The formation of super-long nano-chains during evaporation of metals with a help of intensive impacts

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Abstract. Extended nanostructures, in particular, chains of nanoparticles, are of great interest for microelectronics, biomedicine, and energy. But until now, it was possible to obtain such structures with the lengths not more than a few millimeters. We have developed several techniques based on laser and electric evaporation of metals, which provide the formation of nanochains with the lengths up to 60 cm. A significant factor in the formation of such structures is the constructive participation of turbulent vortices, which create the necessary compression and subsequent agglomeration of the vapors of metals and oxides subjected to the intensive electrical or laser impacts. Research and production of the nano-structures with large surfaces and lengths provide promising opportunities for the direct converters of solar energy and ionizing radiation to electricity, development of new optoelectronic and microelectronic devices as well as highly sensitive biosensors.

1. Introduction
The influence of various nano-dimensional solids on deeper understanding of the mechanisms of natural processes in materials and development of new unique technologies and devices based on nanostructures is expanded monotonously. Nanostructures are applied more and more intensively in biomedical techniques and materials, new methods of generation, storage and transformation of energy, electronic and optical devices with record parameters, information technologies, constructions for aviation and space applications, etc [1 – 5]. Separate nanoparticles and extended structures from nanoparticles of various solids including nano-chains and nano-grids belong to the most popular nano-dimensional objects either in scientific research or in practical development of technologies and installations. So, the amounts of publications devoted to the development and applications of various nanostructures is increasing rather quickly (e.g., see [6 – 32]). It should be emphasized that preparation of these kinds of nanostructures with necessary structures and morphologies is rather a difficult problem. In spite of the formation of the initial nano-particles with definite parameters it is rather problematic to prevent them from spontaneous non-controlled self-coagulation on the one hand and to provide their binding to required nano-chains of nano-grids on the other hand. Big amounts of chemical, electrical, optical, thermo-mechanical methods were studied for these tasks [5 – 21]. Our paper describes several promising results of the formation of chains and laces from oxide and metal nano-particles obtained with applications of electrical and laser impacts on metal raw materials. It is worth to emphasize that we have obtained super-long nano-chains with the record length being about 30 times longer than nanochains described in other publications (50 cm and more in comparison with one centimeter).
2. Experimental techniques and results

2.1. Preparation of chains of nanoparticles via electrical explosion of metal wires and electrical discharge heating

For the experiments with a pulsed electrical discharge, we used a setup consisting of a large-capacity capacitor, a high-voltage power supply for charging it, a circuit that controls the charge, and a high-current switch for supplying an electric pulse from the capacitor. To study in detail the mechanism of the formation of nanostructures formed during the explosion of metal wires, two chambers were used: the first with a volume of 1000 liters for the statistical analysis of the formed structures, and the second with a volume of 5 liters to determine the dependence of the morphology of the forming nanostructures on the composition of the ambient atmosphere. Thus, experiments were carried out on the electric explosion of thin metal wires.

During the electric explosion of a molybdenum wire, the formation of thread-like formations (Fig.1) with a lace-like nano-scale morphology was observed (Fig.2).

Similar structures were also obtained in an experiment with a high-frequency generator (33
Figure 3. Scanning electron microscopy of the lace-like complex structures of PbO

Megahertz). A high-frequency electric discharge melted a metal wire, the melt drops then under the action of the gravity force were falling down, forming chains of nanoparticles along the trajectory of the fall. Rows of nanoparticles parallel to the axis of the structures are observed in the morphology, closed rings also prevail. The most interesting fact is that these agglomerates have macroscopic dimensions in the form of lace ribbons with a length of up to 60 cm and a width of up to 1 mm, which are formed in a fraction of a second in a sphere with a radius of the order of a meter from the exploded wire. Their weight was very light, so they were floating freely in the air for a long time and the rate of their lowering speed did not exceed 1 cm / sec. It was found that these structures were not formed during the explosion of the metal wires in an oxygen-less environment.

