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A novel dual colorimetric fiber based on two acid–base indicators

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ABSTRACT

A novel dual colorimetric fiber based on two acid–base indicators was synthesized by first aminating commercially available polyacrylonitrile fiber with tetraethylenepentamine and then covalently immobilizing ethyl orange moieties through an alkylation reaction and a diazo coupling reaction; finally, the fiber was grafted with phenolphthalein using a Mannich reaction. The functionalized fiber was characterized by elemental analysis, X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier-transfer infrared spectroscopy (FTIR) and UV–vis spectroscopy, and its color-changing properties, response speed, reusability and photostability were all investigated. This fiber exhibits a remarkable color change from deep pink ($pH < 1.1$) to yellow ($1.1 < pH < 13.0$) and then to dark violet ($pH > 13.0$). Moreover, this fiber shows a fast response time (<1 s for 1 M HCl and 1 M NaOH), high photostability (>60 days) and excellent reusability (>300 times).

1. Introduction

Over the past two decades, the development and application of optical sensors and materials based on dyes have grown rapidly [1–7]. Many reversible, solid-state and color-changing sensors have been developed to monitor pH in academic and practical applications [8–13]. For example, a pH sensitive azo-dye (1-hydroxy-4-[4-(2-hydroxyethylsulphonyl)phenylazo]naphthalene) was covalently functionalized to tentagel resin beads to give an optical pH sensor [8]. This azo-dye modified sensor was found to exhibit a dynamic range of pH 5.0 to 12.0 with a color change from yellow to purple. Pararosaniline was attached to macroporous controlled pore glass (CPG) beads to produce an optical pH sensor [9]. This pararosaniline-containing sensor has a sensing range from pH 1 to 11 with a rather slow response time (about 100 min from pH 10.5 to pH 2.0). A halochromic sensor based on a polyaniline film has been prepared and used for in vivo blood pH measurement [10]. However, owing to the oxidization of the polyaniline, the stability of this sensor is unsatisfactory. Pavel et al. loaded several azo-dyes into vinylalcohol-ethylene copolymer films [11], which responded to pH changes from 7.0 to 13.0 with long term stability even under strongly basic conditions. However, the response time and the reusability of the azo-dye modified sensor were not investigated. Cho et al. prepared halochromic resins by covalently attaching carboxylic acid derivatives of sulfthalein dyes onto resin beads [12], which showed color response with changes in pH. The development and application of sol–gel sensors for strong acids (HCl, 1–10 M) and bases (NaOH, 1–10 M) have also been reported [13]. Most of the sensors have only one color change for an acid or a base and use only a single sensor molecule. So research on a dual colorimetric sensor based on two different sensor molecules for acids and bases is still a challenge.

Although a great variety of solid-state optical pH sensors have been studied, most of them were prepared based on membrane or powdered materials instead of fabrics. In recent years, there has been immense interest in studying and developing wearable intelligent textiles for the needs of professional and fashion-loving people [14,15]. Recent developments also illustrate that wearable intelligent textiles may become a key element of ambient intelligence [16]. On the other hand, integrating various sensors into fabrics remains a significant challenge to material science because wearable intelligent materials are strongly restricted by washability, durability and security issues, which increase the difficulty of the research and development. Commercially available fibers generally lack the proper functional groups which can be easily linked to or transformed to sensor molecules. In addition, owing to the steric hindrance effect most pH sensor molecules lose their functions when introduced into fabric carriers. Therefore the development of a colorimetric sensor based on wearable fiber is also a challenge and there are many problems that still need to be resolved.

Polyacrylonitrile fiber (PANF) is resistant to corrosion and mildew and has excellent mechanical strength and stability. PANF is

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also a commercially available material and ubiquitously applied in the clothing industry. Moreover, the fiber contains an abundance of cyano groups which can be easily transformed into various functionalities (such as carboxyl, amide and amidoxime groups) [17–20]. So, PANF is a very suitable starting material for the preparation of a colorimetric fiber. Ethyl orange and phenolphthalein are the most commonly used pH indicators and have remarkable color changes (yellow to red in acid solutions at $pH < 4.5$ for ethyl orange and colorless to violet in basic solutions at $pH > 8.2$ for phenolphthalein). In our previous work, phenolphthalein was immobilized on an ethylenediamine modified PANF using the Mannich reaction and the formed fiber presents remarkable color change (from pale yellow to violet), excellent reusability and recycle stability [21]. However, this fiber only responded to basic solutions. In this work, the design, synthesis and characterization of a novel dual colorimetric fiber based on two acid–base indicators are presented.

2. Experiment

2.1. Reagents

Commercially available PANF with a length of 10 cm and a diameter of 30 ± 0.5 μm (from the Fushun Petrochemical Corporation of China) was used. Tetraethylenepentamine, 4-aminobenzenesulphonic acid, *N*-ethyl-*N*-(2-hydroxyethyl)aniline, phenolphthalein (3,3-bis(4-hydroxyphenyl)phthalide), formaldehyde (37–40% aqueous solution), and the other reagents were all analytical grade and were used without further purification. Water was deionized. The pH buffer solutions were prepared by different combinations of 0.2 M KH_2PO_4, 0.2 M K_2HPO_4, 0.1 M Na_2CO_3, 0.1 M $NaHCO_3$, 0.1 M citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid), 0.2 M HCl and 0.2 M NaOH.

2.2. Apparatus and instruments

Elemental analyses were performed on an Elementar vario EL analyzer. X-ray powder diffraction spectra were recorded with a BDX 3300 X-ray diffractometer (Peking University Instrument Factory) at 0.154 nm. A model XL-30 scanning electron microscope (Philips) was used to characterize the surface of the different modified fibers. FTIR (Fourier-transfer infrared spectroscopy) spectra were obtained with an AVATAR 360 FTIR spectrometer (Thermo Nicolet). The pH values were measured with a model PHS-3C pH meter. UV–vis spectra of the solid fiber samples were recorded on a HP8453 UV–vis spectrometer (Agilent), equipped with an integrating sphere (Shimadzu). The mechanical properties of the different fiber samples were obtained with a model LLY-6 Electronic Single Fiber Strength Tester. The color changes of the colorimetric fiber at different conditions were recorded with a Canon IXUS 95 IS digital camera.

2.3. Synthesis of the dual colorimetric fiber

The synthesis of the dual colorimetric fiber was carried out by three steps as follows:

Step 1 The amination of PANF with tetraethylenepentamine.

