

Humidity paper sensor fabricated by inkjet-printing photosensitive conductive inks

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Abstract: 7-(4-vinylbenzyloxy)-4-methylcoumarin (VM) and maleic anhydride (MA) were polymerized by free radical copolymerization to form the photosensitive alternating copolymer P(VM-alt-MA) (PVMA) and PVMA was used as the soft template to achieve the oxidative polymerization of poly(3, 4-Ethylenedioxythiophene) (PEDOT) to obtain PEDOT:PVMA. Then we used this PEDOT:PVMA aqueous dispersion as the inks for fabricating humidity sensor by inkjet-printing on a paper substrate. This paper sensor can selectively and reversibly detect the water vapor with significant linear relationship.

Keywords: PEDOT, photosensitive, inkjet-printing, humidity sensor

1. Introduction

High electric conductivity, narrow band gap, great environmental stability and high transmittance^[1,2] have given poly(3,4-Ethylenedioxythiophene) (PEDOT) a very bright future in a variety of applications such as OLED^[3], OPV^[4] and sensors^[5]. However, the solubility of PEDOT limited the application of this material. To solve this problem, the water-soluble surfactant was introduced into the system as the soft template of the oxidative polymerization of PEDOT. The surfactant can help disperse PEDOT segments in water and act as a dopant of PEDOT in the presence of counter-ion. Poly(styrenesulfonate) (PSS) is a significant soft template for the polymerization of PEDOT. The PEDOT:PSS dispersion has excellent colloid stability and the conductivity of PEDOT:PSS film can reach to 300 S/cm, which can be as a commercial product used in industrial applications^[6,7].

However, the rigid structure of PEDOT and the strong water absorption of the sulfonate groups led to the low water resistance of PEDOT:PSS which limited the application of these materials. Many research teams have tried to solve this problem by building the cross-linked structure, which can defer the infiltration of water. Thermal curing is a common way to form cross-linked films. Yin et al. synthesized a novel thermal curable template by introducing thermal cross-linkable monomer unit into the PSS chain. In their research, sodium 4-styrenesulfonate (SSNa) and N-(methylol acrylamide) (NMA) were copolymerized to form the thermally curable copolymer P(SS-NMA). Then the P(SS-NMA) was used as soft template to form the

PEDOT:P(SS-NMA) dispersion. The thermal cross-linked structure led to less conductivity blight of the PEDOT:P(SS-NMA) film which compared with the PEDOT:PSS film at high relative humidity. The PEDOT:P(SS-NMA) film could maintain the original shape on the substrate in the water flow while the large portion of the PEDOT:PSS film was broken into pieces^[8].

Recent years, UV curing technology as a new technology is efficient, energy saving and environmental friendly^[9] and has been widely used in electronics^[10], coatings^[11,12], and other fields^[13] to form cross-linked films. Coumarins and their derivatives have been extensively used in various fields including controlling the morphology of micelles or nanoparticles, self-healing materials and controlling the alignment of liquid crystal materials. The cross-linked structure is formed after the photodimerization at the 365 nm UV light irradiation and has the potential to improve the water resistance of the materials. Therefore, in our study, an innovative approach was to synthesize a photosensitive polymeric dispersant with UV curable coumarin groups for PEDOT. Then the PEDOT:PVMA dispersion was used as inks to fabricate the papery humidity sensors by inkjet printing.

7-hydroxy-4-methylcoumarin and 4-vinylbenzyl chloride were undergone the substitution reaction to form the photosensitive styrenic monomer 7-(4-vinylbenzyloxy)-4-methylcoumarin (VM). Then VM and maleic anhydride (MA) were used as monomers to synthesize a photosensitive amphiphilic alternating copolymer P(VM-alt-MA) (PVMA) via conventional radical polymerization. PVMA was used as the soft template to achieve the oxidative polymerization of poly(3, 4-Ethylenedioxythiophene) (PEDOT) meanwhile acted as the dopant of PEDOT, obtaining PEDOT:PVMA aqueous dispersion. The cross-linked PEDOT:PVMA films were transferred to the paper substrate to form a flexible conductive film by inkjet-printing. This film can be used as a novel papery humidity sensor.

