Synthesis of nanometric novel metal based surfactants and evaluation of their biocidal activity

Thesis submitted to

Chemistry Department, Ain shams University

in order to fulfill the requirements for the academic degree
PhD. in chemistry

Thesis presented

by

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Day of promotion:

2012

Acknowledgement

All praises and thanks are to Allah, the Lord of the world, the most Beneficent, the most kind for helping me to finish this work.

I feel grateful to a number of people who supported me to carry out this work. First and foremost, my heartily deep thanks, gratitude and pleasure to ***Prof. Dr. M. A. Mekewi*** *for his encouragement, kind support, his invaluable technical and leader advice, suggestions, discussions and guidance which a real support to complete this thesis.*

Deepest gratefulness and indebtedness to ***Dr. A. M. Badawi*** *professor in Petroleum Research Institute, for his benevolent supervision as referee, enthusiastic attention, and kindly guidance throughout this work.*

I owe deepest thanks to my co-advisor ***Prof. Dr. Sahar Mostafa*** *professor in Petroleum Research Institute for supporting me during this work, her critical reading and discussions and also the useful suggestions to my thesis.*

Last but not least I wish to acknowledge ***my wife*** *for her patience and under-standing during the different stages of my work, whose immeasurable love and supports are always my source of power to overcome all difficulties. She spared no effort until this work comes to existence.*

Adel Elsayed Farrag

To my family and my wife

Abstract

- **Name:** Adel Elsayed Farrag.
- **Title:** Synthesis of nanometric novel metal based surfactants and evaluation of their biocidal activity

By nanoparticles coating on any material surface, mechanical, physical and chemical properties of this material can be modified, leading to creation of unique and new functions. For example, antibacterial, self-cleaning, hydrophobic properties and UV protection of some kinds of material substrates can be achieved through coating a substrate with thin layer of nanoparticles, e.g. ZnO or TiO_2 nanoparticles. This thesis aims to the synthesis and characterization of nanosized zinc oxide particles of different concentrations and various sizes that have highly active surface and provide substrate with added functionality such as antibacterial, hydrophobicity and self-cleaning properties. In the application field the durability of the coating agent is very important factor depends on the affinity of the coating agent or, in the case of polymer coatings, on how well the polymers can bind with the substrate surface. Theoretically, the chemical bond between the coating agent and the substrate surface is the best way to achieve durability.

In the present study, sol-gel based inorganic-organic hybrid polymers were modified/filled with ZnO nanoparticles and were applied to cellulosic cotton (100%) as the substrate surface. These modified inorganic-organic hybrid polymers were based on 3-glycidyloxypropyltrimethoxysilane (GPTMS) which containing an epoxide ring.

ZnO nanoparticles sol has long stability for further processing. Complete coating ZnO/GPTMS sols prepared in this work were stable for several hours which is also sufficient for an industrial application. The most important results are:

- The antibacterial performance of these sol-gel derived hybrid materials was investigated against Gram-negative bacterium *Escherichia coli DSMZ 498* and Gram-positive *Micrococcus lutues ATCC 9341*. The effect of particle size and concentration on the antibacterial performance is examined. Bacteriological tests such as Zone of inhibition test, AATTC Test Method 100-200 and Tetrazolium/formazan test (TTC) were performed in nutrient agar media on solid agar plates and in liquid broth systems using different concentrations and different particle size of ZnO nanoparticles. In this part of thesis a lot of experiments were carried out to be able to understand the ZnO nanoparticle action as antibacterial

agent. This study showed the enhanced antibacterial activity of different concentration and different particle sizes of ZnO nanoparticles against a Gram-negative bacterium and a Gram–positive *Micrococcus lutues* in repeated experiments. This demonstrated that the antibacterial activity of ZnO nanoparticles increases with increasing the concentration of ZnO nanoparticles and also with decreasing the particle size of ZnO nanoparticles.

