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Preparation of the cellulose/silica hybrid containing cationic group by sol–gel crosslinking process and its dyeing properties

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ABSTRACT

The cellulose/silica hybrid (CSH) was prepared by sol–gel crosslinking process. 2,4,6-tri [(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-EBAC) was used as crosslinking agent in the sol–gel process. The dyeing properties of the cellulose/silica hybrid with the traditional reactive dyes were discussed by reflectance spectra, color yield (*K*/*S*) and the colorimetric data of CIELAB. SEM analysis was used to characterize surface structure of the cellulose/silica hybrid. The results show that the cellulose/silica hybrid could be dyed with traditional reactive dyes. The dyeing process for the cellulose/silica hybrid quickly reached equilibrium. *K*/*S* of three different color dyes on cellulose/silica hybrid was much higher than those of them on the traditional cellulose. Cellulose/silica hybrid imparted excellent fastness properties. After dyeing, the reflectance spectra curves and the minimum reflectance wavelengths of the dyed cellulose/silica hybrid and cellulose fabrics had not noticeable change.

1. Introduction

Organic–inorganic hybrid materials have gained much attention due to the remarkable change in properties, such as mechanical, thermal, electrical and magnetic, compared to pure organic polymers. These composite materials are biocompatible, biodegradable and possess low toxicity in biomedical field (Hou, Zhou, & Wang, 2009; Musyanovych, Wienke, Mailander, Walther, & Landfester, 2008; Okada & Usuki, 2006; Wei & Faul, 2008). Several applications have been already developed for this kind of hybrid materials, especially in the field of surface modification of organic and inorganic substrates. The cellulose fiber is one of the excellent natural materials that have wide application in the different technical areas and biomedicine (Hou, Wang, & Wu, 2008; Kulpinski, 2005; Mughhal, Naeem, Aleem, Saeed, & Ahmed, 2008). Besides the traditional use, such as textile materials, cellulose has been explored as a substrate for composite materials because of the presence of several functional groups that may be employed in various activation processes (Fu et al., 2001; Thomas et al., 2008; Xie, Hou, & Sun, 2007, 2008). The researchers attempt to produce modified cellulose with nanoparticles of silicon dioxide. The dispersed inorganic particles govern the properties of hardness, brittleness and transparency, whereas density, free volume and thermal stability depend on the organic host polymer (Lova, Sabine, Isabelle, & Eric, 2008; Xie, Hou, Shi, & Yu, 2007; Yeh, Chen, & Huang, 2007).

The nanoparticles, having a typical nanodiameter (100 nm), are very promising as modifier of polymeric materials, because of their unique structure and special surface properties. The amorphous silicon dioxide nanoparticles are chemical stable and nontoxic. The silicon dioxide nanoparticles can be synthesized by sol–gel techniques. Recently, the sol–gel method has definitely proved its exceptional potential by providing a possibility of synthesizing a significant number of new materials with high degree of homogeneity and purity at a molecular level and with extraordinary physical and chemical properties (Addamo et al., 2008; Dharmaraj et al., 2006; Lou, Zhang, & Chen, 2003; Samuneva et al., 2008). 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. Another advantage of the sol–gel method is that the silicon dioxide particles can be doped or chemically modified with a wide range of active compounds. In order to avoid phase separation, some couple agents such as γ-aminopropylmethyldimethoxylsilane, are used as ends of the organic/inorganic hybrid. In a sol–gel process in situ generated inorganic particles are evenly dispersed at the nanometer scale in the polymeric host matrix, bonding to the polymer through hydrogen or covalent bonds thus forming organic–inorganic hybrid network. In the coloration field, the sol–gel process is applied to modify surface of dyed materials (Pappas, Liatsi, Kartsonakis, Danilidis, & Kordas, 2008; Sequeira, Evtuguin, Portugal, & Esculcas, 2007; Wei, Cheng, Hou, & San, 2008). The cellulose organic/inorganic hybrid is a relatively new type of composites with interesting mechanical, optical, electrical and thermal properties. However, dyeing properties of modified cellulose with nanoparticles of silicon dioxide are scare.

In this paper, the cellulose/silica hybrid by sol–gel crosslinking process is investigated. The compound containing cationic and

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reactive groups, 2,4,6-tri [(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-EBAC), is used as crosslinking agent in the sol–gel process. The dyeing properties of the nanocellulose with the traditional reactive dyes are discussed.

