



(12) **EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 153(4) EPC

(43) Date of publication:  
**15.08.2018 Bulletin 2018/33**

(51) Int Cl.:  
**B22F 9/24 (2006.01)**

(21) Application number: **16852969.1**

(86) International application number:  
**PCT/CN2016/076284**

(22) Date of filing: **14.03.2016**

(87) International publication number:  
**WO 2017/059658 (13.04.2017 Gazette 2017/15)**

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA ME**  
Designated Validation States:  
**MA MD**

- **LIU, Bitao**  
**Chongqing 402168 (CN)**
- **JIN, Rong**  
**Chongqing 402168 (CN)**
- **CHEN, Shanyong**  
**Chongqing 402168 (CN)**
- **YAN, Hengqing**  
**Chongqing 402168 (CN)**
- **GUAN, Youwei**  
**Chongqing 402168 (CN)**

(30) Priority: **09.10.2015 CN 201510645800**

(71) Applicant: **Chongqing University Of Arts And Sciences**  
**Chongqing 402168 (CN)**

(74) Representative: **Becker Kurig Straus**  
**Patentanwälte**  
**Bavariastrasse 7**  
**80336 München (DE)**

(72) Inventors:  
• **LI, Lu**  
**Chongqing 402168 (CN)**

(54) **UNIFORM ASPECT RATIO SILVER NANOWIRES PREPARATION METHOD**

(57) A preparation method for silver nanowires with a uniform aspect ratio, including: dissolving at a certain temperature silver nitrate in glycerol to get a solution A; dissolving at a certain temperature polyvinylpyrrolidone (PVP) in glycerol to get a solution B; mixing uniformly the solution A and the solution B to form a solution C; then, adding a certain amount of a medium into the solution C and mixing uniformly to form a solution D, finally, transferring the solution D into a reaction kettle, putting the reaction kettle into an oven with a set temperature, and ending the reaction after a certain time of reaction. The reactants are centrifuged twice to obtain precipitated silver nanowires. With the addition of the medium, the method can improve the moving speed of ions in a reaction solution, and obtain the silver nanowires with a uniform aspect ratio and nodes. The preparation method is simple and easy to operate, experimentally stable, and suitable for industrial production.

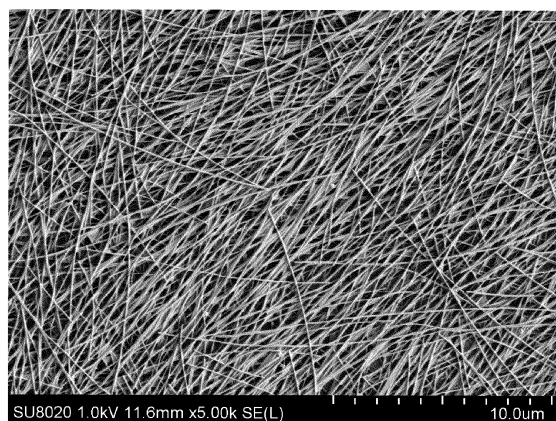


FIG. 1

## Description

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

**[0001]** The present invention relates to a preparation method for silver nanowires, and more particularly, to a preparation method for silver nanowires with a uniform aspect ratio.

