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Fabrication and UV-blocking property of nano-ZnO assembled cotton fibers via a two-step hydrothermal method

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Abstract A novel ZnO/cotton composite, in which ZnO nanoparticles were synthesized directly inside of the lumen and the mesopores of cotton fibers, was fabricated via a simply two-step hydrothermal method in situ using zinc nitrate hexahydrate and hexamethylenetetramine as raw materials. The as-obtained cotton sample was characterized by powder X-ray diffractometer, field emission scanning electron microscopy, and energy-dispersive spectroscopy, respectively. The UV-blocking property of the as-obtained sample was investigated by UV–vis spectrophotometry. The results showed that hexagonal wurtzite nano-ZnO with a diameter of about 30–40 nm was successfully assembled into the lumen as well as the mesoporous structure of the cotton fibers. The UV-blocking property of the modified cotton fibers can be greatly improved by assembling nano-ZnO into the inner of cotton fibers. Comparing with the neat cotton fibers, the UV-blocking ratio of the ZnO assembled cotton fibers inside of KBr disk could reach 80% at 300 nm and 95% at 225 nm, respectively. Therefore, it demonstrated a significant advance in protective functional treatment and provided a potential commercialization.

Keywords Nano-ZnO · Assembly · Cotton fibers · Lumen · Hydrothermal method · UV-blocking

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Introduction

Cotton, one of the most important natural fibers (Adebajo et al. 2006), is widely used as clothing materials due to its excellent characteristics including regeneration, biodegradation, softness, comfort, warmness, and hygroscopic properties. Unfortunately, the UV radiation coming from the space and the environment around human can easily transmit through the ordinary cotton fabrics used in daily life and workshop to cause various pathologies (Bednarska et al. 2000; Takeshita et al. 2006), such as cancer, ageing, Alzheimer's disease, inflammatory disorders, and so on (Liebler 2006; Algaba et al. 2007). Therefore, it is necessary and exigent to develop an efficient fabrication method to achieve the high UV protection properties of cotton fibers. Nano-ZnO is widely used as a catalyst for chemical reactions (Wang et al. 2008), photocatalysts (Parida et al. 2006), photoelectric conversion (Vayssieres et al. 2001; Konenkamp et al. 2002), antibacterial and bactericide (Nair et al. 2009; Applerot et al. 2009), UV-shielding materials (Wang et al. 2004, 2005; Lu et al. 2006), and photoluminescence materials (Dodd et al. 2008). It can efficiently absorb UV radiation coming from the atmospheric ozone layer (Sato and Ikeya 2004) and can be directly used in daily applications. Recently, many studies have been devoted to improve the UV protection function of cotton fabrics using nano-ZnO (Yadav et al. 2006; Kathirvelu et al. 2009; Mao et al. 2009; Zohdy et al.

2009; Farouk et al. 2010; Paul et al. 2010; Wang et al. 2011). Yadav et al. (2006) applied ZnO nanoparticles onto cotton fabrics using acrylic binder. Wang and co-owners also grew nano-ZnO crystallites on cotton fabrics to achieve UV-blocking property (Wang et al. 2004, 2005). Vigneshwaran et al. (2006) treated cotton fabrics with zinc oxide-soluble starch nanocomposites to enhance UV-protective property. Becheri et al. (2008) applied nano-ZnO synthesized via a homogeneous phase reaction on cotton fabrics for UV protecting. The needled-shaped ZnO coated cotton fabric with better UV-blocking property has also been synthesized using hydrothermal method (Mao et al. 2009). In the references above, the combination between nano-ZnO and cotton fabrics was achieved mainly using acrylic binder and mechanical adhesion. The reported preparation methods need complicated processes and various nonfunctional components were introduced into the cotton fabrics, which might reduce the comfort and the machinable properties of cotton fabrics. In this paper, we reported a novel ZnO/cotton composite, in which ZnO nanoparticles were synthesized directly inside of the lumen and the mesopores of cotton fibers via a two-step hydrothermal method in situ. This green method of synthesis is very simple and lower toxicity without using any binder compound. XRD, FESEM, EDS and UV–Vis spectroscopy were used to analyze the as-obtained cotton fibers. The effect of the ZnO content on the UV-blocking property of the as-obtained sample was evaluated by changing the concentrations of zinc nitrate hexahydrate solutions.

