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ORIGINAL PAPER

The influences of enzymatic processing on physico-chemical and pigment dyeing characteristics of cotton fabrics

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Abstract First, a crude cellulase was used to treat cotton fabrics to investigate its influences on the physicochemical properties of cotton. The FTIR and XRD analyses both confirmed the enzymatic treatment could increase the crystallinity of cotton, especially at a higher cellulase dosage. Once treated, the number of dissociable groups (–COOH) in cotton decreased, while that of the reducing groups (–CHO) increased. Second, copper phthalocyanine (CuPc) was selected to prepare an anionic nanoscale pigment dispersion to detect its dyeability on different cotton samples. It was concluded that the enzymatic hydrolysis itself had no significant impacts on the pigment dyeing performance. However, cellulase protein still stayed on the cotton surface after treatment and produced an enhancement effect on the pigment uptake due to strong hydrophobic interactions between them. This could be verified by *K*/*S* measurement and SEM observations.

Keywords Cellulase · Cotton · Copper phthalocyanine · Nanoscale pigment · Enhancement effect

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Introduction

Chemically, cotton is a natural polymer of D-glucose in which individual glucose units are sequentially connected by β-1, 4-glycosidic covalent bonds (Dourado et al. 1999). Natural cotton has a number of superior performances such as good moisture absorbency, outstanding biodegradability and being comfortable to wear as well as easy to color. Therefore, its consumption and market share in the textile industry are considerable (Hashem et al. 2010; Xie et al. 2012). In post-treatment, natural cotton is frequently subjected to enzymatic polishing by cellulase to remove the "fuzz" or "pilling" from the surface to enhance its appearance, hand feeling and commercial value. Cellulase enzymes as a class of glycoside hydrolases containing several endoglucanases (EGs), cellobiohydrolases (CBHs) and β-glucosidases (BGs) have recently received a great deal of attention in the textile industry because of their excellent hydrolytic performance on cellulosic polymers such as cotton, rayon and ramie (Hao et al. 2012b; Henrissat 1994; Saravanan et al. 2009).

As is well known, cellulase polishing has profound influences on the structural, physicochemical and coloring properties of natural cotton. Enzymatic actions on cotton can result in systematic and progressive removal of its primary and secondary walls, which will reduce the fineness of fibers, clear the surface of hairs/pillings, cause weight loss, crack the cotton surface and even result in the rupture of microfibrils (Nithya et al. 2011; Paralikar and Bhatawdekar 1984; Spinelli 1998; Yamade et al. 2005). Gradual degradation by cellulase will also lead to a drop in the molecular weight and tensile strength of cotton, especially at an extended treatment time and high agitation level (Paulo and Almeida 1996; Rousselle and Howley 1998). However, cotton's wettability and moisture regaining will be improved because enzymatic polishing can enlarge its mean pore radius and increase its accessible surface area (Csiszar et al. 2001). Moreover, the handle, softness, crease recovery and dimensional stability of cotton fabrics can be enhanced by enzymatic hydrolysis (Cortez et al. 2002; Gulrajani et al. 1998). After cellulase treatment, some changes in the supramolecular structure of cotton such as the crystallinity and crystallite dimension can also be detected (Akerholm et al. 2004; Cao and Tan 2005; Hao et al. 2014; Nelson and O'Connor 1964).

The dyeability of cotton will also be altered along with the enzymatic treatment (Adeel et al. 2015; Khan et al. 2014; Mori et al. 1996; Zolriasatein and Yazdanshenas 2014). The saturation uptake of anionic dyes greatly depends on the weight loss of cotton resulting from the enzymatic hydrolysis (Mori et al. 1996). The uptake and color strength of reactive dyes on cellulase-treated cotton are expected to be lower than those on untreated cotton at the same dye concentration because of their higher crystallinity (Lv and Zhou 1999). Moreover, cellulase treatment will lead to the formation of some aldehyde groups and consequently produce negative charges in cotton, thus enhancing the electrostatic repulsion forces between dye molecules and cotton to result in lower dye uptake (Zolriasatein and Yazdanshenas 2014). Controversially, some opposite results were also reached by other researchers. Tsatsaroni and Liakopoulou-Kyriakides (1995) found that cellulase treatment could result in improvement in the uptake of anionic natural dyes on cotton. Andreaus et al. (1999) also noticed that the affinity of anionic acid dyes to cotton fabrics can apparently be increased by adsorbed cellulase proteins after the enzymatic process. They attributed this effect to the increased presence of ionic groups on the fabric after cellulase coverage. Anionic nanoscale pigments, as attractive alternatives to anionic soluble dyes, have been widely employed to color cotton because they have a faster adsorption rate, higher coloring efficiency and lower energy consumption (Hao et al. 2009). Nevertheless, the influences of cellulase treatment on the coloring performance of anionic pigments on cotton have never been described in the previous literature.

In this research, a crude cellulase was utilized to treat natural cotton fabrics. First, the enzymatic modifications to the physicochemical and structural properties of cotton were investigated. Second, copper phthalocyanine (CuPc) pigment, with favorable color strength, brightness of shade and fastness properties, was selected to prepare an anionic nanoscale dispersion with the assistance of anionic dispersants. Finally, the influences of cellulase treatment on the dyeability of cotton using this nanoscale pigment were carefully discussed.