2. Experiments

2.1 Materials

7-hydroxy-4-methylcoumarin with a purity of 98% was purchased from Shanghai J&K Chemical Ltd. 4-vinylbenzyl chloride with a purity of 90% was purchased from Sigma-Aldrich Co. LLC. EDOT with a purity of 99% was purchased from Suzhou Yacoo Chemical Reagent Co. Maleic anhydride (MA) with a purity of 99% was purchased from Shanghai Aladdin Reagent Co., Ltd. Anhydrous potassium carbonate, N,N-dimethyl-Formamide (DMF), azodiisobutyronitrile (AIBN), tetrahydrofuran (THF), butylated hydroxytoluene (BHT), ethanol, toluene, hydrochloric

acid, ferric sulfate, ammonium persulfate, phosphorus pentoxide, lithium chloride, potassium acetate, magnesium chloride, sodium chloride and copper sulfate were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd. and used without further purification. PVDF microporous membrane (0.45 μ m) were purchased from Sinopharm Chemical Reagent Shanghai Co. used for purification of PEDOT:PVMA ink.

2.2 Synthesis of PVMA and the PEDOT:PVMA aqueous dispersion

The photosensitive styrenic monomer VM was synthesized as the method of Kim et al ^[14]. The synthetic route of PVMA is shown in Fig. 1. The photosensitive amphiphilic alternating copolymer PVMA was synthesized by radical solution polymerization. A mixture of VM, MA and AIBN dissolved in the mixture solution of THF and DMF was added to a dry 100 mL single-neck flask. The solution was deoxygenated with a nitrogen stream for 15 min at room temperature. The flask was sealed and magnetic stirred in a thermostat bath regulated to 65 °C for 24 h. The final amphiphilic copolymer PVMA was precipitated in toluene, collected by filtration and then re-dissolved in DMF again. After repeating three times, the purified PVMA was dried under vacuum at 70 °C for 72 h.

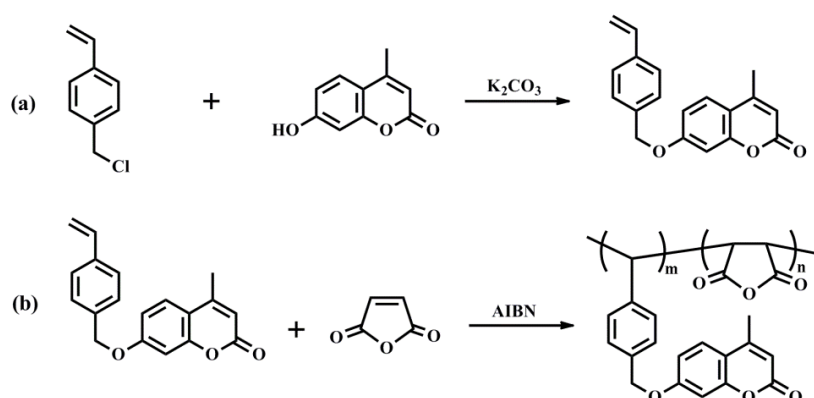


Fig. 1 Synthetic route of PVMA.

The EDOT, PVMA, $(NH_4)_2S_2O_8$ and $(FeSO_4)_3 \cdot 5H_2O$ were dissolved in DI water with the formula, the solid content of the mixture solution is 3.4%. Then the pH values of the mixture were adjusted to 3 by adding the hydrochloric acid. The mixture solution was added to a 100 mL three-neck flask and magnetic stirred in a thermostat bath regulated to 37 °C under the protection of nitrogen for 24 h. Finally, the PEDOT:PVMA aqueous dispersion was dialyzed in water for 3 days and filtered through the PVDF microporous membrane (0.45 μ m) to remove the large aggregates.

2.3 Preparation of the PEDOT:PVMA film

The films of PEDOT:PVMA were constructed on silicon wafers for the water resistance measurements. PEDOT:PVMA films were prepared using droplet coating on clean silicon wafers and dried at 40 °C. The PEDOT:PVMA film was under 365 nm ultrasonic irradiation for 12 h to form the crosslinked PEDOT:PVMA film. For comparison, the uncross-linked PEDOT:PVMA film was prepared without the 365 nm ultrasonic irradiation.