The formation of such lace-like nanostructures can be explained by the processes as follows: since the boiling point of molybdenum is much lower than the temperature of the molten drops themselves, the formed oxide became overheated essentially. This overheating results in abrupt evaporation. Due to the generated high pressure, the vapors are pushed out from the surface of the drop at high speed. As it is well-known, the formation of turbulent vortices is possible at high velocities of gas flows [27 – 31]. The formed turbulent vortices are pushed aside by the oncoming air flow into the rear hemisphere of the drop, where they cool down, forming a lace nanostructure. Since the flow of oxide vapor from the front surface of the droplet continues with the formation of turbulent vortices with solidifying at the rear surface of the droplet, the chain grows and lengthens. This process continues till all of the molten metal turns into a lace ribbon of oxide. It should be noted that for the formation of a continuous chain, the flight speed of the drop should not exceed the rate of the formation near the rear hemisphere of the drop, otherwise the solidified oxide particles do not have time to bind to each other; therefore, the nanochain formation is observed only when the drop is decelerated to a sufficiently low velocity.

2.2. Production of chains of nanoparticles via laser heating and evaporation

In this series of experiments we used a setup that consisted of a 100-watt and 35 watt infrared lasers and focusing lenses. We found out that under focused laser irradiation with an optical power of 35 watts of fusible indium and lead separately, neither in the case of indium nor in the case of lead, the formations of nano-chains were not observed. But upon irradiation of lead-indium alloys with comparable concentrations of components, stable generation of a thin parallel jets of smoke were observed. In these jets we found nanochains (Fig.3) with a lace-like complex structure consisting of nanoparticles of lead and its oxide.

At the same time, the formation of a tube-like agglomerate (Fig. 4) with an outer diameter of up to 4 mm was observed on the substrate.
Figure 4. The tube-like agglomerate on the substrate during laser heating and evaporation of lead-indium alloy

It is known that the melting and boiling points of indium oxide are 1637 °C and 3027 K, respectively, and the melting and boiling points of lead oxide are 613 K and 1262 K, respectively. These data provided the explanation of the formation of nanochains and structures on a substrate as follows: when the lead-indium alloy is heated, the vapors of these metals are transformed into the corresponding oxides, but due to the difference in the melting and boiling points of the resulting substances, indium immediately crystallizes, forming a tube-like structure on the substrate, and lead oxide vapor propagating through this tube, forms the turbulent vortices, due to which nanochains are formed by the solidification of the vapor.

2.3. The evaporation of lead with 100-watt laser
In this experiment a piece of lead was irradiated with focused 100-watt laser beam. At the initial moment the metal melted, and then intense evaporation began at the point of the focusing of the laser beam. It turned out that the evaporation process induced by the continuous-wave laser had pulsed character with the intervals between moments of the intense emissions of the vapor from 7 to 20 s. An aluminum plate with a hole for the beam passage was installed above the crucible with the lead sample. The evaporated material was deposited on this substrate (Fig.5) and lead oxide prevailed in the precipitation layer. Outgoing smoke practically did not rise upward presumably due to the large mass of particles composing it (lead and lead oxide).

Detailed electron microscopic analysis showed that the deposition we obtained is a developed with lace-like structure of nano-chains of lead oxide nanoparticles (Fig.6).

The data obtained make us to suppose that turbulent vortexes are directly involved in the formation of the resulting deposition. In addition, it can be assumed that due to the accumulated vapors of the material near its surface, the laser beam focuses itself, which leads to even more intense evaporation. The layer of the formed lead oxide forms a film that prevents the formed vapors from leaving the surface, which leads to their accumulation in this bubble of oxide film. At the moment when the bubble bursts, an intense release of the accumulated vapor occurs, in which turbulent vortices are formed, contributing to the formation of the resulting developed structure of lead oxide.

2.4. Laser evaporation of copper
In this experiment laser evaporation of copper nanoparticles and sawdust was carried out.
Figure 5. Scanning electron microscopy of the deposition of PbO formed during laser evaporation of lead

Figure 6. Scanning electron microscopy of lace-like structures in the deposition of PbO

Due to the excellent ability of metallic copper to reflect laser radiation in this range of laser wavelength (10.6 µm), as well as the high thermal conductivity of the material, fine fractions of the metal were selected for evaporation under the laser in order to improve the conditions for their heating.

When using nanoparticles, the metal easily evaporated under the laser. Vapors of the resulting oxides were deposited on a copper plate mounted above a ceramic crucible with an evaporated substance.