Experimental

Materials

Pure cotton knit fabrics (120 g/m^2) were provided by Furi Textile Factory, China. They were subjected to conventional scouring and bleaching procedures to remove noncellulosic impurities and further rinsed with 90 °C deionized water for 10 min to eliminate any residual chemicals in them. Total crude cellulase (100 mg/ml protein content) from *T. reesei* was supplied by Haiyi Chemicals, China. The other chemical agents were all of analytical reagent grade.

Enzymatic treatment of cotton

The enzymatic processes were carried out in thermostatic water-bath equipment with mechanical stirring at 120 rpm. Cotton samples (10 g per piece) were submerged in 300 ml cellulase solutions. Two cellulase charges (1 ml/l as low dosage and 3 ml/l as high dosage) were used to evaluate the effect of the cellulase load on the cotton properties. The pH was adjusted to 4.5 using acetate buffer, and the resulting systems were kept at 50 °C for 120 min to complete

the enzymatic modification. Thereafter, one half of the treated cotton (3 ml/l cellulase) was dehydrated by centrifuge to retain the cellulase bound on it and denoted as the cellulase-on sample. The remaining half of the cotton was thoroughly rinsed with 95 °C hot water to totally elinimate the bound cellulase and denoted as the cellulase-free sample.

Preparation of the nanoscale pigment suspension and its dyeing procedure on cotton

Fifteen grams CuPc pigment and 3 g anionic dispersant (copolymer of styrene and maleic acid, Mn: 61,000) were added to 132 g deionized water with the assistance of an IKA stirrer at 10,000 rpm for 20 min. Subsequently, the pigment suspension was further smashed using an M-110EHI microfluidizer at a pressure of 20,000 psi for 30 min to afford a nanoscale pigment suspension.

The untreated, cellulase-free and cellulase-on cotton samples were separately immersed in baths containing nanoscale pigment (4 %, owf) with a 30:1 liquor ratio for 120 min at 50 °C. After adsorption, all samples were immediately introduced to the fixation solutions containing 5 g/l binder FSB (copolymer of styrene and butyl acrylate) at 80 °C for 15 min, rinsed in tap water and finally dried in air.

Measurements

Weight and strength loss of cotton

The cotton samples to be tested were dried in weighing bottles at 105 °C for 2 h and then weighed after cooling in a desiccator. The percentage weight loss (WL %) of cotton after the enzymatic process was determined according to the following equation:

$$\mathrm{WL}\,(\%) = \frac{W_1 - W_2}{W_1} \times 100 \qquad (1)$$

where W_1 and W_2 are the weights of cotton samples before and after enzymatic treatment, respectively.

The tensile strength of cotton was tested according to ISO 13934-1-1999 using a computer-aided YG-2 testing machine. Samples were tested five times, and the average value was offered. The percentage loss in tensile strength (TSL %) was calculated according to the following equation:

$$\mathrm{TSL}\,(\%) = \frac{S_1 - S_2}{S_1} \times 100 \qquad (2)$$

where S_1 and S_2 are the tensile strengths of cotton samples before and after enzymatic treatment, respectively.

Hydrophilicity and moisture regain of cotton

The hydrophilicity of cotton was evaluated using the dynamic wicking test similarly to the previous method (Nithya et al. 2011; Wang et al. 2008). In a capillometer, the cotton samples (40 mm × 5 mm) were suspended vertically with the bottom edge immersed in a thin layer of the colored water. The spontaneous wicking came up, and a millimeter-scale ruler was used to conveniently measure the height of the liquid boundary for a period of 20, 40, 60, 120, 180 and 240 s. Each operation was repeated three times and the average value reported.

The moisture regain test was carried out according to the previously reported method (Kang and Epps 2009). Cotton samples were conditioned at 65 ± 2 % RH and 21 ± 2 °C for 12 h prior to the weight measurement for moisture regain. The measured samples were oven-dried at 105 ± 2 °C for 12 h and then reweighed after this drying process. The drying, cooling and weighing processes were repeated until the change in mass between two successive tests was less than 0.1 % of the cotton mass. The difference between the conditioned and oven-dried mass was calculated in percentage as moisture regain according to the following equation:

$$\text{Moisture regain}\,(\%) = \frac{M - D}{D} \times 100 \qquad (3)$$

where M and D are the masses of conditioned and oven-dried cotton samples, respectively.

The numbers of dissociable and reducing groups in cotton

Polyelectrolyte (polybrene) titration was used to evaluate the dissociable groups (–COOH) in different cotton samples (Zemljic 2008). Typically, all –COOH groups were primarily converted into their sodium form by immersing the fibers in $NaHCO_3$ solution (0.001 M) and adjusting the pH to 9 by NaOH solution (0.1 M). Subsequently, excessive electrolytes were

removed by washing the fibers with distilled water until the conductivity was less than 2 μS/cm; 0.3 g of dry fiber and 40 ml of NaCl solution (0.01 M) were added to a glass beaker, and the pH was set to 7. Excessive cationic polyelectrolytes were added to the suspension. After 30 min stirring to reach the adsorption equilibrium, the solid was filtrated by a Buchner funnel and immediately washed with water to obtain a 55-ml filtrate. Then 10 ml of filtrate was titrated with poly (ethylenesulfonate) solution (1 g/l) using a particle charge detector to determine the end point. Blank samples containing only polyelectrolyte were titrated in the same way as the cotton fibers to eliminate any influence from the glassware or filter. The number of dissociable groups (–COOH) could be calculated by the volume difference of poly(ethylenesulfonate) consumption between the blank and fiber sample.

