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Synthesis of CuAlO₂ nanofibrous mats by electrospinning

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ABSTRACT

Electrospinning as a versatile method for preparation of nanofibers has been used to fabricate the polyvinylalcohol nanofibers containing equal molar of aluminum nitrate and copper acetate. After pretreated at 400 °C, the composite fibrous mats were annealed at 1100 °C in air for 5 h and then the delafossite-structured p-type CuAlO₂ ceramics fibrous mats were obtained. The obtained CuAlO₂ ceramics fibrous mats were characterized by scanning electrical microscope, X-ray diffraction and diffuse reflectance spectroscopy. The direct energy gap of the prepared CuAlO₂ ceramics fibrous mats was measured to be about 3.38 eV. The CuAlO₂ behaved like semiconductors and the thermally activated energy was about 0.25 eV.

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1. Introduction

In recent years, electrospinning technique has been proved to be a versatile method for fabricating nanofibrous materials [1,2]. Up to present, nanofibers such as organic, inorganic and organic–inorganic hybrid materials have been prepared by using electrospinning technique because of their potential applications in tissue engineer, catalysis, electronic and sensor [3–22]. For example, the oxides and ceramics materials such as ZnO, Al₂O₃, SiO₂, TiO₂, V₂O₅, LiCoO₂, NiFe₂O₄ and so on have been prepared through thermally treating the electrospun hybrid fibers of polymers/oxides precursor or the fibers of sol–gel precursors [11–20].

The transparent conducting oxides such as electron doped ZnO, In₂O₃ and SnO₂ are widely and practically used as transparent electrodes in flat panel displays, solar cells, and touch panels [23]. Recently, the delafossite-structured CuAlO₂ films have been found to have the visible-light transmittance as high as 80%, and can be considered as an ideal candidate for transparent p-type conducting oxides [25,26] without intentional doping [24]. Furthermore, its promising potential is also found in applications such as diluted magnetic semiconductors, the all-oxides light emitting device and high-efficient solar cells formed by p-type and n-type transparent semiconductor [27–29]. In some previous reports [30,31], the CuAlO₂ powder has also been used as catalyst for the conversion of solar to hydrogen under visible light.

The methods for preparing $CuAlO_2$ materials include the conventional solid-state reaction, sol–gel method, the hydrothermal method and physical vapor deposition technique [32–35]. The

nanofibrous materials of CuAlO₂ have not been reported now although the CuAlO₂ powders and films have been prepared. In this paper, the ultrathin fibers of polyvinylalcohol containing equal molar of copper acetate and aluminum nitrate are fabricated firstly, and then the CuAlO₂ ceramics fibrous mats are obtained after the hybrid fibrous mats are thermally treated at temperature as high as 1100 °C.

2. Experimental

2.1. Preparation of fibrous mats of CuAlO₂

The raw materials including copper acetate (Cu(CH₃COO)₂·H₂O), aluminum nitrate (Al(NO3)3.9H2O), polyvinylalcohol (PVA) were of analytical grade and purchased from Beijing Chemicals Company. Aluminum nitrate (5 mmol) was dissolved into 10 ml deionic water firstly, then copper acetate (5 mmol) was dissolved into the mixture, and finally, 1.0 g PVA was dissolved into the mixture at about 90 °C under stirring. After having been stirred for about 5 h, the mixture was transferred into a plastic pipette in which a thin Pt rod was connected to a high-voltage power supply. The potential was kept at +15.0 kV during the electrospinning process. The fibers were collected on a grounded aluminum foil about 9 cm below the plastic pipette tip. The fibrous mats peeled off the aluminum foil as stand-free films were dried under vacuum at 100 °C for 12 h, and the dried mats were transferred to a muffle furnace and slowly heated to 400 °C for 8 h and kept at this temperature for 4 h. Then the pretreated fibrous mats were heated to 1100 °C at a rate of 20 °C min⁻¹ and kept in this temperature for 5 h. After the temperature was cooled to room temperature automatically, the obtained samples were collected for the following characterization.

