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(54) **METHOD FOR PRODUCTION OF INORGANIC NANOFIBRES THROUGH ELECTROSTATIC SPINNING**

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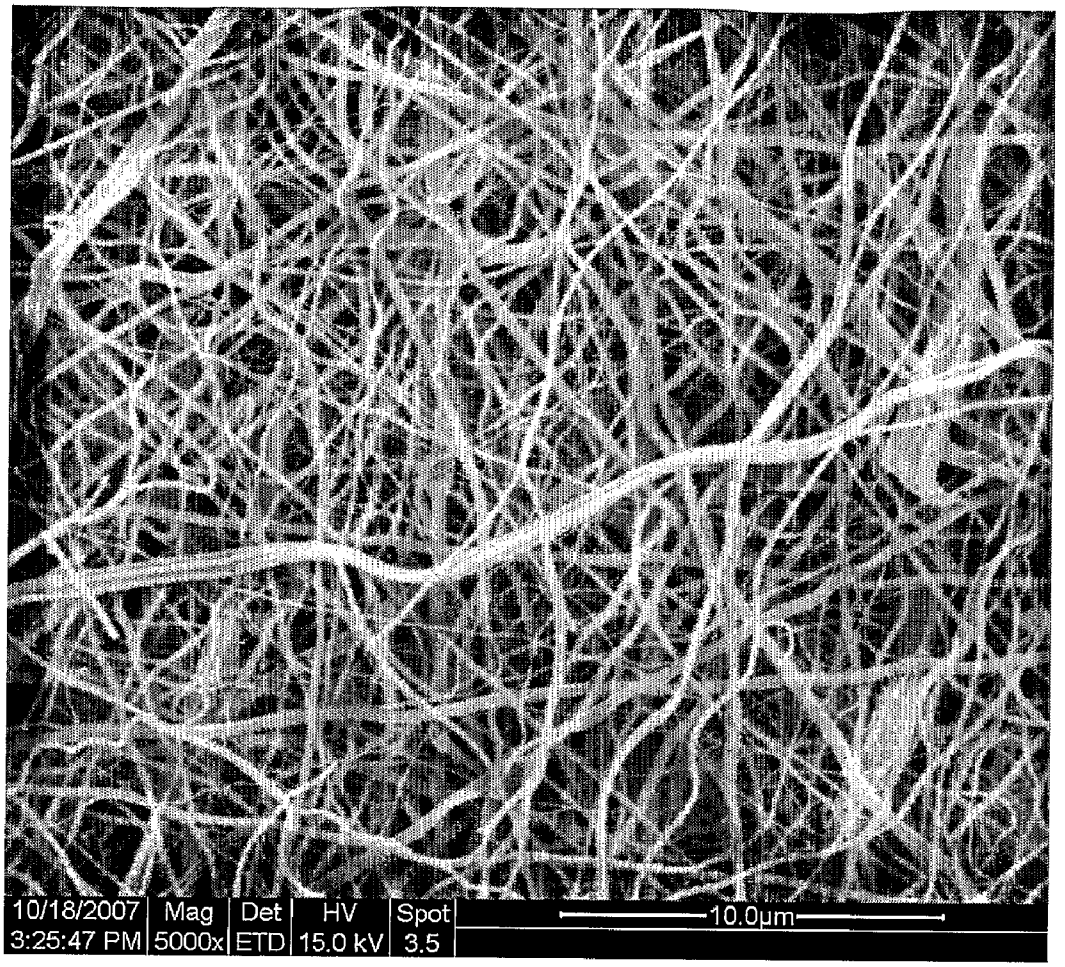
(57) **ABSTRACT**

The present disclosure relates to the production method of inorganic nanofibres through electrostatic spinning of solution, which comprises alkoxide of metal or of semi-metal or of non-metal dissolved in a solvent system on basis of alcohol. The solution is stabilised by chelating agent, which prevents hydrolysis of alkoxide, and after homogenisation it is mixed with solution of poly(vinylpyrrolidone) in alcohol, after then the resultant solution is brought into electrostatic field, in which the electrostatic spinning is running continually, the result of which is production of organic-inorganic nanofibres, which are after then calcinated outside the spinning device in the air atmosphere at the temperature from 500° C. to 1300° C.



