

Microwave Assisted Fabrication of Nano-ZnO Assembled Cotton Fibers with Excellent UV Blocking Property and Water-wash Durability

Yan Li, Yanyan Hou, and Yunling Zou*

College of Science, Civil Aviation University of China, Tianjin 300300, P.R. China
(Received June 26, 2011; Revised September 4, 2011; Accepted September 16, 2011)

Abstract: Nano-ZnO assembled cotton fibers, with excellent UV blocking property and good water-wash durability, have been successfully fabricated using microwave assisted precipitation and crystallization process synchronously in situ for the first time. Here, zinc nitrate hexahydrate was used as zinc resource and sodium hydroxide was used as precipitate. The as-obtained samples were characterized by powder X-ray diffractometer (XRD), field emission scanning electron microscopy (FESEM), and energy-dispersive spectrometry (EDS), UV/Visible spectroscopy and Fourier transformation infrared spectroscopy (FTIR). Wurtzite ZnO with about 30-40 nm in diameter was fabricated in the lumen as well as in mesoporous structures of cotton fibers. The as-prepared samples have excellent UV absorbing activity over a broad range in the region from 225 nm to 380 nm. The crystallinity and UV blocking properties keep unchangeable as the former after being washed for 60 min in 33 l water. FTIR results reveal that there is no peak shift and new peak occurred, which indicates that no chemical bond exist between nano-ZnO and cotton fibers. Mechanical force is the only way to bond nano-ZnO to cotton fibers in the experimental condition. ZnO nanoparticles and wax existing in cotton fibers can combine to a firmly hybrid layer in the surface and the inner of cotton fibers during microwave treatment, which may bring the good water-wash durability.

Keywords: Nano-ZnO, Cotton fiber, Microwave, Water-wash durability, UV blocking

Introduction

UV light coming from the atmosphere and working environment can result in a series of negative health effects such as acceleration of skin ageing, photodermatitis (acne), erythema (skin reddening), and even severe skin cancer. It presents a great prospect to develop textiles with high UV protective property [1]. Nano-ZnO, one of the various inorganic compounds supplying excellent UV blocking properties over a board range of UV wavelength and with a wide direct band gap (3.37 eV) and large exciton binding energy (60 meV), has been considered as one of the most important functional materials [2].

The fabrication of ZnO treated cotton fabrics for improved UV radiation protection has been currently realized by various methods including wet chemical method [3-5], homogeneous precipitation method [6], and hydrothermal method [7]. For example, Wang *et al.* [3] developed a low-temperature growth approach for growing hexagonally oriented ZnO nanorod arrays onto cotton fabrics. Yadav *et al.* [4] prepared ZnO nanoparticles with an average size of 40 nm by wet chemical method and applied them onto cotton fabrics using acrylic binder. Becheri and co-workers [6] synthesized ZnO nanoparticles via a homogeneous phase reaction and applied them on cotton fabrics for UV shielding. Mao *et al.* [7] reported the needled-shaped ZnO coated cotton fabric with better UV-blocking property, has been synthesized by hydrothermal method. According to the references above, the ZnO treated cotton fabrics were obtained by a two-step synthesis process: synthesis of nano-

ZnO and bonding the obtained nano-ZnO to the surface of cotton fabrics. Moreover, in order to increase the washfastness, the ZnO nanoparticles were applied by dipping the fabrics in a solution containing a specific binder [4,5,8,9]. However, the reported preparation methods were complicated and take a long duration. Meanwhile, various nonfunctional components were introduced into the cotton fabrics, which might devastate the comfort and the machinable properties of cotton fabrics. Microwave process enables the rapid and homogeneous heating of the reaction mixture to the desired temperature without heating the entire furnace or oil bath, which saves time and energy [10]. To increase heating efficiency and avoid temperature gradient, microwave heating has been successfully applied for the preparation of a variety of inorganic nanomaterials [11-14].

