

# Effects of content of polyaniline doped with dodecylbenzene sulfonic acid on transparent PANI-SiO<sub>2</sub> hybrid conducting films

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## ABSTRACT

Transparent PANI-SiO<sub>2</sub> conducting films were prepared by hybrid of dodecylbenzene sulfonic acid-doped polyaniline (DBSA-PANI) and 3-glycidoxypropyltrimethoxysilane (GPTMS) through sol-gel route. The influence of content of DBSA-PANI on the structural, electrical and optical properties of the films was investigated. Sheet resistance of the hybrid films was 5.1 kΩ/□ and visible light transmittance was 75%, when the content of DBSA-PANI was 30 wt.%. Thermogravimetric analysis (TG) showed that the obtained films were thermally stable under 120 °C and optical bandgap of the hybrid films was determined from Tauc plots.

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## 1. Introduction

As an important kind of photoelectric material, transparent conducting films have attained many interests. These films can be used in variety of optoelectronic devices such as displays, solar cells and low-e windows [1]. Many kinds of inorganic transparent conducting films have been investigated, such as ITO [2–4], ATO [5,6] and ZAO [7,8], which are high electrical conductivity and high transparency in visible region. However, these films also have some disadvantages, such as poor adhesion property on flexible substrate and high synthetic temperature.

Conducting polymers is also a kind of conducting material. Among various conducting polymers, polyaniline (PANI) has become promising organic air stable-conducting polymer due to its good flexibility, low cost, oxidative stability and unique conduction mechanism [9–11]. However there are some major drawbacks which limit their application, such as low thermal and chemical stability and poor mechanical properties. Organic and inorganic

hybrid materials can obtain the flexibility, weight-light and unbroken transparent conducting films.

Sol-gel process is a suitable technology for preparing the organic-inorganic hybrid films because of low cost, high efficiency, good uniformity and easy treatment of large and complex shape substrates [12,13]. Sols for thin films deposition are mostly prepared from alkoxide precursors such as tetraethyl orthosilicate (TEOS), nevertheless, under acidic conditions, the silanol groups of TEOS are prone to self-condense to form –Si–O–Si– units than form hydrogen bonds with the organic polymers during the sol-gel process [14], which makes it difficult to obtain robust and intact films. On the other hand, water and ethanol are necessary reagent and solvent for sol-gel process in earlier work, but common DBSA-PANI does not dissolve in them. Although water-soluble polyaniline has been reported [15,16], the preparation of water-borne polyaniline is more complex and conductivity of water-soluble polyaniline is lower.

In this work, 3-glycidoxypropyltrimethoxysilane (GPTMS) was used as alkoxide precursors, since its epoxy ring can form a hydroxyl group in acid conditions, which leads to the formation of hydrogen bonds with DBSA-PANI. The hydrolysis-condensation process of GPTMS was started and catalyzed by acetic acid instead of water. The effects of content of DBSA-PANI on the structure, transmittance and conductivity of the hybrid films were investigated by a combination of testing techniques.

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## 2. Experimental

The soluble conducting polyaniline was prepared via emulsion polymerization. For the emulsion polymerization of DBSA-PANI, 0.01 mol aniline and 100 ml of 2.5 wt.% aqueous dodecylbenzenesulfonic acid (DBSA) were taken in a 250 ml reaction vessel and 20 ml of 1 M aqueous hydrochloric acid (HCl) solution was added to decrease the acidity of system. Then, 50 ml of aqueous ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) solution was added dropwise as the initiator in the solution to start the polymerization. The polymerization was allowed to proceed for 6 h with constant stirring at room temperature and terminated by pouring CHCl<sub>3</sub> into the emulsion system. The dark green DBSA-PANI powder was finally recovered.

DBSA-PANI powder was added to the mixed solvent of CHCl<sub>3</sub> and *m*-cresol, and stirred for 3 h at room temperature. Silica sol-gel precursor solution was prepared by the reaction of GPTMS and acetic acid (HAc), and stirred for 2 h. The sol-gel precursor solution was then mixed with the DBSA-PANI solution, and aged for 6 h at room temperature. A constant GPTMS/HAc/*m*-cresol molar ratio was 1/2.5/0.2, and the weight ratio of DBSA-PANI/(SiO<sub>2</sub> + DBSA-PANI) varied from 22 to 40 wt.%, which was marked with P22 to P40.

Dip-coating method was performed as follows: glass slides cleaned by ultrasonic oscillation were immersed in the hybrid solution for 20 s, then withdrawn vertically from the solution at the rate of 1 mm s<sup>-1</sup>. The five layers were needed. After each dip, the samples were dried in air at room temperature for 5 min and then dried at 80 °C for 30 min and cooled down at room temperature.

Thermal stability of hybrid gels was investigated by thermogravimetric measurements. The sample was heated up to 700 °C with the rate of 10 °C min<sup>-1</sup>. The transparence and UV-visible absorption spectra were recorded with UV/VIS spectrometer S53/54. SX1934 digital four-point probe meter in the range of 2 × 10<sup>-3</sup> to 2 × 10<sup>6</sup> Ω/□ was used to measure sheet resistance of hybrid films.

