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Uniform dispersion of silica nanoparticles on dyed cellulose surface by sol–gel method

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ABSTRACT

Cellulose fabric is dyed with Reactive Red B-3BF. Dispersion of silica nanoparticles on dyed cellulose surface is investigated. Novel color cellulose/silica surface is prepared and characterized by FT-IR, AFM and FSEM. The color data of the cellulose/silica surface are discussed by reflectance spectra, color yield (*K*/*S*). The results show that silica nanoparticles form smooth film with high degree of homogeneity on the cellulose surface. The surface color shade of the dyed cellulose can be affected by sol–gel. The *K*/*S* of two sample surfaces have noticeable increase. With increasing silica nanoparticles, the *K*/*S* of samples have further improvement. The thin film imparts low reflectance index and increases color yield.

1. Introduction

In the present century of designer materials, nanoscale modification of material surface for a wide range of biofunctional application is an important topic for future technologies. Organic–inorganic hybrid surfaces have gained much interest due to the remarkable change in properties, such as mechanical, thermal, electrical and magnetic, compared to pure organic polymers (Choi, Harcup, Yee, Zhu, & Laine, 2001; He, Wan, & Xu, 2007; Okada & Usuki, 2006; Sun, Kang, & Mu, 2009). Silica hybrid materials have found application as a coating on implants and medical products, biocatalyst, biosensor and matrix for a controlled release of drugs (Guo et al., 2008; Hou & Dai, 2009; Kataoka et al., 2005). The incorporation of nanoscale particles into polymer surface leads to a strong interfacial interaction and has a significant improvement in rigidity and reinforcement (Hou, Wang, & Yu, 2009; Kulpinski, 2005; Ohno, Tagawa, Itoh, Suzuki, & Matsuda, 2009; Xie, Yu, & Shi, 2009; Xie, Zhang, & Yu, 2009).

Cellulose is highly appreciated for its outstanding characteristics such as non-toxic, biocompatible and biodegradable properties. Besides the traditional use as textile materials, cellulose has been explored as a substrate for composite materials (Fahmy, Aboshosha, & Ibrahim, 2009; Hou, Wang, & Wu, 2008; Hou, Zhou, & Wang, 2009; Samuneva et al., 2008; Xie, Hou, & Sun, 2008). However, the polymer-based nano-surfaces are very difficult to produce by the use of processing techniques common to conventional method. This is due to the strong tendency of the nanoparticles to agglomerate. The sol–gel method has definitely proved its exceptional potential for new hybrid with high degree of homogeneity (Addamo et al., 2008; Azzam, Badawi, Alawady, & Soliman, 2009; Fu et al., 2001; Lova, Sabine, Isabelle, & Eric, 2008; Yeh, Chen, & Huang, 2007). During the sol–gel process, the inorganic mineral, such as tetraethoxysilane (TEOS), is deposited in the cellulose matrix forming hydrogen bond between organic phase and inorganic phase. Some couple agents, such as γ-aminopropylmethyldimethoxylsilane, are used as ends of the organic/inorganic hybrid. Hydrolysis and condensation reactions are basically responsible for polymerization of the inorganic precursors as demonstrated below for the tetraethoxysilane (TEOS) under acidic conditions. The hydrolysis of tetraethoxysilane (TEOS) and γ-aminopropylmethyldimethoxylsilane are shown in Scheme 1.

The uniform dispersion is a theme that runs through chemistry, biology and material science. A wide variety of nano-, micro- or mesoscale uniform dispersions have been generated by diverse methods, including electrophoretic deposition, self-assembly (Hou, Chen, & Zhou, 2009; Lu et al., 2007; Marie, Rotureau, Dellacherie, & Durand, 2007; Wei, Cheng, Hou, & Sun, 2008; Yan & Chen, 2009). Silica materials obtained by the sol–gel process are amorphous, inorganic and porous. Silica nanoparticles possess positive charge ($-NH_3^+$) under acidic sol–gel conditions. If cellulose macromolecules possess anionic functional groups, they may be employed to form organic/inorganic hybrid surface with nano-silica. Reactive dyes are widely used for dyeing of cellulose. They can form covalent bond with the cellulose (Hou & Sun, 2009; Xie & Hou, 2008; Xie, Liu, & Wang, 2009). Because the reactive dyes have