2. Experimental

2.1. Materials

The tetraethoxysilane (TEOS) as precursor and γ-aminopropylmethyldimethoxylsilane (550) as couple agents were obtained from Hangzhou Dadi Chemical Co. Ltd., Hangzhou, China. 2,4,6-tri [(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-EBAC) as crosslinking agent was obtained from Modern Textile Institute, Donghua University, Shanghai, China. The reactive dyes, Yellow B-4RFN (C.I. Reactive Yellow 145), Red B-3BF (C.I. Reactive Red 250) and Blue B-RN (C.I. Reactive Blue 221) were obtained from Shanghai Matex Chemical Company, Shanghai. Scoured and bleached cotton fabrics were obtained from Jinqiu Textile Company, Shaoxing, Zhejiang. Other chemicals were obtained from Shanghai Chemical Reagent Plant.

2.2. Preparation of cellulose/silica hybrid containing cationic group by sol–gel crosslinking process

TEOS 10 g, distilled water 2.5 g, alcohol 25 g, HCl (36.6%) 1 ml were mixed. Then the mixture was stirred for 30 min at 40 °C until a homogeneous solution was obtained.

2,4,6-tri [(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-EBAC) as crosslinking agent was added in the solution. The mixtures were sufficiently mixed by stirring at room temperature.

The cellulose sample was padded with the sol–gel solution 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. For comparison, the sample without the hybrid was cured under the same condition.

2.3. Dyeing of cellulose/silica hybrid fabric

The cellulose/silica hybrid and traditional cellulose fabrics were dyed in an IR dyeing machine (PYROTEC-2000), the liquor ratio being 1:15, sodium sulfate (50 g/l) and sodium carbonate (10 g/l). Fabrics were immersed in the dyebath at room temperature and the temperature was raised to 65 °C at the rate of 1 °C/min and continued at this temperature for 60 min. All the dyed samples were rinsed in hot water and soaped in the solution containing a nonionic 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.

2.4. Measurement of dye exhaustion and fixation

The exhaustion and fixation of dyes on fabric were calculated by measuring the absorbance of the residual dyebath liquor. The percentages of dyebath exhaustion (E%) and fixation (F%) were calculated according to Eqs. (1) and (2), respectively.

$$\mathrm{E}(\%) = [1 - (A_1/A_0)] \times 100 \quad (1)$$

$$\mathrm{F}(\%) = [(A_0 - A_1 - A_2)/A_0] \times 100 \quad (2)$$

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.

Reflectance spectrum was measured with Datacolor SP600$^+$ spectrophotometer.

2.5. Color yield analysis

The color yield (*K*/*S*) of the dyed fabrics was determined by Datacolor SP600$^+$ spectrophotometer. The dye absorbance was measured in the visible spectrum region from 400 to 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. (3)).

$$K/S = \frac{(1-R)^2}{2R} \quad (3)$$

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

2.6. Fastness testing

Color fastness was evaluated according to the respective international standards: fastness to washing, ISO 105-C04, fastness to rubbing, ISO 105-X12.

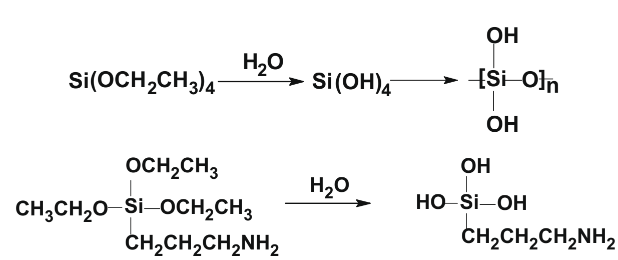
2.7. SEM

For SEM analysis, the fibrous materials were sputtered with gold and then examined with a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

