Surface Dyeability of Cotton and Nylon Fabrics Coated with a Novel Porous Silk Fibroin/Silica Nanohybrid

Wenbin Li,[1,2] Lingli Zou,[1] Xingpin Zhou,[3] Baohua Zhang,[4] Xiaqin Wang,[1,2] Dajun Chen[1]

[1]*College of Materials Science and Engineering, Donghua University, Shanghai 201620, China*
[2]*Key Laboratory of Science & Technology of Eco-Textile, Donghua University/Jiangnan University, Ministry of Education, Shanghai 201620, China*
[3]*Institute of Biosciences and Biotechnology, Donghua University, Shanghai 201620, China*
[4]*Department of Environment and Chemical Engineering, Shanghai University. Shanghai 201800, China*

ABSTRACT: A new and facile approach of surface dyeing was developed for cotton and nylon fabrics coated with a novel porous silk fibroin (SF)/silica (SiO$_2$) nanohybrid. Actually, dyeing of the fabrics occurred in the very thin nanohybrid layers exclusively, while the main body of the fabrics remained intact on the whole. With the assistance of the large surface areas of the porous nanohybrid, dye uptake of the coated cotton fabrics dyed with Acid Red GSF or Disperse Cation Red SD-GRL was enhanced substantially compared with that of the uncoated fabrics as a control. Moreover, dye uptake increased with the SF content in the hybrid, indicating that the SF moiety played a significant role for the surface dyeing process. Color fastness to water of both the dyestuffs was much higher for the coated cotton fabrics compared with that of the uncoated ones. Similar results were obtained for the nanohybrid coated nylon fabrics dyed with Disperse Cation Red SD-GRL as those of the coated cotton fabrics. However, no increase was observed for dye uptake of the coated nylon fabrics dyed with Acid Red GSF owing to saturation of the dyestuff attached on the controlled uncoated nylon fabrics, which concealed the contribution of the nanohybrid layer. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1670–1676, 2007

Key words: silk fibroin/silica nanohybrid; nanosol coating; surface dyeing of fabrics; dyeability; color fastness to water

INTRODUCTION

Silk fibroin (SF), the major component of silk fibers, is a natural fibrous protein, with the primary structure of the repeating sequence well characterized. SF has a wide application prospect in the fields of textiles and biomedical materials owing to its unique chemical and physical properties, such as good biocompatibility, microbial resistance, moisture and oxygen permeability, and handling texture that has distinguished SF from other natural and synthetic fiber-forming polymers. Diverse silk-like fabrics are desired to meet consumers' demands, although the annual output of silk is rather small. So silk-like finishing will be attempted to solve this problem by coating a thin layer of SF on fiber surfaces of cotton, polyester, nylon, silk etc., which imparts the excellent properties of SF to the fabrics to improve wearing comfort while the mechanical properties of the mother fibers remained. For instance, polyethylene terephthalate (PET) fabrics lack reactive groups to locate SF on it. Finishing with SF coating afforded surface-modified PET fabrics better dyeability of acid dyes, washing retainability (WR), and moisture regain.[1]

New classes of nanocomposites have recently arrested much attention as they provide a molecular-level control over the macroscopic properties, although the majority of them have not yet been elucidated. Organic–inorganic nanocomposites have not only surface effects and quantum size effects, but also advantages of inorganic materials, such as rigid-