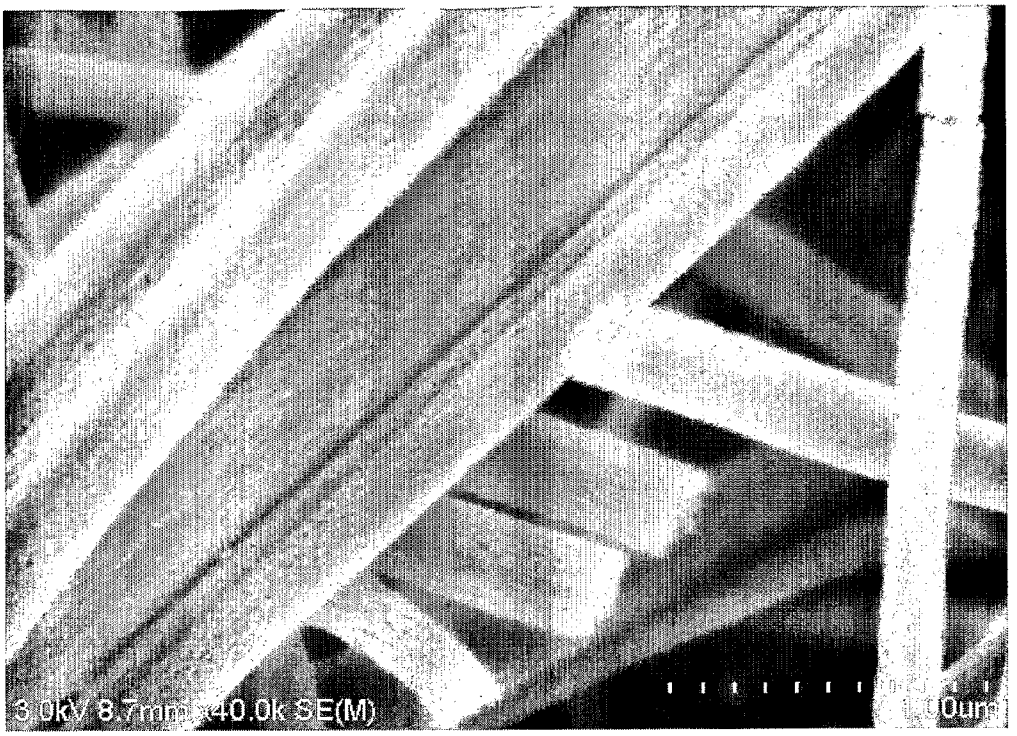
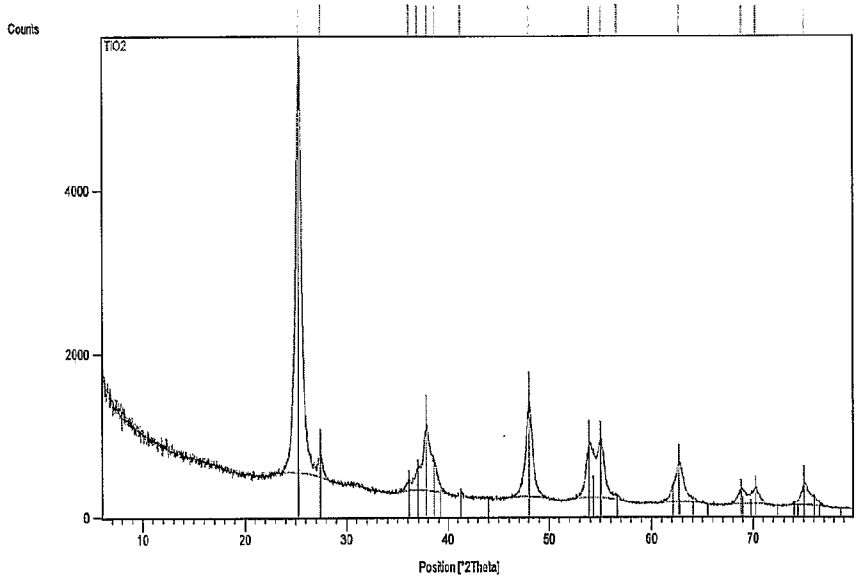

3.0kV 8.7mm x40.0k SE(M)

Fig. 1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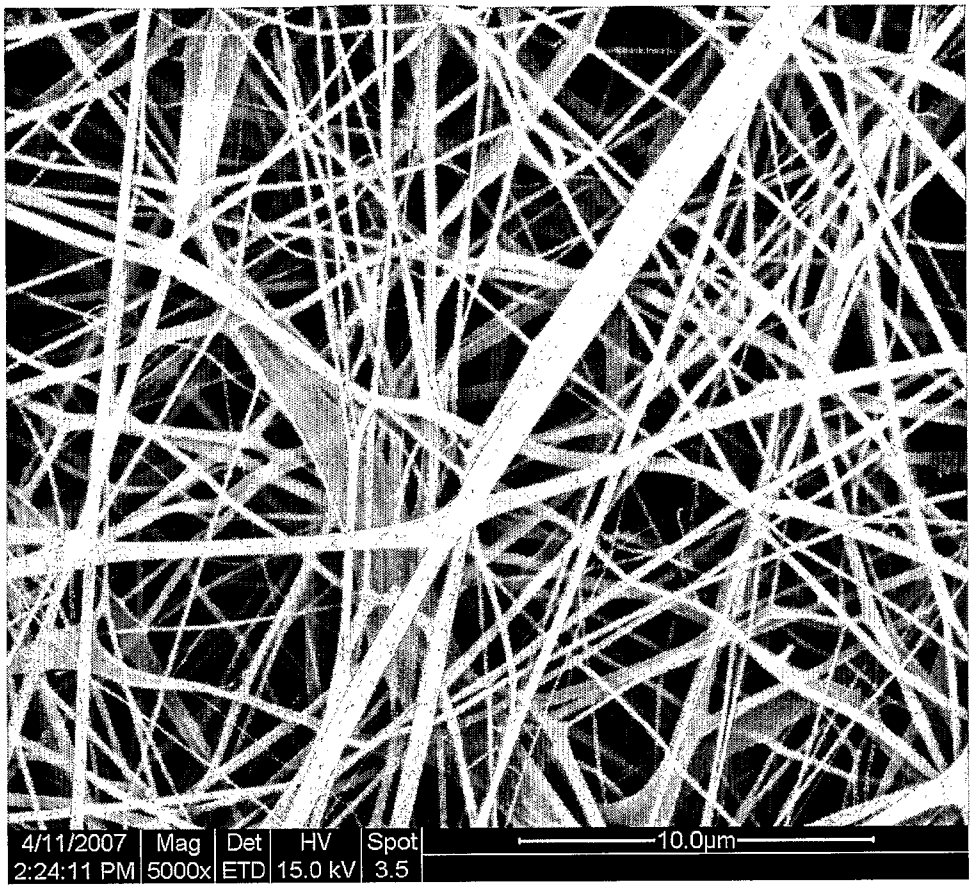
10
20
30
40
50
60
70
Position [°2Theta]

