Multifunctional cotton fabric loaded with Ce doped ZnO nanorods

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Abstract

Ce doped ZnO (Ce-ZnO) nano materials with different Ce molar content were prepared via chemical precipitation method. The morphology of Ce-ZnO was rod like and the size was decreased with the increase of doping amount, and the size of Ce-ZnO was 180 nm in length and 40 nm in diameter when the doping amount is 2.5%. All the samples were treated on cotton fabric, the laden fabric has excellent performance on hydrophobicity, UV resistance and antibacterial activity. The contact angle of fabric loaded with ZnO was 103°, and fabric with 2.5% Ce-ZnO was 148°. The fabric loaded with Ce-ZnO has superior performance of UV resistance. With the increase of doping amount, the antibacterial rates were promoted and then reduced, the antibacterial rates against *S. aureus* and *C. albicans* of fabric with 2.5% Ce-ZnO were promoted to 83% and 85%, however, the antibacterial activity against *E. coli* was reduced to 78%.

Key words: Ce doped ZnO; multifunction; cotton fabric; nano ZnO

1. Introduction

The cotton fabric was widely used in clothing and other articles of daily use due to its softness and comfort, but it also has some poor performance such as proneness to bacteria, susceptibility to UV, hydrophile, etc. As the improvement of living standards and the concept of health, more and more researchers followed with the interests in the multifunctional cotton [1, 2, 3].

Zinc oxide has been known as an important semiconducting material with energy band gap of 3.3 eV, and larger exaction binding energy of 60 meV. Nano ZnO has been widely used in ultraviolet resistance, photo-catalytic degradation, photoelectric materials and energy saving materials [4, 5, 6]. The unique antibacterial function of nano ZnO has also attracted great interest. Nano ZnO is considered as a kind of antibacterial material which is of low toxicity and environmental [7, 8]. It has excellent antibacterial activity against gram positive bacteria and gram negative bacteria. Zinc oxide is one of the typical photo-catalytic antibacterial agents. Under the light condition, the valence band electrons activated to the conduction band, and produced electron (e^-) and electron holes (h^+), these groups exposure to environment and generated $\cdot O^{2-}$, $\cdot OH$ and H_2O_2 , etc. These strong reactive substances reacted with most organic

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composition of bacterial cells to affect the bacterial activity [9]. Therefore zinc oxide was often used to endow textile with good antibacterial properties. Perelshtein et al. used the ultrasound Irradiation method to deposit ZnO nano particles on cotton fabrics, which can serve with potential for antibacterial applications [10]. Gao et al. prepared P(DMDAAC-AGE-MAA)/nano-ZnO composite via free radical polymerization, and the synthesized composite was treated on cotton fibers. The treated fabric has an excellent antibacterial activity to bacteria and fungus [11, 12, 13].

The excitation light of ZnO was in ultraviolet region, which means the low utilization of daylight. Moreover, the electron-hole pair has a high recombination rate due to the charge attraction, and all these would reduce the photo-catalytic antibacterial performance of ZnO. A number of strategies have been adopted to improve the charge separation efficiency and then enhance the photo-catalytic activity such as the semiconductor doping [14].

Doping is an important and effective way to improve the properties of ZnO. Doping with selective elements offers an effective method to adjust the optical, electrical and magnetic properties of ZnO, which is critical for its practical applications [15, 16, 17]. Rare earth elements

became the interests of photoelectric material, electro-magnetic material, etc. There were a lot of researches on enhanced photo-catalytic performance by rare earth doped ZnO [18, 19, 20]. Doping has brought into the virtual band gap, changed the energy structure of semiconductor material, which expand absorption range and improve the utilization of light. On the other hand, rare earth ions have unique electronic structure, and then it can be used as scavenger for photo generated electrons, promoting interfacial electron-hole separation in the photo-catalytic process [21], hence increasing the number of photo charges and improving the photo-catalytic antibacterial activity.