The concentration of reducing groups (–CHO) in cotton samples was evaluated by oxidizing the cotton samples with sodium chlorite (0.3 M sodium chlorite in the presence of 2 M acetic acid solution for 48 h treatment) and then redetermining the –COOH groups in the oxidized ones using polyelectrolyte titration (Lewin and Ettinger 1969).

FTIR and XRD analysis of cotton

FTIR spectra of various cotton samples were recorded using a Fourier transform infrared instrument within the range of 400–4000 cm^{-1}. All the cotton samples were ground into fine powders using a fiber microtome, blended with KBr and finally pressed into ultrathin pellets.

XRD patterns of different cotton samples were recorded using an X-ray diffractometer with Ni-filtered Cu Ka radiation at 40 kV and 30 mA. Scattered radiation was emitted in the range of 2θ from 5 to 40° at a scan rate of 2° min^{-1}. The crystallinity index (CI) was obtained in terms of the ratio of the area arising from the crystalline phase to total area (Lu et al. 2012). A single crystalline peak was extracted by a deconvolution process using PeakFit Software (Sea-Solve Software Inc., Richmond, CA), assuming a Gaussian function for each peak. Iterations were repeated until the maximum F number (>10,000, corresponding to an R^2 value of 0.997) was achieved (Park et al. 2010). The Scherrer equation was utilized to calculate the crystallite size, D (nm), perpendicular to the (200) plane as:

$$D = \frac{K\lambda}{\beta \mathrm{Cos}\theta} \tag{4}$$

where K is the correction factor, θ is the diffraction angle, λ is the X-ray wavelength, and β is the peak width at half maximum intensity in radians (Elazzouzi-Hafraoui et al. 2008; French and Santiago Cintrón 2013).

Characterizations of nanoscale pigment suspension

The nanoscale pigment dispersion was diluted 2000 times using distilled water, and its pH value was set to 7. Subsequently, a Malvern Nano-ZS Zetasizer was used to measure the particle sizes by dynamic light scattering (DLS) and zeta potentials by electrophoretic mobility at 25 °C. Measurements were made five times to ensure the reproducibility, and the average result was quoted. A drop of the diluted sample was placed on a copper grid and observed under a JEOL JEM-1200EX transmission electron microscope (TEM) with an acceleration voltage of 80 kV. The pigment dispersion absorption spectrum was scanned in the range of 450–750 nm using an automatic spectrophotometer.

Microscope analysis

A light microscope (Nikon E600) fitted with a digital camera was employed to observe the fuzz fibers and pigment deposited on the cotton samples. SEM analysis was carried out by mounting the cotton samples on a stub using double-sided adhesive tape. The samples were coated with gold using a sputter coater unit and then viewed using a JSM-6390LV scanning electron microscope (JEOL, Japan) at an accelerating voltage of 10 kV.

K/S measurement

The *K/S* value of cotton samples after pigment coloring was detected with an Xrite-8400 spectrophotometer under illuminant D65 and the 10° standard observer. The absorbance spectrum was scanned in the regions from 450 to 700 nm, and the reflectance at the maximum absorption wavelength was taken to

calculate the K/S value of samples by the Kubelka-Munk equation:

$$K/S = \frac{(1-R)^2}{2R} \quad (5)$$

where K, S and R are the absorption coefficient, scatter coefficient and fractional reflectance at λ_{max}, respectively.

Results and discussion

Influences of enzymatic hydrolysis on the physicochemical properties of cotton

Effect on cotton structure

Aggressive attacks of cellulase focusing on cotton bulk will inevitably modify its structural properties. Infrared spectroscopy is very useful in the structural elucidation of various materials. The infrared spectra of cotton samples, measured by transmission mode, are presented in Fig. 1a. The obvious absorption bands around 3400 and 2900 cm^{-1} can be attributed to the O–H and C–H stretching, respectively. The peak around 1640 cm^{-1} is caused by the adsorbed water molecules (Chung et al. 2004). Absorption bands at 1429 and 1372 cm^{-1} can be assigned to the CH_2 scissoring motion and C–H bending, respectively. The absorbing peak at 1163 cm^{-1} is the representative of antisymmetric bridge stretching of the C–O–C bond (Cao and Tan 2005; Chung et al. 2004). The crystalline structure of cotton is one of the best parameters for understanding its degradation by cellulase. The ratio of the absorptive intensity at 1372 and 2900 cm^{-1} (A_{1372}/A_{2900}) is usually utilized to determine the crystallinity of various cellulosic materials (Akerholm et al. 2004; Nelson and O'Connor 1964). After calculation, the A_{1372}/A_{2900} values for the untreated, low- and high-dosage cellulase-treated cotton are 0.919, 0.927 and 0.933, respectively, which makes clear that the enzymatic treatment can enhance the crystallinity of cotton because the amorphous portion of cotton with a larger enzyme-accessible surface area is more easily attacked by cellulase. XRD analysis is also widely employed to compute the cellulose crystallinity (French and Santiago Cintrón 2013; Langan et al. 2001; Nishiyama 2009; Sugiyama et al. 1991; Wada et al. 1997; Yue et al. 2012). The XRD spectra of different cotton samples are given in Fig. 1b to demonstrate the changes in crystalline structure produced by enzymatic hydrolysis. Several means are employed for calculating the crystallinity of cellulose from the raw spectrographic data of XRD. Segal et al. (1959) proposed a crystallinity Index (CI) as a way of rapidly determining the relative crystallinity of various cellulosic samples. With numerous citations, the Segal CI has been used for over 5 decades to interpret changes in cellulose structure after biological treatments. Although with some faults and limitations, it continues to be used because of its facility and understandability. Recently, French and Santiago Cintrón (2013) offered an updated approach to provide better calculations and explanations for the Segal CI. They concluded that there is a strong relationship

