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Aluminum nanostructures obtained at the interface of two immiscible liquid

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Abstract: **Expanding range of nanostructured materials applications based on aluminum initiates the search for new methods for their preparation. A promising method for the synthesis of aluminum nanostructures using the total energy of pulsed plasma and the energy of the interface is proposed in this article. Aluminum nanostructures have been synthesized by dispersing aluminum electrodes in a microemulsion (water-benzene), in benzene and distilled water, using the energy of a pulsed plasma. Obtained nanostructures of aluminum were subjected to X-ray phase and electron microscopic analyzes. Particle sizes are calculated using the Debye-Scherrer formula. The specific surface area (BET method) and porosity (BJH method) of nanostructures synthesized in microemulsion (water-benzene) were determined by the method of physical nitrogen adsorption.**

Keywords: **pulsed plasma in liquid, nanostructures, microemulsion, interfacial surface, specific surface area, pore volume**

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1. INTRODUCTION

Recently, in connection with the creation of new technologies for producing nanopowders metals and bringing their production to semi-industrial scale, sharply increased interest in the study of nanopowders and nanomaterials. Aluminum nanopowders (ANP) are used as a component metallized mixtures, when obtaining refractory ceramic materials and fuel mixtures during metals processing (welding, cutting and etc.) [1]. According to marketing analysis share of all produced nanopowders aluminum nanopowder is 2.1% (third place among metal powders after Ni and Cu, annual production is ~ 1250 tons) [2]. Nanoparticles aluminum are used as additives to protective corrosion-resistant coatings, sprayed with dispersion. Also nanoparticles aluminum are used in processes sintering ceramics. So, adding 5-10% of aluminum nanoparticles in ordinary aluminum powder improves sintering process of ceramics, with high heat transfer performance and increased density. Intensely the need for nanopowders is growing aluminum and in hydrogen energy [3]. As a result, passivation and stabilization aluminum nanoparticles by coating PE-CVD have demonstrated that nanoparticle technology can be used to improve thermal characteristics and energy density of the fuel [4].

Reducing the particle size of powders aluminum leads to an increase in them the proportion of oxides and hydroxides. High losses metal aluminum and unstable state of aluminum nanopowders (NPA) makes them unsuitable for practical use. Therefore, the problem is reliable passivation of nanopowders with sufficient content metal aluminum [5].

In work [6], annealing was carried out coarse aluminum and NPA, obtained by electric explosion conductors (EEC), in the range 450°-600°C. Research results have shown that both samples contain an oxide coating, and in nano-sized aluminum in the composition of the oxide film was α-Al_2O_3. There is a work that says the structure of the oxide layer affects on the mechanical strength of crystallites metal, thermal expansion and melting point [7].

Very great interest is shown to coated aluminum nanoparticles oxide shell (α-Al_2O_3), which are used for creation of composite materials, with a combination of high heat-conducting and electrical insulating properties. Aluminum nanoparticles with have a protective oxide film high ohmic resistance (due to the formation of a film from high temperature, very strong modification α-Al_2O_3). Similar aluminum nanoparticles used as filler for heat-conducting dielectrics with high breakdown voltage, increased thermal conductivity. Oxide film on surface of nanoparticles provides increased adhesion between them and matrix [8]. The known method obtaining ultrafine powders oxide coated aluminum electric wire explosion, in which oxide layer on the surface aluminum particles form upon contact ultrafine powders with oxygen air, including in mixtures with inert gas - argon [9]. There is a way to get oxide coatings on nanoparticles aluminum [10], according to which the metal placed in a crucible at the bottom of the reactor and subject it to high-frequency heating before evaporation. Despite the considerable number of publications of nanostructures aluminum with a protective film Al_2O_3, synthesis and study of patterns the formation of aluminum nanoparticles covered with a durable oxide film α-Al_2O_3 necessary for their further applications are few and scattered.

Recently, the main focus scientists devoted to the formation nanostructures on interphase surfaces, at the interface between two liquid immiscible phases. Review [11] various approaches to creating ordered structures at interfacial surfaces. Surface energy focused on the interface (phase interface), is excessive compared to energy in volume.

There are many chemical ways obtaining, nanostructures on the interfacial surfaces, e.g. synthesis method semiconductor nanorods cadmium hydroxide from $Cd(C_6H_5N_2O_2)_2$ by surface reaction toluene-aqueous hydroxide solution sodium [12].

