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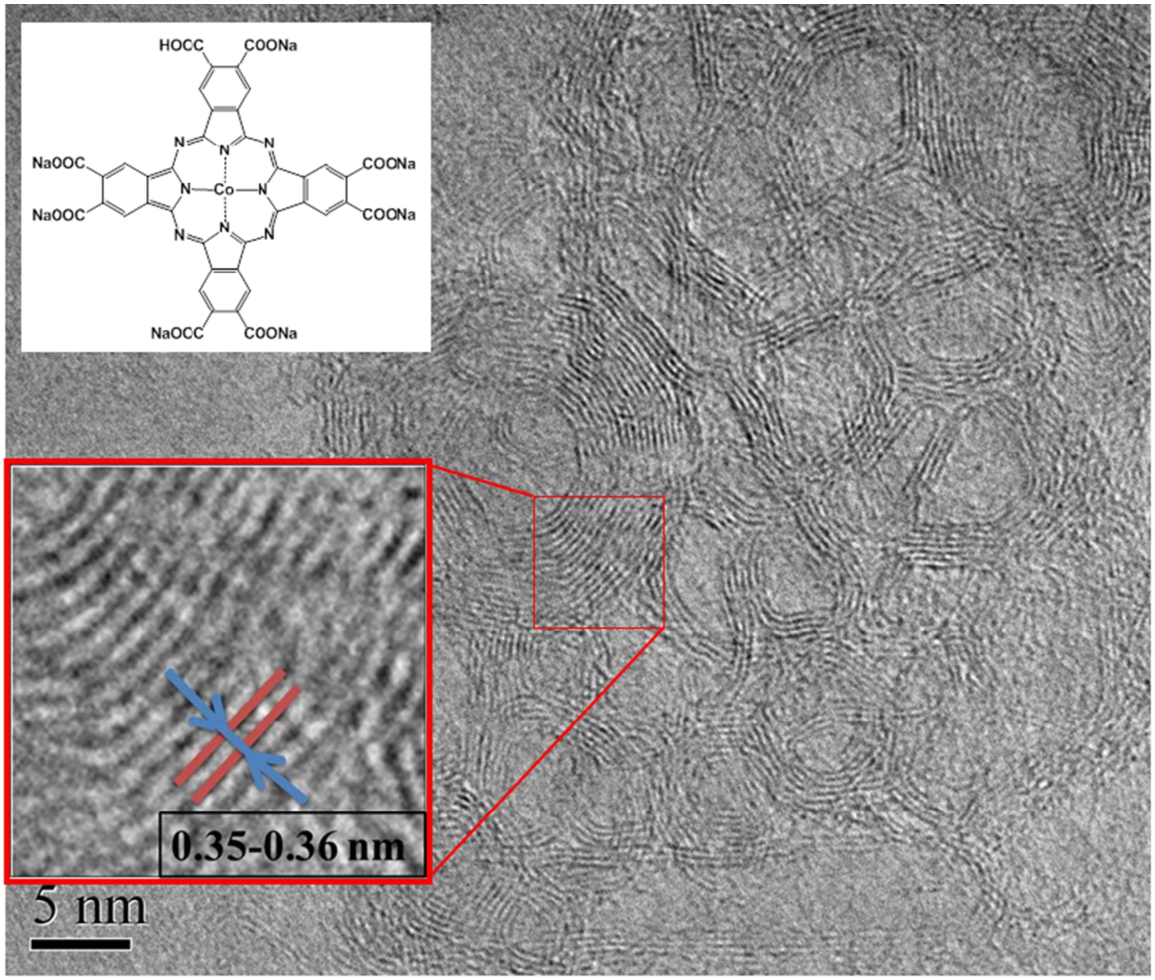

Ultrasonic treatment of theraphthal and MWCNTs dispersions, resulting formation of nano-onion structures in mild conditions.

Preparation of carbon nano-onions by low-temperature unfolding MWCNTs *via* interaction with theraphthal.

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Abstract. Treatment of MWCNTs with water-soluble cobalt octacarboxyphthalocyanine derivative Theraphthal under ultrasonic conditions led to the dispersion and unfolding of MWCNTs producing onion-like carbon nanostructures and graphene sheets. These nanostructures are formed as a result of dispersion and unfolding of MWCNTs using a water-soluble cobalt octacarboxyphthalocyanine derivative theraphthal in ultrasonic treatment conditions. This fact is out of conventional concepts on classic π-π stacking interactions and/or σ-bonding between macrocycles and carbon nanotubes, as well as out of classic high-temperature formation of carbon nano-onions.

