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Fabrication of copper sulfide microstructures with the bottle- and thorny rod-shape

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ABSTRACT

The continuous copper films have been deposited on the surfaces of polyacrylonitrile fibers prepared by electrospinning process. Then the monoclinic-phase Cu_2S thorny rods were obtained under the mixed gas of H_2S and O_2 by using the copper-coated fibrous mats as substrate. The silver could be deposited conveniently on the surface of copper-coated fibrous mats by using sacrificial method. When the silver-gilt copper-coated fibrous mats were used as substrates and treated under the same atmosphere, the monoclinic-phase Cu_7S_4 with bottle- and thorny rod-shape could be obtained. The results revealed the fact that whether silver was present or not, the amount of the copper deposited on the fibrous mats could affect the component and morphology of the formed copper sulfide microstructure. The growing process of these special microstructures of copper sulfide was investigated and the possible mechanism was also suggested.

1. Introduction

In the past decades, much effort has been made in developing methods for synthesizing ordered inorganic crystals with specific sizes, shapes, and hierarchies in consideration of their potential applications in the new materials and devices fields. The architectural control of the nanostructures with special shapes is the cruces for the "bottom-up" approaches toward the fabrication of future nanodevice [1]. Recently, many nanostrucutres and micropatterns have been fabricated by using the metallic particles assembly method [2]. It is well known that the stoichiometric composition of copper sulfide including CuS, $Cu_{1.96}S$, $Cu_{1.94}S$, $Cu_{1.8}S$, Cu_7S_4, Cu_9S_8 and Cu_2S, varies greatly from Cu_2S on the copper-rich side to CuS_2 on the copper-deficient side [3]. Many nanostructures for copper sulfide have been synthesized by using solid-state reaction, precipitation methods, microwave irradiation techniques, pyrolysis of single-source precursors, hydrothermal/solvothermal synthesis [4–11] and so on.

Among the copper sulfides, some can be used as p-type semiconductor component of the solar cells, cold cathodes, sensors and nanoscale switches because of the copper vacancies within the lattice [12–15]. Moreover, the potential applications in photo-thermal conversion, coatings for microwave shields, room-temperature ammonia gas sensor have also been found [16–18] previously. It has been proved that the microstructures of copper sulfide with well-defined morphologies and dimensions can be used in new types of applications and can enhance the performance of photoelectric devices because of the quantum-size effects. Therefore recent endeavor has focused on developing new synthetic methodologies for fabricating microstructures of copper sulfide with controlled shape and size. For example, variously-shaped Cu_2S and Cu_7S_4 such as superlattices, rods, disks, wires, flakes and plates have been prepared in the presence of organic additives or surfactants [19–24], in which the self-assembled organic superstructures and templates with complex patterns can direct the growth of inorganic crystals with controlled morphologies and architectures [25–30]. Recently, the Cu_2S flowerlike dendrites have been prepared by using a simple reaction between $CuSO_4·5H_2O$ and dimethylsulfoxide [31], the hollow cages of Cu_7S_4 have been synthesized by using the cubic cuprous oxide nanocrystals as source based on the Kirkendall effect [32]. Furthermore, monoclinic Cu_2S nanorods arrays could also be fabricated conveniently on the Cu foil substrates through treating the copper foils under the atmosphere of O_2 and H_2S at room temperature [33,34]. However, the Cu_2S and Cu_7S_4 microstructures with complex shapes have not been obtained by using this method based on the solid–gas reaction.

Nowadays, electrospinning technique has been proved to be a useful method for synthesizing the fibrous materials, through which many fibrous materials including inorganic, organic and inorganic–organic hybrid materials have been prepared [35,36]. Moreover, metallic fibers or tubes have also been prepared by combining the electrospinning and electroless plating process [37–40]. The assembly films formed by the metallic nanoparticles on the electrospun organic fibers will exhibit higher reactive activity

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than the bulk materials because of their large surface area. As far as we know, little attention has been paid to the synthesis of semiconductor with specific microstructures by using the assembly films as substrates. In this paper, assembly films of copper particles have been fabricated on the scaffold of electrospun nonwoven polyacrylonitrile fibrous mats by using electroless plating technique. When this kind of copper films is used as substrates, the monoclinic-phase Cu_2S and Cu_7S_4 with bottle- or thorny rod-structures have been fabricated under the mixture of H_2S and O_2 at room temperature.

