

Precursor concentration effect on structure and morphology of ZnO for coatings on fabric substrates

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Abstract: ZnO is a versatile functional material that has a diverse group of growth morphologies. By controlling the growth kinetics, it is possible to change the growth behavior of ZnO structures. Growth of ZnO structures can be achieved in a cheaper way at low temperature using chemical growth techniques such as aqueous chemical growth, nonaqueous solution growth, sol gel and spray deposition. Up to date, there are quite few reports in the literature presenting state of art approaches of use of ZnO material onto textile substrates for several applications as antibacterial, deodorizing and UV protection, and none regarding any systematic approach of direct growth and optimization with respect to the textile support. The successful exploitation of ZnO particles for use in various technological applications requires the development of techniques for controlling its photocatalytic activity. The present contribution presents a study of precursor

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concentration effect on structure and morphology of ZnO for coatings on fabric substrates. ZnO particles were obtained by direct growth onto the respective substrate by aqueous chemical growth using suitable precursors for each growth and then characterized regarding their appearance, size and structure using microscopic techniques and X-ray diffraction.

Keywords: ZnO structuring, textile support, SEM, EDX, XRD.

Introduction

Nanostructured ZnO materials have received broad attention due to their distinguished performance in electronics, optics and photonics. In the last few decades, study of one-dimensional (1D) materials has become a leading edge in nano-science and nanotechnology. With reduction in size, novel electrical, mechanical, chemical and optical properties are introduced. Nano-wire-like structures are the ideal system for studying the transport process in 1D confined objects, which are of benefit not only for understanding the fundamental phenomena in low-dimensional systems, but also for developing new generation nano-devices with high performance. ZnO is a key technological material. The lack of a centre of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors. In addition, ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60 meV) in ZnO crystal can ensure efficient excitonic emission at room temperature and room temperature ultraviolet (UV) luminescence has been reported in disordered nanoparticles and thin films. ZnO is transparent to visible light and can be made highly conductive by doping. ZnO is a

versatile functional material that has a diverse group of growth morphologies, such as nanobelts, nanowires, nanocages, nanocombs, nanosprings, nanorings and nanohelices.¹

By controlling the growth kinetics, it is possible to change the growth behavior of ZnO nanostructures. Growth of ZnO nanostructures can be achieved in a cheaper way at low temperature using chemical growth techniques such as aqueous chemical growth, nonaqueous solution growth, sol gel and spray deposition. All these techniques allow the use of various textile supports for nanostructured ZnO growth having the advantage of a much larger available surface than usual flat substrates leading to an increased surface to volume ratio of the active photocatalyst. Up to date, there are quite few reports in the literature presenting state of art approaches of use of ZnO material onto textile substrates for several applications as antibacterial,² deodorizing³ and UV protection,^{2,4} and none regarding any systematic approach of direct growth and optimization with respect the textile support. More than that, up to our knowledge, there is no available study in the literature about ZnO coated textiles used as photocatalytic active support for gaseous compounds decomposition. Wang et al.⁵ reported a low temperature growth approach to grow hexagonally oriented ZnO nanorod arrays onto cotton fabrics to impart UV-blocking property to fabrics.⁶ Baruah et al.^{7,8} grew ZnO nanowires on nonwoven polyethylene for photocatalytic degradation application. Perelshtein et al.⁹ synthesized and deposited ZnO nanoparticles on the surface of cotton fabrics using ultrasound irradiation for generation of antibacterial applications. Xu et al. [10] reported the fabrication of a ZnO nanorod array film on cotton fibers for making super-hydrophobic surfaces. Goncalves et al.¹¹ reported growth of rod-shaped ZnO particles over wood cellulose fibers using a two-step

process. Xue et al.⁶ reported ZnO nanorod forests wrapping flexible nylon fibers via a wet chemical route and Xiong et al. latex ZnO nanocomposites.¹²

The successful exploitation of nanoparticles ZnO for use in various technological applications requires the development of techniques for controlling its photocatalytic activity. A key factor determining the activity of a photocatalyst is the rate of charge carrier recombination relative to that of interfacial charge transfer. A high rate of charge carrier recombination inevitably decreases the number of free electrons and holes that are available to react with adsorbed molecules and thereby generate free radicals. This can be achieved by structure control and by doping. The present work focuses on micro-nanostructured ZnO growth onto various textile substrates. It targets the achieving large surface to volume ratios together with good textile fiber coverage as an important step through the design of an efficient air photo-catalysis composite active system. The present is basically a study of precursor concentration effect on structure and morphology of ZnO for coatings on fabric substrates. ZnO particles were obtained by direct growth onto the respective substrate by aqueous chemical growth using suitable precursors for each growth and characterized regarding their appearance, size and structure using microscopic techniques and X-ray diffraction.