Theraphthal (**1**, TP, $C_{40}H_9CoN_8Na_7O_{16}$, Mw=1077.46)[1,2] is a water-soluble cobalt phthalocyanine salt with 7 -COONa and 1 -COOH groups on the periphery, used in cancer therapy.[3,4] TP, as well as other metal 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines, their water-soluble sodium salts, and their functional derivatives are known to generate Reactive Oxygen Species (ROS) under certain conditions.[5,6] Related cobalt phthalocyanines have been reported to possess good catalytic properties.[7-11] Multi-walled carbon nanotubes (MWCNTs) are insoluble in water and solvents, but can be dispersed in liquids by various methods like ultrasonication, functionalization, use of surfactants, irradiation, etc.[12,13] Majority of phthalocyanines are not very soluble either. As a result, soluble phthalocyanine-CNTs composites remain less explored.[14,15] An example is a water-soluble composite of oxidized MWCNTs and sulfonic acid sodium salt derivatized copper phthalocyanine, used for applications in bilayer organic solar cells.[16] Here we describe the solubilization of MWCNTs at low bulk temperatures (<50°C) in aqueous media using TP under ultrasonic irradiation which results in changes to and unfolding of MWCNTs including the formation of honeycomb-like/nano-onion nanostructures.

Ultrasonic cleaner Branson-5210 (tank capacity 9.5 L, operating frequency of 40 kHz, output power 469 W) was used for ultrasonication of precursors. High-Resolution Transmission Electron Microscopy (Hitachi H-9500), Scanning Transmission Electron Microscopy (JEOL 1200EX STEM), and IR-spectroscopy (Shimadzu IRPrestige-21) were used for the characterization of final products. Raman spectra (DXR Raman Microscope ThermoScientific) were collected using excitation wavelength of 785 nm (1.58 eV). The chemical composition of one selected sample (diluted TP-MWCNTs dispersions) was investigated by X-ray photoelectron spectroscopy (XPS) on a Perkin-Elmer Phi 560 ESCA/SAM system and the spectra were acquired using a non-monochromated Al Kα excitation source. The Al Kα excitation is characteristic unresolved K $\alpha_{1,2}$ and has a characteristic energy of 1253.6 eV. Survey scans were conducted in the 0 to 1200-eV range at 0.5-eV steps. High-resolution scans were conducted for C 1s peak in the 280 to 294-eV range at 0.1-eV steps. MWCNTs were purchased with *NanoAmorphous Materials, Inc.* (Houston, USA). Different amounts of slightly magnetic MWCNTs (Fig. 1) and **1** (in equal weight ratio, from 0.02 to 0.1% concentration of each component in finely formed dispersions) were ultrasonicated in 30 mL flasks with DI water for 5 h at 42-45°C (Fig. 2). The HRTEM and SEM studies (Fig. 3) of resulting products from diluted dispersions (0.02%) indicate almost complete disappearance of MWCNTs (Fig. 3a) and further formation of honeycomb-like structures, constructed of carbon nano-onions (interlayer distance ≈0.35 nm, Fig. 3b) or their precursors (Fig. 3d). For more concentrated dispersions (Figs. 3c and 4), the measured distances between carbon layers do not confirm existence of MWCNTs, where standard interlayer distances can vary in the range from 0.27 up to 0.42 nm.[17] In this case, polygonal, non-homogenous structures (in some samples CNTs-like species having diameter of 1.7-1.8 nm) are formed (Figs. 3c and 4b). Fig. 4a shows completely unfolded nanotubes in the form of planar graphene sheets. Figs. 3e and 4c show partially destroyed CNTs covered with TP aggregates with distinct sizes. XPS data of TP-CNTs sample (see S5 Supplemental file, graphic a), obtained from dilute dispersions of TP-MWCNTs show mainly the presence of C, O, N, Na and Si. This presence of the Si was from the contamination of glass (the samples were synthesized in a glass vial under ultrasonic treatment and dried on glass surface). Further analysis of the high-resolution XPS spectra of the C 1s peak (see S5 Supplemental file, graphic b) shows that it can be decomposed into the three components at binding energy of 284.4 eV, 286.7 eV and 290.5 eV that can be assigned to sp^2 C=C, C-O (>C=O or C-NH_x) and O-COO, respectively.

In addition, the use of previously COOH-functionalized CNTs obtained by acid treatment of pristine MWCNTs in this experiment at dilute dispersions (0.02%) afforded partially and totally decomposed and unfolded CNTs covered with TP (Fig. 5). We note that, in contrast to MWCNTs, the graphite does not undergo solubilization and destruction in the conditions above. It is also observed that a) low TP concentrations (<0.02%) are unable to disperse MWCNTs even in their smaller quantities; b) MWCNTs can be also solubilized using theraphthal without ultrasound and applying only vigorous stirring, but without formation of onion-like nanostructures; c) ultrasonic treatment of "cobalt(II) nitrate (as a source of cobalt ions) – MWCNTs – water" mixtures without TP does not lead to dispersion of MWCNTs, even in presence of organic or inorganic peroxides which could produce free radicals under sonication in Fenton-like conditions.