ity, size stability, and thermal stability, as well as those of organic materials, for instance, diverse functionality and good processability. Nanocomposites provide a new field for finishing of different sorts of fabrics with customizable chemical and physical properties.[2,3] A major challenge for such organic–inorganic nanocomposites is preparation of novel nanocomposites with high content of the useful component without phase separation. Organic–inorganic polymer hybrids derived from sol–gel reaction are rather promising by themselves as contact lenses,[4] optical waveguides,[5,6] coating and diffusion barriers,[7] gas separation membranes,[8] and so on. A novel porous SF/silica (SiO$_2$) nanohybrid was prepared for the first time by our group (Fig. s1, Supporting Information), which was employed to introduce a thin layer on fabrics.[9] The porous network structure of the nanohybrid could afford great surface areas for hydrogen bonding during the coating and subsequent immobilization of dye molecules. The specificity and accessibility of the rough surfaces of the coated fabrics was supposed to provide numerous linking sites of dyestuffs by taking advantage of great surface areas arising from the micropores with the high surface-to-volume ratio. So the dyestuffs displayed excellent adhesion to the nanohybrid which should be different from size-independent classical materials. Here we describe detailed investigation on new features of dyeability for the nanohybrid coated cotton and nylon fabrics dyed with the acid and cation dyestuffs which were unsuitable for common cotton and nylon fabrics. These dyeing properties depended extremely on the coated nanohybrid layers, as dyeing occurred primarily in the thin nanohybrid layers, almost irrelevant with the main body of the coated fabrics. A new method of surface dyeing for the fabrics was established in this research by making use of large surface areas of the porous nanohybrid for high-level capturing of the dyestuff molecules.

EXPERIMENTAL

Materials

Desized and bleached cotton fabrics were kindly supplied by Textile Experimental Center of Donghua University, nylon 6 fabrics by National Engineering Research Center for Dyeing and Finishing of Textiles of China, cocoons of *Bombyx mori* by Zhejiang Yongkang Co., Acid Red GSF by Shanghai Yiman Textile Chemical Co., and Disperse Cation Red SD-GRL with the color index of 110825 by Shanghai Qingcheng Dyestuff Chemical Co. Acetic acid and tetraethoxysilane (TEOS) were purchased from Shanghai Chemical Reagent Co., Ltd. HCl and methanol were obtained from Pinghu Chemical Reagent in China.

Preparation of dilute nanosol

SF and TEOS with a specified weight ratio were dissolved into distilled water as we reported.[9] To this solution, 0.1M aqueous HCl solution was added dropwise with vigorous stirring as a catalyst for the sol–gel reaction. After being stirred at room temperature for 1 h, the nanosol was used for coating on the fabrics.

Nanohybrid coating finishing

A fabric sample with a size of 5 $\times$ 5 cm^2 was impregnated in the dilute nanosol or a SF solution containing the same amount of SF as in the nanosol with a bath weight ratio of 1 : 50 to avoid thick waterproof coating of raincoats, and then padded through two dips and two nips to achieve an average wet pickup of 70%. Then the fabric sample was dried in an oven at 50°C for 1 h. The dried fabric sample was rinsed with a large quantity of distilled water to remove the unattached nanohybrid. Finally the fabric sample was dried fully at 50°C. A methanol treatment was further carried out by immersing a coated fabric sample in methanol for 30 min to induce transformation of SF from water-soluble random coil (silk I) to water-insoluble β-sheet structure (silk II).[10,11] At last the fabric sample was dried completely at 50°C again.

Dyeing process

The dyeing behaviors of the coated cotton and nylon fabrics were investigated by using Acid Red GSF and Disperse Cation Red SD-GRL as representatives of weak acid and cation dyestuffs. The coated fabrics were dyed with Acid Red GSF (1% owf) at a liquid ratio of 50 : 1 for 15 min under 90°C. After the fabrics were removed out of the dyebath, 0.4 mL of acetic acid was added into the dyebath to adjust the pH 2.6. Dyeing of the fabric was continued for another 45 min. Finally, the loose color was washed off by rinsing the fabric with tap water. During the dyeing process, dye uptake was determined at various dyeing times.

In the same way, the cotton and nylon fabrics were dyed with Disperse Cation Red SD-GR, except the dyeing temperature 98°C, and no addition of acetic acid. The pH value of the dyebath is 6.8. Dye uptake was also tested at different dyeing times.

