

Preparation of cellulose-ZnO hybrid films by a wet chemical method and their characterization

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Abstract Zinc oxide (ZnO) nanoparticles were immobilized on the surface of regenerated cellulose films by a wet chemical method in which the controlled hydrolysis of a Zn(II)-amine complex leads to the formation of ZnO nanoparticles. Cellulose-ZnO materials were characterized by spectral, thermal and optical methods. Scanning electron microscope and atomic force microscope analyses confirmed the formation of ZnO nanoparticles on the surface of the regenerated cellulose film and X-ray diffraction patterns showed the ZnO had the wurtzite structure. The reported method is very simple, and can immobilize the nanoparticles without the aid of a binder or dendritic side group and without high temperature treatments like calcination. ZnO immobilized on biopolymers like cellulose has many potential applications such as strain sensors, biomedical sensors, flexible display devices and optoelectronics.

Keywords Regenerated cellulose · Zinc oxide · Hybrid material · Wet chemical method

Introduction

Cellulose is the most abundant and widespread biopolymer. Owing to its abundance, biodegradability and specific properties cellulose is a very important renewable resource for the development of environmentally friendly, biocompatible and functional materials apart from its traditional and massive use in papermaking and cotton textiles. Cellulose has been extensively used in the fields of membrane separation, pharmaceuticals, cosmetics and the food industry (Klemm et al. 2005). In recent times, applications of cellulose based materials in electronics such as actuators, transistors and energy storage devices have also been reported (Pushparaj et al. 2007; Kim et al. 2006).

On the other hand zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor having a high electron-hole binding energy (60 meV) and important applications in electronics, optics, optoelectronics, lasers, and light-emitting diodes. The piezoelectric and pyroelectric properties of ZnO make it a great candidate for sensors, transducers, energy generators, and photocatalysts for hydrogen production. ZnO is also a “green” material that is biocompatible, biodegradable, and nontoxic for medical applications and environmental science. Nanoscale coating of ZnO on suitable substrates is also important for potential applications for sensors, optical communications, photocatalysts, flexible transistors and solar cells. Moreover, cellulose containing metal or

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semiconductor nanocomposites have been recognized as a very promising material in the field of electronics and catalysis. Recently, metal and semiconductor nanoparticles attached onto the cellulose fibres have been the subject of interest. There are few reports concerning the controlled growth of ZnO particles at the surfaces of cellulosic fibres (Mumalo-Djokic et al. 2008; Goncalves et al. 2009). Cellulose films coated with ZnO nanoparticles constitute an important material for practical applications ranging from the film and paint industry to the technologically appealing area of optoelectronic paper. ZnO nanoparticle coated paper has been prepared by ultrasound assisted coating and antibacterial activity of that material was observed (Ghule et al. 2006).

In this report, we demonstrate the growth of ZnO nanoparticles on the regenerated cellulose films by a wet chemical method, i.e., controlled hydrolysis of Zn(II)-amine complexes. Presence of the hydrophilic groups on the regenerated cellulose can promote the nucleation and growth of the ZnO nanoparticles. Cellulose-ZnO hybrid materials are characterized by spectral, thermal and optical methods and a plausible mechanism for the formation of cellulose-ZnO hybrid films is also discussed.

Experimental

Materials

Cotton cellulose (MVE, DPw 7450) was purchased from Buckeye Technologies Co., USA. Lithium chloride (LiCl; extra pure) was purchased from Junsei Chemical, Japan. Molecular sieves (4 Å, 4–8 meshes) were from Acros Organics, New Jersey, USA. N, N-dimethylacetamide (DMAC) (anhydrous, 99.8%), zinc nitrate and triethanolamine were purchased from Sigma–Aldrich, USA. Anhydrous DMAC was carefully dried with molecular sieves for a week before use.

Preparation of regenerated wet cellulose films

Cotton pulp with a degree of polymerization (DP), 4500, was torn into small pieces. To evaporate absorbed water, the cotton pulp and LiCl (Junsei Chemical) were dried in an oven at 100 °C. The cotton pulp was mixed with LiCl/anhydrous DMAC in

proportion to cotton cellulose pulp/LiCl/DMAC as 2/8/90 by mass. The cellulose was dissolved in the solvent system by heating at 155 °C with mechanical stirring followed by solvent exchange (El Seoud et al. 2000). Cellulose wet films were cast on glass substrates using a doctor blade and the films were treated with a 50:50 (v/v) mixture of isopropyl alcohol and deionized water to obtain freestanding regenerated wet cellulose films. For the comparative study wet films were stretched mechanically and dried under a near infrared lamp. This cellulose film will be mentioned as “pristine cellulose” in this paper.

