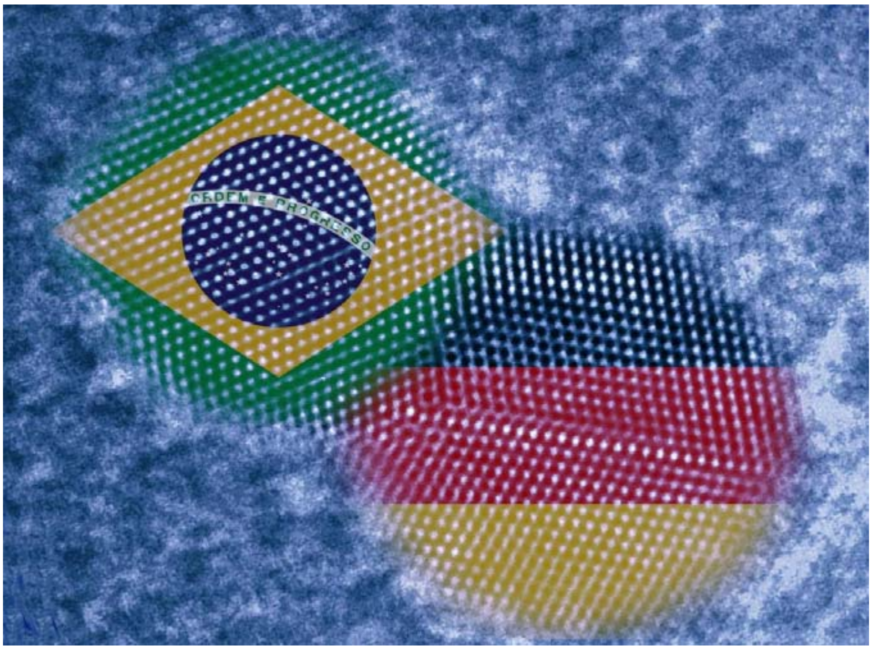

Proceedings

Brazilian - German Workshop on Nanotechnology and Applications

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Preface

It is my pleasure to present to you the Proceedings of the Brazilian-German Workshop on Nanotechnology and Applications which was held on October, 7 and 8, 2009, in Belo Horizonte, Minas Gerais, Brazil.

Nanotechnology provides useful solutions in fields of science and technology ranging from energy, environment, biomedicine and optics to electronics, among others. This workshop aimed at strengthening the Brazilian-German cooperation in nanotechnology and its applications. Our intention has been to bring together scientists and technologists from different communities to communicate and to identify prospective lines of future cooperations.

This Workshop Proceedings contains articles based on the ten talks given during the workshop on topics such as carbon nanomaterials, optics, electronics, as well as nanotechnology for sensors and for magnetic and biomedical applications.

The German partners from Karlsruhe Institute of Technology, Fraunhofer Institute ENAS, sarastro and the INM were very positive about the outcome of this workshop and the pathways for several future cooperations were laid.

We thank all those who contributed to the successful workshop: Dr. Peter William de Oliveira (INM) initiated this workshop already several years ago. Prof. Dr. Alfredo Gontijo de Oliveira (CETEC / UFMG) was the driving spirit on the Brazilian side of the workshop. Dr. Mario Quilitz succeeded in compiling this Workshop Proceedings.

We also express our gratitude to the sponsors: The workshop and the Proceeding volume were supported by the German Federal Ministry of Education and Science (BMBF), the state government of Minas Gerais (Governo de Minas) and the Brazilian Ministry of Science and Technology (MCT).

And last but not least the success of the workshop was also due to the active role of the attendees.

I am optimistic that this workshop will act as a seed, not only for another Brazilian-German workshop on Nanotechnology and Applications in Germany but for many fruitful long term cooperations between the scientific communities of both countries.

E. Arzt

Prof. Dr. Eduard Arzt
Scientific Director and Chairman of the INM – Leibniz Institute for New Materials,
Saarbruecken, Germany

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Sílvia Stanisçuaski Guterres is a Professor of Pharmaceutical Technology in the College of Pharmacy at the Federal University of Rio Grande do Sul, Brazil, since 1989. She received her PhD in Pharmaceutical Nanotechnology from the University of Paris XI, France, in 1995 and nowadays she is an Associate II Professor, teaching pharmaceutical technology and cosmetology for undergraduate pharmacy students at College of Pharmacy and graduate students at the Programa de Pós-Graduação em Ciências Farmacêuticas (PPGCF/UFRGS – UFRGS Pharmaceutical Sciences Graduate Program), have advised more than 30 graduate students (master and Ph.D. levels) from 1997 to 2008. She is a National Council for Scientific and Technological Development (CNPq/Brazil) researcher and leader of the research group entitled *Nanostrucutured Systems for Drug Administration*. Her main research is focused on the development, physicochemical characterization and biological applications of innovative nanocarriers aiming at drug delivery via oral, cutaneous and parenteral routes. She is the director of one of the Brazilian National Nanotechnology Network, supported by the Brazilian Ministry of Science and Technology. She is the Coordinator of a collaborative project between France (Université de Paris-Sud, Prof. Elias Fattal) and Brazil (UFRGS) for Nanotechnolgy (CAPES/COFECUB 540-2005) supported by the Brazilian Ministry of Education. She has published more than 100 research papers and 4 book chapters. She is a member of the American Association of Pharmaceutical Scientists (AAPS), the Brazilian Chemical Society (SBQ), the Centro de Nanociência e Nanotecnologia (CNANO/UFRGS) and the Brazilian Association of Pharmaceutical Sciences (ABCF). She is member of the Editorial Board of the Journal of Drug Science and Technology.

Nanocapsule microagglomerates: innovative carriers to control the release of hydrophilic and lipophilic drugs

Adriana R. Pohlmann, Letícia Sias da Fonseca, Rodrigo Paulo Silveira, Alberto Marçal Deboni, Edilson Valmir Benvenutti, Tânia M. H. Costa, Sílvia S. Guterres

The objective of the work was to develop innovative microagglomerates of polymeric nanocapsules using silicon dioxide by encapsulating both lipophilic and hydrophilic drugs in the same formulation. Our hypothesis was based on an initial attack dose and a maintenance of drug concentration. To achieve our objective a hydrophilic and a lipophilic drug (sodium diclofenac and free acid diclofenac, respectively) have been used. The hydrophilic drug was incorporated in the silica, which was agglomerated with the lipophilic drug-loaded polymer nanocapsules. The formulations were characterized in terms of particle size and polydispersity (PCS and laser diffratometry), surface area (BET), drug quantification (UV), SEM analysis and in vitro drug release experiment. The powders showed physico-chemical properties compatible to an oral drug administration system. The in vitro release experiment clearly showed the ability of the nanocapsule microagglomerate to provide a burst release followed by a sustained profile. In this way, nanocapsule microagglomerates are innovative and versatile carriers useful to simultaneously deliver a hydrophilic and a lipophilic drug. This feature is especially promising in therapeutics when attack and maintenance doses are required.

Nanocapsule microagglomerates: innovative carriers to control the release of hydrophilic and lipophilic drugs

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1. Introduction

In pharmaceuticals, polymeric nanoparticles have been proposed as drug carriers to sustain drug release, increase drug selectivity and effectiveness, improve drug bioavailability, as well as decrease drug toxicity (Couvreur et al., 2002). The polymeric nanoparticles are named nanocapsules or nanospheres depending on their chemical composition. Nanocapsule contain a polymeric wall and an oil core (Jäger et al., 2007), while the nanoparticle is a polymeric matrix stabilized by surfactants (Pohlmann et al., 2007).

In order to improve the physico-chemical stability of drug-loaded polymeric nanoparticles, the spray-drying technique has been employed to dry colloidal suspensions (Guterres et al., 2000). Powders were obtained using colloidal silicon dioxide, as drying adjuvant (Müller et al., 2000; Pohlmann et al., 2002). In parallel, similar powders have been obtained by freeze-drying (Schaffazick et al., 2003). The particles showed spherical shape presenting nanoparticles at their surface. Those systems are able to carry lipophilic drugs encapsulated in the polymeric nanoparticles (Schaffazick et al., 2006).

The spray-drying technique has also been used to prepare organic-inorganic systems, in which the drug was dispersed in agglomerates of silica, the inorganic phase, and the polymeric nanoparticles were used as coating material (Beck et al., 2004). Those organic-inorganic systems were named nanoparticle-coated inorganic microparticles. Each type of those carriers encapsulates either a lipophilic or a hydrophilic drug in the nanoparticles or in the macropores of silica, respectively.

In this context, the goal of the present study was to develop innovative microagglomerates of polymeric nanocapsules using silicon dioxide by encapsulating both lipophilic and hydrophilic drugs in the same formulation. The rational of this approach is to have an initial attack dose and a maintenance of drug concentration. To achieve our objective a hydrophilic and a lipophilic drug (sodium diclofenac and free acid diclofenac, respectively) have been used. The hydrophilic drug was incorporated in the silica, which was agglomerated with the lipophilic drug-loaded polymer nanocapsules. To validate our hypothesis that those formulations are capable to simultaneously provide a burst and a sustained drug release, *in vitro* dissolution profiles were carried out.

2. Experimental

2.1 Preparation of diclofenac-loaded nanocapsules at sodium diclofenac-silica microagglomerates (DicOH-NC@DicONa-silica)

Diclofenac-loaded nanocapsules: Eudragit S100® (1.0 g), diclofenac (0.100 g), capric/caprylic triglyceride (3.0 mL), sorbitan monostearate (0.770 g) were dissolved in

acetone (250 mL). This solution was poured into an aqueous solution (530 mL) containing polysorbate 80 (0.770 g). After 10 min, the acetone was eliminated and the suspension concentrated by evaporation under reduced pressure to a final volume of 100 mL.
Sodium diclofenac-silica: 100 mL of aqueous solution containing 500 mg of sodium diclofenac were added to silica (3.0 g). After 10 min of stirring, the suspension was spray-dried (MSD 1.0, Lab Maq, Brazil) using the following conditions: feeding rate of 0.2 L h^{-1}, air flow rate of 500 N L h^{-1}, atomizing air pressure of 200 kPa, inlet temperature of 150 ± 1 ºC, outlet temperature of 95 ± 2 ºC and nozzle diameter of 1.0 mm.
Microagglomerates: Sodium diclofenac-silica microparticles (3.0 g) were dispersed in the diclofenac-loaded nanocapsule suspensions (100 mL) under magnetic stirring. After 3 min, the mixture was spray-dried using the same operational conditions above.

2.2 Physico-chemical characterization

The pH of suspensions was measured using a potentiometer. The particle size and polydispersity index of nanocapsules were determined by photon correlation spectroscopy (PCS) observing the scattered light at an angle of 90º (goniometer BI- 200M/2.0 version, Brookheaven Instruments, Holtsville, USA; BI9863 detection system; Laser He-Ne source 35mW, 127 model, λ=632.8 nm, Spectra Physics View, USA).
The mean diameter over the volume distribution (d4.3) and particle size distribution (*span*) of microagglomerates were determined using a Malvern Mastersizer 2000 laser diffraction instrument (Malvern Instruments, UK). The samples were dispersed in *iso*-octane, a non-solvent for the materials (n=3). The *span* values were calculated using Equation 1 (Chen and Davis, 2002).

$$span = \frac{d_{90} - d_{10}}{d_{50}} \qquad (1)$$

where d_{90}, d_{10} and d_{50} are the particle diameters determined respectively at the 90th, 50th and 10th percentile of the undersized particle distribution curve.

2.3 Morphological analyses

Scanning electron microscopy analysis were performed using a JEOL Scanning Microscope (JSM-5800, Tokyo, Japan) (20 kV) at 1,000x and 30,000x of magnification (Centro de Microscopia Eletrônica da UFRGS). Samples were analyzed after they have been sputtered with gold and carbon. Energy dispersive spectroscopy elemental analysis (EDS) was performed by a Noran detector using 20 kV and acquisition time of 100 s. The specific surface areas were determined by Brunauer-Emmett-Teller multipoint technique (BET) on a volumetric apparatus using nitrogen as probe. Homemade equipment with a vacuum line system employing a turbomolecular vacuum pump (Edwards *1.5 EXC 120) was used. The samples were previously degassed for 1 h under vacuum at 40 °C. The pressure measurements were made using a capillary Hg barometer and also an active Pirani gauge. The results were systematically compared with an alumina standard reference.

2.5 Drug content and encapsulation efficiencies

The drug was quantified by UV spectroscopy (UV-1601 PC spectrophotometer, Shimadzu, Japan) at 280 nm using a validated method according to the International Conference of Harmonization (1996). The encapsulation efficiency of each formulation was calculated by the correlation between the theoretical and the experimental sodium diclofenac concentrations and expressed as percentages.

2.6 Dissolution efficiency and in vitro *drug release studies*

Drug dissolution profiles were determined by dispersing an exact amount of each powder (equivalent to 0.003 g of drug) in 100 mL of different release media: phosphate buffer pH 1.2

or deionized water. The experiments were carried out at 37.0 ± 0.5 ºC under constant magnetic stirring. Aliquots (3 mL) were withdrawn at pre-determined time intervals and replaced by an equal volume of dissolution medium. The collected aliquots were filtered through a hydrophilic membrane (0.45 µm, Millipore®), and the drug quantified by UV spectroscopy at 280 nm, using the same method described above. Samples prepared without the drug were used as reference. Accuracy was validated by adding sodium diclofenac in the reference samples. Accuracy was 102 ± 4 %.

To compare the drug release profiles, dissolution efficiencies (*DE*) were calculated (Eq. 2).

$$DE = \frac{\int y \times dt}{y_{100} \times t} \times 100 \qquad (2)$$

where $\int y \times dt$ is the area under the dissolution curve up to a time t and $y100 \times t$ is the area of the rectangle described by 100% of drug dissolution at the same time.

3. Results and Discussion

3.1 Preparation and characterization of nanocapsules microagglomerates

The first step was to prepare the diclofenac-loaded polymeric nanocapsule suspension, which had pH of 4.5 ± 0.3, mean particle size of 267 ± 5 nm and polydispersion index lower than 0.2. The physico-chemical characteristics were in accordance with previously reported similar formulations (Beck et al., 2007).

The second step was to agglomerate nanocapsules and the sodium diclofenac-silica by spray-drying. Microagglomerates prepared using or not nanocapsules presented particle sizes and size distributions in the same range with span values below 1.6. SEM analysis at low magnification (Figure 1) showed that silica before and after agglomeration with nanocapsules presented spheroid-like shape, while the sample containing drug DicONa-silica and DicOH-NC@DicONa-silica showed collapsed form. All particles present rugged surfaces. At higher magnification, the photomicrographs showed the nanocapsules on the surface of NC@silica and of DicOH-NC@DicONa-silica, whereas silica and DicONa-silica had rugged surfaces. The nanoparticles observed on the surfaces of the microagglomerates presented mean diameter of 380 nm.

The surface area of the powders decreased after the agglomeration with nanocapsules. DicOH-NC@DicONa-silica and NC@silica showed values of 57 and 78 m^2 g^{-1} (r >0.98), while DicONa-silica and silica showed 164 and 232 m^2 g^{-1} (r = 0.99), respectively. The results can be explained by the decrease in the nitrogen accessibility to the micro and mesopores of the powders in the presence of polymeric nanocapsules as a consequence of the agglomeration process. Encapsulation efficiency values for DicONa-silica and for DicOH-NC@DicONa-silica were, respectively, 76 ± 1 % and 72 ± 1 %.