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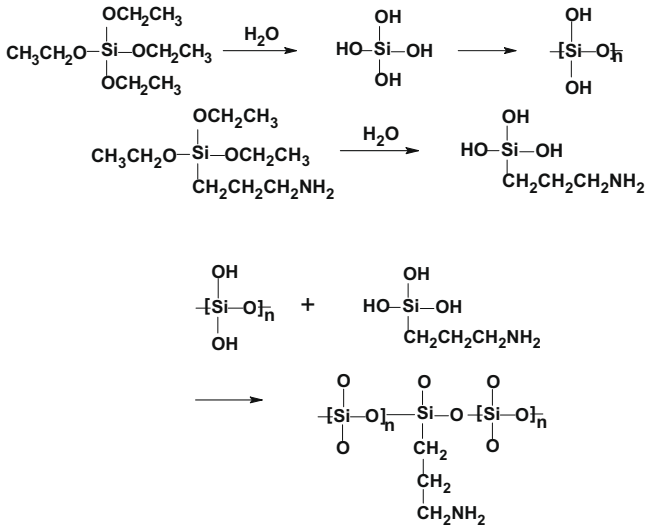
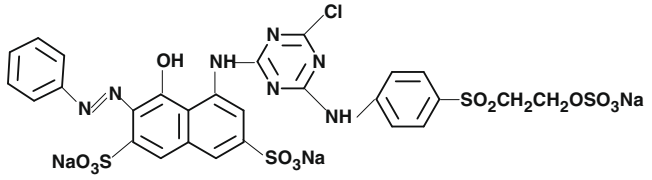


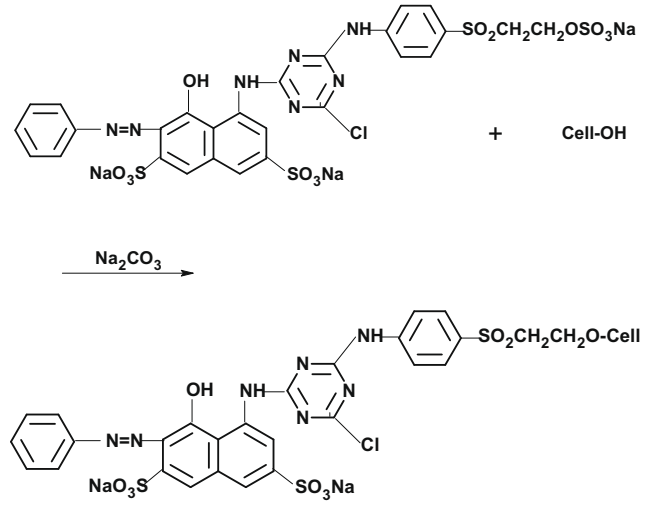
Scheme 1. Condensation of TEOS and γ-aminopropylmethyldimethoxylsilane.



Scheme 2. Chemical structure of Reactive Red B-3BF.

anionic chromospheres, dyed cellulose surface has a lot of anionic groups. After the cellulose has been grafted with reactive dyes containing anionic groups, silica nanoparticles can be dispersed in the cellulose surface. Novel dyed hybrid surface can be obtained.

In this paper, cellulose fibers are dyed with reactive dye (Reactive Red B-3BF). Dispersion of silica nanoparticles on dyed cellulose surface is investigated. Novel color cellulose/silica hybrid surface is prepared and characterized. The color data of the organic/inorganic hybrid surfaces are discussed by reflectance spectra, color yield (K/S) and the colorimetric data of CIELAB.



Scheme 3. Reaction process between Reactive Red B-3BF and cellulose.

2. Experimental

2.1. Materials

Scoured and bleached cellulose fabrics (cotton) were obtained from Jinqiu Textile Company, Shaoxing, China. The tetraethoxysilane (TEOS) as precursor and γ-aminopropylmethyldimethoxylsilane (550) as couple agent were obtained from Hangzhou Dadi Chemical Co., Ltd., Hangzhou, China. The reactive dye, Reactive Red B-3BF (C.I. Reactive Red 250) was obtained from Shanghai Matex Chemical Company, Shanghai. Reactive Red B-3BF was recrystallized in water to remove sodium sulphate before use. Chemical structure of it is shown in Scheme 2. Other chemicals were obtained from Shanghai Chemical Reagent Plant.