Various types of synthesis are known nanoparticles in microemulsions containing immiscible components such as oil and water, as well as some surfactants (surfactants). Water-in-oil microemulsion or reverse microemulsion is a thermodynamically stable microheterogeneous system consisting from reverse micelles (nanoscale water droplets coated with a monolayer (surfactant)) in a non-polar liquid. Synthesis method nanoparticles in reverse microemulsions practically suitable in those cases when too narrow is not required particle size distribution or high concentration of nanoparticles [13].

Well-known synthesis technologies of nanoparticles on the interfacial surfaces, in microemulsions along with their advantages, also have a number of disadvantages, remaining difficult and economically unprofitable. So the search and development of simple and accessible technologies obtaining nanoparticles of aluminum, including including, with a protective oxide film is an urgent task. Successful her the solution provides opportunities for creating materials with improved catalytic, biological, mechanical and electronic properties.

We are offering implementation method available for producing of aluminum nanoparticles at the interface two immiscible liquids (water-benzene), using the pulsed plasma energy. Immiscible in normal conditions water-benzene liquid capable of forming microemulsions with vigorous stirring. Microemulsions have great mobility and large surface phase separation and can serve as a medium for carrying out many chemical syntheses, for example, to obtain nanoclusters and nanostructures of metals [14].

The aim of this work was to synthesize and study of aluminum nanoparticles coated oxide film using energies of pulsed plasma and interphase surface. Developing effective method for the synthesis of aluminum nanopowders with the protective film α-Al_2O_3 opens great prospects for their application in various fields of industry and technology.

2. MATERIALS AND METHODS

The task is being solved dispersion (nanostructuring) aluminum in water-benzene microemulsion, using the pulsed plasma energy created between two electrodes, at an energy of a single pulse 0.04 *J*, frequency of unit impulses - 70 Hz. Microemulsion formed by stirring the mixture (water-benzene) by magnetic stirrer brand MMS-3000 at a rotation speed of 1500 rpm.

To compare results research, nanostructuring aluminum was carried out in microemulsion (water-benzene), distilled water and in benzene. As electrodes used aluminum grade "chemically pure" 99.98% purity. Reagent grade benzene GOST5955-75, manufactured by CJSC LenReaktiv (Russia). The volume of the emulsion where aluminum dispersion was 100 ml, in which 25 ml is benzene, the rest for distilled water.

Pulsed plasma in liquid dielectrics occurs as a result of breakdown interelectrode space at high potential difference between electrodes and relatively low power a source insufficient to excite arc discharge. Single impulse has an extremely short duration (10^{-3}-10^{-5} *s*), high current density (10^6-10^8 A/cm^2) in the affected area, very high temperature in the discharge channel (10^4-10^5K) and pressure 3-10 kbar.

Schematic diagram nanostructuring provided at **Fig. 1**. Here *AC* is a source of constant current; *R1, R2* – load resistances; *C* – capacitor bank; *T1, T2* – thyristors; *D* – diode; *L* – lamp; electrode 1 connected to negative power supply pole; processed electrode 2 connected to the positive pole; liquid medium.

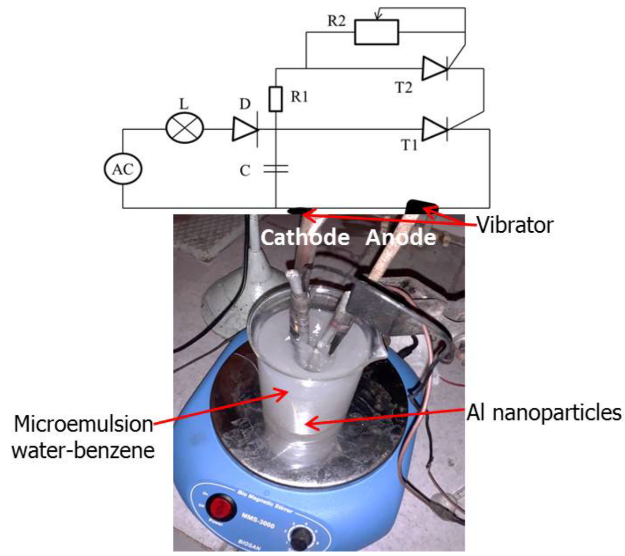

Fig. 1. *Technological scheme of nanostructuring metals in pulsed plasma generated in liquids.*

The energy of a single pulse can steam and melt any conductive material. Further, from the steam and melt nanoparticles of a dispersible material were formed [15]. It was shown [16] that, the mobility liquid medium is favorable for obtaining nanoparticles. Rotation of the emulsion promotes the removal of nanoparticles from high temperature discharge zone, which prevents the growth of nanoparticles.