We note that, according to literature data, carbon nano-onions can be prepared mainly by highly energetic methods, such as heat treatment, detonation, electron beams, arc discharge in liquids, pyrolysis, or combustion.[18-21 and refs. therein] In those reported processes, starting materials are graphite, nanodiamonds, wood wool, naphthalene, or $CuCl_2$ and CaC_2. In our experiments, unusual unfolding of MWCNTs in the conditions of TP addition can be explained by the *in situ* formation of reactive oxygen species in TP solutions under ultrasonic treatment (local temperature in cavitation bubbles is about 5,000 K) and their further attack on MWCNTs surface. It is well-known that cavitation triggers free radical processes, shock waves, cumulative streams, and a number of other phenomena in a system that are localized at collapsing cavitation bubbles. In addition, the combination "ultrasound + TP" at >40°C was recently found[5] to be an excellent combination for tumor treatment, acting on the basis of appearing free radicals (TP promoted the effects of both ultrasound and chemotherapy without changing the general and local tolerability of the treatment). In these conditions, even at low intensity ultrasound in cleaners (20-40 kHz), partial destruction of TP slowly takes place and it is known to be accompanied by formation of

ROS. As a phthalocyanine derivative, TP could be first coordinated[14] to CNT surface *via* π-π-stacking through aromatic macrocyclic ring or through COO^- group(s) (see S1 Supplemental material). The first type of interaction noted above to MWCNTs was already reported for a related cobalt phthalocyanine with $-CO\text{-}NH\text{-}C_6H_4\text{-}C(CF_3)_2OH$ substituents,[22] as well as for non-substituted metal (Co, Cu, Ni, Zn) phthalocyanines.[23] Highly water-soluble, ionic TP transfers MWCNTs to solution and due to the presence of free radicals and resulting surface defects under ultrasound conditions may alter and unfold them forming graphene sheets (Fig. 4a). These sheets can then form CNTs-like species, diameter 1.7 nm, Figs. 3c and 4b). In some cases (in diluted dispersions), at lower TP concentrations, incomplete unfolding of MWCNTs takes place leading to the appearance of circular nanostructures (nano-onions), which are united to honeycomb-like nanostructures due to self-healing of defects in MWCNTs caused by action of free radicals. FTIR-spectra of the dispersion products contain mainly the following bands, cm^{-1}: 2800-3000 (strong, wide, O-H bond stretching in a COOH group of TP and C-C bonds both in carbon phase and TP), 2300-2350 (weak, C-C bonds in both components), 1450-1470 and 1370 (strong, C-H bonds in aromatic macrocycles, C-O bonds in carboxylate groups). These bands are consistent with main bands in FTIR spectra of previously reported carbon nano-onions.[24] Raman spectra of products (Figs. 6 and 7) in the measured range contain two main wide peaks at 1640-1530 (double peak) and 1350-1250 cm^{-1}. Comparing them with previously reported Raman spectra of carbon nano-onions,[19,24,25] MWCNTs and related theraphthal structure containing eight –COONa groups,[26] we note that the first band could be a result of overlapping of two peaks corresponding to the bands in partially destroyed TP, resulting nano-onions, partially destroyed MWCNTs and products of their transformations to other carbon structures mentioned above (see S2 Supplemental material). The involvement in main vibrations (large vibrations are considered only) of N_α (1320 cm^{-1}), C_α (1530 and 1230 cm^{-1}), C_β (1117 cm^{-1}) atoms of TP is observed and not in case of N_β atom (1210 cm^{-1}).[26] In addition, evaluation of evolution processes in both concentrated and diluted TP-MWCNTs dispersions was carried out using Raman spectroscopy (Figs. 6 and 7) and HRTEM (Fig. 8). An obvious gradual disappearance of carbon nanotubes (strong peak at 2700 cm^{-1}, which is expanded and turned to ~2650-2750 cm^{-1}) is observed in both cases and formation of nano-onions (see Fig. 6 and S2 Supplemental table containing a comparison of observed and experimental data) and graphene sheets.

In summary, both pristine and COOH-functionalized MWCNTs can be easily solubilized by dispersion in water using highly water-soluble TP in ultrasonic treatment conditions. Resulting final structure depends on reagent concentrations: in diluted dispersions, the formation of nano-onion structures is observed, meanwhile in relatively concentrated solutions, graphene sheets and non-homogenous structures are found. These observations are different from just π-π stacking interactions and/or σ-bonding reported between macrocycles and carbon nanotubes or typical carbon nano-onion production methods which require high temperatures. Possible applications of these onion-like nanostructures could be in water filtration devices and double layer capacitors, among others.[19,20,25,27] In addition, taking into account that nano-onions are considerably less toxic in comparison to MWCNTs,[19,28,29] an *in vivo* transformation MWCNTs→nano-onions in water under TP assistance could find novel unexpected medical applications. Further investigations on cytotoxicity and elucidation of possible antitumor properties of TP-MWCNTs reaction products are highly recommended, as well as development of low-temperature (bio)degradation methods for carbon nanotubes.[30]