Ce is the most abundant rare earth element in the earth crust. There has been lots of research on its properties due to the fact that it is cheaper, low toxic and environment friendly. Up to know, Ce doped ZnO is used for different applications such as photo-catalytic degradation and luminescent materials [22]. In this work, Ce doped ZnO nano powder has been prepared through simple chemical precipitation method. The different molar percentages of Ce doped ZnO was finished on the cotton fabric. The as-synthesized products were characterized by UV-Visible spectroscopy (UV), X-ray diffraction (XRD) and scanning electron microscope (SEM). The morphology of the cotton fabrics has been observed by SEM. The antibacterial property, UV resistance performance, hydrophobic property of fabric have been investigated.

2. Experimental

2.1. Materials

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, AR, Tianjin Kermel Chemical Reagent Co. Ltd., China), Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.5% metals basis, Aladdin), Sodium hydroxide (NaOH, AR, Tianjin Hongyan Reagent Plant, China), Ethanol (AR, Tianjin Hongyan Reagent Plant, China) were all used without further purification. The bacterium *Escherichia coli* (E. coli, ATCC25922), *Staphylococcus aureus* (S. aureus, ATCC25923), and the fungi *Candida albicans* (C. albicans, ATCC10231) were provided by Xi'an Microorganism Research Institution and incubated at 37 °C on a nutrient agar plate for 24 h before use. All the water used in process was distilled water.

2.2. Preparation of Ce-ZnO nanorods

7.32 g Zinc acetate dehydrate and Cerium nitrate hexahydrate were dissolved into distilled water (Ce /Zn ratios: 0%, 1%, 1.5%, 2%, 2.5%, 3%). 9.33 g sodium hydroxide was dissolved into distilled water to form sodium solution. In the condition of 80°C, the $\text{Zn}(\text{AC})_2$ solution and sodium solution were mixed and stirred for 3 h. Then the Cerium nitrate hexahydrate solution was added and kept stirring for 2 h. The solution then was kept at 90°C for 3 h. The prepared sample was washed by distilled water and ethanol two times through centrifugation respectively. Finally, the light yellow colored powder was obtained after drying. The pure ZnO and CeO_2 were also prepared using this method.

2.3. Characterization of Ce-ZnO nanorods

The crystal structure of Ce-ZnO nano powders was determined by powder X-ray diffraction. The Ce doped ZnO and undoped ZnO powder were subjected to X-ray diffraction (XRD) with a Bruker D8 Advance $\text{CuK}\alpha_1=1.5405 \text{ \AA}$ at room temperature. SEM technique was used to observe the particle sizes, and rough morphology of the particles. The surface morphology of the samples was studied using a scanning electron microscope. The UV-Visible absorption of Ce-ZnO was determined by 61 CRT Spectrophotometer (Shanghai Instrument Factory, China) in the wavelength ranges from 190 to 850 nm using 1 cm quartz cuvettes at room temperature.

2.4. Applied to Cotton Fabric

Cotton knitted fabrics (35 cm × 35 cm) were treated with Ce doped ZnO and undoped ZnO separately. The procedure was simple and shown in Fig 1. The nano materials was dispersed in distilled water, and the samples were immersed in the 30 g/L Ce-ZnO solution or ZnO solution for padding and dried at 95 °C for 5 min in a preheated oven to remove the moisture, and then baked at 125 °C for 10 min. The solution containing no ZnO and Ce-ZnO materials was prepared as a control group.

Fig 1. Schematic diagram of loading cotton fabric with Ce-ZnO nanorods

2.5. Characterization of cotton fabric loaded with Ce-ZnO nanoparticles

2.5.1. Hydrophobic property

The hydrophobic property of the fabric was judged by the contact angle with water. Contact angles (CAs) were measured with 8 μ L deionized water dripping on Data physics OCA 20 (Data physics, Germany) instrument at room temperature. The contact angles were determined by averaging values of 5-6 different points on each sample surface.

