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Carbon Nanotubes films covered with palladium nanocrystals

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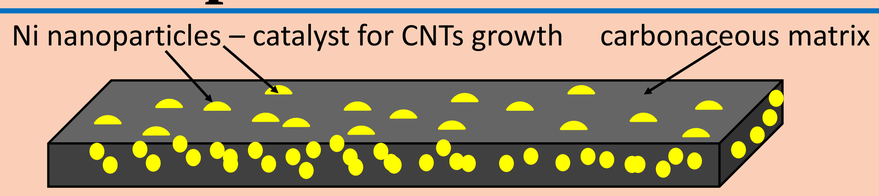
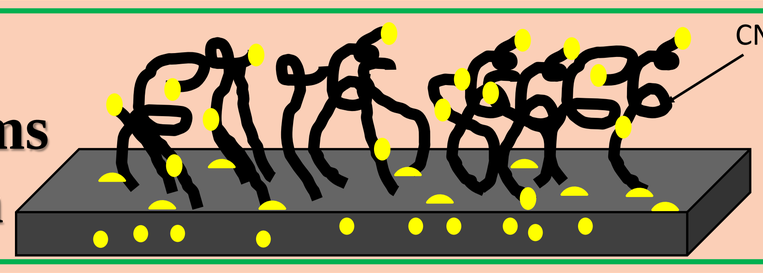
Recently, it has been demonstrated that carbon nanotubes (CNTs) represent a new type of a chemical sensor material capable for detecting small concentrations of molecules with a high sensitivity under ambient conditions. Necessary prerequisite is that the molecules to be detected must have a distinct electron donating or accepting ability, which is fulfilled, for example, by ammonia (NH_3) as a donor and nitrogen dioxide (NO_2) as an acceptor. The adsorption of these molecules on the nanotubes is associated with a partial charge transfer, which alters the charge-carrier concentration or, alternatively, the adsorbed molecules may affect the potential barriers present at the tube–electrode contacts. In any case, the resulting change in the electrical resistance of the nanotube is utilized as a sensor signal. If the nanotube is semiconducting in nature, charge transfer can lead to dramatic changes in the electrical conductance of the nanotube, which serves as the basis for highly sensitive nanotube molecular sensors. For the detection of molecules that are only weakly adsorbed (e.g., H_2, CO), the change in resistance is often too small. A possible method to overcome this drawback is accomplished by the modification of the nanotube sidewalls with nanoparticles made of a suitable metal. For instance, sensitive hydrogen sensors operating at room temperature can be obtained via the deposition of palladium nanoparticles on CNTs, because of high selectivity Pd to hydrogen [1,2].
In this work the method of a preparation CNTs films functionalized by palladium nanoparticles is presented. This is three steps method in which nanocomposites CNTs-Ni-Pd films are obtain. These films were characterized by electron microscopy methods (SEM-scanning electron microscopy, TEM – transmission electron microscopy).

Preparation steps of CNTs-Ni-Pd films

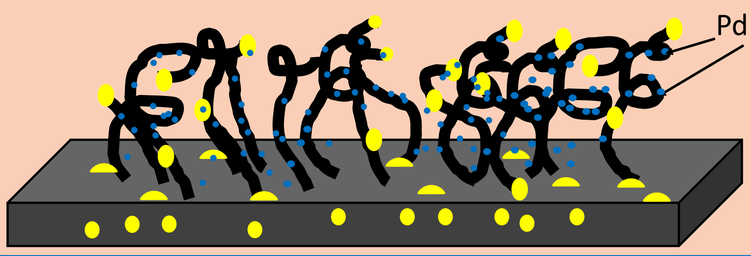
1. PVD (Ni)



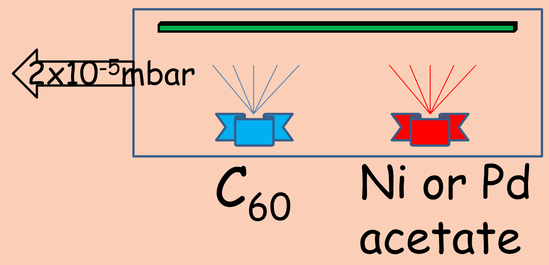
2. CVD CNTs films growth



3. PVD (Pd)

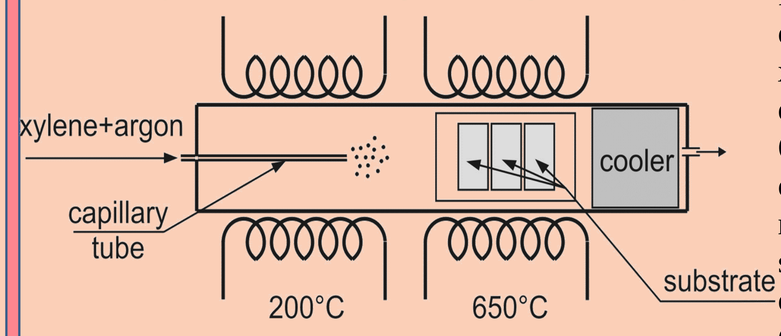


PVD (Physical Vapor Deposition)



In **PVD** process two separated sources containing fullerene C_{60} and nickel acetate or palladium acetate are used to prepare the initial films (1) and to cover by Pd the CVD film (3).