Fig. 2


4/11/2007
2:24:11 PM
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Det
ETD
HV
15.0 kV
Spot
3.5
10.0µm

Fig. 3

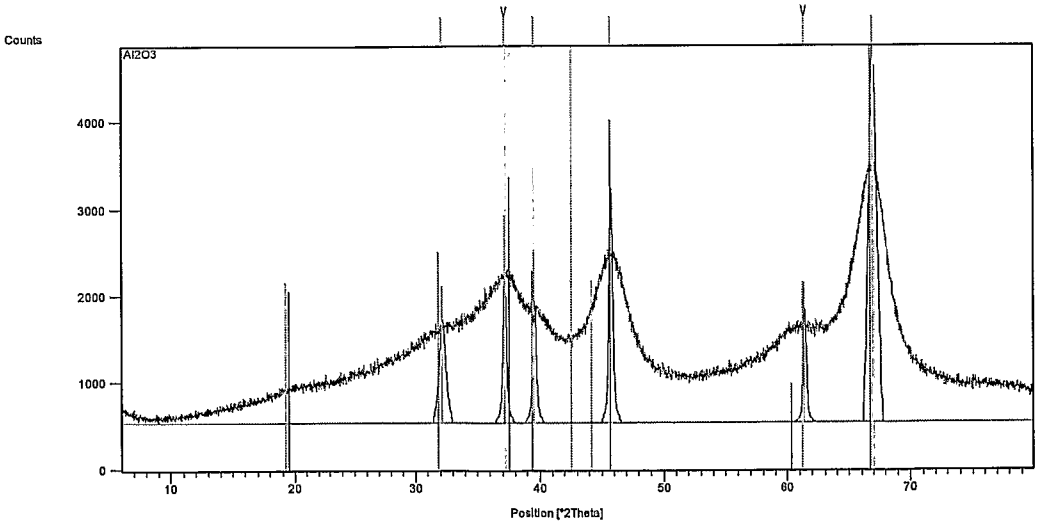
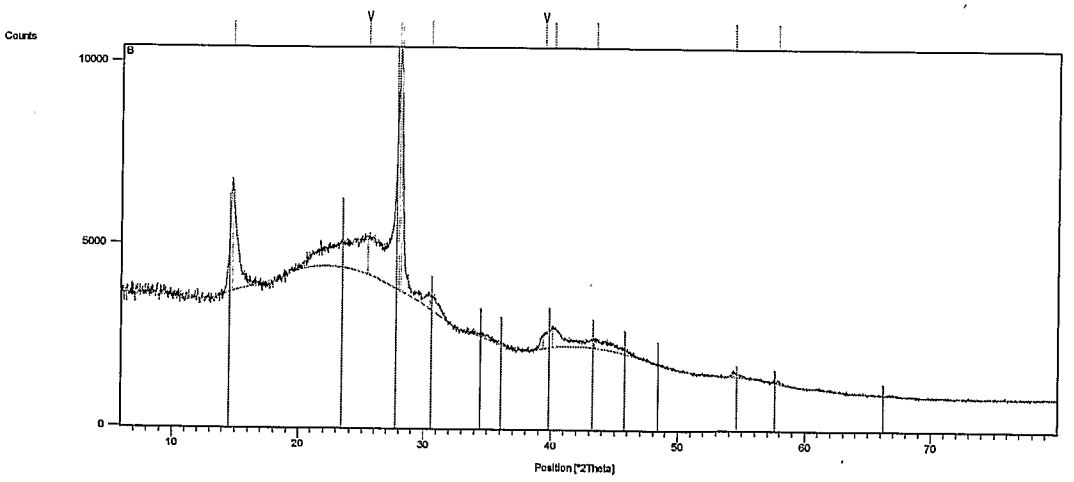

Counts
Al2O3
4000
3000
2000
1000
0
10
20
30
40
50
60
70
Position [°2Theta]