2.4 Fabrication of the PEDOT:PVMA papery humidity sensors

The PEDOT:PVMA aqueous dispersion was used as the based ink to fabricate the papery sensor by inkjet printing. The electrodes were printed to a photographic paper (Eastman Kodak Co.) without any treatment. Inkjet printing was performed on EPSON R230 inkjet printer (Epson (China) Co., Ltd.). The print head cartridges could jet optimally when the surface tension and viscosity of the dispersion solution was approximately 30 mN/m and 18 cps, respectively, based on the measurement of R230 original ink by OCA 40 contact angle measurement (Data Physics Co.) and Brookfield DV-S rotational viscometer (Brookfield Residential Co.). In order to adjust the surface tension and viscosity of the PEDOT:PVMA dispersion solution, some alcohols or other organic reagents was added into the based ink.

2.5 Analysis and Characterization

The chemical structure of VM and PVMA was determined by ¹H-NMR with an AVANCE III 400 MHz Digital NMR spectrometer at 298 K, using DMSO as solvent. Ultraviolet–visible (UV-vis) absorption spectra were recorded on a TU-1901 spectra-photometer (Beijing Purkinje General Instrument). Gel permeation chromatography (GPC) measurement was used to investigate the relative molecular weight and the molecular weight distribution of PVMA with DMF as mobile phase and PS as standard sample by Waters 1515 high performance liquid chromatography. Zeta particle diameter measurements were using a Brookhaven ZetaPALS measurement to study the average particle diameter of the PEDOT:PVMA nanocomposites. Transmission electron microscope (TEM) measurements were carried on a JEOL JEM-2100 microscope operating at 200 KV to study the morphology of the PEDOT:PVMA nanocomposites.

For resistance measurement an Agilent 34401A data acquisition switch equipped with digital multimeter (DMM) and 34401A 20 channel multiplexer switch was used. Data acquisition was done using BenchLink Data Logger Pro. A four wire PEDOT:PVMA sensor pattern on a Kodak photographic paper equipped with sip sockets is connected to an Agilent 34401A multifunction switch/measurement unit. The resistance of the papery sensor was compared with different inkjet

printing layers. To detect the robustness of these sensors, the sensors were folded at different angles and different times for resistance measurement. The equipment was designed to detect the moisture sensitivity of these sensors. Schematic diagram of the equipment was shown in Fig. 2. Different saturated aqueous solutions and desiccant phosphorus pentoxide (P_2O_5) powder were used to achieve the test of moisture sensitivity. Saturated solutions of LiCl, CH_3COOK , $MgCl_2$, K_2CO_3 , NaCl and $CuSO_4$ in a closed vessel were used to yield approximately 11%, 23%, 33%, 43%, 75% and 98% RH levels, respectively. P_2O_5 powder (RH 0%) was used to make a dry air condition for the release of water molecules. The resistance measurement was performed at an ambient temperature of 25 °C. The figure of merit used for the appraisal of moisture sensitivity is the resistance response (R'), determined by $R' = \Delta R/R_0 \times 100\% = (R_{RH} - R_0)/R_0 \times 100\%$, where R_{RH} and R_0 are the electrical resistance of the sensor in the given RH and dry air, respectively.