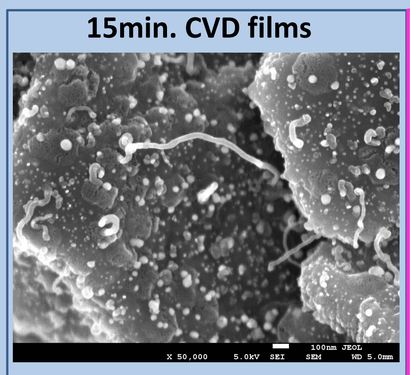
CVD (Chemical Vapor Deposition)

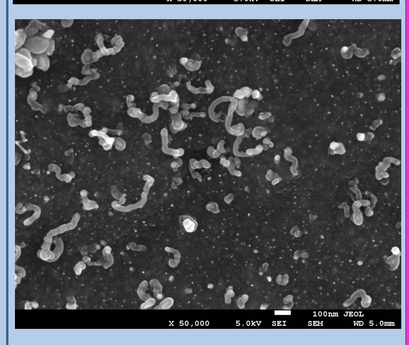


During **CVD** process carbon nanotubes films (2) grown by the decomposition of a hydrocarbon gas which was xylene. CVD process was performed in quartz tube in argon and xylene flow at 650 °C temperatures. In results we obtained films which consisted carbon nanotubes with different densities and sizes and also Ni nanoparticles placed on carbonaceous matrix or inside CNTs.

SEM characterization

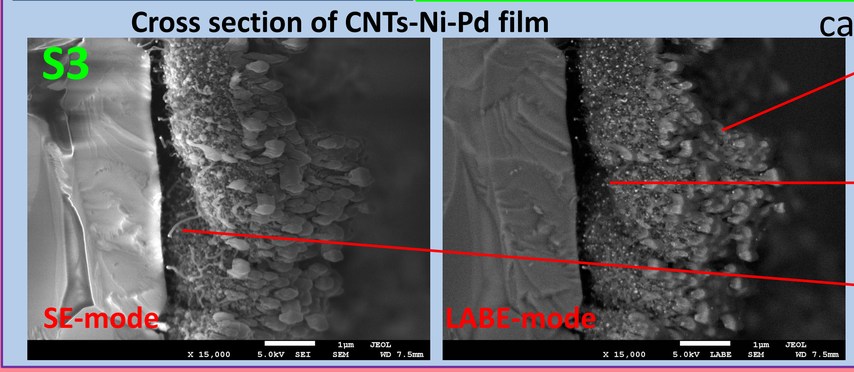
15min. CVD films





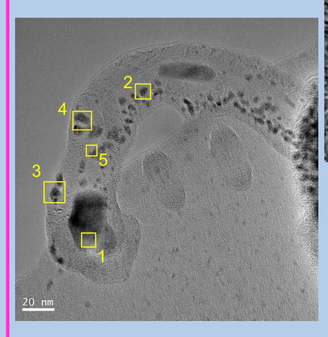
30min. CVD films

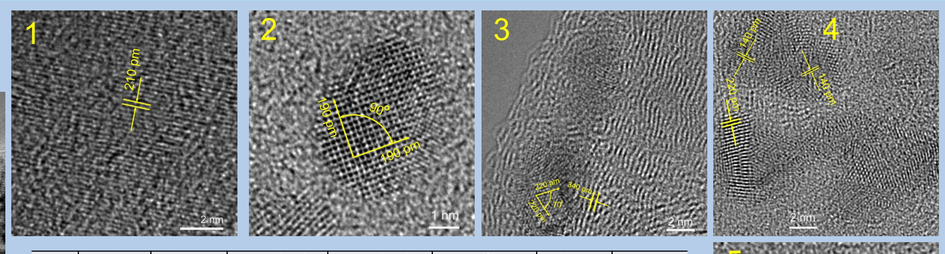
Cross section of CNTs-Ni-Pd film



TEM characterization

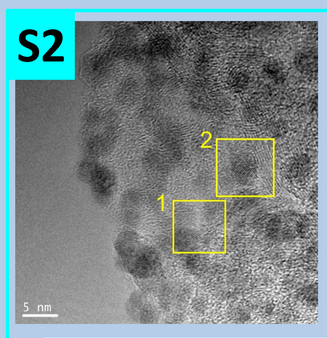
S1

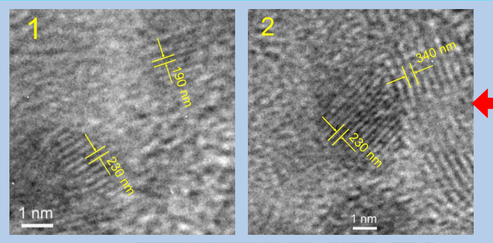




Area	(hkl)_1	(hkl)_2	d_{hkl1} [pm] experimental (literature)	d_{hkl2} [pm] experimental (literature)	a[°] experimental (literature)	Oś pasa	Particle
1	{1 1 1}	-	210 (203)	-	-	-	Ni
2	(2 0 0)	(0 0 2)	190 (195)	190 (195)	90 (90)	[0 1 0]	Pd
3	(1 -1 1)	(1 -1 -1)	220 (225)	220 (225)	71 (70,53)	[1 1 0]	Pd
3	(0 0 . 2)	-	340 (335)	-	-	-	C (CNT)
4	{1 1 1}	-	220 (225)	-	-	-	Pd
4	{2 2 0}	-	140 (138)	-	-	-	Pd
5	{2 0 0}	-	190 (195)	-	-	-	Pd

