# Trial-Manufacture and UV-Blocking Property of ZnO Nanorods on Cotton Fabrics

**Bi Xu, Zaisheng Cai**

*Key Laboratory of Science & Technology of Eco-Textile, Ministry of Education (Donghua University), College of Chemistry and Chemical Engineering, Donghua University, Shanghai, 201620*

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**ABSTRACT:** Oriented ZnO nanorod arrays were prepared on cotton fabrics via a simple two-step process. The ZnO nanocrystals were first synthesized and coated onto cotton substrates by dip-pad-cure process as nucleation seeds, followed by hydrothermal ZnO growth in aqueous solution of zinc nitrate hydrate and hexamethylenetetramine. Field-emission scanning electron microscope images showed the typical ZnO nanorods were 40–60 nm in diameter and 300–400 nm in length. Meanwhile, a few mesoscale ZnO nanorods with diameter of 150–200 nm, length of 600–800 nm, and their congeries were also observed on the cotton fabrics. X-ray diffraction result and Raman spectrum indicated the as-prepared nanorods were of high quality and defect free with hexagonal wurtzite ZnO structure. The as-obtained cotton sample was also characterized with energy dispersive spectroscopy and no impurities were detected. The ZnO nanorods grown on cotton fabrics possessed an ultrahigh ultraviolet protection factor of 379.14 in this study, indicating an excellent protection against ultraviolet radiation in comparison with the untreated cotton fabrics. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3781–3786, 2008

**Key words:** cotton; ZnO nanorods; UV-blocking; hydrothermal; nucleation seeds

## INTRODUCTION

Because of the decreased ozone content of the atmosphere, more ultraviolet (UV) radiation is present in the solar spectrum and causes health problems such as sunburn, allergies, and even skin cancer. Cotton, one of the most popular textile materials, is widely used in the world because of its outstanding properties such as soft, comfort, biodegradation, etc. However, Cotton fabrics offer, in particular, weak protection against UV light and the UV light can easily transmit through the materials with few being absorbed. Therefore, treating cotton fabrics so that they provide protection from UV radiation is an active field of development.

In recent years, one-dimensional (1D) ZnO has been of immense research interest worldwide because of its wide direct band gap of 3.37 eV and large exciton binding energy of 60 meV. As an important II–IV group semiconductor, 1D ZnO is rationally expected to be one of the most important electronic and photonic materials, and thus it is the promising candidate for application in many fields, such as solar cells,[1] UV-cutting materials,[2] catalysts,[3] sensors,[4] antimicrobial materials,[5] etc. Various physical, chemical and electrochemical deposition techniques have been explored to create 1D ZnO nanostructure materials. For instance, pulsed laser deposition,[6] sputter deposition technique,[7] thermal evaporation,[8] and chemical vapor deposition[9] have been successful in growing highly oriented arrays of ZnO nanorods or nanowires on ITO glass, sapphire, $Si/SiO_2$ wafers, etc. However, these methods are not suitable for cotton fabrics since they are operated under rigorous reaction conditions which would destroy the cotton mechanical properties such as feeling and strength.

In this work, a facile method for fabrication oriented ZnO nanorod arrays in aqueous solution on cotton fabrics at low temperature was presented. The cotton fabric was first coated with ZnO nanocrystals as nucleation seeds for the subsequent growth of nanorods in aqueous solution. No special expensive and precise equipments were required during the nanorod growth process. Therefore, it is possible to carry out a large-scale fabrication with a relatively low cost.

## EXPERIMENTAL

### Materials

Desized, scoured, bleached, and mercerized woven cotton fabrics were used as the substrates. All chemi-

*Correspondence to:* Z. Cai (zshcai@dhu.edu.cn).
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cals used in this study including zinc acetate dehydrate (≥99.0, AR), sodium hydroxide (≥96.0, AR), absolute ethanol (≥99.8, AR), zinc nitrate hexahydrate (≥99.0, AR), and hexamethylenetetramine (≥99.0, AR) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China).

### Preparation of ZnO nanocrystals

The ZnO nanocrystals were prepared based on the method of Pacholski[10] with some modifications. The detailed methods were as follows: zinc acetate dehydrate (0.05*M*) was dissolved in ethanol at 60°C under vigorous stirring. Then a solution of sodium hydroxide (0.15*M*) in ethanol was slowly added and stirred for 2 h at 60°C. The ZnO nanocrystals were thus obtained.