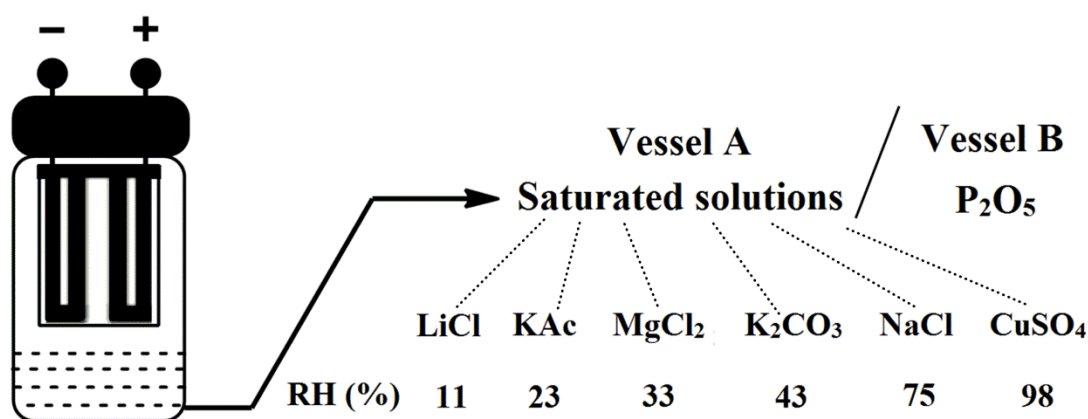


Fig. 2 Schematic diagram of the equipment designed for the detection of the PEDOT:PVMA papery humidity sensors.

3. Results and discussion

3.1 Characterization of PVMA

The 1H -NMR spectra of VM and PVMA are shown in Fig. 3. From the spectrum of VM, $\delta(TMS)$: 2.39(H-8, $-CH_3$); 5.21(H-5, Ar- CH_2 -O); 5.28, 5.30(H-13, CH=); 5.78, 5.82(H-1, Ar-CH=); 6.20(H-9, CO-CH=); 6.69~6.78(H-2, CH=); 7.05~7.14(H-6; H-10, ArH); 7.28~7.58 (H-3; H-4; H-11; H-12, ArH); 7.70(H-7, ArH). From the spectrum of PVMA, $\delta(TMS)$: 1.1~1.9(H-4; H-12, Ar- CH_2 -); 1.9~2.2(H-1; H-2; H-3, CH_2 -); 4.7~5.2(H-11, Ar- CH_2 -O); 5.9~6.2(H-10, CO-CH=); 6.3~7.8(H-5~H-9, ArH), 12.1(assigned to the hydrolysis of MA groups). From the above results, it can be concluded that the expectant polymer have been prepared successfully.

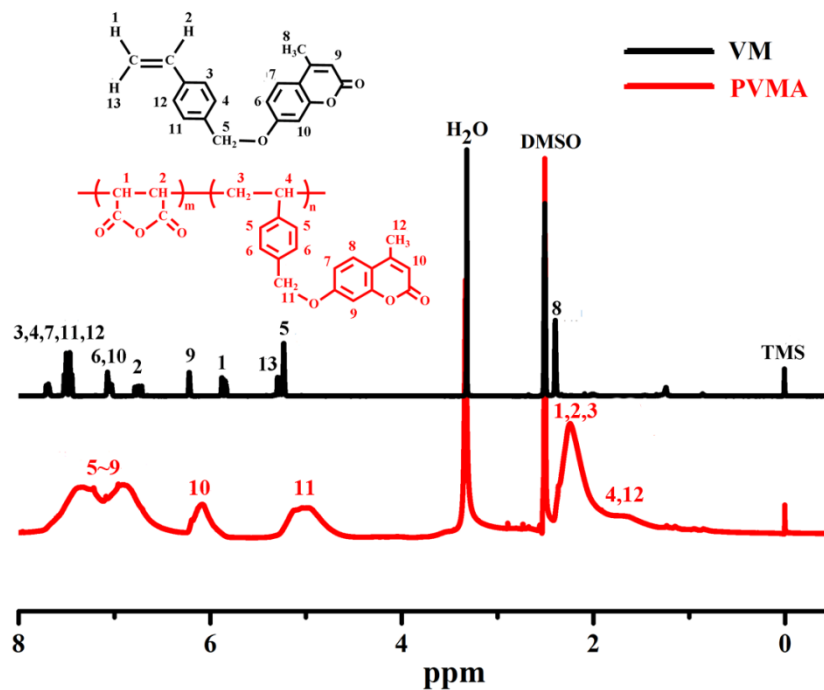


Fig. 3¹H-NMR spectra of VM and PVMA.

