Thin Solid Films 552 (2014) 98–104

Contents lists available at ScienceDirect

Thin Solid Films

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

Fabrication of hydrophobic poly(3,4-ethylenedioxythiophene): Poly(4-styrenesulfonate)/zinc oxide rod conductive film via hydrothermal method and their performance on weather stability and pH buffering ability

Ting-Chang Huang [a], Hui-En Yin [a,e], Wen-Yen Chiu [a,b,c,*], Chia-Fen Lee [d,**]

[a] Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan
[b] Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan
[c] Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan
[d] Department of Cosmetic Science, Chia Nan University of Pharmacy and Science, Tainan, Taiwan
[e] Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan

ARTICLE INFO

Article history:
Received 4 April 2013
Received in revised form 21 November 2013
Accepted 22 November 2013
Available online 2 December 2013

Keywords:
PEDOT:PSS
Zinc oxide
Microrods
pH buffering
Weather stability
Acid/alkali resistance
Hydrothermal growth method

ABSTRACT

The poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) conductive film associated with zinc oxide (ZnO) rods was prepared to improve its hydrophobic property and weather stability. In this study, the ZnO nanoparticles were synthesized in the presence of methanol or ethanol to act as the ZnO seeds that deposited on the PEDOT:PSS film. Then, the ZnO seeds grew on the surface of PEDOT:PSS film to form the PEDOT:PSS/ZnO rod film by hydrothermal method in a weak alkali solution. The surface morphology of PEDOT:PSS/ZnO rod film prepared from different seed solvent and alkali concentrations was investigated. Furthermore, the PEDOT:PSS/ZnO rod conductive films not only maintained the property of good conductivity but also improved its performance in application, such as hydrophobic property, weather stability, pH buffering ability, and acid/alkali resistance.

1. Introduction

Zinc oxide (ZnO) is an important semiconductor, optical and electronic material due to its large band gap energy (3.37 eV) and large exciting binding energy (60 meV) at room temperature [1]. The ZnO film is transparent in the wavelength range 400–1000 nm and exhibits a sharp absorption at 380 nm belonging to UV light range. Meanwhile, the electric conductivity and optical transmittance make ZnO applied in large areas such as solar cell, photonic devices, gas sensors and transparent conductors [2–4]. The particle size, purity and morphology of ZnO greatly influence its optical and electric properties; therefore, ZnO nanostructure has attracted notable attention on the creation of highly oriented arrays [5,6].

In order to obtain one-dimension and well aligned growth of ZnO structure, various methods are used to create ZnO rods and wire with the aspect ratio of length-to-width from 50 to 100, such as template against anodic alumina membranes [7], pulsed laser deposition [8], sol–gel [9], homogeneous precipitation [10], and chemical vapor deposition [11]. Even though these methods can obtain high quality and good array of ZnO rods, the expensive cost from high temperature or high energetic consumption limits its application.

Recently, Govender et al. produced ZnO nanocolumns on tin oxide glass by using aqueous solution at low temperature [12]. It was proposed by Guo that high aspect ratio ZnO rods were prepared via hydrothermal method on indium tin oxide substrates, which were pre-modified with ZnO nanoparticles at low temperature [13]. Further, Lu found that the morphology of ZnO powders was related to the reacting temperature and molar concentration during the synthesizing process [14]. Under different reacting temperatures, ZnO would present as seed and gradually grow from flower-like, ellipsoidal, to rod nanostructure.

Hydrothermal method is one kind of common chemical reactions to prepare nanomaterials from high-temperature aqueous solutions at high vapor pressure, which is also termed hydrothermal synthesis. Meanwhile, the hydrothermal method can reduce the cost and obtain small and uniform dispersion nanoparticles as well.

* Correspondence to: W.-Y. Chiu, Department of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 106, Taiwan. Tel./fax: +886 2 23623259.
** Correspondence to: C.-F. Lee, Department of Cosmetic Science, Chia Nan University of Pharmacy and Science, No. 60, Sec. 1, Erh-jen Rd., Jen-te, Tainan, Taiwan. Tel./fax: +886 6 2667324.
E-mail addresses: ycchiu@ntu.edu.tw (W.-Y. Chiu), D766@ms8.hinet.net (C.-F. Lee).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.11.101

The conductive polymer developments began from 1970s after Shirakawa et al. discovered polyacetylene with high conductivity [15–18]. Subsequently, the Raman spectroscopy was used to study the doping mechanism of bromine and iodine for conductive polymer [19]. In the past 30 years, various conductive polymers were discovered and researched in order to solve the disadvantages and improve the application of polyacetylene. The study of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) conductive polymer was conducted in Bayer Lab in early 1990s. So far, PEDOT:PSS has become one of the commercial conductive polymer products around the world.

There are number of ways to synthesize PEDOT, such as oxidative chemical polymerization, electrochemical polymerization, and in situ polymerization. PEDOT films possess high conductivity (400–600 S/cm), transmittance, electrochemical stability and thermo chemical stability. However, the solubility of PEDOT narrowed its advanced application. Therefore, in 1990, Bayer lab researchers discovered that 3,4-ethylenedioxythiophene (EDOT) could template on a water-soluble polyelectrolyte, poly(styrenesulfonate) (PSS), by oxidative polymerization to form a well-dispersed conductive dispersion PEDOT:PSS in water [20]. In the reaction, Kirchmeyer and Reuter found that PEDOT would use ionic bond to attach PSS closely during polymerization, which showed short segments about 6–18 repeating units [21–23].