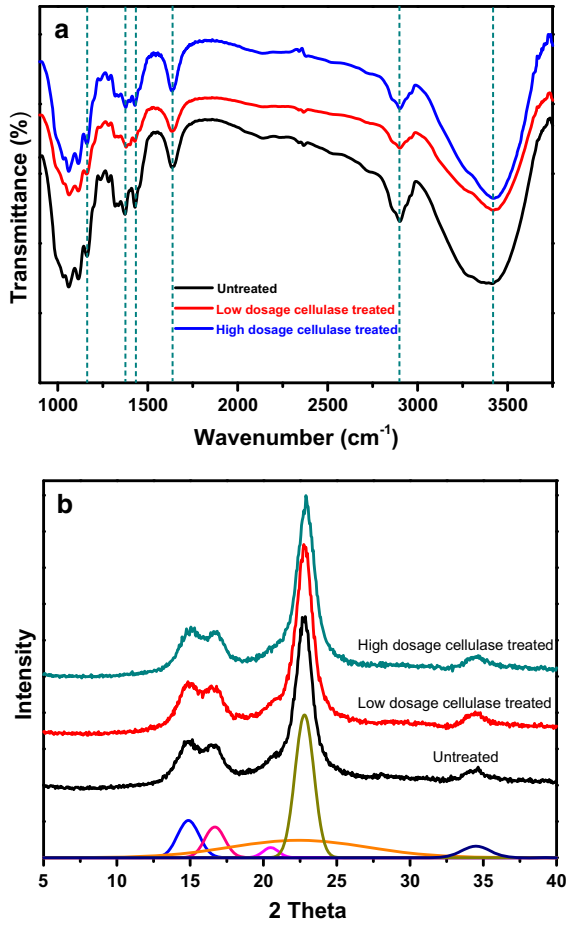

Fig. 1 **a** FTIR spectra and **b** XRD patterns of different cotton samples

between the Segal CI and crystallite size. Besides, some researchers also pointed out that the peak area is more representative of the fraction of crystalline material (Driemeier and Calligaris 2011). Individual crystalline peaks can be extracted by a curve-fitting program from the diffraction intensity profiles (Park et al. 2010). Here, we utilize the XRD deconvolution method to separate amorphous and crystalline contributions to the diffraction spectrum and determine the CI from the ratio of the area of all crystalline peaks to the total area. The CI is calculated to be 62.3, 65.4 and 66.1 % for untreated, low- and high-dosage cellulase-treated samples, respectively, which definitely demonstrates the enzymatic hydrolysis can increase the crystallinity of cotton because amorphous parts of cotton suffer a higher level of hydrolysis. Moreover, information about the average crystallite size can be calculated in terms of this method using the Scherrer formula because the width of the crystalline peak at half maximum height is directly related to the crystallite size. The corresponding values of crystal size perpendicular to the (200) planes are calculated to be 5.50, 6.18 and 6.64 nm for untreated, low- and high-dosage cellulase-treated samples, respectively. This trend is consistent with previous reports by many researchers (Cao and Tan 2005; Wang et al. 2008).

Effect on weight and strength loss

The effects of enzymatic treatment on weight loss and mechanical properties of cotton substrates are presented in Fig. 2a, b, respectively. As shown, the removal of microfibrils and fuzz from the cotton surface can bring about a measurable weight reduction, which increases with increasing cellulase concentration and treatment time. Similarly, a higher cellulase load and treatment duration can result in higher levels of strength loss. The crystalline part of natural cotton, where a number of hydrogen bonds can be formed, is rather rigid and mainly responsible for its axial tensile strength. Therefore, its degradation is usually identified as the main reason for the decline in tensile strength (Lenting and Warmoeskerken 2001).

Effect on the wettability and moisture regain

Wettability of different cotton samples was assessed using a dynamic wicking test in terms of wicking height and is recorded in Fig. 3a. The results reveal that the samples treated with cellulase demonstrate a higher wicking height at the same wicking time as the untreated one. This can be attributed to the greater removal of hydrophobic impurities from the cotton

