(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 547 332 A1**

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

(43) Date of publication:
02.10.2019 Bulletin 2019/40

(21) Application number: **18886729.5**

(22) Date of filing: **21.09.2018**

(51) Int Cl.:
H01B 5/14 *(2006.01)*

(86) International application number:
PCT/CN2018/107054

(87) International publication number:
WO 2019/109711 (13.06.2019 Gazette 2019/24)

(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:
KH MA MD TN

(30) Priority: **07.12.2017 CN 201711280783**

(71) Applicant: **Zhejiang Ouren New Materials Co., Ltd.**
Zhejiang 314100 (CN)

(72) Inventors:
- **XIA, Houjun**
  Jiaxing
  Zhejiang 314100 (CN)
- **YANG, Xiaoming**
  Jiaxing
  Zhejiang 314100 (CN)
- **JIANG, Shufu**
  Jiaxing
  Zhejiang 314100 (CN)

(74) Representative: **Betten & Resch**
Patent- und Rechtsanwälte PartGmbB
Maximiliansplatz 14
80333 München (DE)

(54) FLEXIBLE TRANSPARENT CONDUCTIVE ELECTRODE

(57) A flexible transparent conductive electrode. The flexible transparent conductive electrode consists of a transparent flexible substrate and a silver nanowire coating coated on a surface of the transparent flexible substrate. A preparation therefor comprises steps of : adding a silver nanowire aqueous dispersion, a waterborne acrylic resin, triethylenetetramine, 1-2 parts of methyl p-tolyl sulfone, 0.1-0.3 parts of hydrogenated castor oil, and a composite solvent to a vacuum mixer for vacuum defoaming and uniform mixing to obtain a mixed liquid, the silver nanowire aqueous dispersion having a concentration of 2-10 mg/mL, and the composite solvent being prepared by mixing an alcohol solvent and a ketone solvent; and drying the wet film in a vacuum oven at 150°C for 3-10 min, and taking out the wet film after moisture in the wet film is completely volatilized, to give the flexible transparent conductive electrode. The electrode reduces electrical resistivity, and further avoids accumulation of silver nanowires, ensures uniformity of electrical conductivity, and improves light transmittance.

EP 3 547 332 A1

Description

[0001] The present invention discloses a flexible transparent conductive electrode. The flexible transparent conductive electrode is made of transparent flexible base materials and a transparent flexible substrate coated with a silver nanowire coating. The process of fabricating the flexible transparent conductive electrode comprises a few steps as followings: adding silver nanowire aqueous dispersion, waterborn acrylic resin, triethylenetetramine, 1-2 parts of p-methylsulfonyl toluene, 0.1-0.3 pars of hydrogenated castor oil and a mixture solvent into a vacuum mixer where evenly mixed, vacuum defoamed, and thus the coating is prepared. The concentration of the silver nanowire in the coating is 2-10mg/mL and the mixture solvents used are the mixture of alcohol and ketone. The film is coated with above coating and moved into a vacuum dryer to be dried at 150°C for 3-10min so that the solvents in the coating are completely volatilized and the flexible transparent conductive electrode is obtained. The flexible transparent conductive electrode of the invention has characteristics of the lower conductive resistivity, less stacks of silver nanowires, higher uniformity of conductivity and better optical transmittance comparison with the existing products.

FLEXIBLE TRANSPARENT CONDUCTIVE ELECTRODE

FIELD OF THE INVENTION

[0002] The present invention relates to a technology of silver nanowires, particularly relates to a flexible transparent conductive electrode.