Dried PANF (5.000 g), tetraethylenepentamine (100 mL) and water (33 mL) were added to a three-necked flask. The mixture was stirred and refluxed for 3.5 h. Afterwards the fiber was filtered out and repeatedly washed with water (60–70 °C) until neutral. It was then dried at 70 °C under vacuum overnight to produce aminated fiber (PAN_TF). The weight gain of PAN_TF based on PANF was 35%.

Step 2 General procedure for the immobilization of the ethyl orange moieties.

Alkylation reaction: Dried PAN_TF (2.000 g), *N*-(2-bromo methyl)-*N*-ethylaniline (1.370 g) (prepared from *N*-ethyl-*N*-(2-hydroxyethyl)aniline and PBr_3 in CCl_4 with a yield of 70%) and ethanol (60 mL) were added to a three-necked flask. The mixture was stirred and refluxed for 24 h under nitrogen. Then the mixture was cooled and the fiber was filtered out and washed with ethanol three times. Afterwards, the fiber was washed with 0.1 M NaOH to neutralize the generated hydrogen bromide and repeatedly washed with water (60–70 °C) until neutral. Then the fiber was extracted for at least 36 h by methanol using a Soxhlet's apparatus to remove any non-bonded small molecules. The product was then dried at 70 °C under vacuum overnight to yield the modified fiber ($PAN_{TA}F$) with a weight gain of 18% based on the PAN_TF.

Diazotization and Coupling reaction: 4-Aminobenzene sulphonic acid (0.346 g, 2 mmol) and $NaNO_2$ (0.138 g, 2 mmol) were dissolved in a solution of 1 M NaOH (2.5 mL). The mixture was cooled in an ice bath until the temperature was below 5 °C. Then the solution was added slowly to a solution of concentrated HCl (1 mL, 36%) and ice (2 g). The mixture was allowed to stir in the ice bath (<5 °C) for 20 min to give a white precipitate of diazonium salt. Afterwards, 25 mL deionized water (18 °C) was added to the solution to dissolve the diazonium salt and the temperature was increased to 10 °C. After wetting with deionized water, $PAN_{TA}F$ (1.000 g) was immersed into the solution of diazonium salt and stirred for 1 min with the color changing from yellow to red. Then the fiber was filtered out and washed with 0.1 M NaOH immediately. Afterwards, the fiber was repeatedly washed with water until neutral. It was then dried at 70 °C under vacuum overnight to produce the ethyl orange modified fiber ($PAN_{TAS}F$). The weight gain of $PAN_{TAS}F$ based on $PAN_{TA}F$ was 9%, and the total weight gain of $PAN_{TAS}F$ based on PAN_TF was 29%.

Step 3 General procedure for the immobilization of the phenolphthalein.

Dried $PAN_{TAS}F$ (1.000 g), phenolphthalein (2.000 g), formaldehyde aqueous solution (10 mL) and ethanol (30 mL) were added to a three-necked flask. The mixture was stirred and refluxed for 12 h under nitrogen. Afterwards, the mixture was cooled and the fiber was filtered out and washed with ethanol three times. Then the fiber was extracted for at least 36 h by methanol using a Soxhlet's apparatus to remove any non-bonded small molecules. It was then dried at 70 °C under vacuum overnight to give the dual colorimetric fiber (P-$PAN_{TAS}F$) with a weight gain of 13% based on the $PAN_{TAS}F$.

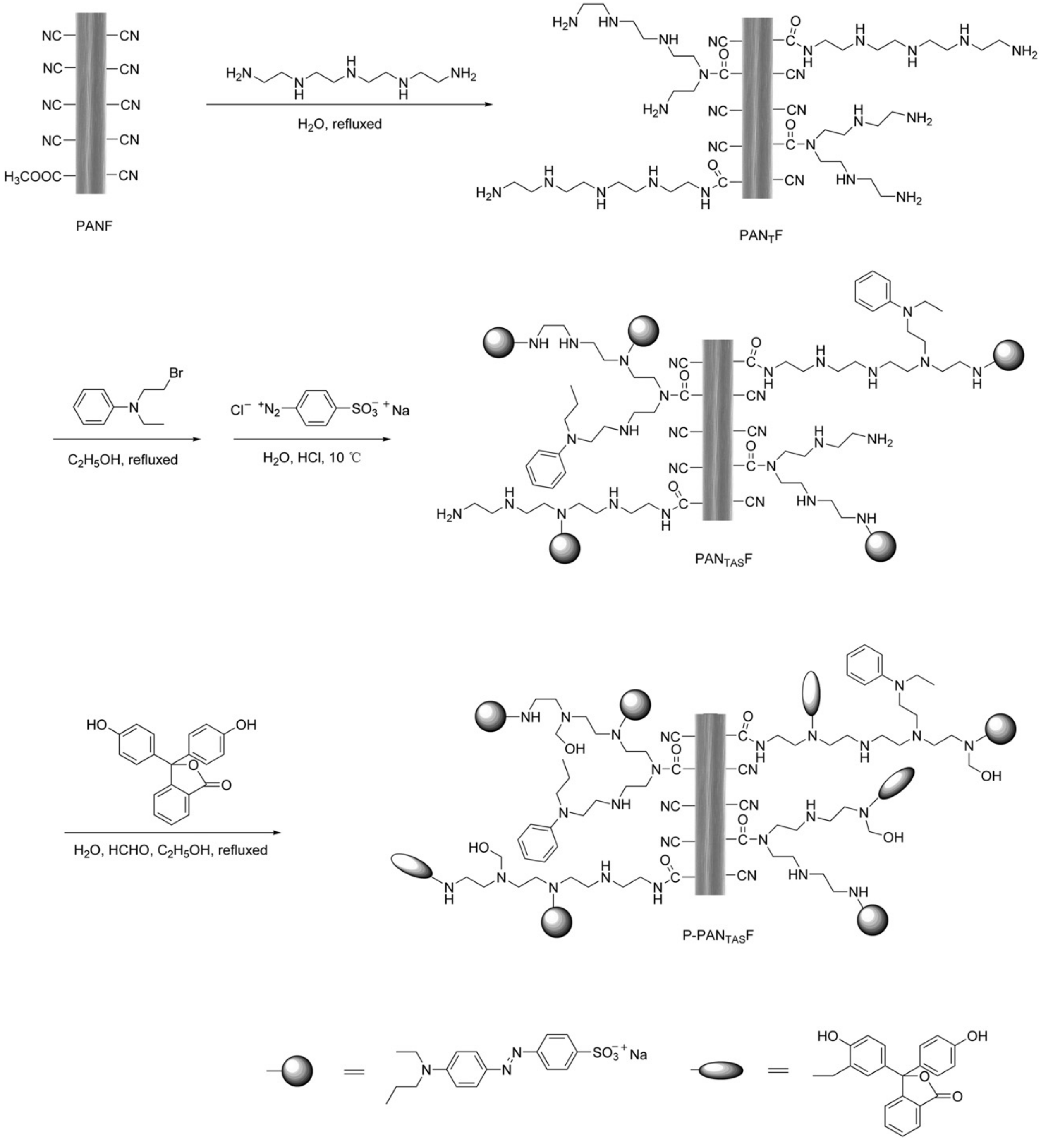
The synthesis of the dual colorimetric fiber is illustrated in Scheme 1.