In this paper, we reported nano-ZnO/cotton fibers were fabricated using microwave assisted route for the first time. Without using any binder compound, the hydrothermal crystallization of nano-ZnO and the bonding between ZnO nanoparticles and cotton fibers were synchronously completed in a short time (30 min). This simple method showed a high-efficiency and rapid in situ fabrication of ZnO nanoparticles with a narrow size distribution on cotton fibers. The as-obtained samples were characterized by XRD, FESEM, EDS, UV/Visible spectroscopy and FTIR. The UV blocking property and water-wash durability of the samples were also studied by measuring the transmission of ultraviolet ray.

Experimental

Materials

All the reagents and solutions including zinc nitrate

*Corresponding author: zouyunling1999@126.com

hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98 wt%), sodium hydroxide (NaOH , 96 wt%), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 wt%) and *N,N,N*-Trimethyl-1-hexadecanaminium bromide (CTABr, $\text{C}_{19}\text{H}_{42}\text{BrN}$, 99 wt%), 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.

Sample Preparation

Samples were prepared as the following procedure: first, 4.5 g zinc nitrate hexahydrate as well as 1.2 g sodium hydroxide was dissolved in 20 ml of distilled water, respectively. White precipitation occurred while the sodium hydroxide solution was slowly dropped into the zinc nitrate hexahydrate solution, keeping the molar ratio of Zn^{2+} to OH^- at 1:2. The precipitate was obtained after single step centrifugal separation and being washed with distilled water. Then the as-obtained precipitate was placed into a conical flask, and 10 ml ammonia in concentration of 25 wt% was gradually added into the flask under magnetic force stirring until the suspension became into a clear solution. After that the solution was transferred into a 100 ml volumetric flask, continually adding distilled water balance with the reticle. Second, 0.01 g CTABr and 0.4 g cotton fibers were dipped into a conical flask filled with 30 ml of the above solution, and then placed into the ultrasonic oscillator (KQ3200DB model, Kunshan, China) with a maximum oscillation frequency of 40 kHz and a power of 100 W for 20 min. Subsequently, the treated cotton fibers, after taken out from the flask and drained, was enclosed into a household microwave oven (Galanz, P80D23N2L0A9 (RO) model) and treated for 10 min under a determined power (136, 296, and 320 W). Finally, the above mixture was transferred into a 100 ml Teflon-lined autoclave with 50 ml distilled water and heated at 150 °C for 3 h. After the hydrothermal treatment, the sample was washed with distilled water thoroughly and dried at 60 °C for 2 h by microwave.

XRD Analysis

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 $\text{CuK}\alpha$ ($\lambda=0.1542$ nm) radiation tube operating at 35 kV and 25 mA at room temperature.

Surface Morphology

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.

UV-blocking Property Measurement

The UV-blocking properties of the assembled cotton fibers

were investigated by transmission spectroscopy using a UV-4501 UV/Visible spectrophotometer. The UV profiles of the untreated cotton fibers were compared to the spectra collected from the same cotton fibers treated with ZnO nanoparticles, and the effectiveness in shielding UV radiation was evaluated by measuring the transmission of UV ray.

FTIR Measurement

Fourier transformation infrared spectroscopy (FTIR) measurement of the samples was collected on a Nicolet 380 spectrometer with the spectral resolution 1 cm^{-1} . The samples were mixed with KBr with the weight ratio about 1:100 and pressed into pellets for characterization.