Experimental section

Materials

All the reagents and solutions including zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, $\geq$98%), sodium hydroxyl (NaOH), hexamethylenetetramine (HMAT, $(CH_2)_6N_4$), absolute ethanol (C_2H_5OH, 99.7%) were of analytical grade and were used without any further purification, which were purchased from Kewei Company of Tianjin University. Cotton fibers were gained from commercial market.

Preparation of the nano-ZnO assembled cotton fibers

The cotton fibers were pre-treated in order to remove various non-cellulose components, such as wax, grease, and other finishing chemicals. The original cotton fibers were immersed in 30 mL 10 wt% NaOH solution placed in a 100 mL Teflon-lined stainless steel autoclave, sealed and heated at 150 °C for 3 h. After hydrothermal treatment, the cotton fibers were rinsed with distilled water up to neutral conditions (pH = 7) and dried using a electric hair dryer.

The preparation of ZnO-assembled cotton fibers was carried out according to the following procedure. Firstly, 29.6 mg zinc nitrate hexahydrate and 14 mg HMTA was dissolved into 25 mL distilled water, respectively, and then the zinc nitrate hexahydrate solution was slowly dropped to the HMTA solution under vigorous stirring to form a growth solution. Secondly, 0.2 g pre-treated cotton fibers were immersed in the above growth solution, vacuuming 1 h and ultrasonic treatment for 30 min in turn, and then the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and hydrothermally treated at 90 °C for 2 h. After fully rinsed with distilled water, the cotton fibers were immersed in one of the growth solutions with determinate amounts of zinc nitrate hexahydrate (74, 223, 370, 520, 743, 838 mg, respectively) again. The corresponding amount of HMTA was 35, 105, 175, 245, 350, 421, and 525 mg in sequence with the molar ratio to zinc nitrate hexahydrate 0.95:1. Finally, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave the same as the above-mentioned and hydrothermally treated at 90 °C for 8 h. After the hydrothermal treatment, the cotton fibers were washed two times with distilled water for 10 min each time in ultrasonic bath, and then rinsed by ethanol three times, and dried by electric blower.

Measurement and characterization

The phases and crystallography of the as-obtained samples were characterized using X-ray diffraction (XRD), which was carried out on a DX-2000 X-ray

diffractometer equipped with a CuKa ($\lambda = 0.1542$ nm) radiation tube operating at 35 kV and 25 mA at room temperature. The morphologies of samples were observed by 1530VP model field emission scanning electron microscopy (FESEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. The samples were gold sputtered to give the samples electronic conductivity under a vacuum prior to the observation. The UV-blocking properties of the assembled cotton fibers were investigated by transmission spectroscopy using a UV-4501 UV/Vis spectrophotometer. The UV profiles of the neat cotton fibers were compared to the spectra collected with the nano-ZnO assembled cotton fibers, and the effectiveness in shielding UV radiation was evaluated by measuring the UV transmission. The samples for UV transmittance testing were prepared using KBr pressed-disk technique in a column mold with inner diameter of 10 mm under the pressure of 30 kg/cm^2. The dosage of KBr powder and the assembled cotton fibers was 120 and 1 mg, respectively.

Results and discussion

XRD analysis

The crystallinity and crystal phase of the treated cotton fibers assembled with ZnO nanoparticles obtained by various amounts of zinc nitrate hexahydrate were examined by the X-ray diffraction (XRD) patterns with Cu-Kα radiation and depicted in Fig. 1. For all the samples, the peaks at 2θ values of 15.2°, 16.7°, 23.1°, and 34.5° corresponding to (101), (101), (002), and (040) are the diffraction peaks of cotton fiber (cellulose I) (JCPDS. No. 03-0226) (Lin et al. 2008). This indicates that the cotton fibers exhibited cellulose I structure. On the other hand, there are also diffraction peaks in curve b–f at 2θ values of 31.77°, 34.42°, 36.25°, 47.54°, 56.60°, 62.86° and 67.96° correspond to the (100), (002), (101), (102), (110), (103) and (112) planes, respectively, and can readily be indexed to the hexagonal wurtzite phase of ZnO (JCPDS No. 36-1451). No peaks corresponding to other materials were detected in the patterns. Moreover, it can be observed that the diffraction peaks of ZnO are not distinctly in Fig. 1a due to the low ZnO content of the as-obtained samples and the peak intensity of ZnO increases when increasing the amount of zinc nitrate hexahydrate as shown in Fig. 1b–d. The peak intensity of cotton fibers at 2θ values of 15.2°, 16.7°, 23.1°, and 34.5° gradually becomes weak with the crystallinity increasing of the nano-ZnO assembled into cotton fibers. It can be proven that nano ZnO particles successfully assembled into the inner structure of cotton fibers, because the obvious crystallinity decreasing of cotton fibers results from the disorder caused by more nano ZnO into the interface between the elementary fibrils (perfect crystalline arrays), which packing cotton fiber architecture (Menachem 2007).