Measurements

Hot-water WR of the SF moiety in a coated layer was evaluated by immersing a coated fabric sample in 100 times (weight) of distilled water at 80°C for 20 min. The fabric sample was turned over and

pressed once every 5 min. WR was calculated as follows.[1]

$$WR\ (\%) = \left(1 - \frac{W_1 - W_2}{W_1 - W_0}\right) \times 100 \qquad (1)$$

where W_0 is the fabric weight before coating, W_1 is the fabric weight after coating, and W_2 is the coated fabric weight after hot-water washing.

Absorption of the dyebath was recorded with a TU-1810 Ultraviolet Spectrophotometer. Standard absorption curves for Acid Red GSF and Disperse Cation Red SD-GRL were derived from a linear relationship between absorption and concentration of the dyestuffs (λ_{max} of Acid Red GSF 534.0 nm, λ_{max} of Disperse Cation Red SD-GRL 532.0 nm). So the concentrations of the residual dyebath were obtained based on the corresponding standard absorption curve. Dye uptake was then determined by comparing the residual concentration of the dyebath C_1 with the original one C_0.

$$Dye\ uptake\ (\%) = \left(1 - \frac{C_1}{C_0}\right) \times 100 \qquad (2)$$

k/s values of the fabrics were measured by a Spectraflash SF600 Micromatch Color Meter. Color fastness to water in terms of washing out rate was tested by using a Roaches Washing Fastness Machine according to National standard GB5713-85 of China, equivalent to ISO105/E01-1982. Color loss due to washing was computed as follows.

$$Washing\ out\ rate\ (\%) = \frac{(k/s)_0 - (k/s)_1}{(k/s)_0} \times 100 \qquad (3)$$

where $(k/s)_0$ and $(k/s)_1$ are the k/s values prior to and after washing with water, respectively. It is worth noticing that k/s value was deliberately used here to calculate washing out rate because of the surface dyeing of the coated fabrics.

RESULTS AND DISCUSSION

Hot-water WR

WR reveals the coating fastness of the nanohybrid to the fabrics to some extent. Table I shows that enhanced WR originated from the methanol treat-

ment of the cotton and nylon fabrics coated with SF or the nanohybrid. X-ray power diffraction patterns confirmed that the methanol treatment induced transformation of SF from water-soluble random coil (silk I) to water-insoluble β-sheet structure (silk II),[9] which facilitated the immobilization of the coating layers on the fabrics. WR was greater than 90% for the nanohybrid-coated cotton and nylon fabrics after the methanol treatment, and increased approximately by 1.5 times of the magnitude greater than that of the corresponding fabrics coated with pure SF after the methanol treatment, although the specific surface areas of the porous nanohybrid layers were extremely larger than those of the pure SF layers. These results proved that the SiO_2 nanoparticles in the nanohybrid were essential to fetter the SF molecules via hydrogen bonding,[9] and hence to avoid release of the SF molecules dissolved by hot water. As we reported, the weight ratio of SF to SiO_2 was 6.46 in the nanohybrid determined by element analysis.[9] However, when all silanol groups were supposed to have participated polycondensation, a theoretical weight ratio of SF to SiO_2 was 8.09, suggesting that numerous silanol groups remained intact in the nanohybrid. The unreacted silanol groups in the nanohybrid were important active centers for formation of physical anchoring sites of the SF molecules. It was found in Table I that the SiO_2 nanoparticles involved in the nanohybrid coating raised WR by $\sim 50\%$ by comparing the WR of the cotton or nylon fabrics coated with pure SF and the nanohybrid either prior to or after the methanol treatment. Therefore, the porous nanohybrid associated with the physical anchoring of the SF molecules with the SiO_2 nanoparticles played significant roles for the fixation of the nanohybrid on the fabrics with the aid of the large surface areas, which contributed to further attachment of the dyestuffs during dyeing as well.