Results and Discussion

Surface Morphology by FESEM

The FESEM photographs of the nano-ZnO assembled cotton fibers are presented in Figure 1(a) and 1(b). It is shown that a large amount of zinc oxide nanoparticles and partly rods locate inside of the lumen as well as in the surface of the ZnO assembled cotton fibers. The photograph with a higher magnification in Figure 1(b) 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. According to Scherrer formula $D=K\lambda/\beta\cos\theta$ and the three peaks locates at 2-theta of 30 to 40° corresponding to Figure 2(a), ZnO

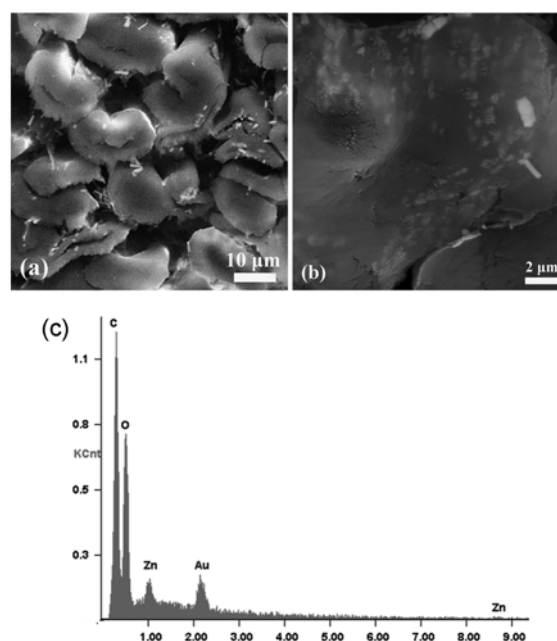


Figure 1. FESEM images of the cross-section of the nano ZnO assembled cotton fibers with (a) a low magnification, (b) a large magnification and (c) the corresponding EDS spectrum obtained in the section area in Figure 1(b).

particle size corresponding to Figure 1(b) can be calculated to be in a very low nanometric range (~30-40 nm). It can be confirmed that ZnO nanoparticles can be successfully assembled into the inner structure through dipping-step and microwave treatment.

The EDS analysis (as shown in Figure 1(c)) reveals the presence of Zn and O atoms, and it confirms that ZnO nanocrystallites occur all over the inner structure of cotton fibers, which is in agreement with the FESEM results. Peaks related to C and Au should be the contributions of the carbon grid and the film that coated the samples, respectively.

XRD Analysis

The X-ray diffraction (XRD) patterns of the nano-ZnO assembled cotton fibers fabricated under different microwave

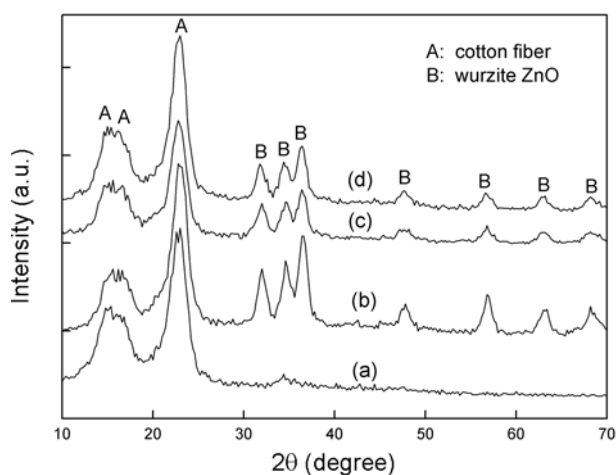


Figure 2. XRD patterns of (a) untreated cotton fiber, and ZnO assembled cotton fibers treated under microwave power of (b) 136 W, (c) 296 W, and (d) 320 W.

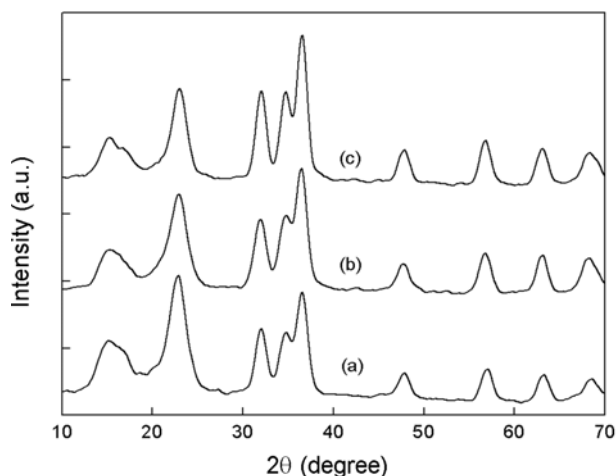
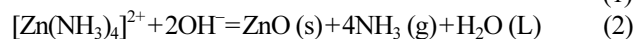
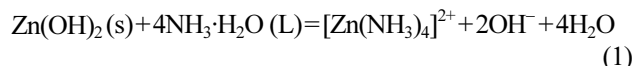