SEM and EDS analysis

Cotton fibers consist of a cuticle, primary wall, secondary wall, and a lumen (Menachem 2007). The lumen is the central cavity or canal at the center of the fiber. Because of the twisted and wrinkled condition of the dried fiber, it often does not appear to be open. When cotton fibers are dissolved in some solution, the lumen often remains as a complete entity and can be rendered visible with fine particles. In this experiment, ZnO nanoparticles were assembled into the lumen through two steps: firstly, the synthesis solution was absorbed into the lumen of cotton fibers, and fine ZnO nanoparticles occurred in the lumen, the mesopores and the surface of cotton fibers under hydrothermal treatment. The ZnO nanoparticles located in the surface of cotton fibers can be washed away. At the

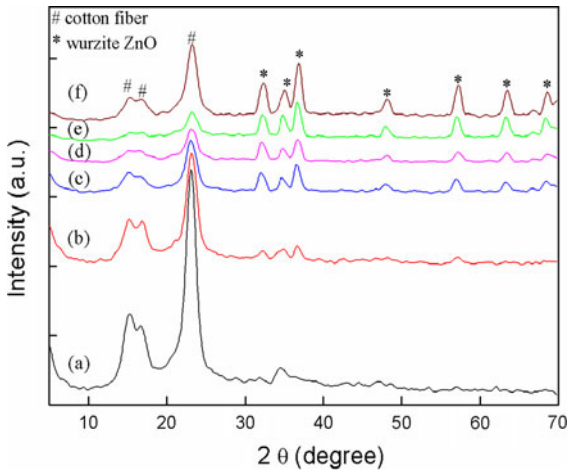

Fig. 1 XRD patterns of ZnO assembled cotton fibers in hydrothermal system with different amounts of $Zn(NO_3)_2{\cdot}6H_2O$: *a* 74 mg, *b* 223 mg, *c* 370 mg, *d* 520 mg, *e* 743 mg, *f* 838 mg

second, the ZnO nanoparticles reserved after washing locate in the lumen and the mesopores of cotton fibers, as the seeds for crystallization, preferentially grow during the second hydrothermal treatment. The FE-SEM photographs of the nano-ZnO assembled cotton fibers are presented in Fig. 2. Figure 2a shows the cross-section of the ZnO assembled cotton fibers and it can be obviously observed that a large amount of zinc oxide nanoparticles and partly rods locate inside of the lumen as well as in the surface of cotton fibers. In the lumen section of the fiber located in the top-middle of Fig. 2a, it can be faintly observed nano-ZnO arrays growing along the lumen axis direction. Figure 2b shows the cross section of the ZnO assembled cotton fibers with a lumen full of ZnO nanorods. The photograph with a higher magnification in Fig. 2c reveals that a lot of mesopores in diameter of about 20–100 nm existing in the primary and the secondary wall of cotton fibers, and a great number of ZnO nanoparticles settle in the mesoporous structure made up of numerous microfibrils, which packing into the primary cell wall and the secondary cell wall of cotton fibers. In Fig. 2d, ZnO particle size can be evaluated to be in a very low nanometric range ($\sim$30–40 nm). In general FESEM observation, it can be confirmed that ZnO nanoparticles can be successfully assembled into the inner structure through the two-step hydrothermal method, it is accordant with the XRD analysis.

EDS was employed to establish the chemical identity of the as-obtained samples and the ZnO fabricated in the interface of cotton fibers. There is a SEM image of the as-obtained sample without visible ZnO nanoparticles on the cross-section of treated cotton fibers (see Fig. 3a) and its corresponding EDS

