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Coating of glass with ZnO *via* ultrasonic irradiation and a study of its antibacterial properties

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ABSTRACT

Zinc oxide (ZnO) nanoparticles were synthesized and deposited on the surface of glass slides using ultrasound irradiation. The structure and morphology of the nanoparticles were studied as a function of the synthesis time. The deposited film was analyzed using characterization methods such as XRD, SEM, AFM, and optical spectroscopy. Zinc oxide submicron crystals with an average diameter of ~300 nm strongly adhered to the glass surface. This method is fast, simple, convenient, economical, and environmentally friendly. The antibacterial activities of the ZnO–glass composites were tested against *Escherichia coli* (Gram negative) and *Staphylococcus aureus* (Gram positive) cultures. A significant bactericidal effect, even in a 0.13% coated glass (wt.%), was demonstrated.

1. Introduction

Zinc oxide (ZnO) has been the topic of high-standard contemporary research because of its wide band gap (3.37 eV) and large exciton-binding energy (60 meV) that cause interesting luminescent, piezoelectric, and photoconducting properties. These properties make this material suitable for many industrial applications in fields such as high frequency surface devices, optical devices, such as UV detector, LDs, and LEDs, and which increasingly attracting more research groups [1–4]. ZnO is an environmentally friendly material and has little toxicity, which is why it is widely used as an active ingredient for dermatological applications in creams, lotions and ointments on account of its antibacterial properties. The antibacterial properties were found in both microscale and nanoscale formulations [5]. The theme of particle-induced reactive-oxygen-species (ROS) production and oxidative injury inside bacterial cells has become an established paradigm underlying the ZnO antibacterial mechanism, as our previous work has demonstrated [6].

The reason why we attempted to coat zinc oxide particles on glass is because it offers the opportunity to keep the glass windows transparent on the one hand, and prevent the penetration of UV radiation on the other hand. Preventing the penetration of the UV radiation might also prevent sensitive electronic components from being damaged. In addition, the coated glass can be used for antibacterial applications. A rigid antibacterial matrix such as coated glass can serve as deodorizing and air-purification functional coating, thus reducing the sterilization cost and manual hours for disinfection of the surrounding domains. It can also avoid secondary pollution and prolong the service life in food industry products.

In this respect, utilizing ZnO as an inorganic antibacterial agent has a key advantage due to its ability to withstand harsh processing and its being more durable, as compared to organic materials [7].

The preparation and characterization of zinc oxide materials of nanometer dimensions with flower-like, snowflake-like, prism-like, prickly sphere-like and rod-like shapes have already been investigated [8]. Recently, some low temperature methods modified with capping agents for the deposition of nanoparticles on the glass substrate were reported, e.g., electroless plating of spin-coated nanoparticles, and polyol reduction precipitation. The coating of nanoparticles with biomolecules, oil, pigments polymers, plastics, etc., with the help of suitable binders and co-binders has been reported as well. Less attention has been paid to nanoparticles of ZnO as coatings, in spite of their known technological applications [9–15].

Sonochemical methods have been proven as being effective for the deposition of nanomaterials on polymeric matrices because of their ability to combine the synthesis of various nanomaterials and their deposition on various substrates in a single operation and without the aid of a binder. Moreover, this coating method is a

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"green" chemistry approach because it does not involve any toxic materials [16]. The additional advantage of this method is the ability to control the particle size of the product by varying the concentration of the precursors in the solution. The chemical effects of ultrasound derive from acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid. During the adiabatic compression phase of oscillating or collapsing bubbles, the high temperatures of several thousand kelvin and a pressure of several hundred bars are reached in a short period of time, preferentially near the solid surface [17,18]. The nuclei of the nanoparticles formed from the precursor solution are thrown at the solid substrate by the microjets and shock waves created after the collapse of the bubble. The speed of these microjets and shock waves is very fast and they throw the just formed nanoparticles at the surface at a very high speed (>100 m/s), causing the nanoparticles to adhere strongly to the solid surface [19].

To the best of our knowledge, this is the first report on the deposition of zinc oxide particles on glass using the sonochemical method.

In this paper, the mechanism and kinetics of the deposition of the ZnO nanoparticles and the influence of glass on the particles' growth were studied by a complex of physico-chemical methods: X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), and optical spectroscopy. We also examined the ability of the coated glass to eradicate two common nosocomial pathogens, i.e. *Escherichia coli* (Gram negative bacterium) and *Staphylococcus aureus* (Gram positive bacterium).