Fig. 4


8/13/2007
2:15:56 PM
Mag
5000x
Det
ETD
HV
15.0 kV
Spot
3.5
10.0µm

Fig. 5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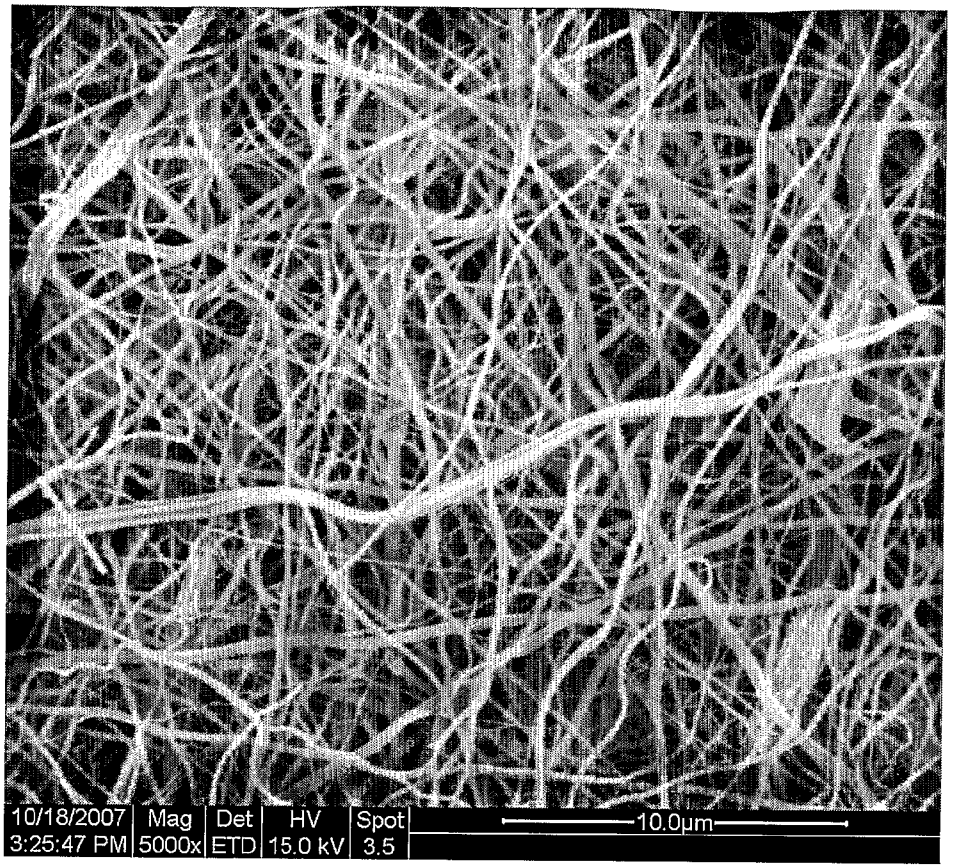
5000
0
10
20
30
40
50
60
70
Position [°2Theta]

Fig. 6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Det
ETD
HV
15.0 kV
Spot
3.5
10.0µm

Fig. 7

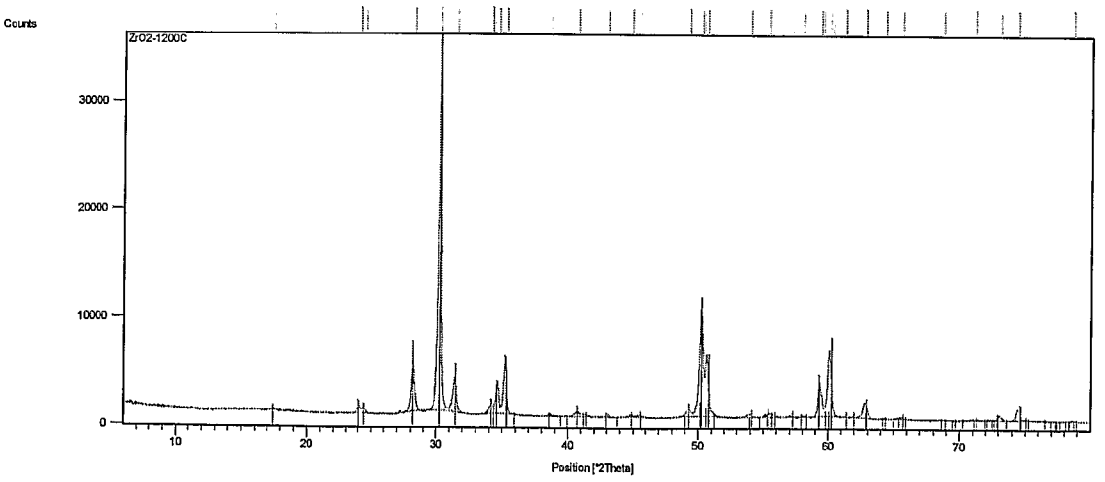
Counts
ZrO2-1200C
30000
20000
10000
0
10
20
30
40
50
60
70
Position [°2Theta]

Fig. 8

METHOD FOR PRODUCTION OF INORGANIC NANOFIBRES THROUGH ELECTROSTATIC SPINNING

TECHNICAL FIELD

[0001] The invention relates to a method for production of inorganic nanofibres through electrostatic spinning of solution, which contains alkoxide of metal or of semi-metal or of non-metal dissolved in a solvent system on basis of alcohol.