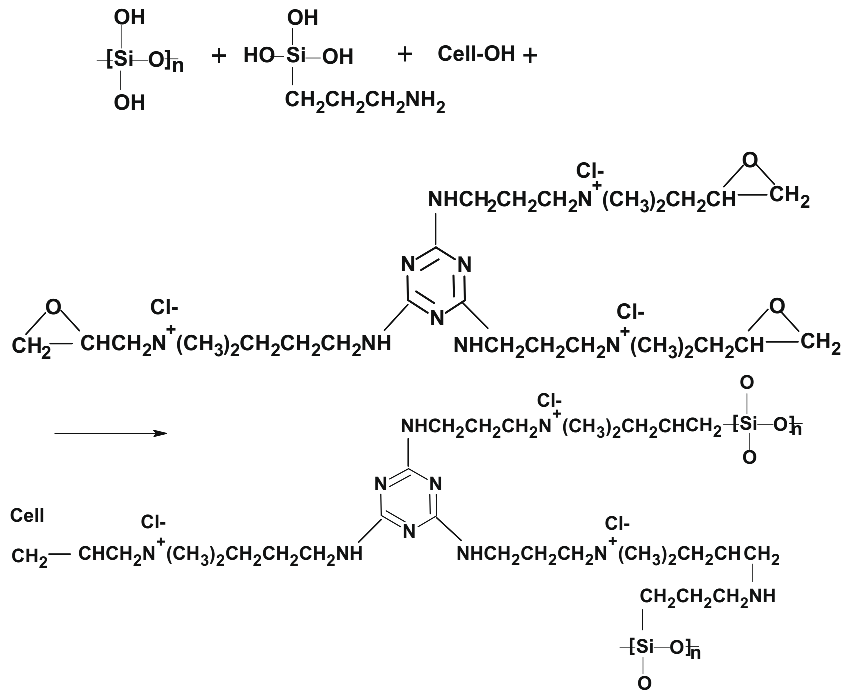
3. Results and discussion

3.1. Preparation of the cellulose/silica hybrid by sol–gel crosslinking process

In the sol–gel process for preparation of glass particles, tetraethoxysilane (TEOS) is usually used as a precursor. Hydrolysis and condensation reactions take place during the process. The product of the polycondensation reaction is a typical inorganic glass type material having only –OH groups on the surface. The organically modified silicone type of materials can be synthesized from the precursor γ-aminopropylmethyldimethoxylsilane as couple agents. Hydrolysis and condensation reactions are shown in Scheme 1. The sol–gel disperse particles have –OH and $-NH_2$ groups. The 2,4,6-tri [(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride as crosslinking agent were used to form covalent bond between the cellulose and inorganic nanoparticles. The crosslinking reactions among hydrolysis products of TEOS, 550 and Tri-EBAC are shown in Scheme 2. SEM analysis of the cellulose/silica hybrid was used to characterize the changes about the surface morphology of the cellulose. Representative SEM micrographs are shown in Fig. 1. Fig. 1b show that there were a lot of the particles on the cellulose surface.



Scheme 1. Hydrolysis of TEOS and 550.



Scheme 2. Chemical structure of cellulose/silica crosslinking hybrid.

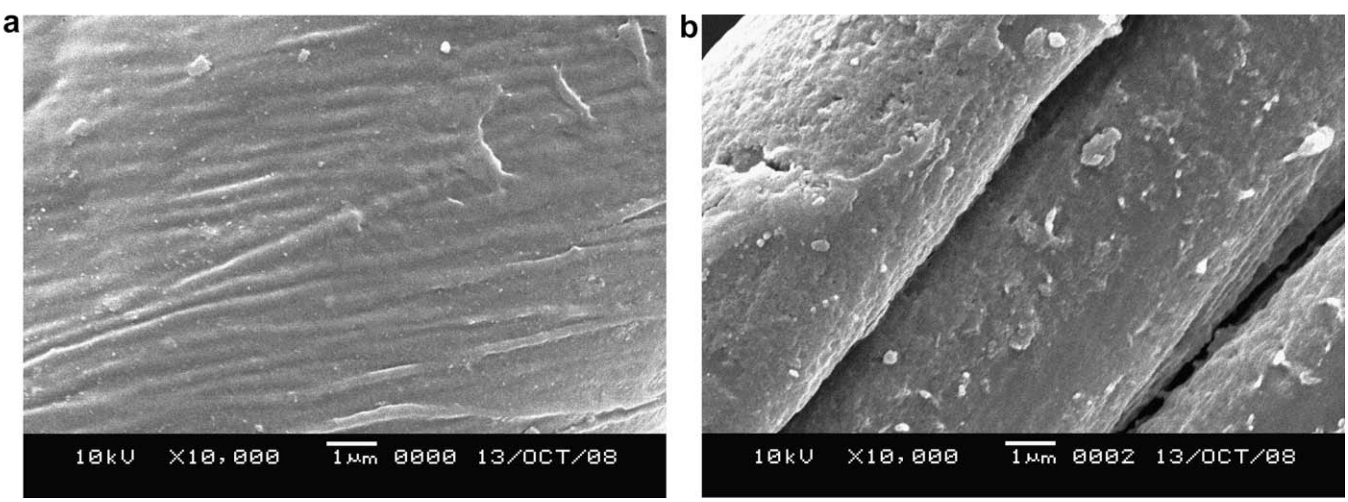


Fig. 1. SEM micrographs of the cellulose and cellulose/silica hybrid fibers. (a) Cellulose fiber, (b) CSH fiber.