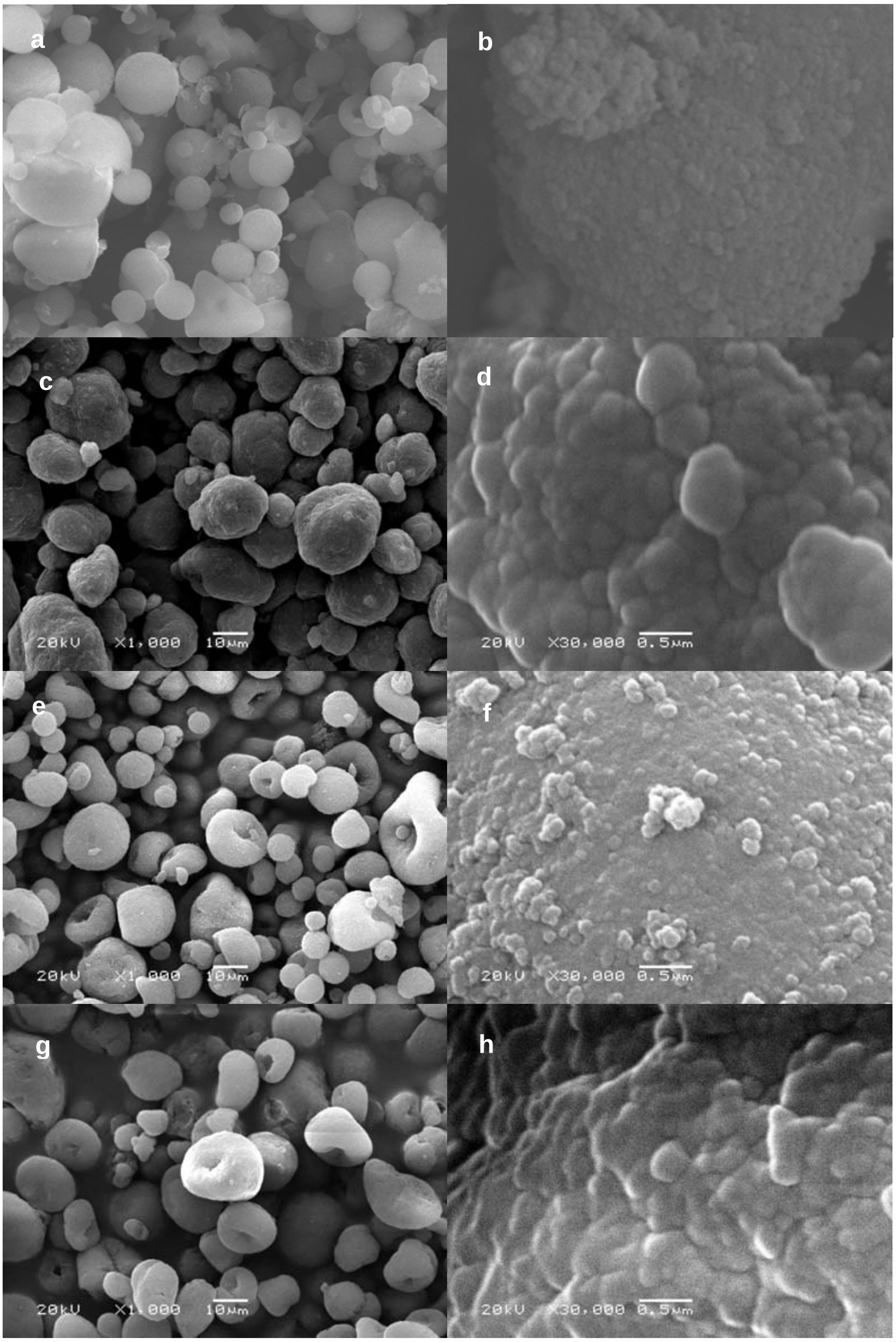

Fig. 1 SEM micrographs of silica at magnitudes of (a) 1,000x and (b) 30,000x; NC@silica at magnitudes of (c) 1,000x and (d) 30,000x; DicONa-silica at magnitudes of (e) 1,000x and (f) 30,000x; and DicOH-NC@DicONa-silica at magnitudes of (g) 1,000x and (h) 30,000x.

3.2 In vitro *drug release studies*

The release experiment was carried out in deionized water in order to verify if the coating material was able to control the release of diclofenac. In water, the pure drug dissolves 92 ±

3% in 5 min. The release profiles of DicONa-silica and DicOH-NC@DicONa-silica showed 101 ± 1 % and 63 ± 3 %, after 5 min, respectively (Figure 2). Within 10 and 60 min, the drug was gradually released from DicOH-NC@DicONa-silica 68 ± 1%. The experiment showed clearly the ability of the nanocapsule microagglomerate to provide a burst release followed by a sustained profile.

Since Eudragit S100®, a gastro-resistant polymer, is the wall of the nanocapsules in the microagglomerates (DicOH-NC@DicONa-silica) a release experiment was also carried out in pH 1.2 to verify the integrity of nanocapsules after the drying process and their ability in controlling the lipophilic drug release. DicONa-silica presented 19 ± 1% of drug released after 5 minutes, which decreased to less than 10%. The high surface area can explain the initial release and the low solubility of diclofenac at pH 1.2 by neutralization is responsible by the re-adsorption of the drug on the powder. DicOH-NC@DicONa-silica, after 5 min, released 3 ± 1% of the drug, which value remained constant within 60 min of experiment. The gastro-resistance was satisfactory and the new microagglomerates (DicOH-NC@DicONa-silica) showed good potential as drug delivery system.

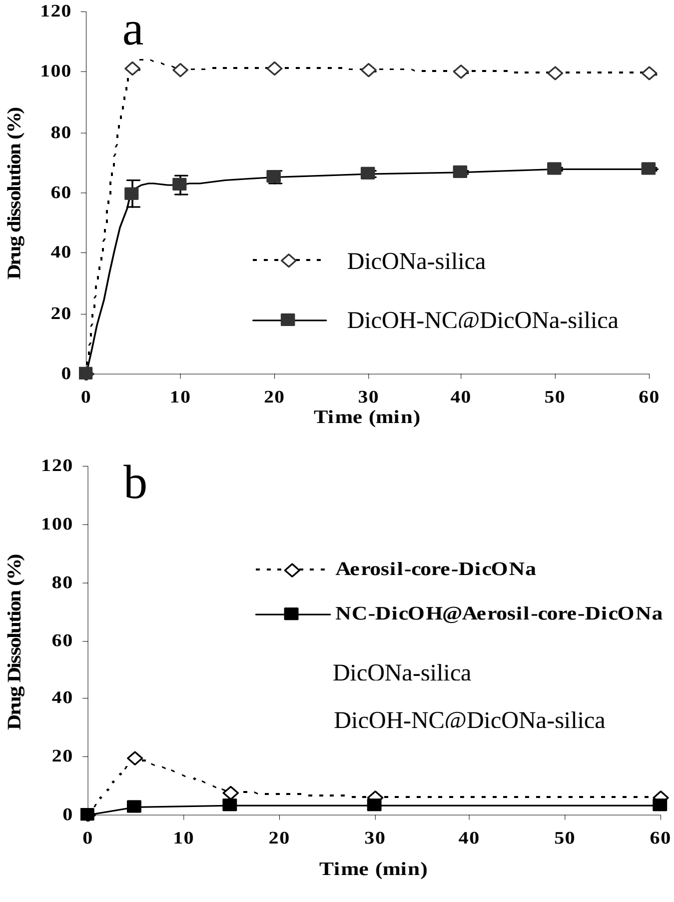

Fig. 2 Drug dissolution profiles from DicONa-silica and DicOH-NC@DicONa-silica: (a) in deionized water and (b) at pH 1.2.

4. Conclusion

The results proved that nanocapsule microaglomerates are versatile carriers to control the simultaneous release of hydrophilic and lipophilic drugs. This feature is especially useful in therapeutics when attack and maintenance doses are required. Further investigations are in progress to confirm the approach *in vivo*.

Acknowledgements

The authors thank Rede Nanocosméticos CNPq/MCT, CAPES, CNPq/Brasília/Brasil, FAPERGS/RS/Brazil, Centro de Microscopia Eletrônica-UFRGS and Dr. Maria Ines Ré from Instituto de Pesquisas Tecnológicas – São Paulo.

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Dr. med. Hanselmann was born 1963 in Ingelheim, Germany. Parallel to school he got the certification as a chemical technician. After school and military service, he studies medicine in Heidelberg, Frankfurt and at the University of Saarland in Germany. After study he worked at the Orthopedic- and Trauma-Department at the University of the Saarland. Parallel to his clinic work he leads a scientific group who worked in the field of molecular biology and biochemistry. His scientific work was focused on the fields of rheumatism, healing processes and sarcoma. 1998 he changed to the Department of Experimental Physics at the University and leads a scientific group who worked on the field of nanoanalytics of biomolecules. From 2000 to 2001 he becomes Chief technology officer in a biotechnological company in Luxemburg. Since 2002 he is CEO of the sarastro GmbH in Saarland, a company which worked in the field of chemical nanotechnology for medical, pharmaceutical, cosmetic and food industry.

The sarastro company
New materials and especially materials which combine different surface or volume properties in one material were from permanent growing importance to the industry and the manufacturers. The need to improve the quality of a product by a simple coating process or to reduce the process time by using the right material leads to an increasing demand for such high-tech materials. sarastro is one of the leading companies for the delivery, development and application of high-end materials used in the field of medicine, food, cosmetics, life science, hygiene and electronics. To guarantee best support to our costumers sarastro had established a quality management system according to DIN EN ISO 9001 : 2000 and DIN EN ISO 13485 : 2003.

The technology
sarastro´s technology based on so called organic/inorganic nanocomposite materials. By using such materials it is possible to change the surface or volume properties in many ways. For example, it is possible to establish functional surfaces like hydrophobic/oleophobic (water and oil repellent), antimicrobial, hydrophilic (antifogging or slippery), gas barrier, conductive printable inks or passive corrosion protection for electronic devices, by a simple coating process. sarastro materials show excellent adhesion, abrasion and chemical resistance, but beside these typical industry required properties sarastro materials are also biocompatible, dermal compatible or show blood compatibility.

New ways to improve surface hygiene by temporary coatings

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In Germany approximately 500,000 patients a year are infected in hospitals by hospital germs, so called nosocomial infections. About ten percent of these infections lead to death. At the end of the 80ies we recognize a range of about 1 to 2% of this types of infections in German hospitals. Until 2006 this rate increase up to 26%. The main cause for these developments is that more and more germs are becoming resistant against antibiotics. An important germ is the so called, Methicillin resistant staphylococcus aureus or MRSA. The central reason for this development is the uninhibited use of antibiotics, but also the immediate environment of the patient is not properly disinfected. These worse hygienic situation supports the risk of infections by contaminated surfaces and equipment. Beside this hospital specific problems, experts have recorded a growing number of germs with a high risk of infection or epidemic disease in our society like SARS, flu, HIV, to name just a few.

What is the answer to these worldwide growing problems, beside improvement of infection control and antibiotic usage?

Aim of this article is the demonstration that temporary antimicrobial coatings, based on organic/inorganic nano-composite materials can contribute to reduce the amount of germs at surfaces and herewith improve infection control in hospitals, public institutions and society.

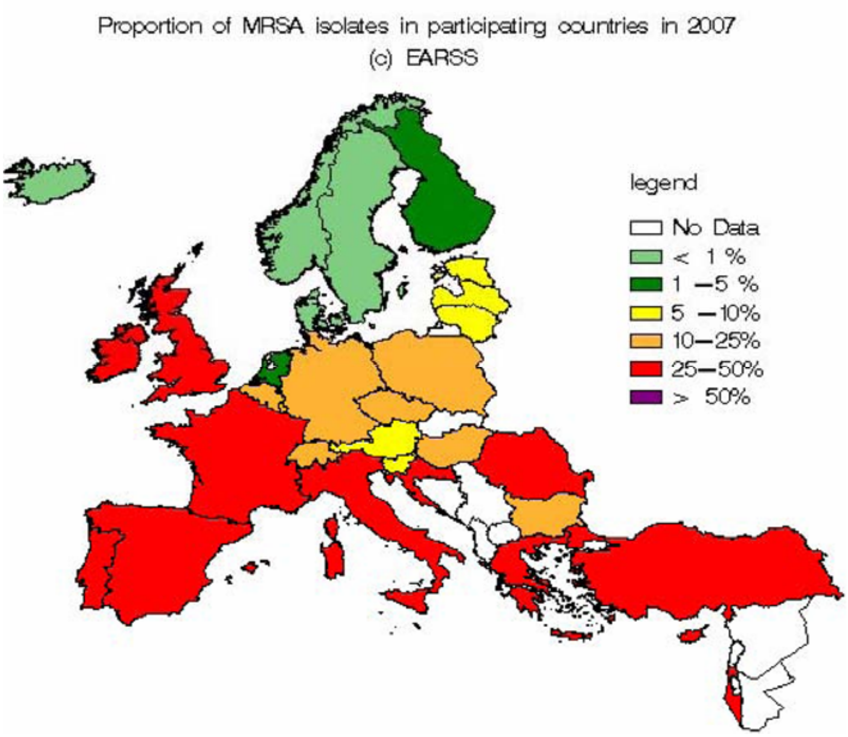


Fig. 1 Amount of MRSA infections in Europe
The different colors to mark the single countries at this figure describe the rate of infection by methicillin resistant staphylococcus aureus in Europe (EARSS), see legend. This overview shows clearly the importants to improve infection control and hygienic circumstances.

Temporary germicide materials, like lasting disinfectants

Although conventional germicides kill over 99% of these germs if used properly, they do not have a lasting effect. Once the germicide has evaporated, the surface, which has just been disinfected no longer, shows any antimicrobial effectiveness. The consequence: As the surfaces in the immediate environment of the patient are only disinfected once a day, this inevitably leads to a gap in hygiene, which allows germs to grow and to be transmitted. To overcome this problem it is necessary to close this hygienic gap by influence the surface in a way that germs can't survive.

Bacoban, developed by sarastro, is a completely new type of disinfectant, which combines a high antimicrobial effectiveness with long-lasting protection against recontamination. The solution has already been licensed for use as a disinfectant of medical products in clinics. It works as a long-lasting germicide – over a period of ten days. This has been proven over and over again in comprehensive laboratory tests as well as in clinical tests (e.g. Strasbourg University, Ministry of Health Luxembourg). At the same time, it has been possible to verify that Bacoban is absolutely safe for humans (tested in an FDA-certified laboratory). Furthermore, the long-term antimicrobial property of Bacoban® was successfully demonstrated in the ASTM tests and several clinical studies, performed and certified by the Fresenius Institute or responsible hygienists in hospitals and universities. The studies revealed that all tested bacteria and fungi (e.g. Staphylococcus aureus, Pseudomonas aeruginosa, E. coli, Aspergillus niger and Candida albicans) were completely destroyed within the first half hour, 10 days after having been applied to the disinfected surfaces, see below. Moreover, Bacoban displays long time effects (also 10 days) against viruses, such as Hepatitis B and C, flu, bird flu, Vaccinia, HIV,BVDV and several others (tested by an DVV, Germany society for prevention of virus disease) approved Laboratory).

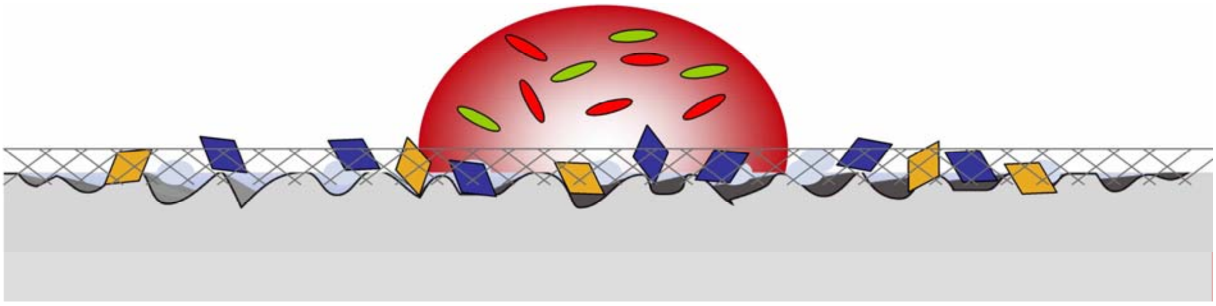
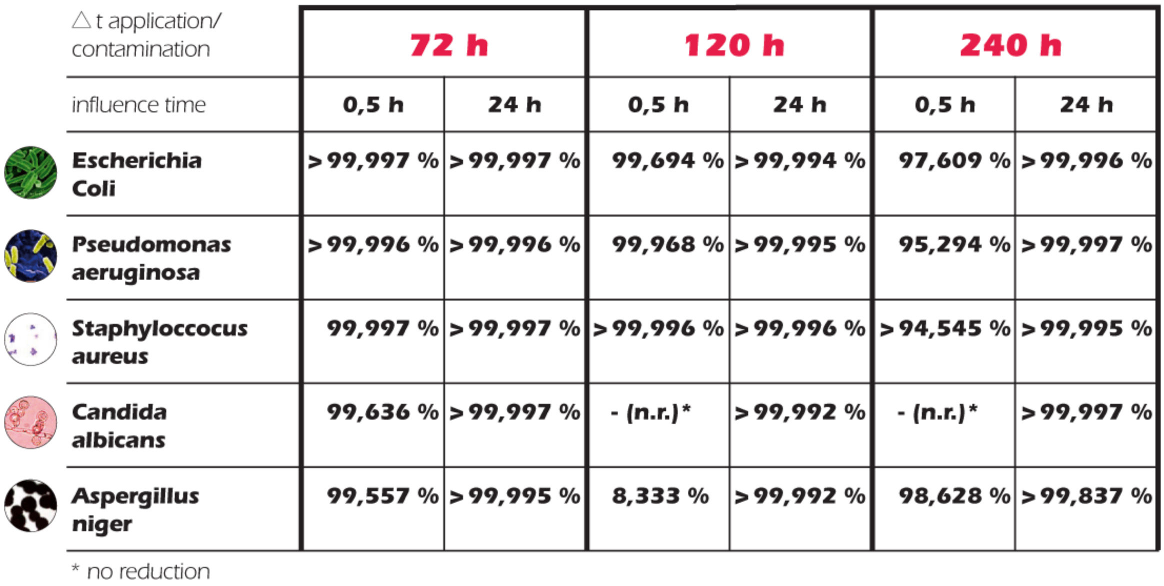


Fig. 2 Schematic illustration of Bacoban function
The figure demonstrate the principle how Bacoban functions. During the evaporation of the solvent a self-organizing process starts, which leads to the development of a film in the nanometer range. The basic structure of this film has an open porosity, which allows the fixation of new formed germicide crystals during the drying process. When, for example, after 10 days a germ containing droplet gets in contact to this surface the water in this droplet penetrates into the structure and solve the germicide crystals. After that the germicide is able to diffuse into the droplet and kill the germs very efficient.



