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Reversible and universal pH sensing cellulose nanofibers for health monitor

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ABSTRACT

Development of an eco-friendly, reversible, and universal pH sensor based on electrospun cellulose nanofiber functionalized with a natural pigment is described in this study. A natural pigment from red cabbage has been extracted and incorporated onto the electrospun non-woven cellulose fibers by means of adsorption and chemical cross-linking techniques. The results revealed that the developed biocomposite is a universal pH sensor which is capable of detecting pH values in the range of 1–14 by indicating the unique color code against each pH. It was also found that the pH sensing was stable at different temperatures and at prolonged time. Moreover, the colors were reversible and the pH sensor was recyclable. Present study opens up new possibilities for using the developed universal pH sensor as a health monitor.

1. Introduction

Naturally humans are visual creatures that we always depend on the information that are represented in visual format. Indeed, many of the instruments starting from telescopes to microscopes to infrared cameras are extensions of our visual senses. It is always preferable to transduce any complex data into visible than any other formats [1,2]. It is well known that colors play a crucial role in our day-to-day life. Chromic materials that reversibly change color upon an external stimulus such as light, heat, and pH, have been attractive to many researchers in recent times, especially in the area of sensors. The chromic fibrous materials are particularly interesting within fiber/textile industry. Halochromic or pH sensitive fabrics are materials that can change color due to change in pH, which can be used for applications such as wound dressing, protective clothing, filtration, etc. [3–5]. Most synthetic dyes are halochromic that changes from one color to another depending on pH. However, they have detrimental effects on the environment and associated with allergic, toxic and other harmful responses [6,7]. The pigments extracted from natural resources are expected to be biocompatible and biodegradable. However, replacing synthetic dyes with natural colorants are challenging, mainly due to the stability of color with respect to light, oxidation, temperature, and pH. Among natural colorants, anthocyanins from red cabbage (*Brassica oleracea* L.) possess preferable properties such as good water solubility, coloration at extended pH range, stability against photodegradation and excellent color resistance at higher temperatures. It was reported that anthocyanins from red cabbage are more stable than the others based on the molecular structure. This is attributed to acyl protection of the hydroxyl groups. Acylated anthocynanins are generally more stable against color fading than the non-acylated anologs [8]. Due to the advantageous properties of anthocyanins from red cabbage, it is preferred as a natural colorant for developing a pH sensor in this study.

Electrospun nanofibers show unique characteristics such as small pore sizes, high porosity, high specific surface area and high absorbant capacity which render them highly suited to be used in chromic sensors [9,10]. Cellulose, the most abundant biomaterial has been demonstrated as a potential raw material for preparation of nanofibers with different functionalities for a variety of applications [11–14]. Nevertheless, the use of natural pigments has been limited due to absence of standard, convenient, and reproducible immobilizing methods. In view of developing a universal and eco-friendly pH sensor, this study is designed in such a way that both the colorant-extract of red cabbage, and the supporting matrix-cellulose nanofibers, are of natural origin. The extract of red cabbage

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was immobilized onto the electrospun cellulose nanofibers by means of adsorption followed by chemical cross-linking using a bifunctional diisocyanate. Further, the dyed-cellulose nanofibers were tested against simulated conditions having different pHs for the purpose of health monitoring.

2. Experimental

2.1. Extraction of natural pigment

The compacted leaves (bulbs) (2× 200 g) of fresh red cabbage (*B. oleracea* L.) were smashed using a domestic blender and soaked in 80% and 100% ethanol (500 mL) for 24 h. Then the extract was filtered and the residue was washed with ethanol (2× 100 mL). The filtrates were concentrated under vacuum and kept on ice chest for 48 h. The residue obtained using 80% ethanol yielded pink colored solid (yield: 1.8 g). Meanwhile, the residue extracted using 100% ethanol resulted in pink colored oil-like product (yield: 1.5 g). The natural colorant extracted from red cabbage is indicated by RC. The RC developed a green color with alcoholic Fe^{3+}, pink-red color with Mg–HCl, and yellow color with NaOH. Purple spot was observed when the residues were exposed to UV and yellow color was developed on exposure to ammonia. The RC responded to Wilson's boric acid test [15], Gibb's test [16], and Molisch's test and did not respond to Horhammer–Hansel test indicating that the extracted residues consist of flavonoids with major constituent as anthocyanin [17–19].

2.2. Electrospinning

A 7–8 wt.% solution of cellulose acetate (CA, M_n = 50,000 g/mol, Aldrich) was prepared using dimethylacetamide/acetone (v/v = 1:2) and electrospun at 10 kV at a tip-to-collector distance of 18 cm at 25 °C and relative humidity of 40–50%. The CA electrospun non-woven fabric (CA-ESNW) was collected on aluminum foil and dried at 25 °C in vacuum for 24 h. The CA-ESNW fabrics were deacetylated in 0.05 M NaOH for 30 h to regenerate cellulose non-woven fabrics (Cs-ESNW) [10,12].