As a result, an oxide deposition was formed on the plate with a developed dendrite-like morphology (Fig.7) consisting of chains of nanoparticles (Fig.8).

In addition to the structure described, large spheres (Fig.9) with a diameter of up to 100 microns are also observed on the plate. The surface of the spheres either consists of individual spheres with a diameter of 0.5 to 5 microns, or it is covered with formations with a morphology similar to the described spraying.

When using copper sawdust, under the laser, they melted into a single drop, boiling took place throughout the entire volume without the formation of an intense steam flow. Following
Figure 7. Scanning electron microscopy of copper oxide dendrite-like deposition

Figure 8. Scanning electron microscopy of chains of nanoparticles in copper oxide deposition

from these facts, it can be assumed that, due to the small size, as well as the oxide layer, which effectively absorbs laser radiation of this range, the nanoparticles instantly evaporated at the initial moment of time, and the resulting melt (Fig.10) was smaller in volume compared to melt from copper sawdust, which led to its greater heating, as a result, more intense evaporation and the formation of dense streams of steam.

Due to the lower atomic weight in comparison with lead, the vapor did not accumulate at the metal surface and pulsations of steam flows were not observed.

3. The formation of extended structures in cryogenic liquids

Fig. 11 presents scanning electron microscopy of the lace-like nanostructure of lead produced by irradiation of a sample of lead immersed into liquid nitrogen with pulsed Nd:YaG laser. It is worth to emphasize the distinct difference between the nanostructures produced by laser evaporation of lead at open air (room temperature) and in liquid nitrogen (77 K temperature). In the last case the long thread-like chains are not observed as well as the evaporation has not the pulsed character being continuous. The lace-like structure reveals the presence of turbulences in the vapor flows. But it can be supposed that the lengths of the vortices in this case are not
Figure 9. Scanning electron microscopy of copper oxide spheres with a dendrite-like surface consisting of nanoparticles

Figure 10. A photograph of copper in the crucible vaporized under the continuous CO₂ laser big enough for the formation of the long nano-chains. So, they are not observed here (e.g., due to much stronger mechanical resistance of the liquid nitrogen and much faster cooling of the vapor).

4. Discussion of the importance of auto-generation of pulsed evaporation and long turbulent vortices for creation of extended nano-structures

Various kinds of extended nano-chains are applied in new types of electronic and optical devices, bio-medical sensors, energy generation and storage, etc. [22 – 26]. Due to the results of the experiments, it was found that an essential role for the formation of thread-like and lace-like structures from nanoparticles belongs to the turbulent vortices created by the intense evaporation of materials. In addition, we find confirmation of this assumption in the papers of the team of authoritative Russian scientist E. Gordon (“Formation of metal nanowires using laser ablation in
Figure 11. Scanning electron microscopy of the lace-like nanostructure of lead produced by irradiation of a sample of lead immersed into liquid nitrogen.

liquid helium” and more late their publications [16, 18, 19, 21]. In these papers the phenomenon of the formation of nano-chains with the morphologies close to the structures obtained in our work was described (Figs. 7.8 in [16]). But in our case the nano-chains were longer significantly (up to 60 cm instead of 1 cm). This difference can be attributed to much better conditions for propagation of long vortices in the open air in comparison with cryogenic liquids. One more factor providing the creation of the longer vortices and subsequent super-long nano-chains for the case of continuous laser irradiation is connected with the auto-generation of the severe pulsations of the evaporation process [27]. The interruption of the evaporation is induced by accumulation of the vapor of irradiated heavy metal (like lead as it was in our cases) in the of the irradiated surface. When the pressure of the accumulated vapor achieves a certain threshold the breakthrough and intensive jet of the vapor is emitted. Due to its high speed the Reynolds number is rather large providing the generation and propagation of the long vortices. The essential amount of experimental and theoretical papers show that this kind of the turbulence facilitates effectively the coagulation of the vapor with formation of extended structures from nano-particles [28-32].

