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ORIGINAL PAPER

# Rapid humidity sensors based on poly (o-phenylenediamine-co-aniline) spherical nanoparticles

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## Abstract

Sensitivity toward humidity, response and recovery time, and reproducibility behaviors of a novel copolymer sensor, obtained by oxidative chemical polymerization of o-phenylenediamine and aniline using D-camphor-10-sulfonic acid dopant, were reported. It is a novel copolymer, and there are very few studies available concerning its synthesis and humidity sensing applications. Humidity-sensitive properties of the copolymer were tested by measuring the resistance of the fabricated films, and good humidity sensitivity was obtained. Moreover, a decrease in resistance with the increase in humidity was observed. Compared to polyaniline (PANI), the humidity sensing property of the copolymer was found to show quicker response and recovery time, higher reproducibility, and higher sensitivity. However, PANI alone exhibited relatively poor sensing property. The response time for the copolymer films at the relative humidity ranging from 11 to 97% was about 38 s, and the corresponding recovery time was about 11 s. The value of sensitivity was about 10. These results indicate excellent sensing character of the new type of copolymer humidity sensors. The obtained sensor is expected to exhibit good humidity sensing behavior in moisture-containing environment.

**Keywords** Humidity sensing · Conductive polymer · Reproducibility · Dopant

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## Introduction

Recently, humidity sensors have attracted progressively more attention on account of their extensive usage in industrial, technology, and laboratory fields and also in everyday life [1–5]. Among different types of humidity sensors, polymer humidity sensors make full use of their strength and show widespread applications especially when they are compared with the ceramic humidity sensors. This is basically attributed to their good flexible properties, smaller-size design, and room temperature operation and flexibility [6, 7]. Therefore, design and fabrication of polymer sensors which possess good sensitivity, low hysteresis, quick response time, and excellent stability are significantly important. In order to promote the sensing characteristics, a general route involves exploration of the fabrication of nanostructured thin films because of high surface area which promotes the process of adsorbing water molecules [8–10].

Polyaniline (PANI) serves as a significantly important conducting polymer enjoying various potential usages in anticorrosion and antistatic coatings, batteries, and sensors [11–14] owing to its desirable characteristics. However, currently, copolymer of aniline (An) and its corresponding derivatives have displayed their charm and turned out to be in spotlight [15, 16]. o-Phenylenediamine (oPD) and An copolymer have been successfully fabricated by electropolymerization and oxidative chemical polymerization [17, 18]. Nevertheless, owing to limited electrode surface area and non-uniform current density, it is difficult to obtain large-area and uniform polymer films by electropolymerization [19]. Therefore, oxidative chemical polymerization method has become significantly more important than before.

Jain et al. [20] reported the behavior of humidity sensors with PANI-based conducting polymers doped with weak acidic dopants. It was observed that over the major range of relative humidity (RH, between 20 and 95%), behavior of these sensors was almost linear and high sensitivity was obtained for PANI doped with D-camphor-10-sulfonic acid (CSA). Poly(o-anisidine) (PoA) and poly(o-phenylenediamine) (PoPD), which are derivatives of PANI, were also reported to be humidity sensitive by Kulkarni et al. and Tonosaki et al. [21, 22]. However, a lot more systematic explorations are still demanded to investigate substituted anilines and to explore the possibility of utilizing them as an alternative to PANI for humidity sensors [23].

In the present study, a novel copolymer sensor was prepared from oPD and An monomers, and CSA dopant. The structure of this new copolymer was characterized in detail by various techniques. The humidity sensing behavior of this novel copolymer was examined, and the results revealed rapid and highly sensitive detection of humidity. To the best of our knowledge, the humidity sensing property of poly(o-phenylenediamine-co-aniline) copolymer has rarely been reported. Therefore, this study utilized a novel perspective to design highly sensitive humidity sensor, which has potential in further research for humidity sensing.