## 3. Results and discussion

UV-vis absorption spectra of DBSA-PANI in chloroform, mixed solvent of chloroform and *m*-cresol, and PANI-SiO<sub>2</sub> sol solution with 30 wt.% DBSA-PANI contents (P30 solution) are shown in Fig. 1. Peaks around 340 and 440 nm are assigned to π-π\* transition of benzenoid rings of DBSA and polaron band transition in the PANI chains, respectively. The absorption band at the wavelength longer than 700 nm is corresponding to n-π\* transition for the *cis*-isomer of the azo linkage [17]. *m*-Cresol is a kind of second dopant for polyaniline, which can promote the conformational

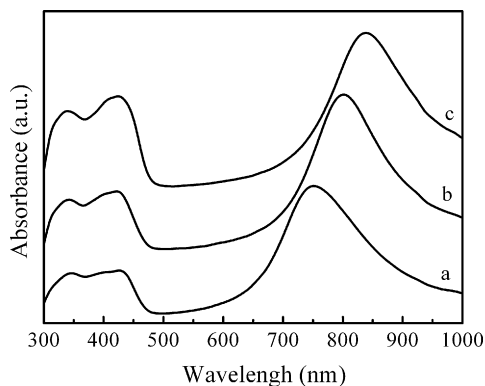


Fig. 1. UV-vis absorption spectra of (a) DBSA-PANI in chloroform, (b) DBSA-PANI in mixed solvent of CHCl<sub>3</sub> and *m*-cresol, (c) PANI-SiO<sub>2</sub> sol solution with 30 wt.% DBSA-PANI contents (P30 solution).

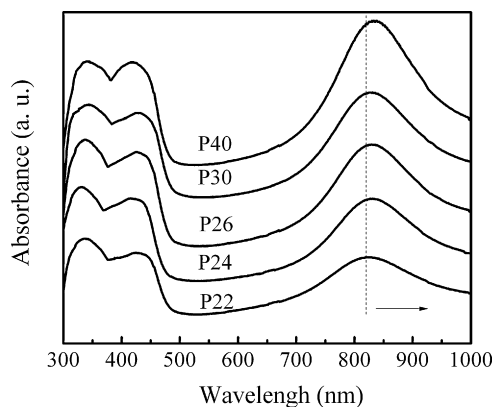


Fig. 2. UV-vis absorption spectra of PANI-SiO<sub>2</sub> hybrid films with different content of DBSA-PANI.

charges of polyaniline backbone from a coil-like conformation to a rod-like conformation and elongate the effective conjugation length. When *m*-cresol was added, the delocalized π bonds on the phenyl group of *m*-cresol induce π-π\* interaction with the phenyl group in the backbone of PANI and the hydroxyl group of *m*-cresol builds strong bonding with amine group of PANI. Therefore, after adding *m*-cresol into solvent, the absorption peak assigned to n-π\* transition shifts from 750 to 800 nm (Fig. 1a and b). Furthermore, 3-glycidoxypropyltrimethoxysilane (GPTMS) is an organoalkoxysiloxane with an epoxy ring, which forms a hydroxyl group in acid conditions. When GPTMS is reacted with DBSA-PANI, the hydroxyl group of inorganic precursors will also form hydrogen bond with DBSA-PANI. As a result, the position of absorption peak of n-π\* transition shifts to 837 nm in the UV-vis spectrum of P30 sol solution (Fig. 1c).

The UV-vis absorption spectra of PANI-SiO<sub>2</sub> hybrid films with different content of DBSA-PANI (Fig. 2) are similar to the spectrum of P30 sol solution. The absorption peak for n-π\* transition shows a red shift from 820 to 837 nm with an increase in the content of DBSA-PANI from 22 to 40 wt.%. The bathochromic shift is reasonable considered that more hydrogen bonds are formed with content of DBSA-PANI increasing and conjugation length of DBSA-PANI increases in the hybrid films [18,19], which can form more integral conductive network during the sol-gel process.

Sheet resistance of PANI-SiO<sub>2</sub> hybrid films with different content of DBSA-PANI is shown in Fig. 3. Sheet resistance decreases sharply with an increase in content of DBSA-PANI and the percolation threshold is found at 30 wt.% content of DBSA-PANI, where the sheet resistance of hybrid films is low as 5.1 kΩ/□. It has been dis-

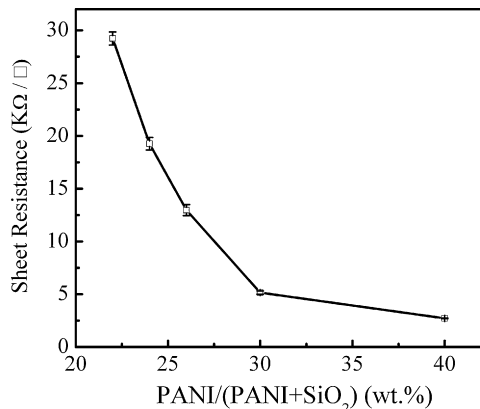


Fig. 3. Sheet resistance of PANI-SiO<sub>2</sub> hybrid films with different content of DBSA-PANI.

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