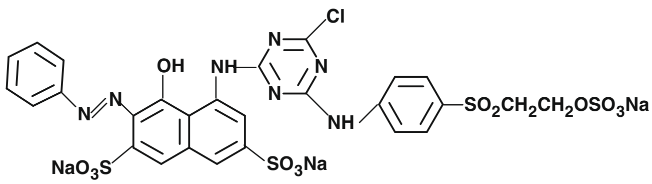
3.2. Dyeing properties of the cellulose/silica hybrid

The cellulose/silica hybrid has a lot of inorganic nanoparticles and organic cationic groups. Compared with the traditional cellulose, the cellulose/silica hybrid exhibits different behavior towards dyeing. Reactive dyes are widely used for dyeing of cellulose and its composites. Reactive dyes are anionic in character and in general owe their water solubility to the presence of sulfonate groups (SO_3^-). The reactive dyes can form covalent bonding with the cellulose (Xie & Hou, 2008; Xie, Hou, & Wang, 2008). Since cellulose/silica hybrid itself adopts a cationic charge in water, these dyes have high intrinsic affinity for the cellulose/silica hybrid fiber.

In order to investigate the dyeing properties of cellulose/silica hybrid, the reactive dye, Red B-3BF, was used for the cellulose/silica hybrid fabric. The chemical structure of Red B-3BF is shown in Scheme 3. The cures of exhaustion and fixation on cellulose/silica hybrid and traditional cellulose are seen in Fig. 2. Fig. 2 shows that the exhaustion and fixation of dyes on cellulose/silica hybrid were higher than those on the traditional cellulose. The dyeing took place rapidly during the first 30 min of the process. After 30 min, the exhaustion and fixation rose slowly. The results show that the dyeing for the cellulose/silica hybrid reached the equilibrium after 60 min. The dyeing for the traditional cellulose did not reach the equilibrium after 60 min. It indicates that the equilibration process for the cellulose/silica hybrid was quick. This behavior may be attributed to the fact that cellulose/silica hybrid has a lot of cationic groups and nanocavity, which improve the absorption of dye anions.

3.3. Color strength of different dyes

In order to investigate the dyeing properties of cellulose/silica hybrid, the different reactive dyes, Yellow B-4RF, Red B-3BF and Blue B-RN were used for the cellulose/silica hybrid fabric. The *K/S*



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

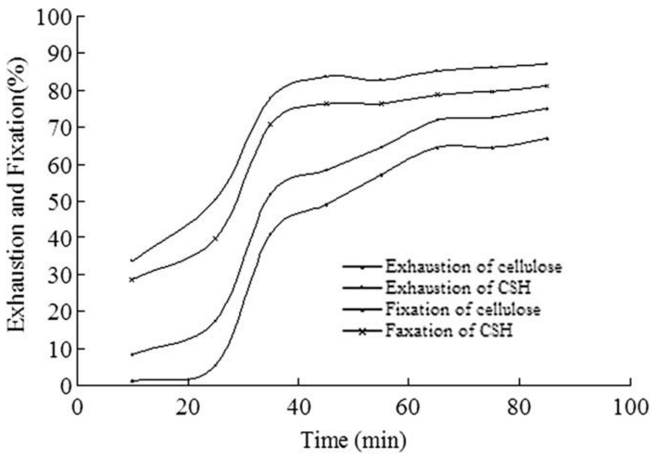


Fig. 2. Exhaustion and fixation of Red B-3BF on cellulose/silica hybrid and traditional cellulose.

cures of dyed cellulose/silica hybrid and cellulose in visual region are seen in Fig. 3. Fig. 3 shows that *K/S* of three different color dyes on cellulose/silica hybrid were higher than those of them on traditional cellulose.

The reflectance spectra of three color cellulose/silica hybrids are seen in Fig. 4. It indicates that the reflectance spectra curves and the minimum reflectance wavelength of the dyed cellulose/silica hybrid and traditional cellulose fabrics had not noticeable change.

3.4. Colorimetric data of the dyed cellulose/silica hybrid

The color parameters *L*, *a*, *b*, were calculated by the tristimulus values *X*, *Y* and *Z*. *L* refers to brightness–darkness with values from 100 to 0 representing white to black. The *a* values run from negative (green) to positive (red). The *b* values run from negative (blue) to positive (yellow).