BACKGROUND OF THE INVENTION

[0003] Metal oxides, especially ITO, has the characteristics of good optical transmittance in visible region and low resistivity which have been hot spots in researches and applications of transparent conductive electrodes in the past 5 decades. However, metal oxides have the disadvantages as limited conductivity, brittle and hard to deform. Concurrently, scarce resources and risen prices are unable to meet the requirements for developing the modern optoelectronic devices. Two dimensional micro-nano new materials and structured thin film electrodes are new fields of transparent conductive electrodes with the development of micro nanotechnology in recent years, such as conductive thin film of polymers, carbon nanotube film, graphene film and metal nanowire film. Unique morphology contributes great flexibility and electron mobility to graphene film, but large scale of production is not mature; uniform dispersion and resistance between carbon tubes limit the inner surface conductivity of carbon tubes film which need a little bit large aspect ratio. Transparent conductive film has advantages of not only great conductivity but also good optical transmission while nanometallic silver wire electrode's are excellent. Micro-nano silver wires can be used as electrode materials with less energy consumption (compared with electrode of oxide thin film) since silver is an electric conductor with great electrical conductivity. At the same time, micro nano structure of metal with plasma effect increases transmittance while diameters of micro silver nanowires' particles are smaller than the incident wavelength of visible light, and perfect photoelectric properties are achieved for electrodes. Simultaneously, micro silver nanowire electrode is benefit for flexible industries and large scale productions with lower cost. Therefore, the micro silver nanowire electrode will be a favorable alternative to ITO transparent conductive electrode. The additives for preparing coating fluid of micro silver nanowires determines performances of the electrode. Therefore, various additives are used to prepare different coating fluid for different properties in order to get better performances. Properties as conductivity and flexural endurance are still to be improved by using current formula. To overcome the problems and go on improving in the prior art are directions for those skilled in this field.

SUMMARY OF THE INVENTION

[0004] The object of the present invention is to provide a flexible transparent conductive electrode, in which silver nanowire coating is used. It can not only reduce the content of silver nanowires, effectively disperse silver nanowires, reduce the conductive resistivity, but also improve the bending resistance to be more than 5000 bending times .

[0005] To achieve the above purpose, the technical scheme adopted by the present invention is a flexible transparent conductive electrode consisting of a transparent flexible substrate and a silver nanowire coating, which the coating is coated on the surface of the transparent flexible substrate and the thickness of the silver nanowire coating is 20-100 microns after dried. The silver nanowire coating comprises following compounds by weight: 100 parts of silver nanowire aqueous dispersion, 5-8 parts of waterborn acrylic resin, 2-5 parts of triethylenetetramine, 1-2 parts of p-methylsulfonyl toluene, 0.2-0.5 parts of polyvinyl alcohol aqueous solution, 0.2-0.4 parts of alkanolamide, 0.3-0.5 parts of isopropoxyethanol, 0.1-0.3 parts of hydrogenated castor oil, 30-40 parts of mixture solvents.

[0006] The process of fabricating the flexible transparent conductive electrode comprises a few steps as followings:

The first step: 100 parts of silver nanowire aqueous dispersion, 5-8 parts of waterborn acrylic resin, 2-5 parts of triethylenetetramine, 0.1-0.3 parts of hydrogenated castor oil and 30-40 parts of mixture slovents are all added into a vacuum mixer where evenly mixed, vacuum defoamed, and then the mixture solution is prepared, in which the concentration of the silver nanowire in the aqueous dispersion is 2-10mg/mL and the mixture solvent is a mixture of alcohol solvents and ketone solvents;
The second step: 1-2 parts of p-methylsulfonyl toluene and 0.2-0.5 parts of polyvinyl alcohol aqueous solution are added into the mixture solution during the process of stirring. The waterborn resin fluid is waterborn polyester resin fluid after evenly mixed for 10min stirring;
The third step: 0.2-0.4 parts of alkanolamide and 0.3-0.5 parts of isopropoxyethanol are added into a vacuum mixer to be continually stirred and evenly mixed. The coating based on the silver nanowires is prepared ;
The fourth step: Transparent flexible substrate is PET film which uniformly coated with the silver nanowire coating by using miceo gravure. The distances between the bars are 15μm and the rolling speed for coating is 80cm/min, a uniform wet film is formed on the surface of the transparent flexible substrate;
The fifth step: The wet film coated with above coating is completely volatilized after dried in a vacuum dryer at 150 °C for 3-10min,and the flexible transparent conductive electrode is obtained.