Experimental

ZnO was chemically grown directly onto PES-Viscose 7DC and 8DC type different substrates from 0.1, 0.05 and 0.01M zinc acetate (ZnAc_2) precursor concentrations in aqueous solutions as presented in Table 1.

Table 1. Growth parameters for ZnO onto PES-Viscose 7DC and 8DC substrates.

Samples on PES-Viscose 7DC and 8DC	Volume	Temperature	Time
0.1 M ZnAC ₂ + 248 μ L NH ₃ 25%	20 mL	95 °C	20 h
0.05 M ZnAC ₂ + 123.5 μ L NH ₃ 25%	20 mL	95 °C	20 h
0.01 M ZnAC ₂ + 24.71 μ L NH ₃ 25%	20 mL	95 °C	20 h

All deposited materials were studied using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). SEM and EDX characterization were performed using a JEOL JSM 6362LV electron microscope equipped with an EDAX INCA X-act Oxford Instrument detector. SEM surface characterization was performed in low vacuum (3-12 Pa) without any sample preparation while EDX characterization and elemental mapping were performed in high vacuum. Elemental mapping of the sample surface was also collected at magnification $\times 10000$ and using large acquisition times (more than 80000 counts) for an accurate definition of surface points. The instrument used for FT-IR characterization is a spectrometer fitted with an ATR module manufactured by Shimadzu. For XRD characterization was used a D8 Discover XRD system from Bruker.

Results and discussions

Crystalline ZnO was successfully deposited onto both kinds of textile substrates. SEM characterization for the samples prepared on both kinds of substrates from the three different precursor concentrations is presented in Figures 1 and 2.