Figure 3. XRD patterns of ZnO assembled cotton fibers dipped in the synthesis solution for (a) one times, (b) two times and (c) three times respectively and treated under microwave power of 320 W for 15 min each times.

power and under different treatment time, are showed in Figure 2 and Figure 3, respectively. For all the samples, the diffraction peaks at 2θ values of 15.2, 16.7, and 23.1° corresponding to (101), (101) and (002) are the diffraction peaks of cotton fiber (cellulose I) [15]. The diffraction peaks in all curve 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 of ZnO respectively, and can readily be indexed to the hexagonal wurtzite ZnO (JCPDS No. 36-1451). No additional peaks corresponding to other materials were detected in the patterns. Moreover, it can be observed that the diffraction peaks of ZnO in Figure 2(b)-(d) did not distinctly change with increasing microwave power from 136 to 320 W. In a contrary manner, the ZnO peaks in the range of large 2-theta clearly decrease with increasing microwave power. It can be understood referencing to reaction equation (1) and (2) of nano-ZnO growth.



The reaction occurs complying to equation (1) under low temperature of 80 °C to produce $[\text{Zn}(\text{NH}_3)_4]^{2+}$, while the reaction occurs according to equation (2) to the left to produce ZnO(s), $\text{NH}_3(\text{g})$ and $\text{H}_2\text{O}(\text{L})$ at more than 80 °C. Therefore, the reaction solution dipped into the lumens and the mesopores of cotton fibers can be extruded out by the gaseous NH_3 produced during microwave treatment. The higher the microwave power, the more the reaction mass is extruded. With hoisting microwave power, lesser reaction solution can be remained inside of cotton fibers and a relatively low quality of nano-ZnO occurs in situ.

Figure 3 shows the XRD patterns of the ZnO assembled cotton fibers through different fabrication times, which including reaction solution dipping process and microwave treatment. It is clearly observed that there is not conscious of differences between the XRD patterns of the samples obtained through one times, two times and three times of fabrication process respectively. It can be explained that the mesoporous structure and the lumens of cotton fibers are occupied by the nanoparticles occur during the first procedure, which block the reaction solution is efficiently absorbed into cotton fibers again during the second and the third procedure. Therefore, the dipping times does not effectively improve the crystallinity of the as-obtained samples.

FTIR Analysis

Figure 4 shows the FTIR spectra of (a) cotton fibers without any treatment, (b) ZnO assembled cotton fibers and (c) nano-ZnO obtained in the same system respectively. With comparison of the three spectra, it is found that all IR peaks of the ZnO assembled cotton fibers are the combination of IR peaks of nano-ZnO and the untreated cotton fibers. Meanwhile, no peak shift and new peak occurs in the tested

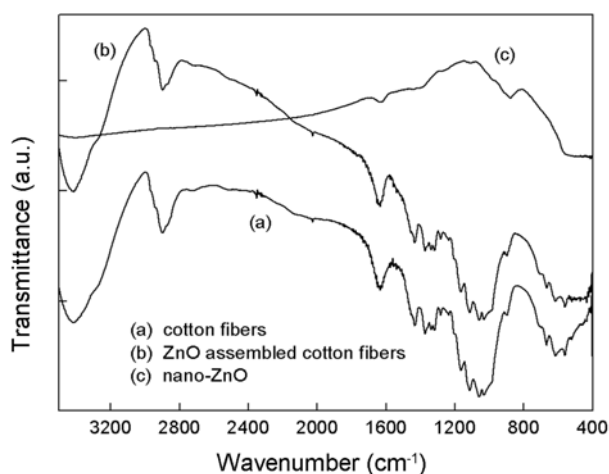


Figure 4. FTIR spectra of (a) cotton fibers without any treatment, (b) ZnO assembled cotton fibers and (c) nano ZnO obtained in the same system respectively.

samples. It can be concluded that there is no chemical bond between nano-ZnO and cotton fibers, mechanical force is the only way to bond nano-ZnO to cotton fibers.

