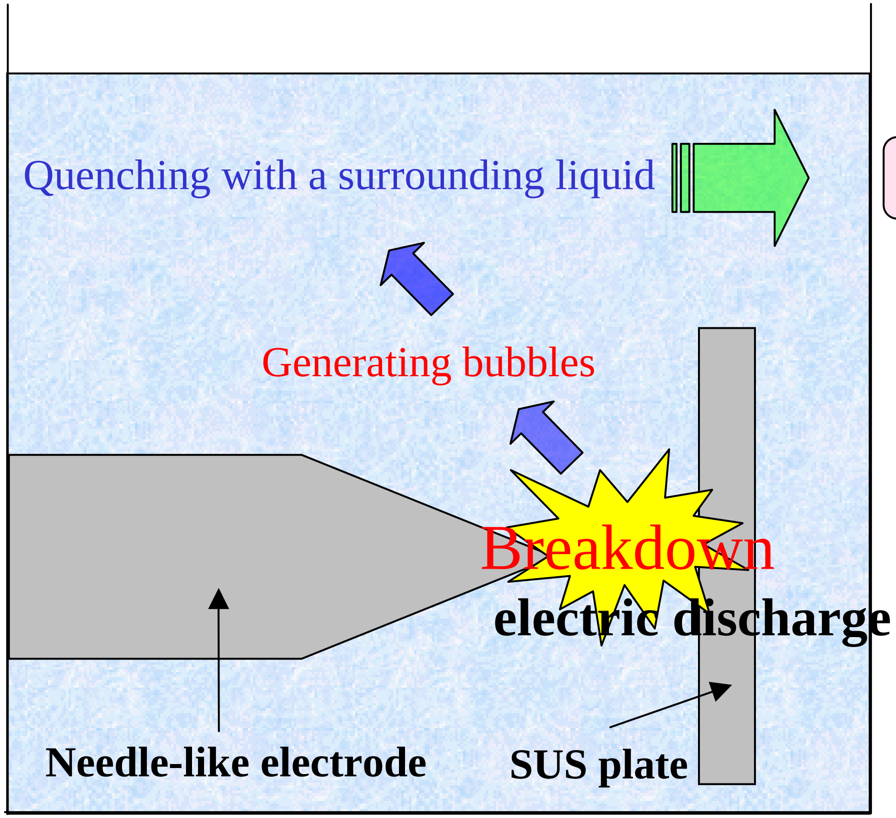
Characteristics of this work

For the conventional technique,

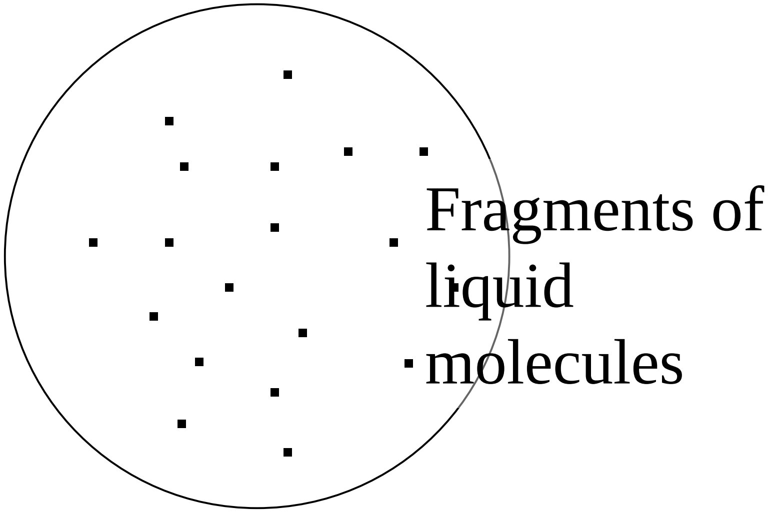
the graphite used for electrode is a source of carbon.

In this research, since metal electrode is used,

an organic liquid becomes the source of carbon.



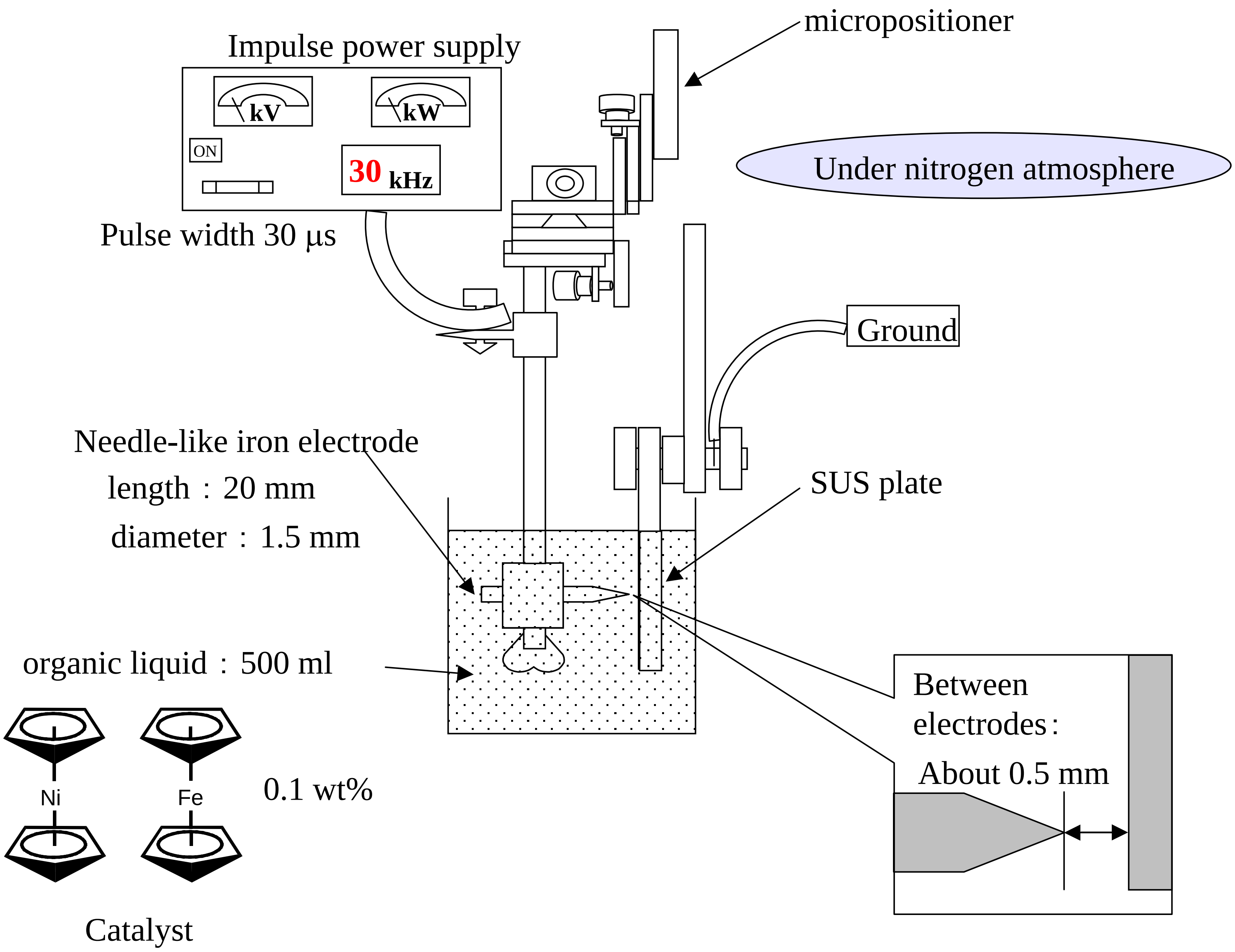
Synthesis of the carbon nano structure



The enlargement of bubbles

Effects of molecular structure of liquid carbon source on the synthesis of carbon nanostructures by arc in liquids method

Experimental apparatus



organic liquids

$CH_3(CH_3)_4CH_3$

hexane

$CH_3(CH_3)_6CH_3$

octane

$CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$

2,2,4-trimethyl pentane

CH_3OH

methanol

$HCHO$

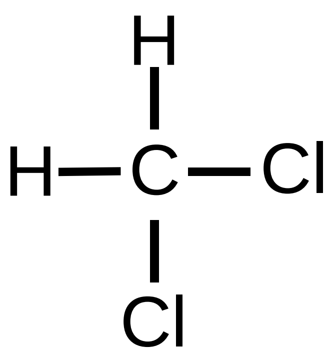
formaldehyde

$(CH_3)_2CO$

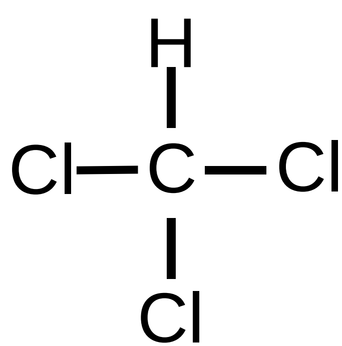
acetone

$C_2H_5OC_2H_5$

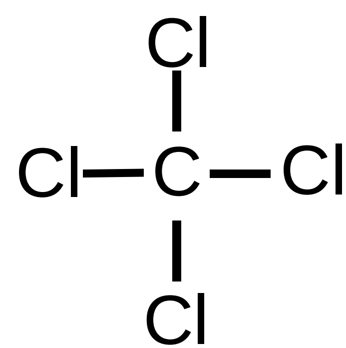
diethyl ether



dichloromethane



chloroform



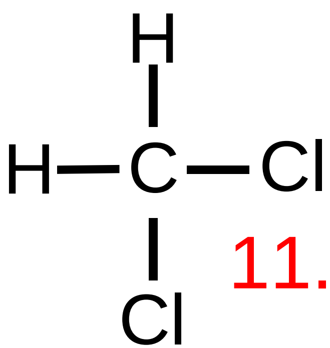
carbon tetrachloride

Electric discharge ／Change in the liquid

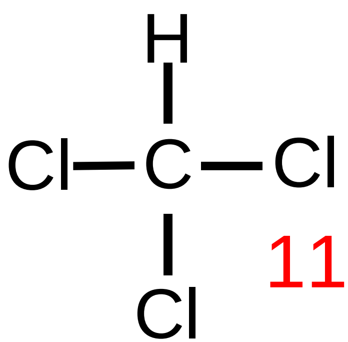
- Electric discharge takes place with intense light and sound.
  ⇒The soot-like products were formed in liquid.
- Chlorine-containing gas was generated.
- Electrode was consumed slightly.
- Temperature of liquid rose by 2 to 5 degrees.