#### 2. Description of Related Art

**[0002]** Based on the properties of high specific surface area, electrical conductivity and thermal conductivity, silver nanowires have a broad application prospect. Especially, the silver nanowires can be used as an alternative material of ITO in fields such as solar energy, OLED, and flexible and large-size touch screen displays, and used in fields such as conductive polymers, composite materials, and electrode printing ink additives. Therefore, the preparation of silver nanowires has become a focus of researchers. At present, there are many documents and patent reports on the preparation methods and applications of silver nanowires. For example, Xia Younan, the first one who prepares silver nanowires with a polyol method, proposed the preparation of silver nanowires with a high aspect ratio by using Pt as seeds and reducing silver nitrate by ethylene glycol (Advanced Materials (2002) 14,883). The polyol reduction method was combined with the hydrothermal method, and a small amount of sodium chloride, ferric chloride, copper chloride and other metal halide were introduced to function with Ag ions to form a colloid, which serves as seeds to prepare silver nanowires. The silver nanowires can be quickly prepared by the combination of the polyol method and the microwave method. However, the silver nanowires thus obtained have a relatively non-uniform aspect ratio, and have a large amount of impurities. For example, Chinese Patent Application No. 200810019828.6 disclosed a batch preparation method for silver nanowires, and Chinese Patent Application No. 201010559335.9 disclosed a method for preparing silver nanowires with controlled diameter by using a cation-controlled microwave method. However, he prepared silver nanowires are less than 30  $\mu\text{m}$  in length, and have a non-uniform aspect ratio. Chinese Patent No. CN 1843670A reported the use of a composite solvent of glycerol and water or ethanol or isopropanol for reduction to prepare silver nanowires. The obtained silver nanowires have a length of 5-200  $\mu\text{m}$  and a diameter of 70-90 nm. Although many preparation methods for silver nanowires have been reported, few of them can obtain silver nanowires with a uniform aspect ratio and no other particles or impurities. Therefore, it is very important to invent a method that has a stable process, has fewer control factors, is simple and quick, can prepare a large quantity of Ag nanowires.

### SUMMARY OF THE INVENTION

**[0003]** The present invention is directed to a preparation method of silver nanowires with a uniform aspect ratio, which is simple, easy to control, and cost-effective.

**[0004]** The present invention is achieved through the following technical solution.

**[0005]** A preparation method for silver nanowires includes the following steps:

- (1) dissolving silver nitrate in glycerol to get a solution A;
- (2) dissolving polyvinylpyrrolidone in glycerol to get a solution B;
- (3) mixing uniformly the solution A and the solution B to form a solution C; and
- (4) adding an ultrapure water medium into the solution C and mixing uniformly to form a solution D, finally, transferring the solution D into a reaction kettle for reaction at  $150^{\circ}\text{C} \pm 10^{\circ}\text{C}$ , and centrifuging the reactants to obtain silver nanowires. The obtained silver nanowires have high purity and a uniform aspect ratio.

**[0006]** Preferably, reaction time in the reaction kettle is 9-10 hours.

**[0007]** To further improve purity and uniformity of the aspect ratio of the silver nanowires, preferably, in step (1), 0.16 g-0.32 g silver nitrate is dissolved at room temperature in 20 ml of glycerol to get the solution A.

**[0008]** More preferably, in step (2), 5 g-7 g polyvinylpyrrolidone is dissolved at room temperature in 80 ml of glycerol to get the solution B.

**[0009]** More preferably, in step (4), 2.5 ml-10 ml of the ultrapure water is added into the solution C and mixed uniformly to form the solution D.

**[0010]** Further, the centrifuging is performed twice.

**[0011]** The present invention has the following beneficial effects:

**[0012]** The preparation method of the present invention is simple to operate, easy to control, cost-effective, and very suitable for large-scale industrial production. The prepared silver nanowires have a uniform aspect ratio, and transparent conductive films based on the silver nanowires have a high transparency of 90-91 %. The silver nanowires have a diameter of up to 30-40 nm and a length of 10-20  $\mu\text{m}$ , and the silver nanowires with the aspect ratio have small resistance, which is beneficial to the improvement of electrical conductivity. In addition, the silver nanowires have no particles and feature high purity.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0013]**

FIG. 1 is a scanning electron microscope (SEM) diagram of a silver nanowire synthesized in Example

1 of the present invention; and

FIG. 2 is a diagram showing transmittance of a conductive thin film made of silver nanowires synthesized in Example 1 of the present invention.

## DESCRIPTION OF THE EMBODIMENTS

**[0014]** The technology of the present invention will be further described below with reference to specific examples.

### Example 1

**[0015]** 0.16 g silver nitrate was dissolved at room temperature in 20 ml of glycerol to get a solution A; 5 g polyvinylpyrrolidone was dissolved at room temperature in 80 ml of glycerol to get a solution B; the solution A and the solution B were mixed uniformly to form a solution C; then, 5 ml of ultrapure water was added into the solution C and mixed uniformly to form a solution D, finally, the solution D was transferred into a reaction kettle, the reaction kettle was put into an oven with a set temperature of 160°C, and the reaction ended after a certain time of reaction.