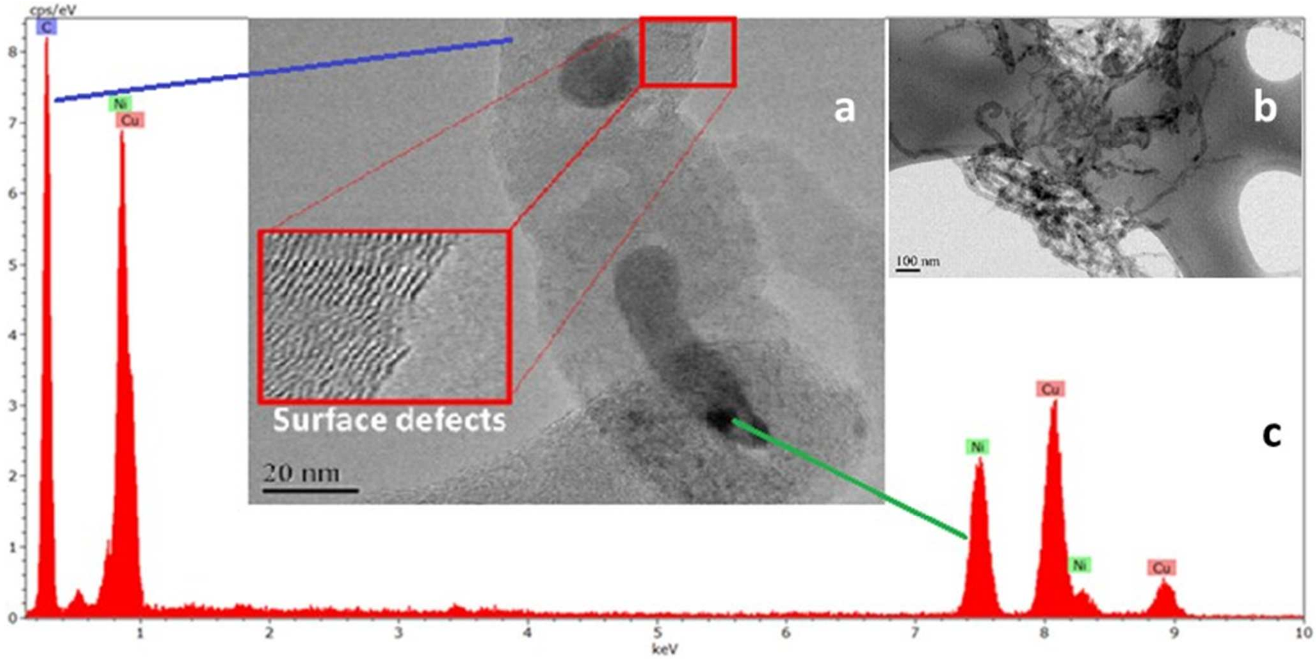


Fig. 1. Commercial MWCNTs before the ultrasonic treatment with TP: a-b) HRTEM images; c) elemental analysis indicating nickel presence as a standard impurity. Standard Cu peak corresponds to the supporting grid.

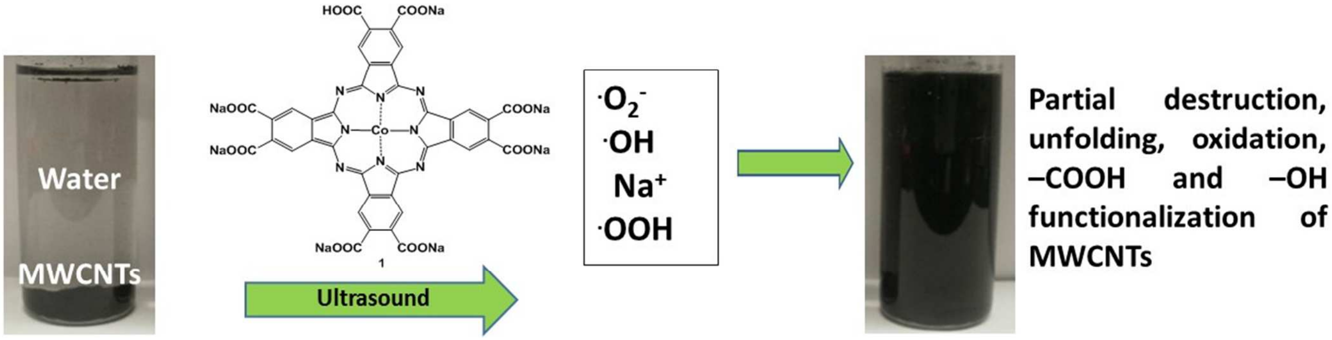


Fig. 2. Results of ultrasonication of pristine MWCNTs in water without TP (left photo) and in the presence of TP (right photo, 1 week aging).