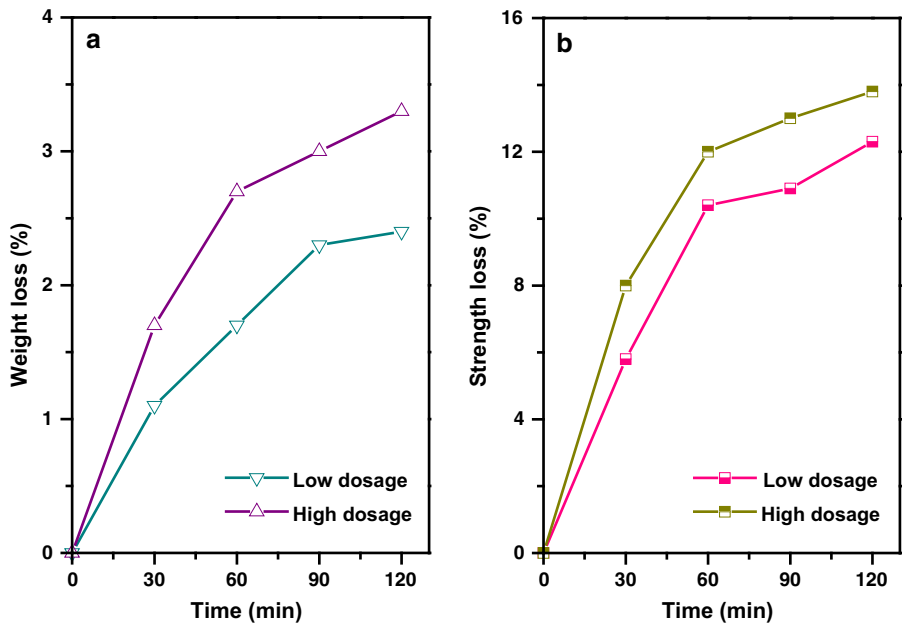

Fig. 2 Effect of cellulase treatment on the **a** weight loss and **b** strength loss of cotton

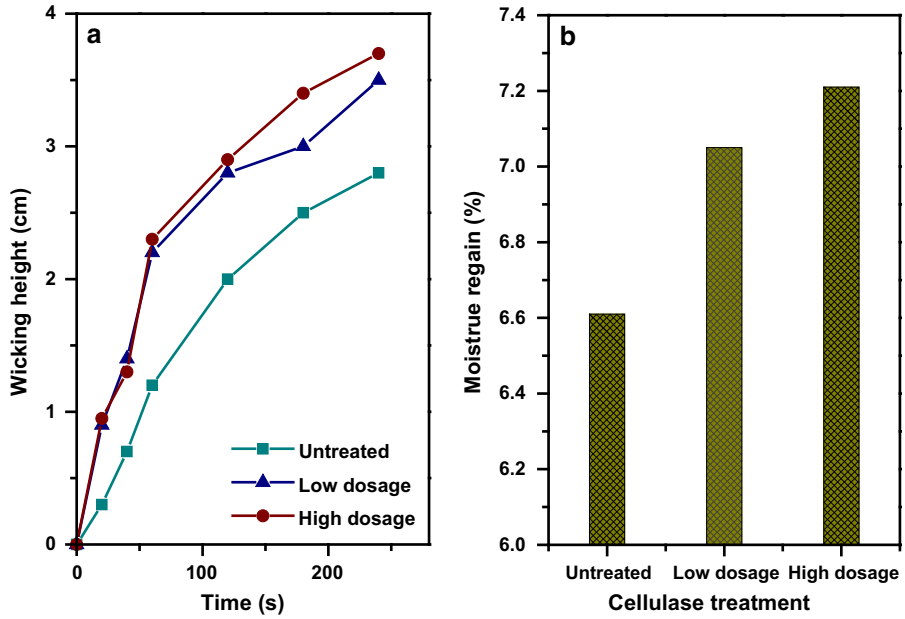

Fig. 3 Effect of cellulase treatment on the **a** wicking height and **b** moisture regain of cotton

surface, increase of the accessible surface area, enlargement of the equivalent capillary pore radius and/or splitting of microfibrils by the cellulase, as reported by many authors (Li and Hardin 1997; Nithya et al. 2011; Pandiyaraj and Selvarajan 2008). These enzymatic modifications can also increase the moisture regain of cotton, as shown in Fig. 3b. The moisture regain of untreated cotton is around 6.60 %, while it increases to 7.05 and 7.21 %, respectively, after low- and high-dosage cellulase treatment because enzymatic actions will lead to the increase of internal pores size and spaces between microfibrils in cotton (Nithya et al. 2011; Ogeda et al. 2012).

Effect on the numbers of dissociable and reducing groups

The correlation between cellulase treatment and the quantity of dissociable groups (–COOH) in cotton was determined using polyelectrolyte titration and is displayed in Fig. 4a, which shows that the number of dissociable groups accessible to titration decreases with the enzymatic action. This is strong evidence supporting that the amorphous domains of cotton are more readily hydrolyzed by cellulase than the crystalline regions because there are scarcely carboxyl groups in the crystalline regions (Park et al. 2007; Zemljic 2008). The effect of enzymatic actions on the number of reducing groups (–CHO) in cotton can also reflect the extent of modifications from cellulase, which is presented in Fig. 4b. It has been observed that the measured number of reducing groups tends to increase with the cellulase load. This means that more cellulase will cause stronger hydrolytic scissions in the cellulose chains, further lower the polymerization degree of cotton and produce more newborn reducing groups at each point of scission (Cavaco-paulo et al. 1996).

Influences of enzymatic hydrolysis on the dyeability of cotton using nanoscale pigment

Characterizations of anionic nanoscale pigment

The anionic CuPc pigment dispersion was prepared and utilized to investigate its dyeing performance on different cotton samples. The dispersion quality of CuPc pigment is vital because of its dyeability such as the color strength, shade and fastness on cotton fabric (Cavaco-paulo et al. 1996; Hao et al. 2011, 2012a, c). The particle size distribution of the pigment suspension was analyzed by light dynamic scattering and is plotted in Fig. 5a, which shows that the pigment has a mean size around 120 nm, and its distribution is quite