[0007] Further improvements of the invention are as follows:

1. In according with the invention, the silver nanowires in the silver nanowire aqueous dispersion has the diameters of 20-150nm and lengths of 50-500mm.
2. In according with the invention, the alcohols is one of methanol, ethanol and isopropanol.
3. In according with the invention, the ketones solvent is one of acetone, butanone, cyclohexanone and isophorone.
4. In according with the invention, the mixture solution is a mixture of alcohols and ketones with 10:(2-4) by weight.

[0008] The invention has the following advantages and characteristics in comparison with the prior art:
The flexible transparent conductive electrode of the invention contains 100 parts of silver nanowire aqueous dispersion, 5-8 parts of water-borne acrylic resin, 0.2-0.5 parts of polyvinyl alcohol aqueous solution, 0.2-0.4 parts of alkyholamide, 0.3-0.5 parts of isopropoxyethylanol as a primary formula, and further adds with 2-5 parts of triethylenetetramine and 1-2 parts of p-methylsulfonyl toluene which reduces the content of silver nanowires, effectively disperses the silver nanowires, reduces the resistivity and improve the bending resistance to be more than 5000 bending times. Furthermore, the formula added with 0.3-0.5 parts of isopropoxyethanol and a mixture solvent of alcohols and ketones with 10: (2-4) by weight, which has advantages of effectively adjusting viscosity and drying rate of the coating further avoiding stacks of silver nanowires, ensuring uniformity of conductivity and improving transmittance.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0009] The following is detailed description of certain embodiments of the present invention.
formulations 1-4: a flexible transparent conductive electrode is comprised of a transparent flexible substrate coated with a silver nanowires coating at a thickness of 20-100μm after the silver nanowire coating is dried. The silver nanowire coating is consist of the following ingredients by weight as shown in Table 1:

Table 1

Ingredients	formulation 1 (parts)	formulation 2 (parts)	formulation 3 (parts)	formulation 4 (parts)
Silver Nanowire Aqueous Dispersion	100	100	100	100
waterborn Acrylic Resin	6	5	6.2	7
Triethylenetetramine	3	2.2	5	4
p-methylsulfonyl toluene	1.8	1	1.5	1.2
PVA Aqueous Solution	0.24	0.4	0.3	0.45
Alkanolamide	0.3	0.35	0.4	0.26
Isopropoxyethanol	0.4	0.5	0.35	0.42
Hydrogenated Castor Oil	0. 15	0.25	0. 1	0.2

(continued)

Ingredients	formulation 1 (parts)	formulation 2 (parts)	formulation 3 (parts)	formulation 4 (parts)
Mixture Solvents	35	32	38	35

[0010] In the formulation 1, wherein the mixture solution is a mixture of methanol and cyclohexanone of 10:2 by weight; In the formulation 2, wherein the mixture solution a mixture of isopropanol and butanone of 10:2.5 by weight; In the formulation 3, wherein the mixture solution is a mixture of ethanol and cyclohexanone of 10:3 by weight in; In the formulation 4, wherein the mixture solution is a mixture of methanol and isophorone of 10:3.8 by weight.

[0011] The process of fabricating the flexible transparent conductive electrode comprises a few steps as followings:

The first step: 100 parts of silver nanowire aqueous dispersion, 5-8 parts of waterborn acrylic resin, 2-5 parts of triethylenetetramine, 0.1-0.3 parts of hydrogenated castor oil and 30-40 parts of mixture slovents are all added into a vacuum mixer where evenly mixed, vacuum defoamed, and then the mixture solution is prepared, in which the concentration of the silver nanowire in the aqueous dispersion is 2-10mg/mL and the mixture solvent is a mixture of alcohol solvent and ketone solvent.

The second step: 1-2 parts of p-methylsulfonyl toluene and 0.2-0.5 parts of polyvinyl alcohol aqueous solution are added into the mixture solution during the process of stirring. The waterborn resin fluid is waterborn polyester resin fluid after evenly mixed for 10min stirring;

The third step: 0.2-0.4 parts of alkanolamide and 0.3-0.5 parts of isopropoxyethanol are added into a vacuum mixer to be continually stirred and evenly mixed. The coating based on the silver nanowires is prepared ;

The fourth step: Transparent flexible substrate is PET film which uniformly coated with the silver nanowire coating by using miceo gravure. The distances between the bars are 15μm and the rolling speed for coating is 80cm/min, a uniform wet film is formed on the surface of the transparent flexible substrate;

The fifth step: The wet film coated with above coating is completely volatilized after dried in a vacuum dryer at 150 °C for 3-10min,and the flexible transparent conductive electrode is obtained.