2.5.2. UV resistance property

The UV resistance property of the cotton fabric was measured by the transmittance. The UV-Visible transmittance spectrum of the cotton fabric was carried out by 61 CRT Spectrophotometer (Shanghai Instrument Factory, China) in the wavelength ranges from 200 to 400 nm at room temperature.

2.5.3. Antibacterial property

The antibacterial activity of the treated fabric was tested against the bacteria *S. aureus*, *E. coli* and the fungi *C. albicans* according to the FZ/T 73023-2006 standard method. The percent reductions of bacteria as the antibacterial rate were calculated according to the following equation:

$$R = (B - A) / B \quad (1)$$

where R is the antibacterial rate (%); A is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over the desired contact period; B is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar immediately after inoculation (at "0" contact time).

3. Results and discussion

3.1. Characterization of Ce-ZnO nanorods

3.1.1. X-ray diffraction (XRD) analysis

Fig 2. XRD pattern of ZnO and Ce doped ZnO

The crystal structure of ZnO and Ce doped ZnO has been studied by XRD. As shown in Fig 2, all the peaks in the pattern can be indexed to the wurtzite phase of ZnO with a hexagonal structure [23, 24]. The figure of Ce-ZnO has no new peak that is related to Cerium, which indicated that the Ce doped into the lattice of ZnO and the Ce^{3+} ions were substituted in the place of Zn^{2+} position [25]. The low angle XRD pattern is shown in Fig 2 b. The XRD pattern of the Ce-ZnO catalyst showed that the 2θ values of (100), (002), and (101) peaks are slightly shifted to higher diffraction angles. This movement of angles indicated the successful incorporation of Ce doped in ZnO lattice [26, 27].

The average crystallite size of the synthesized catalysts has been calculated using Scherrer equation $D = K \lambda / (\beta \cos \theta)$, where D is the crystallite size, K is the shape factor of value 0.943, λ is the X-ray wavelength (0.1541 nm), β is the half-width of the full maximum (HWHM) and θ is the

angle value^[28, 29]. The results were presented in Table 1. It turned out that, with the increase of the doping amount, the crystallite size was decreased gradually, Ce doped into the lattice of ZnO and the formation of new bond between Ce and Zn inhibited the growth of crystal^[30].

Table 1. Crystallite size and band gap energy of ZnO and Ce doped ZnO

Sample	2 θ value (°)	FWHM (°)	Average crystal size (nm)	E _g (eV)
ZnO	36.280	0.328	25.401	3.346
1% Ce doped ZnO	36.400	0.347	24.019	3.342
1.5% Ce doped ZnO	36.340	0.349	23.869	3.333
2% Ce doped ZnO	36.335	0.350	23.783	3.324
2.5% Ce doped ZnO	36.281	0.352	23.667	3.315
3% Ce doped ZnO	36.280	0.330	25.228	3.272

3.1.2. Morphology of Ce-ZnO nanorods

Fig 3. SEM image of ZnO and Ce doped ZnO (a ZnO; b 1% Ce-ZnO; c 1.5% Ce-ZnO; d 2% Ce-ZnO; e 2.5% Ce-ZnO; f 3% Ce-ZnO)

The morphology of undoped and Ce doped ZnO nanoparticles was studied by SEM and shown in Fig 3. All the samples were rod like. With low Ce percentages from 1% to 2.5%, the particle size was gradually reduced with the increase of Ce content. The obtained result was in accordance with the XRD analysis. When the doping amount was 3%, the size of the nano ZnO was significantly increased. ZnO nanorods was about 400nm in length and 60 nm in diameter, and the particle size of 2.5% Ce doped ZnO was 180nm in length and 40 nm in diameter. The aspect ratio was reduced from 20:3 to 9:2, which indicated that the interaction between Zn and Ce inhibited the growth of ZnO^[31].

