NANOPARTICLES APPLICATIONS FOR IMPROVING THE FOOD SAFETY AND FOOD PROCESSING

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Abstract. In the last years, nanoparticles are studied for a number of industrial applications, such as electronics, environmental, synthetic textiles, packaging, pharmaceutical industry, medical care, as well as construction and decoration. They can be classified into two types, organic and inorganic. Organic antibacterial materials are less stable, especially at high temperatures and/or pressures comparing with inorganic antibacterial agents. This fact could be an obstacle for the production necessities. Consequently, inorganic materials such as metal and metal oxides have attracted lots of attention due to their ability to withstand harsh process conditions. From the inorganic materials class, metal oxides such as TiO_2, ZnO, MgO and CaO present special interest, as they are not only stable under harsh process conditions but also generally regarded as safe materials to human beings and animals. Furthermore, the antimicrobial activity of ZnO draws our attention for its possible application in food industry. We resume and we underlined the actual knowledge about ZnO in order to support the researches for obtaining new materials for food industry.

Keywords: antibacterial activity, antifungal activity, nanoparticles, zinc oxide, food safety, hygiene, energy efficiency

1. Introduction

The new challenge of this century is the application of nanotechnology in new fields like food industry. Up to now nanotechnology focused on the medicine, drugs formulation, electronics, textiles, defence industry, cosmetics and agriculture. Potential applications of nanotechnology in the food industry are formulation of food products, food packaging applications, and new materials for food equipments, new sanitizers and also water purification [1, 2].

Nowadays the researchers are attracted by studying inorganic metal oxides (TiO_2, MgO, CaO and ZnO) as antimicrobial agents due to their safety and stability. Because of their unique properties and large number of applications, zinc oxide nanostructures are now one of the main subjects of nowadays research. ZnO nanoparticles are durable, not affect the soil fertility in comparison to traditional antifungal agents. ZnO belongs to the class of metal oxides and is characterized by photocatalytic and photo-oxidising capacity against chemical and microbiological species. Because ZnO is a polar crystal with hexagonal phase, the properties of ZnO are strongly related on the type of the synthesis process and the conditions fulfil during the processing of nanostructures (reaction temperature, concentration of reactants and type of capping agents used). ZnO is an n-type semiconductor with wide direct band gap (3.37 eV), high exciton energy (60 meV) at room temperature which allows it to act as an efficient semiconducting and piezoelectric material. These nanoparticles act as biosensors because of fast electron kinetics and biocompatibility [3]. The advantages of using ZnO nanoparticles are antifungal and antibacterial activities at lower concentrations. Furthermore, different studies conducted in different laboratories show us that the antibacterial activity is influenced not only by nanoparticles concentration but also by the size of the ZnO particles.

Metal nanoparticles (silver, ZnO) are already used as food additive/supplement, packaging materials/storage, refrigerators, storage containers, water purification and anti-bacterial sprays.

2. Experimental details

In 2006, a team of researcher (Lingling Zhang, Yunhong Jiang, Yulong Ding, Malcolm Povey and David York) performed investigation into the antibacterial behavior of suspensions of ZnO nanoparticles (ZnO nanofluids). Especially they investigated the antibacterial behavior of suspensions of zinc oxide nanoparticles (ZnO nanofluids) against *E. coli*. ZnO nanoparticles from two sources are used to formulate nanofluids. The effects of particle size, concentration and the use of dispersants on the antibacterial behavior are examined. The results show that the ZnO nanofluids have bacteriostatic activity against *E.coli*. The antibacterial activity increases with increasing nanoparticle concentration and increases with decreasing particle size (figure 1).

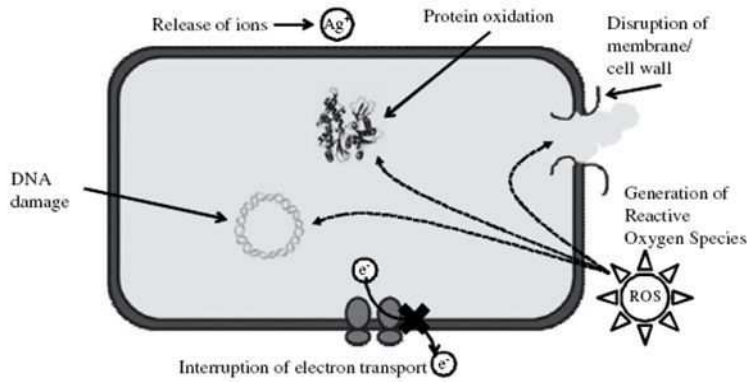

Figure 1. Various mechanisms of antimicrobial activities exerted by nanomaterials [Qilin Li et col.]