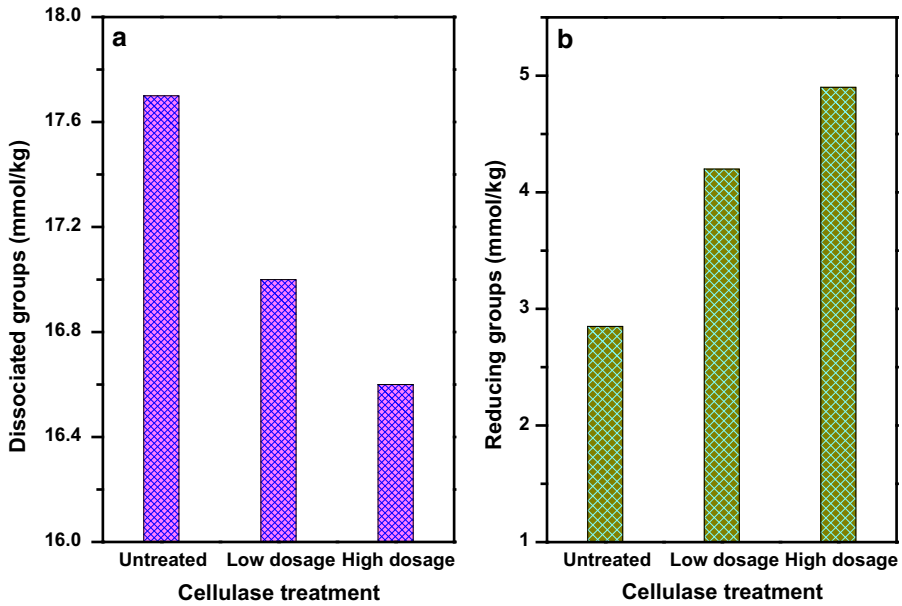

Fig. 4 Effect of cellulase treatment on the **a** dissociable and **b** reducing groups in cotton

narrow. The TEM micrograph of the newly prepared pigment dispersion is presented in Fig. 5b, which shows the nanoscale particles exhibit a good dispersion state in the aqueous medium. The zeta potential of this pigment suspension is shown in Fig. 5c. The pigment particles have a zeta potential around −38.3 mv, which derives from the anchored anionic dispersants on them and plays a substantial role in their dispersability and stability in aqueous medium. The dispersion performance of hydrophobic CuPc in the aqueous system will be poor unless it can be stabilized by sufficient electrostatic or steric interactions. The absorbance spectrum of CuPc, which shows how the absorbance of light depends on the wavelength, was analyzed using a UV-Vis absorption spectrometer and is plotted in Fig. 5d. The nanoscale CuPc pigment exhibits absorption bands in the wavelengths from 600 to 750 nm, which might be attributed to the Q-band of CuPc. Furthermore, two splitting absorption bands are observed at ∼630 and 710 nm, which are likely due to the vibronic coupling in the excited state (Dong et al. 2011; Zhang et al. 2011).

Dyeing properties of nanoscale CuPc pigment on cotton

The exhaustive dyeing operations were separately carried out on different cotton samples under the same conditions. During the dyeing stage, gradual pigment uptake on cotton can be achieved by the movement of pigment particles through the bath bulk and then the fiber-liquid boundary layer to the cotton surface. The uptake of pigment along with exhaustion time and the final color depth of dyed cotton are shown in Fig. 6a, b, respectively, where it is found that the dyeing properties of this nanoscale pigment on different substrates are vastly different. The untreated cotton is barely colored by the pigment particle for 120-min duration because the CuPc pigment is insoluble and lacks sufficient substantivity to cotton in water. Moreover, natural cotton fibers usually carry a few negative charges owing to the presence of some carboxylic acid groups from the oxidation of hydroxyl groups, which will directly repel the anionic pigment particles and result in low uptake efficiency. For the cellulase-free cotton, slightly higher uptake of pigment and color depth are detected because enzymatic hydrolysis can result in the decrease of dissociable carboxyl groups in cotton and thus reduce the repulsive forces between them. Interestingly, the uptake of pigment on the cellulase-on sample is dramatically higher than on the previous two samples. This means that the cellulase protein still present on the cotton surface after biotreatment plays a significant role in propelling the transfer of pigment from the bath to the cotton bulk. As is known, some hydrophobic clusters or domains consisting of nonpolar amino acids, such as Val, Leu, Pro, Met, Trp, Tyr or Phe, exist and