muddy black

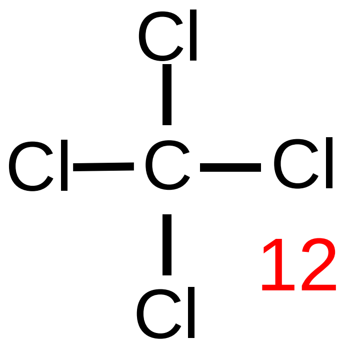
Breakdown voltage〔kV〕



11.0



11.5



12.5

$CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$

11.5

Change in the liquid

slightly black

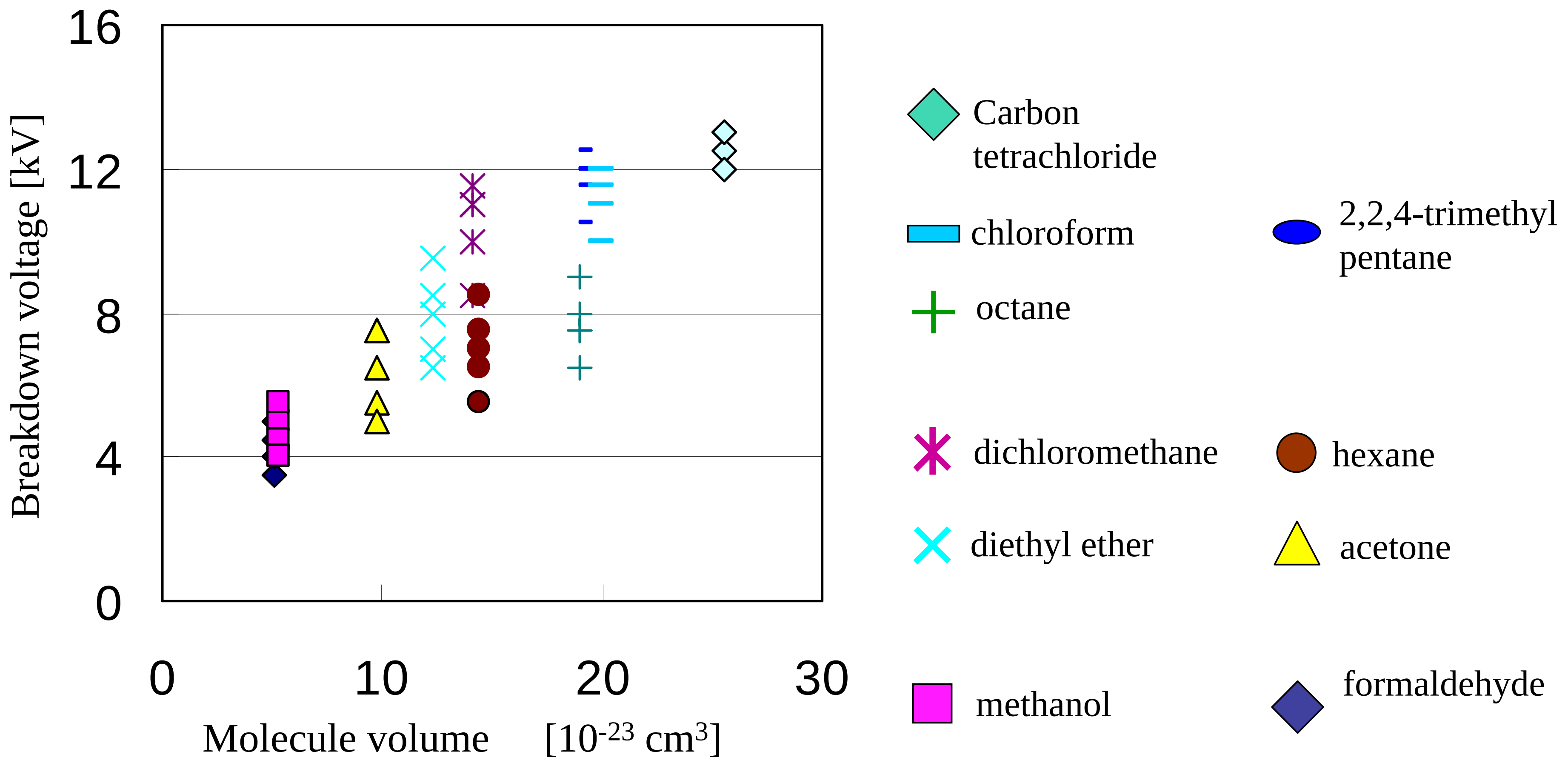
Breakdown voltage〔kV〕

$CH_3(CH_3)_4CH_3$	$CH_3(CH_3)_6CH_3$	$(CH_3)_2CO$
7.5	8.0	7.0

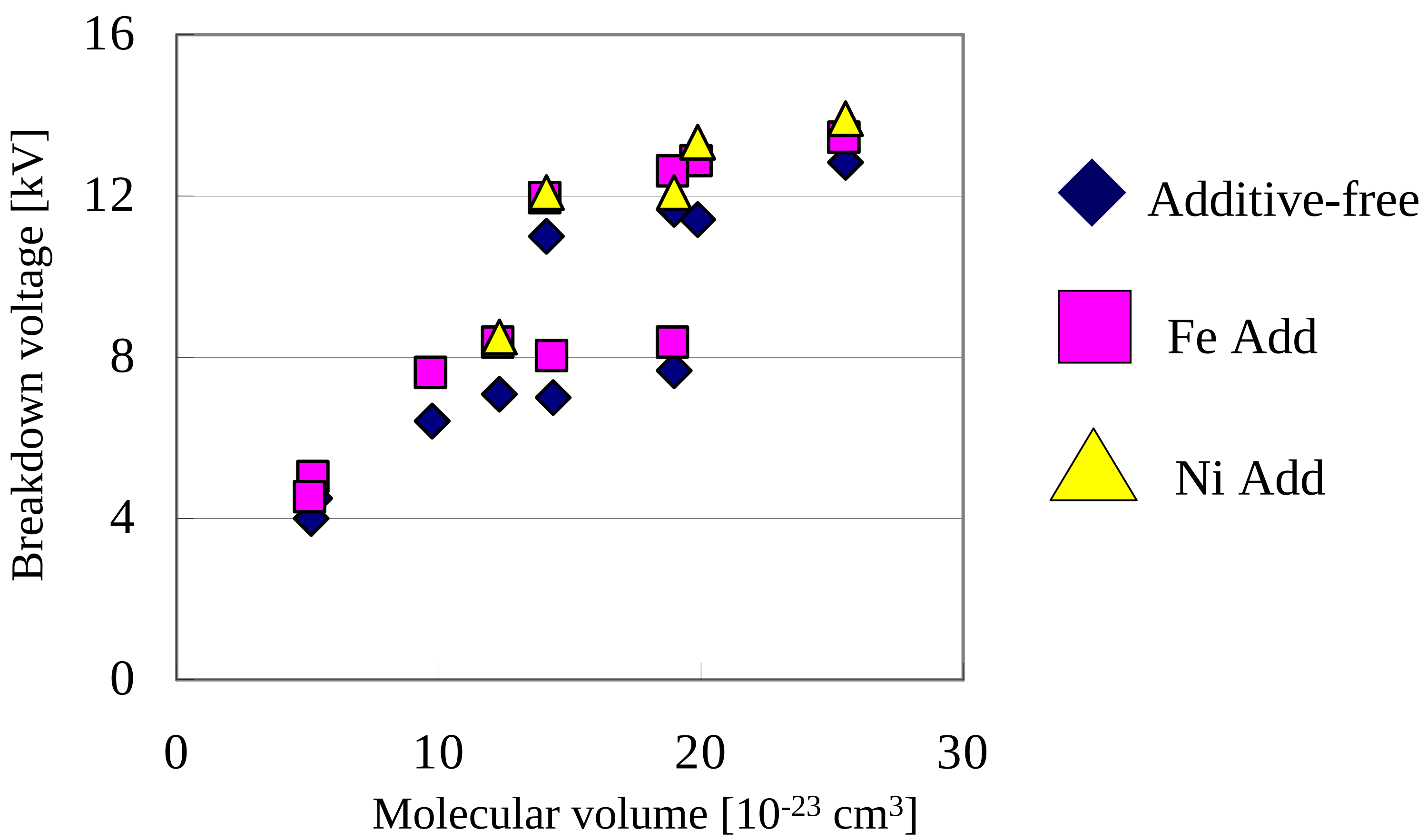
no change

CH_3OH	$C_2H_5OC_2H_5$	$HCHO$
4.5	7.0	4.0

Relation between molecular volume and breakdown voltage



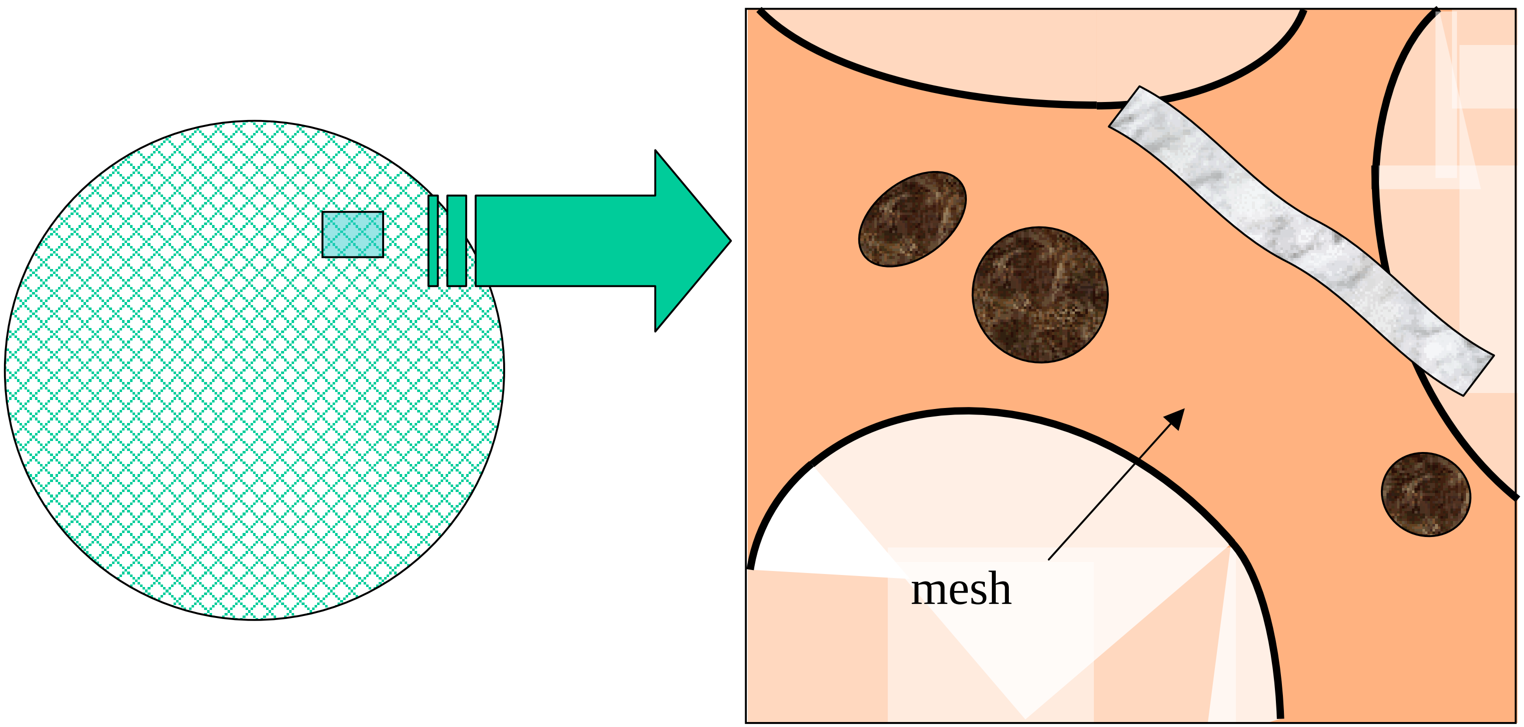
Change of the breakdown voltage by catalyst addition



TEM observation

One drop of liquid after electric discharge on a micro grid.

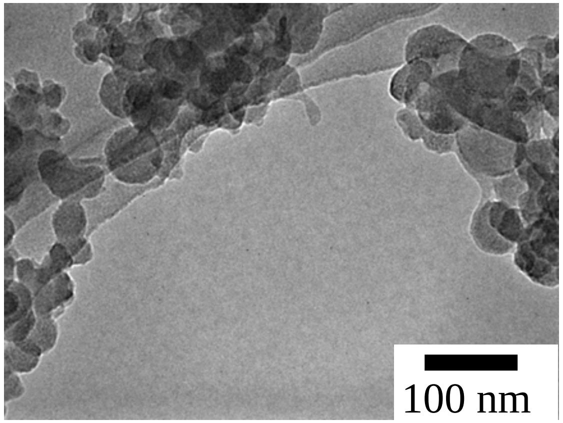
After dried up, TEM observation was performed.