Dye uptake and color fastness to water of Acid Red GSF on coated fabrics

Weak acid dyestuffs are suitable for dyeing of the SF moiety in the nanohybrid. But the uncoated cotton fabrics themselves cannot be dyed well with acid dyes. So Acid Red GSF was chosen for the specific purpose to dye the nanohybrid coated cotton fabrics

TABLE I
WR for the Nanohybrid Coated Cotton and Nylon Fabrics Prior to and After the Methanol Treatment

Fabric	WR for fabrics coated with SF (%)		WR for fabrics coated with the nanohybrid[a] (%)	
	Prior to treatment	After treatment[b]	Prior to treatment	After treatment[b]
Cotton	20.3	34.2	67.7	90.9
Nylon	21.4	37.5	81.8	91.0

[a] The feed weight ratio of SF/TEOS was 7/3.
[b] The methanol treatment was carried out as explained in Experimental.
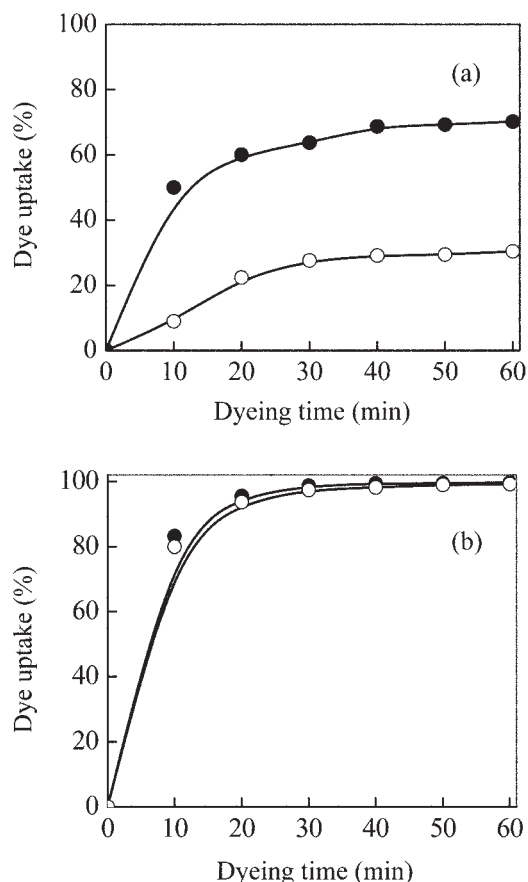
Figure 1 Dye uptake of Acid Red GSF on the (a) cotton and (b) nylon fabrics. —●— coated fabrics, —○— uncoated fabrics. The feed weight ratio of SF/TEOS was 7/3 for the nanohybrid.

so as to make them acid-dyeable. As SF in the nanohybrid is a polyelectrolyte, the net charge is positive when pH decreases below its isoelectric point, or PI, pH 4.5.[12] SF cations are capable of attaching anions of Acid Red GSF via ionic bonding, which accounted for the surface dyeing of the coated cotton fabrics in association with much weaker van der Waals attraction between Acid Red GSF and cellulose macromolecules, The dyeing process of the coated cotton fabrics with Acid Red GSF featuring negatively charged sulfonic acid groups was diffusion-limited. Ionic bonding was formed when the dyestuff stuck irreversibly at first contact with the nanohybrid layer, in contrast to a common multistep dyeing process of acid dyes, adsorption of the dyestuff onto the fiber surfaces, diffusion within fibers and combination with dyeing sites in the interior of the fibers for the uncoated cotton fabric. In Figure 1(a), the equilibrium dye uptake of the coated cotton fabrics was ∼ 70%, whereas it was ∼ 30% for the uncoated cotton fabrics as a control. The disparity in the equilibrium dye uptake illustrated a key role of the nanohybrid, especially the SF moiety, with the large surface areas in the nanohybrid layer. It was also inferred from

Figure 1(a) that the dyeability of the thin nanohybrid layer was much higher than that of the relatively tremendous mass of the cotton fibers, elucidating the unusual properties of the nanohybrid distinct from those of bulk materials. However, the dye uptake was nearly identical for the coated and uncoated nylon fabrics at various dyeing times, as depicted in Figure 1(b). The dye uptake was close to 100% after 30-min dyeing, because there were numerous amino end groups in the nylon macromolecules suitable for dyeing with Acid Red GSF, veiling the dominant effect of the SF moiety presented for the coated cotton fabrics. Incomplete coverage of the nanohybrid on the surface of the coated nylon fabrics could not screen out the fiber interior from the flux of the incoming dyestuff molecules.