[0012] The silver nanowires in the above coating have the diameters of 20-150nm and lengths of 50-500mm:
The tested results of the flexible transparent conductive electrode in the Embodiment 1-4 are shown in Table 2:

Table 2

	Embodiment 1	Embodiment 2	Embodiment 3	Embodiment 4
Resistance(Ω/square) (Four-probe Resistance Tester)	31	30	30	32
Adhesion(Vertical Pulled with 3M600)	No shedding	No shedding	No shedding	No shedding
Transmittance(%)(WGW Optical Haze Meter)	92	92	91	92
Haze(WGW Optical Haze Meter)	1.2	1.3	1.2	1.3
Flexural Endurance(time)	>5000	>5000	>5000	>5000

[0013] The characteristics of the flexible transparent electrode which is provided in the present invention have thus been shown in Table 2 to be achieved in reducing the content of silver nanowires, effectively dispersing the silver nanowires, reducing resistivity and improve the bending resistance to be more than 5000 bending times; and effectively adjusting the viscosity and drying rate of coating fluid, further avoiding stacks of the silver nanowires, ensuring uniformity of the conductivity and improving transmittance.

[0014] The embodiments are only to illustrate the technical conception and characteristics of the present invention, the purpose of which is to enable people familiar with the technology to understand the contents of the present invention and to implement it, and not to limit the scope of protection of the present invention. Any equivalent substitution made with the same idea of the present invention is in the scope of protection of the present invention.

Claims

1. A flexible transparent conductive electrode is **characterized in that** the flexible transparent conductive electrode comprises a transparent flexible substrate and a silver nanowire coating which is coated on the surface of the substrate; The coating on the surface of the transparent flexible substrate is dried in a oven and the thickness of the silver nanowire coating is 20-100μm after dried. The silver nanowires coating comprises following ingredients by weight: 100 parts of silver nanowire aqueous dispersion, 5-8 parts of waterborn acrylic resin, 2-5 parts of triethylenetetramine, 1-2 parts of p-methylsulfonyl toluene, 0.2-0.5 parts of PVA aqueous solution,0.2-0.4 parts of alkanolamide, 0.3-0.5 parts of isopropoxyethanol, 0.1-0.3 parts of hydrogenated castor oil and 30-40 parts of a mixture solution.
   The process of fabricating the flexible transparent conductive electrode comprises following steps:

   step 1, 100 parts of silver nanowire aqueous dispersion, 5-8 parts of waterborn acrylic resin, 2-5 parts of triethylenetetramine, 0.1-0.3 parts of hydrogenated castor oil and 30-40 parts of mixture slovents are all added into a vacuum mixer where evenly mixed, vacuum defoamed, and then the mixture solution is prepared, in which the concentration of the silver nanowire in the aqueous dispersion is 2-10mg/mL and the mixture solvent is a mixture of alcohol solvent and ketone solvent;
   step 2, 1-2 parts of p-methylsulfonyl toluene and 0.2-0.5 parts of polyvinyl alcohol aqueous solution are added into the mixture solution during the process of stirring. The waterborn resin fluid is waterborn polyester resin fluid after evenly mixed for 10min stirring;
   step 3, 0.2-0.4 parts of alkanolamide and 0.3-0.5 parts of isopropoxyethanol are added into a vacuum mixer to be continually stirred and evenly mixed. The coating based on the silver nanowires is prepared ;
   step 4,Transparent flexible substrate is PET film which uniformly coated with the silver nanowire coating by using miceo gravure. The distances between the bars are 15μm and the rolling speed for coating is 80cm/min, a uniform wet film is formed on the surface of the transparent flexible substrate;
   step 5,The wet film coated with above coating is completely volatilized after dried in a vacuum dryer at 150°C for 3-10min,and the flexible transparent conductive electrode is obtained.