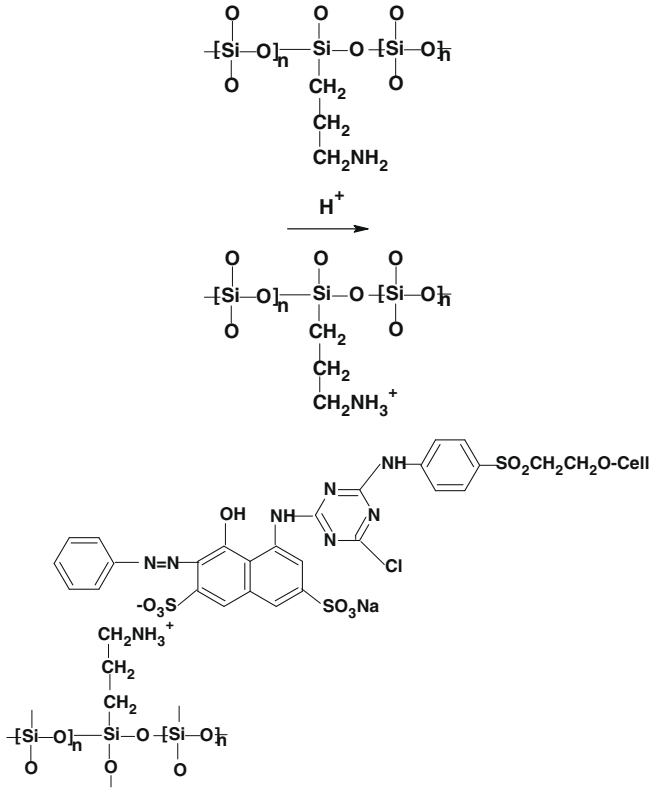
2.2. Dyeing

Cellulose fabrics were dyed in an IR dyeing machine (PYROTEC-2000, Roaches International Ltd., UK), with a liquor ratio of 1:10, sodium sulphate (50 g/l) and sodium carbonate (10 g/l). Fabrics were immersed in the dye bath at room temperature and the temperature was increased to 60 °C at a rate of 1 °C/min. Dyeing was carried out at this temperature for 60 min. After dyeing, the dyed samples were rinsed in hot water and soaped in a solution of a non-ionic surfactant (OP-10, 1 g/l) at 90 °C for 20 min at liquor ratio 1:15. The fabrics were removed, rinsed thoroughly in tap water until the rinsing water was clear and air-dried.

Fixation of the dye on fabric was calculated by measuring the absorbance of the residual dye bath liquor. The percentage of fixation (F%) was calculated according to the following equation:

$$F\ (\%) = [(A_0 - A_1 - A_2)/A_0] * 100 \quad (1)$$

where A_0 and A_1 are the absorbance of the dye solution at λ_{max} before and after dyeing, respectively, A_2 is the absorbance of the soaped dye solution.



Scheme 4. Uniform dispersing mechanism of silica nanoparticles on cellulose surface.

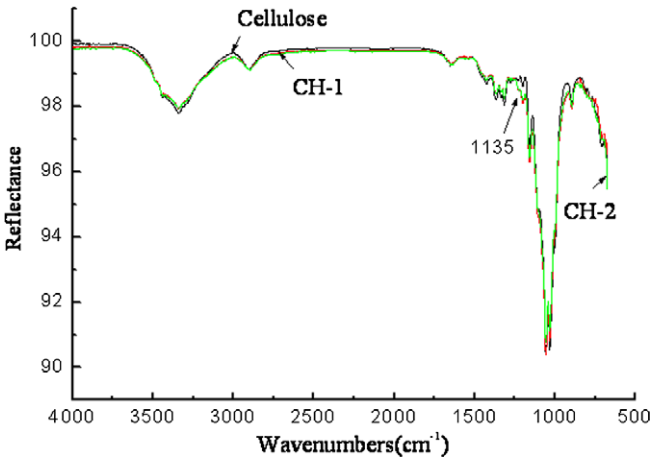


Fig. 1. FT-IR spectra of hybrids CH-1 and CH-2.

2.3. Surface modification of the dyed cellulose with silica nanoparticles by sol–gel process

TEOS 10 g, distilled water 2.5 g, alcohol 25 g, 550 1 g, HCl (36.6%) 1 ml were mixed. Then the mixture was stirred for 30 min at 60 °C until a homogeneous solution was obtained. The solution obtained by sol–gel process was called Sol-A.

Sol-A solutions (10 g and 20 g) are resolved in 90 g water and 1 g HAc, respectively. The mixtures were sufficiently mixed by stirring at room temperature. Two colorless solution containing silica nanoparticles were obtained, and called Sol-1, Sol-2, respectively.