Despite the excellent conductivity and transparency PEDOT:PSS possesses, the water resistance and weather stability of PEDOT:PSS conductive film were very poor. It was presented that the conductivity of PEDOT:PSS films would decrease rapidly under high temperature or high humidity condition [24,25]. Consequently, it was crucial to improve the hydrophobic ability of PEDOT:PSS film for the advanced application. The hydrophobic property could be improved simultaneously by two sorts of methods: low surface free energy composition and surface geometry structure. In this research, PEDOT:PSS film was combined with ZnO rods to make a geometry structure array to prevent water droplet to involve into the hydrophilic PEDOT:PSS conductive film. The resulting PEDOT:PSS/ZnO rod film not only had good hydrophobic property and weather stability, but also possessed excellent pH buffering ability and acid/alkali resistance.

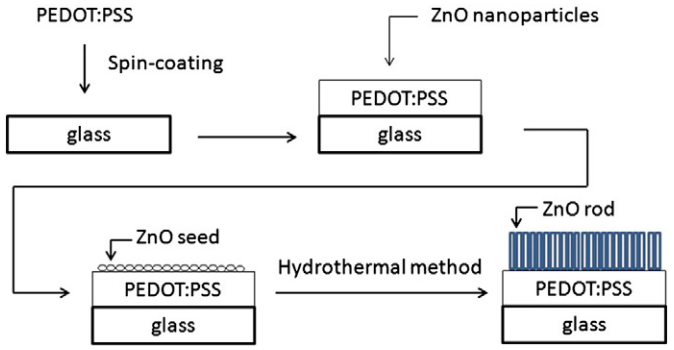
2. Experiments

2.1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), sodium hydroxide (NaOH), methanol, ethanol, hexamethylenetetramine (HMTA), potassium persulfate (KPS, 99 + %), and iron (III) sulfate pentahydrate ($Fe_2(SO_4)_3 \cdot 5H_2O$) were all obtained from Acros. Poly(4-styrenedsulfonic acid) (PSS, MW = 75,000, 18 wt.% aqueous solution) and 3,4-ethylenedioxythiophene (EDOT) were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) was purchased from Scharlau. The buffer solutions with pH 3, 5, and 7 were phthalate aqueous solution and buffer solutions with pH 9 and 11 were borate aqueous solution, which all obtained from Acros. All reagents were used as received. Deionized water (18.2 MΩ·cm) was used throughout the work.

2.2. Synthesis and purification of PEDOT:PSS conductive dispersion

The overall flowchart to prepare PEDOT:PSS/ZnO rods is shown in Scheme 1. PEDOT:PSS conductive dispersion was synthesized using the polymeric template PSS as the charge-balancing counter ions. 1.736 g of PSS (18 wt.%) together with 11.698 g of deionized water was mixed and magnetically stirred for 3 min. Subsequently, 0.125 g of EDOT was added into the mixture and then treated by sonication for 10 min to form the emulsion. The emulsion was then stirred continuously and purged with nitrogen at room temperature. The initiator



Scheme 1. The flowchart of preparing hydrophobic PEDOT:PSS/ZnO rod conductive film.

solutions, 0.2835 g of KPS mixed with 5 g water and 0.0019 g of $Fe_2(SO_4)_3.5H_2O$ mixed with 1 g water, were poured into the flask to start the reaction. After the reaction proceeded at room temperature for 7 h, an additional KPS solution (0.0473 g of KPS dissolved in 2 g of water) was added to complete the reaction. The reaction proceeded for 24 h to obtain the PEDOT:PSS conductive dispersion.

Subsequently, the PEDOT:PSS dispersion was further purified by dialysis with deionized water for four days and the water was renewed every day. The dialysis membrane (MW cutoff = 3500 and flat width = 47 mm) was purchased from Membrane Filtration Product Incorporated. After the dialysis process, the PEDOT:PSS dispersion was placed in a 95 °C oil bath equipped with a reflux condenser for 2 h and then further homogenized for 15 min by using a Hielscher Ultraschallprozessor (Frequency cycle = 0.5, amplitude = 70%) to fully re-disperse the PEDOT:PSS polymer chains in water. Furthermore, the purified PEDOT:PSS dispersion was spin-coated on a glass substrate at 1000 rpm for 50 s, and followed by drying in the oven at 110 °C for 3 min. Then, the dried film was dipped in DMSO for 10 min, and dried again at 110 °C for another 15 min for further use.

2.3. Preparation of PEDOT:PSS/ZnO rod film

The procedures for preparing PEDOT:PSS/ZnO rod film were composed of two steps: (1) the synthesis of ZnO nanoparticles and (2) ZnO rod growth by using hydrothermal method. In the first step, two flasks, which contained $Zn(NO_3)_2 \cdot 6H_2O$ methanol solution and $Zn(NO_3)_2 \cdot 6H_2O$ ethanol solution (0.238 g of $Zn(NO_3)_2 \cdot 6H_2O$ dissolved in 30 ml of methanol or ethanol respectively) were prepared and magnetically stirred at the temperature of 60 °C. Then, the NaOH methanol solution or NaOH ethanol solution (0.128 g of NaOH dissolved in 10 ml of methanol or ethanol) were dropped into the corresponding flasks respectively and continuously stirring at 60 °C for 2 h. After the reaction, the ZnO nanoparticles dispersed in methanol and ethanol were obtained. Finally, the ZnO nanoparticles dispersed in methanol

Table 1
Symbols and ingredients for the synthesis of ZnO rods.

Sample code	Seed solvent	Growth of ZnO rods		
		$Zn(NO_3)_2 \cdot 6H_2O$ (g)	HMTA (g)	Deionized water (g)
M1	Methanol	0.119	0.056	40
M2		0.119	0.112	40
M3		0.238	0.112	40
M4		0.238	0.224	40
E1	Ethanol	0.119	0.056	40
E2		0.119	0.112	40
E3		0.238	0.112	40
E4		0.238	0.224	40