2.4. Acid exchange capacity of the modified fiber (PAN_TF)

Dried PAN_TF (0.200 g) was immersed into 40 mL of 0.100 M HCl for 6 h. The treated fiber was then filtered out and the concentration of the remaining solution was determined by titration with 0.100 M NaOH. The exchange capacity was calculated based on the consumption of the acid [20].

2.5. UV–vis detection of the dual colorimetric fiber

Dried fiber samples (20 mg) were immersed into 10 mL of solutions with different pH values for specific times. The fiber sample was then filtered out and the surface was dabbed with filter paper and dried at 70 °C under vacuum. The absorption spectra of



Scheme 1. The preparation of the dual colorimetric fiber (P-$PAN_{TAS}F$).

these dried fibers were detected by UV–vis spectrometry (background: $BaSO_4$). In order to ensure the reproducibility of the results, all fiber samples were cut into well-proportioned powders.

3. Results and discussions

3.1. Synthesis of the dual colorimetric fiber

The dual colorimetric fiber (P-$PAN_{TAS}F$) was prepared by a three-step process as shown in Scheme 1. The commercially available polyacrylonitrile fiber was heated with tetraethylenepentamine to produce the aminated fiber (PAN_TF). Then PAN_TF was alkylated with *N*-(2-bromomethyl)-*N*-ethylaniline and subsequently coupled with 4-sulfobenzenediazonium chloride to afford the ethyl orange moiety covalently immobilized fiber ($PAN_{TAS}F$). Finally, the $PAN_{TAS}F$ was grafted with phenolphthalein using a Mannich reaction to give the colorimetric fiber (P-$PAN_{TAS}F$). The extent of the modification was monitored by the weight gain and acid exchange capacity of the different modified fibers:

$$\text{Weight gain} = [(W_2 - W_1)/W1] \times 100\%$$

For the amination step, W_1 and W_2 are the weights of PANF and PAN_TF, respectively.

For step 2, W_1 and W_2 represent the weights of PAN$_T$F and PAN$_{TA}$F; or PAN$_{TA}$F and PAN$_{TAS}$F, respectively.

For step 3, W_1 and W_2 represent the weights of PAN$_{TAS}$F and P-PAN$_{TAS}$F, respectively.

The amination reaction was strongly influenced by the reaction time and temperature. The weight gain of the PAN$_T$F could be effectively enhanced by prolonging the reaction time or increasing the temperature. However a higher percentage of weight gain notably reduced the strength of the PAN$_T$F. The details of the amination reaction were discussed in our previous paper [22]. An optimal reaction condition (refluxed for 3.5 h) with a weight gain of 35% was selected to prepare the aminated fiber. The acid exchange capacity of the PAN$_T$F in 0.100 M HCl was determined to be 5.1 mmol/g, indicating that the PANF has been grafted with some of the amino groups. Owing to the cross-linking reaction induced by tetraethylenepentamine, the titration result for the acid exchange capacity was slightly less than the calculated value 5.4 mmol/g (according to the weight gain of 35%). The obtained PAN$_T$F has more amino groups for further reactions than the original polyamide hollow fibers do [23].

In immobilization step 2, the coupling reaction was also influenced by the reaction time and temperature. The coupling reaction on the surface of the PAN$_{TA}$F was difficult to carry out at a low temperature (2 °C). However, prolonging the reaction time at 10 °C resulted in the fiber becoming deep dark. So a mild condition (stirred at 10 °C for 1 min) was selected to prepare PAN$_{TAS}$F. In our previous work, methyl orange failed to be immobilized on the aminated fiber with the Mannich reaction. So this procedure is an effective method to resolve that problem.

In immobilization step 3, in order to avoid the formation of the oligomers or resins of phenolphthalein with formaldehyde under acidic or basic conditions [24], the Mannich reaction was carried out in ethanol without any catalyst. The details of how to deduct the weight gain of the blank reaction have been discussed previously [21,25]. The practical weight gain of the immobilized phenolphthalein using the Mannich reaction for the P-PAN$_{TAS}$F was 9%. After these modifications, a beautiful dual colorimetric fiber (P-PAN$_{TAS}$F) with a fresh yellow color was finally obtained (Scheme S1, Supplementary material).

3.2. *Characterization of the different modified fibers*

The elemental analysis data for PANF, PAN$_T$F, PAN$_{TAS}$F and P-PAN$_{TAS}$F are listed in Table 1. Compared to the original PANF, the carbon content of the PAN$_T$F decreases and the hydrogen content increases as expected, since tetraethylenepentamine has less carbon and more hydrogen than the original PANF. As expected, the introduction of tetraethylenepentamine (nitrogen content, 37.04%) will apparently increase the nitrogen content of the PANF based on the weight gain of 35%. The small increase in nitrogen content of the PAN$_T$F from 21.77% to 22.20% suggests that water is introduced during the reaction of the C≡N groups with tetraethylenepentamine, resulting in the formation of amide and the release of ammonia. Moreover, the nitrogen content of the PAN$_T$F also shows that the cross-linking reaction induced by tetraethylenepentamine and the hydrolysis of C≡N groups is unavoidable. In the PAN$_{TAS}$F, the amounts of carbon, hydrogen and nitrogen all decrease compared to the PAN$_T$F, since the ethyl orange moieties have less carbon, hydrogen and nitrogen than those of the PAN$_T$F. In the P-PAN$_{TAS}$F, the amounts of hydrogen and nitrogen decrease distinctly, and the percentage of carbon increases slightly, as a result of the introduction of the phenolphthalein and formaldehyde molecules.

Table 1
Elemental analysis data for PANF, PAN$_T$F, PAN$_{TAS}$F, and P-PAN$_{TAS}$F.

