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Effects of inorganic acid in DBSA-PANI polymerization on transparent PANI-SiO_2 hybrid conducting films

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ABSTRACT

Transparent hybrid conducting films were prepared by dodecylbenzene sulfonic acid-doped polyaniline (DBSA-PANI) and 3-glycidoxypropyltrimethoxysilane (GPTMS) through a sol–gel process. DBSA-PANI was synthesized via emulsion polymerization, and inorganic acid (nitric or sulfuric acid) was added to adjust the structure of the emulsion system and obtain the higher conductivity of polyaniline. When nitric acid was used in the emulsion system, structure of the hybrid films became more stable and sheet resistance of the hybrid films was lower. Visible light transmittance of the hybrid films was over 75%. Various properties of the hybrid material were analyzed by the infrared spectra (IR), UV–visible absorption spectra, thermogravimetric analysis (TG) and digital four-point probe meter.

1. Introduction

Transparent conducting film is an important kind of photoelectric material, which can be used in flat panel displays, low-e windows, photovoltaics, electrochromic devices and anti-static coatings [1]. Many kinds of inorganic transparent conducting films [2–4] have been investigated due to their high electrical conductivity and high transparency in the visible region. However, they have some disadvantages, for instance, poor adhesion property on the flexible substrate, and hard to be deposited on the polymer substrate due to the high synthetic temperature. Organic conducting material [5–7] is a kind of significant conducting material. However, they also have some disadvantages, such as low thermal stability and poor mechanical properties, which limit their further application. Organic and inorganic hybrid transparent conducting films [8,9] gather the advantages of organic and inorganic materials to obtain the flexible and unbroken transparent conducting films.

Polyaniline (PANI) is an important conducting polymer because of its environmental stability, low cost and promising electrical and optical properties [10,11]. Among various methods of synthesis of conducting polyaniline, emulsion polymerization is known to be one of the most effective methods. Dodecylbenzene sulfonic acid (DBSA) usually works as both surfactant and protonating agent. However, conductivity of polyaniline synthesized by the emulsion polymerization is strongly affected by the pH value of the emulsion solution. To decrease the acidity of the emulsion system and get the higher conductivity of polyaniline, the molar ratio of DBSA/aniline has to be higher than the theoretical value (0.5), which results in the excess DBSA remaining in the polyaniline chains [12,13] and affects the structure of the hybrid films. If the obtained DBSA-PANI is washed several times to remove the excess DBSA, it will lead to the de-doping of DBSA from polyaniline and decrease the conductivity of material [14]. The problem can be solved through adding inorganic acid into the emulsion solution, which increases the acidity of the emulsion system. Furthermore, inorganic acid also adjusts the structure of the emulsion system and becomes the dopant for polyaniline, which enhances the conductivity and visible light transmittance of the soluble polyaniline.

In this work, DBSA-PANI was prepared via the emulsion polymerization and a certain amount of nitric or sulfuric acid was added. Then, the obtained DBSA-PANI was reacted with 3-glycidoxypropyltrimethoxysilane (GPTMS) through the sol–gel route. PANI-SiO_2 transparent hybrid conducting films were finally obtained. The effects of different concentration of nitric or sulfuric acid added in the emulsion system on the structure, transmittance

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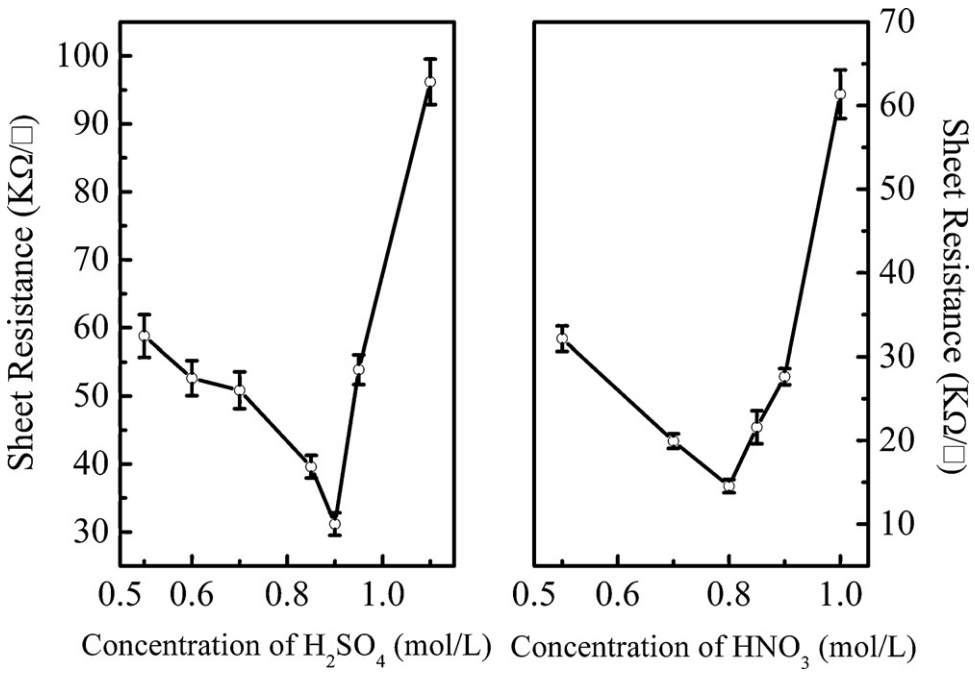

Fig. 1. Sheet resistances of PANI-SiO_2 hybrid films with different concentration of sulfuric acid and nitric acid added in the emulsion system.

and conductivity of the hybrid films were investigated by a combination of testing techniques.