3.2 Characterization of PEDOT:PVMA dispersion

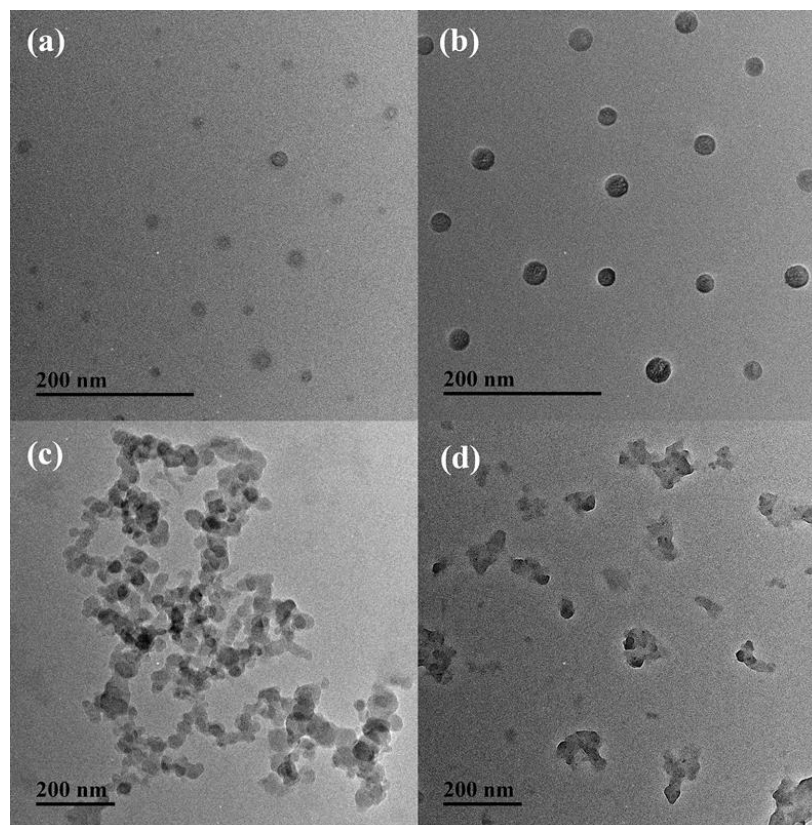


Fig. 4 TEM images of PEDOT:PVMA dispersion. (a) before the polymerization (b) the

polymerization was carried out for 1h (c) the polymerization was carried out for 12h (d) the polymerization was complete.

The TEM images were used for investigating the polymerization process of PEDOT:PVMA aqueous dispersion, shown in Fig. 4. In the Fig. 4(a), EDOT was dispersed in the water by PVMA, forming many microemulsion particles with the particle size of average 18 nm. The Fig. 4(b) is the TEM image when the reaction was carried out for 1 h. From the figure, the particle size of the microemulsion particles is increased to 30 nm, indicating the polymerization proceeding successfully. The Fig. 4(c) is the TEM image when the reaction was carried out for 12 h. As the polymerization proceeded, the growth of the PEDOT conjugated segment caused the π - π stacking force between the thiophene rings and benzene. This interaction led to the aggregation of the microemulsion particles shown in Fig 4(c). Finally, the microemulsion particles ruptured, forming many nano-aggregates stable in aqueous solution, shown in Fig 4(d).

3.3 The result of sensor measurements

Fig. 5 shows the real-time resistance response measurement of the PEDOT:PVMA sensor exposed to different relative humidity. The relative humidity test is carried out through response/recovery cycles for different RH environments between 0% and 11%, 23%, 33%, 43%, 75%, 98% RH. Each cycle is performed by an exposure interval of 1 min followed by a recovery interval of 1 min at dry air. A suddenly decrease in the sensor resistance response is observed with the increasing of RH in a large range of 11~98%. The resistance response values were calculated to be -71.85%, -74.82%, -78.59%, -80.87%, -91.10%, -98.46%, while the sensor exposed to 11%, 23%, 33%, 43%, 75%, 98% RH.

