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Structure and Properties of Platinum, Gold and Mercury Nanowires Grown in Superfluid Helium

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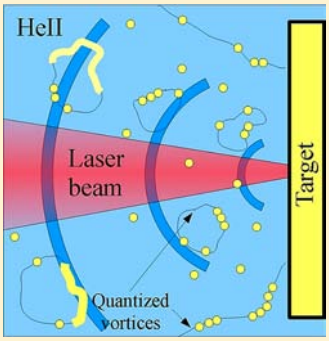
ABSTRACT: Webs consisting of nanowires made of gold, platinum and mercury were produced by the technique based on laser ablation of metals inside superfluid helium. Their morphology and structure as well as their electrical conductivity have been studied. Diameters of gold and platinum nanowires are 4.5 and 3 nm, respectively. Fortunately, they are close to diameters of nanospheres made of these metals, which, as known from the literature, possess anomalous catalytic activity. Web resistivities for all metals up to room temperature are controlled by conductive electron scattering on a wire surface, thus they are almost independent of *T*. Nanowires in the webs are electrically interconnected, and therefore the web can be used as a catalyst without any support. Possible advantages of this type of nanocatalyst are outlined.



SECTION: Physical Processes in Nanomaterials and Nanostructures

Discovery of the high catalytic activity of gold nanoparticles caused a scientific sensation in its time.[1] In general, at the nanometric scale for a lot of metals, for instance, platinum,[2] silver,[3] and nickel,[4] catalytic activity increases with particle's size decrease. However, only for gold does the catalytic effect, entirely absent for the bulk, exist in the narrow range of 3−5 nm, surpassing traditional metallic catalysts.[5] Also, a number of papers[6,7] report the occurrence of very high magnetic susceptibility and even ferromagnetism for gold particles with few nanometer sizes.

Very high catalytic activity appears for thin gold films as well, but as it was demonstrated in ref 8, the effect is expressed on coatings with thickness of 1.5 layer, provided the second layer consists of nanoscale "islands".

The nature of the surprising catalytic size effect is not yet fully understood. It seems that it requires high surface curvature for both nanoparticles and nanofilms.[9] Support of the catalyst, i.e., substrate, whereon metal nanoclusters or the film are deposited, is of importance not only as an electrical contact but as a necessary element of the catalytic process.

At the same time, for nanowires, both the surface curvature and the fraction of atoms belonging to the surface are close to those for spheres with the same radii. Meanwhile, sometimes nanowires are more convenient than nanoparticles. For example, a nanoweb could be used as a catalyst ensuring a charge drain without any support. Also the phenomenon of ferromagnetism should be more expressed in long rods. Research of the nanowire catalytic activity has already begun. In particular, the activity of platinum nanowires as a catalyst of oxygen reduction reaction was shown to be significantly increased with decreasing their radius from 130 to 25 nm.[10] In refs 11 and 12, the networks of Pt and Pt−Ru wires grown by the soft template method and having diameters close to 3 nm showed even more activity in electrooxidation of methanol and CO than the carbon-supported nanoparticle catalyst, and it was attributed to the large amount of grain boundaries in their wires. However, studies of the most interesting gold nanowires are still absent in the literature. The possible reason is the impossibility to produce free-standing gold nanowires with a diameter less than 10 nm, whereas the effect should appear at 5 nm.

Even using our method of metal laser ablation in superfluid helium, we could not obtain a nanoweb with a diameter less than 7 nm.[13] Moreover, because our laser had 20 ns pulse duration, we could not ablate the highly heat-conducting coinage metals. Meanwhile, according to the mechanism

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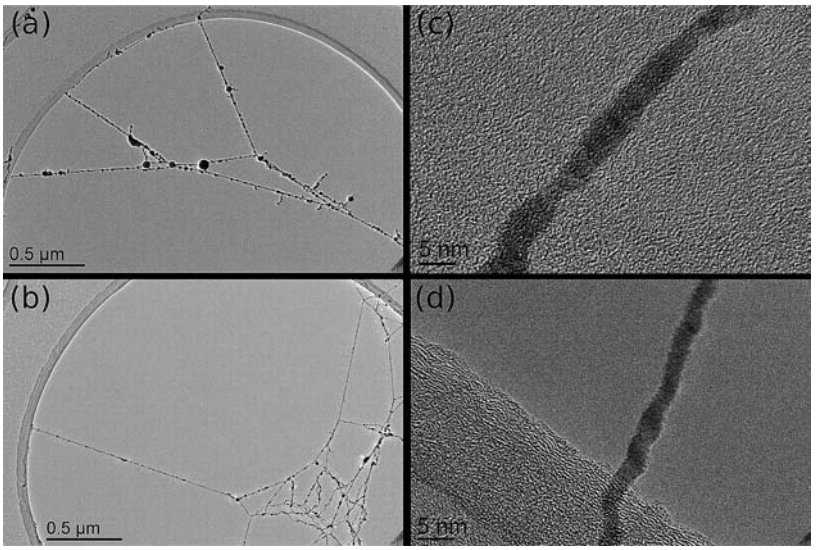