△t application/ contamination	**72 h**		**120 h**		**240 h**	
influence time	**0,5 h**	**24 h**	**0,5 h**	**24 h**	**0,5 h**	**24 h**
Escherichia Coli	**>99,997 %**	**>99,997 %**	**99,694 %**	**>99,994 %**	**97,609 %**	**>99,996 %**
Pseudomonas aeruginosa	**>99,996 %**	**>99,996 %**	**99,968 %**	**>99,995 %**	**95,294 %**	**>99,997 %**
Staphyloccocus aureus	**99,997 %**	**>99,997 %**	**>99,996 %**	**>99,996 %**	**>94,545 %**	**>99,995 %**
Candida albicans	**99,636 %**	**>99,997 %**	**- (n.r.)***	**>99,992 %**	**- (n.r.)***	**>99,997 %**
Aspergillus niger	**99,557 %**	**>99,995 %**	**8,333 %**	**>99,992 %**	**98,628 %**	**>99,837 %**

* no reduction

Fig. 3 ASTM results of Fresenius
Reduction of typical clinical bacteria's and fungus after contact to Bacoban 3, 5 and 10 days after of application. Proven by the ASTM E 2180 Test.

Important for the use of such a product is to identified Bacoban as a new and innovative tool in the hands for hygienists to improve infection control and hygiene in hospitals and public institutions. That means not to prolong the time between the disinfection procedures, because Bacoban has such a potent lasting effect. It means to use Bacoban to close the hygienic gap between the established and standardized daily disinfection procedures.

Beside the significant improvement of surface hygiene the lasting effect has an interesting side effect. The reduction of germs induced and produced smell. Especially, in public toilets a very uncomfortable ammoniac like smell could be noticed. The smell is produced by a bacterial enzyme named urease. This enzyme is able to transform urea into ammoniac, which, also in small concentrations, irritates the olfactory system. Because Bacoban reduced the amount of germs on surfaces permanently also the appearance of smell could be strongly reduced.

Although, Bacoban has such a strong direct and an effective lasting effect, it could be clearly shown, that the material shows no dermal irritation or sensibilization reactions. These data could be shown by certified standard tests in a GLP certified laboratory.

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Nanotechnology for polymer-based sensors and actuators

Jörg Martin, Thomas Otto, Thomas Gessner

Innovative nanocomposites and nanostructures provide completely new chances for the realization of sensor and actuator systems in microsystem technology. So new technologies and favourable properties of modern nanocomposites enable completely new designs – flexible, curved and rough surfaces do not cause obstructions anymore. Large area sensor arrays can be designed to measure distributions of pressure, temperature, moisture or other values fast and reliably.

In our contribution an overview over nanomaterials which are relevant for microsystems technology, including metallic and semiconductor nanoparticles, is given. The effects and mechanisms which are used for sensors and actuators will be explained shortly.

In spite of the fact that nanocomposites are used for sensor and actuator systems for a short time, first sensors have been realized at the Fraunhofer ENAS in Chemnitz. Some of these elements, such as a tactile sensor array, moisture sensors as well as a polymer-based thermoelectric generator are going to be presented.

Due to their manifold properties and appearing effects nanomaterials are a very productive source for development of different microsystems. Therefore an outlook according to further with nanotechnology realizable sensor and actuator systems will be given finally.

Nanotechnology for Polymer-based Sensors and Actuators

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1. Introduction

While a few years ago, nanotechnology was pure research, it has recently gained much importance for practical applications. Not only the steady reduction of structural dimensions in the semiconductor industry, which is in a range less than 100 nm for several years, also the development of new nanoscaled structures and materials as well as the understanding of entirely new effects played a crucial role.

Nanotechnology is already used in many areas of science, technology and medicine. For example, nanoparticles are used to optimize optical elements, to make automotive paints scratch resistant, or they are added to printing inks for banknotes, to make them more secure against forgery [1-3]. So it is not surprising that even for micro systems engineering a large number of materials are available for the development of sensors and actuators. Thereby the substances appear in various forms, as nanoparticles or nanowires etc., as pure material or in composites [4-6].

Polymer nanocomposites are hybrid materials consisting of (mostly inorganic) nanoparticles and a polymer matrix. By modification of the nanoparticles surface it is possible to stabilize these particles in colloidal suspensions and to distribute them homogeneously in matrices [7]. Thus the composites are the connection between the nanoworld and macroscopic components. Their chemical and physical properties are directly influenced by the characteristics of the inclusions (such as quantum effects, magnetic and electrical properties), or on the other hand, new perspectives for applications result just from the combination nanostructure – matrix [5, 6].

So there is a wide range of nanoparticles and innovative polymers available, which - within specific limits - can be combined and adapted according to a particular application. Thus with the same technology, sensors and actuators for very different application fields, such as lab-on-chip systems for medicine and biology, force and position sensors for mechanical engineering or humidity sensors for air conditioning applications, can be manufactured.

In the next chapters a brief specification of smart micro systems will be given as well as some advantages of composite materials will be compared to silicon technology, further technological aspects according to polymer composite materials will be discussed and some examples of realized micro systems based on various composites will be presented finally.

2. Smart micro systems

Smart micro systems such as MEMS (Micro Electro-Mechanical Systems) or MEOMS (Micro Electric Opto-Mechanical Systems) usually consist of several parts with special functionality, including a processor and memory unit, a radio transmitter, a sensor/actuator unit, and a power supply. The whole system and every element have to be designed according to the particular application of the whole system. On question arises for instance concerning the energy supply of such a micro system, e. g. if the system is able to harvest the required energy from its environment (via solar, thermal or vibrational energy [8-10]) or if it is powered by an internal battery.

In reference [11] a battery-driven active radio frequency identification (RFID) label is presented. The intelligent micro system based on silicon technology is able to monitor shock, inclination and temperature during transportation processes to protect sensitive and expensive goods from damage.

To reach the desired multifunctionality of modern smart micro and nano systems various advanced materials have to be combined and integrated, wherefore in most cases different technology approaches are necessary. Here polymers and composites show several advantages compared to classical semiconductor (silicon) technology.

Processes for handling of silicon and the preparation of the starting material, which are often carried out under clean room conditions and at high temperatures, are relatively time-consuming and costly. Large-scale sensors cannot be produced on the basis of silicon, primarily due to cost reasons. Additionally, disadvantages for applications can arise from the mechanical properties, hence sensors and actuators are relatively fragile and cannot be implemented on flexible substrates.

In contrast, polymers and nanocomposites are easily processable at room temperature and under normal atmosphere. Rigid or flexible substrates can act as basis for one or more functional polymer or nanocomposite layers. Further, large sensor arrays are realizeable to determine distributions of pressure, temperature, humidity or other values. Another advantage is the low mass, which is of particular interest in mobile applications.

3. Integration of nanomaterials

As mentioned already, the processing of polymers and nanocomposites is much easier compared to traditional silicon technology. On basis of Figure 1, showing a capacitive sensor array as an example, such process is going to be elucidated in the following.

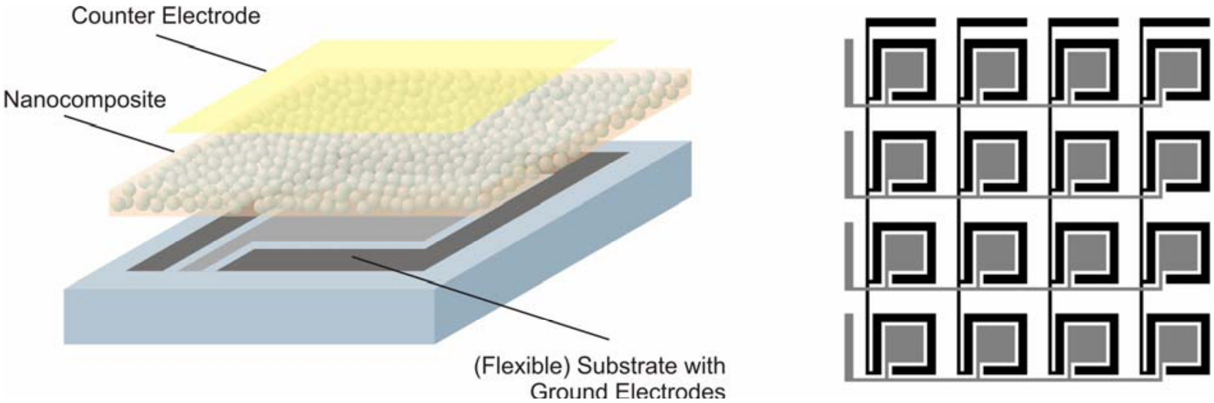

Fig. 1 Capacitive sensor array on the basis of nanocomposites, left: structure of single cell, right: sensor array of 4 x 4 cells.

First, on a substrate, which can have in principle any desired shape or can be even flexible, the base electrodes are deposited. This can be done by vapor deposition or sputtering using shadow masks. Subsequently one or more active composite coatings are applied from a colloidal solution, for instance by spin coating. Then, a counter electrode is applied and the sensor element is going to be contacted finally.

As indicated in Figure 1, right, this setup is very easy to scale and complex sensor arrays with dimensions up to several square centimeters can be fabricated in one step.

However, the above-described technology can be used only up to a particular sensor surface in laboratory scale. For mass production, specifically metalized substrate films will be preferred, which are then structured, for example with lasers. The functional layers may be applied by means of mass printing processes such as offset printing. Likewise, contacting and cross-linking of sensors can be provided by polymer electronics perspectively.

4. Composites and examples of application

Dielectric particles

Typical representatives of this group are metal and semiconductor oxides, such as Al_2O_3, TiO_2 and SiO_2. Here particularly the mechanical and dielectric properties of the materials are significant. Such particles are used already as optical layers for surface refinement and in cosmetics [1, 12]. For micro systems engineering, dielectric particles are interesting in the field of humidity sensor technology.

Here we present first results on the development and characterization of composite-based humidity sensors. In Figure 2 a test pattern with various electrode designs on a glas substrate is shown. The produced new sensors operate on the capacitive principle. The moisture-sensitive capacitor dielectric consists of nanoporous silica particles, which are embedded in PMMA. Water of the ambient air diffuses into the 6 nm pores of the particles and leads to a variation of the dielectric constant of the composite material corresponding to the water vapor content in the air. Therefore a change in relative humidity results in a change of the dielectric constant and hence the capacity of the setup.

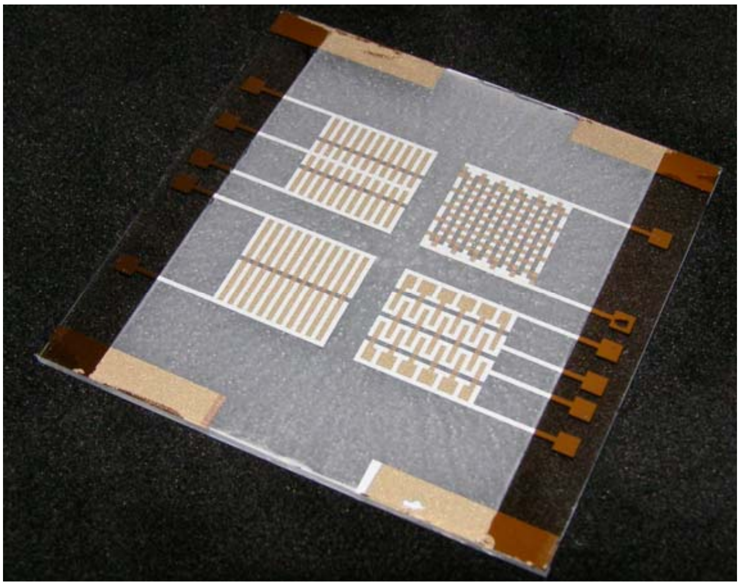

Fig. 2 Silica composite humidity sensors with various electrode layouts.

Several test patterns with different particle sizes and electrode designs have been characterized concerning sensitivity, temperature behavior and response time. By increasing the relative humidity from 20 to 95 % r. h., capacitance changes up to 100 % can be achieved. This result shows the very high sensitivity of the created nanocomposite sensors. In addition, response times in the range of 10-20 seconds for an abrupt humidity change from 20 to 95 % r. h. have been measured. These values are similar or even better than parameters of commercially available capacitive humidity sensors [13].

Metallic nanoparticles and thin films

Metallic nanoparticles and thin metal films also play an important role in micro system technology, especially for sensor applications. The decisive effect is the excitation of surface plasmons, which are particularly pronounced for gold and silver. The spectral position of the resonances depends very sensitively on the dielectric environment of the metal films or particles [14]. Changes of this environment, for example by attachment of a molecule, involve a shift of the resonance. Hence in biotechnology, this mechanism can be used to detect specific molecules in liquids [15].

For micro systems engineering also the manufacture of micro-optical elements on the basis of polymer-metal composite layers is of special interest. It was shown that such layers can be structured directly by means of laser light [16]. Laser light absorption by the metal particles results in coalescence (Ostwald ripening), hence the size distribution of particles is changed locally. A change in size is accompanied with a band shift in the transmission spectrum, since the spectral position of the plasmon resonance is directly dependent on the size of a metal particle. This can be used to create a visual contrast in the composite layer without damaging the layer itself.

As example a Fresnel lens has been created in a plasma polymer-silver composite layer [16]. The lens has a diameter of 19.5 microns and consists of 5 bright and 5 dark zones. This results in a focal length of 15 microns at 633 nm wavelength. Very interesting is the contrast reversal between long and short wavelengths, which is caused by the shift of a broad plasmon resonance band. This effect is not observed in classical zone lenses.

In this way, in addition to lenses, other optical elements can be created and integrated. In combination with photo detector arrays, optical elements on the basis of polymer-metal nanocomposites can be used for instance in mobile detection systems.

Semiconductor nanocrystals

Apart from the above mentioned materials also semiconductor nanoparticles are of interest, e. g. as fluorescent markers in bioanalysis. Here, especially II-VI semiconductor nanocrystals, such as CdSe or CdTe, are used [4].

The fluorescence properties of semiconductor nanoparticles are directly dependent on the size and surface properties of the crystals. The so-called quantum confinement means the confinement of excitons in the particle core and implies that the wavelength of the fluorescence is directly correlated with the core diameter of the crystals [17, 18]. The smaller the particle, the more the emission is in the blue spectral range. The empirical equation (1) describes the dependence of the emission energy on the particle diameter [19, 20]. Herein d is the diameter of the particle, E_{Gap} the band gap of the bulk semiconductor and ε_r the dielectric constant of the semiconductor.

$$E(d) = E_{Gap} + \frac{3.73}{d^{1.39}} - \frac{5.144}{\varepsilon_r d} \qquad (1)$$

Due to this property different colored markers can be realized with just a single base material, which is of great advantage for fluorescence microscopy. In addition, semiconductor crystals show some other advantages compared to dye molecules, such as narrow emission bands and high thermal, chemical, and photo-stability. Beside the usage as fluorescent markers, semiconductor nanocrystals are also suited as integrated light emitters. Perspectively, they should be used as light sources for sensors in micro systems.