Transition from high temperature discharge zones into the surrounding liquid room temperature contributes high temperature, high speed quenching of nanoparticles due to high temperature and pressure gradient due to transience of a single impulse. AT this statement is supported by results. Experimentally it was shown by the authors of [17] that a decrease temperature by only 20 K leads to decrease in the average size of nanoparticles threefold - from 220 to 70 nm. Study of the obtained powders carried out by methods of X-ray phase analysis and transmission electron microscopy.

For aluminum nanostructures obtained at the interface specific surface area (BET) determined and pore volume (BJH) by physical nitrogen adsorption.

3. RESULTS

As a result of dispersion of aluminum electrodes in microemulsion (water-benzene) using pulse energy plasma is collected at the bottom of the reactor gray precipitate that separated from liquid medium by centrifugation. The dried sample was analyzed on the X-ray apparatus Rigaku Geigerflex X-Ray Diffractometer with Cu Kα radiation.

Fig. 2 shows the diffractogram product of destruction of aluminum in microemulsions (water-benzene). Diffractograms analysis established the most intense peaks (111), (200), (220) and (331) refers to metallic aluminum with fcc lattice, crystal parameter lattice a_A = 2.99716 Å.

Reflexes (300) and (036) correspond to trigonal Al_2O_3 with space group – R_3C, parameters crystal lattice $a_Э$ = 3.5864 Å, $a_Э$ = 11.9856 Å, literature data – a_A = 4.759 Å, w = 12.399 Å. To compare research results nanostructures were synthesized aluminum by dispersing aluminum in distilled water and benzene, using pulse energy plasma

Diffractogram of the destruction product aluminum in water contained mainly reflections (111), (200), (220) and (222) (**Fig. 3**), related to metal nanoparticles aluminum with fcc lattice (Fm3m) and crystal lattice parameter $a_Э$ = 2.8811 Å, where a_A = 4.0486 Å. Found diffraction lines with indices 204, 241 monoclinic $Al(OH)_3$ with spatial group P21/n. When

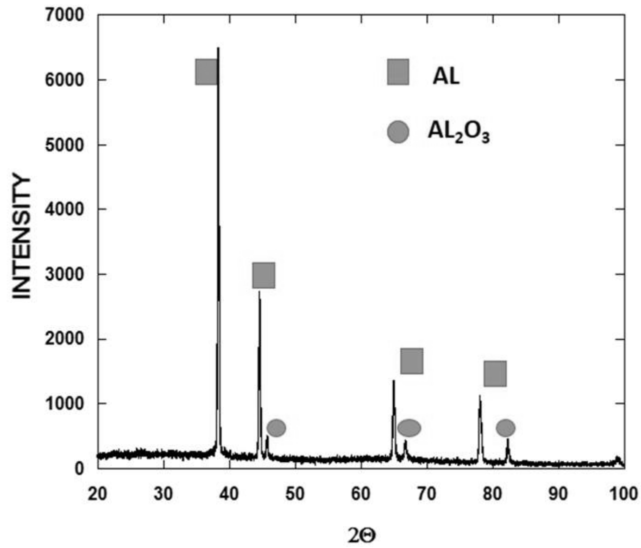

Fig. 2. *Diffraction pattern of Al nanostructures, synthesized in microemulsion (water-benzene), with using the energy of the IPL*

dispersing aluminum metal electrodes in benzene, nanoparticles are formed metal aluminum and carbide aluminum (**Fig. 4**). Most intense peaks correspond to FCC aluminum with the parameter $a_Э$ = 3.0007 Å, for hexagonal carbide aluminum (Al_4C_3) parameters crystal lattices $a_Э$ = 3.9846 Å, $c_Э$ = 24.0548 Å, (a_A = 3.335 Å, c_A = 24.97 Å).