2. The preparation process of the flexible conductive film of claim 1 with silver paste as claimed in claim nanowires, wherein: the silver nanowires of the silver nanowire aqueous dispersion with diameters of 20-150nm and lengths of 50-500mm.

3. The preparation process of the flexible conductive film of claim 1 with silver paste as claimed in claim nanowires, wherein: the alcoholic solvent is one of methanol, ethanol and isopropanol.

4. The preparation process of the flexible conductive film of claim 1 with silver paste as claimed in claim nanowires, wherein: the ketonic solvent is one of acetone, butanone, cyclohexanone and isophorone.

5. The preparation process of the flexible conductive film of claim 1 with silver paste as claimed in claim nanowires, wherein: the mixture solvent is a mixture of alcohols solvent and ketones solvent of 10:(2-4) by weight.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2018/107054

A. CLASSIFICATION OF SUBJECT MATTER

H01B 5/14(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)

H01B

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)

CNPAT; WPI; EPODOC; CNKI: 透明, 导电, PET, 聚对苯二甲酸乙二醇酯, 银, Ag, 纳米线, 墨, 浆料, 丙烯酸, 三乙烯四胺, 对甲砜基甲苯, 聚乙烯醇, 蓖麻油, 干燥, 滚涂, 辊涂, transparent, conduct+, silver, nanowire, ink, slurry, acrylic+, Triethylenetetramine, M-methylsulfone, toluene, Polyvinyl, alcohol, castor, oil, dry, coat+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 108417294 A (ZHEJIANG OUREN NEW MATERIALS CO., LTD.) 17 August 2018 (2018-08-17) description, paragraphs 0004-0009	1-5
A	CN 105273471 A (SUZHOU ATES ELECRONIC TECHNOLOGY CO., LTD.) 27 January 2016 (2016-01-27) description, paragraphs 0012-0023	1-5
A	CN 102208538 A (UNIVERSITY OF ELECTRONIC SCIENCE AND TECHNOLOGY OF CHINA) 05 October 2011 (2011-10-05) entire document	1-5
A	CN 106103610 A (DOWA ELECTRONICS MATERIALS CO., LTD.) 09 November 2016 (2016-11-09) entire document	1-5
A	CN 106910568 A (SUZHOU SICHUANG YUANBO ELECTRONIC TECHNOLOGY CO., LTD.) 30 June 2017 (2017-06-30) entire document	1-5

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

* Special categories of cited documents:

"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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 December 2018	**25 December 2018**
Name and mailing address of the ISA/CN **State Intellectual Property Office of the P. R. China** **No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088** **China** Facsimile No. **(86-10)62019451**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2018/107054

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 103627255 A (SUZHOU COLDSTONES TECHNOLOGY CO., LTD.) 12 March 2014 (2014-03-12) entire document	1-5
A	US 2009166055 A1 (HONEYWELL INTERNATIONAL, INC.) 02 July 2009 (2009-07-02) entire document	1-5

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2018/107054

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	108417294	A	17 August 2018	None			
CN	105273471	A	27 January 2016	CN	105273471	B	06 July 2018
CN	102208538	A	05 October 2011	CN	102208538	B	27 March 2013
CN	106103610	A	09 November 2016	WO	2015137421	A1	17 September 2015
				JP	6353671	B2	04 July 2018
				EP	3118272	A1	18 January 2017
				JP	2015174922	A	05 October 2015
				EP	3118272	A4	11 October 2017
				US	2017015857	A1	19 January 2017
				KR	20160134754	A	23 November 2016
CN	106910568	A	30 June 2017	None			
CN	103627255	A	12 March 2014	CN	103627255	B	20 May 2015
US	2009166055	A1	02 July 2009	WO	2009085934	A2	09 July 2009
				US	7727578	B2	01 June 2010
				WO	2009085934	A3	22 October 2009
				TW	200939251	A	16 September 2009

Form PCT/ISA/210 (patent family annex) (January 2015)