With this respect we have started to investigate the possibilities of semiconductor nanocrystals integration into polymer sensors. In Figure 3 the luminescence of silicon and CdSe nanocrystals is presented. Image 3.a) shows the fluorescence of a porous silicon layer which has been fabricated by etching p-type silicon in a mixture of H_2O_2 and HF [21]. The photoluminescence of three different colloidal nanocrystal–PMMA solutions can be seen in Fig. 3.b). The colloids only differ in the size of the CdSe nanoparticles. The ‘red’ colloid has been then used to create the fluorescent layer which is depicted in 3.c). Therefore the solution has been cast through a mask and has been dried slowly.

Fig. 3 Photoluminescence of a) etched nanoporous silicon, image size: 70 x 70 µm^2, b) colloidal CdSe nanocrystal-polymer suspension and c) casted CdSe nanocrystal-polymer film, image size: 50 x 50 mm^2.

The figure shows that, in principle, direct and indirect semiconductors are suitable as light emitters. But the lifetime of the excited states of CdSe particles is much shorter than that of silicon (some nanoseconds compared to microseconds for Si [22]). This means that the CdSe crystals can be excited more frequently per time interval and thus are emitting more fluorescence photons. Thus regarding emission intensity CdSe seems to be preferable for applications.

Conducting and semiconducting materials for energy harvesting

An important part especially of an energy autarkic micro system, such as a sensor or sensor node for environmental monitoring, is an appropriate power supply. One possibility is the use of a temperature gradient for energy harvesting by means of a thermoelectric generator. The efficiency of thermoelectric materials is characterized by the so-called thermoelectric figure of merit ZT. For conventional used materials, e. g. Bi_2Te_3 or PbTe, this value remained unchanged near 1 for the last 50 years, which is, beside the costs for preparing and integrating such materials, the most prominent reason for a less distinct application of thermoelectric energy harvesting [23].

Nanotechnology provides a completely new chance for improvement of the thermoelectric efficiency. In contrast to bulk materials, with nanostructures it is possible to tune the charge and heat transport properties independently. So calculations have shown that ZT values of 3 or even larger seem to be attainable [24, 25].

Nanocomposites are used for thermoelectric applications for a short time, so far only a few laboratory samples have been reported worldwide [26, 27]. We investigated the thermoelectric properties of some conducting and semiconducting polymers and composites including polyaniline, graphite particles, and graphite fibers. The thermoelectric voltage of graphite-particle polymer composites of various concentrations is depicted in Figure 4. As can be seen clearly, the thermo-voltage increases with increasing graphite content in the composite. For larger concentrations (≥ 50 vol. % graphite) the thermo-voltage drops a little bit, which is most probably the result of an improved thermal conductance.

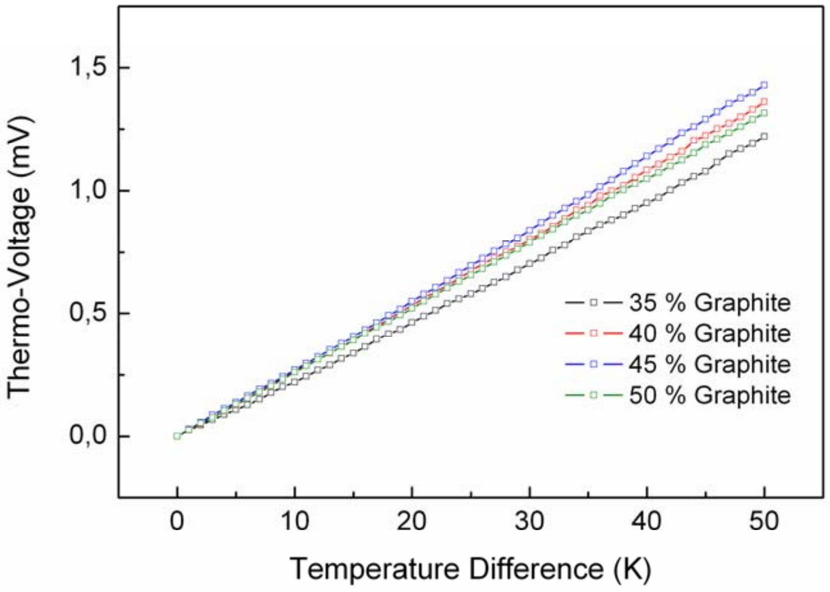

Fig. 4 Thermo-voltage of graphite-polymer composite samples with different graphite volume content (from [28]).

Further a demonstrator based on TTF-TCNQ and graphite composites has been realized and characterized. The generator consists of 5 p-conducting (graphite composite) and 6 n-conducting (TTF-TCNQ/PVK) elements. At a temperature difference of 50 K a thermal voltage of ca. 13 mV has been measured, which is very promising for further studies [28]. Here especially the integration of a large number of elements with a reasonable electrical resistance is one of the future's challenges.

5. Summary

Modern polymers, nanostructures and composites have become very important for micro system technology. Sensors and actuators for very different purposes can be designed and manufactured because of a large variety of available materials. The range spreads from micro systems for biotechnology through force and position sensors to climate sensors for automotive industries.

The advantages of the polymers are in terms of easy processing, implementing of large arrays at low costs and low mass. Furthermore, polymer and composite sensors can be combined with polymer electronics components, thus mass printing processes are available for the production of integrated systems.

Some results concerning the development and characterization of composite-based micro systems, such as humidity sensors or thermoelectric generators have been given. In addition, some aspects of the integration of semiconductor nanocrystals have been mentioned. Perspectively they will be used as light sources for sensors in polymer-based micro systems.

6. Acknowledgements

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Dr. Norman Mechau studied physics at the Brandenburg University of Applied Sciences and at the University of Potsdam. In 2005 he received his PhD in Solid State Physics; the thesis title was “Light induced softening of azobenzenes polymer films”. In 2006 he joined a PostDoc position at Karlsruhe Research Center in the group of Prof. Horst Hahn. Here he started to work in the field of printable electronics. Since 2007 he is leading the group of printable electronics at the same place. His current research interest include the charge transport physics and material science of particulate systems and the development of novel micro structuring and printing techniques for the solution-processed inorganic functional materials.

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Printable electronics from inorganic materials

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Printable electronics offer compelling advantages over more conventional ways of producing electronic circuits. These include the ability of cost effective mass production that can never be obtained using the old CMOS paradigm such as RFID tags that are inexpensive enough to replace bar codes, roll up displays or smart packaging that will allow companies to enhance their offerings and product lines. Ink-jet printing process offers the potential to create specialized circuits in which the materials are deposited additively only in locations where they are needed. This offers a significant cost reduction and a process simplification. Ink-jet printing is potentionally a low-temperature process that may enable manufacturing on flexible substrates and the process is compatible with continuous roll-to-roll processing. In order to build printable inorganic electronic circuits and devices, semiconducting suspensions which can be processed at low temperatures and low-cost manufacturing techniques are necessary. Stabilized suspensions prepared from commercial zinc oxide nanoparticles were used to fabricate field-effect transistors (FETs) by solution processing. The performance of the devices are strongly affected by the nature and concentration of the compounds added to stabilize the nano dispersions. An increase of the field-effect mobility by more than one order of magnitude is observed by increasing the stabilizer concentration from 3 to 13 wt %. However, a decrease in the field-effect mobility is noticed with a further increase in the stabilizer concentration beyond 13 wt.%. The behaviour can be explained by the change in the morphology, the interparticle contact, and the passivation of surface defect sites.

Printable electronic from inorganic materials

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Introduction

Recently, the printing of electrical circuits on flexible substrates has gained importance for building simple and low price devices such as RFID tags, and the search for printable semiconductors that can be processed at low temperatures continues. Solution-processable inorganic semiconducting materials for printable electronics in the form of precursor molecules and nano-particles mainly qualify semiconductors. Than nano-particulate inorganic semiconductors can be easily solution processed by spin coating or ink-jet printing. The advantages of nano-crystals are that the process does not have limitations for processing time and processing temperatures, because the two main processes, the nano-crystal synthesis and the layer formation made by spin coating are essentially independent. However, critical parameters of FETs fabricated from nano-crystals are the morphology of the layers and layer quality as the interface, the interface roughness. Okamura et al. [1] have indicated that if the interface roughness is smaller than the thickness of the accumulation layer of carriers in nano-particulate ZnO layers this leads to a higher field-effect mobility, while if the interface roughness is comparable to or greater than the thickness of the accumulation layer it acts like a geometrical trap for carriers. The influence of a co-polymeric stabilizer in nano-particulate ZnO layers on the FET performance was observed in the work of Bubel et al. [2]. It has been shown that by optimizing the fraction of co-polymeric stabilizer, the field-effect mobility can be improved. The improvement is caused by the improved morphology, because of smaller agglomerates in the dispersion. Further, it was supposed that the co-polymeric stabilizer not only influences the morphological properties of the nano-particulate ZnO layers, but also modifies its electrical characteristics. This is due to the covering and insulating of the nano-particles with the co-polymeric stabilizer which passivates defects states on the surface and thus reduces the intrinsic charge carriers in the nano-particulate ZnO device.

Methods

The electrical characterization of FETs was carried out in a N_2 filled glove-box and with an Agilent Parameter Analyzer 4156C at a constant temperature of 25 °C. The distribution function of the particle diameter in solution was measured using dynamic light scattering method with an ALV-NIBS High Performance Particle Sizer. Morphological measurements were performed with a Veeco Dektak 6M equipped with the *N-Lite* low force package. The dispersion was prepared by 10 percent by weight (wt %) of nano-particulate ZnO powder with sizes of 20-100 nm, produced by Evonik Degussa, suspended in 2-methoxyethanol and a fraction from 0 to 30 wt % of different type of stabilizers was added. The stabilizers were supplied by Evonik Tego Chemie GmbH. One of the stabilizers based on an aqueous solution of a co-polymer system with groups of high pigment affinity (Stab. I). A second stabilizer (Stab. II) consists of a sodium polyacrylate polymer system. The suspensions are dispersed by application of high energy ultra-sound for 10 min followed by 24 hours of magnetic stirring and was then filtered through a filter with a pore size of 2.7 µm. To prepare FET devices, the obtained dispersions were spin-coated on boron doped Si (100) substrates with a resistivity of 2.75 Ω cm and thermally grown SiO_2 of 200 nm. The substrates were annealed on a preheated hotplate for 30 min at 150 °C to evaporate the solvent, which results in nano-particulate ZnO layers with an average thickness of ~300 nm. 100 nm thick Al source and drain electrodes with a large channel ratio of 70 were evaporated through a shadow mask with an electrode spacing of 100 µm and a length of 7 mm.

Results and Discussion

The FET output characteristics were measured for different gate – source voltages V_{GS} for FETs containing from 0 to 30 wt % of each stabilizer. Apart from FETs without stabilizer, which showed ohmic conduction, all FETs showed saturation in enhancement mode by applying a positive gate field. In the following, the transfer characteristics were recorded and the threshold voltage V_{th} was calculated for the saturation regime at a drain – source voltage, see figure 1 (a) and (b). The calculated field effect mobility μ_{FET} for the different stabilizers changes at different concentration of the added stabilizer, shown in figure 1 (c). By varying the fraction of stabilizer from 3 to 30 wt % a steep increase of μ_{FET} for stabilizer one of more than one order of magnitude can be observed up to a concentration of 13 wt %. Adding more stabilizer to the system leads to a slow decrease in μ_{FET}. It can be assumed, that the changes in μ_{FET} are influenced by changes in the layer-morphology and/or the interaction between the nano particles and the added stabilizer itself will influence the system.

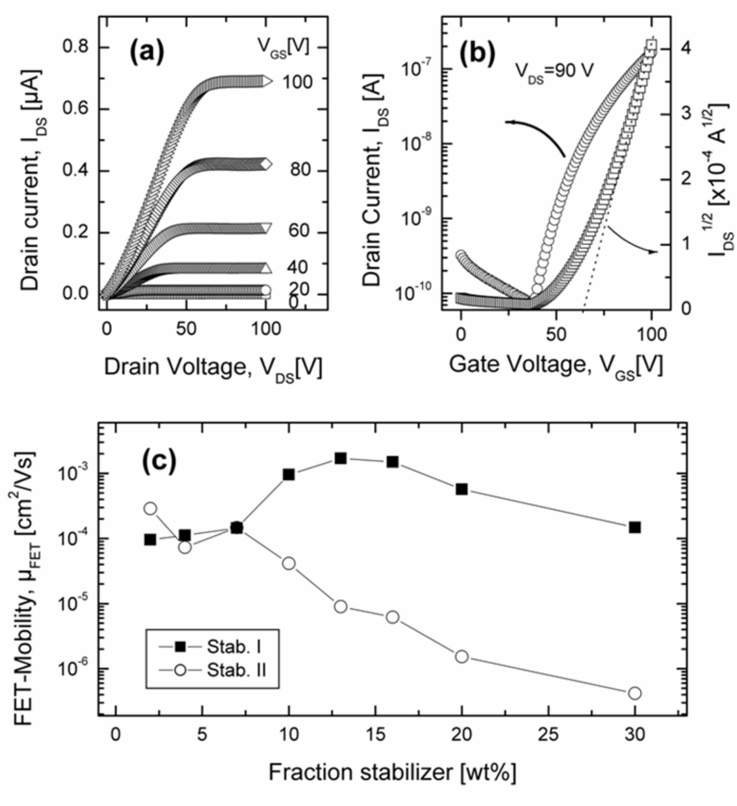

Fig. 1 (a) Output and (b) transfer characteristic of a nanoparticulate ZnO FET of 13 wt% of stabilizer (StabI). (c) FET mobility calculated from transistors processed by spin coating of dispersions containing different fractions of two different stabilizers (Stab I and Stab II).

The dispersion consists not only of primary particles of 20- 80 nm but also of bigger agglomerates of these. When no stabilizer was added to the dispersion, there are agglomerates with a mean diameter of 430 nm. By adding stabilizer to 10 wt %, the diameter distribution is altered to smaller sizes with a mean size between 200 nm and 300 nm. The formation of smaller agglomerates is consistent with an increasing in the negative zeta potential by adding stabilizer to the dispersion, which amplifies the electrostatic repulsion forces and therewith prevents smaller particles from agglomerating. By adding more stabilizer than 10 wt %, there is again a redistribution to smaller agglomerates with a mean size of 180 nm. Accordingly, for smaller agglomerates, it can be expected that the morphology of the spin-coated ZnO nano-particles will improve in terms of density and smoothness, as shown in figure 2. The smoothness of the surface was measured by the root mean square roughness of the layers, done by mechanical profilometer measurements with a Vecco Dektak 6M profiler. It confirmed the expected improvement of the layer morphology with adding stabilizers.

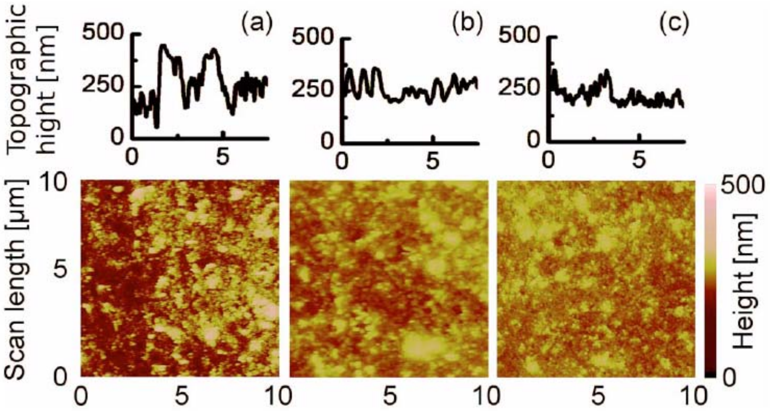

Fig. 2 AFM height profile for (a) 2 wt%, (b) 10 wt%, and (c) 20 wt% of stabilizer (Stab.I) in a solution processed nanoparticulate ZnO Film.

