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(54) **Porous Polymer-coated Copper Electrode, and Preparation Method and Application Thereof.**

(57) The invention discloses a porous polymer-coated copper electrode and a preparation method and application thereof, and relates to the technical field of electrode materials. The porous polymer-coated copper electrode comprises a polymer coating and a copper substrate; the polymer used is polystyrene-b-polyethylene glycol, polystyrene-b-polymethyl methacrylate or polystyrene- b-poly-4-vinylpyridine. According to the invention, a porous polymer coating with controllable aperture and uniform distribution is prepared by a simple block copolymer self-assembly method, so that continuous and uniform deposition of lithium is successfully realized, the growth of lithium dendrites is inhibited, and the cycle life of lithium metal batteries is prolonged.

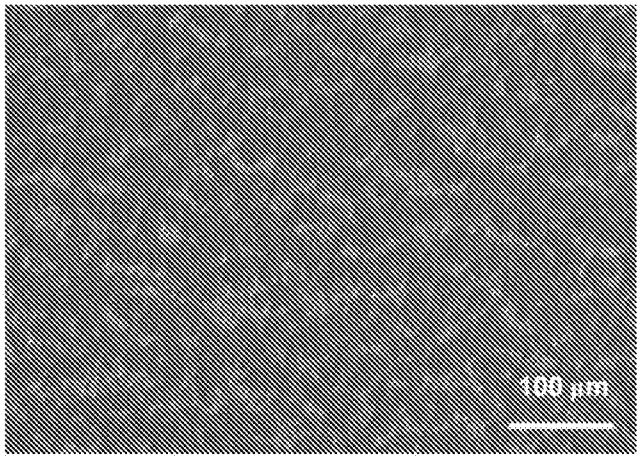


Fig. 1

DESCRIPTION

Porous Polymer-coated Copper Electrode, and Preparation Method and Application Thereof

TECHNICAL FIELD

The invention relates to the technical field of electrode materials, in particular to a porous polymer-coated copper electrode and a preparation method and application thereof.

BACKGROUND

During the electroplating/stripping process of lithium metal battery, the infinite side reaction between active lithium and electrolyte, dendrite growth, infinitely increasing volume effect and other problems lead to the rapid decline of battery capacity and the decrease of battery cycle life. Artificial design of solid electrolyte interface (SEI) film at the electrode/electrolyte interface is the most direct control method to solve the problem of lithium metal battery, so as to improve the battery performance. The "host-free" nature of lithium negative electrode makes its volume change greatly during the cycle, which is also a main reason for the poor performance of lithium metal battery.

Therefore, it is an effective method to design a "host" as a carrier for lithium deposition. Previous methods reported that the method with micro-nano polymer SEI film/separator/solid electrolyte can effectively improve the stability of lithium metal battery. From this, it can be seen that nano-porous channels can be used as the preferred carrier for lithium deposition and guide lithium ions to transport in the pores. However, the previous methods have the defects of complicated process and difficult to effectively control the pore size, and at the same time, it is difficult to realize industrial production.

SUMMARY

The invention aims to provide a porous polymer-coated copper electrode, a preparation method and an application thereof, so as to solve the problems existing in the prior art, ensure the performance of a lithium metal battery and improve the cycle life.

In order to achieve the above objectives, the present invention provides the following scheme:

the invention provides a porous polymer-coated copper electrode, which comprises a polymer coating and a copper substrate; the polymer coating component is polystyrene-b-polyethylene glycol, polystyrene-b-polymethyl methacrylate or polystyrene-b-poly-4-vinylpyridine.

Further, the ratio of hydrophilic block to hydrophobic block of the polymer coating

component is 1-10: 1-10; specifically, in the polystyrene-b-polyethylene glycol, the ratio of polystyrene block to polyethylene glycol block is 1: 10-10: 1; in the polystyrene-b-polymethyl methacrylate, the ratio of the polystyrene block to the polymethyl methacrylate block is 1: 10-10: 1; in the polystyrene-b-poly-4-vinylpyridine, the ratio of the polystyrene block to the poly-4-vinylpyridine block is 1:10-10:1.