Sample	Weight gain (%)	C (%)	H (%)	N (%)
PANF	–	60.12	5.49	21.77
PAN$_T$F	35	58.04	7.15	22.20
PAN$_{TAS}$F	29	57.43	7.10	20.15
P-PAN$_{TAS}$F	13	58.68	6.76	17.75
Ethyl orange moiety[a]	–	54.24	4.80	11.86
Phenolphthalein moiety[a]	–	76.13	4.53	0

[a] Calculated values for the ethyl orange and phenolphthalein moieties.

The XRD (X-ray powder diffraction) spectrum of the PANF (Fig. 1a) shows an intense reflection peak at $2\theta = 17°$ which corresponds to the (100) diffraction of the hexagonal lattice formed by parallel close packing of rod-like molecules. This demonstrates that the PANF adopts a stiff rod-like conformation due to the intermolecular repulsions of the nitrile dipoles [26]. After the amination with tetraethylenepentamine, the reflection peak ($2\theta = 17°$) of the PAN$_T$F decreases (Fig. 1(b)), which indicates a decrease in the polar interactions between molecule chains during the reaction and the breakage of bonds in the inner crystal region [19]. PAN$_{TAS}$F and P-PAN$_{TAS}$F have almost the same XRD spectrum as PAN$_T$F (see Fig. 1(c, d)), which indicates that the inner crystal region of the fiber is not further damaged after the immobilization of ethyl orange and phenolphthalein moieties. This indicates that the strength of this colorimetric fiber has been maintained. The determined breaking strength of P-PAN$_{TAS}$F is 73% of that of PANF (Table S1, Supplementary material), which agrees well with the XRD result.

The SEM (scanning electron microscopy) photographs of PANF, PAN$_T$F, PAN$_{TAS}$F and P-PAN$_{TAS}$F are shown in Fig. 2(a–d). After the amination with tetraethylenepentamine, the surface of the modified fiber becomes rougher. In this work, a tetraethylenepentamine aqueous solution was used in the amination step to produce a weight gain of 35%. The surfaces of the PAN$_T$F, PAN$_{TAS}$F and P-PAN$_{TAS}$F are rougher than those in our previous work [21] in which an aqueous ethylenediamine solution was used to give a weight gain of 13%. After the two immobilization steps, the functionalized fibers (PAN$_{TAS}$F and P-PAN$_{TAS}$F, Fig. 1(c, d)) become rougher than the aminated fiber (PAN$_T$F, Fig. 1(b)). However, except for the coarse surface, no other major flaws are found in the PAN$_T$F, PAN$_{TAS}$F and P-PAN$_{TAS}$F. Therefore the modified fibers still maintain 62%–73% of mechanical strength based on PANF, which is acceptable for further commercial applications (Table S1, Supplementary material).

The samples of PANF, PAN$_T$F, PAN$_{TAS}$F and P-PAN$_{TAS}$F were pulverized by cutting and then prepared in KBr pellets. Their FTIR spectra are shown in Fig. 3. For the FTIR spectrum of PANF (Fig. 3(a)), the 2242 cm^{-1} absorption band is attributed to the C≡N

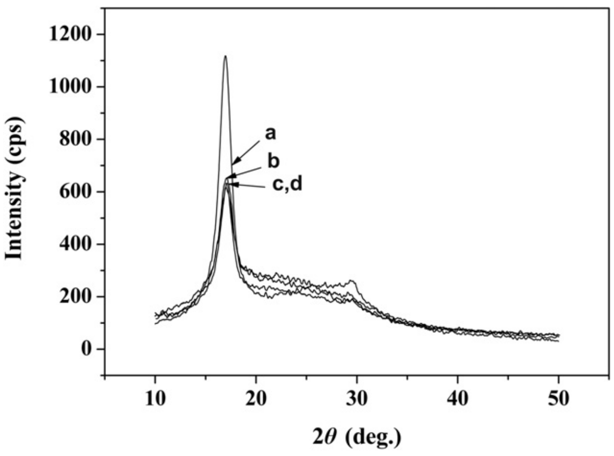


Fig. 1. XRD spectra of (a) PANF, (b) PAN$_T$F, (c) PAN$_{TAS}$F, and (d) P-PAN$_{TAS}$F.

vibration and the 1731 cm^{-1} C═O vibration peak indicates the existence of methyl acrylate units in the copolymer.

The broad absorption bands at 3700–3150 cm^{-1} in PAN$_T$F (Fig. 3(b)) correspond to the stretching vibrations of the N–H and O–H groups. The 2242 cm^{-1} C≡N vibration peak still exists in PAN$_T$F, which suggests that not all the C≡N groups participated in the amination and the hydrolysis. For PAN$_T$F (Fig. 3(b)), the strong absorption band in the region of 1650 cm^{-1} is assigned to the amide I band. The new broad peak at 1560 cm^{-1} is attributed to the overlap of the amide II band (i.e. the C(═O)–N stretching vibrations), and N–H bending vibrations.

For PAN$_{TAS}$F (Fig. 3(c)), the intensities of the peaks at 1560 cm^{-1} and 3700–3150 cm^{-1} decrease compared with those of the PAN$_T$F. This further supports a consumption of N–H groups in the reaction. The new peaks at 1606 cm^{-1} and 1516 cm^{-1} are attributed to the C═C stretching vibrations of the benzene rings, whereas the new peaks at 750 cm^{-1} and 680 cm^{-1} are attributed to the C–H bending vibrations of the benzene rings. These results suggest that the ethyl orange moieties have been covalently grafted onto the fiber.

For P-PAN$_{TAS}$F (Fig. 3(d)), the strengthening of the multiple peaks around 1300–1170 cm^{-1} is assigned to C–O and C–C vibrations from the immobilized phenolphthalein. The new peak at 1760 cm^{-1} is attributed to the C═O vibration in phenolphthalein. Based on the IR spectrum of the pure phenolphthalein [27], these changes in the FTIR spectrum of P-PAN$_{TAS}$F demonstrate the successful introduction of the phenolphthalein via the Mannich reaction.