UV-blocking Property

The UV transmittance spectra of the nano-ZnO assembled cotton fibers, fabricated under different microwave power and different fabrication time, are shown in Figure 5 and Figure 6, respectively. It can be clearly observed that the ZnO assembled cotton fibers have a very low transmittance ratio in the wavelength range of 225 to 400 nm, which means better UV-blocking properties. The effectiveness in shielding UV radiation is due to the UV absorption capacity of ZnO nanoparticles assembled into mesoporous structure and the lumens of cotton fibers. The profile and the

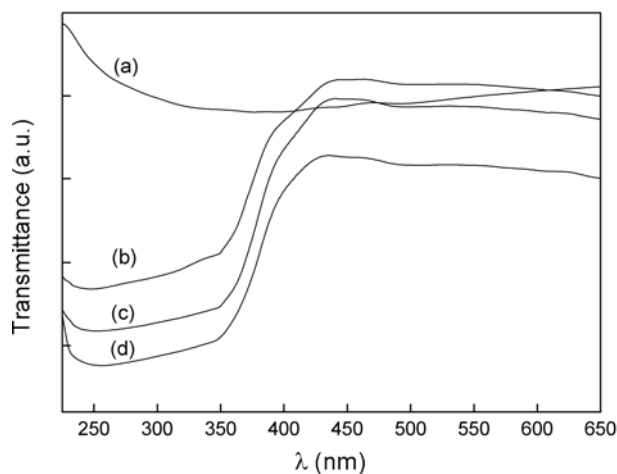


Figure 5. UV transmission spectra of (a) untreated cotton fiber, and ZnO assembled cotton fibers treated under microwave power of (b) 136 W, (c) 296 W and (d) 320 W respectively.

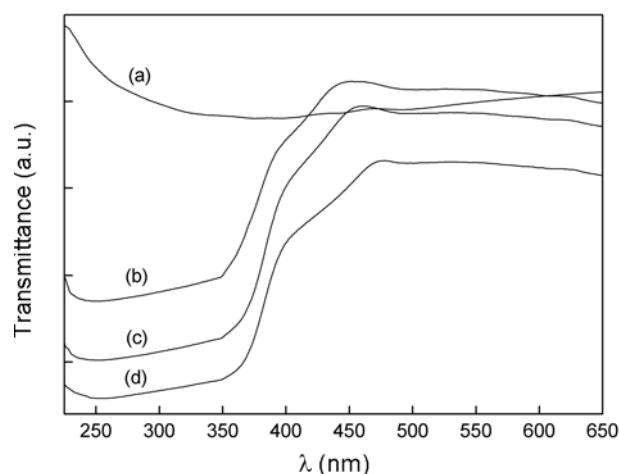


Figure 6. UV transmission spectra of (a) untreated cotton fiber, and ZnO assembled cotton fibers dipped in the synthesis solution for (b) one times, (c) two times and (d) three times respectively and treated under microwave power of 320 W for 15 min each times.

intensities of the UV transmittance peaks of the samples obtained under different microwave power. In Figure 6, the three curves of b-d have the same profile and the peak intensity. It can be concluded that the UV blocking properties of the samples do not increase by repeating the dipping and the microwave irradiation process. The results of UV blocking testing are admirably consistent with that of XRD analysis.