In order to make it clear that the SF moiety in the nanohybrid was the exact reason for the dye uptake increase of the coated cotton fabrics in Figure 1(a), dye uptake of the cotton fabrics coated respectively with three kinds of different hybrids was studied by altering the content of SF in the hybrids. Disparity of dye uptake was evident, as shown in Figure 2. Dye uptake of all the coated cotton fabrics was almost two times of the uncoated ones. The equilibrium dye uptake increased with the SF content in the hybrid layers. As WR for the cotton fabrics coated with pure SF was very low even after the methanol treatment, the dye uptake results of the cotton fabrics coated with pure SF were not compared here. It is conceivable that more Acid Red GSF molecules must have been attached on the surface of the hybrid with more SF. Accordingly, SF was a decisive factor for the increase of the dye uptake.

The dyeing process in Figure 1 was further followed up by color fastness to water measurement for the four kinds of fabrics to understand fully the interaction between the dyestuff and the fabrics. Color fastness to water should be evaluated from
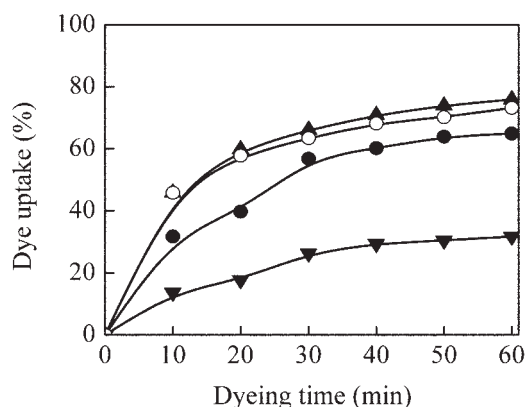

Figure 2 Influence of the SF content in the hybrid layers of the cotton fabrics on dye uptake of Acid Red GSF. The feed weight ratio of SF/TEOS —▲— 9/1, —○— 7/3, and —●— 3/7. —▼— uncoated cotton fabrics.
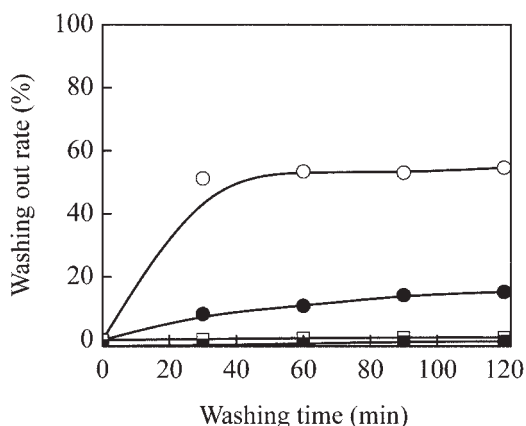
Figure 3 Color fastness to water of the fabrics dyed with Acid Red GSF. —●— coated cotton fabrics, —○— uncoated cotton fabrics, —■— coated nylon fabrics, —□— uncoated nylon fabrics.

two aspects: leakage of the dyestuff from the coated nanohybrid layers and peel of the nanohybrid from the fabrics. The high hot-water WR for both the coated cotton and nylon fabrics in Table I indicated that the latter aspect could be neglected. Figure 3 showed that variation of washing out rate for the coated and uncoated nylon fabrics overlapped and was substantially low, indicating that color fastness to water for the both fabrics was nearly identical. So the interaction between Acid Red GSF and the cationic amino end groups of the nylon macromolecules was strong enough to prevent escaping of the attached dyestuff during washing with water. It should be noted that the significance of the SF moiety in the nanohybrid layer was undiscerned due to the strong electrostatic interaction between Acid Red GSF and the nylon fabrics, in conformity to the dye uptake results in Figure 1. On the contrary, the coated and uncoated cotton fabrics differed noticeably in color fastness to water. Washing out rate of the uncoated cotton fabric rose to 51.2% at a washing time of 30 min, near to the equilibrium value of 53.6%. But washing out rate of the coated cotton fabric was reduced to 8.2% at a washing time of 30 min and increased gradually with washing time to approach 15.2% after washing for 120 min. Therefore, attached Acid Red GSF via van der Waals interaction was prone to segregate from the uncoated cotton fabrics by washing with water. But attached Acid Red GSF via ionic bonding resisted washing efficiently for the coated cotton fabrics.