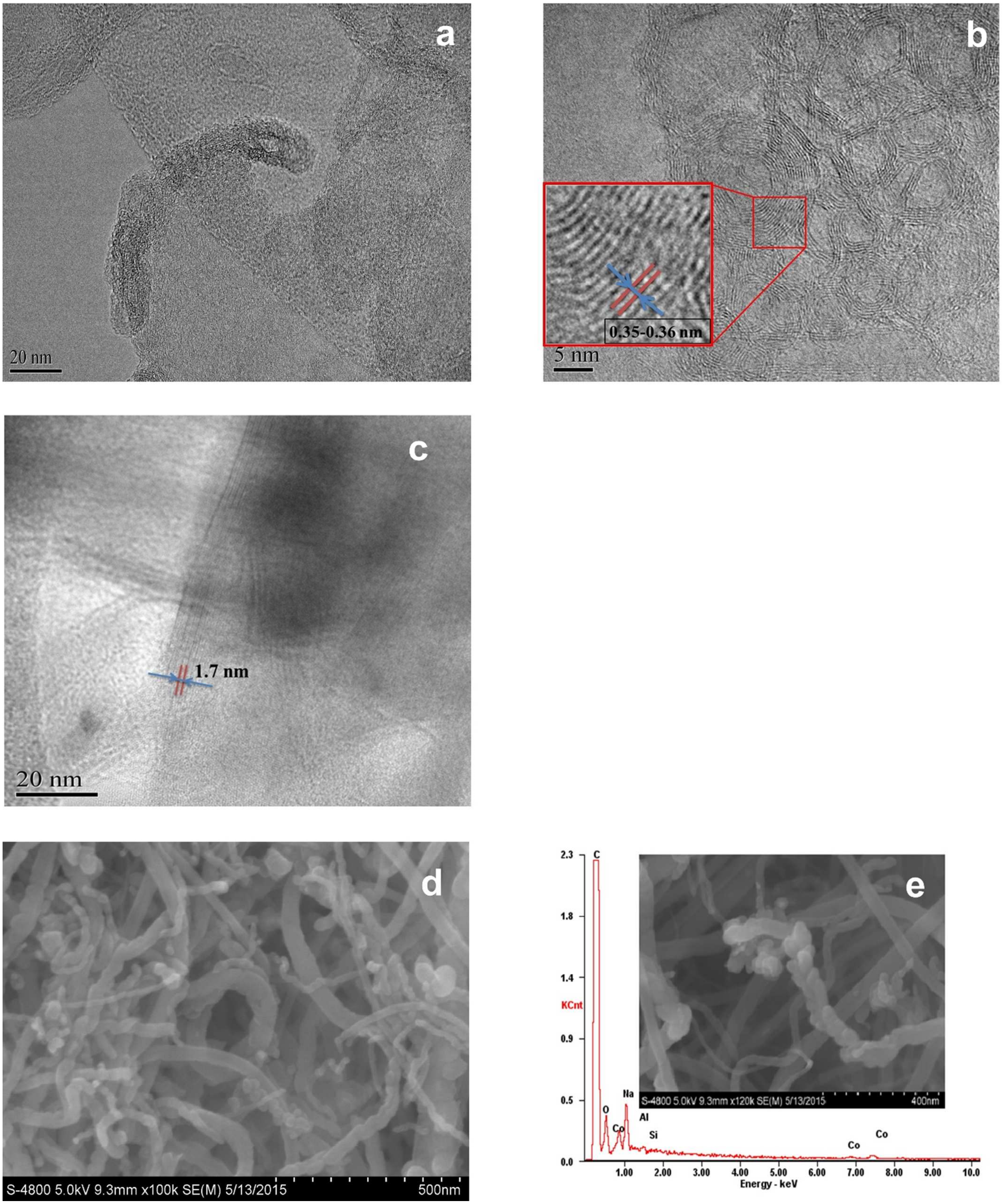

a
20 nm
b
0.35-0.36 nm
5 nm
c
1.7 nm
20 nm
d
S-4800 5.0kV 9.3mm x100k SE(M) 5/13/2015
500nm
e
S-4800 5.0kV 9.3mm x120k SE(M) 5/13/2015
400nm
KCnt
2.3
1.8
1.4
0.9
0.5
0.0
C
O
Co
Na
Al
Si
Co
Co
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.0
Energy - keV

Fig. 3. HRTEM (a-c) and SEM (d, e) images of products observed TP-MWCNT dispersions: a) partially destroyed defected MWCNTs and graphene sheets (diluted dispersions, 0.02 %); b) the interaction product in the form of nano-onions in the system MWCNTs-TP (diluted dispersions, 0.02 %) (see S3 Supplemental material for high resolution image of nano-onion structures); c) the interaction product in the initial system MWCNTs-TP (concentrated dispersions, 0.1 %) (see S4 Supplemental material for high-resolution image); d) SEM image showing precursors of carbon nano-onions in diluted dispersions (1 h ultrasonic treatment); e) SEM image showing initially formed TP aggregates onto CNTs and elemental analysis data.

