Applied Surface Science 363 (2016) 659–663

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

A facile self-assembled film assisted preparation of $CuGaS_2$ ultrathin films and their high sensitivity to L-noradrenaline

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A R T I C L E I N F O

Article history:
Received 18 August 2015
Received in revised form
15 December 2015
Accepted 16 December 2015
Available online 18 December 2015

Keywords:
$CuGaS_2$
Ultrathin film
Self-assembly
Photoluminescent probe
L-noradrenaline

A B S T R A C T

A dense $CuGaS_2$ ultrathin film was prepared in an improved layer-by-layer self-assembled process followed by heat treatment and characterized with X-ray diffraction, scanning electron microscopy, UV–vis spectroscopy, and fluorescence spectroscopy. Meanwhile, the application of the as-prepared $CuGaS_2$ ultrathin film in the trace detection of L-noradrenaline was explored as a photoluminescent probe. The results show that the tetragonal phase $CuGaS_2$ film fabricated on the glass substrate is smooth and dense. And this $CuGaS_2$ ultrathin film can exhibit a strong emission at 829 nm with full width at half maximum of approximate 12 nm. Furthermore, the as-prepared $CuGaS_2$ ultrathin film possesses high sensitivity to L-noradrenaline with a detectable concentration of 2.83 ng cm^{-2} when it is used as a photoluminescent probe, implying that it is a promising candidate in the field of biological and chemical sensing in future.

1. Introduction

Recently, $CuGaS_2$, as a member of the chalcopyrite family, attracts much attention due to its high potential for applications in the fields of thin film solar cell, light emitting diode, infrared radiation and detection, photocatalysis, and preparation of $Cu(In_{1-x}Ga_x)(S,Se)_2$ [1–4]. Many efforts have been devoted to its synthesis and applications. Among these studies, the fabrication of $CuGaS_2$ film is especially striking because high quality films are critical to the applications of $CuGaS_2$ in the fields above. Therefore, it has been an investigation focus to improve the preparation technique of $CuGaS_2$ film.

Nowadays, a series of preparation techniques of $CuGaS_2$ film have been developed, such as sulfurization of Cu–Ga precursors [5], two-stage MOCVD method [6], electrophoretic deposition of Ga–Cu nanocomposite followed by sulfurization [3], thermal evaporation of $CuGaS_2$ powder [7], electron beam evaporation [8], paste coating [9], molecular beam epitaxy [10], helicon-wave- excited-plasma sputtering [2] and so on. However, there are still some shortages in these methods. For example, in general, these synthetic routes often involve expensive specialized apparatus, ultrahigh vacuum system, high temperature treatment, toxic and expensive initial reactants, etc. In addition, it is also a big challenge to control the composition homogeneity of the $CuGaS_2$ film and avoid secondary phases such as Cu_2S-Ga_2S_3 throughout the fabrication process. As a result, it is necessary to improve the preparation technique of $CuGaS_2$ film.

In our previous work, some binary semiconductor films, such as CdS film and HgS film, were fabricated on various solid substrates via an improved layer-by-layer self-assembled technique followed by heat treatment [11,12]. These results motivate us to speculate that it is possible to obtain $CuGaS_2$ film in a similar process. In addition, the self-assembly technique offers opportunities to fabricate the highly ordered multilayer structure, which implies a convenient organization of two-dimensional arrays and three-dimensional networks via electrostatic interaction, intermolecular force, hydrogen bonds and so on. When the self-assembled film is annealed as a precursor, its highly ordered multilayer structure may be favorable to fabrication of stoichiometric $CuGaS_2$ film. However, it is unclear if the $CuGaS_2$ film can be fabricated via the self-assembly technique so far.