Figure 1. Transmission electron microscope JEOL JEM-2100 images of gold and platinum nanowires deposited on a carbon-coated copper grid. Fragments of nanowire bundles in the vicinity of 3 mm-holes in the grid: (a) gold; (b) platinum. The structure of the nanowires at high resolution: (c) gold; (d) platinum.

proposed in ref 13, nanowires formed in He(II) from refractory metals should have smaller thickness than ones of the fusible metals studied in refs 13−15, and 18. According to formula 8 of ref 13, diameters of gold and platinum nanowires are expected to be, at most, half of those for indium and nickel.

Nanowires grown in quantized vortices of superfluid helium eventually form bundles consisting of interconnected parallel-series nanowires. In order to use this nanoweb as a catalyst, the nanowires should be electrically connected with each other, providing voltage application and charge drain during the catalysis.

In order to answer all these questions, we set up the experiments on growing nanowires from gold and its neighbors in the periodical system of elements: platinum and mercury. From our viewpoint, platinum was of same interest as gold, and mercury was chosen not only for contrast and exotics (nobody had produced mercury nanowires before), but also because of its superconducting transition at T = 4.15 K. This allows experimental separation of the contributions of nanowire contacts and wires themselves to the total resistivity.

The experimental setup was described elsewhere.[15] The experimental cell was placed inside a liquid helium cryostat. The temperature of liquid helium was lowered to 1.6 K by its vapor pumping. Atoms and clusters of metal were injected into superfluid helium by ablation of immersed-in-HeII targets by pulse-repetition fiber laser. Nanowires formed in bulk helium partially fell to the carbon-coated copper grids placed in the bottom of low-temperature cell, and partially pinned to the vertical row of needle-like electrodes placed near the target; long bundles of nanowires formed there closed the electrical circuit. After cryostat heating, the grids with the bundles of nanowires deposited thereon were transferred to the electron microscope chamber.

In order to achieve an effective ablation of gold and platinum in superfluid helium, a fiber laser with much shorter pulse than in ref 13 was used. Its characteristics are as follows: pulse duration 0.4 ns, pulse repetition rate 0.5−4 kHz, pulse energy 0.1 mJ, and light wavelength 1.06 μm. Laser beam was focused on the surface of the metal target through cryostat optical windows.

The distance between adjacent electrodes in their vertical row was 1.4 mm. During measurement of nanowire bundle resistance, the total current through it did not exceed 1 mA so that the current through a single nanowire was less than 1 μA. The platinum and gold foils served as targets, and a special L-shaped copper base was applied to hold a mercury drop, which was used after its solidification as a target.

Figure 1 shows that the nanowires grown from refractory metals are really thinner than those grown from fusible metals. Platinum nanowires have a diameter of 3 nm and possess a regular shape, whereas the gold ones are 4.5 nm in diameter and contain clearly visible beads. Naturally, we could not measure the thickness of mercury nanowires vanished under heating, but supposing that they are similar to that made of fusible indium, their diameter is about 8 nm. Of course, TEM images correspond to objects already heated up to room temperature and contacted with the air, and it is important to know their initial structure and shape. One should note that all bundles of nanowires shown on TEM images are strongly stretched, like strings or web (see Figure 1a,b). However, usually the strings and web are pulled by special tools, and it is difficult to find the reason for such tension under nanowire formation in vortices of superfluid helium. They could not be stretched by the thermal expansion on heating, since the difference in expansion coefficients of copper grid and gold or platinum is about 2×10^{-6} K^{-1}, i.e., resulting in the shortening of wire by its heating to 300 K being less than 0.1%, but not a few %, as may be estimated from Figure 1. Moreover, we found that the bundles of copper nanowires grown by a similar technique were stretched already in liquid helium.[16]