## Experimental section

### Materials

The oPD (98%), An (98%) and CSA (99%) were purchased from J&K Scientific Ltd. An was distilled before use and stored at 4 °C. Ammonium persulfate, LiCl, $K_2SO_4$ and N,N-dimethylformamide were obtained from Beijing Chemical Plant. All these reagents were used as obtained in analytical grade. The de-ionized water was used throughout the present study.

### Fabrication of humidity sensor of PANI

0.186 g of distilled An monomer was put together with 10 mL CSA aqueous solution (0.1 M) and stirred for 0.5 h to obtain a mixed solution. Ten milliliter ammonium persulfate aqueous solution (0.2 M) was put into the above solution quickly. A substrate (10 mm × 6 mm × 0.5 mm) with five pairs of Au interdigital electrodes was immersed into the solution. The reaction was kept unstirred for additional 24 h. Finally, a uniform film was formed on the interdigital electrode substrate. The obtained substrate was washed by using de-ionized water and dried in the air.

### Fabrication of humidity sensor of oPD/An copolymer

Typical synthetic processes of oPD/An copolymer nanoparticles were as follows: 0.093 g of distilled An monomer and 0.108 g oPD were mixed with 10 mL CSA aqueous solution (0.1 M) under stirring which lasted 0.5 h. A clear solution was then obtained. Ten milliliter ammonium persulfate aqueous solution (0.2 M) was added to the solution at room temperature. The interdigital electrode substrate was immersed into the mixture. The reaction was kept unstirred for additional 24 h. Finally, a uniform film was formed on the interdigital electrode substrate. The substrate was washed by using de-ionized water and was dried at room temperature.

### Instruments and characterization

Ultraviolet–visible (UV–Vis) absorption spectra were obtained on a Shimadzu UV-3100 spectrometer. The slit width was 2 nm. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5PC spectrometer by using KBr powder-pressed pellet samples. Raman spectra of the polymer films were gained with a Renishaw 1000 model armed with a holographic notch filter and a CCD detector. Air-cooled argon ion laser (Spectra-Physics Model 163-C4260) with the radiation of 514.5 nm was used as the excitation source. Scanning electron microscopy (SEM) was obtained through the microscope of SHIMADZU SSX-550. Thermogravimetric analysis (TGA) test was performed on Pyris 6 Thermogravimetric Analyzer (Perkin-Elmer). The heating rate was 10 °C $min^{-1}$ up to 900 °C by using alumina crucibles under constant $N_2$ flow. The RH was gained with saturated aqueous solutions of LiCl (11%) and $K_2SO_4$ (97%), separately, by using a homemade gas-sensing setup [24].

## Results and discussion

Figure 1 shows the FTIR spectra of CSA-doped PANI and CSA-doped oPD/An copolymers. Figure 1a exhibits the characteristic peaks of PANI being consistent with the literature report [25]. The bands at 1577 and 1510 cm$^{-1}$ correspond to the stretching vibration modes of C=N and C=C in the phenazine ring of PANI, respectively. The band at 1305 cm$^{-1}$ is attributed to the C–N stretching vibration. The band at 1147 cm$^{-1}$ is ascribed to electronic-like absorption peak of N=Q=N (where Q represents the quinoid ring). Figure 1b shows two high wave number bands at 3315 and 3147 cm$^{-1}$, assigned to the typical N–H stretching of the –NH– and –NH$_2$ groups in oPD units, respectively. The band at 1237 cm$^{-1}$ corresponds to the C–N stretching vibration in the benzenoid units. Two bands at 1124 and 619 cm$^{-1}$ represent the in plane and out of plane C–H bending motions of benzenoid rings, respectively [26]. Appearance of the IR bands proved the successful fabrication of the oPD/An copolymers.