- Hydrophilic cellulosic fabrics pretreated with ZnO-containing hybrid polymers surfactants were made superhydrophobic after surface hydrophobization with stearic acid. Drop penetration time (TEGEWA test) and contact angle for cotton fabrics before and after treatment with stearic acid as hydrophobic additive were examined. For the cellulosic fabrics treated with stearic acid only, the water contact angle on the fabric surface remained lower than 50°, treatment with ZnO nanoparticle only did not change the hydrophilic surface of cellulosic fabrics used. However, for the fabrics treated with both inorganic-organic hybrid polymers (GPTMS) filled with ZnO nanoparticle and stearic acid, a contact angle higher than 150° can be obtained.
- Photocatalytic degradation of methylene blue by different ZnO nanoparticles concentrations was also studied. Self-cleaning properties of different ZnO concentrations/GPTMS coated fabrics was also investigated. Photocatalytic activity of ZnO nanoparticles was evaluated in normal laboratory environment, under dark condition and after UV-irradiation.

  Photocatalytic activity of fabrics coated with different ZnO concentrations within the coating layer was evaluated.
- The effectiveness of the novel coating as UV-protection was determined by UV-Vis spectroscopy and by evaluation of the ultraviolet protection factor (UPF). The influences of the coating for some general textile properties e.g. tensile strength, elongation, air permeability, and degree of whiteness, wear-resistance, stiffness as well as the durability of the treatments were investigated.

The use of hybrid polymers modified with the nanometric novel ZnO is working as polymeric surfactant and is therefore a promising approach for the development of the biocidal activity. The inorganic UV-absorber ZnO is highly stable against degradation and it is non-toxic. Literature discusses various (active) species and processes responsible for the antibacterial action of ZnO. Therefore a particular attention is paid to investigate the

possible interaction between the nanoparticles and bacteria. The sol-gel approach used here for the preparation of the coating polymeric surfactant materials guarantees a simple processing easily transferred to textile industry as an application example for testing this biocid nanometric ZnO metal. Furthermore the principles of sol-gel technique allow combining additional properties in a single coating material e.g. abrastion resistance, antibacterial activity, hydrophobic and even self-cleaning properties.

Key Words:

Biocides- ZnO nanoparticles- cellulosic fabrics- self cleaning-photocatalytic- UV protection Nanotechnology-sol gel technique.

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Chapter 1

1. Introduction

1.1. Nanotechnology

Nanotechnology is an emerging area that involves the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanoscale. Also fundamental understanding of physical properties and phenomena.

Nanotechnology is an innovative tool of fabricating materials smaller than 100 nanometers (one nanometer = 10^{-9} meter) [1]. There are different approaches for classification of nanomaterials such as dimension (1, 2 or 3 dimensions < 100 nm), phase composition (single phase, multi-phase solids or systems) as well as manufacturing process (gas phase or liquid phase reaction and mechanical procedures) [1, 3, 4].

The main classes of nanoscale structures are: nanoparticles, e.g. nano metal oxides, nano wire or tubes e.g. carbon nano tubes, nano layers, and nanopores, e.g. aerogel. Both the top-down and bottom-up processes can be used for manufacturing nanostructures, as shown in Figure 1.