Accordingly, the morphology of the nano-particulate ZnO layers is strongly affected for small amounts of stabilizer, whereas higher fractions above 20 wt % have a little effect on the morphology, it is shown figure 3 (a). This can be explained with the covering of the ZnO particle surfaces with adsorbed stabilizer and this is in contrast with the saturation of the zeta potential for stabilizer fractions exceeding 20 wt%. But the improving of morphology cannot explain the entirely difference in field-effect mobility μ_{FET}. In addition, not only the morphology of the layers but also the conductivity of them will influence the field-effect mobility. The conductivity in figure 3 (b) decreases with increasing stabilizer concentration. Above a concentration of 5 wt% of stabilizer the layer-conductivity reduces with an exponential decay. Obviously, for the exponential reduction of conductivity at high concentrations above 5 wt% the stabilizer can be seen as an insulating layer between the individual particles or agglomerates in the ZnO layer. On the other hand, at very low concentrations of stabilizer between 0 and 5 wt%, a steep reduction in conductivity can be observed. A stabilizer fraction below 5 wt% is no way sufficient to cover and therewith insulate the particles completely. Regarding the fact, that there is a relatively high layer-conductivity without any stabilizer, a high density of defects sites, acting as donors, can be considered to exist on the ZnO surface. An indication of surface defect states is the presence of green photoluminescence for the ZnO nano-particles, as shown in figure 3 (c). The green emission between 450 nm and 700 nm originates from defects states at the surface and has been explained as the transition between charged oxygen vacancy and photoexcited holes [3].

However, the steep decay in conductivity at low concentrations of stabilizer below 5 wt%, is attributed to the passivation of surface defect states by the adsorption of stabilizer. A passivation of surface defect states would also explain why layers with more than 3 wt % of stabilizer show field-effect behavior, whereas with less than 3 wt % of stabilizer for conducting layers, no field-effect could be measured. Consequently the stabilizer leads to semiconducting properties and it is needed for successful operation of the particular FET device.

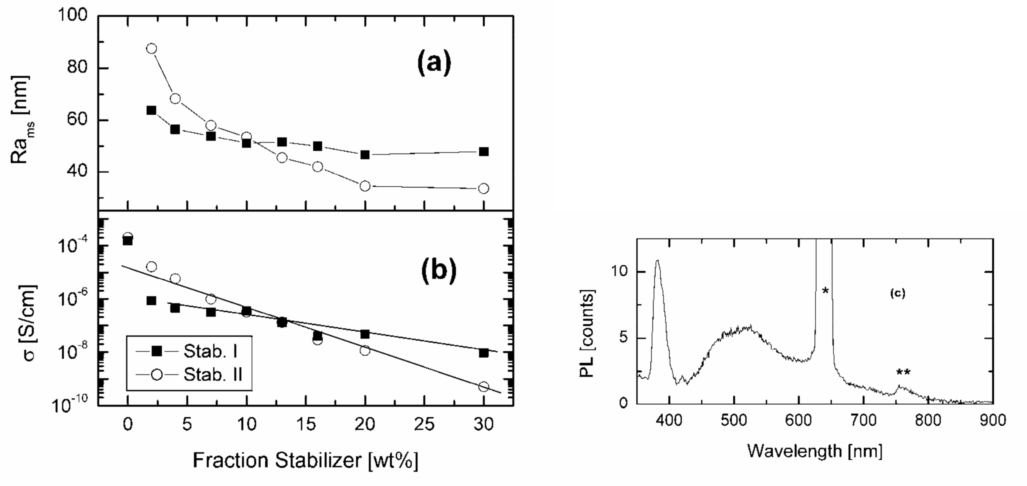

Fig. 3 (a) Roughness and (b) electric conductivity of films with different types and fractions of stabilizers. (c) Photoluminescence spectra at 350 nm excitation of dispersed ZnO nanoparticles. Peak positions are given and second order Rayleigh scattering (*) and fluorescence peak (**) indicated.

Conclusion

It can be concluded that the dispersion and therewith the morphology of the nano-particulate layers can be optimized by choosing the proper amount of stabilizer and the proper stabilizer itself. It has been shown that by optimizing the fraction of the stabilizer, the field-effect mobility can be improved by more than one order of magnitude. This effect is due to the improved morphology and related to smaller agglomerates in the dispersion. Nevertheless, not only the morphology but also the electrical characteristics will be influenced by the stabilizers. It is shown that at high concentrations of stabilizer, the stabilizers build a shell around the particles and act as additional insulating layers between individual particles. Even at very low concentrations the stabilizers passivate ZnO defect states on the surfaces and therewith reduce the density of intrinsic charge carriers in the nano-particulate ZnO device.

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Professor Morais has conducted research on nanomaterials in the past 25 years. He is known for his research on preparation and characterization of magnetic nanoparticles and related material systems (magnetic fluids, magnetoliposomes, magnetic nanoemulsions, and magnetic nanocomposites). He has published over 280 papers on indexed (ISI) technical journals and authored 10 patents. In recent years, Professor Morais presented over 70 invited talk, as for instance at Technical University of Berlin – Germany (2002), Institute for Physical High Technology – Germany (2002), University of Mons-Hainaut – Belgium (2002), University of Ghent – Belgium (2002), University of Central Florida – USA (2002), GE Global Research Center – USA (2002), University of Vienna – Austria (2003), Technical University of Budapest - Hungary (2004), Ruder Boskovic Institute – Croatia (2005), Indian Institute of Technology – Chennai (2006), Koç University – Istanbul (2006), INSA – Lyon (2006), Institute of Nanoscience of Paris – Paris (2007), Institute of Advanced Studies of Madrid – Madrid (2007), Polish Academy of Sciences – Warsaw (2007, 2009), Universidad Nacional Mayor de San Marcos – Lima (2007), King Fahd University of Petroleum and Minerals – Saudi Arabia (2008), Huazhong University of Science and Technology – Wuhan (2008), Tsinghua University – Beijing (2008), Biomaterialetako Ikerkuntza Kooperatiboko Zentroa – San Sebastian (2008), Laval University – Quebec (2009), Institute de Physique et Chimie des Materiaux de Strasbourg – Strasbourg (2009), Leibniz Institute – Saarbrücken (2009). Professor Morais currently supervises undergraduate students, graduate students, and post-docs.

The versatile material platform provided by magnetic fluids

Paulo C. Morais

Magnetic fluids (MFs), consisting of nanosized magnetic particles dispersed in polar or non-polar carrier fluids, offer an extremely versatile material platform to encapsulate the as-suspended particles in different hosting templates. In addition, the nanosized particle surface can be dressed with a huge variety of molecular coating thus providing specificity to the MF sample. Both material systems, namely the encapsulated and the surface engineered nanosized magnetic particles can be engineered to support a long list of biomedical and industrial applications, in fields as different as magnetohyperthermia for cancer treatment and magnetic modulation of thin film transparency.

This article presents a short description of the magnetic fluid material platform, including the co-precipitation chemical synthesis route, the nanoparticle´s surface passivation and molecular dressing, the basic physico-chemical characteristics and some of the applications in the biomedical and industrial fields. The article includes a list of references, mainly comprising the literature produced within the Brazilian Nanobiomagnetism Network (BNN). The included references aimed to provide the reader a short view of the expertise available within the BNN.

The versatile material platform provided by magnetic fluids

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1. Introduction

The successful development of nanoparticulated magnetic material systems (NMMS), either for industrial or biomedical application, requires full access to different levels of information regarding the material's properties. These requirements demand the joint effort of professionals with different backgrounds in unfolding the material's properties and the biological responses. For instance, the pre-clinical tests and the clinical trials addressed to a new magnetic drug delivery system (MDDS) are nowadays expected to be supported by the very knowledge of the interaction between the drug and the template material that carries the drug, site-target the drug and delivers the drug. In between these two far-apart though intimately-connected ends we found the material's preparation routes and the physical and physico-chemical characterization of the drug-loaded and drug-unloaded MDDS (*l*-MDDS and *u*-MDDS). Likewise, the engineering of nanoparticulated magnetic material systems addressed to industrial demands, requires deep understanding of the interaction between the nanosized particle and the hosting template as well as the response of the material system under the action of magnetic field gradients. Most of the currently developing nanoparticulated magnetic material systems, based on the platform offered by the colloidal suspension of chemically-precipitated magnetic nanoparticle, usually named magnetic fluid, include the so-called superparamagnetic iron oxide (SPIO) particle. More specifically, cubic ferrites have been used to produce most of the SPIO-based biocompatible materials [1]. Therefore, as one might expects, different experimental techniques, selected to probe the SPIO-core as well as the SPIO-shell, play a key role in helping characterizing and understand the very properties of the NMMS. This article is intended to emphasize the use of the cubic ferrite-based magnetic fluid [2-4] as an extremely useful material platform in the engineering of NMMS. Examples of recently developed biocompatible and industrial NMMS include magnetoliposome [5], magnetic nanocapsule [6], magnetic nanoemulsion [7], insulating magnetic oil [8], and transparent magnetic fluids [9]. With that purpose in mind the synthesis of the cubic ferrite-based SPIO via alkaline co-precipitation of aqueous-complexes of transition-metal ions, the morphological, the structural, the physical characterization of the as-synthesized nanoparticle, and the peptization of the nanosized particle as a highly-stable magnetic fluid sample will be mentioned in the article. Indeed, applications of complex NMMS for cell-labeling (CL), photodynamic therapy (PDT), magnetohyperthermia (MHT) of cancer cells and tissues, insulating magnetic oil for transformer application and transparent magnetic fluid for optical modulation will be also referred in this article.

2. Magnetic fluid

Magnetic fluid (MF) is a very special colloid in which the suspended nanoparticle posses a permanent magnetic moment [10]. Considering the suspended nanoparticle ferromagnetism (for instance transition metals) and ferrimagnetism (for instance cubic ferrites) are the typical magnetic ordering observed. Nevertheless, due to the reduced particle size, typically in the range of 2-20 nm, the blocking temperature of the peptized nanoparticle occurs below or near room temperature [11]. Therefore, Néel and Brownian relaxation mechanisms compete in describing the thermal relaxation of the magnetic moment of the nanoparticle stabilized in a colloidal suspension at room-temperature [12]. Polar (water-based) as well as non-polar (hydrocarbon-based) solvents are used to peptize the magnetic nanoparticle as a stable colloidal suspension. Stable MF samples containing as much as 15% in particle volume fraction have been produced and shelved for long periods of time [13,14]. Such a long term colloidal stability is provided by efficient particle-particle repulsion interaction. Besides the Brownian motion electrostatic and steric repulsions are the main repulsion mechanisms providing the MF colloidal stability. Electrostatic interaction is the dominant mechanism in ionic MFs, in which the magnetic nanoparticle is suspended in low-pH (2-3) or high-pH (12-13) water-based media [13]. Steric repulsion, on the other hand, is the dominant mechanism accounting for the MF colloidal stability in hydrocarbon-based MFs, in which different non-polar solvents can be used to peptize the magnetic nanoparticle [14]. In both cases the nanoparticle surface has to be properly tailored to provide long term colloidal stability, especially in highly concentrated MF samples. In ionic MFs containing SPIO particles the surface polyoxy-hydroxy native molecular layer plays a key role in providing the mechanism for positively-charging the suspended nanoparticle in low-pH values [15]. In high-pH values, however, a negative surface charge density accounts for the colloidal stability in SPIO-based ionic MFs [15]. Peptization of SPIO particles in non-polar solvents requires a step of surface functionalization with molecules containing a hydrophobic tail facing the bulk solution, thus accounting for the steric particle-particle repulsive interaction mechanism [14]. An aqueous medium may also be used to peptize SPIO particle surface-coated with a molecular layer (single or multi-layered) containing a polar group in the hydrophilic tail facing the polar medium [14]. In more complex systems, such as in the biocompatible magnetic fluid (BMF), both electrostatic and steric repulsive mechanisms may take place simultaneously, providing very stable magnetic colloids at physiological condition. Nevertheless, it is worthwhile mentioning that the MF biocompatibility is assigned only after performing *in vitro* and *in vivo* tests while biocompatibility is usually a dose dependent issue [16-18]. As far as the dispersion of the single magnetic units are concerned figure 1(a) shows a mesoscopic schematic representation of how a typical freshly-synthesized MF sample might looks like in the absence of an applied magnetic field. Figure 1(b) shows an ideal representation of a MF sample, consisting of isolated and surface-coated nanoparticles dispersed in a carrier fluid. Indeed, figure 1(c) shows schematically how the native surface of a SPIO particle, obtained by the co-precipitation route in aqueous medium, might looks like at neutral pH [15]. Besides isolated nanoparticles the presence of dimers, trimers and larger agglomerates are also quoted in figure 1(a). Experimental determination of the relative population of these magnetic units (monomer, dimer, trimer, etc) in a given MF sample can be indirectly performed using zero-field magnetic birefringence for instance [19-22]. Aging processes and/or application of external magnetic fields induce formation of chain-like structures, which had been directly visualized by cryogenic electron microscopy [23].

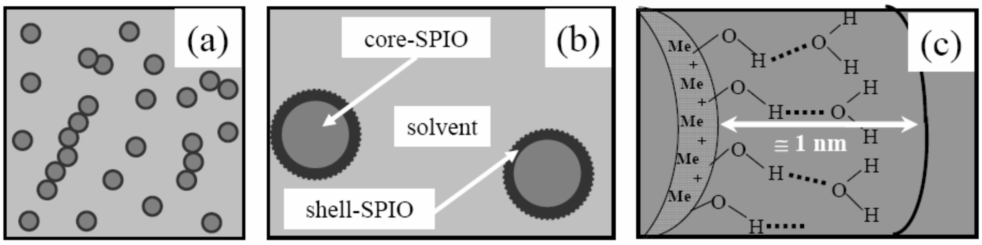

Fig. 1 Schematic representation of (a) the topological scenario of a typical magnetic fluid sample in the absence of an applied magnetic field, (b) the ideal representation of a magnetic fluid sample consisting of isolated and surface-coated nanoparticle dispersed in a carrier fluid and (c) the pH7 native surface of a metal(Me^+)-oxide nanoparticle obtained by co-precipitation in alkaline medium.

The most widely used synthesis route of SPIO-based MF samples described in the literature starts with the co-precipitation of the metal ions from their aqueous salt solution using weak or strong base addition under controlled conditions. Nevertheless, fine control of the particle size and size dispersity is challenging. This is because the morphological characteristics of the end product depend upon many parameters. Among them we found the concentration of all chemical species involved (hydroxyl, metal-ions, and counter ions) in the co-precipitation reaction, the particular counter ions employed, the temperature the chemical reaction takes place, and the stirring speed. From the fundamental point of view the most intriguing dependence is the one related to the stirring speed. In the production of ionic MFs we found the average diameter of cobalt ferrite nanoparticles reducing (below 15 nm) with the increase of the stirring speed (above 1000 rpm) during the co-precipitation step. Figure 2 shows schematically a typical SPIO particle synthesis route employed to precipitate $CoFe_2O_4$ nanoparticles using aqueous solutions of cobalt nitrate (5 mmol/L), iron chloride (10 mmol/L) and sodium hydroxide (1 mol/L), at 95 ^oC and under intense stirring speed. In the first step (see figure 2) the aqueous solution of sodium hydroxide is quickly added to the stirring solution until pH12 is reached. SPIO-based samples with different core-sizes can be precipitated using different stirring speeds. The as-precipitated SPIO particle is fully-charged with a high density of negative surface charge. In the second step the supernadant is removed and nitric acid (2 mol/L) is added to the precipitate till pH3 is reached. At pH3 the SPIO particle is fully-charged with a high density of positive surface charge. Then, the becker containing the precipitate at low pH is left to rest overnight on top of a permanent magnet. The SPIO particle surface passivation is performed in the third step of the synthesis by adding hot ferric nitrate (0.5 mol/L) under continuous magnetic stirring, for about 30 minutes. The peptization of the passivated SPIO particle as ionic MF sample can be accomplished in low-pH as well as in high-pH values by controlling the surface charge density while reducing the ionic strength of the aqueous medium [2-4]. In the first step of the peptization procedure triethylamine water solution (0.1 mol/L) is added dropwise to the low-pH passivated precipitate until pH6 is reached. The precipitate is then washed several times with acetone and distillated water to reduce the ionic strength of the medium. In the second step of the peptization procedure perchloric acid is added to the washed precipitate until pH2 is reached, when peptization of the SPIO particle as ionic MF spontaneously occurs. The picture shown in the central part of figure 2 was taken from a highly-concentrated ionic MF sample in the presence of two permanent magnets placed outside the wall of a glass tube containing a droplet of the sample.