Preparation of cellulose-ZnO hybrid materials

ZnO particles were allowed to grow on the wet cellulose films and then wet cellulose-ZnO hybrid films were stretched (to avoid wrinkles during the drying process) and dried under a near infrared lamp. For the ZnO crystal growth on the cellulose film, 0.005 mol of zinc nitrate is dissolved into 500 mL of deionized water, followed by the dissolution of triethanolamine (TEA) with the same molar ratio (Goncalves et al. 2009). To this solution, wet cellulose films (8 × 8 cm) were added and the reaction was maintained at 90 °C for a period of 6 h with constant magnetic stirring. After 6 h the cellulose-ZnO hybrid material was removed and washed with deionized water and the crystal growth process was repeated with fresh chemicals. Then the wet cellulose-ZnO hybrid materials were stretched mechanically and dried under the near infrared lamp.

Characterization

DMAC regenerated cellulose and cellulose-ZnO hybrid films were analyzed by UV-visible spectroscopy, photoluminescence spectroscopy (PL), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDS) and atomic force microscopy (AFM). UV-Visible spectra of the films were recorded with a Hewlett Packard (8452A) diode array spectrophotometer. XRD was recorded on an X-ray diffractometer (D/MAX-2500, Rigaku), by using Cu K α radiation at 40 kV and 30 mA. TGA was analyzed by using a STA 409 PC/NETZSCH, and analysis was carried out under inert gas (argon) and the samples were heated at a rate of 10 °C/min.

SEM images of the films were taken with a scanning electron microscope (Hitachi S-4200, Japan) to study the morphological difference of the films. AFM images were taken with a DimensionTM 3100 atomic force microscope (Digital Instruments).

Results and discussion

Flexible cellulose-ZnO hybrid films were prepared by a simple and effective wet chemical process. In this method we found crystal growth on both sides of the cellulose film as well as inside the cellulose film. This chemical process involves the alkaline hydrolysis of Zn(II), in which the regenerated cellulose wet film acts as a hydrophilic substrate for the heterogeneous nucleation of ZnO. Figure 1 shows a photograph of cellulose-ZnO hybrid material, which shows crystal growth of ZnO on the surface of regenerated cellulose film. Cellulose-ZnO hybrid films are very flexible. Obtained cellulose-ZnO hybrid films were characterized by spectral, thermal and optical methods.

UV analysis and PL spectra of cellulose-ZnO hybrid material

An UV-visible spectrum of a cellulose-ZnO hybrid film was recorded (Fig. 2). An absorption band at 350 nm confirms the formation of ZnO particles on the regenerated cellulose film. A PL spectrum