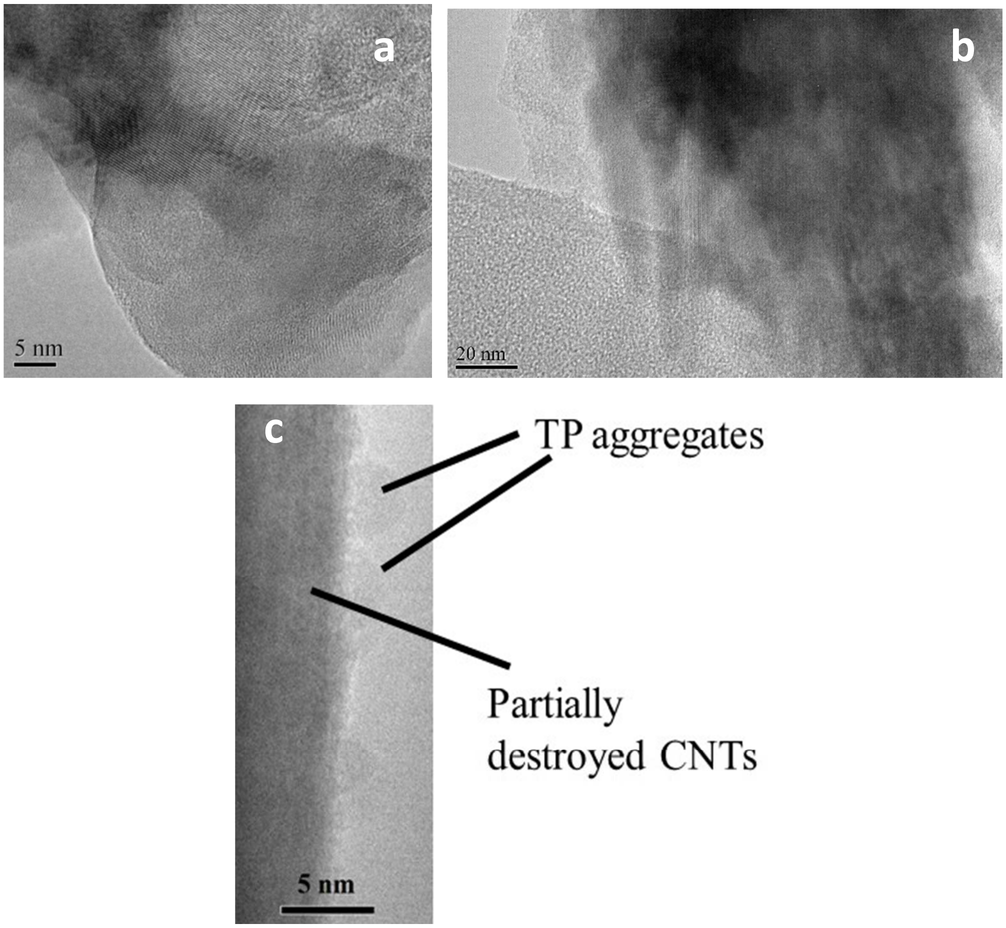


Fig. 4. HRTEM images of the products formed in concentrated TP-MWCNTs dispersions: a) graphene sheets; b) non-homogenous structures with CNT-like species, c) covering of partially destroyed CNTs with TP aggregates.

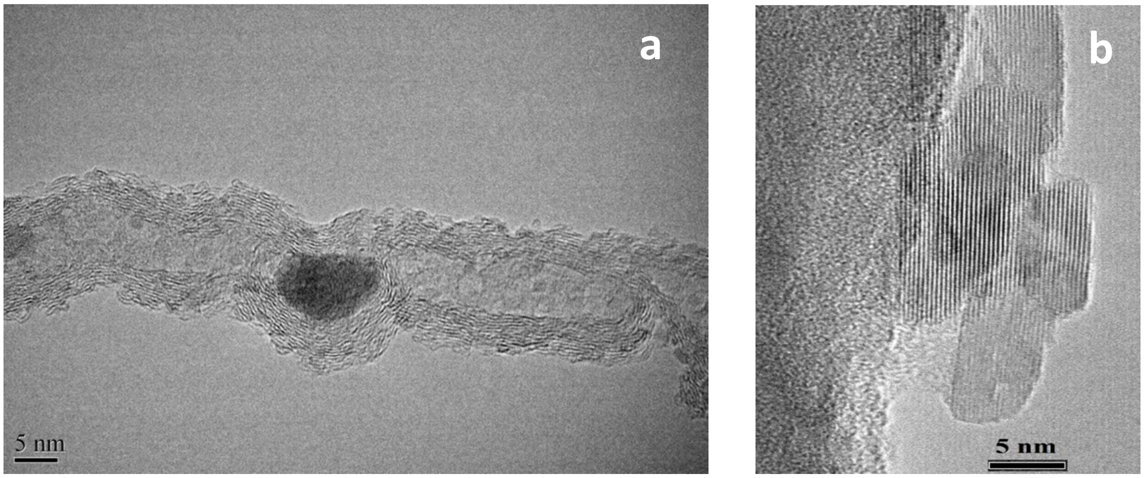


Fig. 5. HRTEM images of a) functionalized MWCNTs-COOH before treatment with TP, b) reaction products of the MWCNTs-COOH with TP.