**[0016]** The Ag nanowire mother solution in the reaction kettle was diluted with alcohol and centrifuged twice to obtain precipitated silver nanowires having a diameter of 30-40 nm and a length of 10-20 μm, which were dispersed in isopropanol. FIG. 1 is a scanning electron microscope (SEM) diagram of a silver nanowire synthesized in Example 1.

**[0017]** The silver nanowires prepared in Example 1 above were formulated into 1g/L silver nanowire slurry, and 500 μL of slurry was uniformly coated on an A4-size transparent film to prepare a transparent conductive film. The sheet resistance of the transparent conductive film was 42 ohm/sq. Then, the transmittance of the transparent conductive film was measured with a UV-Vis spectrophotometer. As shown in FIG. 2, at the visible light wavelength of 550 nm, the transmittance of the transparent conductive film was 90.8%.

### Example 2

**[0018]** 0.16 g silver nitrate was dissolved at room temperature in 20 ml of glycerol to get a solution A; 5 g polyvinylpyrrolidone was dissolved at room temperature in 80 ml of glycerol to get a solution B; the solution A and the solution B were mixed uniformly to form a solution C; then, 2.5 ml of ultrapure water was added into the solution C and mixed uniformly to form a solution D, finally, the solution D was transferred into a reaction kettle, the reaction kettle was put into an oven with a set temperature of 160°C, and the reaction ended after a certain time of reaction.

**[0019]** The Ag nanowire mother solution in the reaction kettle was diluted with alcohol and centrifuged twice to obtain precipitated silver nanowires having a diameter of

30-40 nm and a length of 10-20 μm, which was dispersed in isopropanol.

### Example 3

**[0020]** 0.32 g silver nitrate was dissolved at room temperature in 20 ml of glycerol to get a solution A; 7 g polyvinylpyrrolidone was dissolved at room temperature in 80 ml of glycerol to get a solution B; the solution A and the solution B were mixed uniformly to form a solution C; then, 10 ml of ultrapure water was added into the solution C and mixed uniformly to form a solution D, finally, the solution D was transferred into a reaction kettle, the reaction kettle was put into an oven with a set temperature of 160°C, and the reaction ended after a certain time of reaction.

**[0021]** The Ag nanowire mother solution in the reaction kettle was diluted with alcohol and centrifuged twice to obtain precipitated silver nanowires having a diameter of 30-40 nm and a length of 10-20 μm, which was dispersed in isopropanol.

## Claims

1. A preparation method for silver nanowires, comprising the following steps:
  - (1) dissolving silver nitrate in glycerol to get a solution A;
  - (2) dissolving polyvinylpyrrolidone in glycerol to get a solution B;
  - (3) mixing uniformly the solution A and the solution B to form a solution C; and
  - (4) adding an ultrapure water medium into the solution C and mixing uniformly to form a solution D, finally, transferring the solution D into a reaction kettle for reaction at 150°C±10°C, and centrifuging the reactants to obtain silver nanowires.
2. The preparation method according to claim 1, wherein in reaction time in the reaction kettle is 9-10 hours.
3. The preparation method according to claim 1 or 2, wherein in step (1), 0.16 g-0.32 g silver nitrate is dissolved at room temperature in 20 ml of glycerol to get the solution A.
4. The preparation method according to claim 3, wherein in step (2), 5 g-7 g polyvinylpyrrolidone is dissolved at room temperature in 80 ml of glycerol to get the solution B.
5. The preparation method according to claim 4, wherein in step (4), 2.5 ml-10 ml of the ultrapure water is added into the solution C and mixed uniformly to form the solution D.

6. The preparation method according to claim 1 or 2, wherein the centrifuging is performed twice.
7. The preparation method according to claim 5, wherein the centrifuging is performed twice.

