

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

Adel El Sayed Farrag Mansour

First referee: **Prof. Dr. M. A. Mekewi**

Second referee: **Prof. Dr. A. M. Badawy**

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 TiO₂ 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 lutes* 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 lutes* 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. abrasion 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.

Contents

Contents	vii
1. Introduction	1
1.1. Nanotechnology	1
1.2. Nanotechnology Applications:.....	2
1.2.1. UV protection.....	2
1.2.2. Antibacterial activity.....	5
1.2.3. Water repellent	7
1.2.4. Photocatalytic activity	9
1.2.5. Nano-sol coatings.....	12
1.3. Polymeric Surfactants:	13
1.3.1. Phenolic polymers	13
1.3.2. Alkyd and related polymers	14
1.3. 3. Vinyl type polymers	14
1.3.4. Alkylene oxides block copolymers.....	14
1.4. Literature overview.....	15
1.4.1. Why Nano?.....	15
1.4.2. Production Methods	16
1.4.3. Bottom-up approaches	17
1.4.4. Sol-gel process.....	18
1.5.3. Introduction to the status of research about ZnO	20
1.5.4. GPTMS (3-Glycidoxypropyl)trimethoxysilane	22
2. Experimental part	24
2. 1. Chemicals and materials.....	24
2. 1.1. Textile fabrics	24
2. 1.2. Chemicals.....	24
2. 1.3. Test organism.....	25
2. 1.4. Preparation of microorganisms.....	25
2.2. Preparation methods.....	26

2.2.1. Preparation of ZnO nanoparticles.....	26
2.2.2. Preparation of GPTMS-sol	28
2.2.3. Preparation and application of GPTMS-ZnO-sol	29
2.2.4. Stearic acid modification of fabrics coated GPTMS-ZnO composites	31
2.2.5. Antibacterial properties study	32
2.2.6. Wettability measurements	35
2.2.7. Photocatalytic activity of dyestuff degradation.....	35
2.2.8. Further investigation methods/textile parameter.....	37
3. Results and discussion	41
3.1. ZnO nanoparticles preparation and investigation	41
3.1.1. ZnO nanoparticles for textile coating	41
3.1.2. ATR-FTIR-spectroscopic analysis	52
3.1.3. SEM investigation	53
3.2. ZnO nanoparticles as antibacterial coat for textile.....	58
3.2.1. Evaluation of ZnO-nano coated fabrics for antibacterial activity	59
3.2.2. ZnO sol labeled with FITC	66
3.3. Superhydrophobic cellulosic fabrics prepared by sol-gel coating of ZnO	73
3.3.1. Preview	73
3.3.2. Surface topography of cellulosic fabrics	75
3.3.3. Hydrophobic coatings	77
3.3.4. Non-wetting coatings	79
3.3.5. SEM investigation	80
3.4. Photocatalytic activity of ZnO nanoparticles.....	81
3.4.1. Photocatalytic degradation of methylene blue by of ZnO nanoparticles .	81
3.4.2. Photocatalytic activity of ZnO nanoparticles coated fabrics	86
3.5. ZnO nanoparticles as UV-protection finish for textile.....	88
3.5.1. Effect of ZnO-sol on the performance properties of the fabrics.....	92
4. Conclusion.....	96
5. Appendix.....	99
5.1. Abbreviations.....	99
6. References	100

List of Figures

Figure 1: Two basic approaches to nanoparticles production: top-down (from left to right), and bottom-up (from right to left)	1
Figure 2: Radiation in contact with textile surface	4
Figure 3: Schematic diagram comparing the actions of a man-made photocatalyst (Nano-TiO ₂) with a natural one (chlorophyll).....	10
Figure 4: schematic illustration of photocatalysis mechanism	11
Figure 5: Some possibilities of substrate functionalisation by modified nanosol.....	12
Figure 6: schematic illustration of the relation between the particle size and the corresponding specific surface area.....	16
Figure 7: Production of nanoparticles using top-down method.....	16
Figure 8: Production of nanoparticle using bottom-up method.....	17
Figure 9: Sol-gel technique.....	18
Figure 10: DLS instrument used for measuring ZnO particle sizes.....	28
Figure 11: Chemical structure of the GPTMS	28
Figure 12: Hydrolysis process of the GPTMS polymer.....	29
Figure 13: Inorganic-organic hybrid polymer modified with ZnO sol.....	29
Figure 14: Pad-dry-cure method.....	31
Figure 15: Mechanism of the tetrazolium/formazan system.....	34
Figure 16: Chemical structure of methylen blue (MB)	36
Figure 17: Photochemical reactor (Model RPR-100).	37
Figure 18: Unit structure of cationic and anionic polyelectrolyte	38
Figure 19: Image of ZnO nanoparticle of different concentrations taken certain weeks after synthesis	42
Figure 20: DLS measurements of different ZnO nanoparticle concentrationsError! Bookmark not defined.	
Figure 21: DLS measurements of different ZnO particle sizes	47
Figure 22: Stability of different ZnO /GPTMS sols according to turbidimetric measurements (NTU...Normal-Turbidity-Unit).	49
Figure 23: Assumed structure of fabric-finished with ZnO/GPTMS sol.....	51
Figure 24: ATR-FTIR- Spectroscopy for blank and coated cotton fabrics.....	52
Figure 25: SEM micrographs of (1) cotton fabrics treated with different ZnO nanoparticle concentrations,	55
Figure 26: SEM micrographs of: (1) cotton fabrics and treated with different ZnO particle sizes.....	57
Figure 27: The disc diffusion test of different concentrations of ZnO nanoparticles for the growth inhibition. (a) <i>M.lutues</i> and (b) <i>E.coli</i>	60
Figure 28: The disc diffusion test of different ZnO particle sizes for the growth inhibition of: (a) <i>M.lutues</i> and (b) <i>E.coli</i>	61