Further, the thickness of the polymer coating is 80-300 nm.

The invention also provides a preparation method of the porous polymer-coated copper electrode, which comprises the following steps:

dissolving the polymer in an organic solvent, and coating the obtained polymer solution on the surface of metal copper to obtain the porous polymer-coated copper electrode.

Further, the organic solvent includes toluene, chloroform, acetone, cyclohexane or acetic acid.

Further, after the polymer solution is coated, the steps of cleaning and removing hydrophilic blocks are also included.

Further, the cleaning agent used for cleaning is water or acetic acid.

The invention also provides the application of the porous polymer-coated copper electrode in lithium ion batteries.

The invention discloses the following technical effects:

according to the invention, through a simple block copolymer self-assembly method, two blocks are separated in the solvent evaporation process, and then an enriched phase is washed by a selective solvent to form a porous structure, so that a porous polymer coating with controllable aperture and uniform distribution is prepared, continuous and uniform deposition of lithium is successfully realized, the growth of lithium dendrites is inhibited, and the cycle life of lithium metal batteries is prolonged.

BRIEF DESCRIPTION OF THE FIGURES

In order to explain the embodiments of the present invention or the technical scheme in the prior art more clearly, the drawings needed in the embodiments will be briefly introduced below. Obviously, the drawings described below are only some embodiments of the present invention, and other drawings can be obtained according to these drawings without creative work for ordinary people in the field.

Fig. 1 shows the morphology of polystyrene-b-polyethylene glycol-coated current collector prepared in Example 1 of the present invention;

Fig. 2 is a coulombic efficiency diagram of polymer-coated current collectors prepared in Example 1, Example 4 and Comparative Example 1 of the present invention;

Fig. 3 is a diagram of lithium deposition morphology of different electrodes; wherein A is the lithium deposition morphology of pure copper electrode in Comparative Example 1, and B is the lithium deposition morphology of porous polymer-coated electrode in Example 1.

DESCRIPTION OF THE INVENTION

A number of exemplary embodiments of the present invention will now be described in detail, and this detailed description should not be considered as a limitation of the present invention, but should be understood as a more detailed description of certain aspects, characteristics and embodiments of the present invention.

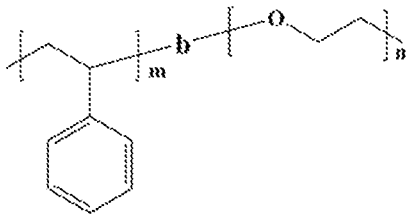
It should be understood that the terminology described in the present invention is only for describing specific embodiments and is not used to limit the present invention. In addition, for the numerical range in the present invention, it should be understood that each intermediate value between the upper limit and the lower limit of the range is also specifically disclosed. The intermediate value within any stated value or stated range and every smaller range between any other stated value or intermediate value within the stated range are also included in the present invention. The upper and lower limits of these smaller ranges can be independently included or excluded from the range.

Unless otherwise specified, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention relates. Although the present invention only describes the preferred methods and materials, any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present invention. All documents mentioned in this specification are incorporated by reference to disclose and describe methods and/or materials related to the documents. In case of conflict with any incorporated document, the contents of this specification shall prevail.

It is obvious to those skilled in the art that many improvements and changes can be made to the specific embodiments of the present invention without departing from the scope or spirit of the present invention. Other embodiments will be apparent to the skilled person from the description of the invention. The description and example of that present invention are exemplary only.

The terms "including", "comprising", "having" and "containing" used in this article are all open terms, which means including but not limited to.