BACKGROUND ART

[0002] Inorganic materials feature a number of properties, thanks to which they are suitable for usage in many technical fields, e.g. in electrotechnics, medicine, industry, etc. For example, TiO_2, SiO_2, Al_2O_3, ZrO_2 and B_2O_3 belong to the important inorganic substances. At inorganic nanofibres there are combined properties of nanofibrous materials, like an organised one-dimensional structure with properties of nanomaterials, especially with high specific surface, and with physical-chemical properties of inorganic substances as hardness, thermal resistance and structure of electron stripes. Therefore the resultant nanofibres are suitable for production of composite materials, catalysts, electrochemical elements, etc.

[0003] At present, there are known various methods for production of nanoparticles from inorganic materials. Production of inorganic nanoparticles, namely from SiO_2 and Al_2O_3, is disclosed in WO2007/079841.

[0004] Nanoparticles from inorganic material, which may be produced through the above mentioned or other suitable method, could also be incorporated into a structure of nanofibres, which may be realised e.g. by adding the nanoparticles into polymer solution and consequent production of nanofibres from this solution. Presence of inorganic nanoparticles in polymer nanofibres renders specific properties to these nanofibres. Nevertheless the substantial portion of these nanoparticles is formed of polymer component.

[0005] At present the pure inorganic nanofibres are produced by discontinual methods of electrostatic spinning at usage of nozzle or needle spinning electrode, into which the solution is supplied, which may be represented by a precursor of given inorganic elements, or the polymer solution containing alkoxide of respective metal or non-metal as a source of inorganic basis of fibres.

[0006] The known solutions used for production of anorganic nanofibres through electrostatic spinning from nozzles cannot be used for continual production of nanofibres, because alkoxides are time-unsteady and are easily subject to degradation of alkoxide through hydrolysis, this even through action of air humidity, which occurs still before their spinning. To date for electrostatic spinning there was not used any solution of alkoxide, that would be stable enough and could be used for continual production of inorganic nanofibres.

[0007] The goal of the invention is to develop a continual production method of inorganic nanofibres through electrostatic spinning, which would remove disadvantages of the background art.

The Principle of Invention

[0008] The goal of the invention has been achieved through a method for production of inorganic nanofibres according to the invention, whose principle consists in that, the alkoxide solution of metal or of semi-metal or non-metal is in a solvent system on basis of alcohol stabilised by chelating agent, which prevents hydrolysis of alkoxide, and after homogenizing is mixed with solution of poly(vinylpyrrolidone) in alcohol, after then the resultant solution is brought into electrostatic field, in which continually on long-term basis the electrostatic spinning is running, the result of which is production of organic-inorganic nanofibres, which are outside the spinning device calcinated after then in the air atmosphere at the temperature from 500° C. to 1300° C.

[0009] By stabilisation of solution the hydrolysis of alkoxides by action of air humidity and other impacts of working environment is prevented, so that the process of electrostatic spinning runs continually and in the long-term. In the published works, in case of nozzle electro-spinning, they use the solutions of alkoxide of metal in alcohol in combination with poly(vinylpyrrolidone). Alkoxide is stabilised by additive of acetic acid (see Journal of America Ceramic Society 89[6] 1861-1869(2006), Science and Technology of Advanced Materials 6(2005)240-245). Usage of this solution in case of electrostatic spinning from opened surface is possible in laboratory scale, nevertheless at the process lasting longer than half an hour the degradation of solution and hydrolysis of alkoxide occurs. This effect prevents industrial utilization of in literature described compositions of solutions for production of ceramic nanofibres through the method of electrostatic spinning from opened surface.

[0010] For the purpose to increase the electrical conductivity of solution and to increase efficiency of production process, it is possible to add into the solution a concentrated acid, which is according to the claim **3** preferably selected from the group of hydrochloric acid, nitric acid, phosphoric acid.

[0011] In preferred embodiment of the method the chelating agent is composed of β-diketone, while the most suitable β-diketone seems to be acetylacetone, at whose usage the stabilisation of solution is permanent.

[0012] Alcohol in solution of poly(vinylpyrrolidone) is selected from the group of ethanol, 1-propanol, 2-propanol or their mixtures.

[0013] In advantageous embodiment the poly(vinylpyrrolidone) has an average molecular weight within 1000000-1500000 g/mol and its weight concentration in solution is within the range from 4 to 9%, while the most preferred seems to be the poly(vinylpyrrolidone) having average molecular weight of 1300000 g/mol.

[0014] Alkoxide of metal is preferably selected from the group of titanium tetrabutoxide, titanium tetraisopropoxide, aluminium tri-sec-butoxide, aluminiumtriisopropoxide or zirconium tetraisopropoxide.

[0015] Alkoxide of semi-metal is preferably tetraethoxysilane or borium triethoxide.

[0016] To achieve a good stabilisation of alkoxide solution it is preferred if the ratio of alkoxide and chelating agent in solution is within 1:0.8 to 1:2.2.