2. Experimental

2.1. Coating procedure

All the reagents were purchased from Aldrich, were of analytical chemical purity and were used without additional purification. The ZnO nanoparticles were deposited on a glass slide by the sonochemical irradiation of the Zn^{2+} ions precursor in a water–ethanol solution. This solvent is considered as an environmentally friendly solution. Zinc acetate tetrahydrate $Zn(Ac)_2{\cdot}4H_2O$ was used as a precursor for this reaction. Typically, the zinc acetate was dissolved in a water:ethanol = 1:9 mixture to obtain a 0.05 mol/L concentration of Zn^{2+} ions. The pH of the solution was adjusted with the addition of ammonia to pH 8. The glass slide was then inserted into the reactor and the sonication was done with an immersed Ti-horn (20 kHz, 750 W at 70% efficiency) for a fixed period of time. After the reaction the sonochemically coated glass was washed with water and ethanol and allowed to dry in air at room temperature. The ZnO content on the glass was determined by volumetric titration with ethylenediaminetetraacetic acid (EDTA) after treatment of the sample in 0.5 M solution of HNO_3 [20].

2.2. Characterization

The structural characterization of the silver films was done by X-ray diffraction (XRD) using a Bruker D8 diffractometer (with Cu $K\alpha$ = 1.5418 Å radiation). The morphology of ZnO nanoparticles on the glass substrate was studied by scanning electron microscopy (SEM) with a JEOL-JSN 7000F device. The samples were also examined by atomic force microscopy (AFM) with a Nanoscope Dimension 3100 Controller instrument. The transmission optical spectra were recorded on a CARY 100 Scan UV spectrometer covering a wavelength region from 200 to 600 nm. The determination of ZnO nanoparticles in the washing solution was conducted by dynamic light scattering (DLS) performed with a Coulter particle analyzer (Malvern Zetasizer).

2.3. Antibacterial test

The antibacterial activity of ZnO was tested against the Gram negative *E. coli* (strain 1313) as well as against the Gram positive *S. aureus* (strain 195) bacteria. Both strains were obtained from the Bacteriological Laboratory of the Meir Hospital, Kfar Sava, Israel. A typical procedure was as follows: cultures of the bacteria were grown overnight on nutrient agar (Difco, Detroit, MI). On the morning of the experiment, these cultures were transferred into a flask containing nutrient broth (NB) at an initial optical density (OD) of 0.1 at 660 nm and allowed to grow at 37 °C with aeration. When the cultures reached an optical density of 0.3 OD at 660 nm (the beginning of the logarithmic phase), they were centrifuged and washed twice with a saline solution (NaCl 0.145 M) at pH 6.5 to yield a final bacterial concentration of approximately 10^8 CFU ml^{-1}. A sample of a ZnO coated glass slide (1 cm × 1 cm) cm) was placed in a vial (with an inner diameter of 2.5 cm) containing 4.5 ml of saline. The strain cells were then pipetted (500 μl) into the vial. The initial bacterial concentration in the vial was approximately 10^7 CFU ml^{-1}. To ensure that any decrease in bacterial number was likely to be due to exposure to a coated glass treatment, two controls were included in the experiment, one with the absence of bacteria and a coated glass (negative control), and the second with the bacteria at the appropriate concentration in saline with the presence of an uncoated glass (positive control). The bacterial suspensions were incubated and shaken on a rotary shaker at 180 shakes min^{-1} and 37 °C for up to 4 h. Samples of 100 μl each were taken at a specified time, diluted tenfold in saline, and then transferred onto nutrient agar plates (Difco). The plates were allowed to grow for 24 h at 37 °C and then counted for viable bacteria. The viable bacteria were monitored with a colony counter by counting the number of colony-forming units from the appropriate dilution on nutrient agar plates. The survival fraction, N/N_0, was determined by calculating the colony-forming units per milliliter of the culture. The term N_0 denotes the number of colony-forming units at the beginning of the treatment before adding the coated glass, and N stands for the number of colony-forming units after the treatment for the indicated time of each sample.

3. Results and discussion

Our previous studies in which ZnO nanoparticles were synthesized indicated that the yield of the product and the particle size are strongly dependent on the rate of particle collision and on the concentration of the reagents during the sonochemical synthesis. That is why experimental parameters such as the time and concentration of the precursor were selected as important factors for the optimization of the sonochemical reaction. Due to the limited length of this paper, we will only discuss time as a variable parameter of the reaction. A full discussion of the mechanism of the ZnO ultrasonic synthesis has already been provided in detail in our previous work [6]. It should be noted that the glass substrates were coated on both sides. This is because the ultrasonic waves pushed the just-formed ZnO nanoparticles not only in a straight line from the ultrasonic horn, but also in a turbulent manner. It should also be emphasized that the coating was stable and could not be removed by a simple washing procedure with water, or ethanol and/or acetone. The methods we used for the leaching examination were DLS and transmission electron microscopy (TEM) after placing the coated glasses in each of the above-mentioned solvents for duration of 7 days. The DLS and TEM studies did not reveal a presence of any nanoparticles in the leaching solution. That means that the sonochemically deposited ZnO nanoparticles are strongly anchored to the glass substrate.