2.3. Immobilization of natural pigment

The extracted solid natural pigment RC was dissolved in 80% ethanol at the concentration of 20 mg of pigment per 100 μL of solvent. The Cs-ESNW was cut into 2 cm × 2 cm (each 1.5–2.0 mg) and placed on a small glass-petri disk. The pigment solution was dispensed onto the Cs-ESNWs at the concentration of ca. 1, 5, 10 and 20 mg of pigment/mg of Cs-ESNW and kept at 30 °C for 10 h followed by drying at 25 °C for 24 h. The pigment molecules were fixed on the matrix using hexamethylene diisocyanate (10%, v/v in n-hexane) for 60 min at 50 °C. Then the cross-linked matrix was washed with n-hexane repeatedly, dried at room temperature, and stored in desiccator at room temperature until further use. The natural colorant loaded into Cs-ESNW was designated as RC/Cs-ESNW.

2.4. Characterization

The morphologies of Cs-ESNW, and RC/Cs-ESNW nanofiber mats were observed under a JEOL JSM-5900 scanning electron microscopy (SEM) after sputtering the samples with platinum for 120 s. To detect the presence of natural pigment in the fiber, the elemental analysis using Energy dispersive X-ray analysis (EDAX) was performed on the RC/Cs-ESNW mats.

2.5. Color measurements

The following buffer solutions were used to test the color schemes of the RC/Cs-ESNW nanofibers having RC content of 5 mg/mg of ESNW: for pH 1–2, hydrochloric acid–potassium chloride buffer; for pH 3–6, citrate buffer; for pH 7–8, phosphate buffer; for pH 9–10, carbonate–bicarbonate buffer. In the case of pH 11–14 the combination of HCl–NaOH was used. For comparing the color schemes of precursor RC and RC/Cs-ESNW nanofibers, the CIE $L^*a^*b^*$ (International Commission of Illumination) color space coordinates were determined. In CIE $L^*a^*b^*$, L^* is lightness, a^* is the position between green and red, and b^* is the position between yellow and blue. Photographs of the RC solutions and RC/Cs-ESNW nanofibers at different pH were taken under same lighting conditions and analyzed for L^*, a^*, b^* and RGB values by ADOBE PHOTOSHOP 7.0. The RGB – red, green, and blue values of a color determines the color space of a color. The colors of the RC and RC/Cs-ESNW nanofiber mats each pH were compared with the other pHs by calculating the total color difference (ΔE) as shown in Eq. (1).

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (1)$$

where, ΔL is the difference in brightness, Δa is the redness difference, and Δb is the yellowness difference between the samples [20,21].

2.6. Stability and recycle usage of pH sensor

The stability of the pH sensor was performed under different temperature and longer storage period. The pH sensitive RC/Cs-ESNW mats were incubated at two extreme temperatures −50 °C and 100 °C for 24 h. Then the pH sensitivity was examined at three different pHs viz. 2, 5, and 10. In another set of experiment, the RC/Cs-ESNW mats were tested with solutions having pH from 1 to 14. Then the samples were dried at 25 °C under vacuum and reused for examination with solutions having pH 2. Similarly, the samples were dried and reused for color test using buffers having pH 5 and 10. Further the effect of storage time at room temperature was also studied.

3. Results and discussion

3.1. Morphological studies

The morphologies of Cs-ESNW and RC/Cs-ESNW composite nanofiber mats are shown in Fig. 1. The precursor Cs-ESNW mat was consisting of fine nanofibers having average fiber diameter $\varphi = 228 \pm 118$ nm (Fig. 1a). The optical images presented in Fig. 1c shows the surfaces of the RC/Cs-ESNW nanofiber mats with different concentrations of RC extract. The experimental feed of 1 mg of pigment per 1 mg of Cs-ESNW mat did not give sufficient visible color as seen in Fig. 1c (left). The increase in the concentration of pigment from 1 mg to 5, 10, and 20 mg/mg of Cs-ESNW gave enriched natural color of RC extract. After immobilization of RC extract onto the Cs-ESNW by chemical cross-linking, the fiber diameters were slightly increased (Figs. 1b and 2).

The major constituents of red cabbage are flavonoids in the form of anthocyanins, vitamins B_1 and B_2 (sources of nitrogen), vitamin B_6 (source of phosphorous), and potassium [20,21]. EDAX performed on the RC/Cs-ESNW nanofibers indicated the successful incorporation of RC extract into the nanofibers by evidencing the presence of elements such as nitrogen, phosphorous, and potassium (Fig. 3). Further, the cross-linking reaction between the molecules present in RC extract and the cellulose were confirmed by means of FT-IR spectroscopy (Fig. 4). The cross-linking reaction can occur in mainly two possible ways. On one hand, the