2. Experimental

2.1. Materials and reagents

Polyacrylonitrile (PAN) and sodium borohydride ($NaBH_4$) were purchased from Aldrich Company. Tetrabutylammonium bromide (TBAB), sodium ethylenediamine tetra-acetate (Na_2EDTA) and copper foils were purchased from Beijing Chemical Company. The gold salt was synthesized by using the method of previous literature [37], and all other chemicals employed in this study were of analytical grade.

2.2. Electroless plating copper on the fibrous mats surface

TBAB (10 mg) was dissolved into 1.0 ml dimethylformamide (DMF) firstly, and then 90 mg PAN powder was added to the mixture and dissolved at 70 °C to form a transparent solution, finally, gold salt (15 mg) was added to form a brown-red transparent solution. The mixture was transferred into a plastic pipette with a tip whose inner diameter was about 0.5 mm. A thin platinum rod was put into the plastic pipette and connected to a high-voltage power supply which kept a voltage of 13–15 kV during the electrospinning process. A sheet of filtrate paper placed on the grounded aluminium foil was employed as collector, 12–15 cm below the pipette tip. The obtained PAN/gold salt hybrid fibrous mats were cut into round disks with diameters of about 5.0 cm and placed into the circulatory filter. Then the dilute $NaBH_4$ solution (1 mM, 200 ml) was used to reduce the gold salt embedded in the fibers through circulatory filtrating. So the gold nanoparticles (GNPs) formed in the PAN fibers after this procedure, and subsequently, the fibrous mats were washed by water thoroughly.

The transparent bright-blue copper plating solution was obtained by currently dissolving 4.0 g sodium hydroxide, 5.1 g Na_2EDTA and 2.5 g copper sulfate pentahydrate in 100 ml water under stirring, then 3.2 ml formaldehyde aqueous solution (37%) was added into the mixture and the pH value of the solution was adjusted to about 12.5. The plating solution was filtrated three times before use in order to remove the formed precipitation and the other impurity. The copper plating process was carried out by circularly filtrating the 100 ml plating solution through the fibrous mats containing GNPs for 10, 20 and 30 min at 30 °C, then the obtained copper-coated fibrous mats corresponding to the different plating times were defined as 10S, 20S and 30S, respectively. During the process, the GNPs embedded in the fibers were used as the catalytic center for the reductive reaction of Cu^{2+}. The obtained copper-coated fibrous mats were rinsed with water to remove the plating solution and loose copper particles on the mats surface, and then dried in vacuum condition.

2.3. Fabrication of the copper sulfide nanostructures

The silver-gilt layer on the copper surface was obtained after the copper-coated mats were immersed in the 15 mM $AgNO_3$ solution for different times (3, 6 and 9 min) and washed thoroughly with water. The as-prepared copper-coated fibrous mats and the silver-gilt copper-coated fibrous mats were placed into an obturator to react with H_2S gas for 72 h at about 16 °C. In order to clarify the growing process of the microstructure, the morphologies of the samples were recorded after the substrates were treated with H_2S gas for different times.

2.4. Instruments and characterization

The scanning electron microscopy (SEM) images were taken on a JEOL-JSM-6700F scanning electron microanalyser and operated at 15 kV, and the energy dispersive X-ray spectroscopy (EDS) attached to the scanning electron microscope was used to analyze the component of the obtained microstructures. The transmission electron microscopy (TEM) micrographs were recorded on a JEOL-JEM-1011 transmission electron microanalyser. The X-ray powder diffraction XRD patterns were recorded by using a Bruker D8 Advance X-ray diffractometer with a Cu Ka radiation.