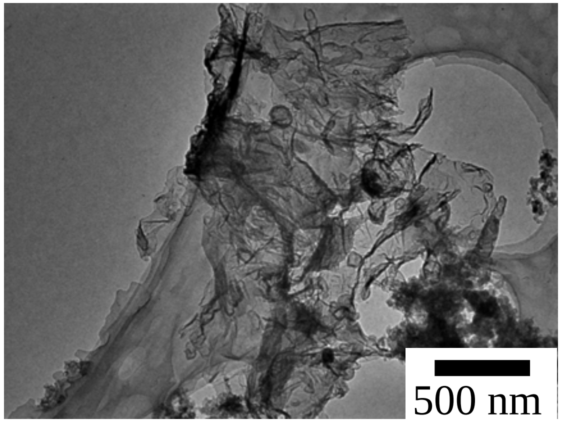
Classification of products

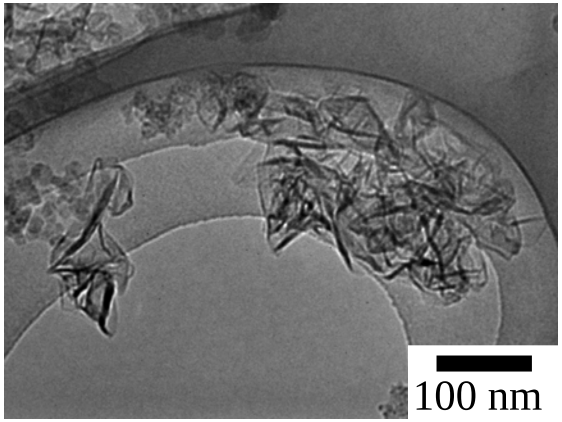
The products observed on a micro grid were classified into the following three types.

①Amorphous particle



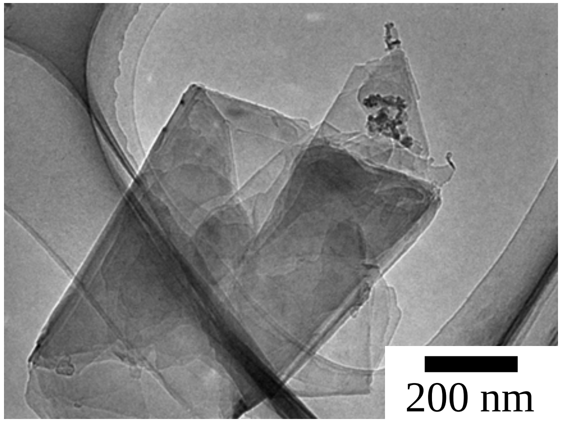
②Crystalline substance

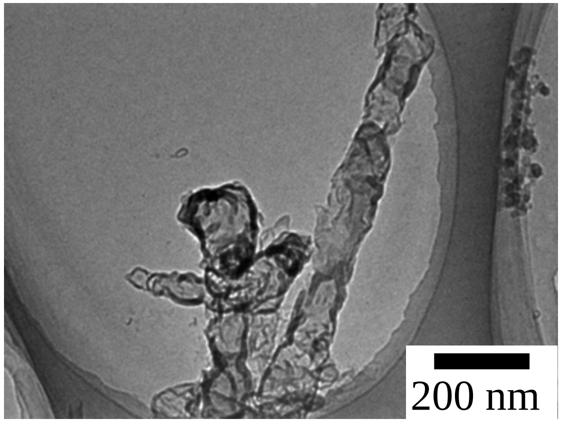




③Unique structure

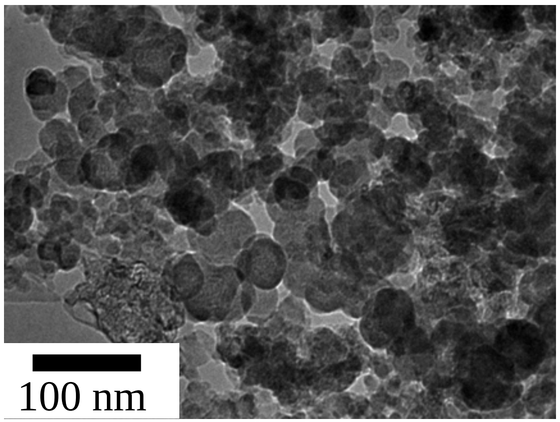
Those what with peculiar structure different from ① or ②.

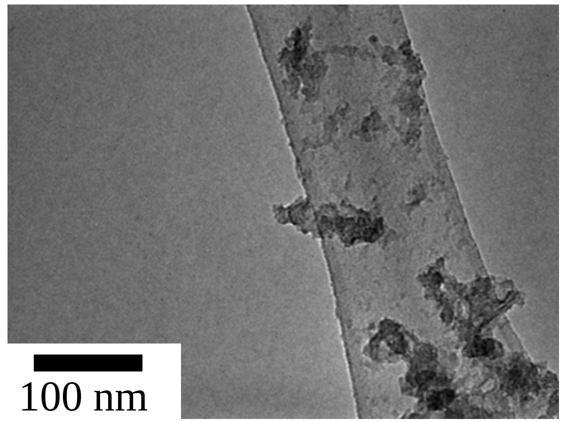




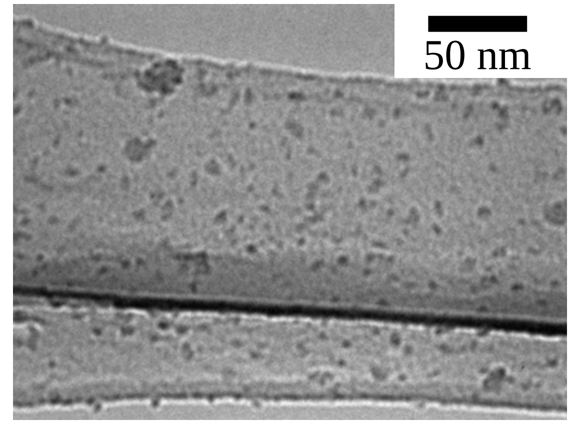
Catalyst-free system

Without catalyst, amorphous particles of diameter 5-100 nm were dominant and no unique structure was observed.

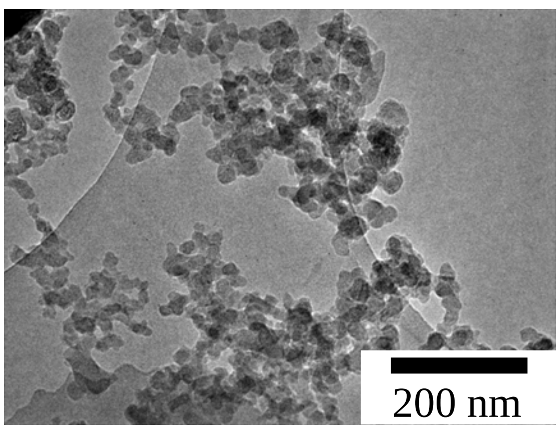


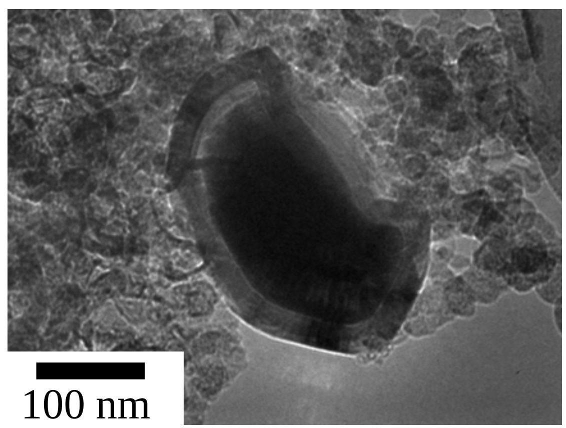


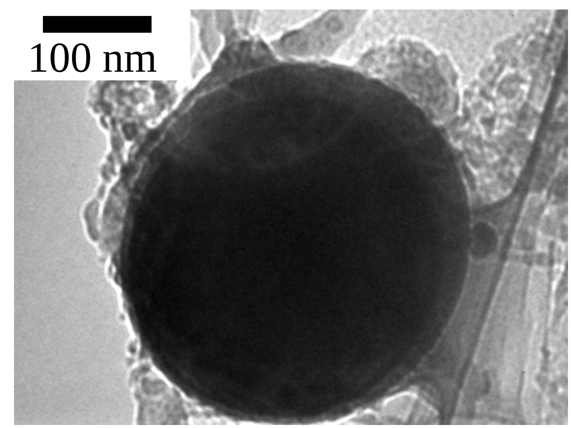
torn form



Scattered state





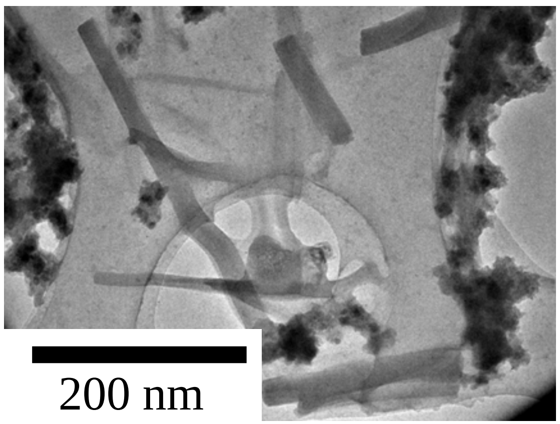


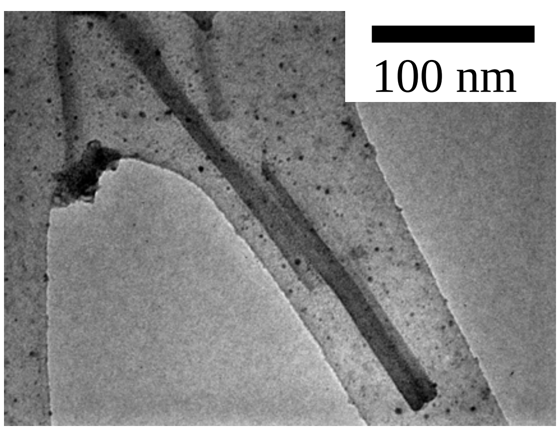
Graphite ball

Example of unique structure products①

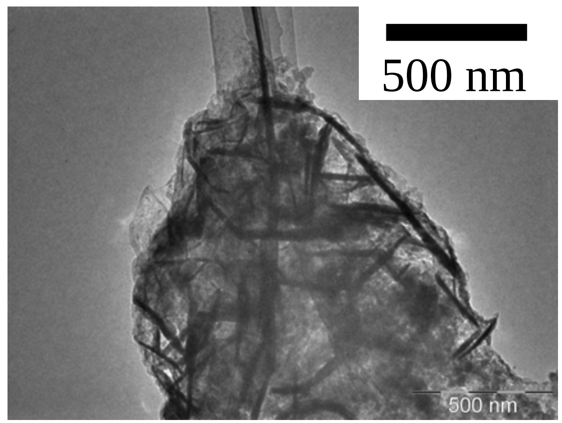
With addition of catalyst, unique carbon nanostructures were observed on some parts of micro grid.