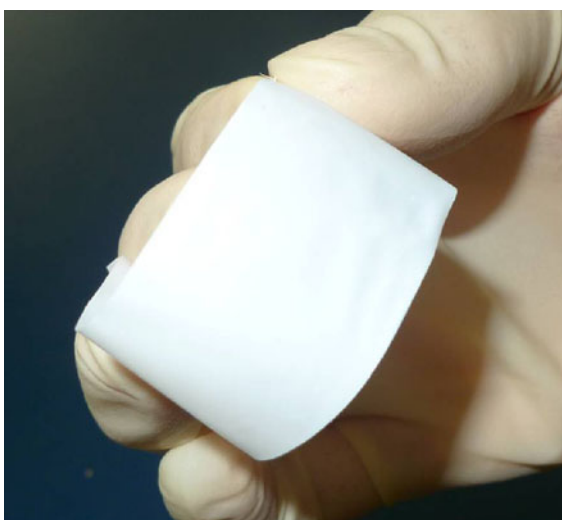


Fig. 1 A cellulose-ZnO hybrid film

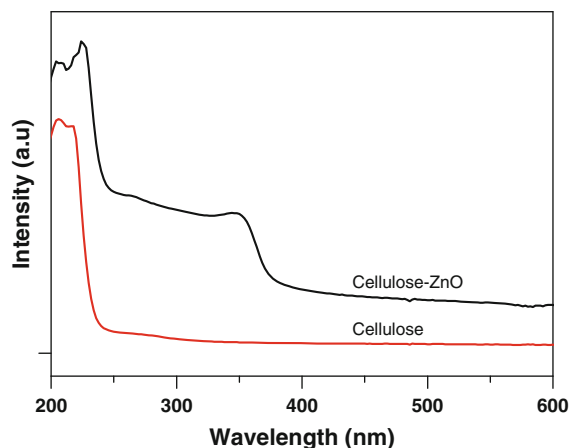


Fig. 2 UV-visible spectra of a cellulose-ZnO hybrid film and pristine cellulose

(Fig. 3) of a cellulose-ZnO hybrid film was recorded by exciting at 350 nm, which shows a strong UV emission at 390 nm (3.2 eV) and a relatively weak visible emission at 472 nm (2.6 eV). The UV emission band of ZnO has been well demonstrated to be related to the exciton emission (Spantel and Anderson 1991). Although the mechanism of green emission by ZnO crystals has not been clearly identified, models related to various defects, which can provide recombination centers within the band gap, have been suggested. A singly ionized oxygen vacancy has been reported to be responsible for the green emission in ZnO, and this emission results from the recombination of a photogenerated hole with the singly ionized charge state of this defect (Vanheusden et al. 1996).

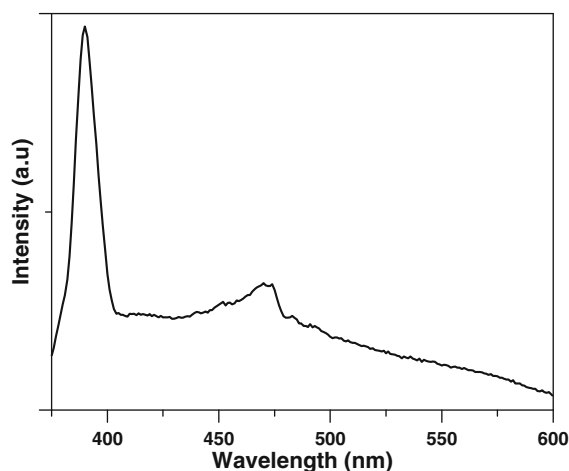


Fig. 3 A PL spectrum of a cellulose-ZnO hybrid film

XRD and TGA analyses

XRD patterns were recorded from a cellulose-ZnO hybrid material and the pristine cellulose precursor. Figure 4 shows characteristic peaks for the wurtzite structure of ZnO [3] at 2θ value of 31.7° (100), 34.4° (002), 36.2° (101), 47.5° (102), 56.6° (110), 62.8° (103), 67.9° (112) and 69.1° (201) in addition with a broad peak at 21° for the regenerated cellulose. Relatively sharp peaks show that the ZnO crystals were well crystallized. In other words, crystallinity of the ZnO was not affected by the hydrophilic nature of cellulose.

TGA pattern of the cellulose-ZnO hybrid film is shown in Fig. 5. For comparative purposes, the TGA

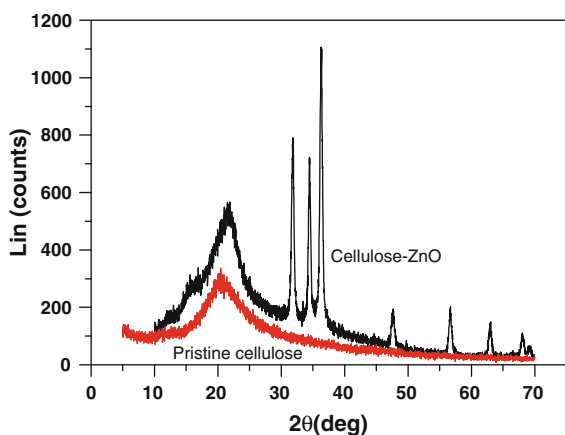


Fig. 4 XRD patterns of a cellulose-ZnO hybrid film and pristine cellulose

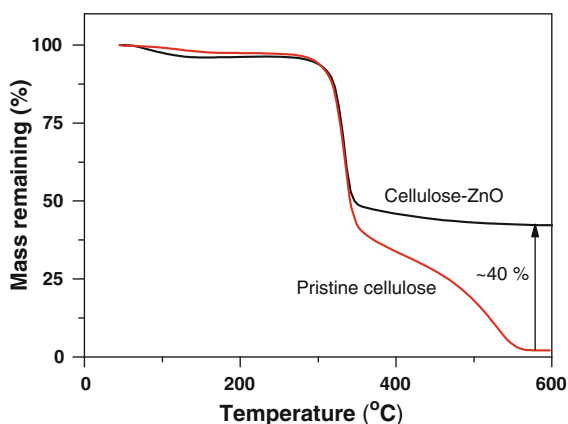


Fig. 5 TGA patterns of a cellulose-ZnO hybrid film and pristine cellulose

curve for cellulose is also presented, indicating that the two main steps observed correspond to the thermal degradation of cellulose (Dahiya and Rana 2004). Assuming complete degradation of the cellulose occurs by 600°C , the cellulose-ZnO hybrid films have $\sim 40\%$ ZnO by mass.