In the invention, the structure of polystyrene-b-polyethylene glycol is as follows:



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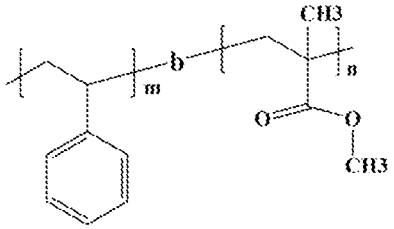
The structure of polystyrene-b-polymethyl methacrylate is as follows:



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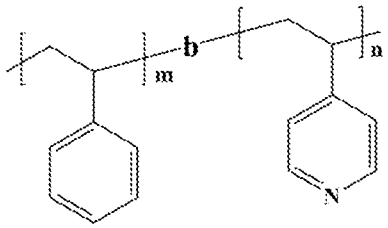
The structure of polystyrene-b-poly-4-vinylpyridine is as follows:



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Example 1

Step 1: dissolve polystyrene-b-polyethylene glycol with polystyrene block: polyethylene glycol block = 10: 1 in cyclohexane to prepare 8 mg/mL polystyrene-b-polyethylene glycol solution.

Step 2: using spin coater to spin-coat polystyrene-b-polyethylene glycol solution on the copper electrode to prepare a polystyrene-b-polyethylene glycol coating with the polymer coating thickness of 80 nm, and then washing in deionized water for 30 minutes to remove the polyethylene glycol block to obtain a current collector with the polystyrene-b-polyethylene glycol coating (the coating thickness is 80 nm).

Step 3: assemble the button battery and test the cycle performance of the battery, as follows:

in a glove box filled with argon and with water and oxygen values less than 0.1 ppm, lithium tablets with a diameter of 14 mm and a thickness of 1 mm, a separator with a diameter of 18 mm (Celgard 2325), 1 mol/L of lithium bis (trifluoromethyl) sulfonyl imide, and an electrolyte of 1,3 dioxolane/ethylene glycol dimethyl ether (v/v=1:1) containing 2wt% lithium nitrate were used to assemble the button battery with model of CR2025. The diameter of the current collector with polymer coating was 16 mm. The assembly sequence is negative shell, elastic sheet, gasket, lithium

sheet, interlayer, separator, porous polymer-coated copper electrode and positive shell, and the battery is sealed by an electric packaging machine. When assembling a half batter, the lithium sheet is the working electrode and the porous polymer-coated copper electrode is the counter electrode.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 175 cycles.

The morphology of the polystyrene-b-polyethylene glycol-coated current collector prepared in Example 1 of the present invention is shown in Fig. 1.

Example 2

Step 1: dissolve polystyrene-b-polyethylene glycol with polystyrene block: polyethylene glycol block = 1: 10 in cyclohexane to prepare 8 mg/mL polystyrene-b-polyethylene glycol solution.

Step 2: using spin coater to spin-coat polystyrene-b-polyethylene glycol solution on the copper electrode to prepare a polystyrene-b-polyethylene glycol coating with the polymer coating thickness of 80 nm, and then washing in deionized water for 30 minutes to remove the polyethylene glycol block to obtain a current collector with the polystyrene-b-polyethylene glycol coating (the coating thickness is 80 nm).

Step 3: assemble the button battery and test the cycle performance of the battery. The assembling steps of button battery are the same as those in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 200 cycles.

Example 3

Step 1: dissolve polystyrene-b-polyethylene glycol with polystyrene block: polyethylene glycol block = 1: 1 in chloroform to prepare 8 mg/mL polystyrene-b-polyethylene glycol solution.

Step 2: using spin coater to spin-coat polystyrene-b-polyethylene glycol solution on the copper electrode to prepare a polystyrene-b-polyethylene glycol coating with the polymer coating thickness of 80 nm, and then washing in deionized water for 30 minutes to remove the polyethylene glycol block to obtain a current collector with the polystyrene-b-polyethylene glycol coating (the coating thickness is 80 nm).

Step 3: assemble the button battery and test the cycle performance of the battery. The assembling steps of button battery are the same as those in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 135 cycles.

Example 4

Step 1: dissolve polystyrene-b-polyethylene glycol with polystyrene block: polyethylene glycol block = 10: 1 in chloroform to prepared 8 mg/mL polystyrene-b-polyethylene glycol solution.