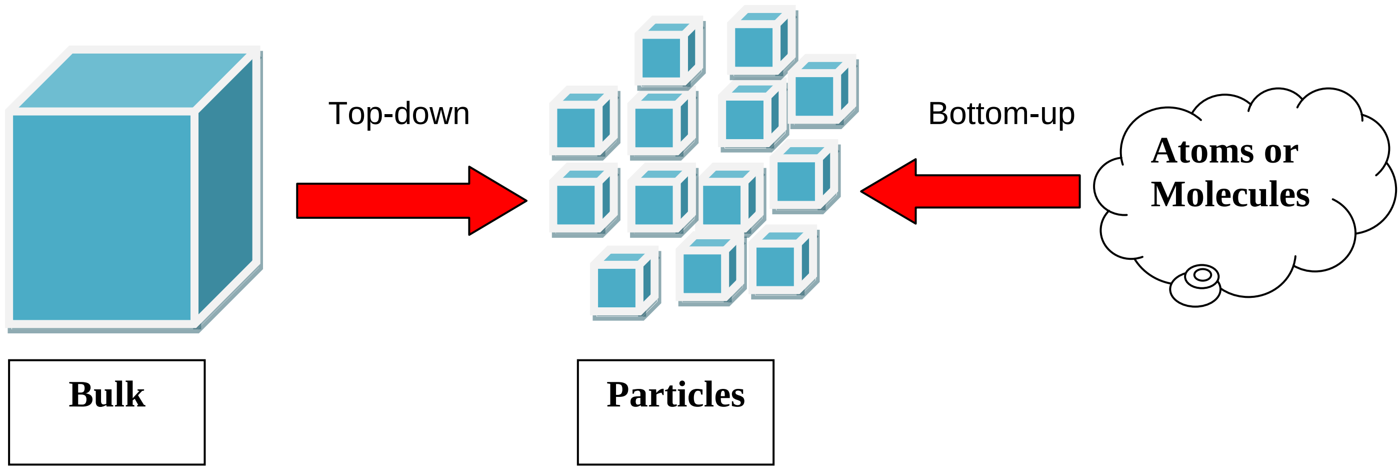

Figure 1: Two basic approaches to nanoparticles production: top-down (from left to right), and bottom-up (from right to lifte) [5]

Inorganic-based nano-structured materials can be categorized in two main groups namely: **i)** inorganic nanoparticles and their nanocomposites, e.g. TiO_2, Al_2O_3, ZnO, Ag, Cu nanoparticles, carbon nano tubes, nano layer clay and their nano composites and **ii)** inorganic nano-structured loaded organic carriers, e.g. cyclodextrin loaded with or nano- and micro- capsules having inorganic nanoparticles [6].

Recently, nanotechnology has become one of the most important emerging technologies in the textile industry for many reasons such as: more effective, less water/energy/chemicals consumption and cost, less changes to physico-mechanical properties of the treated textiles, better quality, functionality and durability of important properties, and the most important is less environmental impacts [4].

1.2. Nanotechnology Applications:

As the use of high performance materials and the increasing concern over environmental and ecological issues have grown, the urgent need for innovative technologies, e.g. nanotechnology, to impart the demanded functional properties and to cope with the need for revolutionary material products to face the great challenges in the global market without adversely affecting the environment has grown accordingly.

The imparted functional properties of the products are determined by: type of substrate, coating formulation, coating technique, available equipments, and performance requirements as well as economical and ecological aspects.

The wave of nanotechnology has shown a great potential in textile coating to improve existing substrate performances as well as to develop and impart extraordinary functions such as antimicrobial, UV protection properties, oil and water repellency, maintaining fabric breathability, flam-retardant functionality and self cleaning properties [1].

1.2.1. UV protection

Over exposure to UV radiation (Table 1), especially UV-B (280-320 nm) can cause premature ageing and sunburn of the skin as well as degradation of textile materials [7]. Therefore there is a great demand for the UV-protection substrate materials. The enhancement in UV-protection functionality depends on nature of textile fibres, fabric construction, dyeing and coating conditions, using of certain

additives such as UV-absorbers and brightening agents, as well as laundering conditions of the garments [8]. Reducing the exposure time to UV-radiation along with using protective clothes with high UPF (ultraviolet protection factor) values in addition to sunscreens are the main options of protection [9].
Table 1 shows the characteristics of solar radiation striking the earth's surface.