The dyed samples were immersed in the solutions for 1 h and then padded to give 80% wet pick-up. The dry temperature and time were 105 °C and 1.5 min, respectively. The cure temperature was 150 °C, and cure time was 1.5 min. The fabrics were removed, rinsed thoroughly in tap water and air-dried.

For comparison, the dyed samples without the hybrid were cured under the same conditions.

2.4. Measurements

FT-IR spectra of the samples were measured by a OMNI Sampler of the Nexus-670 FT-IR-Raman spectrometer (Nicolet Analytical Instruments, Madison, WI) using a single ART reflecting method.

For FSEM (field emission scanning electron microscope) analysis, the samples were sputtered with carbon and then examined with a S-4800 field emission scanning electron microscope (HITACHI Corp., Japan).

Atomic force microscope (AFM) image was obtained with SPM Multimode-Nanoscope IIIa (Digital Instruments, USA) at room temperature, in tapping mode.

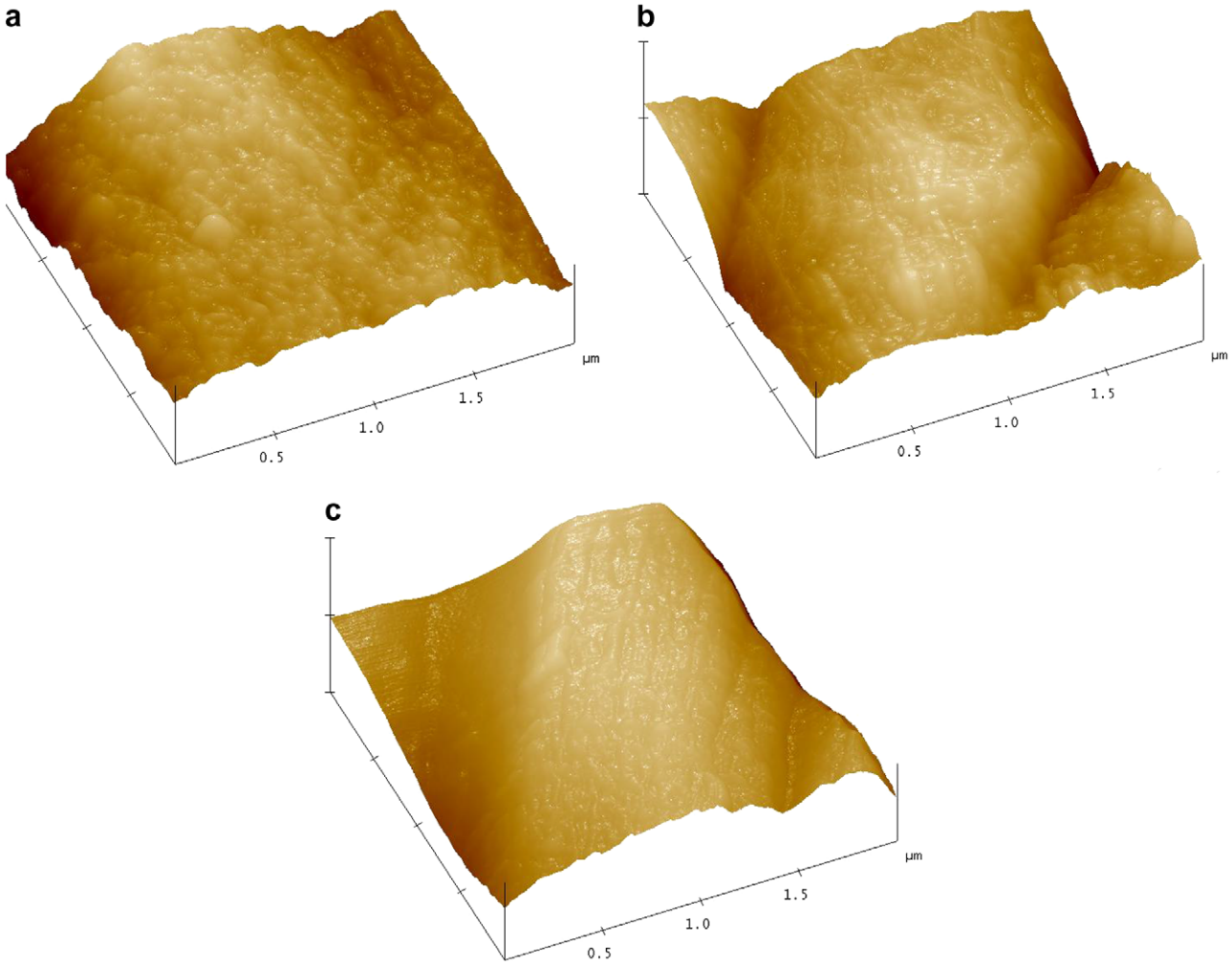


Fig. 2. AFM three-dimensional images of dyed cellulose-based hybrids: (a) control cellulose fiber; (b) CH-1 hybrid; and (c) CH-2 hybrid.

