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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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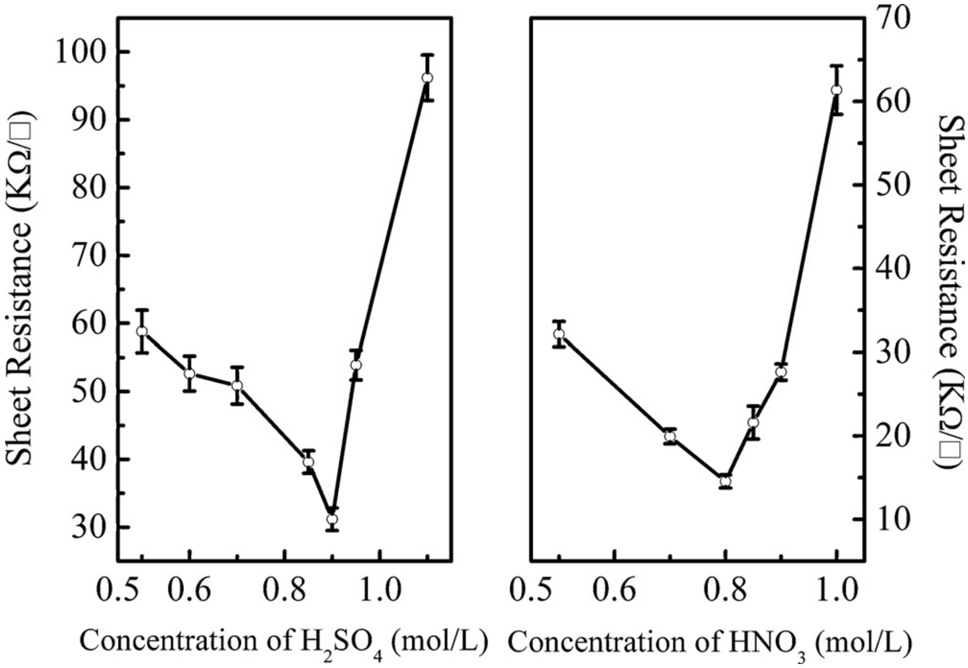

Fig. 1. Sheet resistances of PANI-SiO_2 hybrid films with different concentration of sulfuric acid and nitric acid added in the emulsion system.

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

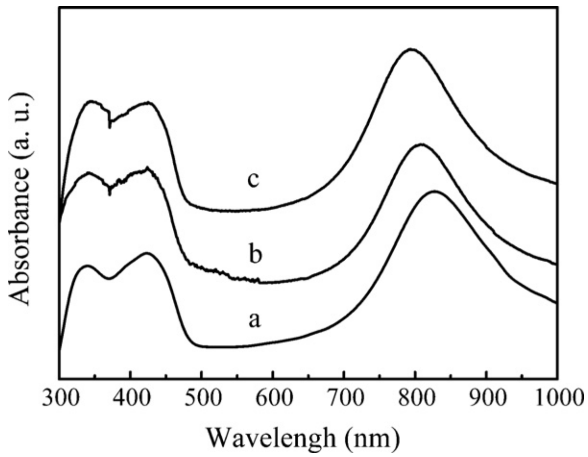

Fig. 2. UV–visible absorption spectra of PANI-SiO_2 hybrid films with (a) no inorganic acid, (b) 0.8 mol/L nitric acid and (c) 0.9 mol/L sulfuric acid added in the emulsion solution.

0.9 mol/L sulfuric acid added in the emulsion solution. The absorption peak in the range of 800–820 nm is assigned to n–π^* transition for the cis-isomer of the azo linkage [19,20]. After inorganic acid is added into the emulsion system, a clear blue shift is observed, which is due to the decrease of conjugation length of DBSA-PANI [21,22]. When inorganic acid is added into the emulsion solution, polyaniline is co-doped with DBSA and inorganic acid. Partly doped DBSA is replaced by the inorganic acid and more excess DBSA is existed in the emulsion solution, which results in the screening effect of H^+ and anions of partly dissociation of excess DBSA [23]. The screening effect leads to the coil-like conformation of polyaniline, which decreases the effective conjugation length of polyaniline. Furthermore, a much clearer hypsochromic shift is observed, when 0.9 mol/L sulfuric acid is added into the emulsion solution. Therefore, it can be believed that more doped DBSA is replaced and becomes the excess DBSA, which means the doping of sulfuric acid for polyaniline is easier in this case.