Although we could not monitor the structure and morphology of the nanowire bundle at low temperatures, we were able to measure the electrical resistance of bundles shorting the electrodes as soon as they have grown. According to the accepted viewpoint,[17] the resistivity of nanowires, ρ, at high T is determined by the scattering of conduction electrons on phonons, resulting in a quasi-linear $\rho(T)$ dependence with a slope sensitive to the metal's nature. With decreasing T, the resistance becomes controlled by electron scattering on the wire surface, weakly depending on temperature and being

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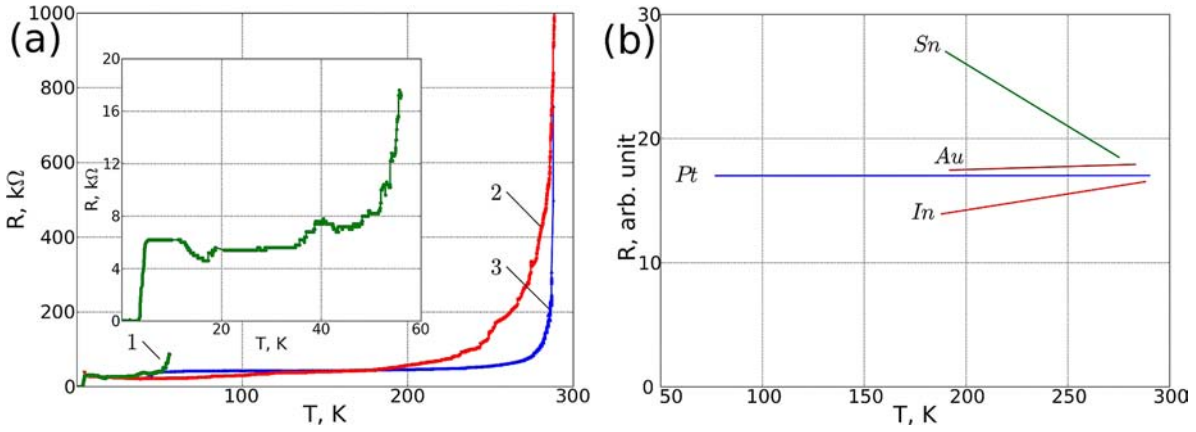

Figure 2. Electrical resistance, R, of the 1.4 mm long bundles of nanowires versus temperature: (a) 1 – mercury; 2 – gold (in the figure scale, the curve for platinum almost coincides with that for gold); 3 – tin (dependence for mercury is in 5:1 scale); the inset shows R versus T dependence for mercury in real scale. (b) The temperature dependences of resistance for annealed bundles of nanowires made of gold, platinum, tin, and indium (see text for the details of annealing).