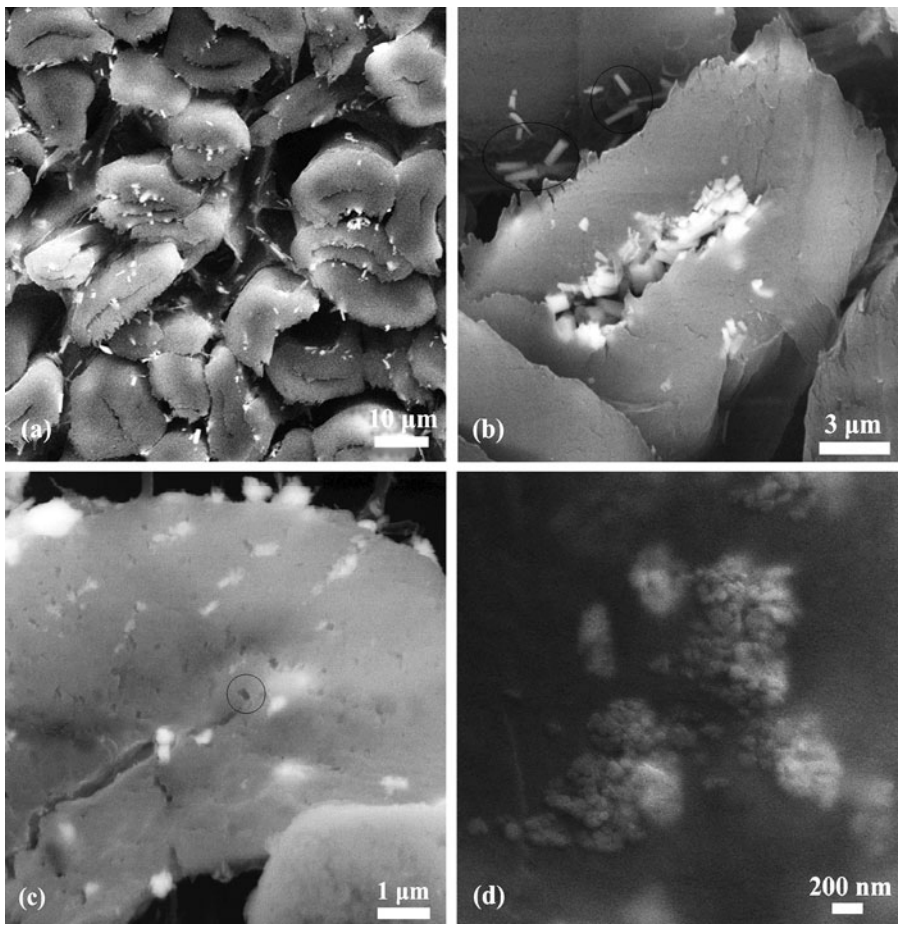

Fig. 2 SEM images of **a** the cross-section of the nano-ZnO assembled cotton fibers in low magnification, **b** the lumen of the ZnO assembled cotton fiber, **c** the cross-section of a cotton fiber and **d** high magnification images of the cross-section of the ZnO assembled cotton fiber

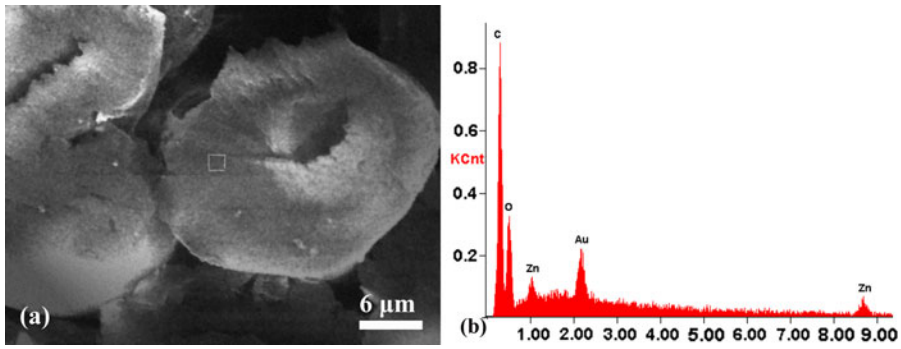

Fig. 3 SEM image of the cross-section of the nano ZnO assembled cotton fibers and the corresponding EDS spectra obtained in the area without visible nano-ZnO particles

spectra as showed in Fig. 3b. The EDS analysis reveals the presence of Zn and O atoms, and the atomic ratios of Zn:O fits almost 1:1 stoichiometry of Zn and oxygen, respectively. The result confirms that a lot of ZnO nanocrystallites occur all over the inner structure of cotton fibers, and this is in agreement with the FESEM results (see Fig. 2). Peaks related to C and Au should be the contributions of the carbon grid and the film that coated the samples, respectively.

UV-blocking property

The solar UV radiation is actually composed of UV-A (400–315 nm), UV-B (315–290 nm) and UV-C (290–200 nm). These radiations are present in natural terrestrial sunlight in different amounts due to the filtering activity of the upper atmosphere and local conditions (latitude, altitude and clouds). UV-C and most of UV-B are filtered by the ozone layer (Ghule et al. 2006; Paul et al. 2010). Here, UV spectra were recorded for untreated and treated cotton fibers by measuring the transmission.