3. Results and discussion

3.1. Fabrication of copper-coated fibrous mats

From the SEM images shown in Fig. 1A, we can find that the PAN/GNPs hybrid fibers' surface is fairly smooth and the average diameter of the fibers is about 380 nm. The smooth surface indicates that the size of the GNPs embedded in the fibers is very small. From the TEM image (inserted image in Fig. 1A), it can be seen that the size of the GNPs is about 10 nm although some GNPs integrate into large clusters (>50 nm). When the copper plating solution is filtrated through the PAN/GNPs hybrid fibrous mats repeatedly, the GNPs rooted on the fibers surface will catalyze the reductive reaction of the Cu^{2+} initially and copper will be deposited on the fibers surface. From the SEM images shown in Fig. 1B–D, it is found clearly that the amount of deposited copper increases with the increase of the copper plating time. For example, the copper layer is not large enough to form uniform continuous layer on the fibers surface and many gaps are observed on the surface of the copper-coated mats in 10S (Fig. 1B) because the copper plating process lasts only for 10 min. However, the fibers' surfaces are coated with copper completely in 20S when the plating time increases to 20 min (Fig. 1C), the average diameter of the copper-coated fibers is about 850 nm and the gaps dispersed in the mats have been partly filled by the deposited copper. When the copper plating time increases to 30 min further, more copper has been deposited on the fibers surfaces (Fig. 1D), the diameter of the fibers becomes thicker than 1 μm and the contour of the fibers becomes blurry. The finally obtained copper-coated fibrous mats such as 20S and 30S show a typical copper reflective color and the copper layers exhibit good uniformity.

3.2. Fabrication of Cu_2S microstructure on the copper-coated fibrous mats

When the copper-coated fibrous mats 10S are used as substrates to react with the mixture of H_2S and O_2, there are not any special microstructures observed except that the surfaces of the fibers are coated by the formed Cu_2S particles. So in the following experiments, fibrous mats coated with more copper such as 20S and 30S are chosen as the substrate to fabricate the microstructures of copper sulfide. When the copper-coated fibrous mats 20S are treated with H_2S and O_2 gas in an obturator at room temperature for 72 h, the micro-ribbons with thickness, width and length of about 500 nm, 1.5 μm and several micrometers, respectively, are formed on the surface of 20S (Fig. 2A). These ribbons exhibit larger size than the nanorods reported previously [33]. It is interesting to find that the thorny rods have formed when the copper-coated fibrous mats 30S are treated under the same condition (Fig. 2B), and