[0017] For the electrostatic spinning itself, the alkoxide solution in electrostatic field is to be found on surface of active zone of the spinning mean of a spinning electrode.

[0018] At the same time it is preferred, if the alkoxide solution is into electrostatic field for spinning transported by surface of the spinning electrode, which is preferably formed of rotating spinning electrode of an oblong shape, which extends by a section of its circumference into the solution being subjected to spinning.

DESCRIPTION OF THE DRAWING

[0019] The drawing represents in the FIG. **1** produced TiO_2 nanofibres, and in the FIG. **2** their XRD spectrum, the FIG. **3** represents Al_2O_3 nanofibres and the FIG. **4** their XRD spectrum, the FIG. **5** represents B_2O_3 nanofibres and the FIG. **6** their XRD spectrum, the FIG. **7** represents ZrO_2 nanofibres and the FIG. **8** their XRD spectrum.

EXAMPLES OF EMBODIMENT

[0020] Spinning solution for production of inorganic nanofibres, especially of TiO_2, SiO_2, Al_2O_3, ZrO_2 and B_2O_3, by means of electrostatic spinning contains as a source of inorganic basis an alkoxide of respective metal, semi-metal or non-metal, which is dissolved in a suitable solvent, e.g. in ethanol, **1**-propanol or 2-propanol. To stabilise the solution of alkoxide, especially to prevent its hydrolysis, an addition of chelating agent as stabiliser is necessary. The most suitable chelating agent is 6-diketone, e.g. acetylaceton. Molecular ratio between alkoxide and chelating agent should be within the range from 1:0.8 to 1:2.2. To improve the spinning ability of the solution also supporting polymer is added into it, which may be represented by e.g. poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol or viscosity number K-90, while its weight concentration towards a total weight of solution is from 4 to 9% by weight.

[0021] The process of electrostatic spinning depends on concentration, or more precisely on viscosity, surface tension and other parameters of alkoxide solution. The exact composition of alkoxide solution depends on temperature and humidity of environment and parameters of electrostatic spinning, such as rotation and type of electrode, distance between electrodes and applied voltage.

[0022] In particular example of embodiment for production of SiO_2 nanofibres for production of solution a mixture of 250 g of ethanol and 39 g of acetylacetone was used, in which there was carefully dissolved 100 g of tetraethoxysilane. After homogenisation the obtained solution was carefully mixed with solution of 35.2 g poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 747.9 g of ethanol. After following homogenisation the resultant solution was acidified with concentrated hydrochloric acid.

[0023] The resultant solution of tetraethoxysilane was used for production of SiO_2 nanofibres by means of electrostatic spinning. There was used a device for electrostatic spinning of polymer solutions comprising a spinning electrode and against it arranged collecting electrode, while the spinning electrode comprised rotatably mounted spinning mean extending by a section of its circumference into a solution of tetraethoxysilane being present in a reservoir. The rotating spinning mean, thanks to its rotation, carried out the solution of tetraethoxysilane into a electrostatic field induced between the spinning electrode and the collecting electrode, while a portion of surface of rotating spinning mean being positioned against the collecting electrode represents an active spinning zone of the spinning mean. During spinning the solution of tetraethoxysilane was present in electrostatic field on surface of active spinning zone of the spinning mean of the spinning electrode. Rotating spinning mean may be construed e.g. according to the CZ patent 294274 or according to the CZ PV 2006-545 or CZ PV 2007-485. At concrete spinning of solution of tetraethoxysilane described above a portion of solution, about 125 ml, was poured into storing vessel and this was equipped with a spinning rotating cylindrical electrode. The vessel with the electrode was positioned into a device for production of nanofibres through electrostatic spinning. As a substrate material any fabric, foil, etc., may be used. The obtained organic-inorganic nanofibrous layer comprised the nanofibres having thickness of 30-1000 nm.

[0024] The nanofibrous organic-inorganic layer was consequently calcinated in a furnace in air atmosphere at temperature from 600 to 800° C. at production of pure amorphous SiO_2 nanofibres.

[0025] Similarly, the following solutions of alkoxides were subject to electrostatic spinning.

[0026] For production of TiO_2 nanofibres for preparation of solution the mixture of 250 g of ethanol and 29.4 g of acetylacetone was used, in which 100 g of titanium tetrabutoxide was dissolved. After homogenisation the obtained solution was carefully mixed with solution of 35.2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 758.8 g of ethanol and after then acidified with concentrated hydrochloric acid. The resultant solution was subject to spinning through electrostatic spinning. The nanofibrous organic-inorganic layer was calcinated in furnace in air atmosphere at the temperature of 500° C. The crystallic form (structure) of resultant TiO_2 of inorganic nanofibres was purely of anatase.

[0027] In further example of embodiment for production of $Li_4Ti_5O_{12}$ nanofibres for preparation of solution the mixture of 250 g of ethanol and 29.4 g of acetylacetone was used, in which 100 g of titanium tetrabutoxide was dissolved. After homogenisation the obtained solution was carefully mixed with solution of 35.2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol and 24 g of dihydrate of lithium acetate in 758.8 g of ethanol. The resultant solution was subject to electrostatic spinning. The nanofibrous organic-inorganic layer was calcinated in furnace in air atmosphere at the temperature of 750° C. The resultant inorganic fibres showed the phase of $Li_4Ti_5O_{12}$ with addition of anatase and rutile less than 5%.