Color yields (K/S) of dyed fabrics were determined by a Datacolor SP600$^+$ spectrophotometer (Datacolor, USA). The tristimulus values of dyed samples were measured in the visible spectrum region 360–700 nm, and the reflectance at the wavelength of maximum absorption (λ_{max}) was used to calculate the color yield of dyed fabrics by the Kubelka–Munk equation (Eq. (2)).

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

where K is the absorption coefficient of the substrate, S is the scattering coefficient of the substrate and R is the reflectance of dyed fabric at λ_{max}.

3. Results and discussion

3.1. Graft of cellulose with reactive dye

The reactive dye, Reactive Red B-3BF, has reactive groups. Dye molecules can form covalent bond with the hydroxyl of cellulose molecules under alkaline condition. Reactive mechanism is shown in Scheme 3. In this paper, 5% (o.w.f,) Reactive Red B-3BF was employed to dye cellulose fabric. The G presented the graft quantity in cellulose with reactive dyes. Graft quantity in cellulose (G) was calculated according to the following equation:

$$G = \text{amount of dyes fixed on cellulose/cellulose matrix} = \frac{M_{dye} \times F}{W_{fiber}} \quad (3)$$

where M_{dye} is amount of used dyes, W_{fiber} is amount of used cellulose fiber.

According to Eqs. (1) and (3), the percentage of fixation (F%) and the graft quantity in the cellulose (G) were calculated. Fixation (F%) and the graft quantity (G) of Reactive Red B-3BF on cellulose are 85.2% and 4.8 mmol/100 g, respectively.

3.2. Dispersion of silica nanoparticles on dyed cellulose surface by sol–gel process

In order to obtain nano-sized surface with high degree of homogeneity and purity at a molecular level, molecule uniform disperse is a novel method. Dyed cellulose surface with reactive dye possesses anionic groups ($-SO_3^-$). Silica nanoparticles have cationic groups. Silica nanoparticles containing cationic groups can be attracted into dyed cellulose surface. Silica nanoparticles have been dispersed in matrix surface and self-assembled on the cellulose surface by electrostatic and hydrogen bonding. Two cellulose-based hybrids dispersed and self-assembled with Sol-1, Sol-2 were obtained and called CH-1 and CH-2, respectively. The dispersing and self-assembly mechanism of the hybrid surface by sol–gel process is shown in Scheme 4. FT-IR spectra of hybrids CH-1 and CH-2 are shown in Fig. 1. The FT-IR spectra of hybrids exhibit that the bands at 1135 and 708 cm^{-1} are assigned to ν_{as}, ν_s of –Si–O–Si– vibrations.

3.3. Surface morphology of modified cellulose with nanoparticles

Atomic force microscope three-dimensional image (AFM) can be used to characterize any changes about the surface morphology of the cellulose/silica hybrids. AFM of cellulose/silica hybrids and control cellulose fiber are shown in Fig. 2. AFM images show that surface morphology of the cellulose/silica hybrids has obvious difference from the surface morphology of the control cellulose. The AFM graphs show the topography of the hybrids with the low distribution profiles of smooth surface. It can be seen that the cellulose/silica hybrids has smooth surface.

Representative FSEM micrographs of cellulose fiber and the hybrid (CH-2) are shown in Fig. 3. In Fig. 3, (a) is the FSEM of cellulose fiber, and (b) is the FSEM of CH hybrid fibers. It can be seen that the surface of the cellulose/silica hybrid fiber is smooth. Nanoparticles can form good film with high degree of homogeneity and purity at a molecular level on the cellulose matrix. FSEM and AFM for the cellulose/silica hybrids are in very good agreement.