Step 2: using spin coater to spin-coat polystyrene-b-polyethylene glycol solution on the copper electrode to prepare a polystyrene-b-polyethylene glycol coating with the polymer coating thickness of 80 nm, and then washing in deionized water for 30 minutes to remove the polyethylene glycol block to obtain a current collector with the polystyrene-b-polyethylene glycol coating (the coating thickness is 80 nm).

Step 3: assemble the button battery and test the cycle performance of the battery. The assembling steps of button battery are the same as those in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 130 cycles.

Example 5

Step 1: dissolve polystyrene-b-polyethylene glycol with polystyrene block: polyethylene glycol block = 1: 1 in cyclohexane to prepare 8 mg/mL polystyrene-b-polyethylene glycol solution.

Step 2: using spin coater to spin-coat polystyrene-b-polyethylene glycol solution on the copper electrode to prepare a polystyrene-b-polyethylene glycol coating with the polymer coating thickness of 80 nm, and then washing in deionized water for 30 minutes to remove the polyethylene glycol block to obtain a current collector with the polystyrene-b-polyethylene glycol coating (the coating thickness is 80 nm).

Step 3: assemble the button battery and test the cycle performance of the battery. The assembling steps of button battery are the same as those in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated 180 cycles.

Example 6

Step 1: dissolve polystyrene-b-polyethylene glycol with polystyrene block: polyethylene glycol block = 1: 10 in chloroform to prepare 8 mg/mL polystyrene-b-polyethylene glycol solution.

Step 2: using spin coater to spin-coat polystyrene-b-polyethylene glycol solution on the

copper electrode to prepare a polystyrene-b-polyethylene glycol coating with the polymer coating thickness of 80 nm, and then washing in deionized water for 30 minutes to remove the polyethylene glycol block to obtain a current collector with the polystyrene-b-polyethylene glycol coating (the coating thickness is 80 nm).

Step 3: assemble the button battery and test the cycle performance of the battery. The assembling steps of button battery are the same as those in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 125 cycles.

Example 7

Step 1: dissolve polystyrene-b-polyethylene glycol with polystyrene block: polyethylene glycol block = 1: 10 in cyclohexane to prepare 16 mg/mL polystyrene-b-polyethylene glycol solution.

Step 2: using spin coater to spin-coat polystyrene-b-polyethylene glycol solution on a copper electrode to prepare a polystyrene-b-polyethylene glycol coating with polymer coating thickness of 120 nm, and then washing in deionized water for 30 minutes to remove the polyethylene glycol block to obtain a current collector with the polystyrene-b-polyethylene glycol coating (the coating thickness is 120 nm).

Step 3: assemble the button battery and test the cycle performance of the battery. The assembling steps of button battery are the same as those in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 180 cycles.

Example 8

Step 1: dissolve polystyrene-b-polyethylene glycol with polystyrene block: polyethylene glycol block = 1: 10 in cyclohexane to prepare 25 mg/mL polystyrene-b-polyethylene glycol solution.

Step 2: using spin coater to spin-coat polystyrene-b-polyethylene glycol solution on a copper electrode to prepare a polystyrene-b-polyethylene glycol coating with polymer coating thickness of 300 nm, and then washing in deionized water for 30 minutes to remove the polyethylene glycol block to obtain a current collector with the polystyrene-b-polyethylene glycol coating (the coating thickness is 300 nm).

Step 3: assemble the button battery and test the cycle performance of the battery. The

assembling steps of button battery are the same as those in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 150 cycles.

Example 9

Step 1: dissolve polystyrene-b-polymethyl methacrylate with polystyrene block: polymethyl methacrylate block = 1: 1 in cyclohexane to prepare 8 mg/mL polystyrene-b-polymethyl methacrylate solution.

Step 2: using spin coater to spin-coat polystyrene-b-polymethyl methacrylate solution on the copper electrode to prepare a polystyrene-b-polymethyl methacrylate coating with polymer coating thickness of 80 nm, and then washing in acetic acid for 30 minutes to remove the polymethyl methacrylate block to obtain a current collector with the polystyrene-b-polymethyl methacrylate coating (with a coating thickness of 80 nm).