3.3. *The pH sensitivity, response time, photostability, reusability and durability of P-PAN$_{TAS}$F*

The pH sensitivity and response time are crucial parameters for colorimetric fiber. The possible color-changing mechanism of P-PAN$_{TAS}$F in acid and base solutions is drawn in Scheme S2 (Supplementary material). It is well known that ethyl orange changes from orange to red in acidic solutions when a quinoid structure forms [28]. For phenolphthalein, the color changes from colorless to violet in basic solutions as a result of the formation of a dianion structure [29]. In addition, the further formation of a colorless trianion structure causes the color to decay quickly over time. The transition curves of the absorption of P-PAN$_{TAS}$F versus pH are shown in Figs. 4 and 5. The maximum absorption of ethyl orange is at 474 nm in neutral solution and at 510 nm in acidic solutions (pH < 3.0) [30,31]. The maximum absorption of the P-PAN$_{TAS}$F in acidic solutions is 570 nm. The large red shift may be due to the buffering action of the amino groups on the fiber and changes in its

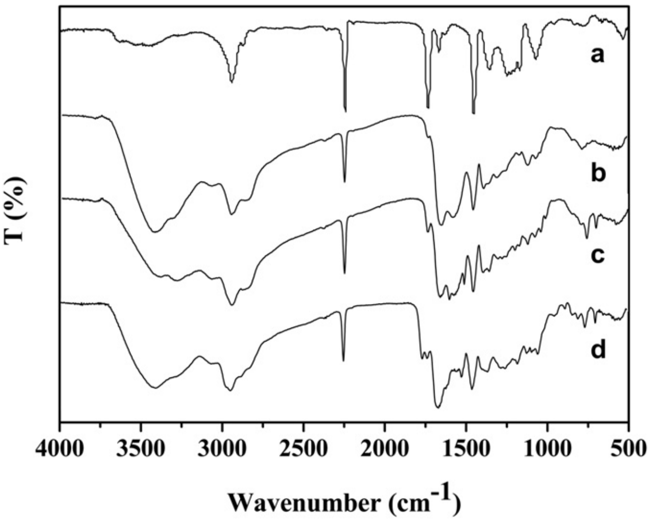


Fig. 3. FTIR spectra of (a) PANF, (b) PAN$_T$F, (c) PAN$_{TAS}$F, and (d) P-PAN$_{TAS}$F.

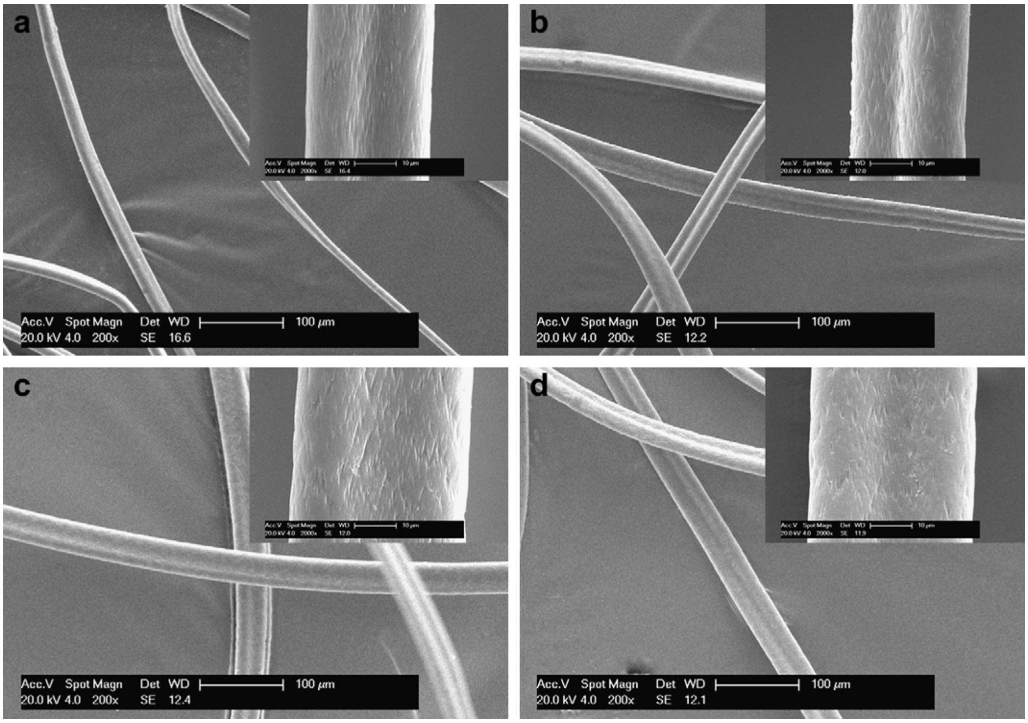


Fig. 2. SEM photographs of (a) PANF, (b) PAN$_T$F, (c) PAN$_{TAS}$F, and (d) P-PAN$_{TAS}$F.

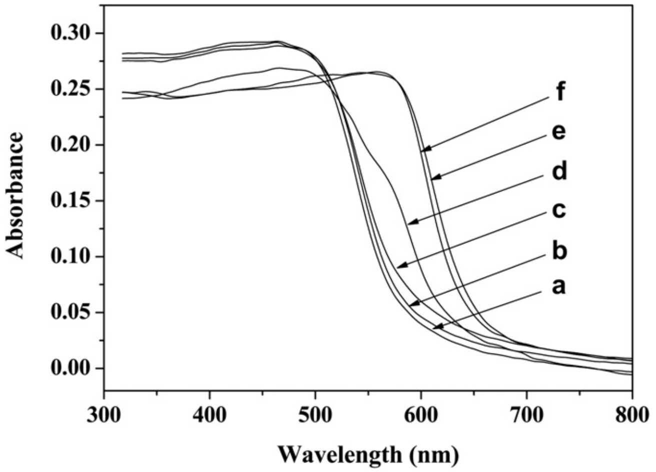


Fig. 4. Absorption spectra of P-PAN$_{TAS}$F in aqueous solutions at pH (a) 7.0, (b) 3.1, (c) 2.2, (d) 1.1, (e) 0.5, and (f) 0.2.

microenvironment. Compared to phenolphthalein ($\lambda_{max} = 553$ nm) and our previous halochromic fiber ($\lambda_{max} = 574$ nm) [21], the maximum absorption of P-PAN$_{TAS}$F in basic media is 600 nm. The red shift may be due to the effect of the ethyl orange moieties and changes in its microenvironment [24]. Moreover, the corresponding dynamic ranges shift from pH 3–5 to 0–1 in acidic solutions and from pH 8–11 to pH 13–14 in basic solutions. The reason for these phenomena may lie in the buffering action of the amino groups on the modified fiber. Furthermore, changes in the microenvironment and the increase of the dimensional effect may also influence the color-changing process.