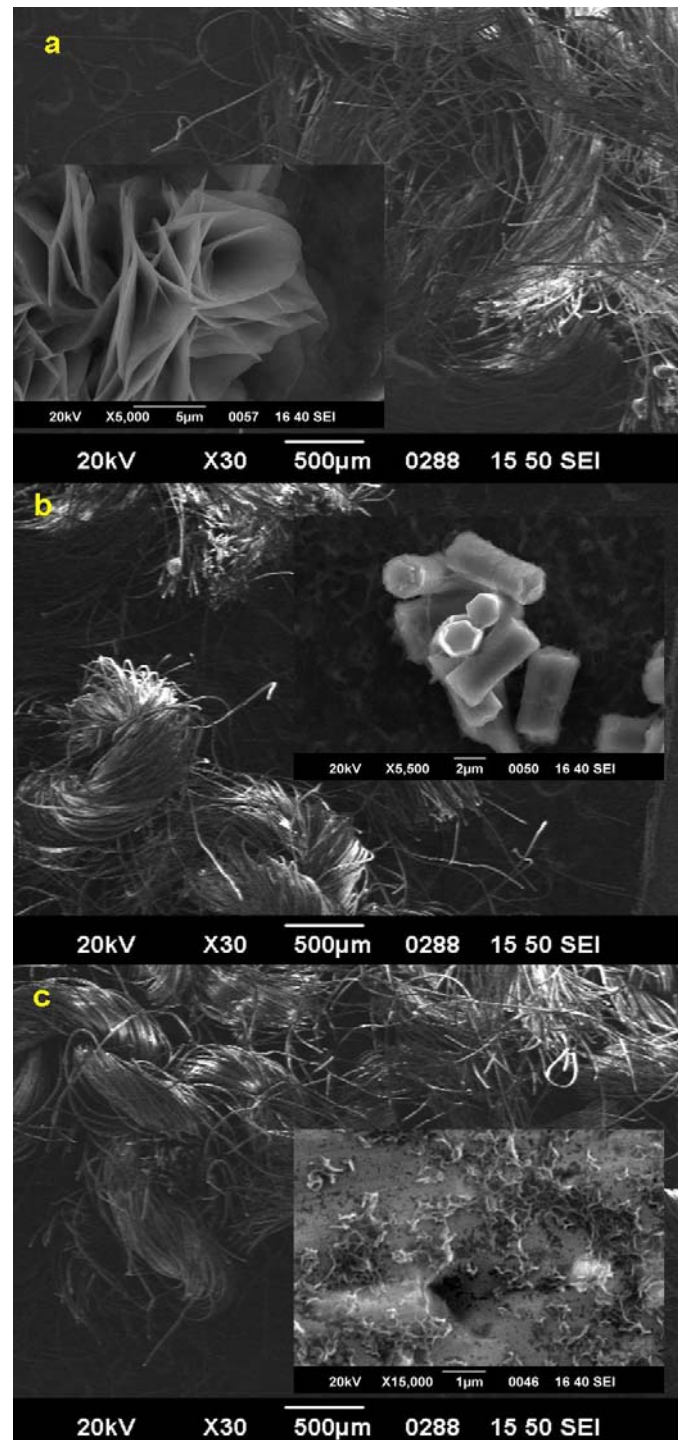


Figure 1. SEM images of ZnO coated PES-Viscose 7DC from precursor concentrations **a** 0.01 M ZnAC₂ + 24.71 μL NH₃ 25% **b** 0.05 M ZnAC₂ + 123.5 μL NH₃ 25% **c** 0.1 M ZnAC₂ + 248 μL NH₃ 25%.