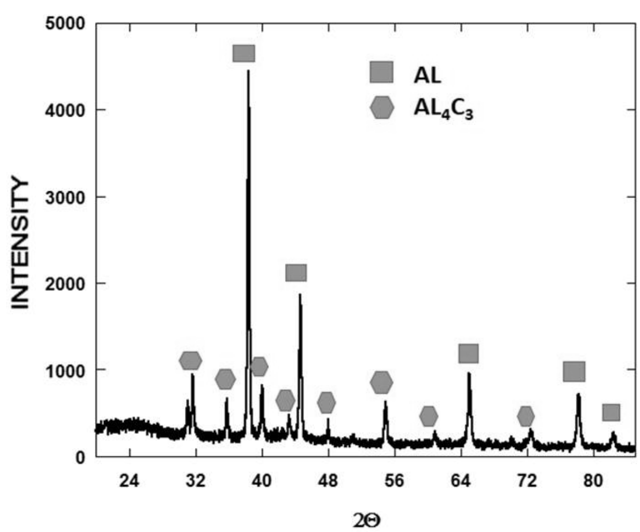

Fig. 4. *Diffraction pattern for Al nanostructures, synthesized in benzene, using energy IPL.*

4. DISCUSSION

According to the results of the study of the phase composition when dispersing aluminum in different environments using energy pulsed plasma can be observed changing the parameters of crystal gratings. Crystalline parameter gratings of massive fcc metal aluminum was $a_А$ = 4.0486 Å, and the parameters crystal lattices for nanoparticles FCC aluminum obtained in microemulsion was $a_Э$ = 2.99716 Å, in a medium benzene - $a_Э$ = 3.0007 Å, distilled water – $a_Э$ = 2.8811 Å.

Also happens changing the parameters of crystal lattices of nanoparticles of aluminum oxide (Fig. 2) and aluminum carbide (Fig. 4), in comparison with literary the parameters of the crystal gratings of massive aluminum oxide and aluminum carbide.

Besides the main phases metallic aluminum in aluminum dispersion product in microemulsion (Fig. 2), found high-temperature phase α-Al_2O_3, from nanoparticle protector film metallic aluminum. Stabilization aluminum nanoparticles provided not only high temperature high-speed quenching, but also oxide film. Education is film, as shown earlier, gives nanoparticles high ohmic resistance [8]. Formation protective film α-Al_2O_3 around aluminum nanoparticles dictated mainly by conditions synthesis – one of the most localized and efficient high-energy effects of pulsed plasma and energy the interface of the microemulsion.

When aluminum is dispersed in distilled water and benzene in addition to the main phase of the nanoscale aluminum, $Al(OH)_3$ and Al_4C_3 are formed, where the formation of oxide films.

Study of morphology and determination of product dispersion destruction of aluminum in microemulsion (water-benzene) were carried out by TEM pictures shown in **Fig. 5**. The size of aluminum nanoparticles is set using ImageJ program measuring diameters of 100 nanoparticles per TEM images. TEM image of the product nanostructuring of aluminum in microemulsions (water-benzene) (Fig. 5) visible spherical nanoparticles, sizes which are in the range from 6 to 50 nm. When nanostructuring aluminum in aluminum nanoparticles