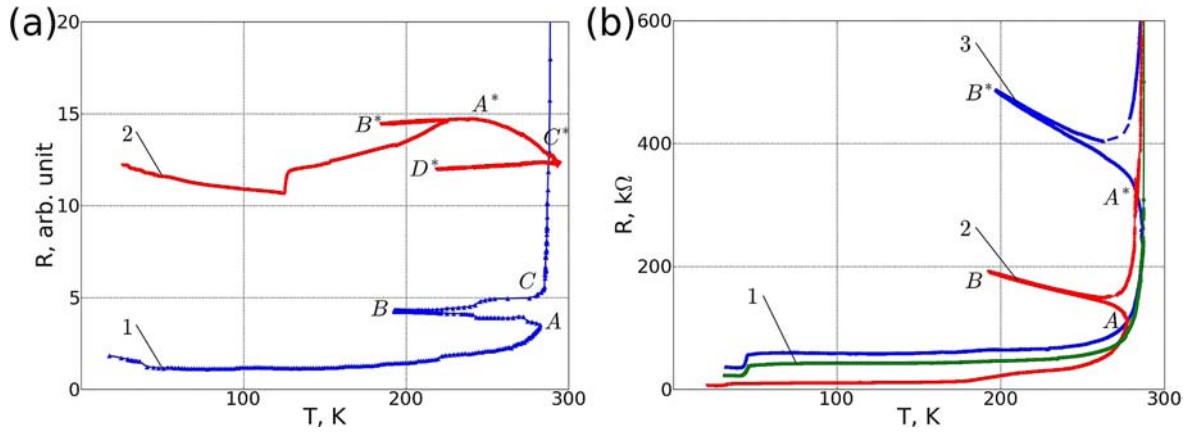

Figure 3. (a) Effect of annealing under slow (about 10 h) heating on the resistance R of the bundles of gold (1) and platinum (2) nanowires. At the point A (A*) the jacket of the fridge was filled by liquid nitrogen, and the temperature of the cell slowly (for 5 h) decreased and then at the point B (B*) liquid nitrogen was removed to restart slow warming. The bundle of platinum nanowires survived heating up to the room temperature, after which it was subjected to recooling (C* → D*) and subsequent heating (D* → C*) procedures. (b) Effect of annealing under slow (about 10 h) heating on the resistance R of the bundles of tin nanowires with 8 nm diameter. 1 – permanent heating; 2, 3 – heating followed by slow cooling by liquid nitrogen started from point A (A*) and finished at point B (B*), correspondingly.

insensitive to the nature of the metal. Such transition from a quasi-linear temperature-dependent resistance to the almost constant residual resistance takes place at $T \approx 50$ K for nanowires studied in the literature.[17] For our nanowires, it should occur at higher temperatures due to their smaller diameters.

We used a two-wire method of resistance measuring, so it was fundamentally impossible to separate resistances of nanowires from resistances of wire-electrode and wire–wire contacts. Therefore in the interpretation we have used the following arguments. The measured resistance of mercury nanowire bundle in its superconductive state at 1.6 K was about 1 Ω. This value corresponds to the resistance of connection wires and contacts. Under mercury transition to the normal state caused by heating the resistance of bundle increased up to 6 kΩ (see Figure 2 inset). Based on TEM results, including those from refs 18 and 19, we assume that the bundle topology for different metals is similar. Supposing that the residual resistivity for any metal is almost same, we estimate the resistance of nanowire bundles made of platinum and gold as being 4–10 times higher than that for mercury ones because of their lower diameters. Thus during preparation of gold and platinum samples, the laser ablation was continued until the measured bundle resistances fell down to about 30 kΩ (i.e., 5 times larger than for mercury). We think that in this case, structures of gold and platinum nanoweb specimen should be similar to the structure of the mercury specimen. In any case, measured resistance for them can be regarded as belonging mainly to the resistance of the wires themselves, and not to the contacts between them.

Temperature dependencies of resistance of nanowire bundles were measured during the slow self-heating of the cell first in liquid helium and then in a helium gas at ambient pressure. Typically, three bundles of nanowires, closing three pairs of electrodes, were grown, and measurements were carried out simultaneously for all of them in order to exclude sporadic jumps of resistance associated with abrupt changes in percolation in the bundle.

The $R(T)$ dependencies shown in Figure 2 demonstrate the long plateaus (at low temperature, the mercury nanowires undergo a transition from the superconducting to the normal state observed as a sharp large jump in the resistance at about T

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= 4.2 K, which is close to the transition temperature in the bulk metal). At higher temperatures, the $R(T)$ dependencies for all metals show some small reproducible steps at temperatures about 35 K (mercury), 230−240 K (gold), and 120 K (platinum). Such changes could be attributed to nanowire structure relaxation. Indeed, for the massive platinum, a jump of resistance was observed just at the same temperature T = 120 K, and it was explained as a consequence of annealing of defects.[20] In all three metals, as it was found earlier for indium and tin nanowires, the $R(T)$ plateau was followed by an irreversible sharp increase in resistance started at 50 K for mercury and at 260 K for gold and platinum. Such behavior was natural to attribute to changes in percolation inside the netlike bundle of nanowires due to their stretching. The stretching is caused by nanowire shortening under its shape change from cylindrical to "peapod". Partially such process of pulling proceeds even in HeII for just formed nanowires, the temperature increase revives the process of tensioning. Such changes in shape can occur only by the metal atoms motion along the surface of wires, and therefore for fusible metals the process of beads development resulting in a network tensioning should begin at lower temperature. This has been verified experimentally: the gold nanowires, stretched over the holes in the carbon-coated copper grid as shown in Figure 1a, being heated in the TEM microscope chamber demonstrated the beads further development and then the wires breakdown. Likewise, under the cryostat heating, the tension of wires in a bundle, closing the circuit, caused the individual wires breakage, so more and more fragments were excluded from the percolation chains up to the complete break of the contact.