Dye uptake and color fastness to water of Disperse Cation Red SD-GRL on coated fabrics

Cation dyestuffs are appropriate for dyeing negatively charged polyacrylonitrile fibers with brilliant colors. However, they are seldom applied to dye cot-

ton or nylon fabrics. Disperse Cation Red SD-GRL was selected as the representative cation dyestuff for the nanohybrid coated cotton and nylon fabrics, so as to clarify the surface dyeing of the cotton and nylon fabrics. The net charge of the SF moiety in the nanohybrid was negative when pH 6.8 of the dyebath exceeded its PI. So the SF anions are capable of attaching Disperse Cation Red SD-GRL via ionic bonding. On the other hand, slightly negatively charged polar silanol groups in the SiO_2 phase of the nanohybrid were also able to interact with Disperse Cation Red SD-GRL via electrostatic interaction at pH 6.8.[13] In Figure 4, the equilibrium dye uptake was 15.4% for the uncoated cotton fabrics, but it rose to 60% after coating, roughly four times of that of the uncoated cotton fabrics. Similarly, the equilibrium dye uptake was 70.8% and 20.6% for the coated and uncoated cotton fabrics, respectively. The primary reason of the dye uptake increase was that the negatively charged nanohybrid and their greater surface areas motivated the dyeing processes essentially.

It seemed that both the negatively charged SF moiety and slightly negatively charged silanol groups in the nanohybrids interacted with Disperse Cation
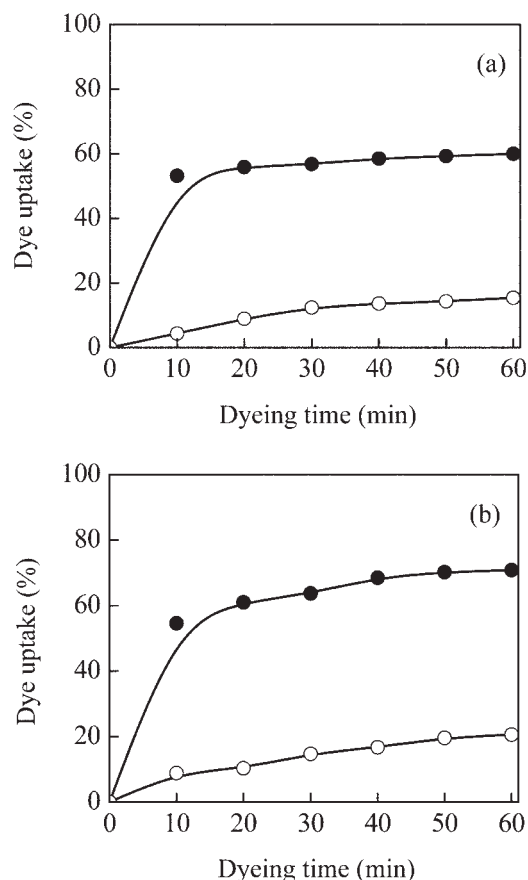