The response time of the P-PAN$_{TAS}$F at pH 0.5 and 13.6 are shown in Fig. 6. When quickly immersed into the aqueous buffer solution at pH 0.5, the P-PAN$_{TAS}$F became red orange in 5 s, deep pink within 1 min and equilibrated in 5 min. The response time decreased with decreasing pH. When the pH was decreased to 0.1, the color changes took place within 1 s. In the basic condition (at pH 13.6), a similar phenomenon was observed and it was discussed in our previous paper [21]. The color changes of the P-PAN$_{TAS}$F in 1 M HCl and 1 M NaOH aqueous solutions over time were recorded and are shown in Fig. 7. These photos show that the color of the P-PAN$_{TAS}$F changed from yellow to red orange in 1 M HCl in <1 s and then

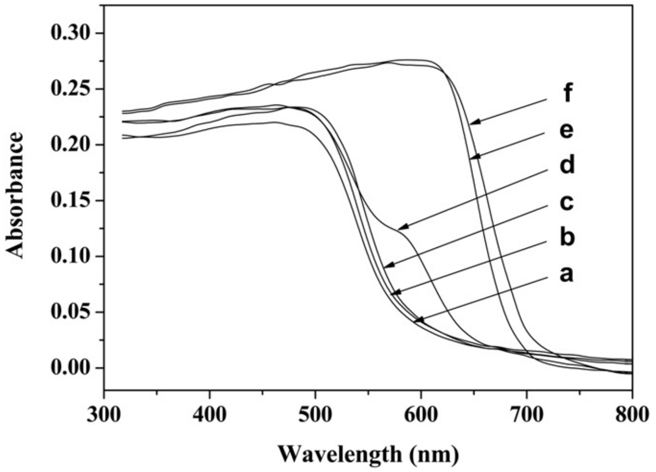


Fig. 5. Absorption spectra of P-PAN$_{TAS}$F in aqueous solutions at pH (a) 7.0, (b) 10.8, (c) 11.9, (d) 13.0, (e) 13.6, and (f) 14.0.

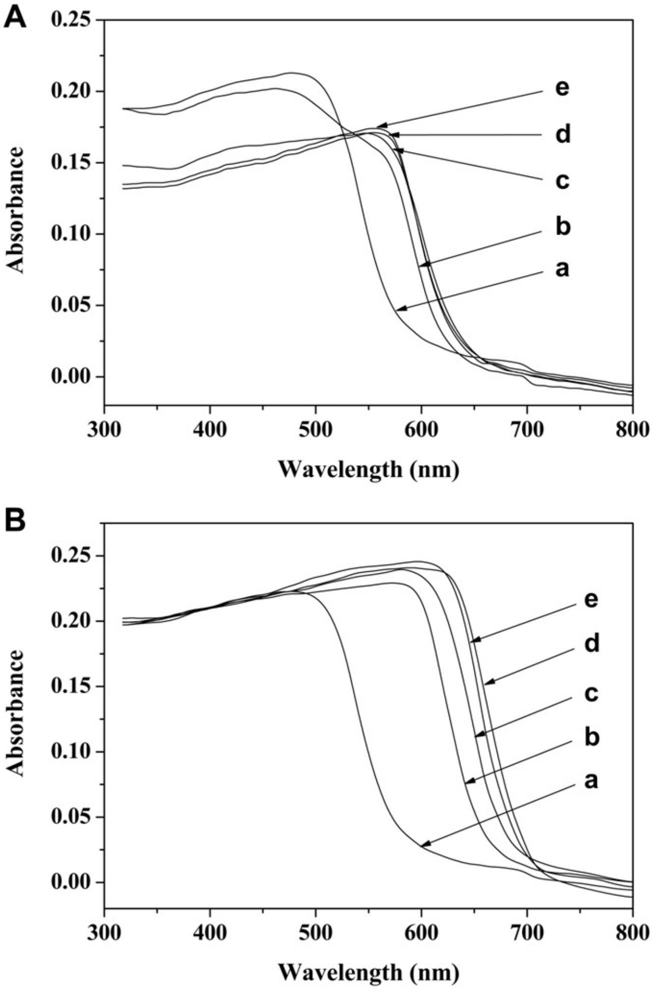


Fig. 6. Absorption spectra of P-PAN$_{TAS}$F in aqueous buffer solutions at (a) 0 min, (b) 1 min, (c) 2 min, (d) 5 min, and (e) 10 min. (A) at pH 0.5, (B) at pH 13.6.

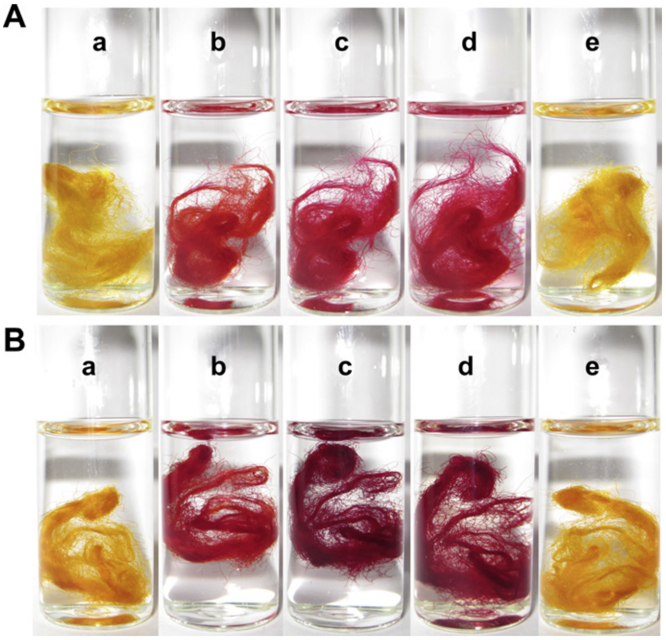


Fig. 7. The color-changing properties of P-PAN$_{TAS}$F in aqueous solution after (a) 0 s, (b) 1 s, (c) 20 s, (d) 24 h, and (e) neutralization. (A) 1 M HCl, (B) 1 M NaOH.