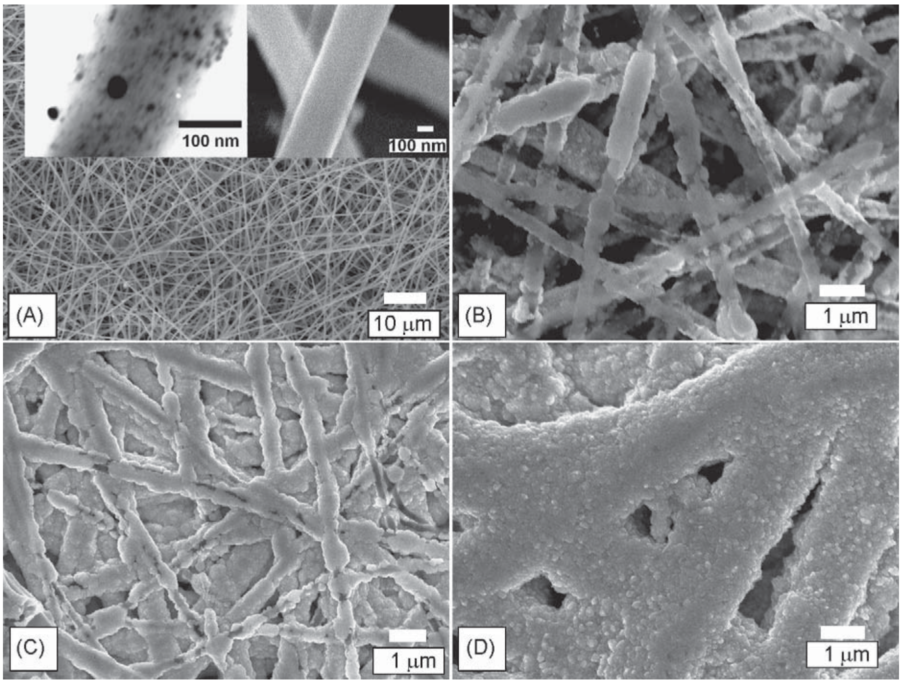

Fig. 1. The SEM image of (A) PAN/GNPs hybrid fibrous mats and the copper-coated fibrous mats prepared by electroless plating copper for 10 min (B) 10S, 20 min (C) 20S and 30 min (D) 30S.

that the main rods have a diameter of about 400 nm and the length about several micrometers, furthermore, many small thorns with lengths about 200–500 nm and diameters about 50 nm grow almost vertically out of the main rods (Fig. 2C). The EDX data reveal that the molar ratio of copper and sulfur element is about 1.91, nearly close to 2, in good agreement with the stoichiometric component of Cu_2S, which indicates that Cu_2S is the main component of the microstructure surface. From the results mentioned above, it can be seen that the amount of plating copper exerts strong influence on the morphology of the formed Cu_2S, and that the copper-coated fibrous mats such as 30S containing more plating copper than 20S are favorable to form the thorny rods of Cu_2S. We can also find from the XRD pattern (Fig. 2D) that the finally obtained samples contain mainly the cubic Cu and the monoclinic Cu_2S phase.

3.3. Fabrication of Cu_7S_4 on the silver-gilt copper-coated fibrous mats

It is surprising to find that the silver deposited on the copper surface has an obvious influence on the component and morphology

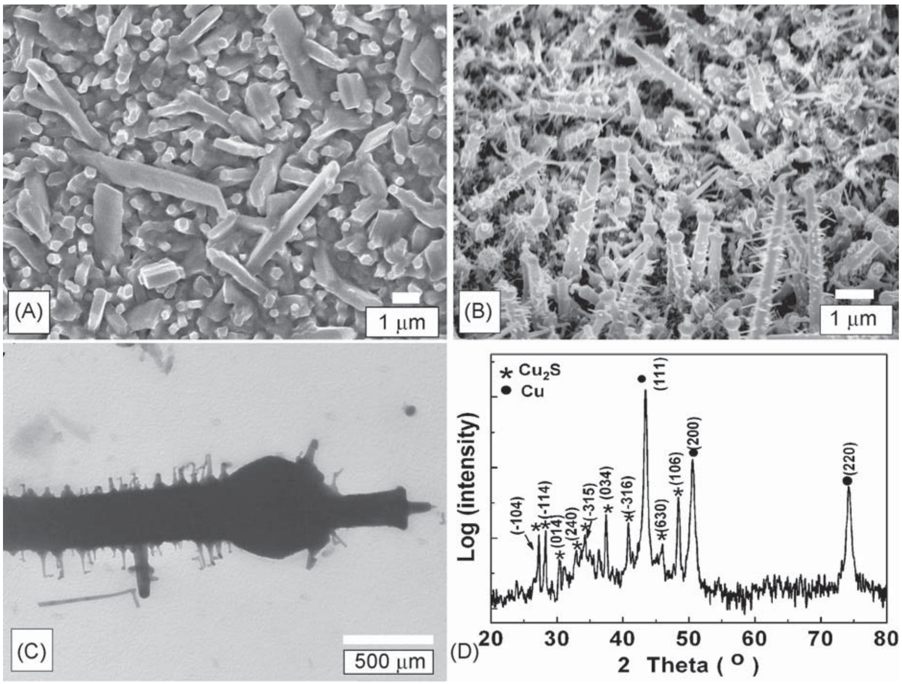

Fig. 2. The SEM images of the Cu_2S microstructures obtained by treating the substrate (A) 20S and (B) 30S under the mixture of H_2S and O_2 atmosphere for 72 h at 16 °C, (C) the TEM image and (D) the XRD pattern of the sample shown in (B).