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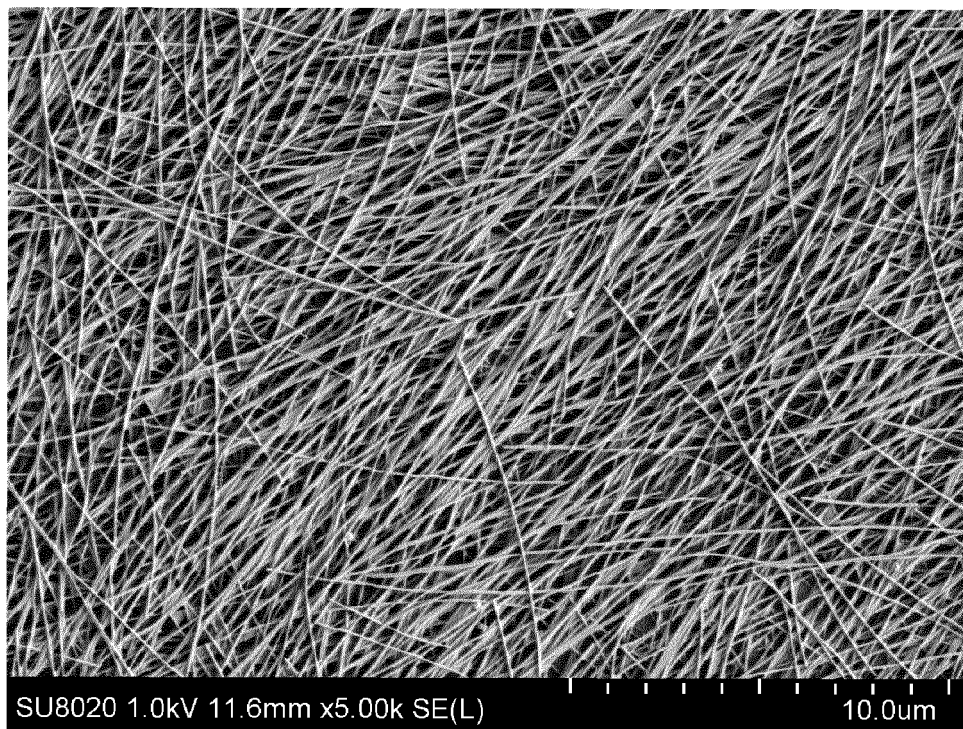


FIG. 1

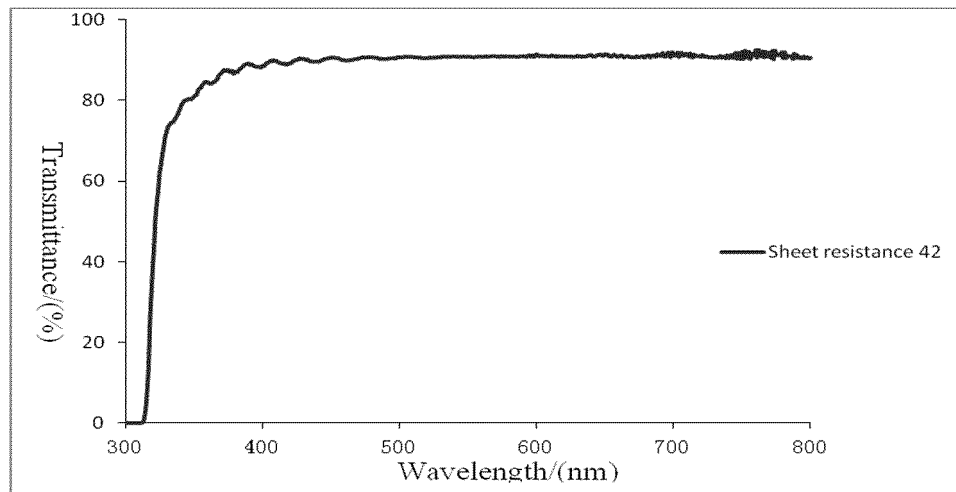


FIG. 2

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/076284

## A. CLASSIFICATION OF SUBJECT MATTER

B22F 9/24 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS, CNTXT, CNKI, EPODOC, WPI: silver nanowire, linear, silver nitrate, length-diameter ratio, Ag, AgNo3, PVP, polyvinylpyrrolidone, glycerol, silver, nano, wire, length-diameter, ratio, centrif+, medium, simple, easy