[0028] In another example of embodiment for production of solution of TiO_2 nanofibres the mixture of 250 g of 2-propanol and 29.4 g of acetylacetone was used, in which 100 g of titanium tetrabutoxide was dissolved. After homogenisation the obtained solution was mixed with solution of 35.2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 758.8 g of ethanol, and after then acidified with concentrated hydrochloric acid. The resultant solution was subject to spinning through electrostatic spinning. The nanofibrous layer was calcinated at the temperature of 700° C. Crystallic form of resultant nanofibres was partially of anatase and partially of rutile, that is witnessed by the picture represented in the FIG. **1** and XRD spectrum of nanofibres represented in the FIG. **2**.

[0029] In further exemplary embodiment for production of solution for production of TiO_2 nanofibres the mixture of 250 g of 1-propanol and 29.4 g of acetylacetone acidified with 0.3 g of phosphoric acid was used. In the given mixture 100 g of titanium tetrabutoxide was dissolved. After homogenisation the obtained solution was mixed with solution of 35.2 g poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 758.8 g of ethanol. The resultant Solution was subject to spinning through electrostatic spinning. The nanofibrous layer was calcinated at the temperature of 500° C. Crystallic form of resultant inorganic TiO_2 nanofibres was purely of anatase.

[0030] At further example of embodiment for production of solution for production of TiO_2 nanofibres the mixture of 250 g of ethanol and 58.8 g of acetylacetone was used, in which 100 g of titanium tetrabutoxide was dissolved. After homogenisation the obtained solution was mixed with solution of 35.2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 729.4 g of ethanol and after then acidified with concentrated hydrochloric acid. The resultant solution was subject to spinning through electrostatic spinning. The nanofibrous layer was calcinated at the temperature of 700° C. Crystallic form of resultant TiO_2 nanofibres was partially of anatase and partially of rutile.

[0031] For production of solution for production of TiO_2 nanofibres according to further example of embodiment the mixture of 150 g ethanol and 29.4 g of acetylacetone was used, in which 100 g of titanium tetrabutoxide was dissolved. After homogenisation the obtained solution was mixed with solution of 35.2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 272.1 g of ethanol, and after then acidified with concentrated hydrochloric acid. The resultant solution was subject to spinning through electrostatic spinning. The nanofibrous layer was calcinated at the temperature of 500° C. Crystallic form of resultant TiO_2 nanofibres was purely of anatase.

[0032] In another embodiment for production of solution for production of TiO_2 nanofibres the mixture of 250 g ethanol and 35.2 g of acetylacetone was used, in which 100 g of titanium tetraisopropoxide was dissolved. After homogenisation the obtained solution was mixed with solution of 42.2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 977.7 g of ethanol and after then acidified with concentrated hydrochloric acid. The resultant solution was subject to spinning through electrostatic spinning. The nanofibrous layer was calcinated at the temperature of 500° C. Crystallic form of resultant TiO_2 nanofibres was purely of anatase.

[0033] For production of Al_2O_3 nanofibres the mixture of 500 g of 2-propanol and of 40.7 g of acetylacetone was used, in which 100 g of aluminium tri-sec-butoxide was dissolved. After homogenisation the obtained solution was mixed with solution of 62.1 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 1366.9 g of ethanol and after then acidified with concentrated hydrochloric acid. The resultant solution was subject to spinning through electrostatic spinning. The nanofibrous layer was calcinated at the temperature of 700° C. The resultant inorganic fibres showed a pure □-Al_2O_3 crystallic structure, which is witnessed by the picture represented in the FIG. **3** and XRD spectrum represented in the FIG. **4**.

[0034] In another embodiment for production of solution for production of Al_2O_3 nanofibres the mixture of 350 g of 2-propanol and 40.7 g of acetylacetone was used, in which 100 g of aluminium tri-sec-butoxide was dissolved. After homogenisation the obtained solution was mixed with solution of 62.1 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 827 g of ethanol and after then acidified with concentrated hydrochloric acid. The nanofibrous layer was calcinated at the temperature of 800° C. The resultant inorganic fibres showed a pure □-Al_2O_3 crystallic structure.

[0035] In another embodiment for production of solution for production of Al_2O_3 nanofibres the mixture of 500 g of 2-propanol and 49 g of acetylacetone was used, in which 100 g of aluminium triisopropoxide was dissolved. After homogenisation the obtained solution was mixed with solution of 74.9 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 1772.2 g of ethanol and after then acidified with concentrated hydrochloric acid. The resultant solution was subject to spinning through electrostatic spinning. The nanofibrous layer was calcinated at the temperature of 700° C. The resultant inorganic fibres showed a pure □-Al_2O_3 crystallic structure.

[0036] For production of B_2O_3 nanofibres the mixture of 500 g of ethanol and 68.6 g of acetylacetone was used, in which 100 g of borium triethoxide was dissolved. After homogenisation the obtained solution was mixed with solution of 71.5 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 1644.3 g of ethanol and after then acidified with concentrated hydrochloric acid. The resultant solution was subject to spinning through electrostatic spinning.