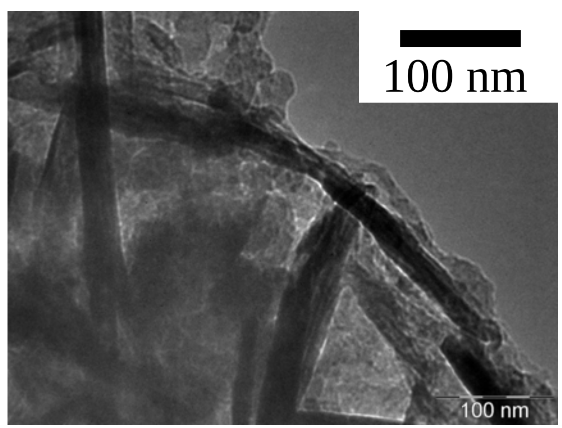
MeOH＋Fe



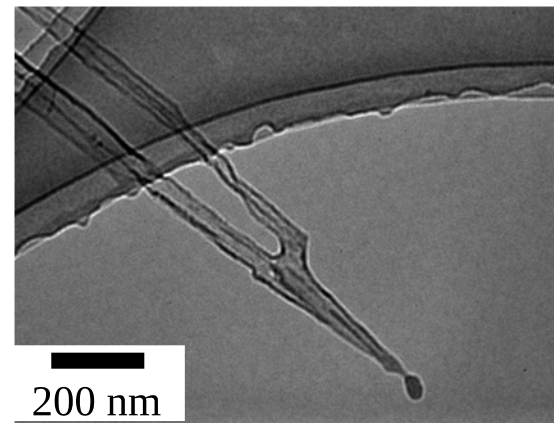


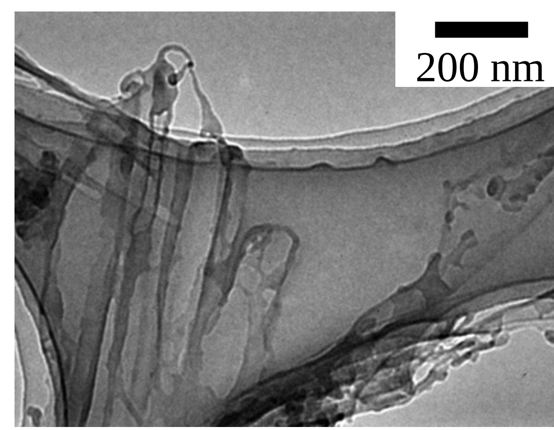
$CHCl_3$＋Ni





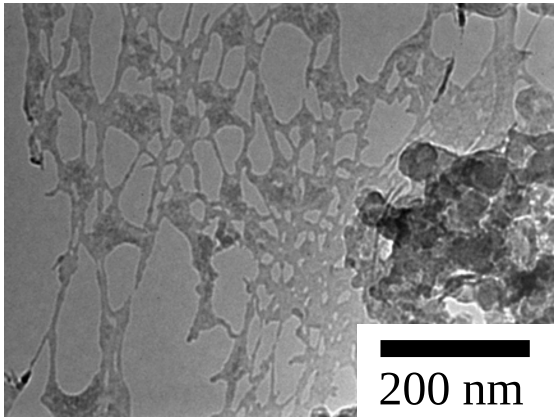
CCl_4＋Ni

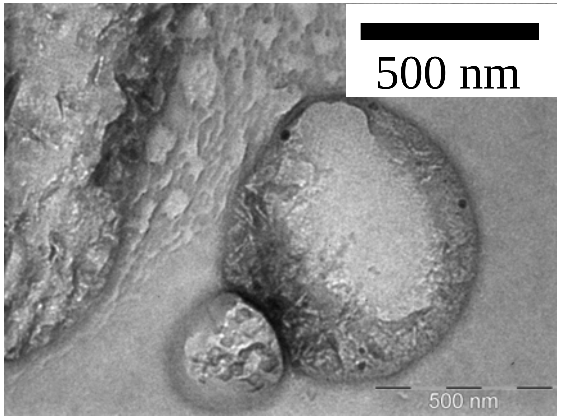




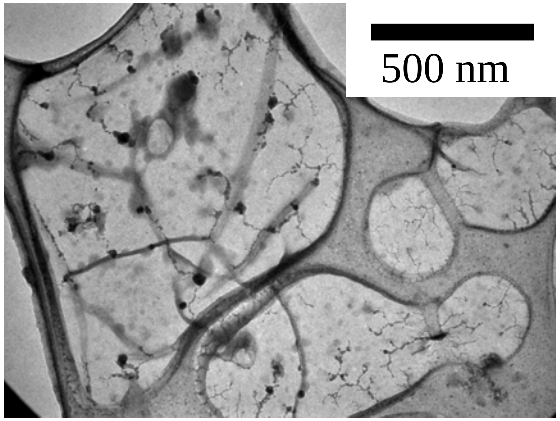
Example of unique structure products②

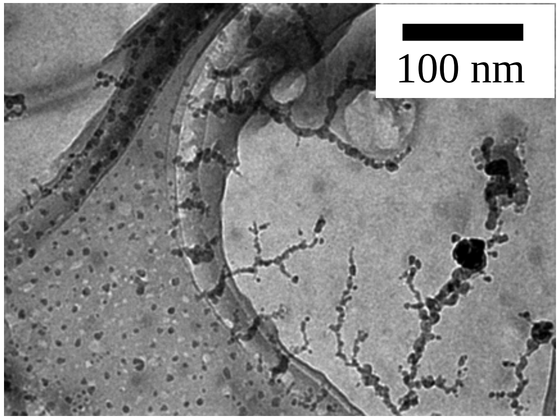
$CH_2Cl_2 + Ni$

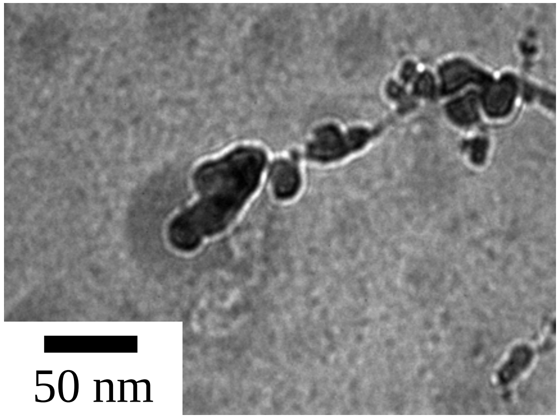


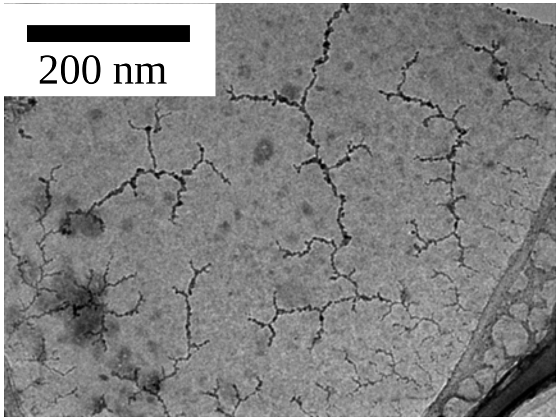


$CH_3C(CH_3)_2CH_2CH(CH)_3CH_3 + Ni$



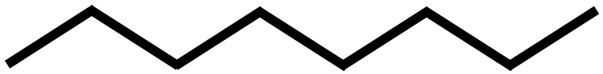




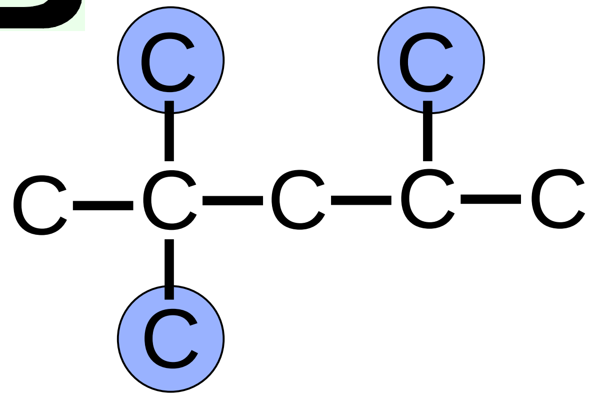


Influence of fragmentation on products

octane＋Fe **8.5** light

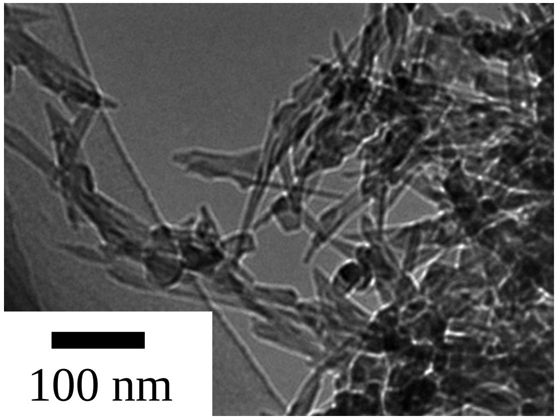


2,2,4-trimethyl pentane＋Fe **11.5** Deep-black



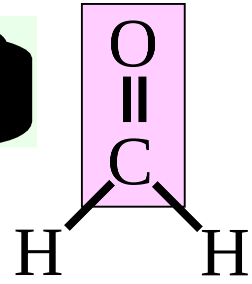
A classification of a products

	octane＋Fe	2,2,4-trimethyl pentane＋Fe
Amorphous particle	50%	65%
Crystalline substance	50%	30%
Unique structure	0%	5%