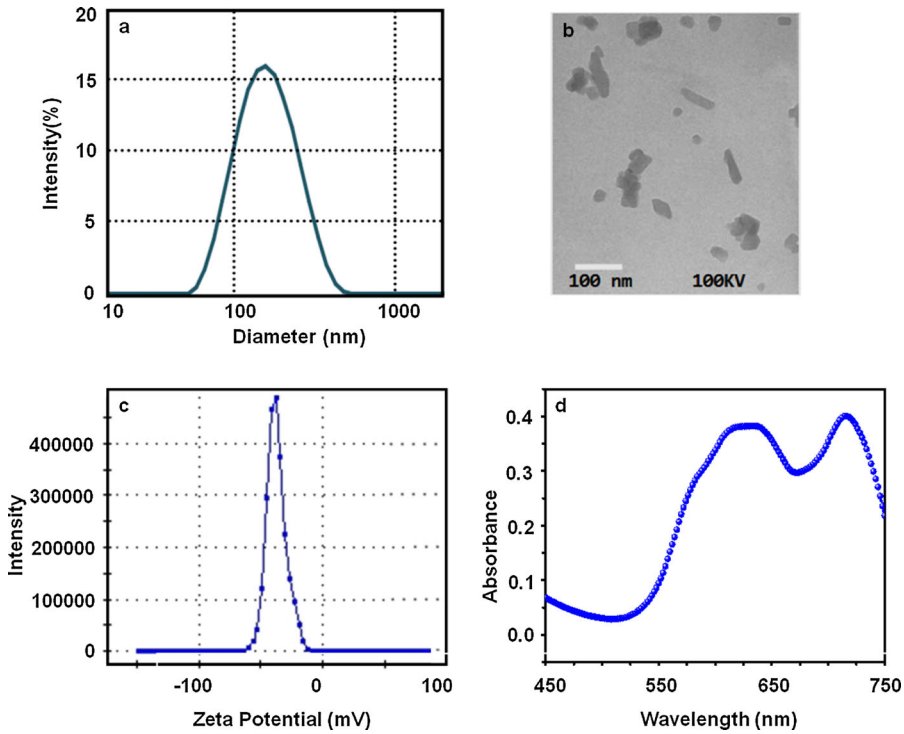

Fig. 5 **a** Particle size distribution, **b** TEM image, **c** zeta potential and **d** absorption spectrum of the nanoscale pigment

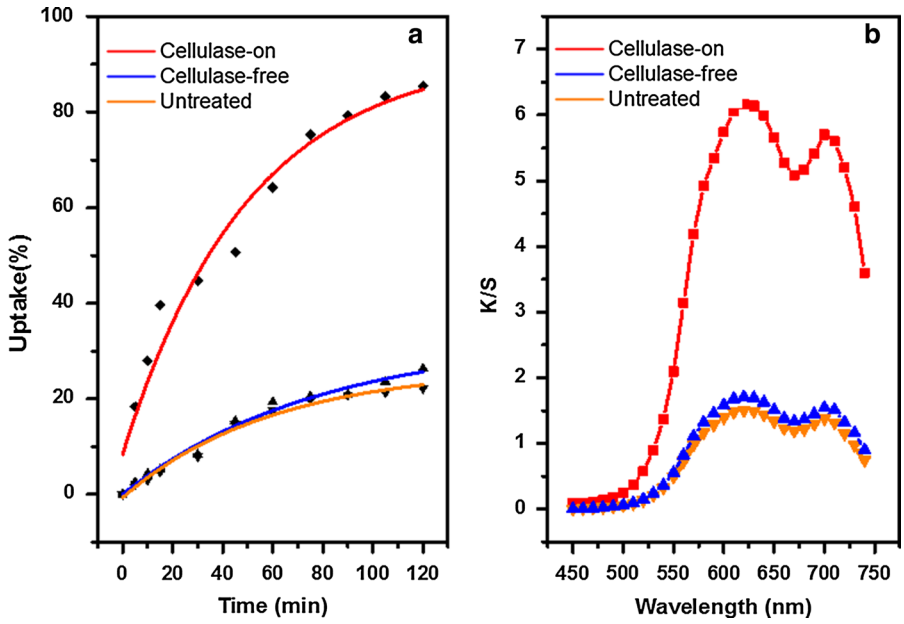

Fig. 6 **a** Pigment uptake on different cottons along with dyeing time and **b** *K*/*S* values of different cottons after pigment dyeing

distribute on the cellulase surface (Gusakov et al. 2000), which will produce strong hydrophobic interactions with hydrophobic CuPc pigment and eventually promote its uptake and final color depth on cotton. This can be defined as the cellulase-enhanced effect on pigment uptake, and a schematic representation of this mechanism is illustrated in Fig. 7. Besides, the heterogeneous charge distribution of bound cellulase

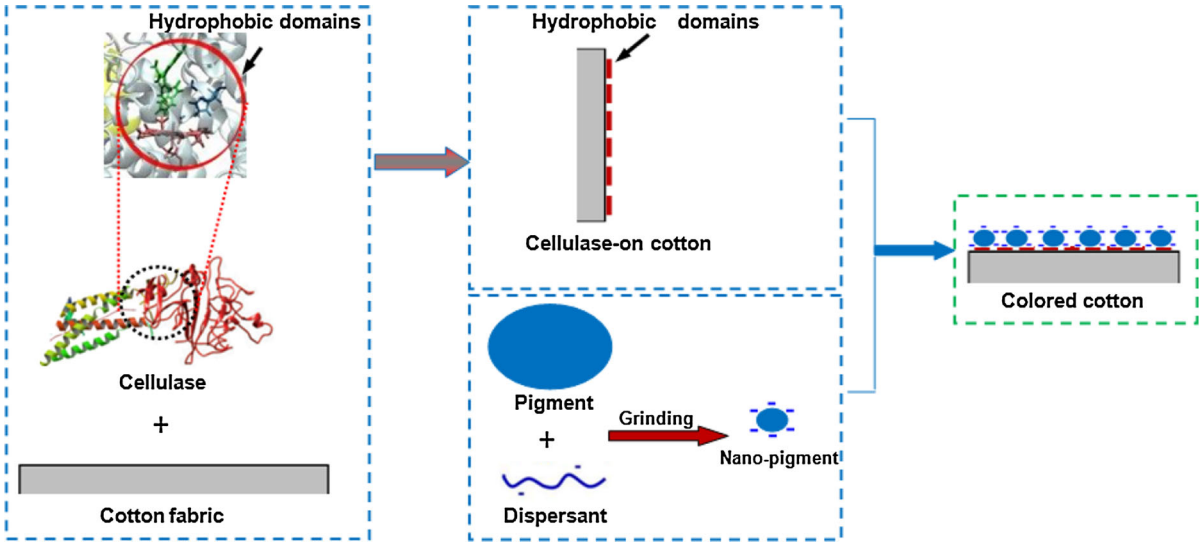

Fig. 7 Schematic representation of the cellulase-enhanced effect on pigment uptake