3.1.3. UV-vis absorption spectrum analysis

Fig 4. UV-vis absorption spectrum of synthesized ZnO and Ce doped ZnO

Figure 4 shows the UV-vis absorption spectrum of ZnO and Ce doped ZnO recorded in the 190-850 nm wavelength range. All the spectra showed the typical broad absorption of ZnO^[32]. The shift in the absorption peaks lightly towards higher wavelength was observed after Ce doping.

Moreover, there was no significant peak observed in the spectrum of ZnO, but it detected a significant absorption at 199 nm with Ce doping. The UV absorption edge was red-shifted with Ce doping, indicating a reduction in the band gap, which was also reported by others researchers [33]. However, when the content of Ce was 3%, there was a new broad absorption appeared at 320nm, which was related to CeO₂[34].

The band gap of the synthesized samples was calculated according to the equation: $E_g \text{ (eV)} = hc/\lambda_g(1.6 \times 10^{-19})$, in which h is the Planck's constant of $6.63 \times 10^{-34} \text{ J}\cdot\text{s}$, c the speed of light ($3 \times 10^8 \text{ m s}^{-1}$) and λ_g is the wavelength (m)[35, 36], and reported in Table 1. It showed that the band gap gradually decreased with the increase of Ce doping amount and the change in the band gap values must be slightly influenced by the bond of Zn and Ce[37]. The results of UV-vis indicated that Ce doping can enhance the UV absorption of ZnO.

3.2. Performance of Cotton Fabric Loaded with Ce-ZnO Nanorods

3.2.1. Morphology of the cotton fabric

Fig 5. SEM image of cotton fabric finished with ZnO and Ce doped ZnO (a b cotton fabric; c d cotton fabric finished with ZnO; e f cotton fabric finished with 2.5% Ce-ZnO)

The morphology of cotton fabric loaded with ZnO and 2.5% Ce doped ZnO was studied by SEM and shown in Fig 5. As shown in Fig a and b, the surface of cotton fabric was smooth without any particles. After loaded with ZnO and Ce doped ZnO, the surface of cotton fabric was rough. ZnO and Ce doped ZnO were densely and uniformly distributed over the cotton fibers. Under the same concentrations, the Ce doped ZnO loaded more on the cotton fabric (Fig 5 e) compare with undoped ZnO (Fig 5 c), and the Ce doped ZnO can be observed clearly inside the cotton fabric (Fig 5 f). The SEM and XRD of ZnO and Ce-ZnO showed that the size of nano ZnO rods has reduced after doping. Therefore Ce doped ZnO with a smaller size was easier to gather and load, even reaching deeper parts of the fiber.

3.2.2. Hydrophobic property of cotton fabric

Fig 6. Contact angle with water of cotton fabric loaded with ZnO and Ce doped ZnO

Figure 6 shows the contact angle with water of cotton fabric load with ZnO and Ce doped ZnO. The surface is considered as hydrophobic when the contact angle is greater than 90°[38]. Cotton fabric possesses excellent hydrophobicity. From Fig 6 it can be clearly seen that all the

fabric treated with ZnO or Ce doped ZnO was hydrophobic. The contact angle of fabric coated with ZnO was 103°, and the contact angle of fabric loaded with 1% Ce-ZnO was 107°. With the doping amount increased, the contact angle increased significantly, and it reach to 148° when Ce content was 2.5%. However when the Ce mole percent was 3%, the contact angle decreased to 118°, but the cotton fabric still has good hydrophobic property.