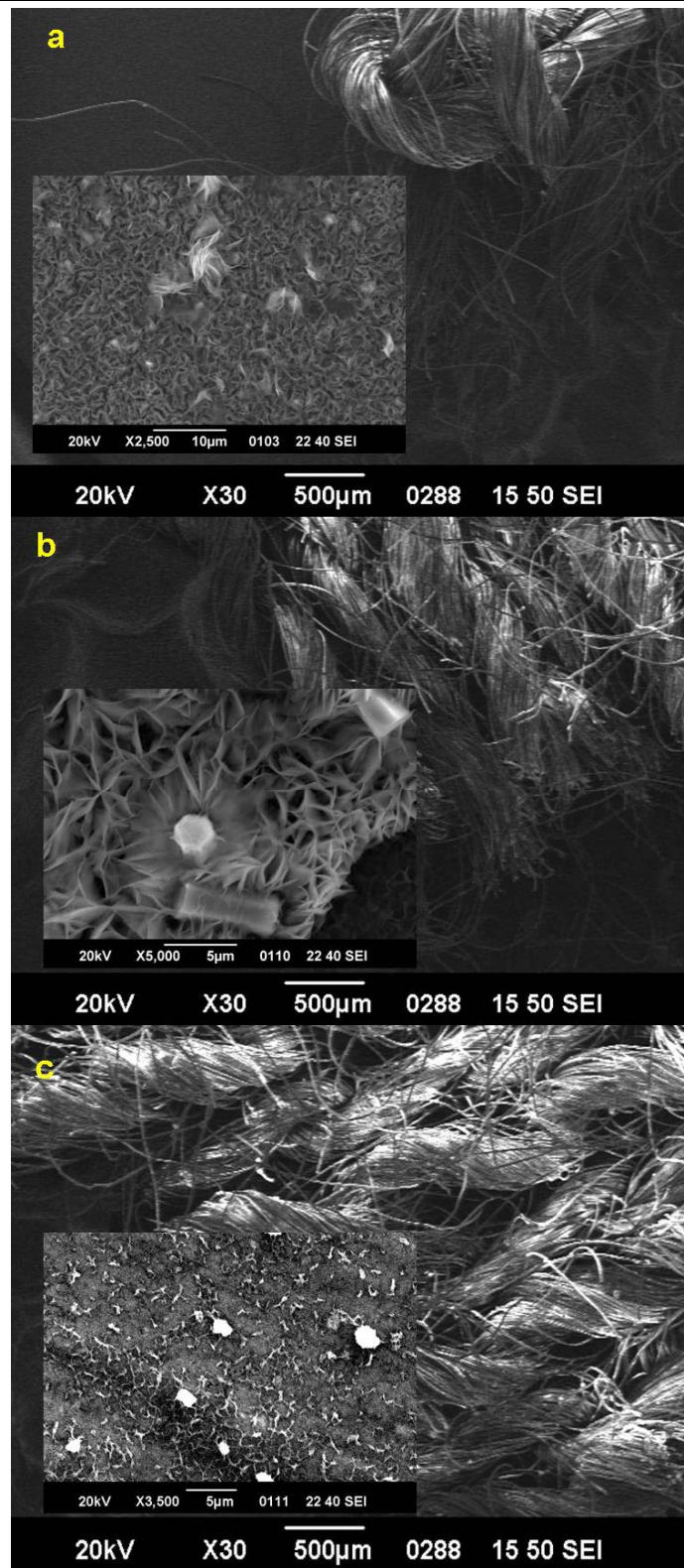


Figure 2. SEM images of ZnO coated PES-Viscose 8DC from precursor concentrations **a** 0.01 M ZnAC₂ + 24.71 μL NH₃ 25% **b** 0.05 M ZnAC₂ + 123.5 μL NH₃ 25% **c** 0.1 M ZnAC₂ + 248 μL NH₃ 25%.

As presented in Figures 1 and 2 ZnO growth is strongly influenced by precursor concentration as well as the substrate nature. Growth from 0.01 M ZnAC₂ + 24.71 μL NH₃ 25% precursor solution leads to ZnO structuring as walls-like structures while 0.05 M ZnAC₂ + 123.5 μL NH₃ 25% and 0.1 M ZnAC₂ + 248 μL NH₃ 25% promote the formation of large hexagonal ZnO micro and nano crystals onto textile fibers. XRD analysis, showed the presence of wurtzite ZnO (1 0 1), (1 0 0), (0 0 2) [JCPDS Card No. 36-1451] crystalline structure with highest peak intensity for (1 0 1) crystalline orientation and the best crystallinity for a 0.05 M precursor concentration. In the case of PES-Viscose 8DC ZnO shows slightly enhanced crystallinity. XRD diffractograms for both kinds of substrates are presented in Figure 3 a and b.

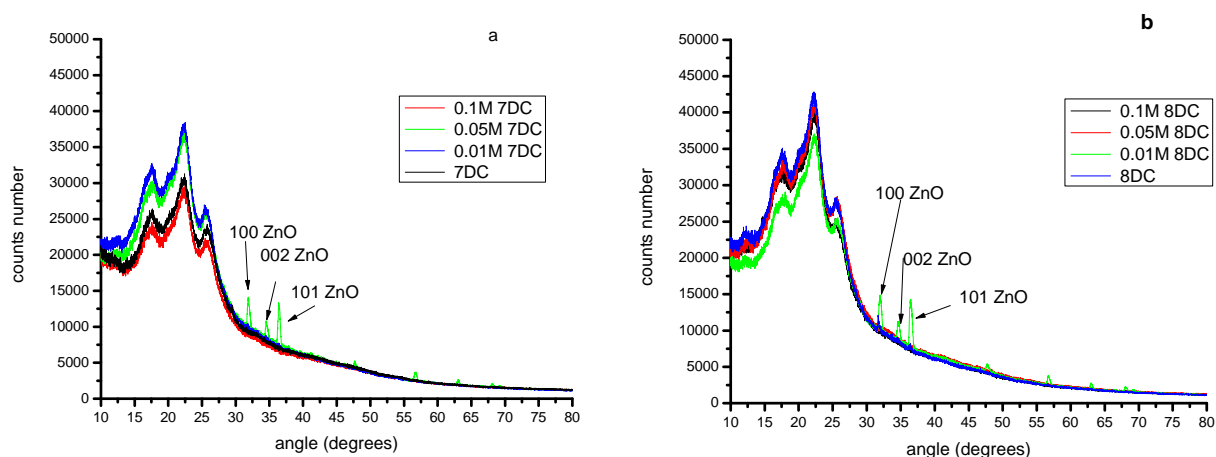


Figure 3. XRD diffractograms of ZnO coated PES-Viscose **a** 7DC and **b** 8DC from precursor concentrations 0.01 M ZnAC₂ + 24.71 μL NH₃ 25%, 0.05 M ZnAC₂ + 123.5 μL NH₃ 25% and 0.1 M ZnAC₂ + 248 μL NH₃ 25%.