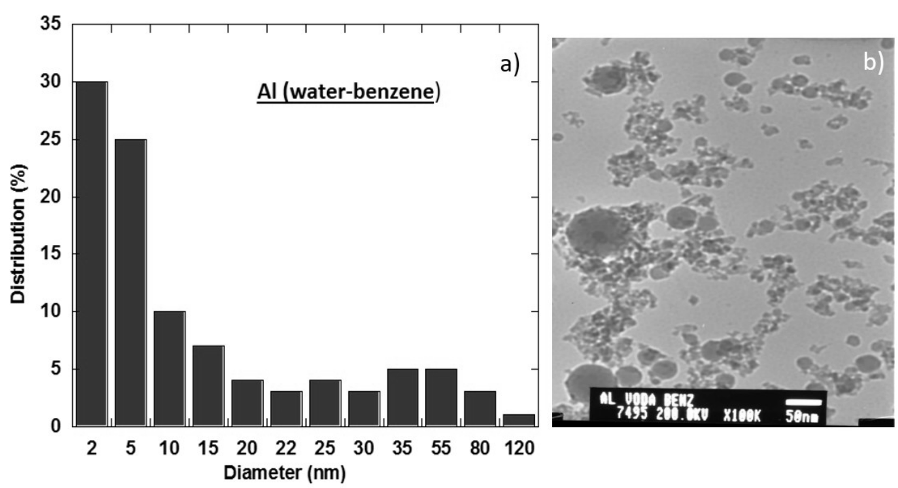

Fig. 5.*a) Histogram of particle distribution over sizes; b) TEM images of Al in microemulsion (water- benzene).*

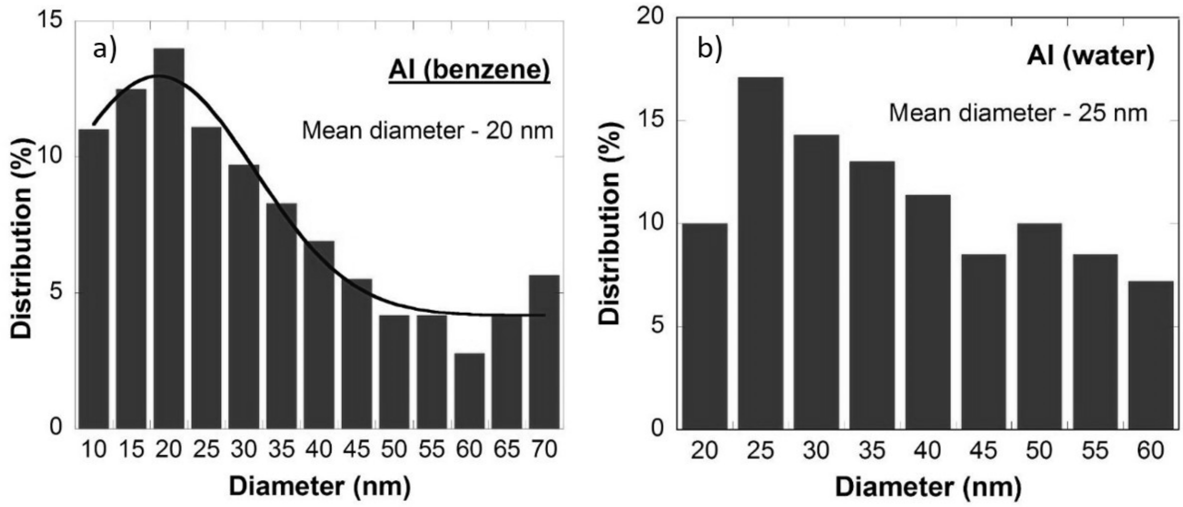

Fig. 6. *Particle size distribution for Al nanostructures obtained: a) in benzene, b) in distilled water.*

are formed in water with sizes 20-60 nm (average size 25 nm). Nanoparticle reflection lines detected aluminum hydroxide, the size of which calculated based on X-ray phase data analysis (55-200 nm).

In benzene at a given energy single pulse metal aluminum nanoparticles were formed with sizes 10-70 nm (average size 20 nm) (**Fig. 6**). Except aluminum nanoparticles in the product of aluminum dispersion in benzene, carbide nanoparticles are formed aluminum Al_4C_3. Thus, for the synthesis of nanoparticles aluminum with oxide tread film is the optimal medium microemulsion - water-benzene. In clean the synthesis of similar nanoparticles is possible in water aluminum, but are formed in water except high temperature oxide film aluminum hydroxide nanoparticles with less density and, therefore, less durability. In light of the above protective film of aluminum nanoparticles, synthesized in water, looser, those. these nanoparticles are more susceptible to oxidation than nanoparticles of aluminum from microemulsions.

4.1. Specific surface area and pore volume aluminum nanoparticles synthesized in microemulsion (water-benzene)

Physical gas adsorption method one of the methods for determining the specific surface area, porosity (micro-, mesoporosity), pore volume, distribution pore sizes of solids. Most common adsorbate for these targets is nitrogen. Sorption study carried out at the boiling point of the liquid nitrogen in the pressure range from minimum possible up to saturated vapor pressure nitrogen at a given temperature. Surface of nanostructures of aluminum, synthesized in microemulsion (water-benzene), using energy PI, studied by the BET method (BET – Bruner-Emmett-Teller method, Brunauer-Emmett-Teller) and BJH (BJH – Barrett-Joyner-Khalenda, Barrett-Joyner-Halenda).