Figure 4 shows the transmittance plotted against the wavelength for untreated cotton fibers and the treated cotton fibers with different contents of ZnO nanoparticles. Compared to the neat cotton fibers as shown in Fig. 4a, the transmittance ratio of the nano-ZnO assembled cotton fibers is obviously low in the wavelength range of 210–380 nm (see Fig. 4b–f). This result indicates that the ZnO assembled cotton fibers showed better UV-blocking properties than the neat cotton fibers and the effectiveness in shielding UV radiation is due to the UV absorption capacity of ZnO nanoparticles. Moreover, Fig. 4c–f show a marked UV blocking property in the wavelength range below 370 nm, indicating the better UV-protection of the assembled cotton fibers with the higher amounts of zinc nitrate hexahydrate. It can be concluded that the UV absorption efficiency increased when increasing the ZnO content of cotton fibers. The transmittance value (%) of samples (a), (b), (c), (d), (e) and (f) at 300 and 225 nm respectively, which were read from the curves in Fig. 4, were listed in Table 1. The UV blocking ratio (R, %) can be calculated according to formula (1).

$$R(\%) = (Tc - Tz)/Tc \quad (1)$$

In where, Tc and Tz are respectively, the transmittance value (T, %) of the neat cotton fiber sample (a) and the ZnO assembled cotton fiber samples (b), (c), (d), (e) and (f). The calculation results show that the UV blocking ratio of the ZnO assembled cotton fibers reaches 80% at 300 nm and 95% at 225 nm respectively, when compared to the neat cotton fibers. Considering the characteristics of KBr pressed-disk technique, the high UV blocking ratio was achieved in

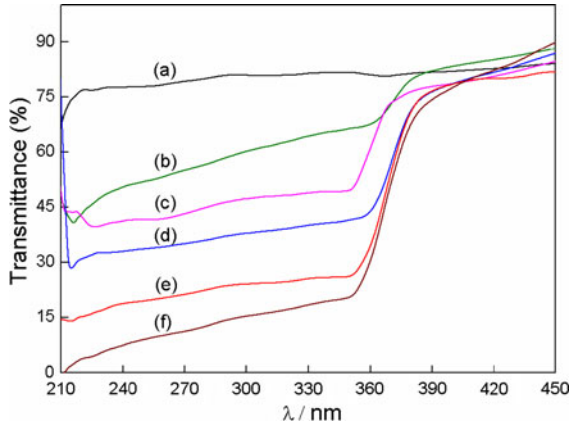

Fig. 4 UV transmission spectra of *a* neat cotton fibers and the ZnO assembled cotton fibers in hydrothermal system with different amounts of $Zn(NO_3)_2{\cdot}6H_2O$: *b* 370 mg, *c* 520 mg, *d* 743 mg, *e* 838 mg, *f* 1048 mg

Table 1 UV blocking ratio and transmittance of the ZnO assembled cotton fibers

	(a)	(b)	(c)	(d)	(e)	(f)
300 nm						
T, %	80.8	60.1	47.1	37.9	23.8	15.2
R, %	0	25	41	53	70	80
225 nm						
T, %	76.8	45.9	39.9	31.9	15.8	4.2
R, %	0	40	48	59	79	95

cases of that the amount of the ZnO assembled cotton fibers added into the testing sample is lower than 1 wt% and the large section in the testing UV-ray line was not covered by cotton fibers. Therefore, it can be reasonably foreseen that the UV blocking property of the fabrics weaved using the as-obtained ZnO assembled cotton fibers should remarkably excellent.

Conclusions

Nano-ZnO assembled cotton fibers were successfully synthesized via a two-step hydrothermal method in situ using zinc nitrate hexahydrate and hexamethylenetetramine as raw materials. The XRD results indicate that the prepared ZnO was hexagonal wurtzite phase. SEM results show that ZnO with about 30–40 nm in size was formed in the lumen as well as in the mesopores of the treated cotton fibers. The UV tests indicate a significant increment of the UV absorbing activity in the ZnO-assembled cotton fibers, and the UV blocking ratio of the ZnO assembled cotton fibers reaches 80% at 300 nm and 95% at 225 nm respectively, comparing with the neat cotton fibers. Such results can be exploited for the protection of the body against solar radiation and for other technological applications.

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