It seems that both the shape of nanowires and their morphology are strictly the functions of the bundle annealing temperature T_{anneal}, indeed after annealing the resistance of bundle remains constant under any subsequent variation of temperature provided $T < T_{anneal}$. It is demonstrated by Figure 3. The reproducible $R(T)$ dependencies of annealed bundles should reflect real characteristics of nanowire. So resistivities of both gold and platinum thin nanowires are nearly constant at least up to room temperatures. This is the evidence for the conductivity control by electron scattering on the surface of the nanowires at these conditions.

As already mentioned, the transition from quasi-linear temperature dependence to the plateau should occur for poorly electrically conductive metal at lower temperatures than that for gold and platinum. Unfortunately, the bundle of mercury nanowires breaks at rather low T, so we have carried out the similar experiments with nanowires made of tin and indium. Figure 3b summarizes the results of a series of similar experiments for tin nanowires with a diameter of 8 nm. For tin nanowires, the measured resistance even decreases with temperature growth. Such behavior is typical for nanowires made of other poor metals, namely, Bi[21] and Sb.[22] Even for bundles of zinc nanowires, the typical metal $R(T)$ dependence exhibited for wires with d = 15 nm changes for nanowires with d = 9 nm into $R(T)$ dependence similar to what we observed for tin; whereas for thinner Zn nanowires with d = 4 nm, a drop of the resistance with temperature growth was even more expressed.[23]

The $R(T)$ dependencies for annealed bundles of nanowires summarized in Figure 2b show that the resistance of all studied metals at low and close to room temperatures is determined by the scattering of the conductive electrons on the surface of the wires; the indium nanowire residual resistance, however, decreases with temperature decrease, but much weaker than ∞T. Thus we could suppose that the resistivity should be almost similar in all metals, and it is not mandatory to produce the wirings in microchips from highly conductive metals.

Our method does not allow variation of nanowire thickness. However, diameters of platinum and gold nanowires grown in superfluid helium are fortunately close to the diameters of spherical nanoparticles in which the catalytic properties as well as ferromagnetism were pronounced.

Of course, the technique of nanowire production in superfluid helium is intended solely for research and can not be the basis for real technology, but nevertheless the amount of produced catalyst is desirable to be sufficient for the direct registration of catalytic process products. As can be seen from Figure 4, the nanowire bundles grown on electrode tips during 30 min long laser ablation are already visible to the naked eye. In such conditions we were able to introduce into superfluid helium about 1 mm^3 of metal per hour with around 10% nanowire production efficiency, so that it is possible to obtain wire with total length of 1000 km and total surface area of approximately 10^2 cm^2. It is easy to estimate that such surface area of catalyst is sufficient for products registration by means of mass-spectroscopy or chromatography.

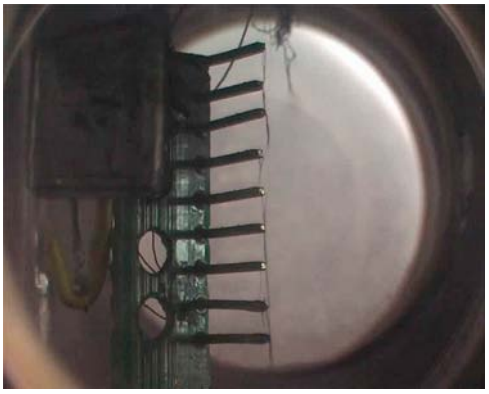

Figure 4. The photo of platinum nanowire bundles grown in superfluid helium made through cryostat windows. The nanowires preferably pinned to the tips of adjacent electrodes closing the electrical circuit.

As shown by our study, the annealed nanoweb saves its pass-through electrical conductivity at ambient conditions, so as a catalyst it does not need a conductive support. We are planning to precipitate the nanowebs on a microporous glass filter in liquid helium, in order to organize in a chemical reactor the flow of reagents through this filter.

Our reasoning that nanowires have to be as effective catalysts as nanoparticles is plausible but not strictly conclusive, and it should be tested experimentally. First of all, the surface smoothness and crystal structure of nanowires are quite different from that of the nanospheres for which the catalytic effect is already proven. These nanospheres, produced usually by molten droplets cooling, possess, due to the surface tension, the perfect shape and a smooth surface; additionally, the fast cooling promotes a metal amorphization.[24] As seen from Figure 1, our gold nanowires have, in contrast to nanospheres, a beadlike shape and crystalline structure, and according to the study of the catalytic effect on thin gold films,[8] it should contribute to catalytical activity.

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Notes

The authors declare no competing financial interest.

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