SEM, EDS and AFM analyses

To study the surface and cross sectional morphology of the cellulose-ZnO hybrid materials, SEM analysis was performed. Figure 6a and b show the surface morphology of the hybrid material. The ZnO material on the cellulose film has a fairly narrow size distribution centered around 250 nm. It is interesting to observe that the formation of the ZnO lying parallel to the direction of cellulose fibre in regenerated cellulose (Fig. 6b). Cross sectional analysis shows ZnO nanoparticles were formed not only on the surface of the cellulose but inside the film as well (Fig. 6c).

To find the elemental composition of the cellulose-ZnO film, EDS analysis was performed. Figure 7 shows the EDS pattern of the cellulose-ZnO hybrid film which confirms the presence of zinc and oxygen. Figure 8a shows a representative AFM picture of cellulose-ZnO material, where observed granules by SEM analysis are aggregates of tiny ZnO nanoparticles. The single line section profile (Fig. 8b) shows that the height variation is around 100 nm.

Mechanism of the formation of cellulose-ZnO hybrid films

To understand the mechanism of the cellulose-ZnO hybrid film formation, two different reactions were carried out. In the first reaction, wet cellulose film was introduced to the aqueous solution of zinc nitrate and TEA and then the temperature was gradually increased to 85°C and the reaction mixture was kept under constant stirring at 85°C for 6 h. This reaction yields cellulose-ZnO hybrid films. In the second reaction, an aqueous solution of zinc nitrate and TEA was heated to 85°C and after 1 h wet cellulose films were introduced to the reaction mixture and the reaction mixture was kept under constant stirring at 85°C for another 5 h. In this case, the formation of cellulose-ZnO hybrid films was not observed because

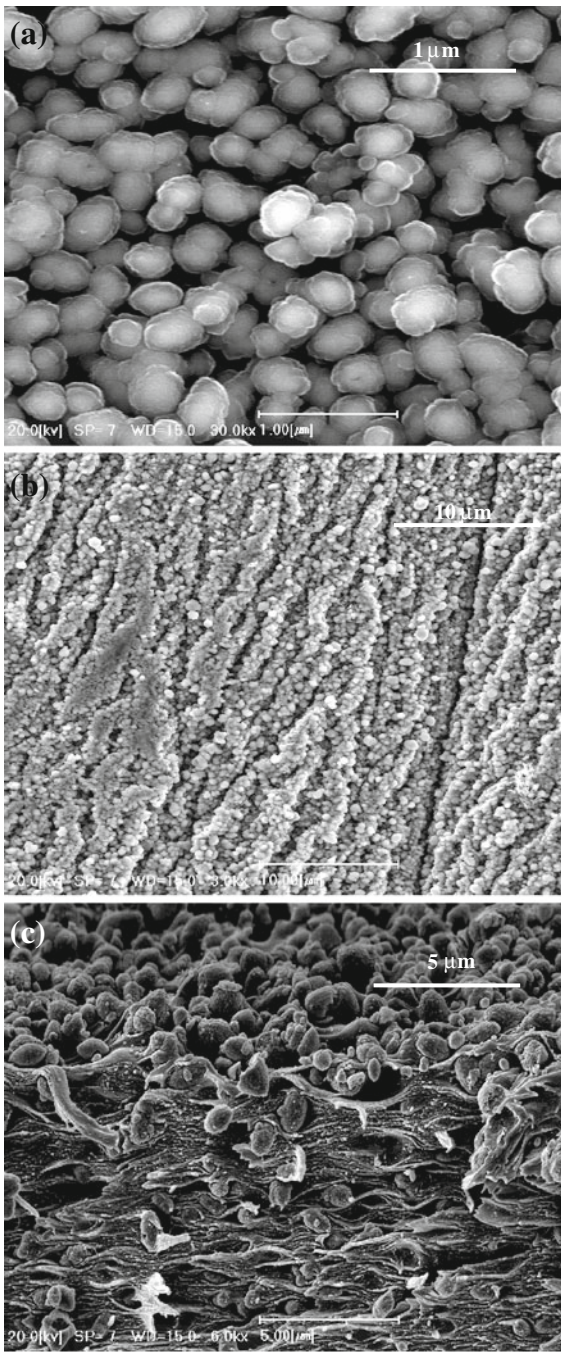


Fig. 6 a, b SEM images of cellulose-ZnO hybrid film surfaces and, c a cross sectional SEM image of a cellulose-ZnO hybrid film