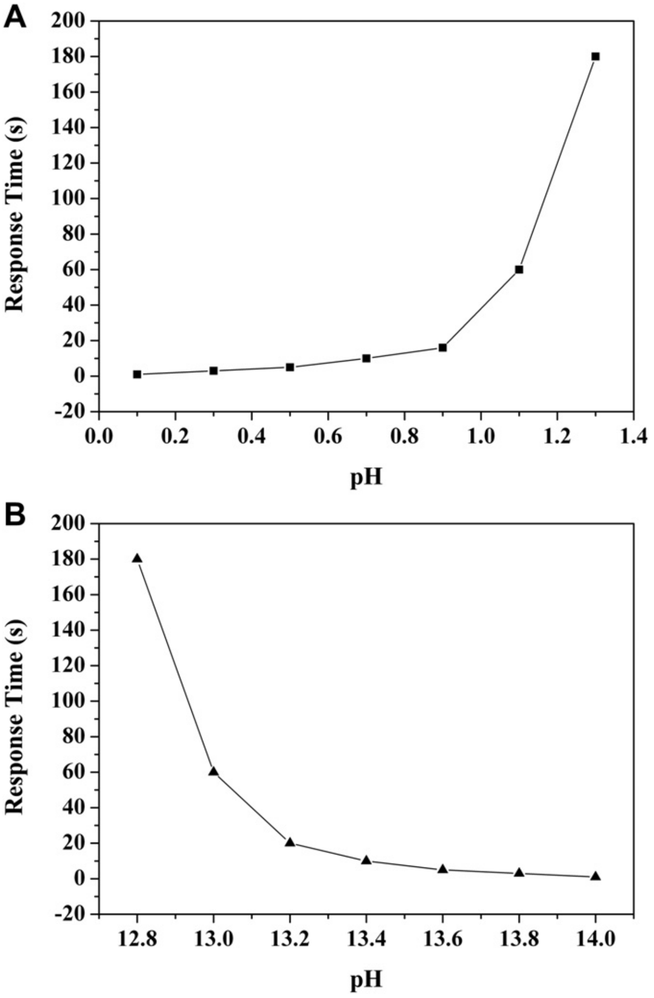


Fig. 8. Naked-eye response time of the color change of P-PAN$_{TAS}$F at different pH. (A) HCl solutions, (B) NaOH solutions.

changed to deep pink in <20 s (Fig. 7A (b, c)). A similar phenomenon was also observed in 1 M NaOH (from yellow to dark violet, Fig. 7B (b, c)). After soaking in 1 M HCl for 24 h or longer, the color of the P-PAN$_{TAS}$F was effectively maintained (Fig. 7A (d)). However, the color of the P-PAN$_{TAS}$F in 1 M NaOH changed from dark violet to red orange (Fig. 7B (d)), which was also observed and discussed in our previous work [21]. After soaking in 1 M HCl or 1 M NaOH for 24 h, the color of P-PAN$_{TAS}$F changed back to yellow after neutralization (Fig. 7A (e) and B (e)). In general, response time is greatly affected by the diffusion speed of the analyte. Fibers are known to have larger specific surface areas than granular materials. Compared to polymer beads and films, fibers also have good kinetic properties due to short diffusion paths from the analyte to the fiber surfaces. Therefore, the response time of the P-PAN$_{TAS}$F is faster than most of the recently reported granular materials [9].

Naked-eye response time is the time a person takes to react to the color change by naked-eye. For self-protection applications, detection with the naked-eye is more important than instrumental detection. The naked-eye response times of the P-PAN$_{TAS}$F in different pH aqueous solutions were measured by naked-eye and a stopwatch. The results are shown in Fig. 8. With pH increasing from 0.1 to 1.3, the naked-eye response time increases from 1 s to 180 s (see Fig. 8A). Whereas in basic media, the naked-eye response time decreases remarkably as the pH increased (see Fig. 8B). This further shows that the response time of the P-PAN$_{TAS}$F decreases with increasing concentrations of acids or bases.

Long life, reusability and photostability are also essential for functional materials. When immersed into an aqueous solution at pH 0.5, the P-PAN$_{TAS}$F changed its color to deep pink and did not decay after 24 h (see Fig. 9A (a, b)). The maximum absorption at 553 nm for free phenolphthalein occurs at pH 11, and it decays quickly because of the formation of the colorless trianion structure [24]. However, the absorption of the P-PAN$_{TAS}$F did not decay even when it was dipped into a solution at pH 13.6 for 24 h (see Fig. 9C (a, b)).

To verify its reusability, the P-PAN$_{TAS}$F was treated repeatedly with both pH 0.5 and pH 13.6 solutions. After 300 times, the fiber still responded very well to the acid (pH 0.5, deep pink) and base solutions (pH 13.6, dark violet). The absorption spectra of the P-PAN$_{TAS}$F after 300 times at pH 0.5, 7.0 and 13.6 were the same as unused P-PAN$_{TAS}$F (see Fig. 9A (a, c), B (a, b) and C (a, c)), which demonstrates excellent reusability and durability. The P-PAN$_{TAS}$F was also exposed to direct sunlight for 60 days, and the optical properties did not show any changes (see Fig. 9A (a, d), B (a, c) and C (a, d)).

To study the color-changing ability and stability of the P-PAN$_{TAS}$F in strong acid and base solutions, the color changes of the P-PAN$_{TAS}$F in 4 M HCl and 4 M NaOH were recorded over time and are shown in Fig. 10. These photos show that P-PAN$_{TAS}$F could be immersed into 4 M HCl and 4 M NaOH for 24 h without deterioration (see Fig. 10A (b, d) and B (b, d)). After neutralization, the P-PAN$_{TAS}$F changed back to yellow and then responded to the 4 M HCl and NaOH for the next cycle (see Fig. 10A (e, f) and B (e, f)). Even in concentrated HCl (36%) and NaOH (30%), the same phenomena were observed. All these experiments prove that this colorimetric fiber has good kinetic properties and is stable in strong acid and base solutions.

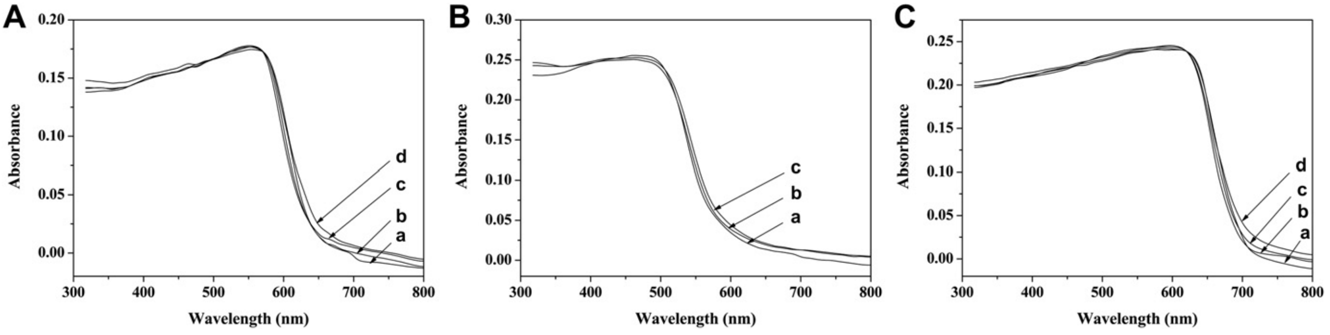


Fig. 9. Absorption spectra of P-PAN$_{TAS}$F. (A) at pH 0.5: (a) first cycle, 10 min, (b) first cycle, 24 h, (c) after 300 cycles, and (d) exposed under sunlight for 60 days; (B) at pH 7.0: (a) P-PAN$_{TAS}$F, (b) after 300 cycles, and (c) exposed under sunlight for 60 days; (C) at pH 13.6: (a) first cycle, 10 min, (b) first cycle, 24 h, (c) after 300 cycles, and (d) exposed under sunlight for 60 days.