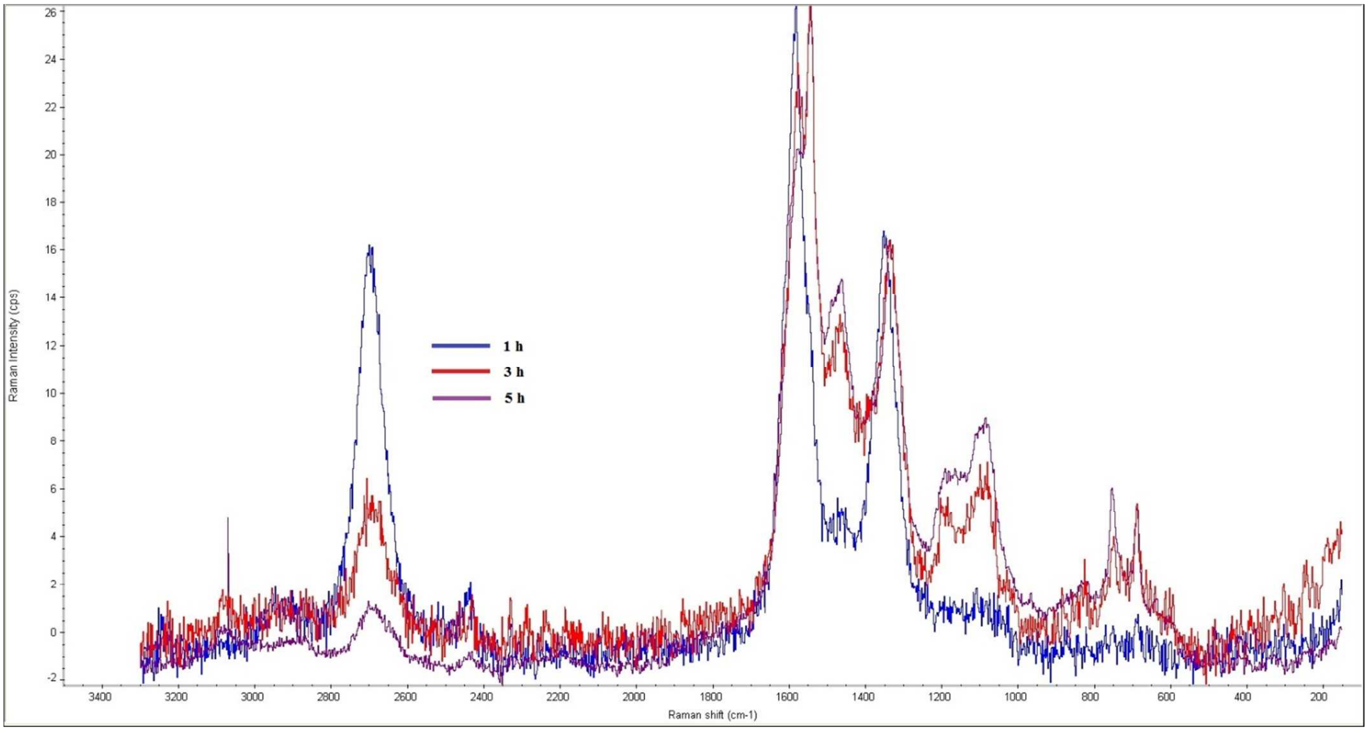


Fig. 6. Raman studies of evolution processes in concentrated TP-MWCNTs dispersions.