Elemental EDX analysis was performed in order to verify if except the observable ZnO structures, there is also a uniform coating of the textile fibers. Elemental mapping of Zn and O distributions together with the corresponding EDX spectra are presented in Figures 4 and 5.

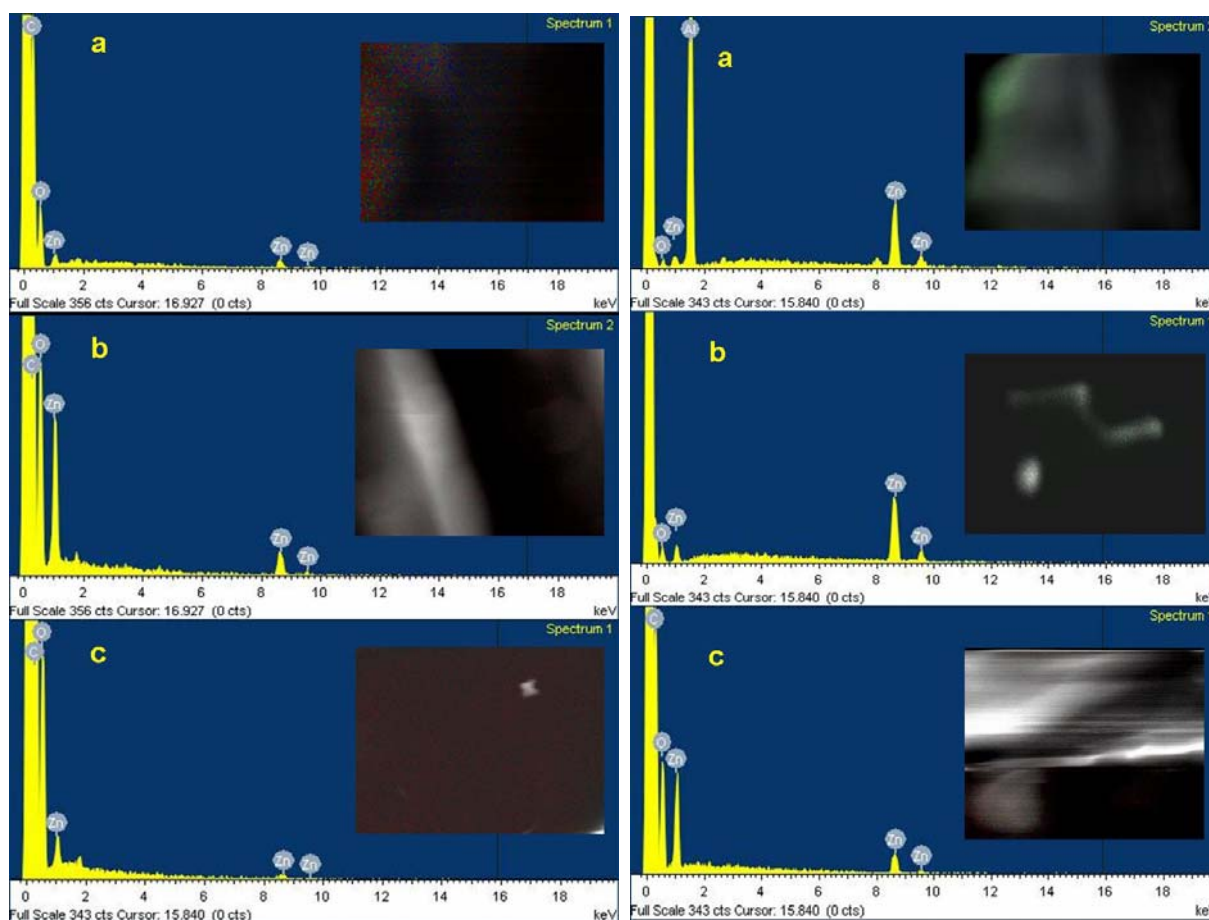


Figure 4. EDX spectra and elemental mapping of ZnO coated PES-Viscose 7DC from precursor concentrations **a** 0.01 M ZnAC_2 + 24.71 μL NH_3 25% **b** 0.05 M ZnAC_2 + 123.5 μL NH_3 25% **c** 0.1 M ZnAC_2 + 248 μL NH_3 25% (red C, green O, blue Zn).