The UV–Vis spectra of CSA-doped PANI and CSA-doped oPD/An copolymers were obtained by dispersing each of them in *N*,*N*-dimethylformamide, separately. The obtained spectra are shown in Fig. 2. The major absorption bands at about 330 and 597 nm in Fig. 2a are assigned to the *π*–*π** electron transition of benzenoid units and the exciton-like transition (the conducting form) in quinoid diimino units of PANI [27]. Figure 2b exhibits the spectra of CSA-doped oPD/An copolymers, showing three typical absorption bands. The absorption band centered at 273 nm is assigned to the *π*–*π** transitions of the benzenoid and quinoid structures. The absorption band centered at 366 nm is assigned to the *π*–*π** transition associated with the phenazine ring conjugated to the two lone pairs of nitrogen in the –NH$_2$ groups [28, 29]. These two bands are characteristic of PoPD. The band at 560 nm is assigned to the red-shift of the band of 597 nm corresponding to exciton-like transition in quinoid diimino units of PANI. These results confirmed that the oPD/An copolymers were prepared successfully.

The TG curves of CSA-doped PANI and CSA-doped oPD/An copolymers are shown in Fig. 3. Overall, the curves reveal that the decomposition of the two

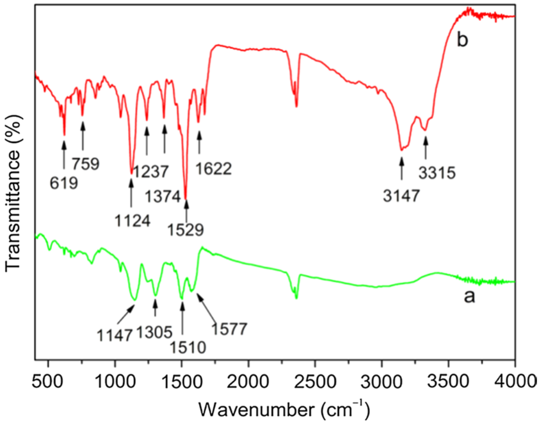


**Fig. 1** FTIR spectra of (a) CSA-doped PANI and (b) CSA-doped oPD/An copolymer

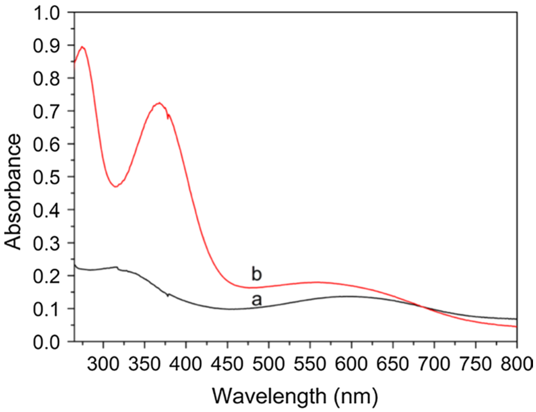


**Fig. 2** UV–Vis spectra of (a) CSA-doped PANI and (b) CSA-doped oPD/An copolymer

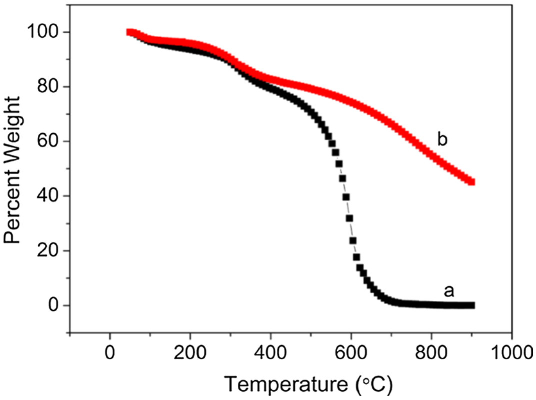
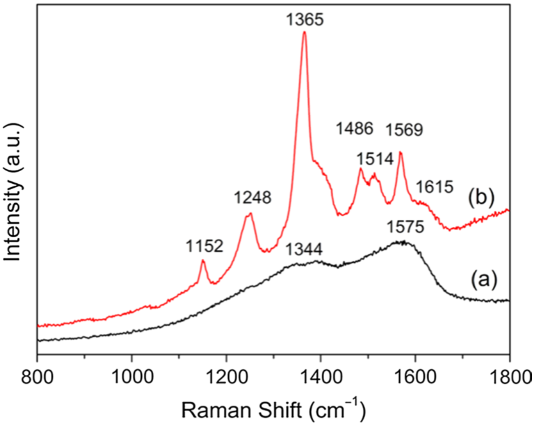