Step 3: assemble the button battery and test the cycle performance of the battery. The assembling steps of button battery are the same as those in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 165 cycles.

Example 10

Step 1: dissolve polystyrene-b-poly-4-vinylpyridine with polystyrene block: poly-4-vinylpyridine block = 1: 1 in chloroform to prepare 8 mg/mL polystyrene-b-poly-4-vinylpyridine solution.

Step 2: using spin coater to spin-coat a polystyrene-b-poly-4-vinylpyridine solution on a copper electrode to prepare a polystyrene-b-poly-4-vinylpyridine coating with the polymer coating thickness of 80nm, and then washing in deionized water for 30 minutes to remove the poly-4-vinylpyridine block to obtain a current collector with the polystyrene-b-poly-4-vinylpyridine coating (the coating thickness is 80 nm)

Step 3: assemble the button battery and test the cycle performance of the battery. The assembling steps of button battery are the same as those in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 160 cycles.

Comparative example 1

The button battery was assembled with copper electrode (bare copper) as the current collector,

and the cycle performance of the battery was tested. The assembly steps of the button battery were the same as in Example 1.

Under the condition of current density of 1 mA/cm^2 and capacity of 1 mAh/cm^2, it is stably circulated for 60 cycles.

Fig. 2 is a coulombic efficiency diagram of polymer-coated current collectors prepared in Example 1, Example 4 and Comparative Example 1. It can be seen from Fig. 2 that the structure of block polymer has a very obvious influence on the cycle stability of the battery. The coating formed without porous structure only slightly improves the cycle stability of the battery, but the cycle stability of the battery is greatly improved after the porous structure is formed. Thus, the invention provides a method for preparing the electrode coating of the battery with high cycle stability.

Fig. 3 is a diagram of lithium deposition morphology of different electrodes, where A is the lithium deposition morphology of pure copper electrode in Comparative Example 1, and B is the lithium deposition morphology of porous polymer-coated electrode in Example 1. It can be seen that the invention successfully realizes the continuous and uniform deposition of lithium by using the porous polymer coating.

The above-mentioned embodiments only describe the preferred mode of the invention, and do not limit the scope of the invention. Under the premise of not departing from the design spirit of the invention, various modifications and improvements made by ordinary technicians in the field to the technical scheme of the invention shall fall within the protection scope determined by the claims of the invention.

CLAIMS

1. A porous polymer-coated copper electrode, comprising a polymer coating and a copper substrate; the polymer coating component is polystyrene-b-polyethylene glycol, polystyrene-b-polymethyl methacrylate or polystyrene-b-poly-4-vinylpyridine.

2. The porous polymer-coated copper electrode according to claim 1, wherein in the polystyrene-b-polyethylene glycol, the ratio of polystyrene block to polyethylene glycol block is 1: 10-10: 1; in the polystyrene-b-polymethyl methacrylate, the ratio of the polystyrene block to the polymethyl methacrylate block is 1: 10-10: 1; in the polystyrene-b-poly-4-vinylpyridine, the ratio of the polystyrene block to the poly-4-vinylpyridine block is 1:10-10:1.

3. The porous polymer-coated copper electrode according to claim 1, wherein the thickness of the polymer coating is 80-300 nm.

4. A preparation method of the porous polymer-coated copper electrode according to any one of claims 1-3, characterized by comprising the following steps:

dissolving a polymer in an organic solvent to obtain a polymer solution, and coating the obtained polymer solution on the surface of metal copper to obtain a porous polymer-coated copper electrode.

5. The preparation method according to claim 4, wherein the organic solvent comprises toluene, chloroform, acetone, cyclohexane or acetic acid.

6. The preparation method according to claim 4, wherein after the polymer solution is coated, the step of cleaning is further comprised.

7. The preparation method according to claim 6, wherein the cleaning agent used for cleaning is water or acetic acid.

8. An application of the porous polymer-coated copper electrode according to any one of claims 1-3 in lithium ion batteries.