The infrared spectra (IR) of PANI-SiO_2 hybrid gels with no inorganic acid, 0.8 mol/L nitric acid and 0.9 mol/L sulfuric acid added in the emulsion solution are shown in Fig. 3. The peaks at 1610 and 1494 cm^{-1} are corresponding to C=C ring stretching of quinoid and benzenoid structure, respectively [24,25]. The peak in the range of 3400–3100 cm^{-1} is due to the hydrogen bonding between amines (–NH–) and protonated imines (–NH^+) in the regularly aligned polyaniline chains [26,27]. The peak at 1106 cm^{-1} is assigned to the Si–O–Si group, which indicates the formation of hybrid cross-linking network. The double peak at 2947 and 2878 cm^{-1} is attributed to the aliphatic C–H stretching mode, which is due to the long alkyl tail of DBSA [28]. It is found that the peaks of C=C ring stretching of quinoid and benzenoid become stronger when inorganic acid is added into the emulsion system, which means that more conducting polyaniline is polymerized. However, the peak at 3461 cm^{-1} for hybrid gels with no inorganic acid shifts to 3306 cm^{-1} for hybrid gels with 0.9 mol/L sulfuric acid and becomes weaker (Fig. 3a, c). It means the hydrogen bonds between regular polyaniline chains are weakened because of the screening effect of DBSA for polyaniline. As DBSA-PANI with a coil-like conformation is harder to interact with the inorganic precursor [29], the hybrid structure of the obtained films is affected and stability of the hybrid films becomes lower.

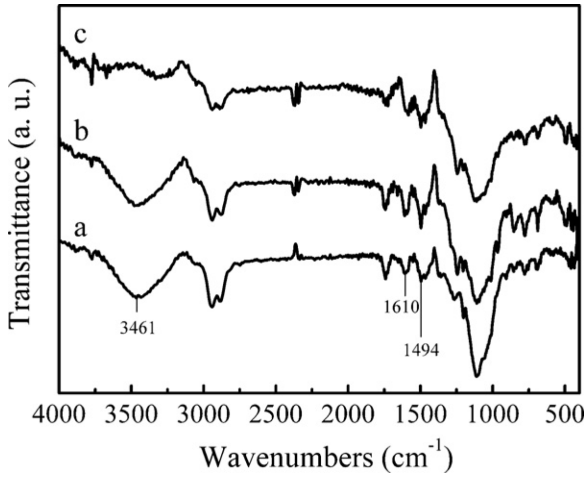

Fig. 3. Infrared spectra (IR) of PANI-SiO_2 hybrid gels with (a) no inorganic acid, (b) 0.8 mol/L nitric acid and (c) 0.9 mol/L sulfuric acid added into the emulsion system.

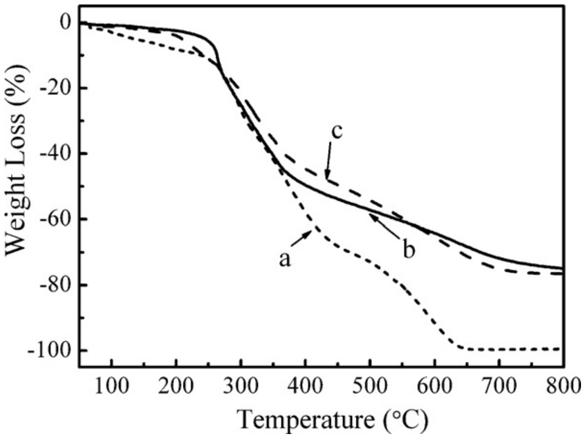

Fig. 4. Thermogravimetric analysis (TG) of (a) DBSA-APNI with 0.8 mol/L nitric acid, PNAI-SiO_2 hybrid gels with (b) 0.8 mol/L nitric acid and (c) 0.9 mol/L sulfuric acid added in the emulsion solution.