**Fig. 3** TGA curves of (a) CSA-doped PANI and (b) CSA-doped oPD/An copolymer

samples occurs in two steps. The first step occurs at about 270 °C, and it corresponds to the decomposition of the acid dopant. The next phase happens at 464 °C because of the decomposition of the polymer chains [30]. Noteworthily, the oPD/An copolymers are more thermally stable than PANI. Decomposition of the polymer components in oPD/An above 464 °C is much slower than those in PANI. Therefore, a good thermally stable material was prepared by chemical oxidation polymerization in the present study.

Figure 4 shows Raman spectra of the CSA-doped PANI and CSA-doped oPD/An copolymers by using the 514.5 nm laser line excitation. The spectrum of PANI (Fig. 4a) shows typical Raman shifts at 1344 and 1575 cm$^{-1}$, which are assigned to the C–N$^{\bullet+}$ and C=C stretching modes in benzenoid ring, respectively [31]. Figure 4b demonstrates that the Raman shift at 1486 cm$^{-1}$ is assigned to the C=N stretching mode, indicating the presence of imine sites in the polymer structure [32]. A strong Raman shift at 1365 cm$^{-1}$ corresponds to the C–N$^{\bullet+}$ stretching vibrations-delocalized polaronic charge carriers. Existence of this band proves high concentration of the C–N$^{\bullet+}$ carrier in the oPD/An copolymers. The Raman shift at 1514 cm$^{-1}$

**Fig. 4** Raman spectra of (a) CSA-doped PANI and (b) CSA-doped oPD/An copolymer



is assigned to the N–H bending deformation of protonated amines. The Raman shift at 1248 cm$^{-1}$ is ascribed to the C–N stretching mode of the polaronic units. The Raman shift concerning the C–C deformation of benzenoid rings is observed at 1615 cm$^{-1}$ [33].

Figure 5a shows a representative SEM image of PANI with added CSA, exhibiting the existence of nanotubes with mean diameter of 200 nm and mean length of more than 1 µm. However, the morphology of the CSA-doped oPD/An copolymers was found to be spherical, as shown in Fig. 5b. The particles are uniform in size and are about 320 nm in diameter.

Figure 6 shows typical response curves of the CSA-doped PANI film and the CSA-doped oPD/An copolymer film. Figure 6a exhibits the response curve for CSA-doped PANI, revealing low sensitivity and long response-recovery time. The sensitivity is defined as $S=(R-R_0)/R_0$, where $R$ is the resistance of the sample for RH at 11%, and $R_0$ is the resistance of the sample for RH at 97%. The sensitivity of the CSA-doped PANI film is 0.7, and the response time is 74 and 126 s for the humidity absorption and desorption processes, respectively. Figure 6b shows that the sensitivity of the CSA-doped oPD/An copolymer films is about 10