### Coating processes

The as-prepared ZnO nanocrystals were coated onto the cotton fabric sample by dip-pad-cure process. The cotton sample was dipped into the ZnO nanocrystal solution for 2 min and then padded with an automatic padder (Rapid Labortex Co., Taipei, Taiwan) with a nip pressure of 2.80 kg/cm$^2$. The padded substrate was air-dried for 15 min and then cured at 170°C for 10 min in a preheated oven to ensure ZnO nanocrystal particles adhere to its surface. This process was repeated three times to form a dense film of crystal seeds.

### Growth of ZnO nanorods

The cotton fabric coated with ZnO nanocrystals as aforementioned was immersed in an aqueous solution of zinc nitrate hexahydrate (0.03*M*) and hexamethylenetetramine (0.03*M*) at 90°C for 3 h with continuous oscillation by an atmosphere laboratory dyeing machine (Longling Electronic Co., Shanghai, China).[11] The cotton substrate was then taken out from solution, rinsed with deionized water, and dried at 70°C for 20 min.

### Instruments and characterization

The morphology of the nanorod arrays grown on cotton sample though the above procedures was observed by scanning electron microscope (SEM, JSM-5600LV, operating at 15 keV) and field-emission scanning electron microscope (FESEM, JSM-7401F, operating at 5 keV). The composition was determined by energy dispersive spectroscopy (EDS, Inca Oxford, attached to the SEM, operating at 20 keV). The structural characterization of the as-prepared nanorods was analyzed by X-ray diffraction (XRD, Rigaku D/max-rA) spectra with the Cu K$\alpha$ line of 1.54 Å. The room-temperature Raman spectrum was recorded on a Nicolet Nexus 670 FT-Raman spectrometer with the 1064 nm radiation from a Nd : YAG laser. The ultraviolet protection factor (UPF) of the sample was measured using UV-1000F ultraviolet transmission analyzer according to New Zealand Standard AS/NZS 4399 : 1996.

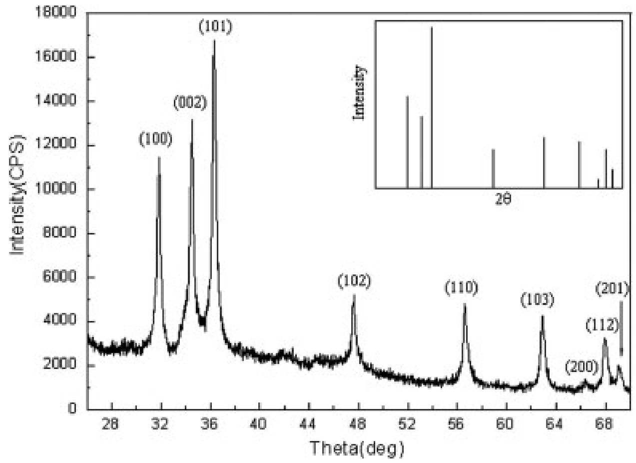


**Figure 1** XRD pattern of the nanorods grown on cotton fabric. The top right image is the standard XRD pattern of wurtzite ZnO.

## RESULTS AND DISCUSSION

Oriented ZnO nanorod arrays were grown on the cotton fiber surface through a two-step process, i.e., the preparation of ZnO nanocrystals and coating them onto the cotton fibers, subsequently hydrothermal ZnO growth in an aqueous solution of zinc nitrate hydrate and hexamethylenetetramine at 90°C for 3 h.

### XRD

Figure 1 shows the XRD pattern of the as-prepared products grown on cotton fabrics. All diffraction peaks are indexed as typical hexagonal wurtzite ZnO structure with lattice constants $a$ = 3.249 Å and $c$ = 5.206 Å (JCPDS 36-1451). No diffraction peaks from other impurity phases are found, confirming that the products are pure ZnO. Compared with the standard XRD pattern of wurtzite ZnO shown in the top right image of Figure 1, the (0 0 2) diffraction peak is remarkably enhanced, implying that the ZnO nanorod arrays are grown along the *c*-axis orientation.

### SEM and EDS

SEM photographs of the cotton samples before and after treatment are presented in Figure 2.