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                    | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | CN 104785794 A (CHONGQING UNIVERSITY OF ARTS AND SCIENCES), 22 July 2015 (22.07.2015), see description, paragraph [0006], and figures 1-4             | 1-7                   |
| PX        | CN 105081351 A (CHONGQING UNIVERSITY OF ARTS AND SCIENCES), 25 November 2015 (25.11.2015), see description, paragraphs [0003]-[0005], and figure 1    | 1-7                   |
| PX        | CN 105081350 A (CHONGQING UNIVERSITY OF ARTS AND SCIENCES), 25 November 2015 (25.11.2015), see description, paragraphs [0003]-[0005], and figure 1    | 1-7                   |
| PX        | CN 105081348 A (CHONGQING UNIVERSITY OF ARTS AND SCIENCES), 25 November 2015 (25.11.2015), see description, paragraphs [0003]-[0005], and figures 1-2 | 1-7                   |
| A         | CN 103170645 A (SHENZHEN INSTITUTES OF ADVANCED TECHNOLOGY, CHINESE ACADEMY OF SCIENCES), 26 June 2013 (26.06.2013), see the whole document           | 1-7                   |
| A         | CN 104607655 A (SOOCHOW UNIVERSITY), 13 May 2015 (13.05.2015), see the whole document                                                                 | 1-7                   |
| A         | CN 103100724 A (SHENZHEN INSTITUTES OF ADVANCED TECHNOLOGY, CHINESE ACADEMY OF SCIENCES), 15 May 2013 (15.05.2013), see the whole document            | 1-7                   |

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| * Special categories of cited documents:                                                                                                                                | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                                              |
| "A" document defining the general state of the art which is not considered to be of particular relevance                                                                |                                                                                                                                                                                                                                                  |
| "E" earlier application or patent but published on or after the international filing date                                                                               | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                                                                     |
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| "O" document referring to an oral disclosure, use, exhibition or other means                                                                                            | "&" document member of the same patent family                                                                                                                                                                                                    |
| "P" document published prior to the international filing date but later than the priority date claimed                                                                  |                                                                                                                                                                                                                                                  |

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|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| Date of the actual completion of the international search<br>21 June 2016 (21.06.2016)                                                                                                                             | Date of mailing of the international search report<br>14 July 2016 (14.07.2016) |
| Name and mailing address of the ISA/CN:<br>State Intellectual Property Office of the P. R. China<br>No. 6, Xitucheng Road, Jimenqiao<br>Haidian District, Beijing 100088, China<br>Facsimile No.: (86-10) 62019451 | Authorized officer<br><br>LI, Yizhi<br>Telephone No.: (86-10) 62085501          |

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/076284

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------|-----------------------|
| A         | KR 20110071526 A (CEMS CO., LTD.), 29 June 2011 (29.06.2011), see the whole document | 1-7                   |

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.

**PCT/CN2016/076284**

| Patent Documents referred<br>in the Report | Publication Date | Patent Family  | Publication Date |
|--------------------------------------------|------------------|----------------|------------------|
| CN 104785794 A                             | 22 July 2015     | None           |                  |
| CN 105081351 A                             | 25 November 2015 | None           |                  |
| CN 105081350 A                             | 25 November 2015 | None           |                  |
| CN 105081348 A                             | 25 November 2015 | None           |                  |
| CN 103170645 A                             | 26 June 2013     | CN 103170645 B | 21 October 2015  |
| CN 104607655 A                             | 13 May 2015      | None           |                  |
| CN 103100724 A                             | 15 May 2013      | CN 103100724 B | 08 April 2015    |
| KR 20110071526 A                           | 29 June 2011     | None           |                  |

Form PCT/ISA/210 (patent family annex) (July 2009)

## REFERENCES CITED IN THE DESCRIPTION

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

### Patent documents cited in the description

- CN 200810019828 [0002]
- CN 201010559335 [0002]
- CN 1843670 A [0002]

### Non-patent literature cited in the description

- **XIA YOUNAN.** the first one who prepares silver nanowires with a polyol method, proposed the preparation of silver nanowires with a high aspect ratio by using Pt as seeds and reducing silver nitrate by ethylene glycol. *Advanced Materials*, 2002, vol. 14, 883 [0002]