3.4. Effect of silica nanoparticles on surface color properties of dyed cellulose

The surface color shade of the dyed cellulose can be affected by dispersion. The investigation on color shade of dyed cellulose hybrids is scarce (Jeon, Mather, & Haddad, 2000; Xie, Hou, & Zhang, 2009). Silica nanoparticles deposited smooth transparent film on the cellulose matrix. The structure of the hybrid thin film on the dyed cellulose is shown in Scheme 5. The surface color yield (K/S) of the hybrids was determined by a Datacolor SP600$^+$ spectrophotometer in the visible spectrum region 360–700 nm. K/S curves of the color samples are shown in Fig. 4.

Compared with the control sample, the K/S of two hybrid samples (CH-1 and CH-2) had noticeable increase. With increasing sil-

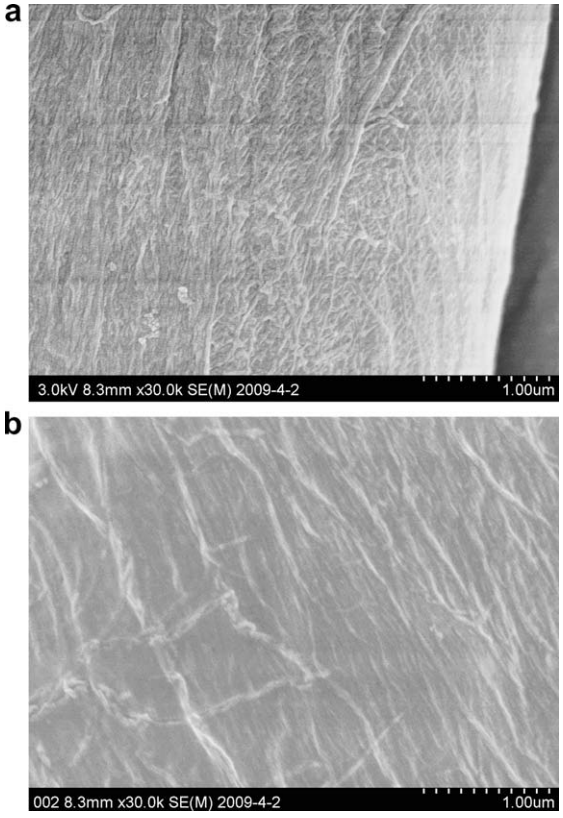
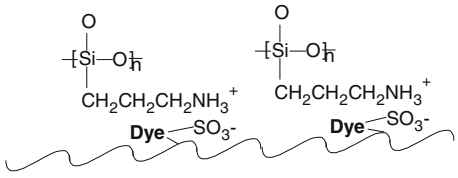


Fig. 3. FSEM micrograph of the cellulose-based hybrids: (a) control cellulose fiber and (b) CH-2 hybrid.



Scheme 5. Structure of the hybrids on the dyed cellulose.

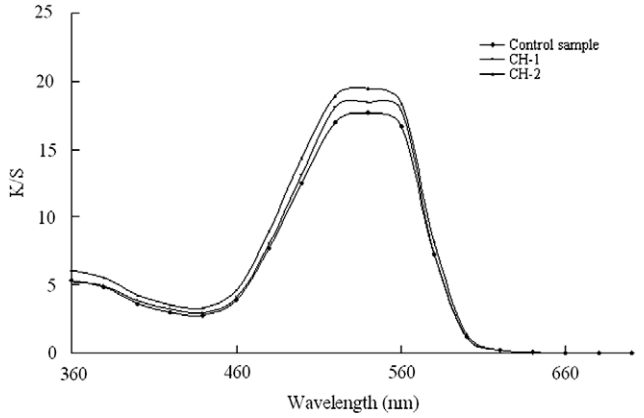


Fig. 4. *K*/*S* curves of the cellulose-based hybrids.

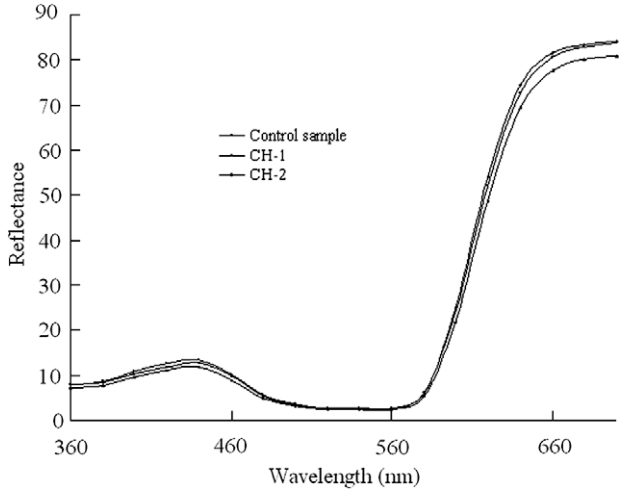


Fig. 5. Reflectance spectra of the cellulose-based hybrids.

ica nanoparticles, the *K*/*S* of hybrid sample surface (CH-2) had further improvement. It further demonstrates that the thin film from silica nanoparticles had been formed. The thin film imparted low reflectance index and increased color yield.