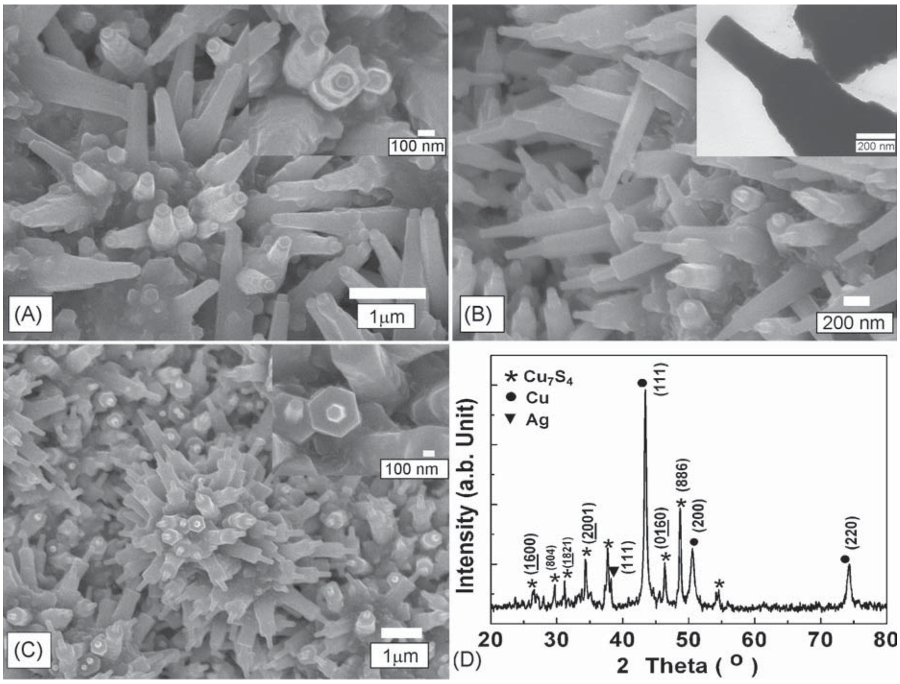

Fig. 3. The SEM images of the Cu_7S_4 microstructures prepared from 20S decorated with different amount of silver by controlling the reaction time as (A) 3 min, (B) 6 min (inserted image: TEM), (C) 9 min and (D) the XRD pattern of the sample shown in (C).

of the formed copper sulfide microstructure. When the copper-coated fibrous mats are immerged into the 15 mM $AgNO_3$ solution for different times, different amount of silver can be deposited on the plating copper surface easily. The deposited silver exhibits two kinds of morphologies, silver particles and fern-leaf-shaped dendrites. The morphology and the amount of the silver are mainly affected by the replacement reaction time. The EDX spectra reveal that the formed dendrites contain the elements of silver and copper (see supporting materials). This result is different from the previous literature [41,42] in which pure silver dendrites are obtained by using the pure copper foils as the sacrifice to reduce the silver ion. The reason may be that the plating copper films exhibit larger surface area and higher reactivity than bulk copper, which will make the replacement reaction occur quickly, so some copper particles would be enwrapped by the formed silver, and then the silver-copper bimetallic dendrites have formed.

