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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