Washing Durability

The water-washing durability test of the ZnO assembled cotton fibers were carried out in a domestic washer (XQB45-846B National, Panasonic). Three samples of the treated cotton fibers with mass of 0.3 gram were carried in a small gauze pocket and washed for 20, 40, and 60 min in 33 l

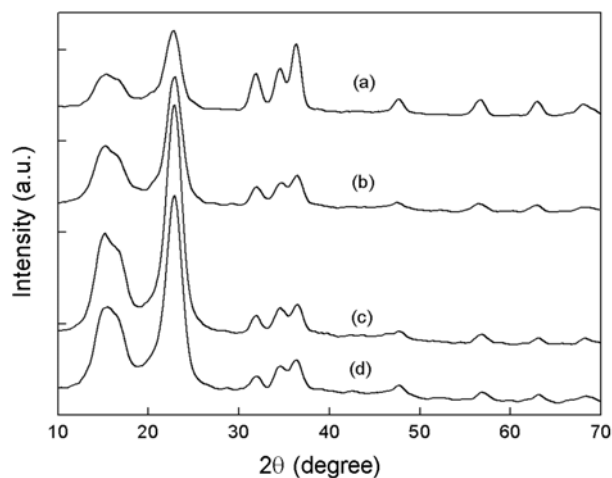


Figure 7. XRD patterns of the ZnO assembled cotton fibers after washing for (a) 0 min, (b) 20 min, (c) 40 min and (d) 60 min respectively.

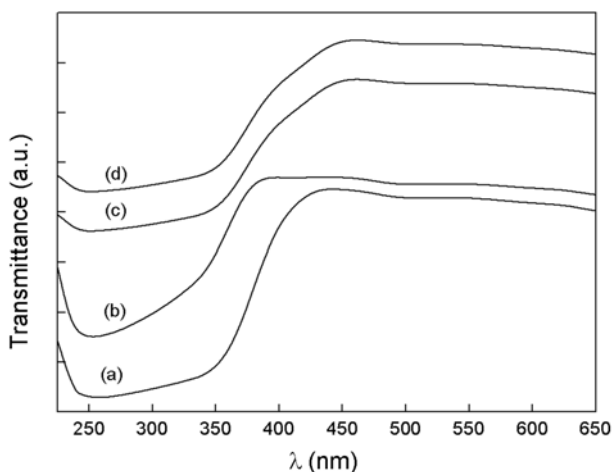


Figure 8. UV transmission spectra of the ZnO assembled cotton fibers after washing for (a) 0 min, (b) 20 min, (c) 40 min and (d) 60 min respectively.

water respectively. Then, the samples were characterized using XRD and UV transmission measurement. Figure 7 shows that ZnO crystallinity of the samples slightly decreases and the crystallinity of cotton cellulose obviously increases after washed for 20 min. Comparing between samples (b), (c) and (d), the peak intensity of wurzite ZnO inside of the treated cotton fibers has no changes after washed for 20, 40, and 60 min respectively. It can be concluded that ZnO nanoparticles are strongly bonded to the surface and the inner structure of cotton fibers. The crystallinity decreasing in the primary washing process is due to the slight abrasion of the nanoparticles located in the surface of cotton fibers. The crystallinity recovering of cotton cellulose may be due to OH^- into cotton structure again, which is lost during microwave treatment. Figure 8 shows that there are no obvious difference between the UV transmittance curves of the samples after washing for 0, 20, 40, and 60 min respectively, and all samples present an excellent UV blocking property. In this experiment, after washing for 60 min, the pocket used to load cotton fibers samples was torn, but the ZnO crystallinity of ZnO assembled cotton fibers still kept at high value as same as the former. It is confirmed that the ZnO assembled cotton fibers possess a very excellent washing durability. In general, the mechanical bond and physical joining do not guarantee the remarkable washing durability. We presume that ZnO nanoparticles and wax existing in cotton fibers can combine to achieve a firm composite layer in the surface and the inner of cotton fibers during microwave treatment, which may bring the good washing durability. The unclear interaction between ZnO nanoparticles and cotton fibers should be studied in detail.