Reflectance spectra of the hybrids were measured and shown in Fig. 5. It indicates that both the shapes of the reflectance spectra curves and the minimum reflectance wavelength of the fabrics with and without the hybrid had not noticeable change.

4. Conclusion

Cellulose fabric is dyed with Reactive Red B-3BF. Fixation and the graft quantity of Reactive Red B-3BF on the cellulose are 85.2% and 4.8 mmol/100 g, respectively. Novel color cellulose/silica hybrid surfaces are obtained by dispersion in the cellulose. The AFM and FSEM graphs show the topography of the hybrid surfaces with the low distribution profiles of smooth surface. Nanoparticles form good film with high degree of homogeneity on the cellulose surface. The color shade of the dyed cellulose can be affected by dispersion. The *K*/*S* of two hybrid samples have noticeable increase. With increasing silica nanoparticles, the *K*/*S* of hybrid sample has further improvement. The thin film imparts low reflectance index and increases color yield. However, the reflectance spectra of the hybrids have not noticeable change.

References

Addamo, M., Augugliaro, V., Paola, A. D., Garcia-Lopez, E., Loddo, V., Marci, G., et al. (2008). Photocatalytic thin films of TiO_2 formed by a sol–gel process using titanium tetraisopropoxide as the precursor. *Thin Solid Films, 516*, 3802–3807.

Azzam, E. M., Badawi, A. M., Alawady, A. R., & Soliman, A. (2009). Synthesis and characterization of self-assembling some thiol surfactants on gold nanoparticles. *Journal of Dispersion Science and Technology, 30*, 540–547.

Choi, J., Harcup, J., Yee, A. F., Zhu, Q., & Laine, R. M. (2001). Organic/inorganic hybrid composites from cubic silsesquioxane. *Journal of American Chemistry Society, 123*, 11420–11430.

Fahmy, H. M., Aboshosha, M. H., & Ibrahim, N. A. (2009). Finishing of cotton fabrics with poly(N-vinyl-2-pyrrolidone) to improve their performance and antibacterial properties. *Carbohydrate Polymers, 77*, 845–850.

Fu, B. X., Hsiao, B. S., Pagola, S., Stephens, P., White, H., Rafailovich, M., et al. (2001). Structural development during deformation of polyurethane containing polyhedral oligomeric silsesquioxanes (POSS) molecules. *Polymer, 42*, 599–611.

Guo, X., Guo, H., Fu, L., Zhang, H., Carlos, L. D., Deng, R., et al. (2008). Synthesis and photophysical properties of novel organic–inorganic hybrid materials covalently linked to a europium complex. *Journal of Photochemistry and Photobiology A: Chemistry, 200*, 318–324.

He, J., Wan, Y., & Xu, L. (2007). Nano-effects, quantum-like properties in electrospun nanofibers. *Chaos, Solitons and Fractals, 33*, 26–37.

Hou, A., & Dai, J. (2009). Crystal morphology change of C.I. Disperse Blue 79 in supercritical carbon dioxide. *Dyes and Pigments, 82*, 71–75.

Hou, A., Chen, S., & Zhou, Y. (2009). Self-assembly of the polysiloxane modified with cationic and perfluorocarbon groups on the polyester surface and its effect on the color shade of the dyed polyester. *Journal of Polymer Research*. doi:10.1007/s10965-009-9274-y.

Hou, A., & Sun, Y. (2009). Modified cellulose fiber with the tertiary amino and quaternary groups and its dyeing properties. *Journal of Dispersion Science and Technology, 30*, 643–648.

Hou, A., Wang, X., & Wu, L. (2008). Effect of microwave irradiation on the physical properties and morphological structures of cotton cellulose. *Carbohydrate Polymers, 74*, 934–937.

Hou, A., Wang, X., & Yu, Y. (2009). Preparation of the cellulose/silica hybrid containing cationic groups by sol–gel crosslinking process and its dyeing properties. *Carbohydrate Polymers, 77*, 201–205.