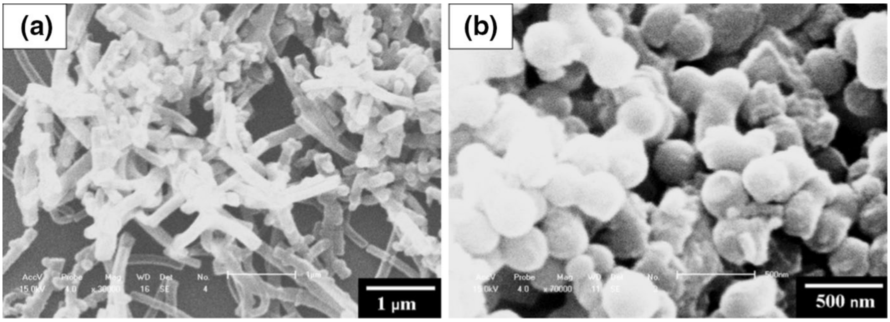


**Fig. 5** SEM images of **a** CSA-doped PANI and **b** CSA-doped oPD/An copolymer

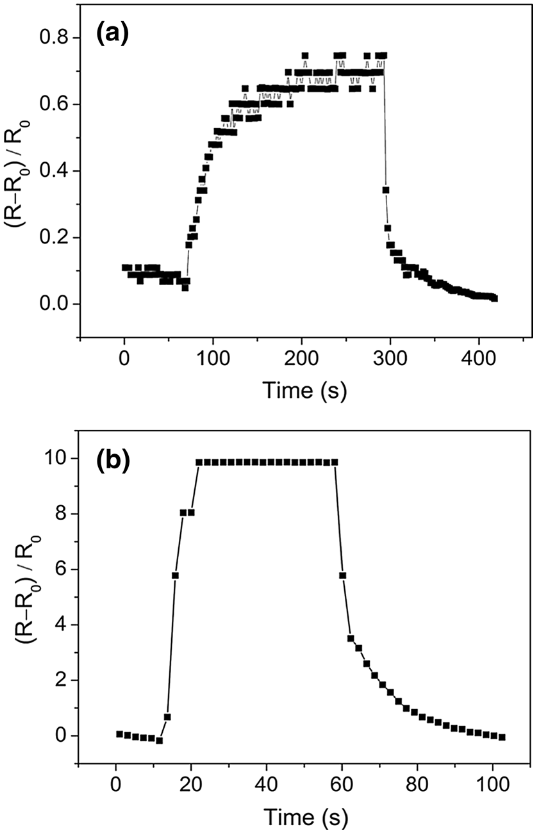
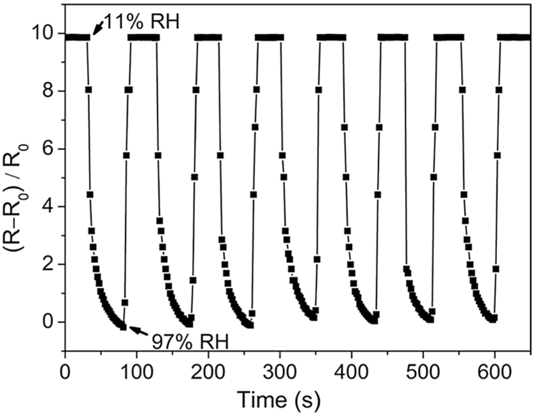


**Fig. 6** The response and recovery characteristic curves of the films of **a** CSA-doped PANI and **b** CSA-doped oPD/An copolymer

for the RH between 11 and 97%. The time required for humidity adsorption and desorption was 38 and 11 s, respectively. Compared to PANI nanotubes, oPD/An copolymers nanoparticles exhibited significantly improved sensitivity and response–recovery behavior.

Figure 7 exhibits that the sensitivity of the CSA-doped oPD/An copolymer films remains constant during seven cycles. This indicates that the copolymer may act as a potential candidate for a reusable sensor material in humidity sensing. The cycling curve proves that the copolymer has good reproducibility and reliable sensitivity. Such good humidity sensing property has relation with the water–adsorption and proton transfer mechanism. Initially, water molecules are physically adsorbed on the surface of the copolymer, and then, the hydronium ($H_3O^+$) ion is formed at the surface with increasing number of water molecules. Under this condition, proton transfer occurs finally. The mechanism can be explained in terms of acid–base reaction as shown in Fig. 8. From this mechanism, we deduced that the interaction between water molecules and the surface of the CSA-doped oPD/An copolymer was dominated by chemisorption, while physisorption played a minor role. Numerous charged sites and hydrogen bond