Conclusion

Nano-ZnO assembled cotton fibers, with excellent UV

blocking property and good water-wash durability, has been successfully fabricated using microwave assisted precipitation and crystallization process synchronously in situ, using zinc nitrate hexahydrate and sodium hydroxide raw materials. The FESEM and XRD results show that wurzite ZnO with about 30-40 nm in diameter was formed in the lumen as well as in the mesoporous structures of the treated cotton fibers. The UV testing show the as-prepared samples have an excellent UV absorbing activity and a high washing durability. FTIR results revealed that there is no chemical bond between nano-ZnO and cotton fiber, mechanical force is the only way to bond nano-ZnO to cotton fibers in the experimental condition. Without any additionally nonfunctional reagents, wax existing in cotton fibers can be taken as the binder between nanoparticles and cotton fiber. ZnO nanoparticles and wax existing in cotton fibers can combine to achieve a firm composite layer in the surface and the inner of cotton fibers during microwave treatment, which may bring the good washing durability. The unclear interaction between ZnO nanoparticles and cotton fibers should be studied in detail.

Acknowledgements

The work was supported by the National Natural Science Foundation of China (Grant No. 51002183) and jointly supported by the National Natural Science Foundation of China and the Civil Aviation Administration of China (Grant No. 61079010). We are also grateful to the Research Fund of Civil Aviation University of China (No. 2011kys04).

References

1. R. Paul, L. Bautista, M. D. la Varga, J. M. Botet, E. Casals, V. Puentes, and F. Marsal, *Text. Res. J.*, **80**, 454 (2010).
2. C. H. Xue, R. L. Wang, J. Zhang, S. T. Jia, and L. Q. Tian, *Mater. Lett.*, **64**, 327 (2010).
3. R. H. Wang, J. H. Xin, X. M. Tao, and W. A. Daoud, *Chem. Phys. Lett.*, **398**, 250 (2004).
4. A. Yadav, V. Prasad, A. A. Kathe, S. Raj, D. Yadav, C. Sundaramoorthy, and N. Vigneshwaran, *Bull. Mater. Sci.*, **29**, 641 (2006).
5. N. Vigneshwaran, S. Kumar, A. A. Kathe, P. V. Varadarajan, and V. Prasad, *Nanotech*, **17**, 5087 (2006).
6. A. Becheri, M. Dürr, P. Lo Nostro, and P. Baglioni, *J. Nanoparticle Res.*, **10**, 679 (2008).
7. Z. P. Mao, Q. P. Shi, L. P. Zhang, and H. T. Cao, *Thin Solid Films*, **57**, 2681 (2009).
8. K. Qi, X. Chen, Y. Liu, J. H. Xin, C. L. Mak, and W. A. Daoud, *J. Mater. Chem.*, **17**, 3504 (2007).
9. K. Du, R. H. Wei, Q. D. Chen, J. H. You, and H. B. Yang, *Front Phys. China*, **4**, 505 (2009).
10. T. Krishnakumar, R. Jayaprakash, N. Pinna, V. N. Singh, B. R. Mehta, and A. R. Phani, *Mater. Lett.*, **63**, 242 (2009).

11. D. Sharma, S. Sharma, B. S. Kaith, J. Rajput, and M. Kaur, *Appl. Surf. Sci.*, **257**, 9661 (2011).
12. M. Marandi, G. Hajisalem, N. Taghavinia, and M. Houshiar, *J. Lumin.*, **131**, 721 (2011).
13. A. Kajbafvala, S. Zanganeh, E. Kajbafvala, H. R. Zargar, M. R. Bayati, and S. K. Sadrnezhad, *J. Alloy Comp.*, **497**, 325 (2010).
14. N. Kijima, M. Yoshinaga, J. Awaka, and J. Akimoto, *Solid State Ionics*, **192**, 293 (2011).
15. H. Lin, L. R. Yao, Y. Y. Chen, and H. Wang, *Fiber. Polym.*, **9**, 113 (2008).