The thermogravimetric curves (TG) of conducting polyaniline with 0.8 mol/L nitric acid and PNAI-SiO_2 hybrid gels with 0.8 mol/L nitric acid and 0.9 mol/L sulfuric acid added in the emulsion solution are shown in Fig. 4. As shown in TG curve of polyaniline with 0.8 mol/L nitric acid (Fig. 4a), about 10.8% weight loss is observed between 100 °C and 240 °C, which is due to the de-doping of DBSA. The de-doping of DBSA leads to more excess DBSA in the polyaniline chains, which affects the thermal stability of polyaniline at lower temperature. When the conducting polyaniline is reacted with inorganic precursor, the polyaniline chain is dispersed into the stable –Si–O–Si– network structure through the hydrogen bonding interaction between polyaniline and the terminal hydroxyl group of inorganic precursor, which improves the thermal stability of the samples. Thus, there is no clear weight loss for the PNAI-SiO_2 hybrid gels with 0.8 mol/L nitric acid at lower temperature (Fig. 4b). Furthermore, the whole weight loss of the hybrid gels is less than that of the conducting polyaniline. Moreover, it is also observed that the thermal stability of the hybrid gels with 0.8 mol/L nitric acid is better than ones with 0.9 mol/L sulfuric acid (Fig. 4b, c). The decomposition temperature of DBSA [30] for hybrid gels with 0.8 mol/L nitric acid is from 240 °C to 370 °C, while the decomposition temperature for hybrid gels with 0.9 mol/L sulfuric acid begins at 190 °C. Then the weight loss up to 700 °C is corresponding to the decomposition of polyaniline itself and total weight loss for the hybrid gels with 0.9 mol/L sulfuric acid is also more than that with 0.8 mol/L nitric acid. The result is consistent with the analysis of IR (Fig. 3). Moreover, it has little influence on the decomposition temperature of samples with the concentration of nitric acid increasing and the hybrid gels with 0.8 mol/L nitric acid are most thermally stable (Fig. 5).

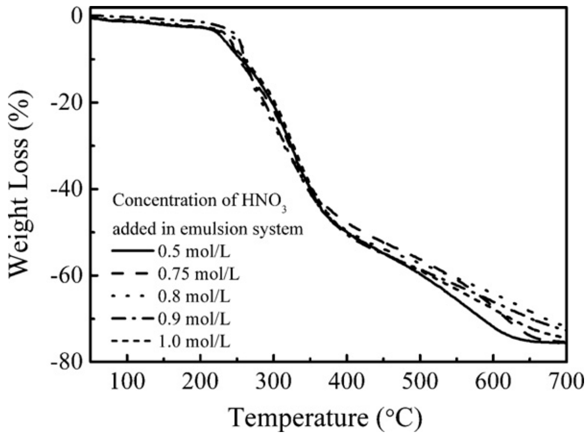

Fig. 5. Thermogravimetric analysis (TG) of PNAI-SiO_2 hybrid gels with different concentration of nitric acid added in the emulsion solution.

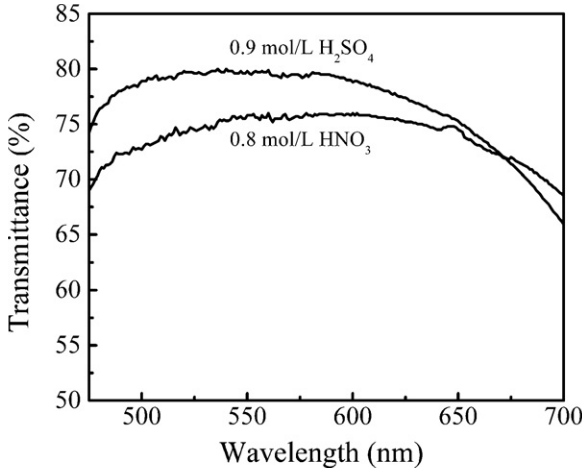

Fig. 6. Optical transmittance of PANI-SiO_2 hybrid films with 0.8 mol/L nitric acid and 0.9 mol/L sulfuric acid added in the emulsion solution.

Optical transmission spectra (T) of the PANI-SiO_2 hybrid films with 0.8 mol/L nitric acid and 0.9 mol/L sulfuric acid are shown in Fig. 6. The visible light transmittances of the hybrid films with sulfuric acid and nitric acid reach 80% and 75%, respectively. Therefore, the obtained films are transparent. However, in the earlier analysis (Fig. 2), it has been known that doping of sulfuric acid for polyaniline is easier and sulfuric acid will replace the DBSA, when sulfuric acid is add into the emulsion solution. Therefore, a smaller amount of DBSA in the hybrid films increases the transparence of the hybrid films [31].

4. Conclusions

In this work, DBSA-PANI was synthesized by the emulsion polymerization, which was using nitric acid or sulfuric acid to adjust the structure of the emulsion system. Then, DBSA-PANI was reacted with GPTMS through the sol–gel process to obtain the hybrid transparent conducting PANI-SiO_2 films. Inorganic acids improve the structure of the emulsion system and increase the conductivity of PANI-SiO_2 hybrid films. However, if too much inorganic acid is added into the emulsion solution, it will become the main dopant for polyaniline and replace the DBSA and affect the stability of the hybrid films. Therefore, when concentrations of nitric acid and sulfuric acid are 0.8 mol/L and 0.9 mol/L, sheet resistances of the hybrid films reach 14.5 kΩ/□ and 31.1 kΩ/□, respectively. Additionally, doping and de-doping of sulfuric acid for polyaniline are much easier comparing with nitric acid.

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