Conclusions
We have developed five new techniques of the formation of extended nano-structures from various metals subjected to electrical and laser impacts: electrical explosion of thin metal wires, melting of metal wires by high frequency electrical discharges, evaporation of solids by continuous-wave infrared lasers with 10.6 µm and 0.9 µm lengths of radiation, evaporation of solids immersed into liquid nitrogen by pulsed infrared laser. The chemical compositions of the nanostructures obtained by these means are regulated by variations of the content of the ambient atmosphere (air, argon, liquid and gaseous nitrogen). The analysis of the experimental observations manifests active participation of turbulent vortices in the formation of these nanostructure for all of the methods described above.

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References

[1] S Soni, A Salhotra, M Suar, 2015, *Engineering Science Reference* (USA), 1950 p.
[2] Journal of Pharmaceutics and Nanotechnology, 2016, 4, Special Issue: Reviews on Pharmaceutics and Nanotechnology
[3] A Neyes, R Saletti, 2018 *Nanoparticles in Life Sciences and Biomedicine*, 435 p.
[4] W Mattheu, B Noiurnikan 2021 *Emerging Nanotechnologies for Renewable Energy* 624 p.
[5] T Chen 2018, *Semicond. Nanocryst. and Metal Nanopart.: Phys. Propert. and Device Applic.* 425
[6] F Christian 2013, *Frontiers in Energy* 7, 5 – 18.
[7] C Huttei 2018, *Gas-Phase Synthesis of Nanoparticles*, Wiley (USA), 314 p.
[8] J P Merlin, S S Rajan, 2020 *J Cancer Sci. Treatment* 2, 87-89
[9] F E Kruis, H Fissan, and A Peled, 1998 *J of Aerosol Science* 29, 511-535.
[10] K K Harish, V Nagasamy, B Himangshu, K. Anuttam 2018, *Biomed J Sci & Tech Res* 4(2).
[11] M Kim, S Osone, T Kim, H Higashi, T Seto, 2017. *KONA Powder and Particle Journ* 34, 80 – 90.
[12] Boguslavsky L.I. 2010, *Fine Chemical Technologies* 5(5) 3-12 (In Russ.)
[13] M Yadi, et.al., 2018 *Artif Cells Nanomed Biotechnol* 46(3) 336-S343.
[14] D Sharma, et.al., 2019 *Arabian Journ. Chemistry* 12 3576-3600.
[15] A Eljas, M Saravanakummar 2017, *IOP Conf. series: Materials, Science and Engineering* 263 032019
[16] E Gordon, et.al. 2011 *Journal of Low Temperature Physics* 165(3) 166-176
[17] N V Klassen, P V Provotorov, A E Ershov, V N Kurlov, V V Solodovnikov 2015 A device for the formation of superlong nanochains, Patent of Russia №153513 from July 20,
[18] E Gordon, et.al. 2017, *J. Phys. Chem. A* 121(48) 9185–9190
[19] E B Gordon, A V Karabulin, M I Kulish, V I Matyushenko, M E Stepanov, 2017, *Mendeleev Communications* 27 484-386
[20] S V Stovbun, A A Skoblin, 2019 *Phys.Chem. Chem. Phys.* 21 5771-5779
[21] E Gordon, et.al. 2020 *High Energy Chemistry* 54 164-169
[22] C Fang, et.al. 2008 *Applied Physics Letters* 92 263108
[23] X Yuan, et. al. 2017 *ACS Energy Letters* 7600223
[24] A Ruiz-Sanchez, et.al. 2017 *Journ. Mater. Chem B* 5 7262
[25] V T Tran, et.al. 2014 *Sensors and Actuators B: Chemical* 203 817-823
[26] N V Klassen, P V Provotorov, A E Ershov, 2015 A device for the direct transformation of ionizing radiation to electricity , Patent of Russia №154180 from July 21
[27] S Bugaychuk, 2014, *OSA Advanced Photonics Congress, Nonlinear Photonics* 27-31 July, Barcelona, Spain, JMSA.26
[28] S Friedlander, 2000 Smoke, dust and haze: fundamentals of aerosol dynamics, Oxford University Press (USA), 430 p.
[29] S Garrick, 2011, *Aerosol Science and Technology* 45(10) 1272-1285.
[30] S Garrick, 2015 *Journ. Nanotechnology* 2015, 642014
[31] J Lin et.al. 2016 *Appl. Mat. Mech. 37*(10) 1275-1288
[32] M Shigeta, 2020 *Plasma Chemistry and Plasma Processing* 40 775-794