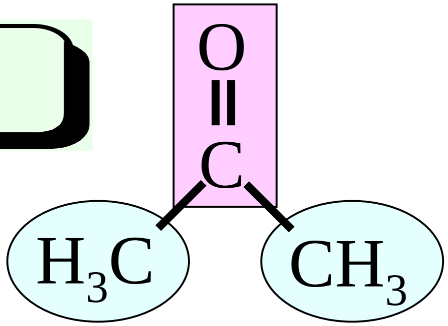


Influence of functional group on products

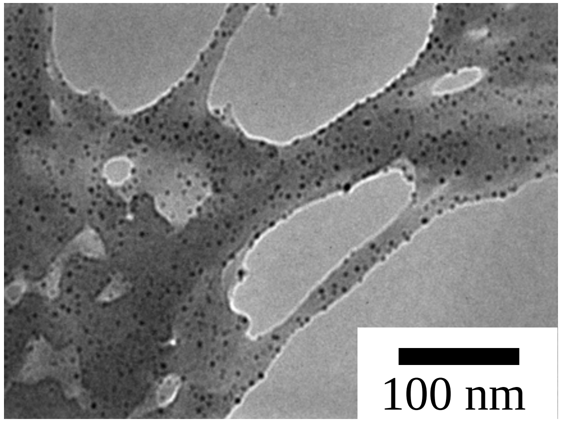
formaldehyde＋Fe

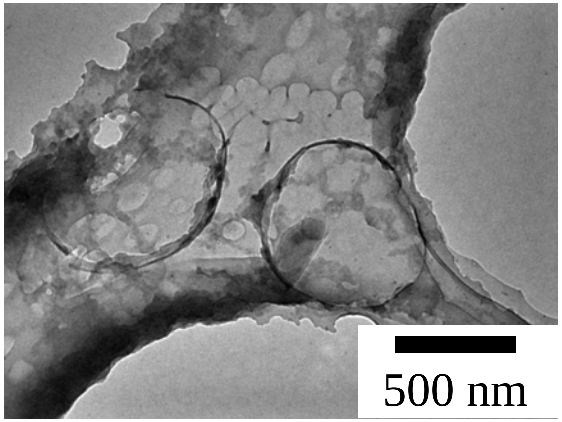


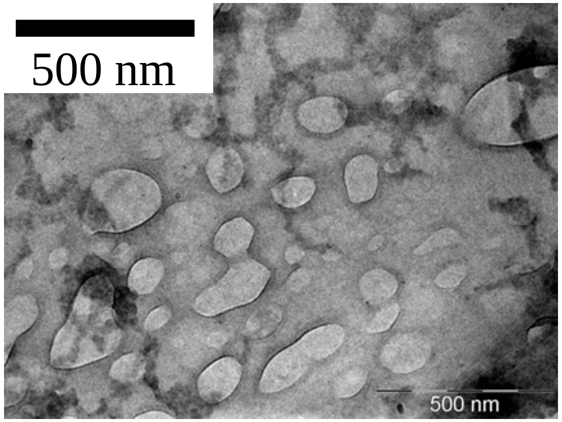
acetone＋Fe

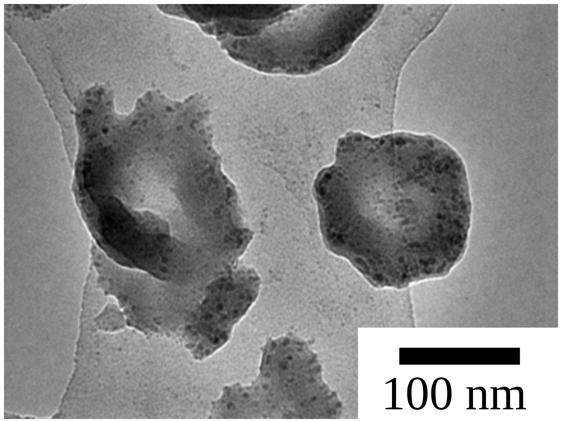


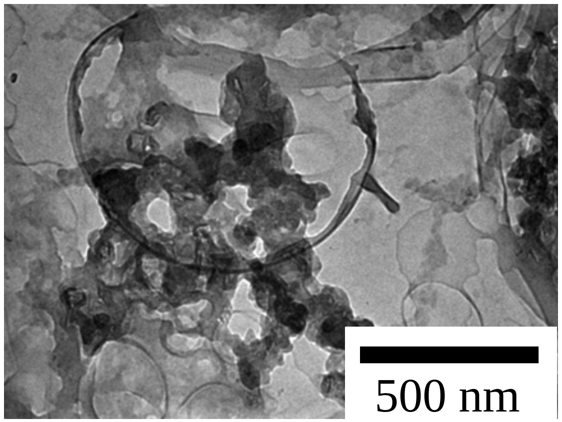
70 percent of a domain is the shape of amoeba.







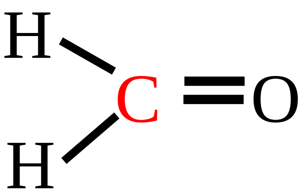




Relationship between main chain structure and crystalline products

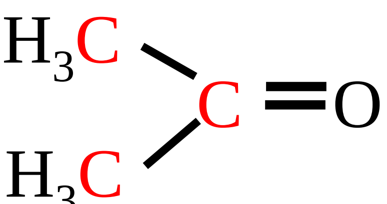
The fraction of a crystalline particle

CH_3OH 2-3%

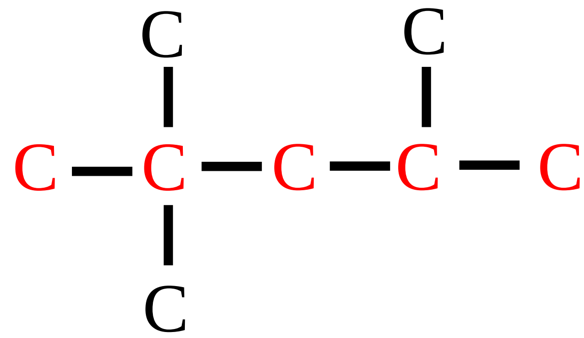


0%

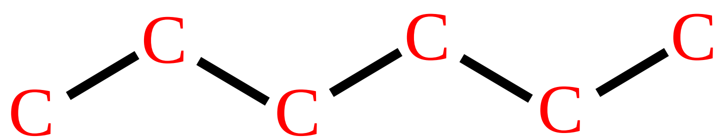
$C_2H_5OC_2H_5$ 2-3%



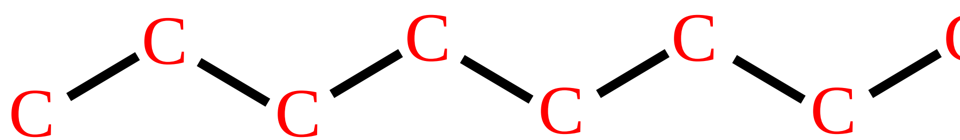
5%



30%



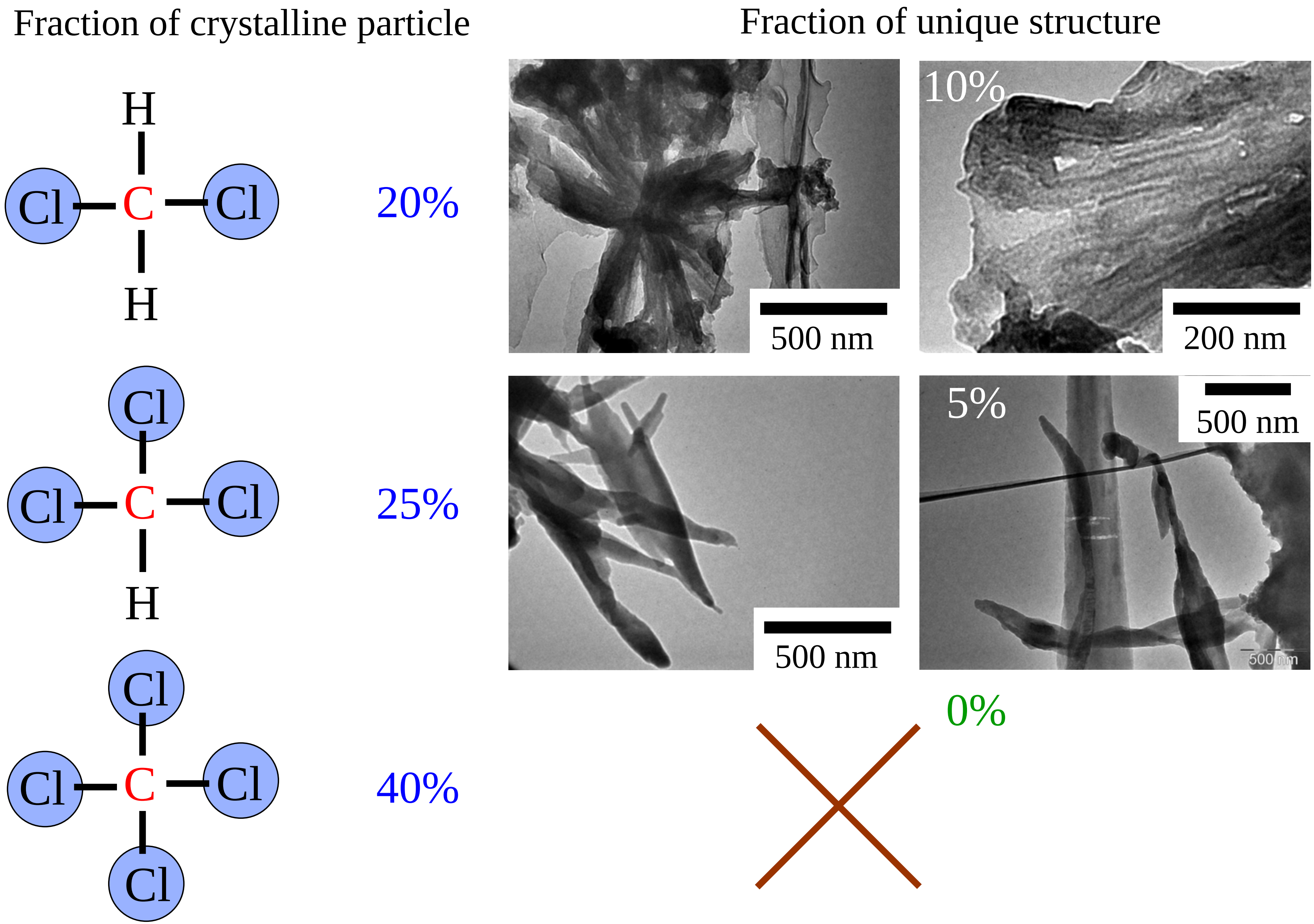
30%



50%

The fraction of crystalline particle increases with main chain length of source molecule.

Specificity of chlorine-containing compounds



conclusions

・Without catalyst, only amorphous particles with diameter 5-100 nm were obtained. By addition of catalyst (Ferrocene, Nickelocene) carbon nanostructures were obtained.

・The functional group and small fragmentation of each liquid had great effects on obtained structure.

・The longer the main chain of liquid molecule is, the more the crystalline products were obtained.

・The chlorine-containing compound exceptionally did give crystalline products despite the number of C is one.

Synthesis of carbon nanostructures by pulsed electric discharge between metal electrodes using fluorine-containing organic liquid

Experimental conditions (Time change)

HFE-7200

$C_4F_9OC_2H_5$

Soot-like products were formed: 12.5 mg / A･s ≒ 30 times of previously reported rate.

Electric discharge conditions

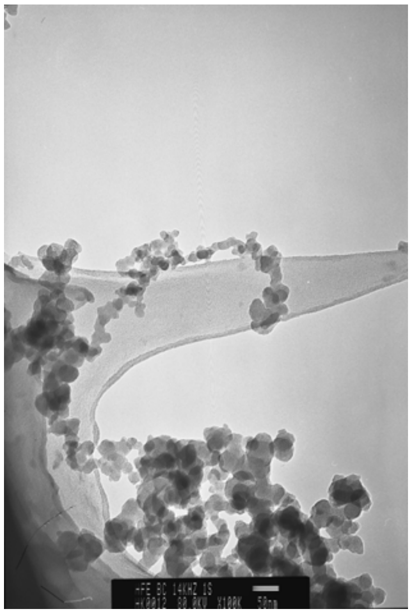
	volt.(kV)	power(kW)
14kHz-5s	5.0	0.25
14kHz-10s	6.5	0.25
14kHz-15s	8.0	0.40
14kHz-20s	6.0	0.30

Atomic concentrations

mol%	C	F	O	F/C	O/C
14kHz-5s	80.48	7.08	12.44	8.797	15.46
14kHz-10s	78.81	8.85	12.34	11.23	15.66
14kHz-15s	81.07	14.98	3.96	18.48	4.89
14kHz-20s	80.4	12.23	7.37	15.21	9.17
HFE-7200	28.57	66.67	4.76	150	16.66

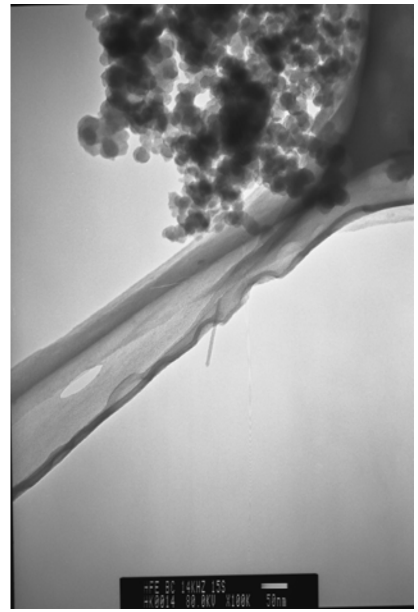
TEM observation (Time change)

Amorphous particle | **Carbon nanotube**

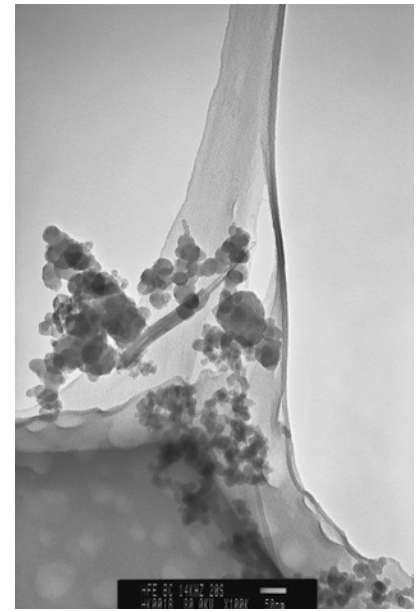


1) 14kHz-5s

2) 14kHz-10s



3) 14kHz-15s



4) 14kHz-20s

100nm

The carbon particle of about 5 - 100nm was observed.
Some CNTs appeared with prolonged discharge time.