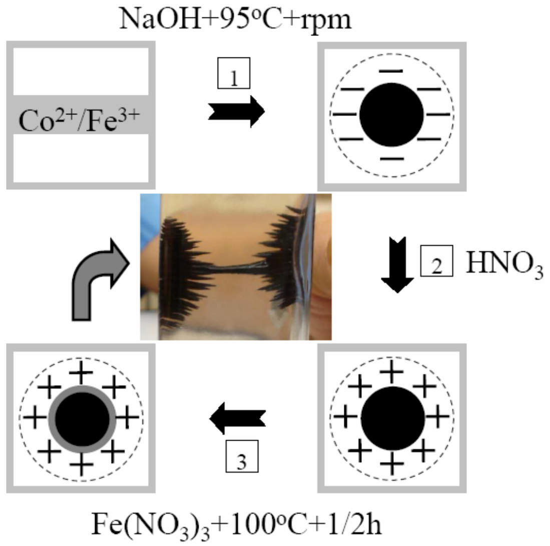

Fig. 2 Schematic representation of the alkaline chemical co-precipitation route for SPIO, with the purpose of producing stable magnetic fluid samples.

One way to control the SPIO particle core-size is by changing the stirring speed during the first step of the synthesis. It is found that the higher the stirring speed the smaller the average mean particle diameter. However, the standard deviation associated to the lognormal particle size distribution does not change when the SPIO particle core-size increases by about 50% [2]. The understanding of the SPIO particle growth mechanism through chemical condensation reaction in aqueous solution under vigorous stirring has not been addressed in the literature, despite the huge impact it may have from the fundamental and applied viewpoints. However, the reduction of the average SPIO particle core-size as the stirring speed increases may indicate that the nanoparticle growth process is mainly dominated by the diffusion of the on growing nanoparticle throughout the medium instead of the diffusion of the aqueous cations into the nanoparticle surface. This seems to be an obvious conclusion, once cations are everywhere in the reaction medium while the SPIO phase represents a small volume fraction. Nevertheless, the distinction between normal and anomalous diffusion of the SPIO particle may hold the key to understand the growth process. Under normal diffusion the SPIO growth process may keep the same growth kinetics along the mean free path whereas under anomalous diffusion the growth kinetics may switch between two distinct pathways, with very different growth velocities. The two distinct growth pathways may occur during a sequence of short flies or during the long flies, the two scenarios typical of the anomalous diffusion [24]. Anomalous diffusion of particles inside a turbulent fluid has been already reported in the literature [25]. Under such a scenario, the SPIO growth is more likely to occur during a sequence of short flies, when space localization is much higher. As the stirring speed increases the time the SPIO particle spends during a sequence of short flies also increases, allowing the onset of a higher density of nucleation sites in the reaction medium, with consequent reduction of the average SPIO core-size.

Ultra-stable BMF samples based on cobalt-ferrite surface-coated with citrate anions has been prepared as described in what follows [4]. Firstly, cobalt-ferrite is precipitated as schematically described in step-1 of figure 2. Then, in step-2 (see figure 2), the as-precipitated SPIO phase is washed with distillated water, following the treatment with citric acid aqueous solution (0.05 mol/L) under slight stirring for 45 min in order to promote the SPIO surface-coating. The citrate-coating step can be performed under different pH values as a strategy to fine control the SPIO citric acid surface-grafting. In step-3 (see figure 2) the citrate-functionalized SPIO particle is washed several times with acetone in order to remove any excess of citric acid and afterwards dried using a nitrogen gas flux. In the final step the dried citrate- functionalized SPIO particle is dispersed in distilled water and kept under slight stirring for 24 h, before centrifugation at 1000 rpm for 2 min. The obtained MF sample is adjusted to pH7 and salinity 0.9% NaCl in order to produce the highly-stable BMF sample. Similarly, following the standard procedure described in the literature [26] the meso-2,3-dimercaptosuccinic acid (DMSA) can be used to produce surface-coating maghemite (γ-Fe_2O_3) nanoparticles. As-precipitated γ-Fe_2O_3 nanoparticle with an average diameter value (core sizes) of 9.3 nm was surface-coated with DMSA and used to produce stable BMF samples. The stock BMF sample can be stabilized around pH7 and salinity of 0.9% NaCl (physiological condition). With the purpose of biological applications the stock BMF sample (concentration around 10^{16} particle/cm^3) can be used to produce different diluted samples, quoted for instance as 1:2, 1:4, 1:20, 1:50, and 1:100. Sample 1:4, for instance, is produced by mixing one volume of the stock BMF sample with three volumes of physiological solution.

The produced MF samples can be further used as an exceptional and highly-flexible platform to synthesize more complex NMMS. Starting with different MF samples [2-4] the peptized SPIO can be encapsulated as magnetoliposome [5], magnetic nanocapsule [6], or incorporated into magnetic nanoemulsion [7]. The *ex-situ* incorporation of SPIO particle using the MF technological platform provides full control for nanoparticle concentration in the hosting template with excellent uniformity. In addition, by controlling the chemical compatibility between the molecular-coated SPIO and the hosting matrix the protocols used for SPIO template incorporation provides the opportunity for the addition of biologically-active molecules into the end product, which can be tailored as a MDDS. Magnetic drug delivery system consisting of biocompatible magnetic fluid (BMF), magnetoliposome (ML), magnetic nanoemulsion (MNE) and magnetic nanocapsule (MNC) are presently being produced and biologically-tested worldwide [4-7].

3. Applications

Functionalized maghemite nanoparticles were successfully used for labeling Swiss mice erythrocytes, opening up new perspectives of biological and medical applications of MDDS, including strategies to overcome the brain blood barrier [27]. Incorporation of zinc phthalocyanine [28], pheophorbide [29] and chlorine [30] into the shell layer of a MF has been recently described. The MDDS comprising SPIO particles (magnetite or maghemite) plus photosensitizers (phthalocyanine, pheophorbide, or chlorine) were engineered to synergetically act as a dual therapeutic agent for cancer treatment, using photodynamic (PDT) and magnetohyperthermia (MHT) therapies. Likewise, zinc phthalocyanine has been incorporated into cobalt-ferrite based magnetoliposome to produce a MDDS [7] aiming to enhance the tumor damage using PDT and MHT therapies after minimum drug administration. A new MDDS was also produced via encapsulation of zinc phthalocyanine [31] and Foscan [32] into maghemite-based magnetic nanoemulsions. Interesting aspects regarding MNE formulation are the enhanced drug solubilization, good thermodynamic stability and easily-achieved scaling up for mass production [33]. Whereas surface passivation of the peptized SPIO particle needs to be properly addressed to prevent chemical degradation and aging effect PDT and MHT may promote phase changes of the magnetic component in a MDDS. Therefore, a more detailed investigation of the effects of SPIO surface passivation while preventing undesirable sample aging and phase changes due to illumination with visible light or thermal annealing is required to support long-term biocompatibility of a MDDS.

The heat transfer efficiency between the inner and the outer parts of electrical transformers is an important technological issue and can be improved either by changing the design of the device and/or by replacing the materials used to build their parts. As far as the heat transfer efficiency is concerned, however, device design appears to be reached the limit considering the available materials employed, thus residing upon the materials engineering the future to improve the device performance. Among the possibilities provided by materials engineering the use of diluted magnetic fluids, based on insulating mineral or vegetal oil as the carrier liquid, has been proposed as a very promising technological approach [34,35]. Difficulty in implementing this technology in a large scale resides mainly on controlling the colloidal stability of the insulating oil-based refrigerating magnetic fluid while operating under low nanoparticle volume fraction and higher temperature conditions [36]. These two conditions together favour desorption of the stabilizing molecular coating layer dressing the suspended magnetic nanoparticle, quickly aging the refrigerating MF with loss in operation efficiency and risk for the device. In addition, reduction of the nanoparticle surface grafting coefficient exposes the surface, allowing phase transformation of the core material (via oxidation for instance). Stable maghemite-based MF samples are usually obtained from oxidation of freshly-precipitated magnetite nanoparticles. Nevertheless, it has been suggested that oxidation at this nanoscale seems to be size-dependent, allowing partial oxidation of polydispersed samples [37]. Investigations of magneto-optical properties of MF samples, such as birefringence, magnetochromatics, field-dependent transmission, and magnetically-modulated refractive index have been reported in the literature. Optical applications of MF samples, however, are limited to relatively lower particle concentrations, due to optical transparency factors. Nevertheless, the static magnetic birefringence (SMB) and the optical transmissivity (TR) of a new ionic magnetic fluid containing cadmium ferrite ($CdFe_2O_4$) nanoparticles dispersed in low-pH aqueous medium revealed unexpected higher optical transparency in the visible wavelength [38]. A comparative analysis of the unusual optical properties of the $CdFe_2O_4$-based MF sample was carried out with respect to the optical properties of a typical aqueous MF sample containing surface-coated maghemite (γ-Fe_2O_3) nanoparticles. The two samples were chosen to have similar average nanoparticle sizes and size dispersions. It was found that the new material is over one order of magnitude more

transparent than the typical γ-Fe_2O_3–based MF sample, making the former a promising candidate for magneto-optical applications. In addition, using the SMB experimental setup (polarizer and analyzer perpendicular to each other) a strong, low-field peak on the intensity of the transmitted light was observed. The observation of that peak was assigned to the anomalously high value of the sample's birefringence. Combination of both properties, the high optical transparency in the visible wavelength range and the negative differential intensity of the transmitted light at low fields, would be extremely useful in the design of high performance optical components.
In order to investigate the magnetic material phase stability and identify the thermally- and optically-induced production of new magnetic phases different experimental techniques, including morphological, structural, magnetic and optical have been employed. High-resolution microscopy provides direct observation of the nanoparticle shape, average size, size dispersion and spatial distribution in hosting matrices [39-44]. Correct interpretation of all the size-dependent material properties relies on the knowledge of the morphological and topological characteristics of the sample provided by high-resolution microscopy micrographs. X-ray diffraction (XRD) is also a standard technique for probing the materials' crystal structure, providing the average size of the nanosized particle via evaluation of the corrected full width at half height of a characteristic diffraction line [45]. Mössbauer spectroscopy for instance provides very useful information regarding material's degradation and phase transformation in SPIO-based materials [46-56]. Likewise, photoacoustic spectroscopy has been recently employed for probing molecular species attached to the nanoparticle surface, thus providing valuable information regarding the aging of magnetic fluids after dilution of the stock sample by the addition of extra solvent [57-62].

4. Conclusion

This article highlights the use of magnetic fluid as an excellent material platform to produce more complex nanosized magnetic material systems addressed to biomedical and industrial applications. Nanosized magnetic materials consisting of magnetoliposomes, magnetic nanocapsules, magnetic nanoemulsions and specially-designed magnetic fluids have been described.

Acknowledgements

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Brazilian Institute of Science and Technology of Carbon Nanomaterials

Marcos A. Pimenta

The activities and goals of the “Brazilian Institute of Science and Technology of Carbon Nanomaterials” are discussed. In the research field of “Nanotubes and Fullerenes” our team is working on the (i) sample production (synthesis and chemical processing); (ii) basic research and characterization; (iii) applications and devices and (iv) toxicity. In the field of Graphenes, our current activities are (i) the production of graphenes (mechanically and chemically exfoliated and CVD) and (ii) basic research, with special emphasis to the optical and electronic properties

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1. Introduction

The success of nanoscience and nanotechnology might represent a revolution in larger-scale in the fields of energy, health, information technology and emergent phenomena. It is not surprising that carbon is playing a key role in the development of nanoscience and nanotechnology. From one side, carbon-based structures give rise to life. From another side, carbon is the silicon upstairs neighbor in the periodic table, with more flexible bonding and unique physical, chemical and biological properties, holding the promise of a revolution in electronics. Three are the important aspects that make carbon materials special for facing the nano-challenges listed in the previous paragraph: in the sp^2 configuration, the chemical bonding are stronger than in the sp^3 configuration, making graphene (the single sheet of sp^2 atoms) stronger than diamond to tensile strength. Bucky balls, tubes, horns can be built from graphene, these structures being stable and strong enough for the most different types of characterization and processing. The delocalized electronic states in graphene are highly unusual, since they behave like relativistic massless Dirac fermions, and are responsible for ultimate optical and transport - both thermal and electronic - properties. Different from most of the materials, such as polymers, sp^2 nano-carbons allow us to accurately access their properties both from the experimental and the theoretical approaches, because it is a simple system, formed by only one type of atom in a periodic hexagonal structure. Being able to model the structure is crucial for the development of our methodologies and knowledge.

Although the ideal concept of a sp^2 carbon system starts with the two-dimensional graphene sheet, the three-dimensional graphite, formed from the packing of graphene layers, is one of the longest-known and longest-used materials found in the nature. Of all materials, graphite has the highest melting point (4200K), the highest thermal conductivity, and it also conducts electricity (room temperature electron mobility: 20000 cm^2/Vs). Graphite and the related carbon fibers have been commercially used for decades. Their applications range from use as conductive fillers and mechanical structural reinforcements in composites (e.g., in the aerospace industry) to electrode materials (e.g., in batteries), with an estimated market of 14 billion dollars.

The early years of nanoscience, in the 1980's, are usually associated with developments in nanoscopy techniques, as well as with the Nobel-prize-awarded discovery of the fullerene C_{60} [1]. Therefore, from the beginning this new science frontier has been associated with forms of carbon that are different from the previously known ones - diamond and graphite. A few years later, the discovery of the carbon nanotubes [2] further extended the interest of the scientific community on that class of materials. Carbon nanotubes are considered today one of the most important materials in nanoscience and nanotechnology, since they exhibit unique electronic, structural, thermal, mechanical and chemical properties. They have been used to produce devices such as transistors and diodes, electron emitters for displays, supercapacitors for charge storage, biological and gases sensors. When mixed to different materials as polymers and fibers, carbon nanotubes change dramatically the mechanical and electrical properties of these materials.

In 2004, graphene was obtained experimentally [3], and it is today certainly the most important star on the horizon of materials science and condensed matter physics. This material consists of a single atomic layer of graphite, and is a basic building block for graphitic materials of all other dimensionalities. Despite its short history, graphene has already revealed a large spectrum of new physics and potential applications. Due to its unusual electronic spectrum, graphene corresponds to a new paradigm of “relativistic” condensed matter physics, since the charge carriers (electrons and holes) can be described by massless relativistic (Dirac) fermions [4]. Graphene can now be obtained by chemical route in larger quantities, with possible uses in scalable devices. We are certainly observing today the graphene “gold rush” in materials science and condensed matter physics Finally, in 2008, graphene nanoribbons (GNR) were synthesized by chemical route [5]. These stripes of graphene, with widths in the nanometer scale, present semiconducting properties that - unlike graphene and metallic nanotubes - allow their direct use in field-effect transistors with very large on-off ratios.

2. The “ Brazilian Institute of Science and Technology of Carbon Nanomaterials”

The “Brazilian Institute of Science and Technology of Carbon Nanomaterials” is hosted by the Physics Department at Universidade Federal de Minas Gerais (UFMG) and formed by other 19 Research Institutions, Universities and Companies belonging to 8 different states in Brazil (CDTN, UFJF, UFU, UFV, UFSJ, UFSJ-Ouro Branco, UFOP, Magnesita and Nacional de Grafite, in the State of Minas Gerais; INMETRO, UFF and UFRJ in Rio de Janeiro; UFABC and USP-RP in São Paulo; UNIFRA and UFRG in Rio Grande do Sul; UFPR in Paraná; UEFS in Bahia; UFMA in Maranhão, and UFP in Pará). The team of the Institute consists of 54 researchers. About half of them (25) belongs to the host Institution (UFMG) and the remaining ones are distributed among the research institutions, universities and companies around the country (see figure 1).

Our team has been pioneer in Brazil in the study of the science and applications of carbon nanotubes and other carbon nanomaterials. We have researchers working in the synthesis, purifications and functionalization of carbon nanotubes, a group of scientists working with fundamental properties of carbon nanotubes, researchers performing theoretical models and simulations about these materials, and.researchers developing devices and applications such as gas sensors, biological sensors, photovoltaic devices, fuel cells, and field effect transistors (FET) using nanotubes. We also have researchers working in the field of toxicology of carbon nanotubes, and two Companies associated with our proposal: Nacional de Grafite (production of graphene samples and electrodes for nanotube production) and Magnesita (thermally insulating composite materials with nanotubes). Our team has also started producing graphene by exfoliation and characterizing its electronic, magneto-transport and vibrational properties.

The current activities of the Institute aims at, developing novel and relevant investigations on the physics, chemistry, and applications of carbon nanomaterials; forming high quality human resources at different levels - from undergraduate to postdoctoral -on the field of carbon nanomaterials; mantaining a network of top researchers and groups in the field within the country, and collaborators abroad, to produce science of excellence in the field in a collaborative way; and fostering the research in the field in emerging centers and universities in the State of Minas Gerais and in other states of the Federation; transfering the knowledge from our research and expertise to the society, as well as a series of seminars and other activities directed to the community in general, and to elementary and high schools.