[0037] The nanofibrous layer was calcinated at the temperature of 500° C. The resultant inorganic fibres showed B_2O_3 crystallic structure with amorphous addition, which is witnessed by the picture represented in the FIG. **5** and XRD spectrum represented in the FIG. **6**.

[0038] For production of ZrO_2 nanofibres the mixture of 500 g of ethanol and 30.6 g of acetylacetone was used, into which the solution of 142.9 g of zirconium tetraisopropoxide in 1-propanol was added. After homogenisation the obtained solution was mixed with solution of 56.4 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 1193.8 g of ethanol and after then acidified with concentrated hydrochloric acid. The resultant solution was subject to spinning through electrostatic spinning. The nanofibrous layer was calcinated at the temperature of 700° C. The resultant inorganic fibres showed ZrO_2 mixture of monoclinic and tetragonal crystallic structure, which is witnessed by the picture represented in the FIG. **7** and XRD spectrum represented in the FIG. **8**.

[0039] In all cases the long-term continual spinning process was achieved and thickness of produced nanofibres was from 30 to 1000 nm.

[0040] Production of nanofibres from the above mentioned solutions of alkoxides is not limited only to the described electrostatic spinning device with rotating spinning electrode, but it is possible to use also other types of spinning electrodes, at which the solution of alkoxide in electrostatic field for spinning is to be found on surface of active spinning zone of a spinning mean of a spinning electrode. Spinning of alkoxide solution runs successfully also on wire spinning electrodes according to the CZ PV 2007-485, at which the active spinning zone of the wire has during the spinning process a stable position towards the collecting electrode and alkoxide solution is to the active spinning zone of the wire supplied either by applying or by movement of the wire in direction of its length. In this case, the solution of alkoxide in electrostatic field for spinning is to be found on surface of active zone of the wire of spinning mean. The described solutions of alkoxides can of course be used also for discontinuous production of nanofibres at usage of nozzle or needle as a spinning electrode.

INDUSTRIAL APPLICABILITY

[0041] The mentioned method for production of nanofibres ensures a sufficient stability of the solution being subject to spinning for entire period of spinning, and it is a key aspect for continuous production of inorganic nanofibres. Application

of layers of inorganic nanofibres is important in many technical fields and industry, e.g. for production of composite materials, catalysts and electrochemical active elements.

1. A method for production of inorganic nanofibres through electrostatic spinning of solution, which comprises alkoxide of metal or of semi-metal or of non-metal dissolved in a solvent system on basis of alcohol, wherein the solution is stabilised by acethylacetone, which prevents hydrolysis of alkoxide, and after homogenisation it is mixed with solution of poly(vinylpyrrolidone) in an alcohol, after then the resultant solution is brought into electrostatic field, in which the electrostatic spinning is running continually, the result of which is production of organic-inorganic nanofibres, which are after then calcinated outside the spinning device in air atmosphere at the temperature from 500 ° C. to 1300° C.

2. The method according to claim **1**, wherein, to increase the electrical conductivity of the solution, a concentrated acid is added into the solution.

3. The method according to claim **2**, the wherein the acid is selected from the group of hydrochloric acid, nitric acid, phosphoric acid.

4. (canceled)

5. The method according to claim **1**, wherein the alcohol in solution of poly(vinylpyrrolidone) is selected from the group of ethanol, 1-propanol, 2-propanol or their mixtures.

6. The method according to claim **1**, wherein the poly (vinylpyrrolidone) has an average molecular weight within the range of 1000000-1500000 g/mol and its weight concentration in the solution is within the range from 4 to 9%.

7. The method according to claim **6**, wherein the poly (vinylpyrrolidone) has average molecular weight of 1300000 g/mol.

8. The method according to claim **1**, wherein the poly (vinylpyrrolidone) has viscosity number K within the range from K-70 to K-95 and its concentration in solution is in the range from 4 to 9%.

9. The method according to claim **8**, wherein the poly (vinylpyrrolidone) has viscosity number K-90.

10. The method according to claim **1**, wherein the alkoxide of metal is selected from the group of titanium tetrabutoxide, titanium tetraisopropoxide, aluminium tri-sec-butoxide, aluminium triisopropoxide, zirconium tetraisopropoxide.

11. The method according to claim **1**, wherein the alkoxide of semi-metal is selected from the group of tetraethoxysilane, borium triethoxide.

12. The method according to claim **1**, wherein the molecular ratio of alkoxide and chelating agent in solution is from 1:0.8 to 1:2.2.

13. The method according to claim **1**, wherein the alkoxide solution in electrostatic field for spinning is to be found on surface of active spinning zone of the spinning mean of the spinning electrode.

14. The method according to claim **12**, wherein the solution of alkoxide is transported into electrostatic field for spinning by surface of the spinning electrode.

15. The method according to claim **12**, wherein the spinning electrode is formed of rotating spinning electrode of an oblong shape, which extends by a section of its circumference into the spinning solution.

* * * * *