2. Experimental

In the typical emulsion polymerization, 0.01 mol aniline and 100 mL of 2.5 wt% aqueous DBSA were taken in a 250 mL reaction vessel. Then, 20 mL of a certain concentration of nitric or sulfuric acid was added. The emulsion solution was initiated by adding 50 mL of aqueous ammonium persulfate ($(NH_4)_2S_2O_8$) solution and stirred for 6 h at room temperature (the molar ratio of aniline to $(NH_4)_2S_2O_8$ was 1). Finally, the polymerization was terminated by pouring $CHCl_3$ into the emulsion system and dark green DBSA-PANI powder was finally recovered.

DBSA-PANI powder was dissolved in the mixed solvent of $CHCl_3$ and m-cresol, and silica sol precursor solution was prepared with GPTMS and acetic acid by the way described earlier [15]. Then, two kinds of solution were mixed and stirred for 6 h at room temperature. The concentration of precursor solution was 0.5 mol/L and the weight ratio of DBSA-PANI to SiO_2 was 3/7.

PANI-SiO_2 hybrid films were deposited by dip-coating method on glass slides and dried in air at room temperature for 5 min and dried at 80 °C for 30 min, repeating the procedure for each layer. Five layers were needed.

The structure and properties of PANI-SiO_2 films were studied by the following methods. Infrared spectra of the hybrid gels were measured with Nicolet AVATAR360 FT-IR spectrophotometer in the range of 4000–400 cm^{-1}. Visible light transparence and UV–visible absorption spectra were recorded on the UV/VIS spectrometer S53/54. Thermal stability of the hybrid gels was investigated by the thermogravimetric measurements. The samples were heated up to 700 °C with the rate of 10 °C min^{-1}. SX1934 digital four-point probe meter in the range of 2×10^{-3} to 2×10^6 Ω/□ was used to measure sheet resistance of the hybrid films.

3. Results and discussion

Sheet resistances of PANI-SiO_2 hybrid films with different concentrations of nitric acid and sulfuric acid added in the emulsion system are shown in Fig. 1. Sheet resistance of the hybrid films with no inorganic acid added in the emulsion solution is 137 kΩ/□. By increasing concentrations of sulfuric acid and nitric acid to 0.9 mol/L and 0.8 mol/L, sheet resistances of the hybrid films decrease to 31.17 kΩ/□ and 14.55 kΩ/□, respectively. Then with a further increase of the concentrations of inorganic acids, sheet resistances increase. DBSA-PANI is the main conducting component in the hybrid films. Furthermore, it is reported that conductivity of DBSA-PANI is affected by the pH value of the emulsion solution when DBSA-PANI is polymerized. The conductivity of DBSA-PANI is high when pH value is close to 0 [12,16]. However, acidity of DBSA is low. When the ratio of DBSA to aniline is raised to increase the acidity of the emulsion solution, large amounts of the excess DBSA remain in the polyaniline chains. That affects the structure of the hybrid films. Moreover, the conductivity of polyaniline can also be improved by the high extent of aggregation of aniline and high diffusion rate of oxidant, when polyaniline is synthesized in the emulsion system [17]. At a higher concentration of DBSA, more "gel-like" structures are formed when aniline is reacted with DBSA in the process of the emulsion system, which increases the viscosity of the emulsion system. The higher viscosity of the emulsion system increases the extent of aggregation of aniline and decreases the diffusion rate of oxidant. When inorganic acid is added into the emulsion solution, a part of aniline molecule will be reacted with inorganic acid and less "gel-like" structures will be formed, which decreases the viscosity of the emulsion system. As a result, the extent of aggregation becomes smaller, but the diffusion rate of oxidant is accelerated. Therefore, it can be thought that inorganic acid has the contrary effects on the conductivity of polyaniline. Thus, sheet resistance of the hybrid films exhibits a minimal value due to the contrary effects. Also, when the added concentration of inorganic acid is too high, inorganic acid will be incorporated into the polymer chains and become the main dopant for polyaniline, which makes the polyaniline insoluble. Moreover, de-doping of small molecular inorganic acid is easier when polyaniline is reacted with inorganic precursor. The structures have been discussed in our earlier works [15,18]. The water molecules are formed during the processes of hydrolysis-condensation reaction of GPTMS and hydrogen bonding formation between polyaniline and terminal hydroxyl group of inorganic matrix in the sol–gel route. The water molecule may lead to the de-doping of unstable and volatile inorganic acids. Therefore, sheet resistances of the hybrid films increase fast, when concentrations of nitric acid and sulfuric acid are higher than 0.8 mol/L and 0.9 mol/L, respectively. Furthermore, sheet resistance of the hybrid films is higher, when 0.9 mol/L sulfuric acid is used in the emulsion solution. The reason for the change of sheet resistance of the hybrid films is going to be further discussed.

Fig. 2 shows the UV–visible absorption spectra of PANI-SiO_2 hybrid films with no inorganic acid, 0.8 mol/L nitric acid and