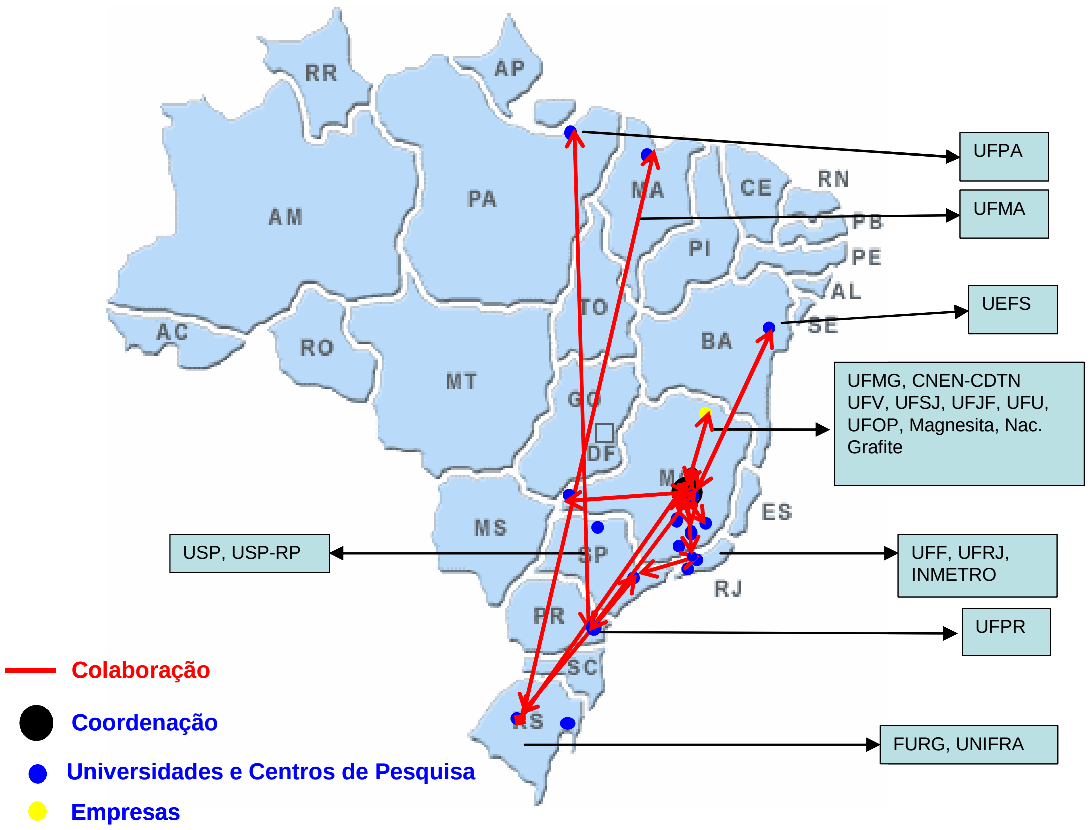

Fig. 1 Map indicating the research centers and companies of the Institute.

Although the core mission of our Institute is basic science, we have spotted some possibilities of technology transfer. We are working in the development of a wide range of different processes and applications based on carbon nanomaterials that have an enormous potential to be transferred to the productive sector. We can quote as an example, the development of large scale production systems of carbon nanotubes to fulfill the national needs of this important material. It is worth noting that due to the increased attention that carbon nanotubes had withdraw in the last years, some countries have recently hindered its exportation for development countries, such as Brazil, as a strategy to slow down its development in nanotechnology. Researchers at UFMG have developed recently a large scale carbon nanotube production method targeted at the Brazilian market. We plan to transfer this technology in the future to companies interested in producing and marketing carbon nanotubes. One of them, “NACIONAL DE GRAFITE”, showed interest in the development and production of electrodes used in the growth of carbon nanotubes, as well as their application in batteries. Other potential applications include: energy (photovoltaic devices and super capacitors); Chemical and petrochemical industry (insumes for the production of carbon nanotubes); iii) health care (development of biosensors and biocomposites). Thus, there is a great potential to include by-products of our research in the innovation law and hence contribute to the industrial development of the country.

3. Conclusions

The activities of the “Brazilian Institute of Science and Technology of Carbon Nanomaterials” can be described according to the following classification: in the research field of “**Nanotubes and Fullerenes”** our activities are focused on the (i) sample production (synthesis and chemical processing); (ii) basic research and characterization; (iii) applications and devices and (iv) toxicity. In the field of **Graphenes**, our current activities are

(i) the production of graphenes (mechanically and chemically exfoliated and by CVD) and (ii) basic research, with special emphasis to the optical and electronic properties

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Transparent, conductive oxides for coating applications

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Transparent, conductive oxides (TCOs) applied as coatings find multiple applications in various areas such as flat panel display setups, as electrodes in touch-screen panels, electrochromic devices, solar cells and in architectural applications for example as IR reflectors.

The favored material in the class of TCOs is still ITO – Sn-doped In_2O_3 – due to its unique combination of high transparency and electrical conductivity. Though already very good, the potential of the ITO coatings with regard to their conductivity leaves some space for future improvements. Also ITO as a material has some serious drawbacks, such as limited availability and high costs. This work presents some strategies to overcome these obstacles.

One way to enhance the conductivities of alternative materials is to use carbon nanotubes as a dopant. This strategy was tested for ATO (Antimony-doped Tin Oxide), Titan dioxide and AZO (Aluminium-doped Zinc oxide). The results for these materials are presented.

In coatings of ITO on glass or polymeric foils usually silica-based binders are used. They have the disadvantage to reduce the contact between the highly conducting grains and thus reduce overall conductivity in the composite. The matrix between the nanoparticles can be improved by several measures. Experiments with relevance in this direction are discussed.

A third strategy aims at the reduction of costs in the process of ITO fabrication. Here one way to go is to use an electrochemical synthesis method. Results of the line of development are presented.

Other strategies comprise the suitable processing of materials with a lower intrinsic conductivity or the search for materials with high intrinsic conductivity close to that of ITO. Examples are presented and discussed.

Transparent conductive oxides for coating applications

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1. Introduction

Transparent conductive oxides (TCOs) an unusual combination of material properties as they are on one hand provide highly electrically conductive and on the other hand show high optical transmission as well. Usually glasses or ceramics are known for high optical transparency and metals for high electrical conductivity. The combination of both properties is rare and restricted to a comparably small group of materials. Therefore, when used in coatings, TCOs find multiple applications in various areas such as electrodes in touch-screen panels or for other flat panel display setups [1-5], in electrochromic devices [6-8], in photovoltaics [9,10], for electromagnetic shielding [11,12] or for gas-sensing [13,14].

A forthcoming area comprises the application in OLEDs for lighting. As lighting consumes about 25 % of the global electrical energy, the replacement of energy saving lamps by OLEDs has a huge potential for saving energy. The OLEDs require transparent conductive electrodes. Here TCOs can be used [15-17].

Low emissivity coatings are an interesting issue in architecture. Instead of letting the heat generated by infrared radiation into the room after passing the window glass, the infrared radiation with wavelengths beyond 2 μm is reflected directly at a layer coated onto the window glass thus reducing the need for climatization in the room. This is an item especially in tropic countries where a big amount of electricity is used for climatization. Here transparent conductive oxides such as ITO can be used as IR reflectors [18,19].

The favored material in the class of transparent conductive oxides is still ITO – Tin-doped indium oxide – due to its unique combination of high transparency and electrical conductivity.

The processing of a typical TCO material can be illustrated using the example of ITO, indium tin oxide. ITO is synthesized via a precipitation from a solution which means by a controlled growth process. After calcination and reduction processes, a powder of Tin-doped Indium oxide with an average grain size of 20 to 30 nm is obtained. By addition of suitable surface modifiers and solvents a suspension is produced, which can be used to manufacture coatings. Application of the coatings is performed usually by means of wet chemical coating techniques. While smaller samples (up to 10 cm x 10 cm) are prepared via spin coating or bar coating, larger samples are coated via dip- or roll-to-roll processes. Curing of the coatings depends on the substrates to be coated. While coatings on substrates like glass can be cured thermally, coatings on polymeric substrates have to be cured by UV- or IR-irradiation which normally requires the addition of suitable photo initiators.

As the latter techniques allow coating on polymer foils it was only natural to use printing techniques for the coating of foils. Printing techniques have many advantages: They are easily up-scalable, allow continuous processing and direct patterning without any etching or other additional structuring processes and – last but not least – provide a cost efficient method of application. With all these features the process is suitable for the production of printed electronics.

When the physical properties of the various coatings are compared - especially for the conductivities - one observes big differences between those prepared on polymeric substrates and those prepared on glass where the conductivities are higher by one order of magnitude. The difference is even higher if films are compared to pellets made of chemically synthesized indium tin oxide. While films made by chemical processes rarely exceed conductivities of 1 $\mathrm{Scm^{-1}}$, with sintered pellets conductivities up to more than 1000 $\mathrm{Scm^{-1}}$ can be achieved [20]. This remarkable difference, a gap of three orders of magnitude, raises the question what – if the pellets can be considered as the upper limit of conductivities obtainable for chemically synthesized samples – causes the low conductivities in the films.

If one only looks at the isolated nanoparticles, their intragranular conductivities are comparable. Therefore it can be assumed that the intergranular conductivities are causing the above mentioned differences. In the case of the films there are always binder phases present to keep the nanoparticles together and in case of the films on polymeric substrates additional photo starters are needed to initiate the curing process. The binder phases are usually silica based systems e. g. MPTS (methacryloxypropyltrimethoxysilane), a bifunctional organosilane. The role of this compound as a binder phase is at least three fold: First, it “glues” together the nanoparticles, second, it provides adhesion of the film to the substrate and in its third role it gives mechanical stability to the composite film. Though already very good, the potential of the ITO coatings with regard to their conductivity leaves some space for future improvements. Here especially the matrix between the nanoparticles can be improved by several means.

This work provides some strategies to overcome the above mentioned obstacles. Some results will be shown and discussed.

Other problems are associated with the mainly used material, indium tin oxide. Despite of many parallel activities ITO is still the premiere material of choice. Nevertheless it has several serious disadvantages. Among the most severe drawbacks, the first is the possible future inavailability which is due to the worldwide limited reservoir of indium containing minerals. Sooner or later the material will not be available at a reasonable cost which will not only create a shortage of the resources but will cause an imponderability in the process of the manufacturing. The other main drawback closely related to the first are the high costs of indium tin oxides which is now about 2500 € per kg.

The strategies to overcome the material and system obstacles introduced above comprise four main lines:

The first line to improve the conductivities in TCO materials aims at enhancing the conductivity by doping. This means that materials with lower intrinsic conductivities are doped by suitable conductive materials to achieve an enhanced overall conductivity of the respective composite. In the long range the conductivities obtained by this or any other method or by combining various approaches, have to be in the range of the conductivities of indium tin oxide. Here the use of carbon nanotubes as dopants proved to be useful. This first route is established for several systems. i.e.: ATO (Antimony doped tin oxide, SnO_2 : Sb), titania (TiO_2) and AZO (Aluminum doped zinc oxide, ZnO : Al). Results were reported and discussed. An outlook on further strategies will be given.

The second strategic line comprises the enhancing of the matrix conductivity by modifications of the matrix phase. Here the binder phase is the main focus of the work. For this second route first results indicate a remarkable feasibility. The first material system was successfully tested as a matrix conductivity improving material.

In a third line of strategy alternative routes of synthesis for ITO were investigated. They can partially replace ITO in its expensive forms by the use of cheaper educts and processes. Here some work was already performed. It will be described and results will be discussed.

Finally a fourth line aims at enhancing the intrinsic conductivity of alternative materials. This implies as a rule the search for suitable processes to enhance the intrinsic conductivity. However it can also include the search for new alternative materials as replacements for indium tin oxide. Compared to the other strategies this line requires much more basic work and the thorough investigation of many physicochemical, structural and microstructural aspects of the selected materials. This line up to now is investigated only to a minor extent which is due to its high complexity.

2. Experimental

Enhancing of conductivity by doping:
As already mentioned the first route is established for several systems. i.e.: ATO, TiO_2, and AZO. Preperation includes the precipitation of nanoparticles from precursors and the formation of a suspension. This suspension is combined with a suspension containing the functionalized CNTs. Resulting sols are usually stirred, ultrasonicated and microfluidized subsequently. Coatings were usually prepared by spin-coating on a borofloat glass. Curing respective sintering procedure depends on the substrates and process history.
Due to lack of space experimental details are described elsewhere: For ATO processes are described in more detail in [21, 22]. For TiO_2 and AZO more details are found in references [23, 24] and [25] respective.

Enhancing the matrix conductivity:
For the second route first test results indicate the principle feasibility. The first metal oxide (M_nO_m) system was tested as a matrix conductivity improving material.
Preperation includes the precipitation of nanoparticles from precursors and the forming of a suspension. To this suspension the dopant components are added in partial substitution of the binder phase. Resulting sols are used to prepare coatings by spin-coating on borofloat glass or by other coating techniques such as gravure printing on polymeric foils. Curing and sintering procedure depend again strongly on the substrates and process history.
Due to lack of space the experimental details will be described elsewhere [26-27].

Alternative routes of synthesis for indium tin oxide:
Alternative routes of synthesis for ITO can partially lead to the replacement of expensive precursors or expensive process steps in the preparation of ITO, thus making the process cheaper.
Various attempts to reduce costs in the conventional forms of synthesis of indium tin oxide nanoparticles or nanoparticulate coatings have been performed.
One alternative described below comprises an electrochemical synthesis from metal electrodes. For the electrochemical synthesis and its experimental details see [20]. Methods for characterization of this samples are also described in this reference.

Enhancing the intrinsic conductivity of alternative materials and search for alternatives to replace ITO:
The search for alternative materials ideally replacing ITO is an ongoing process which was probably started at the time ITO was first used as a TCO. In the search for alternative materials and for processes to alter intrinsic conductivities of the transparent oxide materials many techniques were employed (see e. g. references [28-31]). Due to lack of space it is not possible to describe all the synthesis and characterization techniques used.

3. Results and discussion

Enhancing of conductivity by doping:
In our previous work the route of enhancing the conductivity by doping was established for several systems. These systems include ATO, TiO_2, and AZO. The only dopant tested in this regard are functionalized CNTs. Experiments to compare the effect of CNTs with that of other doping materials are on the way.
Figure 1 illustrates the effect of doping an ATO (antimony doped tin oxide, SnO_2 : Sb) ceramic with carbon nanotubes. The sheet resistivities are shown versus temperature of sintering. The sample with CNT doping is denoted ATO/MWNT because the doping consists of multi-walled carbon nanotubes (MWNT). An effect of reduction of the sheet resistivity by the doping is visible at lower temperatures. Though a clearly significant effect is seen, it is less than one order of magnitude. At sintering temperatures above 300 °C the effect of the doping becomes very small and at temperatures beyond 500 °C the doped samples show

even higher resistivities than the undoped. This is due to the thermal destruction of the nanotubes and presumably the formation of carbon species with no conductivity.

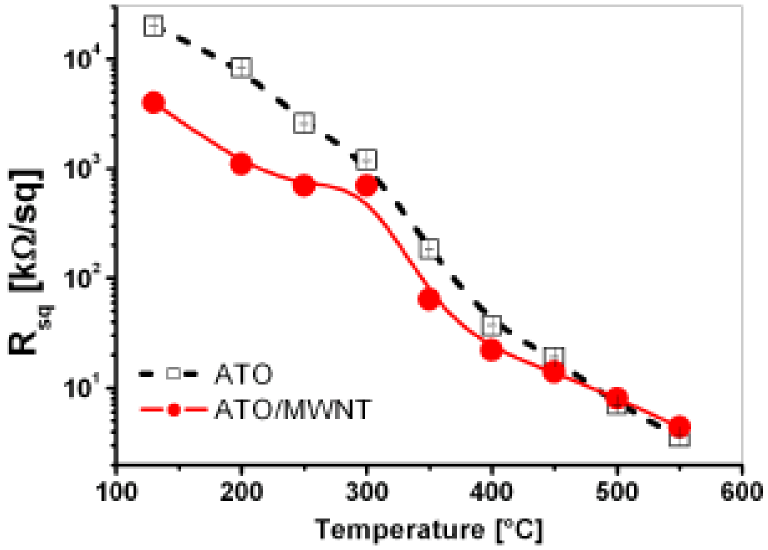

Fig. 1 Comparison of sheet resistances of ATO (antimony doped tin oxide) and ATO doped with CNTs [21].