**Fig. 7** Long-term response and recovery curves of the oPD/An copolymer doped with CSA at 11% and 97% RH



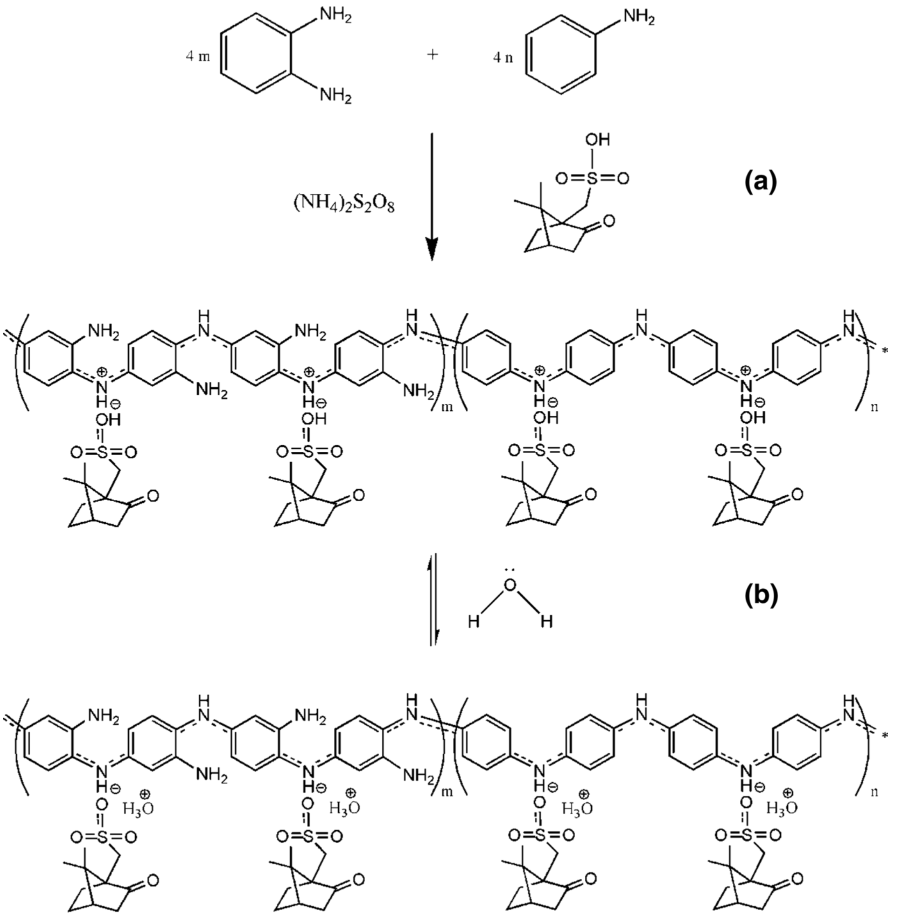


**Fig. 8** The schematic illustration of **a** the oxidative chemical polymerization of oPD/An copolymer doped with CSA and **b** the acid–base reaction mechanism of humidity sensing

accepting/donating sites (–NH–, –N=, $=NH^+$–, $–NH_2^+$–, etc.) are present within the copolymer. These charged or polar sites aid in shifting the equilibrium toward the formation of protons, which can either increase the doping level of the copolymer or conduct charge themselves through the network of absorbed water molecules. Hydrogen bond between copolymer chains through water molecules have also been suggested to contribute to the increase in conductivity [34–37].

Noteworthily, the humidity adsorption period takes much more time than the humidity desorption period on the thin film of the CSA-doped oPD/An copolymer. Although numerous charged sites and hydrogen bond accepting/donating sites are present in the copolymer, it becomes difficult when the $H_3O^+$ enters into the main chain of the copolymer at high humidity, because of larger steric hindrance of CSA. However, the water molecules are easy to take off from the copolymer in dry atmosphere. Thus, quick recovery occurs at low humidity.

## Conclusion

An o-phenylenediamine/aniline (oPD/An) copolymer doped with D-camphor-10-sulfonic acid (CSA) was synthesized by oxidative chemical polymerization. FTIR spectroscopy and UV–Vis spectroscopy showed the successful fabrication of the doped copolymer. Thermal studies indicated that the copolymer exhibited better thermal stability than PANI. Humidity-sensitive behavior of the copolymer was tested by measuring the resistance of the fabricated films at 11 and 97% relative humidity. The response and recovery time was 38 and 11 s, respectively. High sensitivity and quick response to water vapor make the films to be potential candidate for humidity sensors.

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