Experimental conditions (Frequency change)

Electric discharge conditions

	volt.(kv)	power(kw)
5kHz−10s	8.5	0.15
14kHz−10s	6.5	0.25
30kHz−10s	5.5	0.20
45kHz−10s	7.5	0.25
60kHz−10s	7.0	0.25

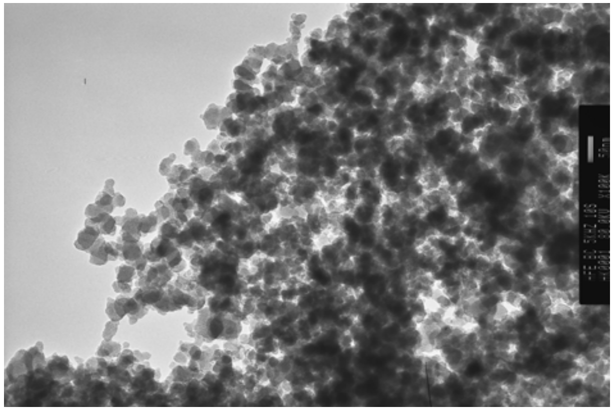
Surface atomic concentrations

mol%	C	F	O	F/C	O/C
5kHz−10s	80.82	13.92	5.25	17.22	6.50
30kHz−10s	80.55	13.59	5.87	16.87	7.29
45kHz−10s	80.44	12.69	6.86	15.78	8.53
60kHz−10s	80.37	12.4	7.23	15.43	9.00

TEM observation (Frequency change)

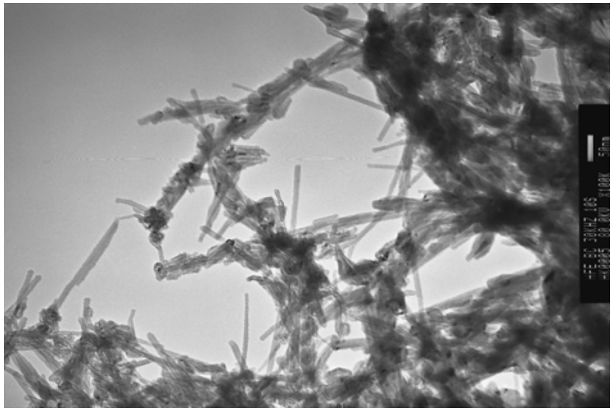
Amorphous particle

Carbon nanotube



1) 5kHz-10s

2) 14kHz-10s

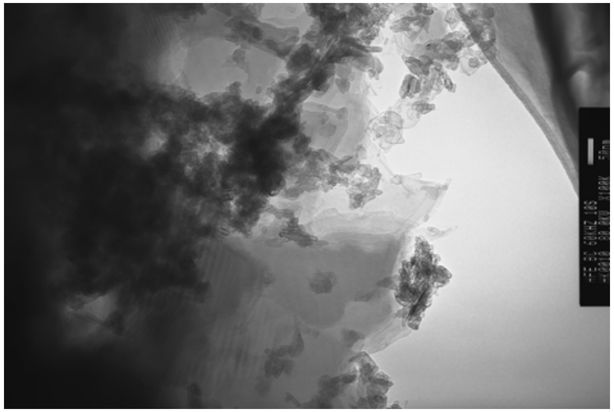


2) 30kHz-10s

About 10nm diameter carbon nanotube was observed except for 5kHz-10s.

Most CNTs were observed in 30kHz-10s.

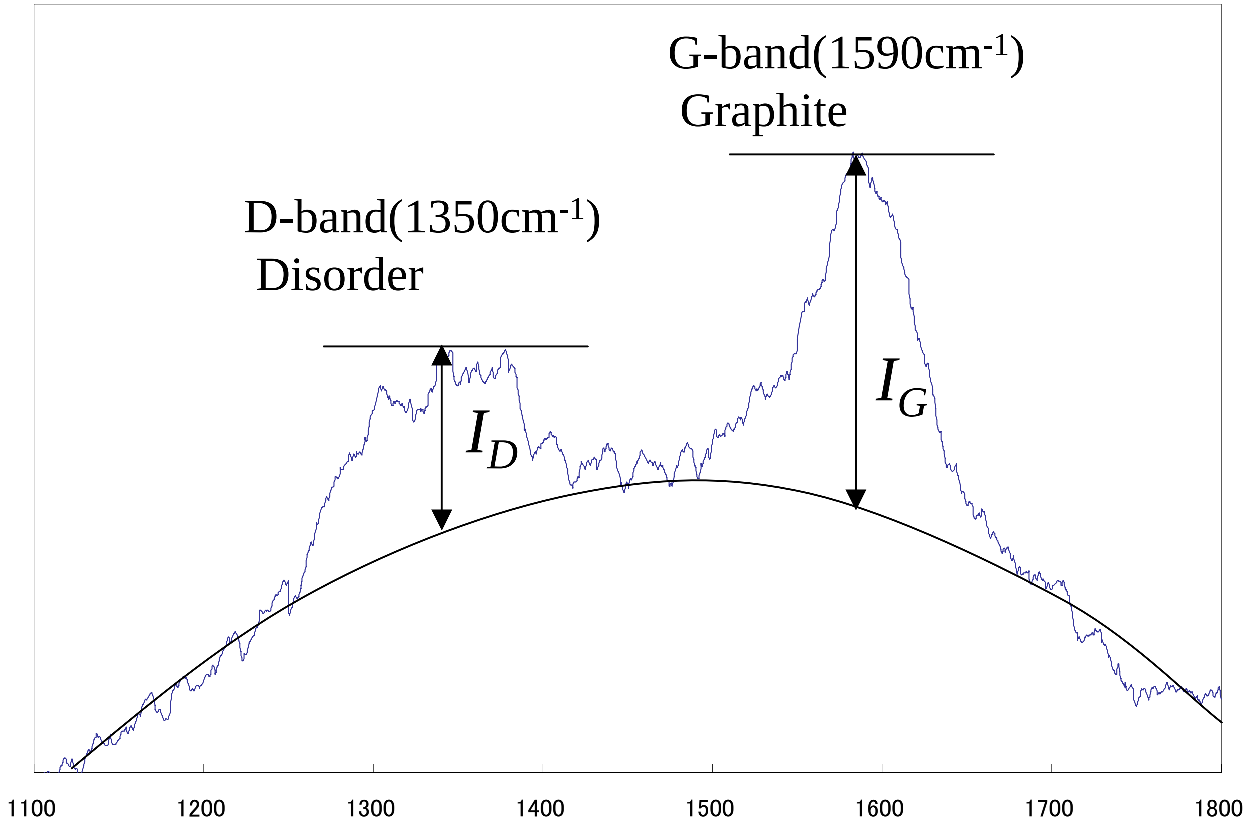
3) 45kHz-10s



4) 60kHz-10s

100nm

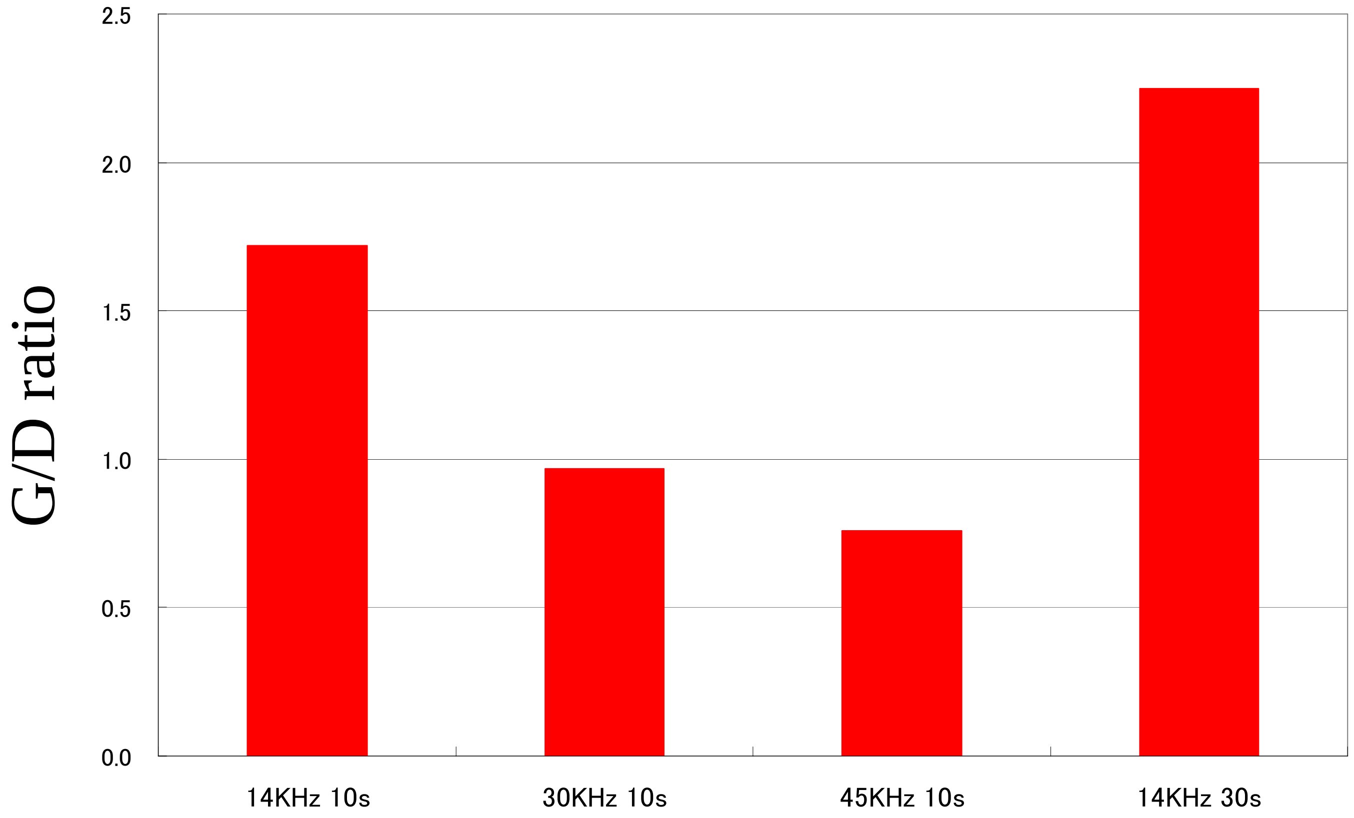
Raman spectrum



$$G/D\ ratio = I_G / I_D$$

The Raman measurement result was caliculated for the rate of a graphite and an amorphous.

G/D ratio (Frequency & time change)



The G/D ratio decreased according to the increase in electric discharge frequency.
When electric discharge time was extended, the G/D ratio increased.