Hou, A., Zhou, M., & Wang, X. (2009). Preparation and characterization of durable antibacterial cellulose biomaterials modified with triazine derivatives. *Carbohydrate Polymers, 75*, 328–332.

Jeon, H. G., Mather, P. T., & Haddad, T. S. (2000). Shade memory and nanostructure in poly(norbornyl-POSS) copolymers. *Polymer International, 49*, 453–457.

Kataoka, K., Nagao, Y., Nukui, T., Akiyama, I., Tsuru, K., Hayakawa, S., et al. (2005). An organic–inorganic hybrid scaffold for the culture of HepG2 cells in a bioreactor. *Biomaterials, 26*, 2509–2516.

Kulpinski, P. (2005). Cellulose fibers modified by silicon dioxide nanoparticles. *Journal of Applied Polymer Science, 98*, 1793–1798.

Lova, R., Sabine, C., Isabelle, V., & Eric, D. (2008). Effect of nanoclays on the dyeability of polypropylene nanocomposite fibers. *Coloration Technology, 124*, 86–91.

Lu, X., Gong, S., Meng, L., Li, C., Liang, F., Wu, Z., et al. (2007). Novel fluorescent amphiphilic block copolymers: Controllable morphologies and size by self-assembly. *European Polymer Journal, 43*, 2891–2900.

Marie, E., Rotureau, E., Dellacherie, E., & Durand, A. (2007). From polymeric surfactants to colloidal systems: 4. Neutral and anionic amphiphilic polysaccharides for miniemulsion stabilization and polymerization. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 308*, 25–32.

Ohno, T., Tagawa, S., Itoh, H., Suzuki, H., & Matsuda, T. (2009). Size effect of TiO_2–SiO_2 nano-hybrid particle. *Materials Chemistry and Physics, 113*, 119–123.

Okada, A., & Usuki, A. (2006). Twenty years of polymer–clay nanocomposites. *Macromolecular Materials and Engineering, 291*, 1449–1476.

Samuneva, B., Djambaski, P., Kashchieva, E., Chernev, G., Kabaivanova, L., Emanuilova, E., et al. (2008). Sol–gel synthesis and structure of silica hybrid biomaterials. *Journal of Non-Crystalline Solids, 354*, 733–740.

Sun, H., Kang, S., & Mu, J. (2009). A facile preparation of the Co_3O_4 villiform nanostructure. *Journal of Dispersion Science and Technology, 30*, 500–502.

Wei, Y., Cheng, F., Hou, G., & Sun, S. (2008). Amphiphilic cellulose: Surface activity and aqueous self-assembly into nano-sized polymeric micelles. *Reactive & Functional Polymers, 68*, 981–989.

Xie, K., Yu, Y., & Shi, Y. (2009). Synthesis and characterization of cellulose/silica hybrid materials with chemical cross-linking. *Carbohydrate Polymers*. doi:10.1016/j.carbpol.2009.06.019.

Xie, K., & Hou, A. (2008). Synthesis, properties and application of cationic reactive disperse dyes containing quaternary group. *Journal of Dispersion Science and Technology, 29*, 436–439.

Xie, K., Hou, A., & Sun, Y. (2008). Chemical graft of cellulose with the ion-pair emulsion containing the reactive groups and its dyeing properties. *Journal of Dispersion Science and Technology, 29*, 1385–1390.

Xie, K., Hou, A., & Zhang, Y. (2009). Color analysis of the nano-structured dyed cellulose materials containing inorganic particles. *International Journal of Nonlinear Sciences and Numerical Simulation, 10*, 759–765.

Xie, K., Liu, H., & Wang, X. (2009). Surface modification of cellulose with triazine derivative to improve printability with reactive dyes. *Carbohydrate Polymers, 78*, 538–542.

Xie, K., Zhang, Y., & Yu, Y. (2009). Preparation and characterization of cellulose hybrids grafted with the polyhedral oligomeric silsesquioxanes (POSS). *Carbohydrate Polymers, 77*, 858–862.

Yan, Y., & Chen, Q. (2009). Rapid synthesis of monodisperse polystyrene microspheres and self-assembly of colloidal crystals on mica. *Journal of Dispersion Science and Technology, 30*, 575–580.

Yeh, J. T., Chen, C. L., & Huang, K. S. (2007). Synthesis and properties of chitosan/SiO_2 hybrid materials. *Materials Letters, 61*, 1292–1295.