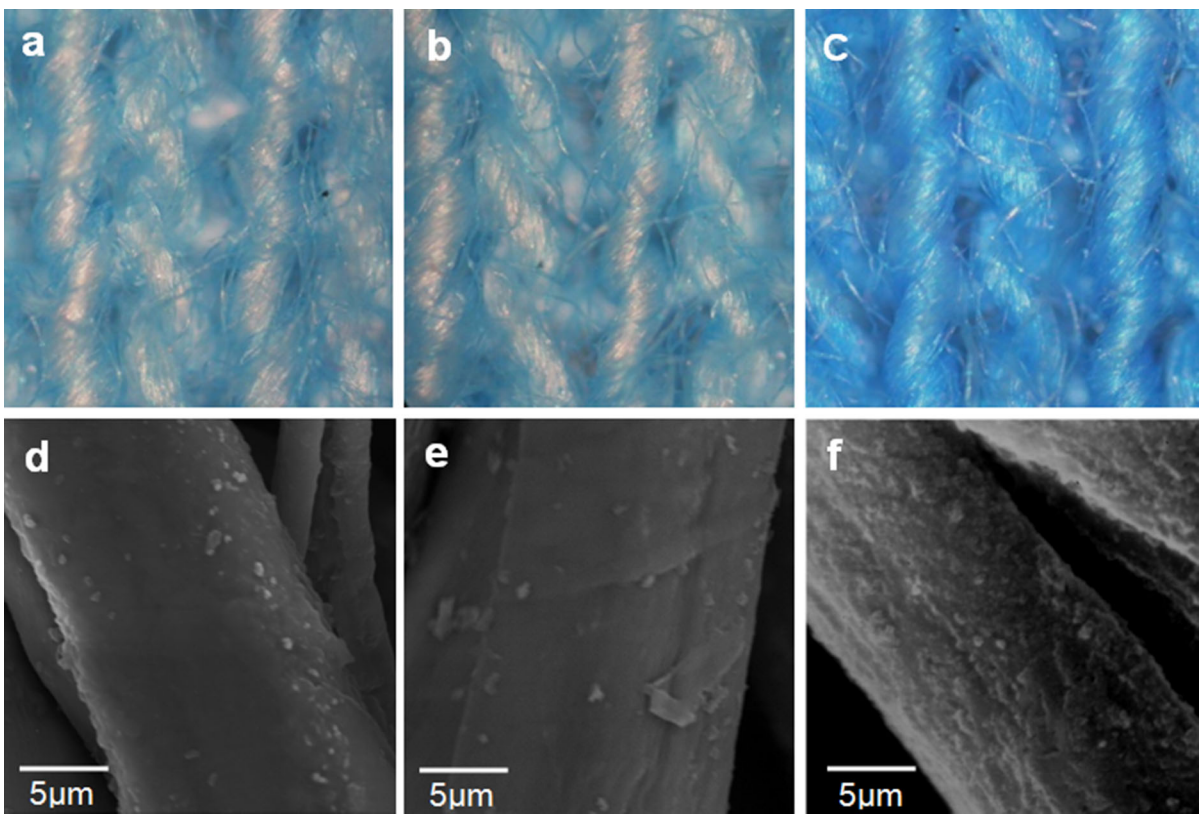

Fig. 8 Digital photos of **a** untreated, **b** cellulase-free and **c** cellulase-on cotton after pigment dyeing and SEM images of **d** untreated, **e** cellulase-free and **f** cellulase-on cotton after pigment dyeing

may also contribute to the uptake of anionic pigment on cotton (Adamczyk et al. 2011). More directly, the images of colored cotton samples were taken by microscopes and are shown in Fig. 8a–f. Consistent with above results from *K/S* measurement, a small number of pigment particles can be found on the untreated and cellulase-free cotton samples, whereas plentiful pigment particles are easily observed on the cellulase-on one. It is noted that these pigment particles are mainly precipitated on the cotton surfaces instead of diffusing into the fiber, and some of them aggregate together because the space for holding them on cotton is rather narrow relative to the aqueous bath.

Conclusions

Cellulase treatment could produce some impacts on the physicochemical properties of cotton. Both FITR and XRD analysis made clear that the enzymatic treatment enhanced its crystallinity. The dynamic wicking test disclosed that the enzymatic process would increase the wettability of cotton. In addition, the moisture regain of cotton was increased from 6.60 % to 7.05 and 7.21 % after low- and high-dosage cellulase treatment. After enzymatic processing, the number of dissociable groups in cotton decreased while the reducing groups increased. The anionic CuPc pigment dispersion was prepared, and its dispersion quality was characterized by DLS and TEM analysis, which showed that the pigment particles had an average size of 120 nm with an irregular slice shape. This nanoscale pigment had distinct dyeing performances on different cotton samples. It had low uptake on the untreated and cellulase-free cotton during the 120-min dyeing process but much higher uptake on the cellulase-on cotton. Cellulase protein still present on the cotton surface after biotreatment played a significant role in propelling the transfer of pigment from the bath to the cotton. It was the hydrophobic interactions between cellulase and pigment that led to the enhancement of pigment uptake and thus its final color depth on cotton.

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