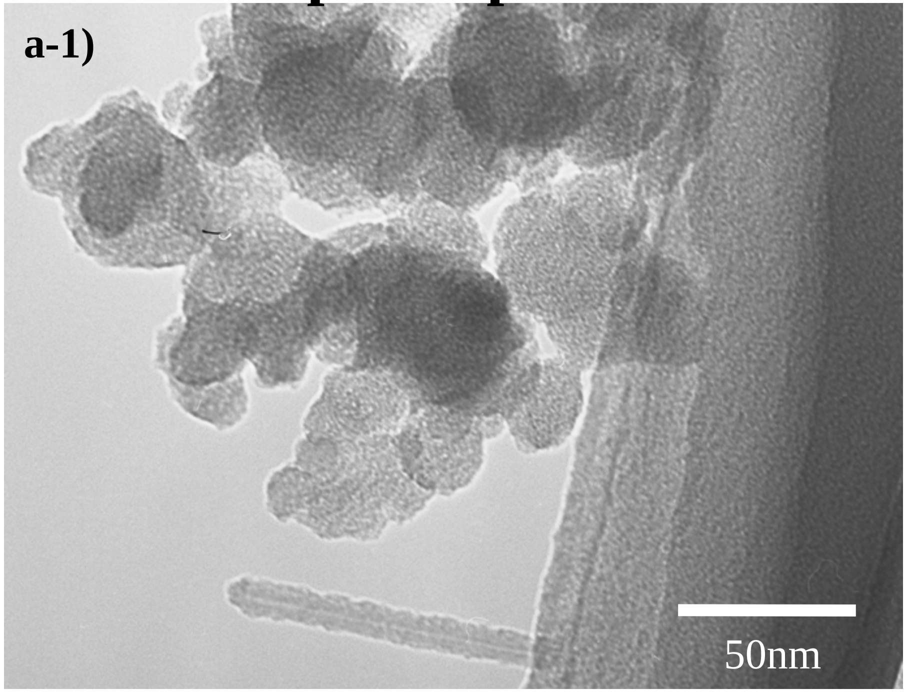
Surface atomic concentrations (Change in catalyst concentration)

Catalyst addition		atomic concentrations(mol%) C	F	O	Fe	Composition ratio(%) F/C	O/C
The amount change of catalysts	0.01%	80.77	14.11	3.82	1.30	17.47	4.73
	0.05%	76.24	14.12	7.69	1.95	18.52	10.09
	0.10%	81.54	12.98	4.39	1.08	15.92	5.38
	0.30%	78.71	15.49	4.18	1.63	19.68	5.31
	0.50%	81.69	11.90	5.04	1.36	14.57	6.17
	HFE-7200	37.50	56.25	6.25	0.00	150.00	16.67
Time change	20s	79.53	15.46	3.33	1.67	19.44	4.19
	30s	78.57	15.03	4.80	1.60	19.13	6.11
Frequency change	30kHz	75.79	14.79	7.59	1.83	19.51	10.01
	45kHz	77.68	15.68	5.16	1.48	20.19	6.64

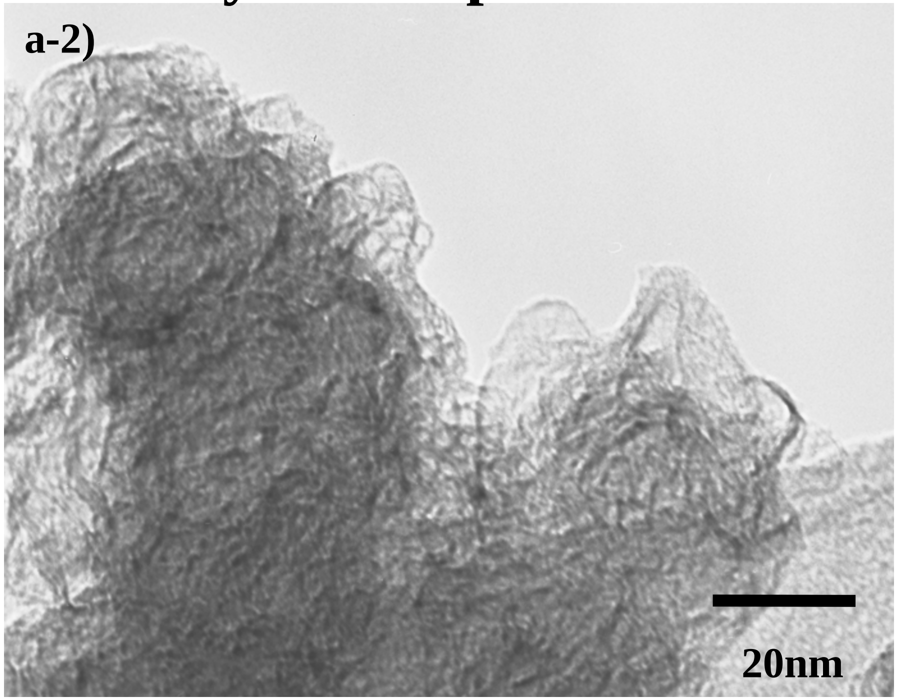
Addtion-free		atomic concentrations(mol%) C	F	O	Composition ratio(%) F/C	O/C
Time change	10s	78.81	8.85	12.34	11.23	15.66
	15s	81.07	14.98	3.96	18.48	4.89
	20s	80.40	12.23	7.37	15.21	9.17
Frequency change	30kHz	80.55	13.59	5.87	16.87	7.29
	45kHz	80.44	12.69	6.86	15.78	8.53

TEM observation (Change in catalyst concentration) 1

Amorphous particle



A crystalline particle

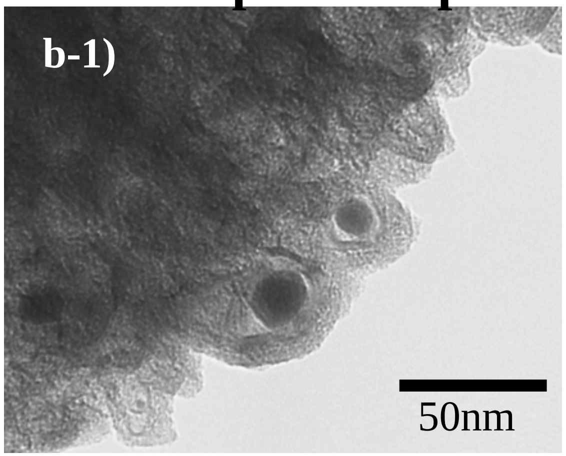


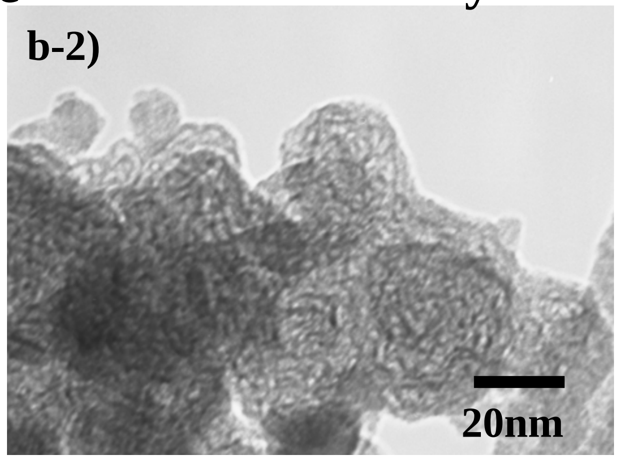
Electric discharge conditions:14kHz,10s, a-1 a-2:Fe0.01%

The carbon particle of about 5 - 100nm was observed for all products. Although CNT was hardly observable, particles of entangled CNT were observed.

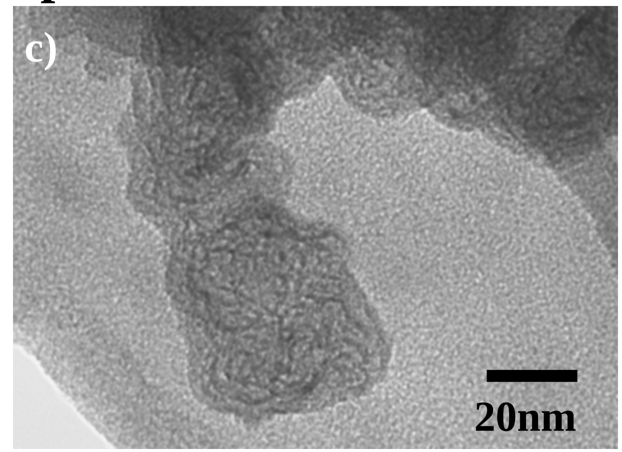
TEM observation (Change in catalyst concentration) 2

Metal encapsulated particle

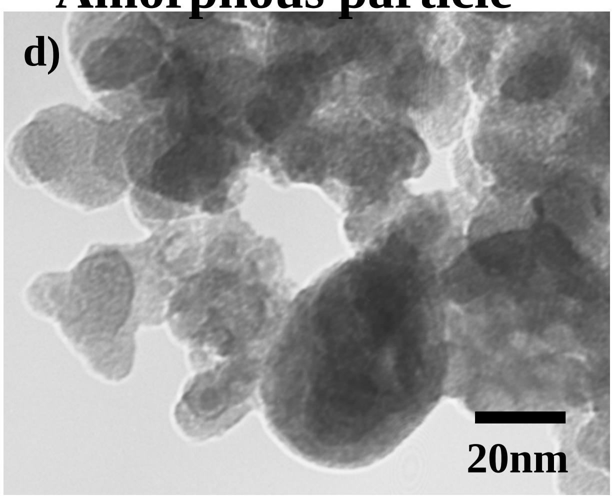


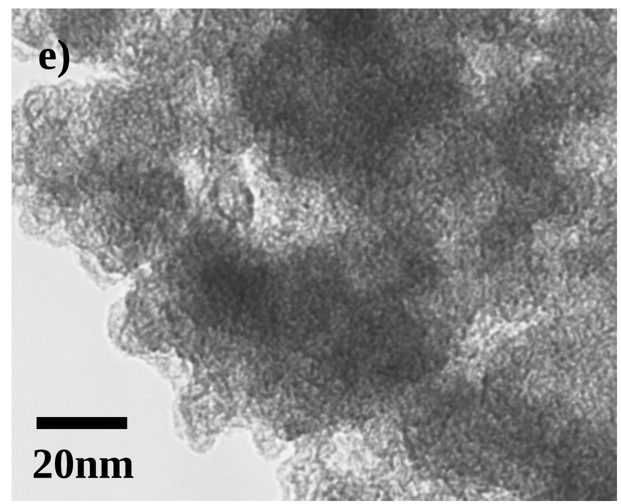


A crystalline particle



Amorphous particle

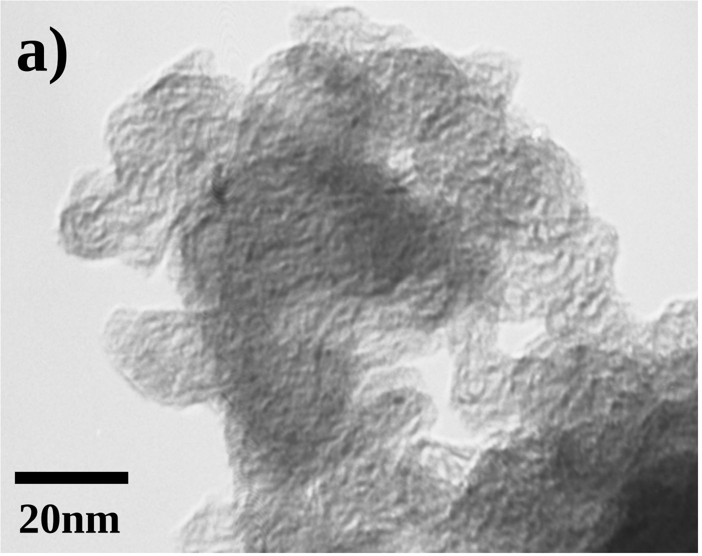


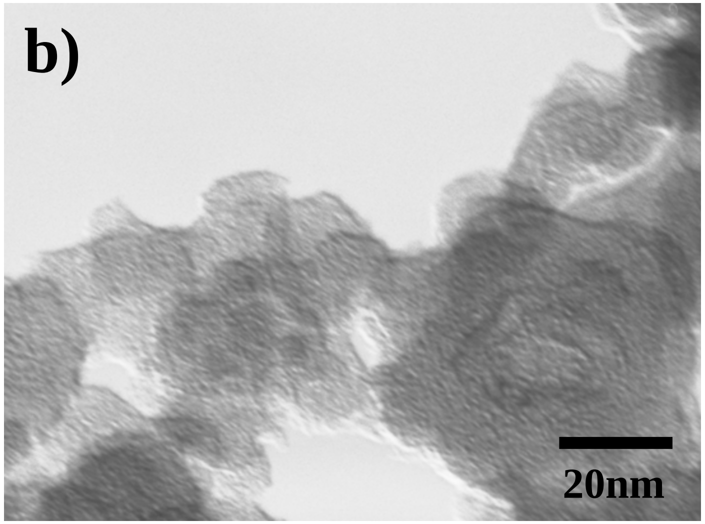


Electric discharge conditions:
14kHz,10s, b-1 b-2:Fe0.05%,c:Fe0.1% d:Fe0.3% e:Fe0.5%