2.2. Characterization

The scanning electron microscopy (SEM) images were taken on a JEOL-JSM-6700F field-emission scanning electron microanalyser (Tokyo, Japan) and operated at 15 kV after the samples were coated with a layer of platinum by spraying under vacuum. XRD patterns were measured by a Bruker D8 Advance X-ray diffractometer by using Cu K α radiation (λ = 0.15406 nm). The electrical conductivity during the heating process was measured by the conventional four-point probe method, and during which a controlled temperature cell set was used. The optical properties of

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Fig. 1. FE-SEM images of the electrospun hybrid fibers and CuAlO₂ fibrous mats. (A) The electrospun fibrous mats of PVA containing equal molar ratio of aluminum nitrate and copper acetate; (B) the pretreated hybrid fibrous mats at 400°C and the insetted figure is the large-scale SEM image of the pretreated fibrous mats; (C) the obtained CuAlO₂ fibrous mats prepared by thermally treating the pretreated mats at 1100°C in air for 5 h. Photo picture of the fibrous mats: (D) the dried hybrid fibrous mat, (E) the pretreated hybrid fibrous mat at 400°C, and (F) the CuAlO₂ fibrous mat prepared at 1100°C.

the CuAlO₂ fibrous mats were measured by using a Cary 500 UV-VIS-NIR spectrophotometer equipped with an integrated sphere in which $BaSO_4$ was used as a reference. The spectra were recorded in the range of 220–1200 nm at room temperature in air.

3. Results and discussion

From Fig. 1A which shows the SEM image of dried as-prepared hybrid fibers of PVA in which the amounts of aluminum nitrate and copper acetate are 1:1 in molar ratio, we can find that the diameters of the fibers are almost uniform (\sim 350 nm) and the surfaces of the fibers are fairly smooth. The color of the hybrid fibrous mats changes from light blue to yellow-blue when the mats are dried at 100 °C at vacuum; while turns black after the dried fibrous mats are thermally treated at 400 °C for 5 h because the metal salt can be decomposed to form the Cu- and Al-related oxides during the thermal treatment at 400 °C. Furthermore, we can also find that the surface of the hybrid fibers becomes coarse (Fig. 1B) after they are annealed at 400 °C in comparison with the as-prepared hybrid fibers (Fig. 1A), and that the fibers are formed by the particles with an average diameter of about 100 nm. Moreover, it is found that after thermal treatment at 400 °C, the diameters of the fibers are about 350 nm, which is similar to the diameter of the dried fibers. However, the gaps between the fibers have become small, which can be contributed to the shrinkage of the fibers caused by the decomposition during the thermal treatment. When the fibrous mats treated at 400 °C are annealed at 1100 °C for 5 h, we find the surfaces of the fibers become smooth. The reason may be that the small particles shown in Fig. 1B have sintered at 1100 °C, which makes the smooth surfaces formed on the fibers (Fig. 1C). We can also find that the diameters of these fibers are about 300 nm and the gaps dispersed in the fibrous mat become smaller because of the shrinkage.

In fact, the shrinkage of the hybrid fibrous mats is always occurred during thermal treatment and the pictures of the fibrous mats after thermal treatment process at certain temperature are shown in Fig. 1D–F. For example, after the as-prepared fibrous mat with area of about 66 cm^2 being selected to prepare the CuAlO₂ fibrous mat is dried under vacuum at $100 \,^\circ$ C, there remains about



Fig. 2. XRD patterns of the CuAlO₂ precursor and the obtained CuAlO₂. (a) The pretreated fibrous mats at 400 °C, (b) the powdery CuAlO₂ precursor prepared by decomposing the mixture of Al(NO₃)₃·9H₂O and Cu(CH₃COO)₂·H₂O, (c) the CuAlO₂ fibrous mats and (d) the powder of CuAlO₂ prepared by decomposing the mixture of Al(NO₃)₃·9H₂O and Cu(CH₃COO)₂·H₂O, is mixture of Al(NO₃)₃·9H₂O and Cu(CH₃COO)₂·H₂O with a equal molar ratio.



Fig. 3. (A) $(\alpha h\nu)^2$ versus $h\nu$ plot derived from the optical transmission curve (see the inset) obtained from a CuAlO₂ fibrous mats. (B) Temperature dependence of the conductivity (σ) for the CuAlO₂ fibrous mats.

 56 cm^2 (Fig. 1D) and the decrease of the area is about 15%. When the dried mat is heated at 400 °C, the reserved area is about 17 cm² and the shrinkage is about 74% (Fig. 1E). Finally, there remains only about 12 cm² (Fig. 1F) after the pretreated mats are annealed at 1100 °C, the total shrinkage of the mat is about 82%. The organic component of the hybrid fibers will be decomposed and the inorganic components retained during the thermal treatment process, and retained inorganic components such as Al and Cu oxide contact each other so closely that CuAlO₂ forms at high temperature, at the same time obvious shrinkage can be observed during the process of thermal treatment.