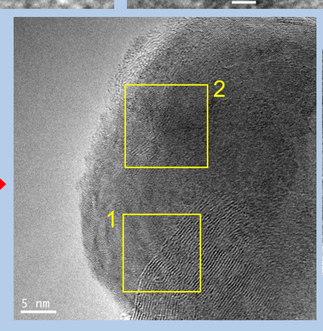
S2

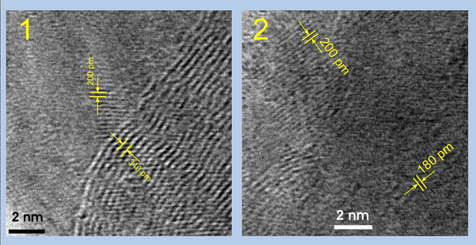




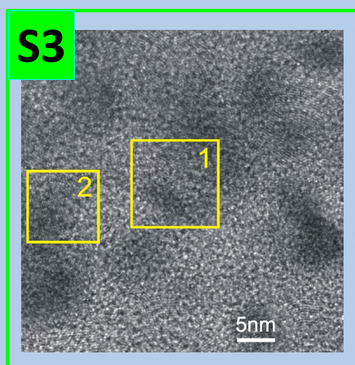
Area	(hkl)_1	d [pm] experimental (literature)	Particle
1	{1 1 1}	230 (225)	Pd
1	{2 0 0}	190 (195)	Pd
2	{1 1 1}	230 (225)	Pd
2	(0 0 . 2)	340 (335)	C (CNT)

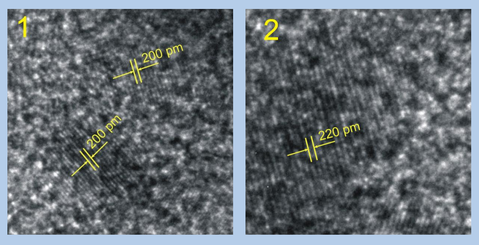
Area	(hkl)_1	d [pm] experimental (literature)	Particle
1	{1 1 1}	200 (203)	Ni
1	(0 0 . 2)	340 (335)	C (CNT)
2	{1 1 1}	200 (203)	Ni
2	{2 0 0}	180 (176)	Ni

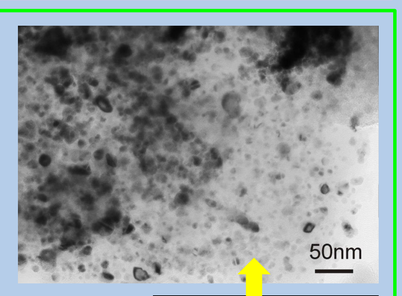


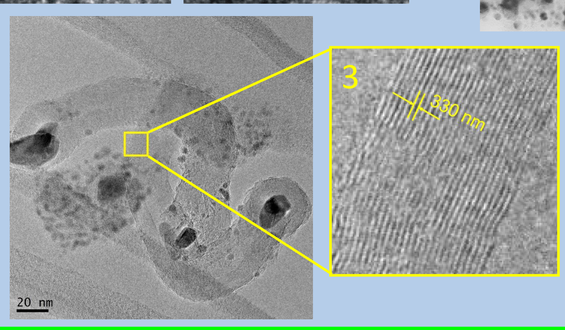


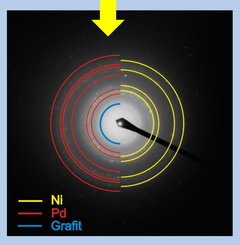
S3











Area	(hkl)_1	d_{hkl1} [pm] experimental (literature)	Particle
1	(1 1 1)	220 (225)	Pd
2	{1 1 1}	200 (203)	Ni
3	(0 0. 2)	330 (335)	graphite

*) In tables the interplanar distans of are presented

Conclusions

We obtained carbon nanotubes decorated with Pd nanoparticles.
SEM investigations:

- CNTs diameters (films after CVD) 20 to 70nm lenghs from 100nm to 1µm.
- Ni nanoparticles - catalyst of CNTs growth – are visible inside CNTs and on the surface.
- After third step CNTs films covered by carbonaceous-palladium mixture which enlarging CNTs initial size

TEM investigations

- Films obtained in three steps method contain: carbon (CNTs), Ni and Pd
- Ni nanoparticles are inside CNTs and Pd nanoparticles decorated nanotubes which allow to attached various molecules to CNTs

[1] Small 2005, 1, No. 2, pp.180 –192
[2] Adv. Mater. 2001, 13, No. 18, pp. 1384-1386

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