TEM observation (Frequency change)

Crystalline particle | **Amorphous particle**

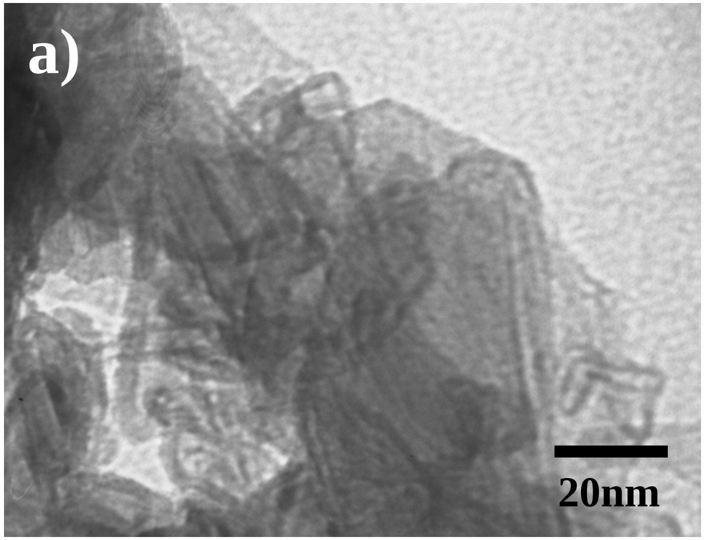




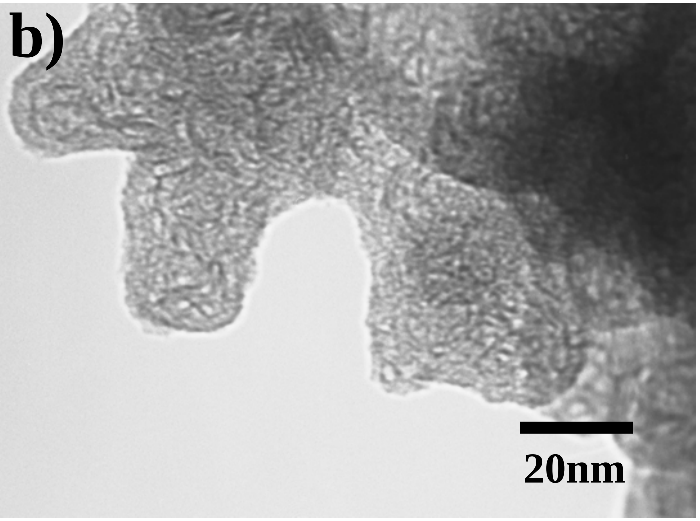
Electric discharge conditions:10s Fe0.1%,a:30kHz,b:45kHz

TEM observation (Time change)

CNT

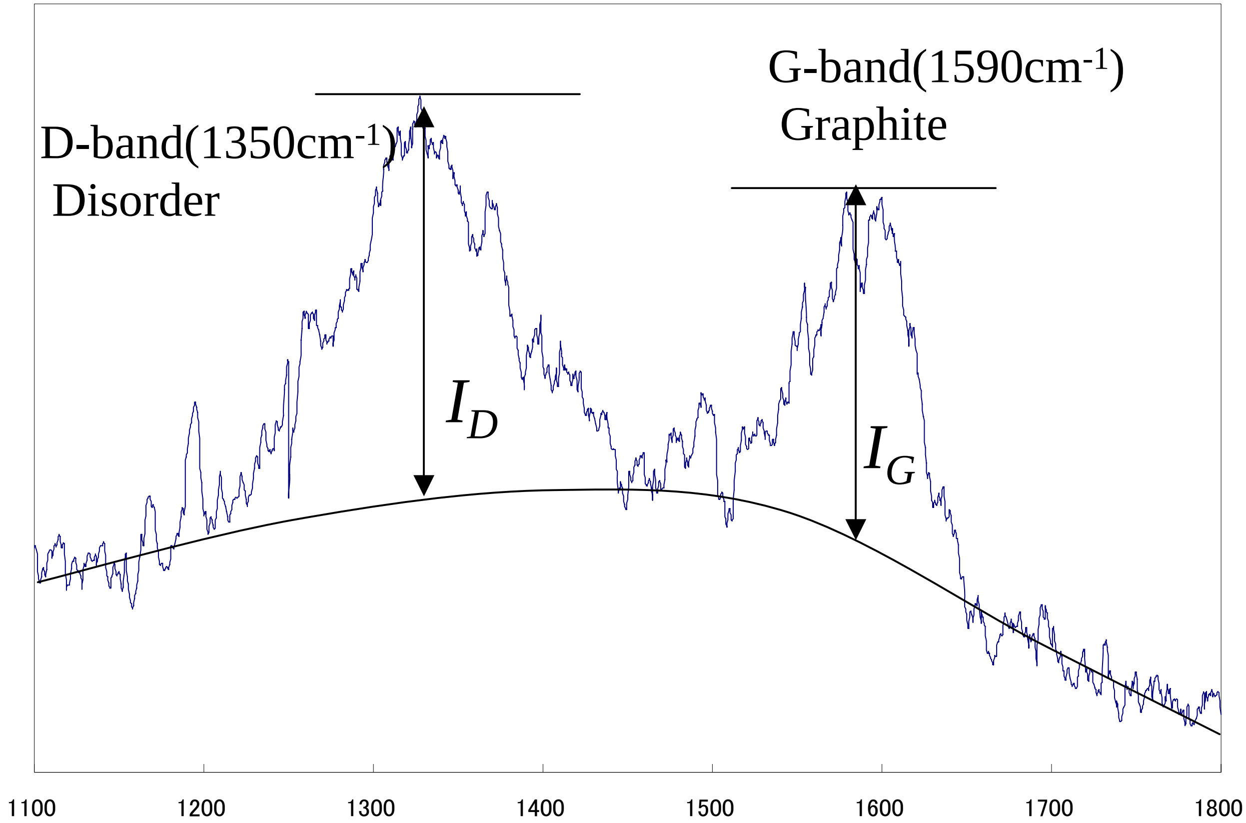


Crystalline particle



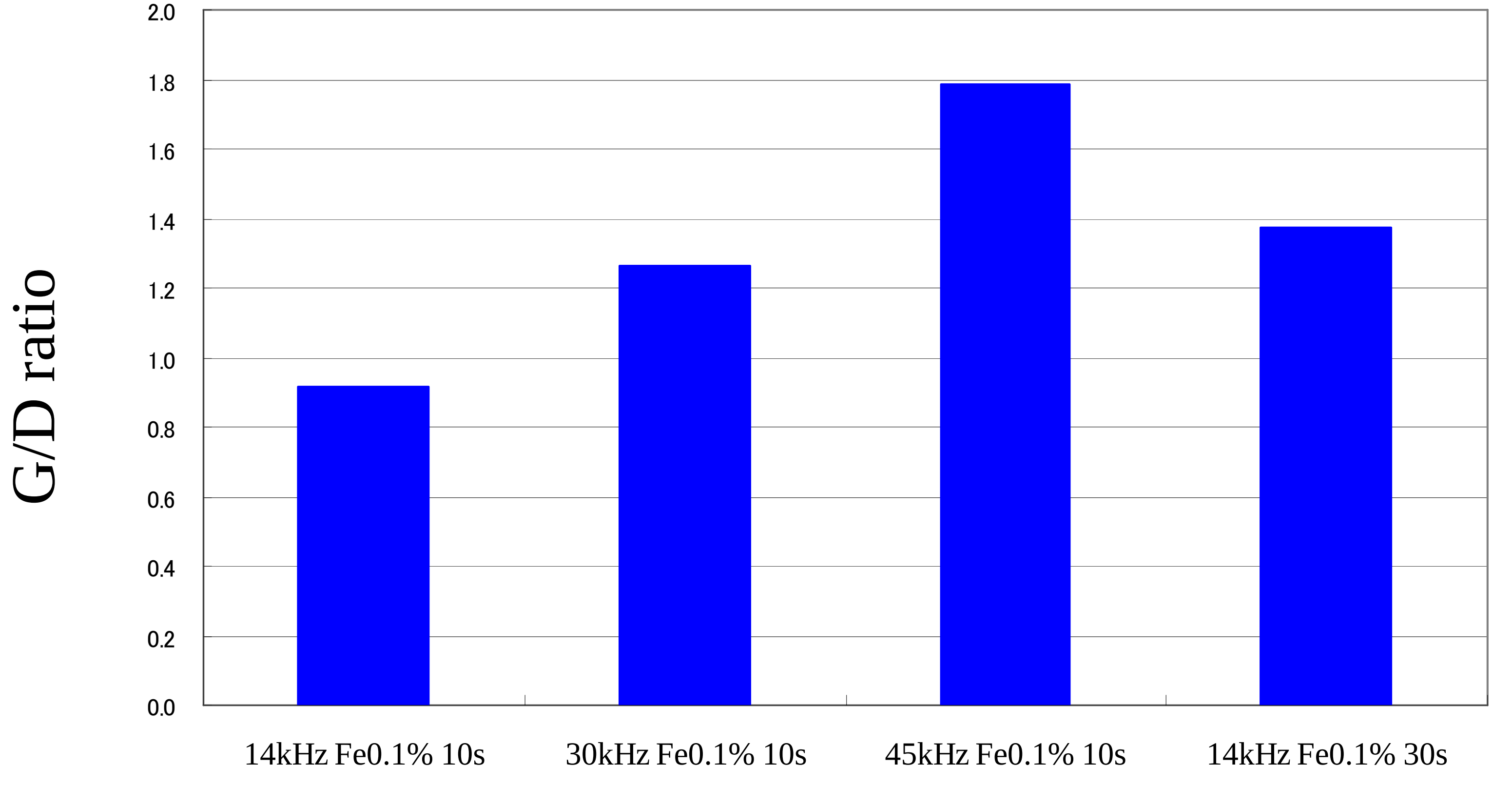
Electric discharge conditions :14kHz,Fe0.1% ,a:20s,b:30s

Raman spectrum



G/D ratio = I_G / I_D

G/D ratio (Change in catalyst consentration)



The G/D ratio decreased according to the decrease in electric discharge frequency.

When electric discharge time was extended, the G/D ratio increased.

Conclusions

•Carbon nanostructures were prepared by pulse-modulated discharge in fluorine-containing organic liquid without using graphite electrodes.
•The formation rate of product was found to be about 30 times faster than that by the “arc in liquid” method previously reported.
•The product consists of nanoparticles and MWCNTs with fluorine on their surface.
•Crystallinity increased according to frequency.