From the XRD patterns shown in Fig. 2, we can find that the obtained pretreated fibrous mats show the typical diffraction peaks of monoclinic-structured CuO (PDF 45-0937) without any trace of the Al-related phases after the hybrid fibrous mats (Fig. 2a) are heated at 400 °C, which indicates that the copper acetate dispersed in the hybrid fibers has been decomposed during the pre-thermal treatment process, and that the absence of Al-related phases may be originated from the amorphous phases of the related Al compound. The result in this paper is different from the previous report [34] in which the CuAlO₂ precursor is prepared by decomposing the equal molar amount of Cu(CH₃COO)₂·H₂O and Al[OCH(CH₃)CH₂CH₃]₃ mixture at 300 °C and the resulted precursor mainly contains the cubic Cu₂O because the Al[OCH(CH₃)CH₂CH₃]₃ in the mixture can act as a reducer. In our experiments, Al(NO₃)₃·9H₂O is used as an aluminum source in which the nitrate is an oxidizer, so the monoclinic CuO is the main decomposed product for $Cu(CH_3COO)_2 \cdot H_2O$. In order to make a comparison, the powdery CuAlO₂ precursor has also been prepared by decomposing the equal molar ratio of Al(NO₃)₃·9H₂O and Cu(CH₃COO)₂·H₂O at 600 $^{\circ}$ C, which shows a similar XRD pattern (Fig. 2b) to that of the pretreated fibrous mats. The color of the pretreated fibrous mats changes from black to gray when the fibrous mats are annealed at 1100 °C in air for 5 h, which indicates that the CuAlO₂ fibrous mats have formed. The XRD patterns also show that the hexagonal-phased CuAlO₂ fibrous mats (a = 2.8504 Å, b = 16.9067 Å, R3m-166, JSPDS 35-1401) without any detectably undesired phases have been synthesized. We can also find that the diffraction peaks located at 15.8°, 31.7°, 48.4° and 66.2° corresponding to the diffraction of (003), (006), (009) and (0012) planes exhibit stronger intensity than that of the (101) and (012) planes (Fig. 2c), which are similar to the CuAlO₂ films deposited on the sapphire surface [35] by epitaxial growth, but different from the CuAlO₂ powders prepared by solidstate reaction, sol-gel method and decomposing Al(NO₃)₃·9H₂O and Cu(CH₃COO)₂·H₂O mixture (Fig. 2d) in which the (101) and

(012) planes exhibit higher diffractive peaks than (003), (006) and (009) planes [30–34].

It is known that the chains of the macromolecule can be aligned along with the direction of fibers when the electrospun solution is ejected from the nozzle [22]. On the other hand, the cations would be fixed in the matrix of the aligned molecule chains because the hydroxyl groups of the PVA exhibit some coordinative action with the cations of Cu^{2+} and Al^{3+} . This special structure of hybrid fibers may act as template more or less and direct the formation of the $CuAlO_2$ with stronger intensity on (003), (006), (009) and (0012) planes.

The diffuse reflectance spectroscopy has been used to determine the optical properties of pure CuAlO₂ fibrous mats. The direct energy gap is determined by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion, which intercepts the energy axis $h\nu$. Here, we can use the absorbance value to substitute the α value because as the absorption coefficient, α , which depends on the wavelength, is proportional to the absorbance. As presented in Fig. 3A, the direct optical transition is observed at 3.38 eV through the $(\alpha h\nu)^2$ versus $h\nu$ plot and corresponded to the direct energy gap, which is close to the previously reported values [35].

The temperature dependence of the conductivity for the CuAlO₂ fibrous mats is plotted and shown in Fig. 3B. It can be seen that in the measured temperature range the conductivity is thermally activated. The plotting of the ln σ versus 1/T shows that the electrical conductivity follows the Arrhenius law: $\sigma = \sigma_0 \exp(-\Delta E/kT)$. And the $\Delta E = 0.25$ eV is obtained from the slope of the linear portion (Fig. 3B). The close activation energy has also been reported in previous literature [25] through measuring the thin films of delafossite-structured CuAlO₂. All the results mentioned above indicate that we have successfully fabricated the fibrous mats of CuAlO₂ through combining the electrospinning technique and thermal treatment.

4. Conclusion

Summarily, delafossite-structured CuAlO₂ ceramics fibrous mats have been prepared by thermally decomposing the electrospun fibers of PVA containing equal molar ratio of $Al(NO_3)_3 \cdot 9H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$. The XRD patterns of the obtained pure CuAlO₂ ceramics fibrous mats are similar to that of CuAlO₂ deposited on the sapphire surface. The diffuse reflectance spectroscopy reveals that the direct energy gap of the CuAlO₂ fibrous mats is about 3.38 eV, and that the prepared CuAlO₂ fibrous mats behave like semiconductors and the thermally activated energy near room temperature is about 0.25 eV.

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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.2009.05.009.

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