Table 1: Spectrum of the sun light

Spectrum of the Sunlight	**Wave length range [nm]**	**Fraction of the total energy [%]**	**Energy [Watt/m^2]**
UV-A UV-B UV-C	320-400 280-320 200-280	3.9 0.4 0	44 4 -
visible light	400-800	51.8	580
infrared	800-3000	43.9	492

Nano-structured materials based on ZnO-nanoparticles (having some advantages such as lower cost, white appearance, UV-blocking property and not harmful) can be used to impart outstanding UV-blocking property to the finished textiles [10].
When straight light falls onto a textile, part of the radiation is reflected, the material absorbs another part and the remainder transmitted through it as shown in Figure 2.

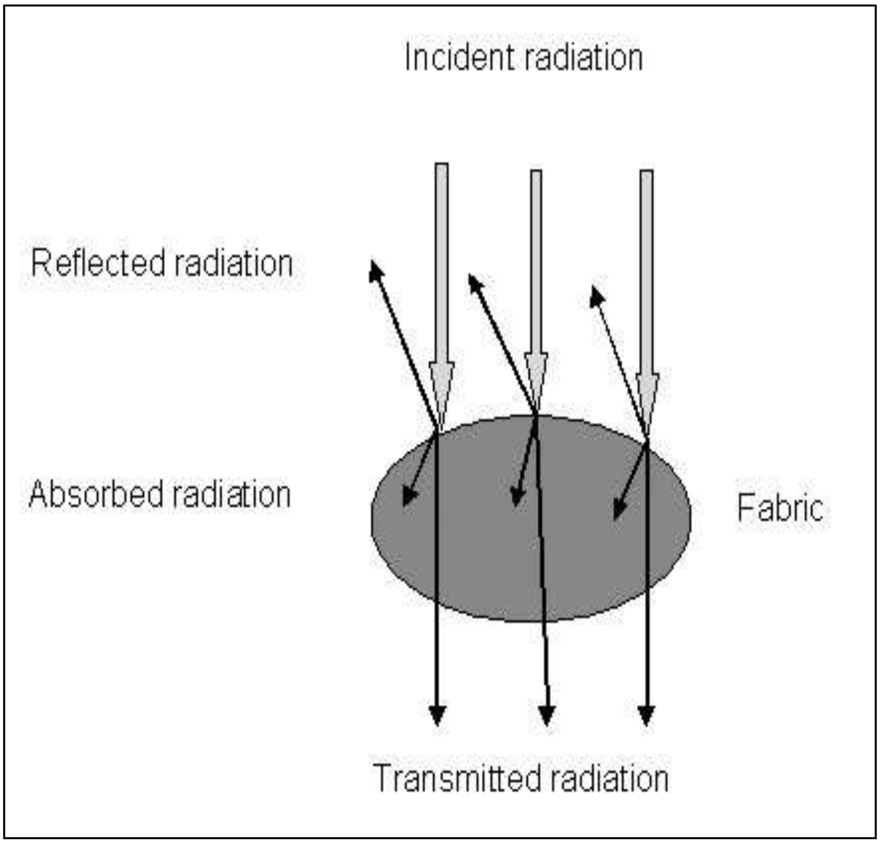

Figure 2: Radiation irradiating a textile surface

1.2.1.1. Evaluation of UV protection

UPF is the abbreviation of the ultraviolet protection factor. It indicates how much longer a person wearing the textile can stay in the sun before the start of skin reddening occurs compared to an unprotected person [11-13]. UPF has been adopted to create awareness among the end users of the negative impacts and effects of UV-radiation. The UV protection factor is determined by using the following equation[11, 12].

$$UPF = \frac{\sum_{\lambda = 280\,nm}^{400\,nm} E_\lambda \, S_\lambda \, \Delta\lambda}{\sum_{\lambda = 280\,nm}^{400\,nm} E_\lambda \, S_\lambda \, T_\lambda \, \Delta\lambda}$$

where:

E(λ) = the solar irradiance [W m^{-2} nm^{-1}],

S(λ) = the erythema action spectrum,describing the harmfulness of the different wavelengths,