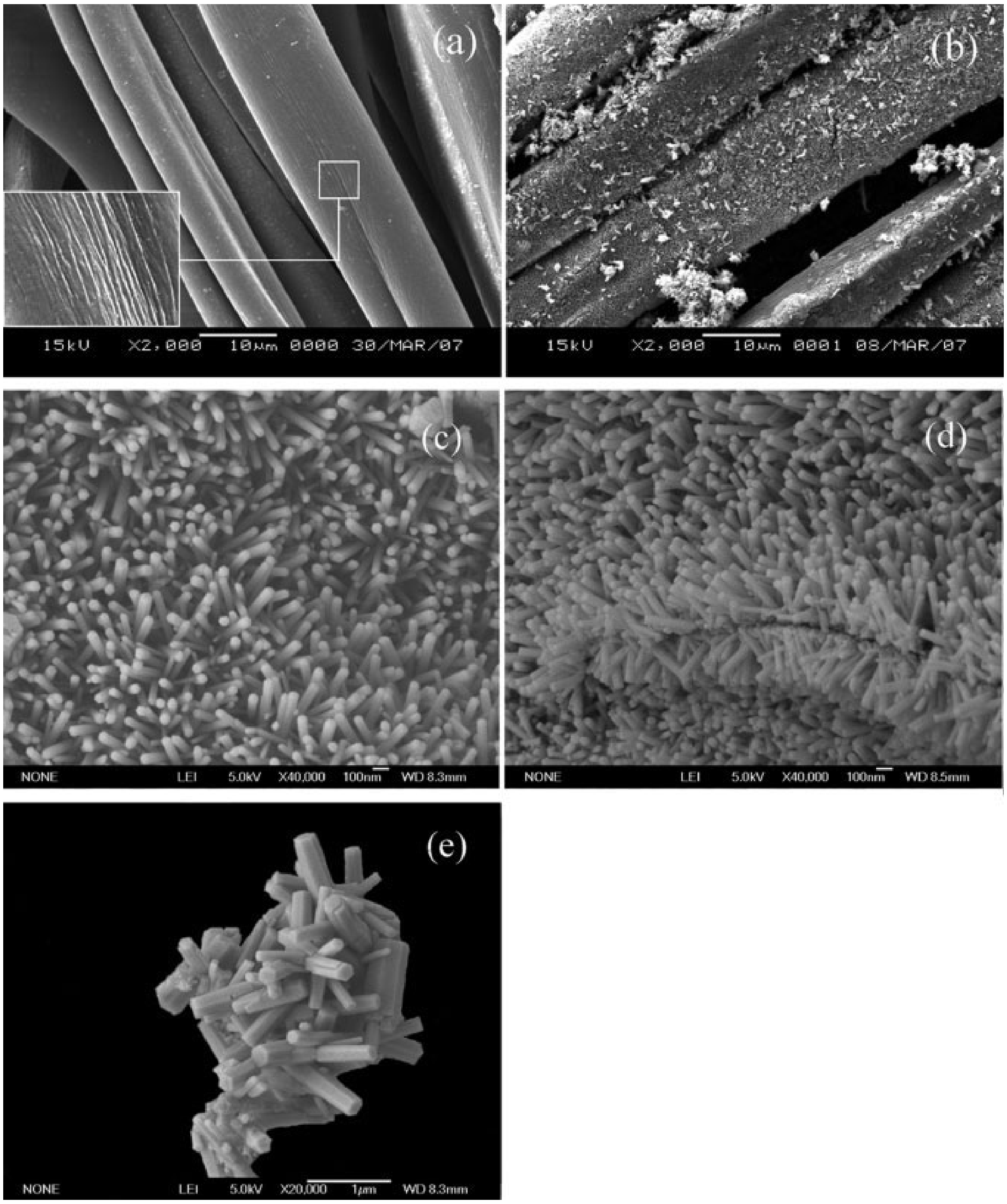


**Figure 2** SEM images of (a) untreated cotton fibers; (b) low magnification of treated cotton fibers; (c, d) large magnification of ZnO nanorod arrays grown on different part of single cotton fiber; (e) mesoscale nanorods synthesized between two adjacent cotton fibers.

The morphology of untreated cotton fibers is demonstrated in Figure 2(a). Besides the smooth surface, grooves and cracks can also be clearly observed on the untreated cotton fibers. The magnified SEM image of the grooves is shown in the lower left insert of Figure 2(a). The SEM images of ZnO nanorod arrays grown on cotton fabrics via the two-step process are shown in Figure 2(b–d). Figure 2(b) shows that oriented ZnO nanorods are densely and uniformly distributed over the entire cotton fibers. Meanwhile, a few mesoscale white nanorods and their congeries lying on the ZnO nanorod arrays and between adjacent cotton fibers can also be observed. Figure 2(c,d) are two FESEM pictures of nanorod arrays grown on different part of the cotton fiber in large magnification. Figure 2(c) is a top-view image of nanorod arrays grown on the smooth surface area of the cotton fiber while the nanorod arrays grown around the grooves are demonstrated in Figure 2(d). Both of Figure 2(c,d) shows the well faceted nanorods with a typical diameter of 40–60 nm and a length of 300–400 nm in given growth conditions.