Particle concentration is observed to be more important than particle size under the conditions of this work. The results also show that the use of two types of dispersants (Polyethylene Glycol (PEG) and Polyvinylpyrrolidone (PVP)) does not affect much the antibacterial activity of ZnO nanofluids but enhances the stability of the suspensions. SEM analyses of the bacteria before and after treatment with ZnO nanofluids show that the presence of ZnO nanoparticles damages the membrane wall of the bacteria. Electrochemical measurements using a model DOPC monolayer suggest some direct interaction between ZnO nanoparticles and the bacteria membrane at high ZnO concentrations [3].

The study concerning mechanistic investigation into antibacterial behavior of suspensions of ZnO nanoparticles against *E. coli* was followed in 2008 and 2009 by Lingling Zhang, Yunhong Jiang, Yulong Ding, Nikolaos Daskalakis, Lars Jeuken, Malcolm Povey, Alex J. O'Neill, David W. York. They found that aqueous suspensions containing $4.45 \cdot 10^{-5}$ - $1.25 \cdot 10^{-3}$ M ZnO particles exhibit a strong antibacterial activity against *E. coli* under the dark conditions. The dominant mechanisms of such antibacterial behaviour are found to be either or both of chemical interactions between hydrogen peroxide and membrane proteins, and chemical interactions between other unknown chemical species generated due to the presence of ZnO particles with the lipid bi-layer. The effect of direct physical interactions between nanoparticles and biological cells are found to play a relatively small role under the conditions of this study [3].

Qilin Li, Shaily Mahendra, Delina Y. Lyon, Lena Brunet, Michael V. Liga, Dong Li and Pedro J.J. Alvarez, in 2008, published the study "Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications". Resuming their results, we found that the challenge to achieve appropriate disinfection without forming harmful disinfection by products by conventional chemical disinfectants, as well as the growing demand for decentralized or point-of-use water treatment and recycling systems calls for new technologies for efficient disinfection and microbial control. Several natural and engineered nanomaterials have demonstrated strong antimicrobial properties through diverse mechanisms including photocatalytic production of reactive oxygen species that damage cell components and viruses (e.g. TiO_2, ZnO and fullerol), compromising the bacterial cell envelope (e.g. peptides, chitosan, carboxyfullerene, carbon nanotubes, ZnO and silver nanoparticles (nAg)), interruption of energy transduction (e.g. nAg and aqueous fullerene nanoparticles (nC60), and inhibition of enzyme activity and DNA synthesis (e.g. chitosan). Although some nanomaterials have been used as antimicrobial agents in consumer products, including home purification systems as antimicrobial agents, their potential for disinfection or microbial control in system level water treatment has not been carefully evaluated. Their paper reviews the antimicrobial mechanisms of several nanoparticles, discusses their merits, limitations and applicability for water disinfection and biofouling control, and highlights research needs to utilize novel nanomaterials for water treatment applications [4].

Antimicrobial properties of chitosan/poly (vinyl alcohol) films containing ZnO nanoparticles and plasticizers were studied by a team of Brazilians researcher (Denice S. Vicentini, Arthur Smania Jr., Mauro C.M. Laranjeira) from Santa Catarina University (2008-2009). In their study ZnO nanoparticles were prepared by the Pechini method from a polyester by reacting citric acid with ethylene glycol in which the metal ions are dissolved, and incorporated into blend films of chitosan (CS) and poly (vinyl alcohol) (PVA) with different concentrations of polyoxyethylene sorbitan monooleate, Tween 80 (T80).

The prepared films were characterized by infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), swelling degree, degradation of films in Hank's solution and the mechanical properties [5]. Besides these characterizations, the antibacterial activity of the films was tested, and the films containing ZnO nanoparticles showed antibacterial activity toward the bacterial species *Staphylococcus aureus*. The observed antibacterial activity in the composite films prepared in this work suggests that they may be used as hydrophilic wound and burn dressings.