Figure 29: Reduction rate of the cotton 100% fabric treated with ZnO (10%, 30 nm) in GPTMS sol against <i>E.coli</i> & <i>M.lutues</i>	63
Figure 30: Reduction rate of the cotton fabric treated with different particle sizes of ZnO-sol.....	64
Figure 31: the change of formazan colour.....	65
Figure 32: Absorbance of formazan for cotton 100% fabrics coated with different ZnO nanoparticle concentrations in GPTMS-sol.....	66
Figure 33: Cell imaging with FITC-ZnO nanoparticles	69
Figure 34: SEM micrographs ZnO and <i>M.lutues</i>	71
Figure 35: SEM micrographs ZnO with <i>E.coli</i>	72
Figure 36: Schematic diagram of ZnO in GPTMS-sol preparation and coating process to get hydrophobic cellulosic fabric surface.....	74
Figure 37: SEM micrographs of: (a) blank cotton fabric, (b) cotton fabric treated with ZnO/GPTMS (31nm) and stearic acid, (c) cotton fabric treated with ZnO/GPTMS (650 nm) and stearic acid	76
Figure 38: Results of a Martindale test investigating the durable non-wetting coating of the treated after 20.000 scrubbing cycles.	79
Figure 39: SEM micrographs of: (a) cotton fabric treated with GPTMS-ZnO (10%-30 nm)-stearic acid before Martindale test, and (b) cotton fabric treated with GPTMS-ZnO (10%-30 nm)-stearic acid after 20.000 scrubbing cycles.	80
Figure 40: Discoloration efficiency of different concentrations of ZnO nanoparticles under different conditions.	82
Figure 41: UV-Vis absorption spectra of decolourization of methylen blue (20 mg/l) by different concentrations of ZnO (30nm) nanoparticles	83
Figure 42: UV-Vis spectra of photocatalytic decolourization of MB dye by using different concentrations of ZnO nanoparticles (0,1, 0,5 and 1 g/l) after 1h in (a) normal laboratory environment, and (b) dark.	84
Figure 43: Decolorization of MB dye on cotton fabric surface.....	87
Figure 44: UPF value of Cotton and CO/PET substrates treated with different conditions.	90
Figure 45: Results of a Martindale test investigating the wear resistance of the ZnO in GPTMS-sol (10%) treated samples after 20.000 scrubbing cycles	94
Figure 46: SEM of a Martindale test investigating the wear resistance of the ZnO in GPTMS-sol (10%) treated samples after 20.000 scrubbing cycles compared to the untreated sample.....	95

List of Tables

Table 1: Spectrum of the sun light	3
Table 2: Preparation of higher ZnO nanoparticle concentrations	27
Table 3: Percentage of ZnO in GPTMS to get different ZnO concentrations	30
Table 4: Specifications of the textiles used for all the experiments.	24
Table 5: Preparation and characterization of higher ZnO nanoparticle concentrations	42
Table 6: ZnO nanoparticles prepared in different solvents.....	47
Table 7: ZnO nanoparticle content on fabric treated with different ZnO concentrations	50
Table 8: Drop penetration time (TEGEWA test) and contact angle for cellulosic fabrics before and after treatment with stearic acid as hydrophobic additive [after 2 washing cycles].....	78
Table 9: Effect of increasing the concentration of ZnO-sol on the UV-protection properties of cotton and cotton blend fabric samples after treatment.	89
Table 10: Effect of increasing the concentration of ZnO-sol on the UV-protection properties of cotton and cotton blend fabric samples after treatment and 5 laundering cycles.	91
Table 11: Effect of increasing the concentration of ZnO-sol on some performance properties of cotton and cotton blend fabric samples.....	93

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.