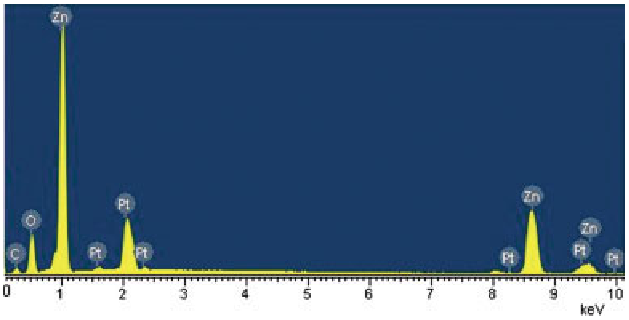


**Figure 3** EDS analysis of the ZnO nanorod arrays on cotton fabric. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Lots of experiments have revealed that the diameter and length of ZnO nanorods can be controlled by adjusting the reaction parameters such as the temperature, concentration, reaction time, and the ZnO seeds coated on the substrate.[12,13] A few mesoscale nanorods with the length of 600–800 nm, diameter of 150–200 nm and their congeries are also observed which is displayed in Figure 2(e). Well-faceted top and side surfaces with a hexagonal cross section can clearly be revealed in Figure 2(e). Figure 3 shows the chemical composition of the ZnO nanorods grown on the cotton fabrics determined by EDS. Only oxygen and zinc are detected except the background weak signals of platinum coating layer (Pt) and the carbon element coming from the cotton substrate. It is found that ZnO nanorods are nearly stoichiometric with little excess of Zn. This is in accordance with the XRD result and confirms that the nanorods are primarily ZnO.

## Raman spectrum

Raman scattering is an effective and nondestructive method to investigate the crystallization, structure, and defects in the nanostructure materials. With a wurtzite hexagonal structure, ZnO belongs to the space group C4 6v ($P6_3mc$), in which one primitive cell includes two formula units where all the atoms occupy the $C_{3v}$ symmetry. Group theory predicts the existence of the following optic modes: $A_1 + 2B_1 + E_1 + 2E_2$ at the Γ point of the Brillouin zone where $A_1$, $E_1$, and $E_2$ modes are Raman active while $B_1$ is forbidden.[14,15] Furthermore, the $A_1$ and $E_1$ are infrared active and split into longitudinal optical (LO) component and transverse optical (TO) component.[16]

**TABLE I**
**Raman Active Phonon Mode Frequencies (in $cm^{-1}$) for Bulk ZnO**

| $E_2$ (low) | $A_1$ (TO) | $E_1$ (TO) | $E_2$ (high) | $A_1$ (LO) | $E_1$ (LO) |
|---|---|---|---|---|---|
| 101 | 380 | 407 | 437 | 574 | 583 |

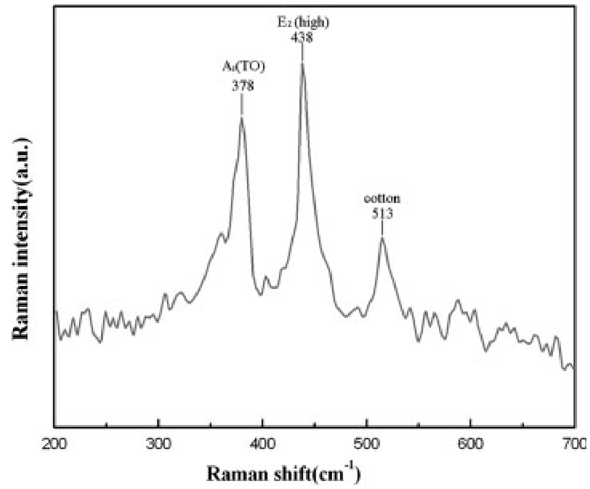


**Figure 4** Raman spectrum of ZnO nanorods on cotton fabric.

The frequencies of the Raman-active phonon modes reported previously for bulk ZnO are presented in Table I.[17]

Figure 4 demonstrates the Raman-scattering spectrum of the as-prepared ZnO nanorod arrays on cotton fabrics. In this Raman spectrum, three characteristic peaks are observed at 378, 438, and 513 $cm^{-1}$. The Raman band at 378 $cm^{-1}$ is attributed to $A_1$ (TO) mode. The sharp and strong peak at 438 $cm^{-1}$ is assigned to ZnO nonpolar optical phonons $E_2$ (high) mode. Raman band at 513 $cm^{-1}$ is originating from the cotton substrate. It is generally accepted that the $E_1$ (LO) is related to the formation of defects in ZnO.[18,19] Therefore, the presence of high intensity $E_2$ (high) mode with absence of $E_1$ (LO) peak in the Raman scattering further confirms that the synthesized ZnO nanorods are of high quality and defect free by this low-temperature aqueous solution route.