L-noradrenaline [1-(3,4-Dihydroxyphenyl)-2-aminoethanol, LNE] is an endogenous adrenoceptor agonist [13]. Many central nervous system functions and various diseases are related to its concentrations in the nervous tissue and biological body fluid [14]. Moreover, LNE as a stimulant has been on the Word Anti-Doping Agency's 2005 Prohibited list. As a result, the determination of trace LNE has become an attractive and hot topic. And several analytical methods have been established. Here, the electroanalytical technology has been widely applied in the biological and chemical sensing due to its low cost, sensitivity, simplicity and high accuracy [15–45]. Therefore, most of analytical methods used in the detection of trace LNE are based on electroanalytical

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http://dx.doi.org/10.1016/j.apsusc.2015.12.132
0169-4332/

technology so far. It is well known that the photoluminescent probe method is a rapid, simple, low-cost and sensitive detection method. However, there are few papers on the photoluminescent probe method in the detection of trace LNE. Hence, it is meaningful to explore a sensitive photoluminescent probe which can be applied in the detection of trace LNE.

Our previously reported experimental results indicate that $CuGaS_2$ possesses high sensitivity to L-noradrenaline in water with a detectable concentration of 5.0×10^{-7} mol·L^{-1} when it used as a photoluminescent probe [46], implying that $CuGaS_2$ is a promising photoluminescent probe for the detection of trace LNE. However, from the practical point of view, it is inconvenient using $CuGaS_2$ powder as a photoluminescent probe. To overcome this technical shortage, an alternative approach is to use the $CuGaS_2$ film fabricated on a solid substrate. Unfortunately, in the case of the $CuGaS_2$ film, most of the studies reported were focused on the application of $CuGaS_2$ film in the field of solar cell. There is no paper on the application of the $CuGaS_2$ film in the detection of trace LNE. Hence, it is still unclear whether the $CuGaS_2$ film is a suitable probe for the detection of trace LNE or not so far.

In the present work, the single-phase $CuGaS_2$ ultrathin film was prepared by annealing the $(-Cu^{2+}-\text{dithiol}-Ga^{3+}-\text{dithiol}-)_n$ self-assembled film on the glass substrate. Moreover, the possible application of the as-prepared $CuGaS_2$ film as a photoluminescent probe was explored for the detection of trace LNE. The results suggest that the as-prepared $CuInS_2$ ultrathin film possesses an emission with high color purity and great potential as a photoluminescent probe for the detection of trace LNE.

2. Experimental

2.1. Materials

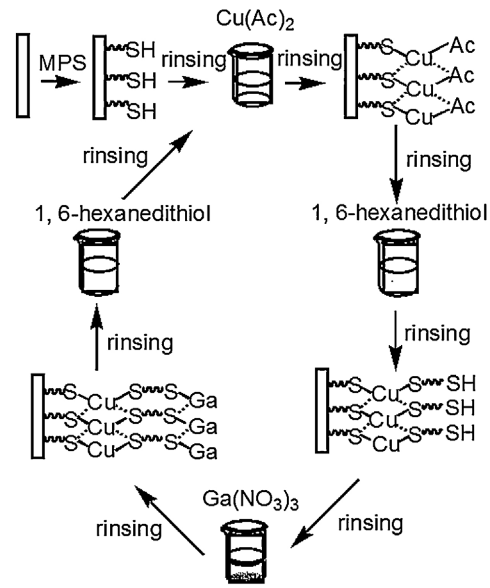
Gallium nitrate hydrate (99.999%) and LNE (98%) were purchased from Alfa Aesar. The other reagents were analytical grade and obtained from Sinopharm Chemical Reagent Co. Ltd (China). All reagents were used without further purification.