3.2.3. UV and visible light absorption

Fig 7. UV-vis spectrum of cotton fabric finished with ZnO and Ce doped ZnO

The UV resistance of cotton fabric was researched by UV-vis spectrum and showed in Fig 7. Apparently, the pristine cotton fabric does not display the property of ultraviolet resistance, whose transmittance was above 83% [39] and the UV transmittance of fabric coated with ZnO and Ce doped ZnO was reduced evidently. Both ZnO and Ce doped ZnO given cotton fabric an excellent UV resistance. The fabric loaded with Ce doped ZnO has a lower UV transmittance than the fabric loaded with undoped ZnO. With the increase of the doping amount, the ultraviolet transmission of cotton fabric reduced, and the minimum reached to 30% when the doping amount was 2.5%. When the doping amount was 3%, the transmission of fabric was increased because the particle size of Ce doped ZnO has increased which can be observed in SEM.

3.2.4. Antimicrobial property

Fig 8. Antibacterial activities of the fabric treated with ZnO and Ce doped ZnO

ZnO was considered as an efficient antibacterial agent against both Gram-negative and Gram-positive bacteria. The antibacterial activities of the cotton fabric treated with ZnO and Ce doped ZnO were evaluated against *S. aureus*, which stand for Gram-positive bacteria, the *E. coli* was representative of Gram-negative bacteria and *C. albicans* was stand for Fungus.

Figure 8 showed the antibacterial activities of the cotton fabric treated with ZnO and Ce doped ZnO. The antibacterial rates of fabric laden with ZnO against *S. aureus* and *C. albicans* were 74% and 70%. The antibacterial activities of cotton fabric with Ce doped ZnO were more effective against *S. aureus* and *C. albicans*, and the antibacterial activities are increased and then decreased with the doping amount increasing. The fabric loaded with 2.5% Ce-ZnO has a superior antibacterial activity against *S. aureus* and *C. albicans*, and the antibacterial rates were reaching to 83% and 85%. Combining the SEM results, we know that the size of Ce-ZnO reduced after doping, and the smaller sized nanoparticles could enhance the dissolve activity of Zn^{2+} ions [40]. Thus fabric treated with Ce doped ZnO has a better antibacterial performance. Ce was also considered as a scavenger to capture electrons, and then reduced the recombination rate of

electron-hole pair to generate more reactive oxygen species, such as H_2O_2 , $\cdot\text{O}_2^-$, and $\cdot\text{OH}$, which are toxic to the cells as they damage cellular constituents, then improved the photo-catalytic antibacterial activity of ZnO [41]. Moreover compare to the ZnO, doping with Ce has improved the absorption rate of light thereby enhanced the photo-catalytic antibacterial performance of ZnO [42].

Although the impact tendency of doping amount to antibacterial rate against *E. coli* was same with the other two bacterial, the all antibacterial rate against *E. coli* was reduced after Ce doping compared with the antibacterial rate against other two bacterial. The best antibacterial rate of fabric with 2.5% Ce doped ZnO against to *E. coli* is 78%, which was decreased compared to the fabric laden with ZnO (83%), and similar results were reported by other researchers who attributed the change to the different structures of *E. coli*. [43]

4. Conclusions

ZnO and different molar percentages of Ce doped ZnO were synthesized by simple chemical precipitation method. The synthesized nanoparticles were characterized by XRD, UV-Visible spectroscopy and SEM. The average crystallite size was decreased after doping, the absorption peaks of Ce-ZnO was slightly shifted towards higher wavelength. All the samples were rod like and Ce-ZnO has a smaller size compared to pure ZnO. All the samples were loaded on the cotton fabric, ZnO or Ce-ZnO endows the cotton fabric with excellent hydrophobic property, UV resistance and broad spectrum antibacterial activities against Gram positive, Gram negative bacteria and fungus. The fabric treated with Ce-ZnO has a better performance than the fabric loaded with ZnO in the hydrophobic and UV resistance. Compared with the fabric loaded with ZnO, the fabric finished with Ce-ZnO has more effective antibacterial activity against *S. aureus* and *C. albicans*, and the antibacterial rates of fabric treated with 2.5% Ce-ZnO were reaching to 83% and 85%. But fabric treated with Ce-ZnO has a lower activity against to *E. coli*.

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