## Mechanism

In this study, ZnO nanorods were grown in aqueous solution of zinc nitrate and hexamethylenetetramine.[20] The main chemical process is supposed as:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_20 \rightarrow NH_4^+ + OH^- \quad (2)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

The formation of ZnO nanorod in this process is related to the anisotropy of the ZnO material. It is reported that polar {0 0 0 1} plane has roughly a 60% higher cleavage energy than the nonpolar {1 0 0

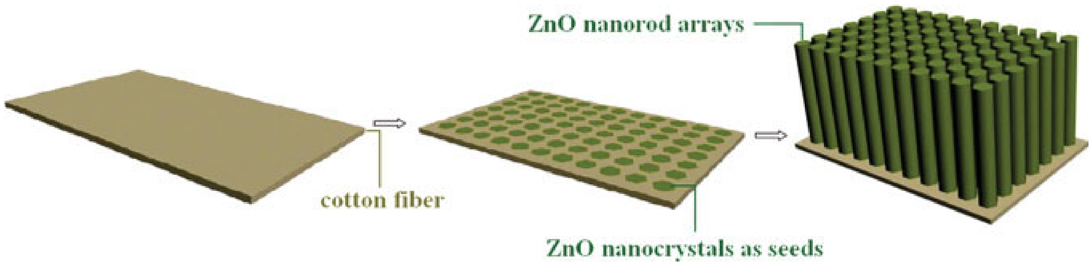


**Figure 5** Growth mechanism of ZnO nanorod arrays. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

0} plane.[21,22] The crystal planes which have higher surface energy possess faster growth velocity, and the crystal surfaces with faster growth velocity are easier to disappear while the surfaces with slower velocity will gradually dominate the morphology of the crystal. Therefore, the polar nature of positively or negatively charged ZnO surface and its anisotropic growth character result in the formation of the ZnO nanorod.[23] The undercoat of ZnO nanocrystals as nucleation seeds on the cotton fabric plays an important role in achieving high density of uniform ZnO nanorod arrays.[24] Two processes including nucleation and crystal growth are required for crystallization in a supersaturated solution. The interface energy between ZnO/substrate is usually smaller than that of ZnO/solution.[25,26] As a result, the nuclei tend to form on the substrate (heterogeneous nucleation) than in the solution (homogeneous nucleation) at a lower saturation ratio. On the one hand, introducing the seed layer can effectively lower interface energy between the crystal nuclei and the substrate and hence decrease the nucleation barrier.[27] On the other hand, the crystalline texture substrate is beneficial for the matching lattice between the ZnO seeds and cotton substrate.[28] So heterogeneous nucleation will take place preferentially on the ZnO seed surface, and well-aligned ZnO nanorod growth will be formed. Because of the flexible property of cotton fabrics, some of the nanorods deviated from vertical slightly. Figure 5 depicts the possible growth mechanism of ZnO nanorod arrays on cotton fabric. However, a few mesoscale ZnO nanorods and their congeries are observed and they are supposed to be formed through the homogeneous nucleation.[29,30]

## UPF

''Ultraviolet Protection Factor'' defined in Australian/New Zealand standard AS/NZS 4399: 1996 has now been widely adopted to characterize the ability of a fabric to block UV light. The UPF rating indicates how much UV radiation is absorbed by the fabric. For example a fabric with a UPF rating of 50 only allows 1/50th of the hazardous UV radiation falling on the surface of the fabric to pass through it, the fabric blocks 98% of the sun's harmful UV rays. The UPF rating of less than 15, between 15 and 50, and more than 50 (50+) are generally classified as bad, good, and excellent UV-blocking properties for fabrics, respectively. The cotton fabric with a UPF value less than 15 is generally not adequate to provide sufficient protection against UV radiation for outdoor activities. UV protective clothing with a greater UPF should be developed to provide high levels of UV protection in a variety of conditions. ZnO is one of the most important semiconductors and the as-prepared ZnO nanorod arrays on the cotton fabrics can absorb light with energy of $h\nu$ that matches or exceeds their band gap energy ($E_g$) which lies in the UV range of the solar spectrum. Meanwhile, ZnO is very efficient at scattering UV radiation. UV light absorption and light scattering of the ZnO nanorod arrays contribute to excellent UV-shielding property. The UPF values of cotton fabrics were directly measured using UV-1000F ultraviolet transmission analyzer in this study. Figure 6 displays the transmittance spectra of the two cotton fabric samples and their corresponding UPF values. The