2.2. Fabrication of $CuGaS_2$ ultrathin film

The $CuGaS_2$ ultrathin film was fabricated on the glass substrate according to the method similar to that described by Zhang et al. [11], as shown in Scheme 1. In a typical preparation, a well-cleaned glass substrate was immersed into toluene (10 mL) containing 3-mercaptopropyltrimethoxysilane (MPS, 1 vol.%), and the toluene was refluxed at 383 K for 3 h. Then, the substrate was rinsed several times with toluene and dried in nitrogen flux. The construction of the $(-Cu^{2+}-\text{dithiol}-Ga^{3+}-\text{dithiol}-)_n$ multilayer film involved the following eight steps: (1) immersion of the substrate modified with MPS into the ethanol solution of copper acetate (0.02 mol·L^{-1}) for 2 min; (2) rinsing with ethanol; (3) immersion of the substrate into the ethanol solution of 1,6-hexanedithiol (0.05 mol·L^{-1}) for 2 min; (4) rinsing with ethanol, (5) immersion of the rinsed substrate into the ethanol solution of gallium nitrate (0.02 mol·L^{-1}) for 2 min; (6) rinsing with ethanol; (7) immersion of the substrate into the ethanol solution of 1,6-hexanedithiol (0.05 mol·L^{-1}); (8) rinsing with ethanol. By repetition of steps 1–8 in a cyclic fashion, the alternating $(-Cu^{2+}-\text{dithiol}-Ga^{3+}-\text{dithiol}-)_n$ multilayer film with 100 cycles was achieved. Finally, the multilayer film prepared was annealed at 623 K for 2 h in N_2 ambient to obtain the $CuGaS_2$ ultrathin film on the glass substrate.

2.3. Detection of trace LNE

LNE solution (1 μmol·L^{-1}) was prepared using deionized water at room temperature. In order to accurately determine the surface



Scheme 1. Formation of the $(-Cu^{2+}-\text{dithiol}-Ga^{3+}-\text{dithiol}-)_n$ self-assembled film on the glass substrate.

concentration of LNE on the $CuGaS_2$ ultrathin film, LNE solution was uniformly dropped onto the $CuGaS_2$ ultrathin film (3×1.5 cm^2) using a microsyringe, and then the $CuGaS_2$ ultrathin film was dried at room temperature. Next, the fluorescence spectra of the $CuGaS_2$ ultrathin film were measured immediately. The excitation wavelength was 550 nm. The slit widths of excitation and emission were both 5 nm. The fluorescence intensity at 829 nm was used for the detection of LNE. The surface concentration of LNE on the $CuGaS_2$ ultrathin film was calculated according to Eq. (1).

$$C_s = \frac{V \times C_{LNE} \times M_{LNE}}{S} \quad (1)$$

where C_s is the surface concentration of LNE on the $CuGaS_2$ ultrathin film, V is the volume of the LNE solution dropped, C_{LNE} is the concentration of the LNE solution, M_{LNE} is the molar mass of LNE, S is the area of the $CuGaS_2$ ultrathin film.

2.4. Characterization

The crystal structure of the sample was identified with a PAN analytical Xpert Pro MRD X-ray diffractometer (Netherlands).

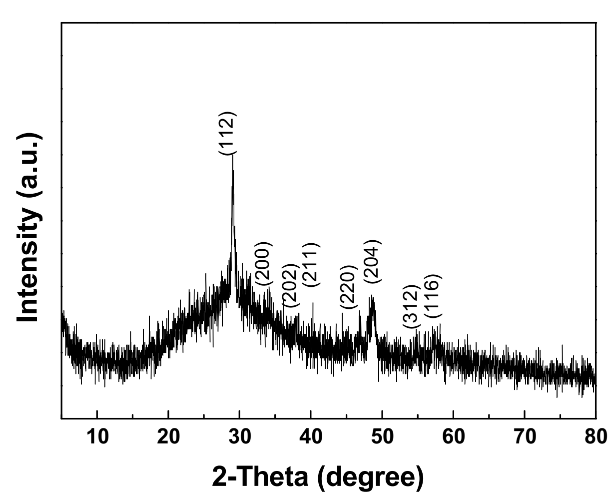


Fig. 1. XRD pattern of the as-prepared $CuGaS_2$ ultrathin film.