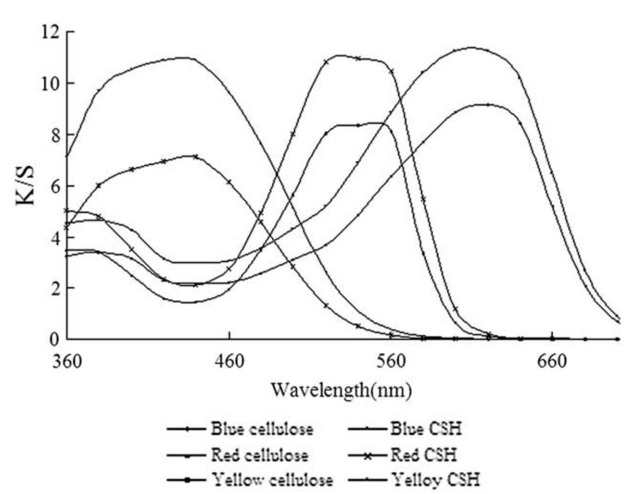


Fig. 3. *K/S* curves of dyed cellulose/silica hybrid and traditional cellulose.

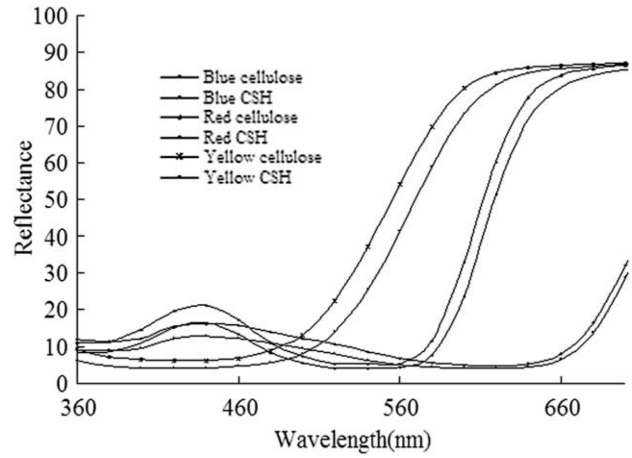


Fig. 4. Reflectance spectra of dyed cellulose/silica hybrid and traditional cellulose.

The color yield change ($\Delta K/S$) was calculated using Eq. (4).

$$\Delta K/S = (K/S)_1 - (K/S)_0 \quad (4)$$

$(K/S)_1$ and $(K/S)_0$ represent *K/S* of the dyed CSH and traditional cellulose, respectively.

Colorimetric data of the dyed samples are summarized in Table 1. The results in Table 1 show that the $\Delta K/S$ significantly increased. The decreases of *L* values were obvious. The *a, b, c* values changed. The *a* values of all dyed CSH noticeably increased. Compare with the dyed cellulose, the color shades of the dyed CSH moved from green to red. This means that the color of the dyed sample became dark.

3.5. Fastness properties of the dyed cellulose/silica hybrid

The fastness properties of dyed cellulose/silica hybrid and cellulose fabrics were measured. The results are summarized in Table 2. It can be seen that wet rubbing fastness of the dyed CSH was similar with that of the dyed traditional cellulose. The washing fastness of the dyed CSH was better than that of the dyed traditional cellulose. This can be explained by the fact that the CSH has a lot of cationic groups in macromolecular. These results show that the CSH could be dyed with traditional reactive dyes and imparted excellent fastness properties.

Table 1
Colorimetric data of dyed CSH and traditional cellulose.

Samples		λ_{max} (nm)	$\Delta K/S$	*L*	*a*	*b*	*c*
Yellow	Cellulose	430	0	74.16	27.91	71.57	76.82
	CSH	430	3.37	68.27	36.26	72.15	80.75
Red	Cellulose	510	0	47.06	57.33	−3.47	57.44
	CSH	510	3.32	42.46	55.94	−2.01	55.98
Blue	Cellulose	630	0	34.92	−4.11	−19.50	19.93
	CSH	630	2.19	39.29	−2.12	−18.65	18.77

Table 2
Fastness properties of dyes on CSH and traditional cellulose fabric (2% owf).

Samples		Fastness to rubbing		Fastness to wash	
		Dry	Wet	SC	SW
Cellulose	Yellow	4–5	4	4	4
	Red	4–5	3–4	3	3
	Blue	5	3–4	3–4	3–4
CSH	Yellow	5	4	4	4
	Red	5	3–4	3–4	3–4
	Blue	5	3–4	4	4

SC, staining on cotton; SW, staining on wool.

4. Conclusions

Cellulose/silica hybrid by sol–gel crosslinking process was prepared. There were a lot of the organic/inorganic particles on the cellulose surface. The cellulose/silica hybrid can be dyed with traditional reactive dyes. The dyeing took place rapidly during the first 30 min of the process. The equilibration process for the cellulose/silica hybrid was quick. *K/S* of three different color dyes on cellulose/silica hybrid was much higher than those of them on traditional cellulose. Cellulose/silica hybrid imparted excellent fastness properties.

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