After the copper-coated mats (20S) are decorated with silver through controlling the replacement reaction times (3, 6 and 9 min), the silver-gilt copper-coated fibrous mats are used as substrate to react with the mixture of H_2S and O_2 gas for 72 h in an obturator at room temperature (16 °C). We can find from Fig. 3 that the bottle-shaped microstructures have formed on the silver-gilt copper-coated mats surface, and that the top end of the bottle-shaped microstructures shows the shape of hexagonal prisms. The diameters of the thin part at the bottle top are about 120 nm and the length is about 50 nm, and the diameters of the thick part at the bottle bottom are about 350 nm and the length is about 2 μm (Fig. 3A) when the copper-coated fibrous mats contain less amount of silver (replacement reaction time is 3 min). When the substrates of 20S containing more amount of silver (replacement reaction time is 6 and 9 min) are treated under the same condition, the length of thin part of the bottle increases to about 300–400 nm (Fig. 3B and C). The EDX spectra show that the bottle-shaped microstructures mainly contain the elements of copper and sulfur but no silver element can be detectable on the microstructures surface, and that the value of Cu/S is about 1.78. Furthermore, we find from the XRD pattern that the obtained samples contain the cubic-phase Cu, monoclinic-phase Cu_7S_4 and little amount of cubic Ag (Fig. 3D). In previous reports, Cu_7S_4 is usually synthesized by reacting Cu_2O and sulfur source in solution [32], so it is interesting to obtain the Cu_7S_4 at room temperature by reacting Cu with the mixture of H_2S and O_2 in the presence of silver on the copper surface. Based on the above results, we can find that the silver deposited on the plating copper surface may promote the formation of monoclinic-phase Cu_7S_4 with the bottle-shaped microstructures.

When the copper-coated fibrous mats such as 30S which contains more amount of copper than 20S, are treated with the same procedure as 20S, it can be seen from the SEM images shown in Fig. 4 that not only the bottle-shaped microstructures (Fig. 4A and B) but also the thorny nanorods with lengths of several tens micrometers have formed on the substrate surface (inserted figures in Fig. 4A and B), and that many small thorns have grown out from the side surface of the bottles. The TEM images show that the diameter of the thick rods is about 500 nm, and that the small thorns have a length of about 100 nm and a diameter about 50 nm, which is almost vertical to the long thick rods surface (Fig. 4C). The XRD pattern (Fig. 4D) indicates that the sample contains the monoclinic-phase Cu_7S_4, little amount of cubic-phase Cu and Ag. In comparison with the results shown in Fig. 3, we can find that in the presence of Ag, the thorny rod- and bottle-shaped microstructures will be favorable to form at the same time when the substrates contain more amount of plating Cu. However, when the copper foils are used as substrates to react with the mixture of H_2S and O_2, the similar microstructures have not been obtained whether the decorated silver is present or not.

3.4. The mechanism for the formation of the microstructure

In order to clarify the growing process of the microstructures, after the substrates decorated with silver are treated with H_2S gas for different times, the SEM images are recorded and shown in Fig. 5. From which we can find that the structures of copper-silver bimetallic dendrites have been destroyed after the substrates react with the mixture of H_2S and O_2 gas for 2 h. The reason may be that the formation of metal sulfide causes the substrate mass to increase, and that the metal sulfide has less density than metal. The surface of the substrates is fairly smooth and the final microstructure cannot