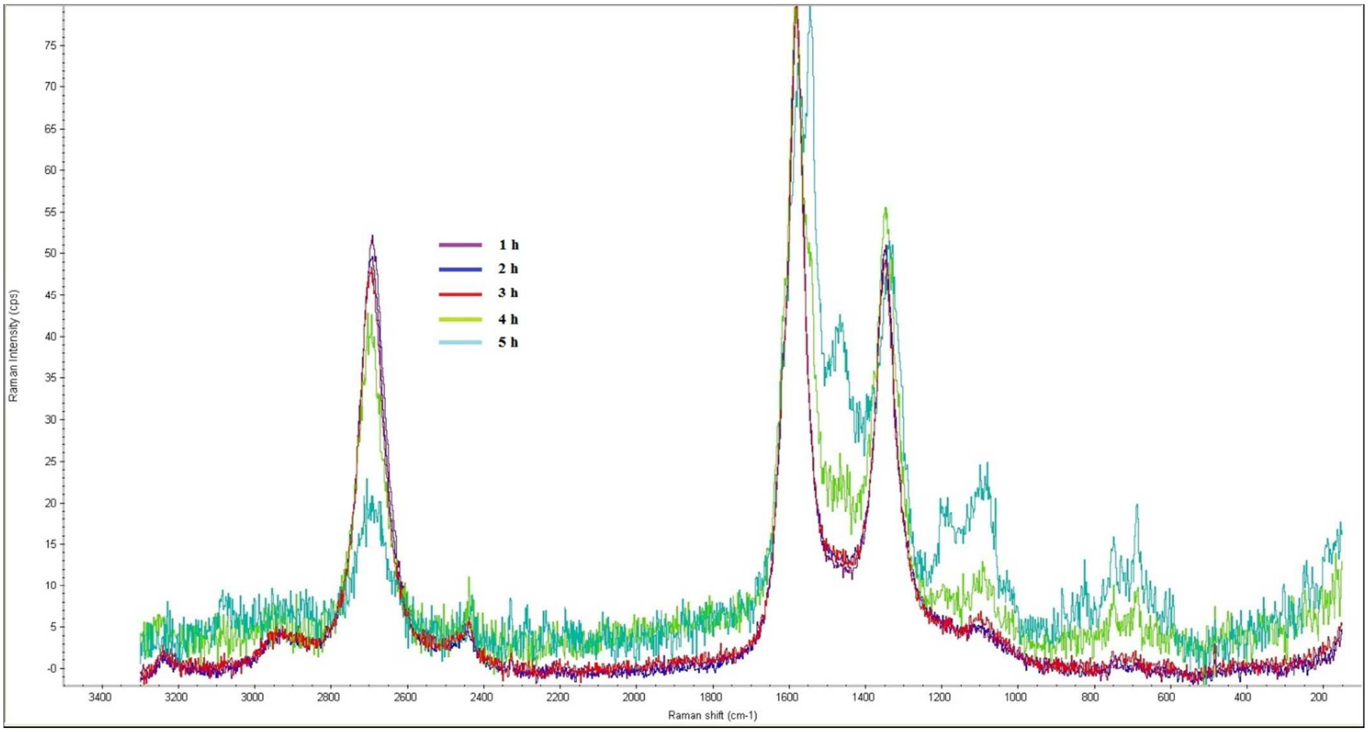
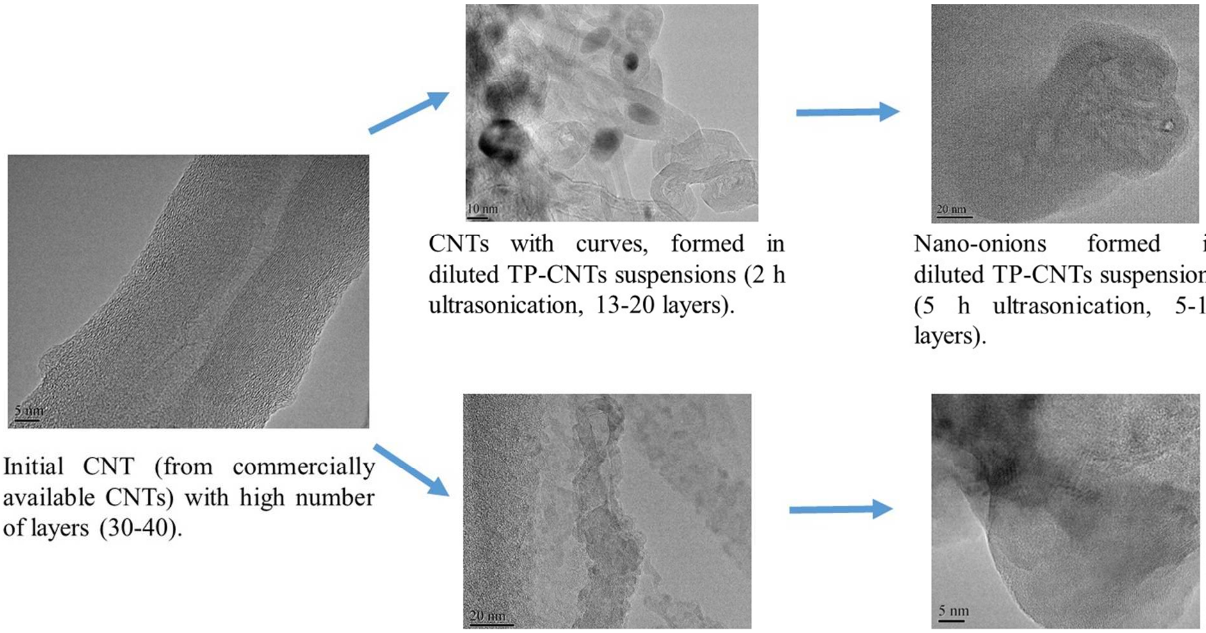


Fig. 7. Raman studies of evolution processes in diluted TP-MWCNTs dispersions.



Initial CNT (from commercially available CNTs) with high number of layers (30-40).

CNTs with curves, formed in diluted TP-CNTs suspensions (2 h ultrasonication, 13-20 layers).

Nano-onions formed in diluted TP-CNTs suspensions (5 h ultrasonication, 5-12 layers).

Partially destroyed and shortened CNTs (4-8 layers) after 3 h ultrasonication in concentrated TP-CNTs suspensions.

Practically destroyed CNTs and graphene sheets after 5 h ultrasonication in concentrated TP-CNTs suspensions.

Fig. 8. HRTEM images of process evolution in diluted (up) and concentrated (down) TP-CNTs dispersions.

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