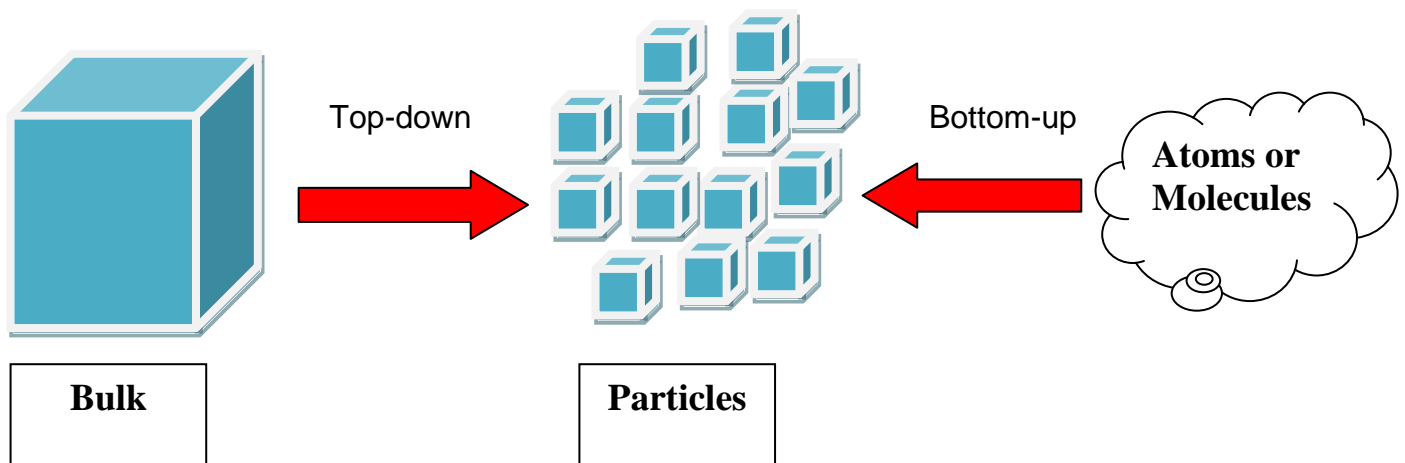


Figure 1: Two basic approaches to nanoparticles production: top-down (from left to right), and bottom-up (from right to left) ⁵

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	320-400	3.9	44
UV-B	280-320	0.4	4
UV-C	200-280	0	-
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.

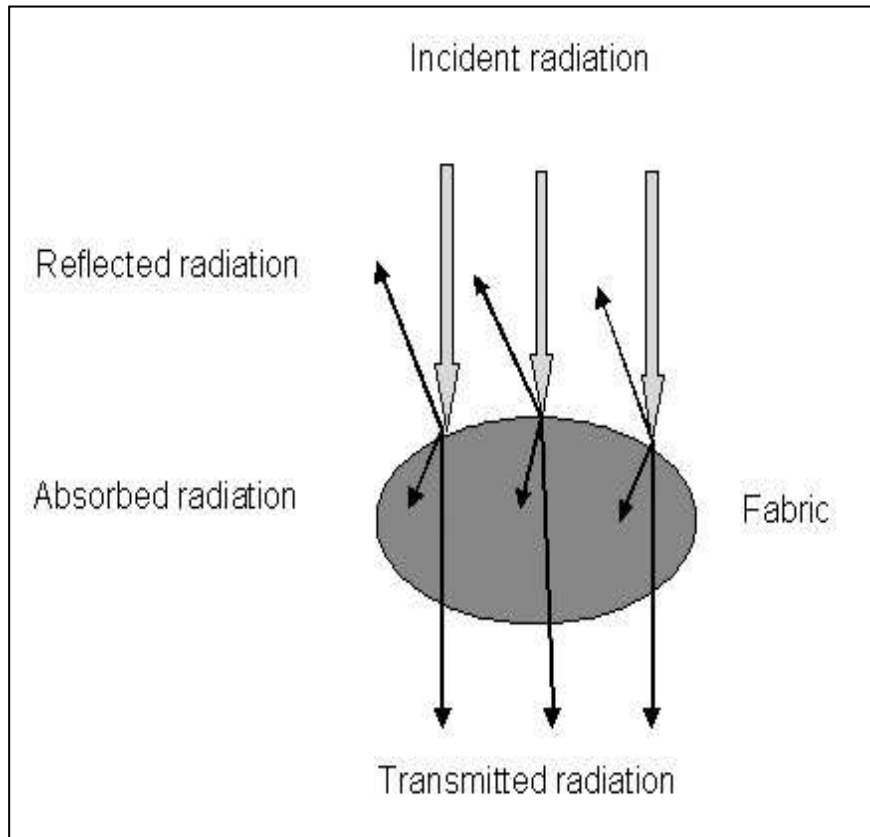


Figure 2: Radiation irradiating a textile surface

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 person¹¹⁻¹³. 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}.

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

where:

$E(\lambda)$ = the solar irradiance [$\text{W m}^{-2} \text{ nm}^{-1}$],

$S(\lambda)$ = the erythema action spectrum, describing the harmfulness of the different wavelengths,