PATENTANSPRÜCHE

1. Eine poröse polymerbeschichtete Kupferelektrode, umfassend eine Polymerbeschichtung und ein Kupfersubstrat; die Polymerbeschichtungskomponente ist Polystyrol-b-Polyethylenglykol, Polystyrol-b-Polymethylmethacrylat oder Polystyrol-b-Poly-4-vinylpyridin.

2. Die poröse polymerbeschichtete Kupferelektrode nach Anspruch 1, wobei in dem Polystyrol-b-Polyethylenglykol das Verhältnis von Polystyrolblock zu Polyethylenglykolblock 1: 10-10: 1 beträgt; im Polystyrol-b-Polymethylmethacrylat ist das Verhältnis des Polystyrolblocks zum Polymethylmethacrylatblock 1: 10-10: 1; im Polystyrol-b-Poly-4-vinylpyridin ist das Verhältnis des Polystyrolblocks zum Poly-4-vinylpyridinblock 1:10-10:1.

3. Die poröse polymerbeschichtete Kupferelektrode nach Anspruch 1, wobei die Dicke der Polymerbeschichtung 80-300 nm beträgt.

4. Ein Verfahren zur Herstellung der porösen polymerbeschichteten Kupferelektrode nach einem der Ansprüche 1-3, dadurch gekennzeichnet, dass es die folgenden Schritte umfasst:

Lösen eines Polymers in einem organischen Lösungsmittel, um eine Polymerlösung zu erhalten, und Auftragen der erhaltenen Polymerlösung auf die Oberfläche von metallischem Kupfer, um eine poröse polymerbeschichtete Kupferelektrode zu erhalten.

5. Das Herstellungsverfahren nach Anspruch 4, wobei das organische Lösungsmittel Toluol, Chloroform, Aceton, Cyclohexan oder Essigsäure umfasst.

6. Das Herstellungsverfahren nach Anspruch 4, wobei nach dem Auftragen der Polymerlösung ein weiterer Schritt der Reinigung erfolgt.

7. Das Herstellungsverfahren nach Anspruch 6, wobei Wasser oder Essigsäure als Reinigungsmittel zur Reinigung verwendet wird.

8. Eine Anwendung der porösen polymerbeschichteten Kupferelektrode nach einem der Ansprüche 1 bis 3 in Lithium-Ionen-Batterien.