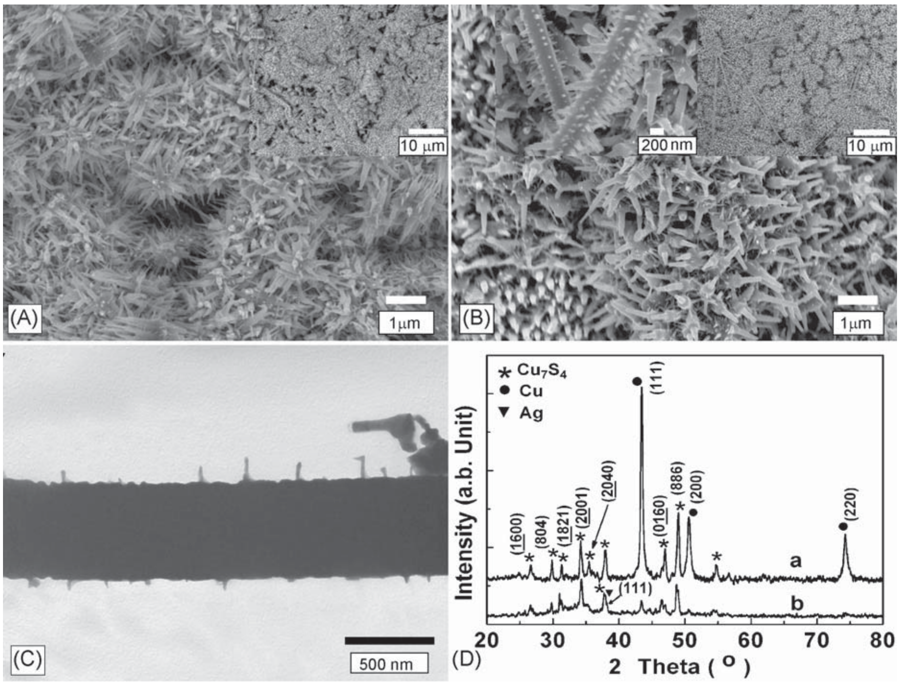

Fig. 4. The SEM images of the Cu_7S_4 microstructures prepared from 30S decorated with different amount of silver by controlling the replacement reaction time as (A) 3 min, (B) 9 min, (C) the TEM image of the thorny rods shown in (B) and (D) the XRD patterns of the sample shown in (A) (a) and in (B) (b).

be observed yet (Fig. 5A). The elements of copper, silver and sulfur are detected on the substrates surface by using EDX technique. After the substrates are treated with the same atmosphere for 12 h, the surface of the substrates becomes coarse, and some thick rods with diameter of about 300 nm have grown out of the substrates surface (Fig. 5B). The rods surfaces contain mainly the element of copper, sulfur and very small amount of silver. When the reaction time increases to 24 h, we can find that the thin rods with diameters of about 100 nm have grown out from the tops of the thick rods (Fig. 5C). After the substrates are treated under the same atmosphere for 36 h further, not only the bottle-shaped microstructures, but also the long rods with tens of micrometers length are observed on the surface of the substrate (Fig. 5D, inserted figure).

According to our experiments and the previous results [33,34], the suggested growing process for these bottle-shaped and thorny rod-shaped microstructures is shown in Fig. 6. When the plating copper layers decorated with silver are treated with the mixed gas of H_2S and O_2, the Ag and Cu can react with oxygen to form the Ag_2O and Cu_2O on the substrates surface firstly, at the same time, the Ag_2O can react with copper to form CuO [43], the formed Ag_2O, CuO

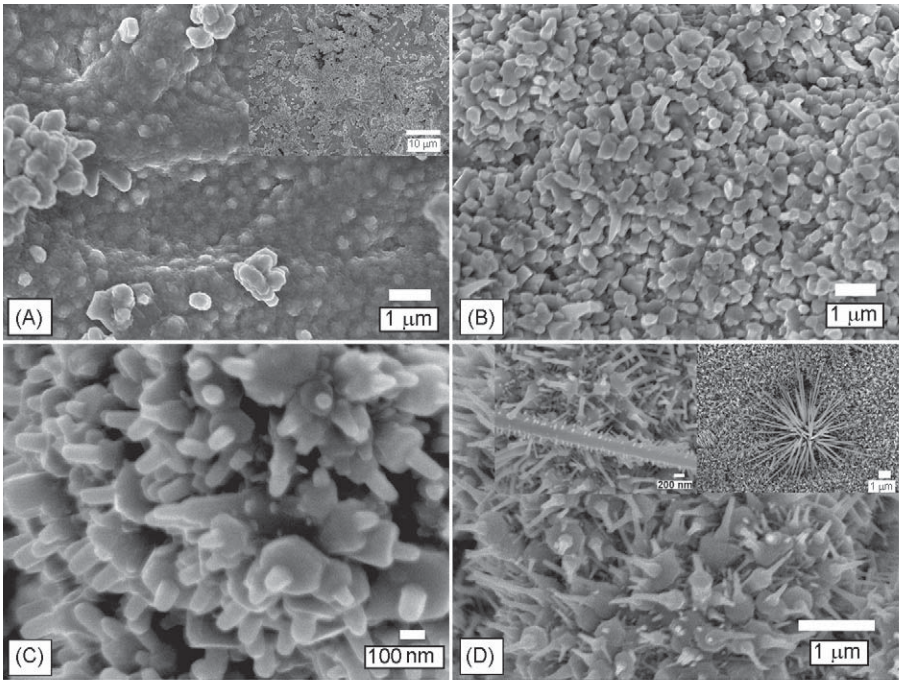

Fig. 5. The SEM images after the silver-gilt copper-coated fibrous mats 30S (depositing Ag for 9 min) are treated in H_2S and O_2 mixture for different time (A) 2 h, (B) 12 h, (C) 24 h and (D) 36 h.