In addition, chitosan was studied in [6]. Novel chitosan/Ag/ZnO (CS/Ag/ZnO) blend films were prepared via a new method of sol-cast transformation. The blend films were characterized by UV-vis absorption spectroscopy (UV–vis), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Energy Dispersive X-Ray Fluorescence Spectrometry (EDX). The results revealed that ZnO and Ag nanoparticles (NPs) with spherical and granular morphology had uniform distribution within chitosan polymer. The product had excellent antimicrobial activities against *B. subtilis*, *E. coli, S. aureus, Penicillium, Aspergillus, Rhizopus* and yeast. And CS/Ag/ZnO blend films had higher antimicrobial activities than CS/Ag and CS/ZnO blend films. Moreover, the blend films almost maintained the initial colour of chitosan, which have potential application as antibacterial materials [6].

"Antibacterial activity of ZnO nanoparticles prepared via non-hydrolytic solution route" was published in 2010 by some Koreans author (Rizwan Wahab, Amrita Mishra, Soon-Il Yun, Young-Soon Kim, Hyung-Shik Shin) from Chonbuk National University, Jeonju, South Korea. The antibacterial activity of ZnO nanoparticles has been investigated and presented in that paper. Nanoparticles were prepared via non-hydrolytic solution process using zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and aniline ($C_6H_5NH_2$) in 6 h refluxing at 65°C (figure 2).

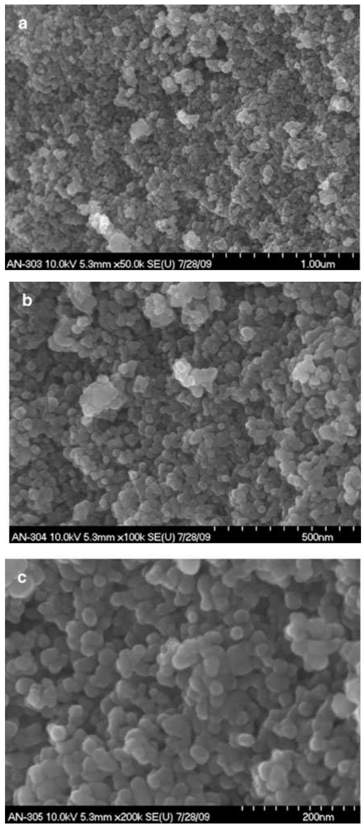

Figure 2. FESEM images ZnO – NPs; (a,b) show the low magnification images, whereas (c) shows the high magnification image [Rizwan W. et col.]

In the presence of four pathogens such as *Staphylococcus aureus*, *Escherichia coli*, *Salmonella typhimurium*, and *Klebsiella pneumoniae*, the antibacterial study of zinc oxide nanoparticles were observed. The antibacterial activity of ZnO nanoparticles (ZnO-NPs) were studied by spectroscopic method taking different concentrations (5–45 μg/ml) of ZnO-NPs. Their investigation revealed that the lowest concentration of ZnO-NPs solution inhibiting the growth of microbial strain is found to be 5 μg/ml for *K. pneumoniae*, whereas for *E. coli*, *S. aureus*, and *S. typhimurium*, it was calculated to be 15 μg/ml. The diameter of each ZnO-NPs lies between 20 and 30 nm as observed from FESEM and transmission electron microscopy images. The composition of synthesized material was analyzed by the Fourier transform infrared spectroscopy, and it shows the band of ZnO at 441 cm^{-1}. Additionally, based on morphological and chemical observations, the chemical reaction mechanism of ZnO-NPs was also proposed [7].

S. L. Patil, S. G. Pawar, A. T. Mane, M. A. Chougule and V. B. Patil, researcher from Materials Research Laboratory, School of Physical Sciences, Solapur University, Maharashtra, India, published in 2010 "Nanocrystalline ZnO thin films: optoelectronic and gas sensing properties". They deposited nanocrystalline Zinc oxide thin films by sol–gel spin coating technique and then they analyzed before and after a suitable thermal annealing in order to test their applications in various reducing and oxidizing gases. ZnO thin films were highly sensitive and selective for NH_3 gas. The spectrophotometric and conductivity measurements have been performed in order to determine the optical and electrical properties of zinc oxide thin films [8]. The structure and the morphology of such material have been investigated by high resolution electron microscopy and small area electron diffraction. The average particle size was between 60–70 nm .