In **Fig. 7** presented nitrogen adsorption and desorption isotherms for nanostructuring product aluminum (nano-sized aluminum + aluminium oxide). Based on the analysis specific surface area

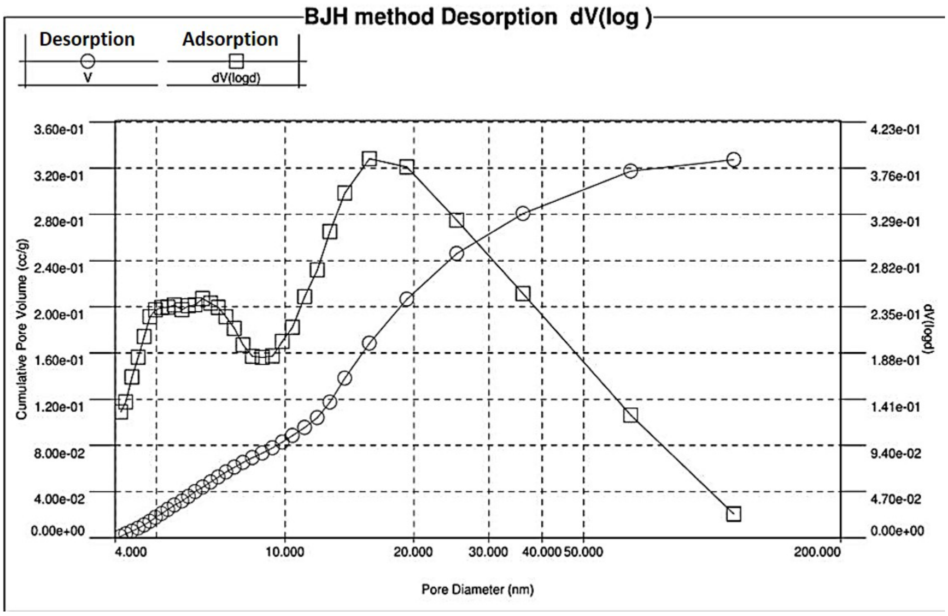

Fig. 7. *Isotherms of adsorption and desorption nitrogen, nano alumina.*

was 96.7 m^2/g, pore volume 0.33 cm^3/g, average pore diameter 5 nm. The data obtained allows us to attribute sample to mesoporous systems in which pore diameter is in the range of 2-50 nm, which is confirmed by the presence of a loop hysteresis. The pore shape can be attributed to wedge-shaped pores, with narrowing in one or at both ends [18]. The authors of [19] synthesized α-Al_2O_3 using the sol-gel method with subsequent heat treatment at temperatures over 1400°*C*. Specific surface of the obtained powder Al_2O_3 amounted to 51 m^2/g, which is almost 2 times less than the sample obtained us in microemulsion. Probably, high energy impact single pulse allows synthesize smaller nanoparticles aluminum with an oxide film, i.e. with more specific surface area.

5. CONCLUSION

Aluminum nanoparticles were synthesized in microemulsion (water-benzene), using pulse energy plasma in the interface. X-ray diffraction analyses results when dispersing aluminum on phase boundary, in microemulsion (water-benzene) are mainly formed aluminum nanoparticles coated protective film of nanoscale high temperature alumina modifications.

Translucent method electron microscopy (TEM) product morphology studied electrospark dispersion aluminum in microemulsion (water-benzene). TEM images show mostly spherical nanoparticles aluminum. Aluminum nanostructures, obtained at the interface, more dispersed, possibly due to additional energy saturation the energy of the interface, in comparison with nanostructures obtained in benzene and distilled water. So way, it can be argued that exactly additional energy generated by interface in microemulsion (water-benzene), affects the formation high-temperature phase α-Al_2O_3. Specific surface for nanocomposite (nanostructures) of aluminum, obtained at the interface, almost 2 times more than for nanoparticles, synthesized by the sol-gel method. Aluminum nanoparticles with tread film from its high-temperature oxide were synthesized by us in one stage and for the first time.

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