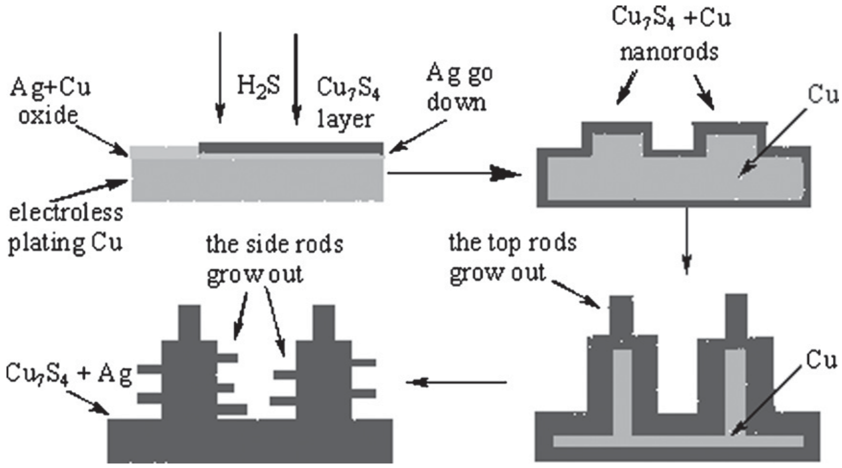

Fig. 6. The simple illustrate for the formation process of the copper sulfide microstructures.

and Cu_2O will subsequently react with H_2S gas to form Ag_2S, CuS and Cu_2S. On the other hand, the copper can also directly react with Ag_2S to form Cu_2S, so the formed Cu_2S comes from two reactions in this case, one is that Cu reacts with Ag_2S, and the other is that Cu_2O reacts with H_2S. Finally the copper sulfide Cu_7S_4 has formed because CuS and Cu_2S have formed at the same time. As a result, the silver will go down the copper sulfide layer, so there is very little amount of silver element detected on the microstructure surface. Furthermore, the plating copper layers exhibit larger surface area and higher reactive activity than the bulk copper, so the growing rate of Cu_7S_4 rods is relatively high, the formed rods grow out from the small cracks of the surface layers and they grow up so quickly that some copper particles are enwrapped in the rods. With the increase of the reaction time, the erosive gas diffuses into the inside of the rods, so the enwrapped copper can react with the erosive gas continuously to form the new Cu_7S_4 which grows out of the small cracks of the rods, so the thin rods are formed on the top and the side surface of the thick rods. Finally, the Cu_7S_4 microstructures with bottle- or thorny rod-shape are formed. When the copper-coated fibrous mats 30S are treated with the same atmosphere in the absence of silver, the growing processes of the Cu_2S microstructure are also investigated and the similar growing process is observed.

4. Conclusions

Summarily, the Cu_2S with thorny rod-structures and Cu_7S_4 with bottle-shape and thorny rod-shape structures have been prepared by using the electroless plating copper-coated fibrous mats as substrates to react with H_2S and O_2 mixture. The experimental results reveal that the amount of plating copper has an important influence on the morphology of the obtained copper sulfide microstructure, and that more amount of plating copper is beneficial to form the thorny rods structures. When the copper-coated fibrous mats decorated with silver are treated with the same atmosphere, the bottle-shaped microstructures have been obtained. With the increase of the plating copper amount, the thorny rods with hundreds of micrometers length are formed on the substrate surface besides the bottle-shaped microstructures. These special microstructures of copper sulfide could be used in the field emission, solar cell or other potential application fields.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matchemphys.2009.11.025.

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