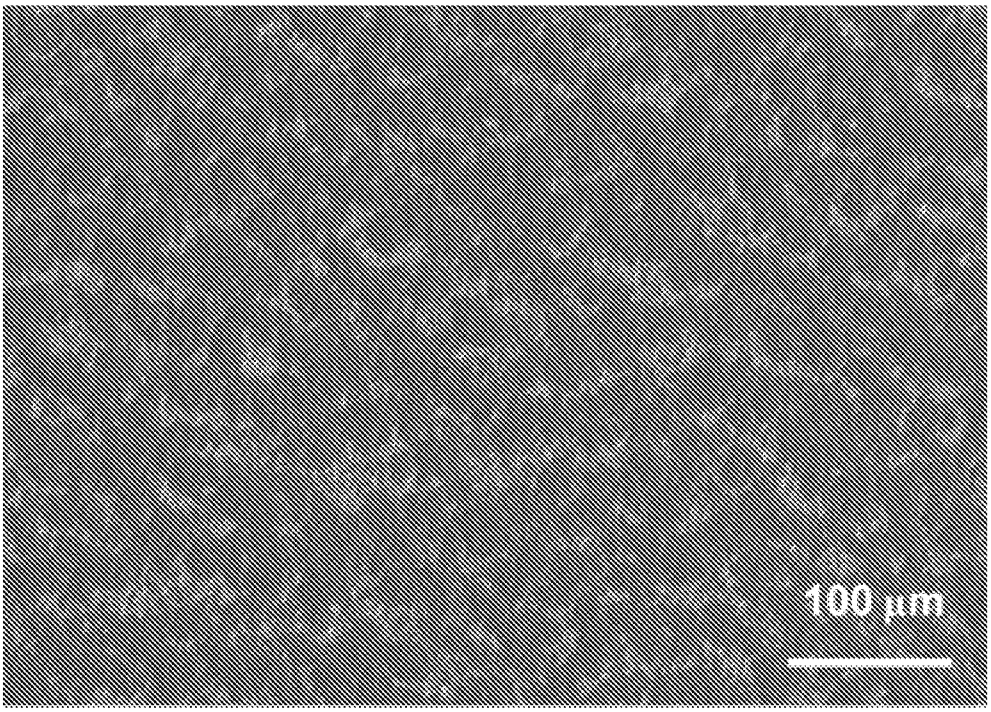
100 μm

Fig. 1

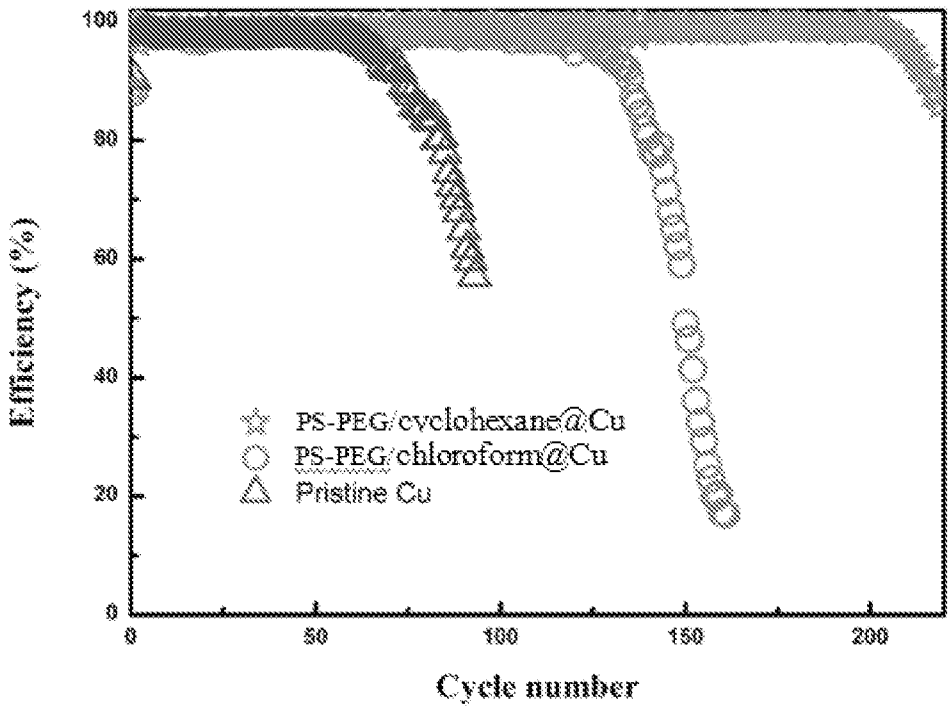
Efficiency (%)
Cycle number
0
20
40
60
80
100
0
50
100
150
200
PS-PEG/cyclohexane@Cu
PS-PEG/chloroform@Cu
Pristine Cu

Fig. 2

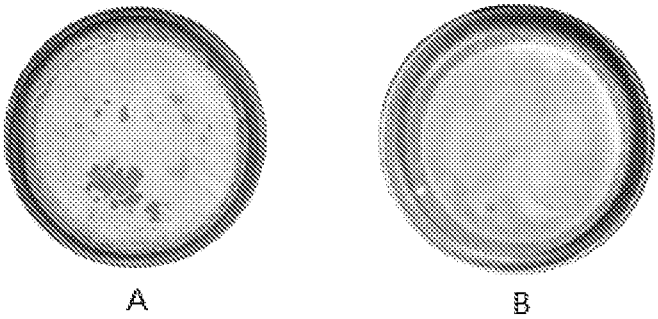

Fig. 3