Figure 4 Dye uptake of Disperse Cation Red SD-GRL on the (a) cotton and (b) nylon fabrics. —●— coated fabrics, —○— uncoated fabrics. The feed weight ratio of SF/TEOS was 7/3 for the nanohybrid.
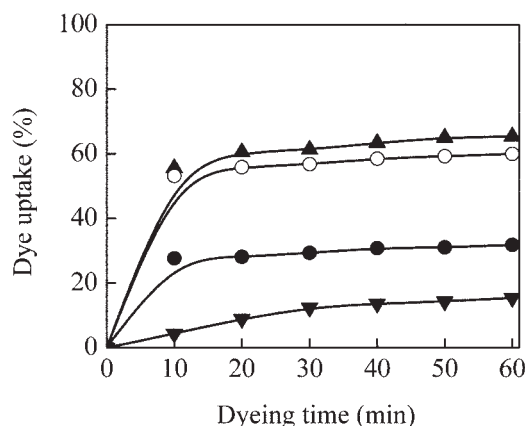
Figure 5 Influence of the SF content in the hybrid layers of the cotton fabrics on dye uptake of Disperse Cation Red SD-GRL. The feed weight ratio of SF/TEOS —▲— 9/1, —○—7/3, and —●— 3/7. —▼— uncoated cotton fabrics.

Red SD-GRL, and thus contributed to the increase of dye uptake in Figure 4. So the SF content was varied to identify either the SF moiety or the SiO$_2$ nanoparticles, or both, controlled the dyeing processes. Equilibrium dye uptake in Figure 5 was 65.4%, 60.0%, and 31.8% for the cotton fabrics coated with the hybrids of the initial feed weight ratios of SF/TEOS 9/1, 7/3, and 3/7, respectively. But equilibrium dye uptake diminished to 15.4% for the uncoated cotton fabrics. So dye uptake increased with the SF content in the hybrid, coincident with the results from Figure 2. Consequently, the SF moiety dominated the dyeing processes rather than the SiO$_2$ nanoparticles in the nanohybrid due to insufficient negative charges of the polar silanol groups.

Color fastness to water was measured to check interaction between Disperse Cation Red SD-GRL and the coated cotton or nylon fabrics with the dyeability of Disperse Cation Red SD-GRL shown in Figure 4. The washing out rate of the coated cotton and nylon fabrics, shown in Figure 6, decreased to less than 10%, 1/7–1/6 of that of the corresponding uncoated ones. That is, the nanohybrid retarded the loss of Disperse Cation Red SD-GRL during washing. The uncommon properties of the nanohybrid offered, both the fabrics, strong attraction with the cation dyestuff. Migration of Disperse Cation Red SD-GRL from the coated nanohybrid was inhibited efficiently because ionic bonding of the dyestuff with the nanohybrid was much stronger than van der Waals interaction between the dyestuff and the uncoated cotton or nylon fabric. So the color fastness to water of the coated fabrics was much higher than that of the uncoated fabrics.

CONCLUSIONS

The SF/SiO$_2$ nanohybrid derived from sol–gel reaction was utilized to introduce the thin nanohy-

brid coating layers on the cotton and nylon fabrics. WR representing hot-water WR was greater than 90% for both the nanohybrid coated cotton and nylon fabrics, indicating that the SiO$_2$ nanoparticles in the nanohybrid were essential to fetter the SF molecules via hydrogen bonding, and hence to avoid release of the SF molecules dissolved by hot water. The SF moiety in the nanohybrid is a polyelectrolyte, the net charge was positive when pH of the dyebath was below its PI. So SF cations attached the anions of Acid Red GSF via ionic bonding, which interpreted the increase of dye uptake for the coated cotton fabrics in association with the great surface areas of the nanohybrid. However, no increase was observed for dye uptake of the coated nylon fabrics dyed with Acid Red GSF owing to saturation of the dyestuff attached on the controlled uncoated nylon fabrics, which concealed the contribution of the nanohybrid layer. Conversely, SF was negatively charged when pH of the dyebath exceeded its PI. As a result, the SF anions interacted with Disperse Cation Red SD-GRL via ionic bonding, which also led to the increase of dye uptake of Disperse Cation Red SD-GRL for the coated cotton and nylon fabrics along with the great surface areas of the nanohybrid. Furthermore, dye uptake of Acid Red GSF increased with the SF content in the hybrid layers. More Acid Red GSF molecules must have been attached on the surface of the nanohybrid with more SF. Therefore, SF was a decisive factor for the increase of the dye uptake. Similar results were obtained as well for the coated cotton fabrics dyed with Disperse Cation Red SD-GRL. Color fastness to water of the coated cotton fabrics dyed with Acid Red GSF or Disperse Cation Red SD-GRL increased severalfold in comparison with the
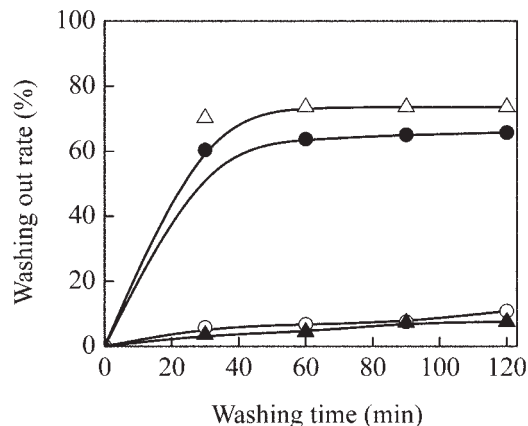