Lili He and colleagues have investigated the antifungal activities of ZnO nanoparticles against two important postharvest fruit diseases fungi: *B. cinerea* and *P. expansum*. The mode of action of ZnO nanoparticles on the growth of fungal hyphae was studied by scanning electron microscopy (SEM) and Raman spectroscopy [8]. In conclusion, ZnO nanoparticles at a concentration greater than 3 mmol l^{-1} can significant inhibit the development of *B. cinerea* and *P. expansum*. The nanoparticles studied were more effective against *P. expansum* than *B. cinerea*. Also the sizes of ZnO nanoparticles are very important and the nanoparticles with sizes of ~70 nm have significant antifungal properties against *B. cinerea* and *P. expansum* The data acquired from SEM and Raman spectroscopy indicate that there may exist different mechanisms of ZnO nanoparticles against the two different fungal species [9].

Sawai and Yoshikawa [10] conducted a quantitative evaluation on antibacterial activity of some metal oxide powders like ZnO, MgO and CaO. The most effective against *Staphylococcus aureus* was ZnO. Another study conducted by a team coordinate by Ken Hirota [11] has revealed the the antibacterial activity of a ZnO ceramics against Escherichia coli. As a very important conclusion is that using ZnO nanoparticles strongly inhibit the development of pathogenic microorganisms when it is used in small concentration.

Li and colleagues have investigated the durability of anti-bacterial activity of nano-ZnO functionalized cotton fabric to sweat. They have treated cotton fabrics at a concentration of 11 g/L ZnO and padded them to 100% wet pick-up. The durability of anti-bacterial activity of the finished fabric in alkaline, acidic and inorganic salt artificial sweat solution has been evaluated. Results showed better salt and alkaline resistances than acid resistances for the treated fabrics. A negative surface charge has been deduced for ZnO nanoparticles and illumination can increase anti-bacterial performance compared to normal conditions [12, 13].

Tetrapod-like nano-particle ZnO was also used for producing acrylic composite resin. ZnO nano-belts, nanowires, nanotubes and nanocages have been also produced by Pan et al. [14].

Xu and Cai [13] have grown ZnO nanorods on cotton fabric samples through the dip-pad-cure process. However, the control mechanism of nanorod growth has not been described. They have tried to cover the prepared nanorod with a super hydrophobic agent to produce a cotton fabric with super hydrophobic properties based on the Cassie and Baxter theory (equation 1)

$$\cos\theta = f_1 \cdot \cos\theta_S - f_2 \cdot \cos\theta_V , \qquad (1)$$

where

f_1 is the fraction of fluid area in contact with the substance

f_2 is the fraction of the fluid area in contact with air

θ indicates the contact angle at a surface composed of solid and air

θ_S and θ_V are the corresponding water contact angles on smooth solid surface and vapour surface.

The equation can be used for hydrophobic surfaces that trap air in the hollows of the rough surface and the liquid–air contact angle (θ_V) is 180º [13, 14, 15].

Emamifar, A., et al. [16] made studies on nanocomposite LDPE films including Ag or ZnO by melt mixing in a twin-screw extruder. The film was obtained from LDPE resin pellets and ZnO particle powder with an average diameter of about 70 nm. They studied the materials obtained on fresh orange juice trying to establish the shelf life. The results show that the packages containing the nanomaterials prolonged the shelf life of orange juice up to 28 days without pasteurization or a sterilization of the product. For this objective, the team observed two microbial parameters: yeast and moulds count and total aerobic bacteria in orange juice. To complete the study a sensorial study was also conducted. The shelf life of fresh orange juice was prolonged without any negative effects on sensorial parameters.

3. Conclusions

These results suggest that ZnO nanoparticles could be used as antifungal and antibacterial agents. Further studies are needed to develop new types of nanoparticles and to investigate the feasibility of incorporating ZnO nanoparticles into films, coatings and other packaging materials in order not only to increase the barrier properties of packaging materials but also to protect the food packed against microbial spoilage during the shelf life. For food industry another research direction is replacing the use of high temperatures (pasteurization or sterilization) with nano-structures. This nanostructures can be use in the composition of filters which are capable to retain the microorganisms before packaging. Furthermore, such a treatment would improve energy efficiency of dairies or juices factories, improving the shelf life and the quality of products by a minimal processing of the raw material.

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