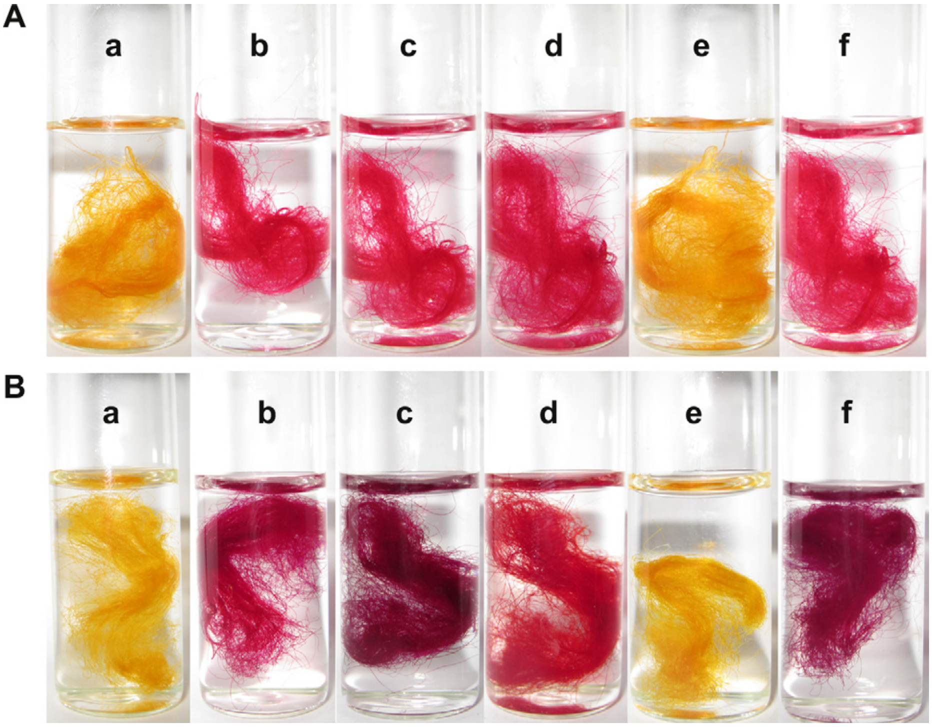


Fig. 10. The color-changing properties of P-PAN$_{TAS}$F in aqueous solution after (a) 0 s, (b) 1 s, (c) 20 s, (d) 24 h, (e) neutralization, and (f) next cycle 20 s. (A) 4 M HCl, (B) 4 M NaOH.

Fig. 11. The color-changing properties of P-PAN$_{TAS}$F in (a) CH_3COOH, 4 M, (b) citric acid, 4 M, (c) H_3PO_4, 4 M, (d) HNO_3, 4 M, (e) HCl, 4 M, (f) HBr, 4 M, and (g) H_2SO_4, 4 M. (h) Na_2CO_3, saturated aqueous solution, (i) $Ca(OH)_2$, saturated aqueous solution, (j) Na_3PO_4, saturated aqueous solution, (k) $Ba(OH)_2$, saturated aqueous solution, (l) Na_2SiO_3, saturated aqueous solution, (m) KOH, 4 M, and (n) NaOH, 4 M.

The color-changing properties of the P-PAN$_{TAS}$F in other commonly used concentrated acid and base solutions are shown in Fig. 11. The acidity of CH_3COOH (pH 1.9) was too weak to induce color change in the P-PAN$_{TAS}$F (Fig. 11(a)). Citric acid (4 M) caused the color of P-PAN$_{TAS}$F to change to red-orange and was easily distinguished from the other acids, which shows that the P-PAN$_{TAS}$F is also applicable to strong organic acids (Fig. 11(b)). The P-PAN$_{TAS}$F responded to all the tested strong mineral acid solutions with color changes from orange to deep pink (4 M H_3PO_4, HCl and H_2SO_4) or red (4 M HNO_3 and HBr). Saturated Na_2CO_3 (pH 12.6) did not cause a color change in the P-PAN$_{TAS}$F because its pH sensitivity starts at 13.0 (Fig. 11(h)). As expected, the color of the fiber changed from yellow to dark violet in strong basic solutions such as saturated $Ba(OH)_2$, Na_2SiO_3 and 4 M KOH (Fig. 11).

These experiments show that the color changes of the P-PAN$_{TAS}$F occur for most strong acids and bases, and P-PAN$_{TAS}$F is a good dual colorimetric sensor for various strong acids and bases that are harmful to the skin. This is especially important in the application of skin protection because the harmfulness of acidic and basic solutions to the skin worsen with increasing acidity and alkalinity.

4. Conclusions

A novel dual colorimetric fiber based on two acid–base indicators has been prepared by first aminating commercially available polyacrylonitrile fiber with tetraethylenepentamine and then immobilizing ethyl orange moieties covalently through an alkylation reaction and a diazo coupling reaction; finally, the fiber was modified with phenolphthalein covalently using a Mannich reaction. This modified fiber responds to acids and bases with a remarkable color change from yellow to deep pink or to dark violet with a fast response time (<1 s in 1 M HCl or 1 M NaOH). The color changes of the P-PAN$_{TAS}$F can be induced by various strong acids and bases with a large range of concentrations. The P-PAN$_{TAS}$F also shows excellent reusability (>300 times), high photostability (>60 days under direct exposure to sunlight) and recycle stability (color-changing ability does not fade after being recycled 300 times). These attractive features of this colorimetric fiber based on a wearable PANF make it a useful sensor fiber which has the potential to manufacture automatic leak detection wrappers for acids and bases and self-monitoring exposure suits for people who work in environments contaminated by hazardous acids and bases.

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Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2011.08.015.

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