Figure 6 Color fastness to water of the fabrics dyed with Disperse Cation Red SD-GRL. —○— coated cotton fabrics, —●— uncoated cotton fabrics, —▲— coated nylon fabrics, —△— uncoated nylon fabrics.

uncoated cotton fabrics. So was the coated nylon fabrics dyed with Disperse Cation Red SD-GRL. The attached dyestuffs via ionic bonding resisted washing efficiently for the coated fabrics.

In brief, the unusual properties of the SF/SiO$_2$ nanohybrid distinct from those of bulk materials were employed to increase the dyeability of the cotton and nylon fabrics via the new surface dyeing approach for the nanohybrid coated fabrics with the assistance of the large surface areas of the nanohybrid in pursuit of altering dyeability of fabrics. Actually, dyeing of the fabrics occurred in the very thin nanohybrid layers exclusively, while the main body of the fabrics remained intact. Other physical properties of the coated fabrics, such as abrasion resistance and biocompatibility, are in current process. Introduction of the novel nanohybrid to the fabrics in this work opens up new vistas for finishing of fabrics with nanomaterials to achieve unique chemical and physical properties.

References

1. Wei, Z.; Gu, Z. J Appl Polym Sci 2001, 81, 1467.
2. Mahltig, B.; Bottcher, H. Melliand Textilberichet 2002, 83, E50, 251.
3. Textor, T.; Bahners, T.; Schollmeyer, E. Prog Colloid Polym Sci 2001, 117, 76.
4. Philipp, G.; Schmidt, H. J Non-Cryst Solids 1984, 63, 283.
5. Xu, C.; Eldada, L.; Wu, C.; Norwood, R. A.; Shacklette, L. W.; Yardley, J. T. Chem Mater 1996, 8, 2701.
6. Faraggi, E. Z.; Sorek, Y.; Levi, O.; Avny, Y.; Davidov, D.; Neumann, R.; Reisfeld, R. Adv Mater 1996, 8, 833.
7. Schmidt, H.; Wolter, H. Non-Cryst Solids 1990, 121, 428.
8. Tamaki, R.; Chujo, Y.; Kuraoka, K.; Yazawa, T. J Mater Chem 1999, 9, 1741.
9. Wang, X.; Zou, L.; Jiang, D. J Appl Polym Sci 2007, to appear.
10. Yamada, K.; Tsuboi, Y.; Itaya, A. Thin Solid Films 2003, 440, 208.
11. Tsukada, M.; Gotoh, Y.; Nagura, M.; Minoura, N.; Kasai, N.; Freddi, G. J Polym Sci B: Polym Phys 1994, 32, 961.
12. Cheng, Q.; Peng, T.-Z.; Hu, X.-B.; Yang, C. F. Anal Bioanal Chem 2005, 382, 80.
13. Lei, C.; Shin, Y.; Liu, J.; Ackerman, E. J. J Am Chem Soc 2002, 124, 11242.