Figure 5. EDX spectra and elemental mapping of ZnO coated PES-Viscose 8DC from precursor concentrations **a** 0.01 M ZnAC_2 + 24.71 μL NH_3 25% **b** 0.05 M ZnAC_2 + 123.5 μL NH_3 25% **c** 0.1 M ZnAC_2 + 248 μL NH_3 25% (red C, green O, blue Zn).

EDX analysis confirmed the presence of ZnO onto the textile fibers the best coating corresponding to 0.06 M precursor concentration.

ATR FTIR characterization was also performed onto all deposited samples and the characteristic transmittance spectra are presented in Figures 6 a and b.

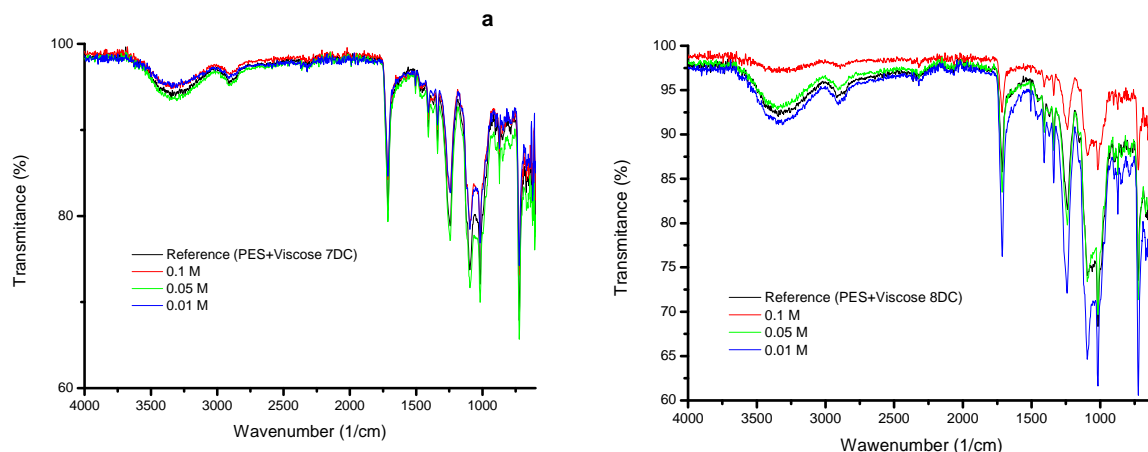


Figure 6. ATR FTIR transmittance spectra of ZnO coated PES-Viscose **a** 7DC and **b** 8DC from precursor concentrations 0.01 M ZnAC_2 + 24.71 μL NH_3 25%, 0.05 M ZnAC_2 + 123.5 μL NH_3 25% and 0.1 M ZnAC_2 + 248 μL NH_3 25%.

The characteristic picks for viscose are: 3330 –OH stretching, 2910 –CH and CH_2 stretching, 1010 and 1080 –CO and ring stretching, the picks characteristic for PES are: 732 – $(\text{CH}_2)_4$ –, 1240 – ester group, 1340 – CH_3 geminal bending and 1710 –CO stretch, the pick that appears for both polymers is 1400 – CH_2 bending. Most of characteristic absorptions of ZnO are overlapping with the picks of the substrate and the only one that is not overlapping with anything is the one at 2370 which is very faint and cannot be used for quantitative estimations.

Conclusions

ZnO was chemically grown directly onto PES-Viscose different substrates from 0.1, 0.05 and 0.01 M precursor concentrations solutions. Characterization by SEM and XRD shows that 0.05 M precursor concentration is the optimum for highly crystalline ZnO growth. EDX characterization proved that ZnO coat the fiber surface. Due to low conductivity of textile coated samples, accurate elemental composition could not be achieved. ATR-FTIR proved that the textile substrate does not undergo any degradation during the deposition of ZnO. The characteristic

absorption bands for ZnO are present in the spectra but are fairly weak therefore no quantitative estimations can be made.

Acknowledgements

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