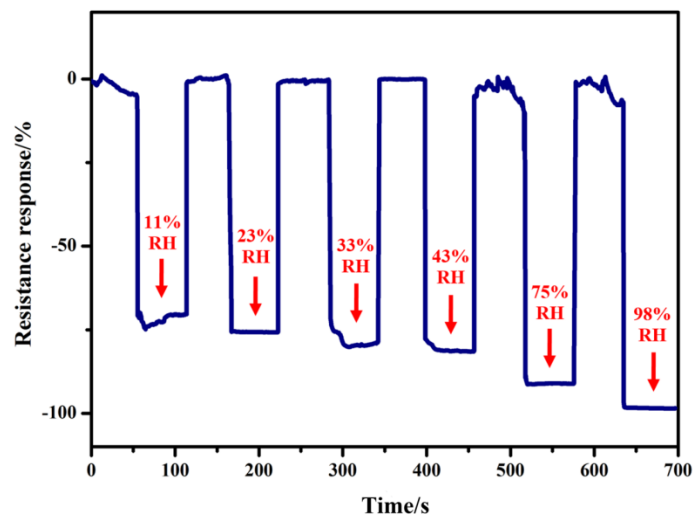


Fig. 5 Resistance response measurement of the PEDOT:PVMA sensor under switching RH.

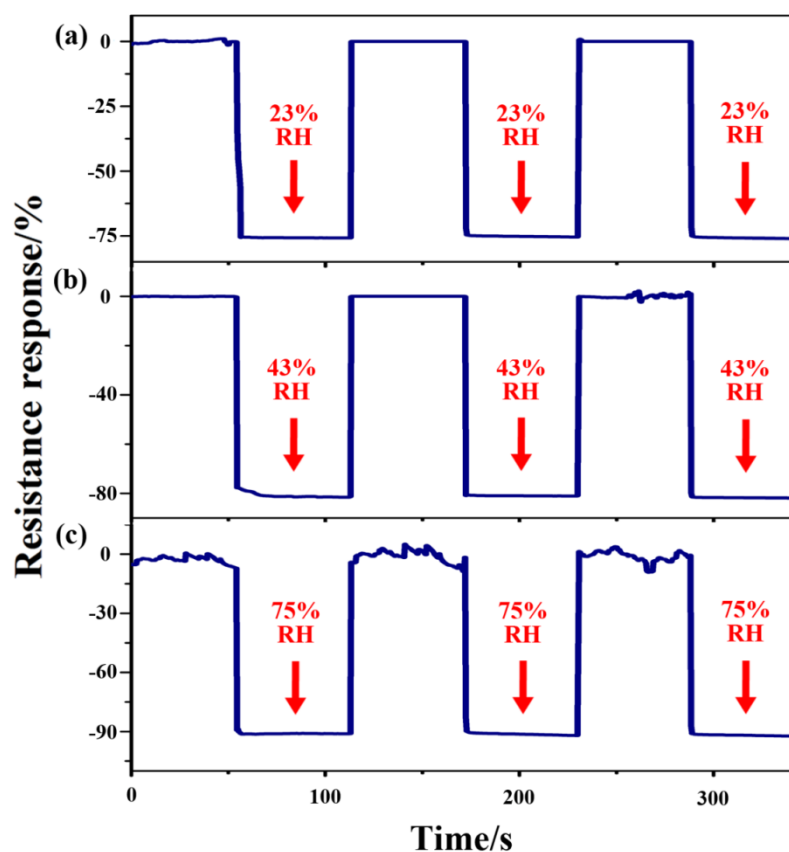


Fig. 6 Repeatability of PEDOT:PVMA sensor for (a) 23% (b) 43% (c) 75% RH at room temperature.

Fig. 6 shows the repeatability of PEDOT:PVMA sensor performs under the same experimental conditions. The repeatability characteristics is measured for 3 cycles repeatedly for 23%, 43% and 75% RH. This papery sensor exhibited a superb response–recovery behavior and excellent repeatability for humidity sensing.

4. Conclusion

In conclusion, we developed a facile method to prepare a stable aqueous dispersion of PEDOT:PVMA using a novel photosensitive copolymer PVMA. Furthermore, the water resistance of the PEDOT:PVMA film can be improved with the photo-dimerization of PVMA. And the photo-crosslinked films can be transferred to form flexible films by inkjet printing. We designed the electrode patterns by the graphics software CorelDRAW and fabricated the papery humidity sensors by inkjet printing. The robustness of these photo-crosslinked papery sensors acted very excellently. For the measurement of humidity sensor property, these sensors exhibited

not only superb sensing behavior to moisture sensitivity, but also good repeatability. We believe this material will have a bright future for the organic electronics.

Acknowledgements

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