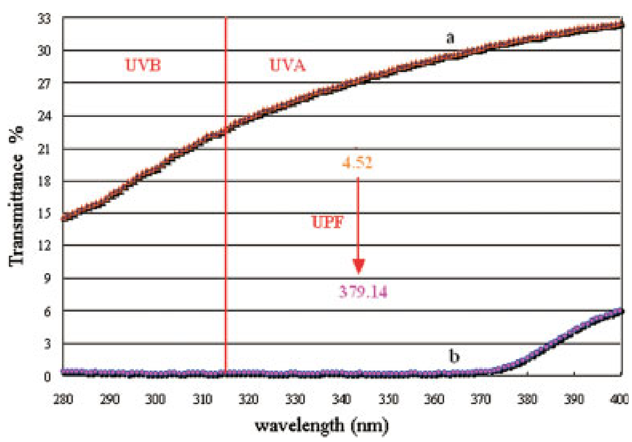


**Figure 6** Transmittance spectra of (a) untreated cotton fabric sample; (b) cotton fabric with ZnO nanorods grown onto it via a two-step process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

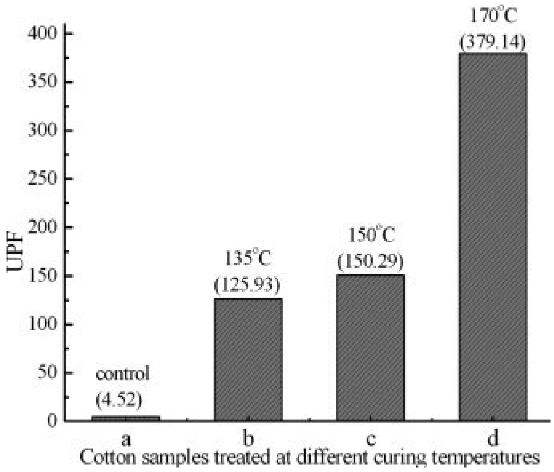


**Figure 7** The UPF value of (a) original cotton fabric sample; (b–d) cotton fabrics cured at 135, 150, and 170°C, respectively.

transmittance of the treated fabric decreases drastically compared with the untreated cotton fabric and almost no UV light transmits through the fabrics in the region of 280–374 nm. The untreated fabric shows a weak protection against UV radiation because of its low UPF value of 4.52 while the treated fabric reveals an ultrahigh UPF value of 379.14 and this high UPF results in an excellent protection against UV radiation in comparison with the untreated cotton fabrics. Curing temperature in the coating process plays an important role in preparing UV-blocking cotton fabrics. Different curing temperatures (135, 150, 170°C) were chosen to investigate the effects on UV-shielding property and the corresponding UPF values of the cotton fabrics treated at different curing temperatures were shown in Figure 7. It is obvious that UPF value of cotton sample (d) treated at 170°C is much higher than the others. Great UPF increment is obtained while improving the curing temperature from130 or 150 to 170°C. This phenomenon may be simply explained as follows: the higher curing temperature, the more ZnO and better ZnO crystallization produced, which is beneficial for the following ZnO nanorod growth. High curing temperature would affect the cotton property to some extent and more research work is being done in our group to eliminate or minimize the harmful effect on cotton fabrics.

## CONCLUSIONS

In summary, oriented hexagonal ZnO nanorod arrays were grown on cotton fibers via a simple two-step process at low temperature. The typical nanorods prepared are 40–60 nm in diameter and 300–400 nm in length. Meanwhile, a few mesoscale ZnO nanorods with diameter of 150–200 nm, length of 600–800 nm, and their congeries are also observed on the cotton fabrics. The nanorods grown on cotton fabrics with an ultrahigh UPF of 379.14 in this study provide an excellent UV protection against UV radiation, which are desirable for use in multiple fields such as functional material devices, composites, and optoelectronic industries in the future.

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