ZnO particles were precipitated away from the cellulose surface. This inference clearly explains that zinc precursor first attaches to the hydrophilic wet

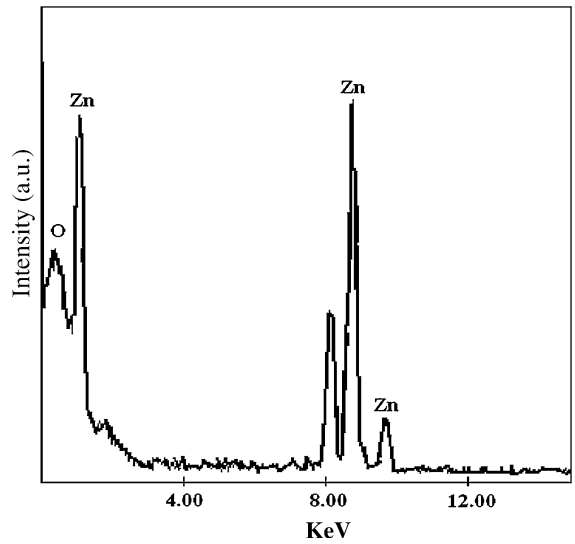


Fig. 7 An EDS pattern of the surface of a cellulose-ZnO hybrid film

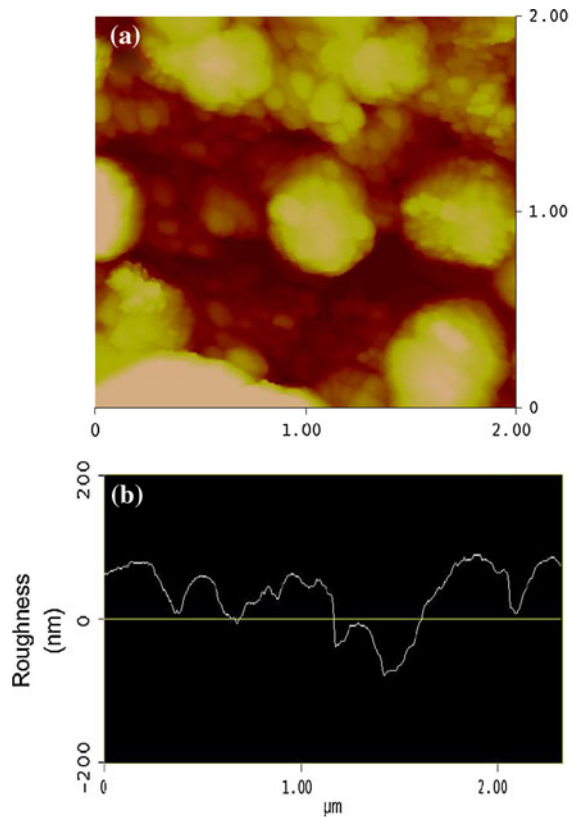


Fig. 8 a AFM image and, b section analysis of a cellulose-ZnO film

cellulose film and then undergoes alkaline hydrolysis to produce ZnO nanoparticles, whereas already formed ZnO nanoparticles do not attach to the wet cellulose film.

Conclusions

Cellulose-ZnO hybrid materials are prepared by a simple one pot wet chemical method. This method can achieve immobilization without the aid of a binder or dendritic side groups and does not involve high temperature treatment. PL spectrum showed strong emission at 390 nm and weak emission at 472 nm. TGA analysis showed the hybrid material has around 40 wt% of ZnO nanoparticles. SEM images showed a uniform formation and surface and cross sectional morphology of the material. The mechanism of the formation of the cellulose-ZnO hybrid films was based on the fact that the zinc precursor first attaches to the hydrophilic wet cellulose film and then undergoes alkaline hydrolysis to produce ZnO nanoparticles. ZnO immobilized on biopolymers like cellulose has potential applications in strain sensors, biomedical sensors, flexible display devices and optoelectronics.

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