It is worth noticing, that despite of the reduction of the resistivity, the absolute values of the achieved resistivities are far from being good. This is a consequence of the poor quality of the carbon nanotubes which show non-uniform properties. Also the resistivity of the ATO ceramics are far from optimum.

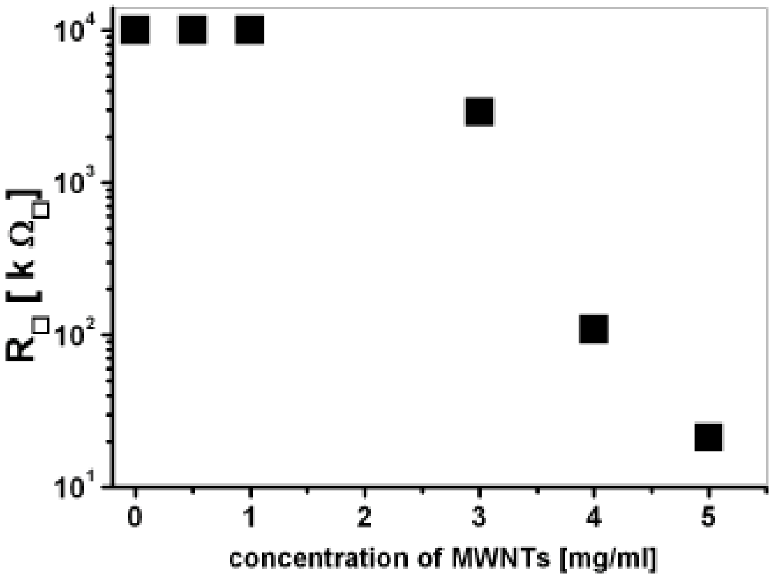

Fig. 2 Comparison of sheet resistances of titanium oxide undoped and doped with various concentrations of CNTs. CNTs are reported as MWNT (multi walled carbon nanotubes) [27].

Attempts to incorporate CNTs in a matrix of titania lead to the results depicted in Figure 2. In these experiments the conditions of sintering are constant. The sheet resistivities are shown versus the concentration of MWNTs in the TiO_2 matrix. Up to a concentration of more than 1 mg MWNTs per ml suspension the resistivities of the composites remain rather constant. At higher concentrations of more than 3 mg/ml the resistivities started to decrease. The decrease in dependence of the increasing concentration of carbon nanotubes reflects the percolative forming of transport paths in the composite microstructure. With a reduction of nearly three orders of magnitude the effect of the CNT doping is comparably pronounced, but however still the absolute values of the resistivities are too high for application.

The experiments with AZO (Aluminum doped zinc oxide, ZnO : Al) doped with carbon nanotubes are still ongoing. So far values of sheet resitivities of around and below 10^1 kΩ/sq could be obtained with AZO containing coatings.

In tests with carbon nanotubes applied as transparent coatings without an additional ceramic matrix even higher resistivities were obtained. This again points towards non-uniform microstructural features of the commercially produced carbon nanotubes.

Future cooperations with the Brazilian network for carbon materials bear the chance to combine well characterized carbon nanotubes with ceramic composites to obtain better electrical properties.

Enhancing matrix conductivity:

Whenever binder phases are present in a coating to keep the nanoparticles together, to generate adhesion to the substrate or to provide mechanical stability the usually used binder phases are silica based compounds such as MPTS (methacryloxypropyltrimethoxysilane), a bifunctional organosilane. As silica is an insulator the contact between the conductive ITO grains is interrupted and limited to a very small number of conduction paths. Thus especially the matrix between the nanoparticles can be improved by several means. Our strategy comprises the improvement of the matrix conductivity by the introduction of in-situ forming conductive compounds which is incorporated in the composite in partial or complete replacement of the binder. This attempt was successfully evaluated for the first M_nO_m (metal oxide) system. Figure 3 illustrates the results.

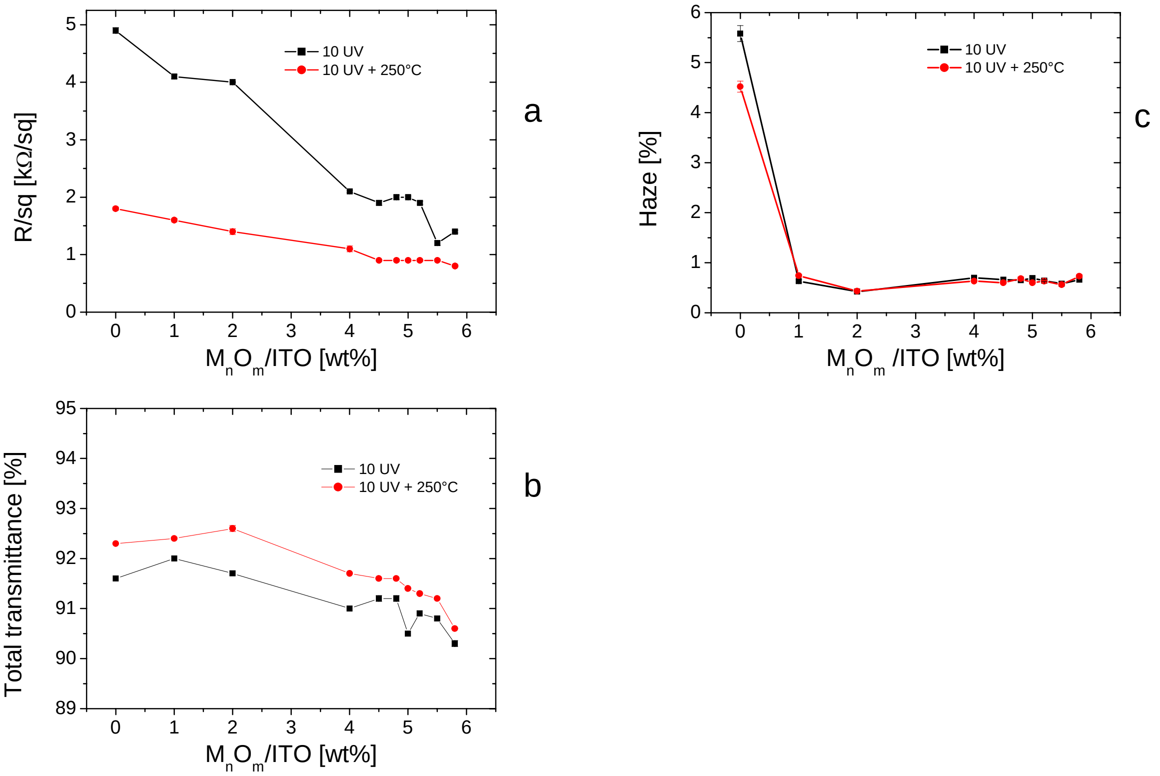

Fig. 3 Partial replacement of the binder phase by a higher conductive phase which is formed in-situ in the matrix leads to various effects on the physical properties. Increasing content of additive metal oxide phase like leads to: a) reduction of the sheet resistance, b) slight reduction of transmission and c) a reduction of haze [26].

The partial replacement of the binder phase by a higher conductive metal oxide phase being formed in-situ in the matrix leads to various effects on the physical properties. An increasingcontent of the added metal oxide phase first reduces the observed sheet resistance (a). The amount of incorporated replacement material into the binder composition however has some limits: The binding function must not be too much reduced. Also a loss of mechanical stability can only be tolerated up to a certain extent. At higher amounts of additive phase cracks and mechanical deteriorations of the coatings can be observed. The effect of decrease in resistivity on the other hand is not as high as desired but it shows the principle feasibility of the method. The other diagrams (b) and (c) in Figure 3 illustrate the effects on transmittance which is slightly reduced with an increasing additive phase content and on haze which is also reduced. For this effect relatively small amounts between 1 and 2 % of additive phase are sufficient. A side effect of the method is the faster UV hardening of the coatings on polymer foils.

Alternative routes of synthesis for indium tin oxide:
In an alternative process nanoscaled indium tin oxide (ITO, In_2O_3 : Sn) was prepared via an electrochemical method from metal electrodes in an aqueous system which contained ammonium acetate as a conductive salt. Figure 4 depicts the set-up for the electrochemical synthesis according to this method.

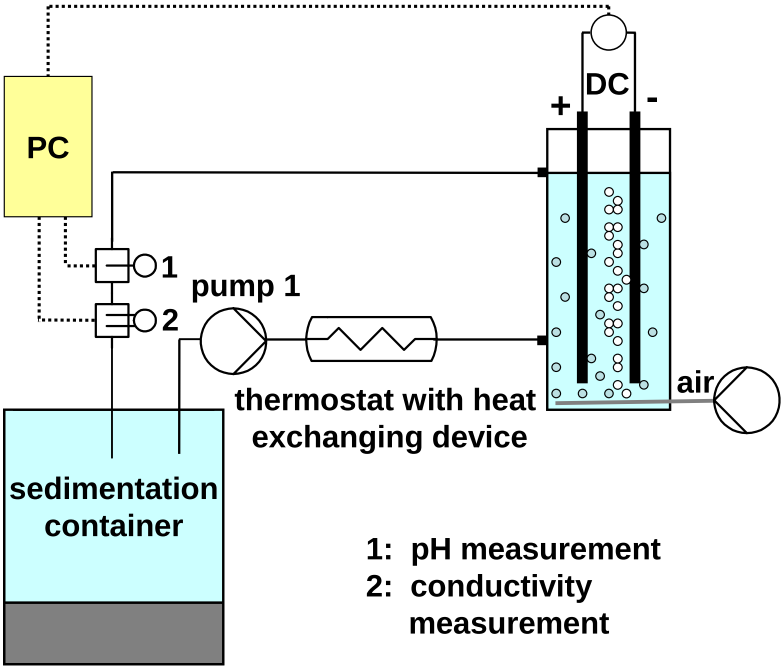

Fig. 4 Set-up for the electrochemical synthesis of ITO via an electrochemical technique [20].

As an intermediate product nanocrystalline $In(OH)_3$ was obtained which in turn serves as a precursor for the subsequent calcinations and - associated with tin doping - resulted in ITO powders. Depending on the atmosphere the dehydration of tin doped $In(OH)_3$ started at 150 °C, and a solid solution of cubic ITO was formed between 190 °C and 300 °C. At sintered samples which were post-treated in various ways, electrical conductivities up to 1400 Scm^{-1} were observed.

Enhancing the intrinsic conductivity of alternative materials and search for alternatives to replace ITO:
As mentioned the fourth strategy aims at enhancing the intrinsic conductivity of alternative materials.
It is reasonable to search for suitable processes to enhance the intrinsic conductivity.

Due to the very complex nature of the physical and chemical properties of transparent oxide materials there is a large variety of parameters which influence the combination of optical transparency and electrical conductivity. The resistivity is influenced by the charge carriers, by their concentration and mobilities. The charge carriers depend also on the defect chemistry which sets the equilibria of the defect interactions such as association and trapping of charge carriers, the relation between electronic and ionic charge carriers and so on. Last but not least structural and microstructural parameters strongly influence the resistivities but also the optical properties as transparency, absorption, reflectivity and haze.

Processes which are used to improve the intrinsic conductivity of alternative materials have to take into account all these dependencies. Some promising methods are found in thermal post-treatments, treatments under special atmospheres and other techniques.

The strategy can also include the search for new alternative materials as replacements for indium tin oxide.

In principle four families of TCO materials are known so far. They can be divided either along structural classifications or after the predominant type of electrical charge carriers:

Tetrahedrally-coordinated cations are present in zinc oxide or in AZO (ZnO : Al). These materials are n-type conductors.

Other n-type conductors show octahedrally-coordinated cations like CdO, ATO and SnO_2, $CdIn_2O_4$, Cd_2SnO_4, and others and form a second family of compounds. The most prominent member of this group however is ITO itself.

There are two other families which comprise both p-type conductors. One family has structures with linearly-coordinated cations. These include the members of the structure type ABO_2, the so called delafossites. A typical example is the TCO compound $CuAlO_2$.

The fourth family is less common and is built of cage frameworks, like mayenite, which has the composition $12CaO{\cdot}7Al_2O_3$.

So far mostly materials like ITO, ATO and AZO are considered to be good candidates. All of them are members of the n-type families. Clearly, the search should be widened to find other potential TCOs for the future.

4. Conclusion

The most popular material in the class of TCOs is still ITO – Sn-doped In_2O_3 – due to its unique combination of high transparency and electrical conductivity. Though already very good, the potential of the ITO coatings with regard to their conductivity leaves some space for future improvements. Some of the conditions in bindered composite coatings made of nanoparticles and additional phases limit the achievable conductivities. ITO itself is the material of choice due to a lack of other suitable candidates, but it still has some serious drawbacks including limited availability and its high price.

Several strategies to improve the situation are discussed in this article.

An important strategy aimed at the enhancement of the conductivity of alternative TCO materials by doping with carbon nanotubes. Results on ATO, titania and AZO are presented here: However despite principally promising results the absolute values of the achieved conductivities are rather small.

The matrix between the nanoparticles leaves much space for improvement as can be seen from a comparison of coatings and sintered pellets. It can be achieved by a partial replacement of the insulating binder phase by conductive alternatives. The first metal oxide system shows promising but still not sufficient increases in conductivities.

Alternative synthetical methods can reduce costs and supply materials with altered properties. An electrochemical synthesis from metal electrodes is proposed.

Last but not least there is a strategy, to improve the intrinsic conductivities of alternative materials by altered process technologies or to look after new alternative TCO materials.

As stated above especially the latter lines of work will require much more basic work and the thorough investigation of many physicochemical, structural and microstructural aspects of the selected materials. Therefore these areas are investigated so far only to a minor extent due to their very complex nature.

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Large area production of optical coatings and devices by the sol-gel process

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Coating Technology

Thin films technology occupies an important key position in the development of modern device technologies. For example the combination of high optical transmission in the visible range (between 380 nm to 780 nm) with high electronic conductivity, makes them an essential component for various types of displays (LCD, EL displays or touch screen panels), thin film solar cells and anti-reflective applications. Beyond the electrical conductivity, the closely related IR reflectivity and the photocatalytic effect opens a broad field of applications as heat insulating windows in architectural (low-emissivity glasses), security (electromagnetic shielding) or domestic areas (ovens, refrigerators) [1]. The thickness of such coatings is in the range of approx. 100 nm and thickness variations of only $\leq \pm 2$ % are demanded for high quality coatings. The most common coating techniques are PVD (Physical Vapor Deposition) [2] and CVD (Chemical Vapor Deposition) [3,4].

An advantage for the commercialization of the PVD or CVD process is that the process equipment including technology and material can be readily bought from suppliers. In the case of the wet coating area no standard equipment is available for large scale applications and the technological know-how has to be generated in the user's company. A similar situation is observed for the coating material, since coatings based on commercially available organic polymer materials are of interest only in a few application fields.

Wet coating materials are not standardized, not easily available and therefore have also to be developed by the users. Both factors, the non-availability of standard equipment and the non-availability of appropriate coating materials, seem to be the main draw back, and therefore wet coating techniques have not yet gained the same significance for large area/high volume applications as e.g. magnetron sputtering. This is in opposition to the large potential connected to chemical material synthesis, which allows generating highly functional coating materials with interesting properties for glass surfaces and, in addition to this, the equipment costs may be only a fraction of the costs of other techniques [5].

Nanostructured inorganic or mixed inorganic-organic materials became of interest for many areas in the last decade. Many coatings and devices have already been prepared with tuned properties between glasses and polymers, with improved optical properties, or with improved mechanical or resistance to chemicals. In addition to the molecular inorganic or inorganic-organic hybrid network, the magnetic, electric, optical or catalytic properties of nanoparticles resulting from the inorganic amorphous, crystalline, glassy or metallic state of matter also can be used for the material design [6].

Nanoparticles are usually fabricated by using chemical synthesis under specific conditions. During a precipitation process from liquid phases, surface modification agents have been added during or shortly after the formation of the precipitates. These interfere with the nucleating and growing particle to avoid agglomeration and to control size. Nanoparticles from many systems have been fabricated. It was shown that 6 nm SiO_2-nanoparticles containing nanocomposite hybrid sols can be dried in form of crack-free films up to 14 μm thickness after one step of dip-coating process and densification process at 450 °C. This is attributed to the increase of relaxation ability and flexibility. The nanoparticulate inorganic amorphous coating is insoluble in water and can be used as protective coating against acid attack. Boehmite nanoparticles were used to serve as condensation catalysts to prepare very hard transparent coatings for polycarbonates and an overcoat with polymerizable nanoparticles was used to produce anti-reflective and ultra hard coatings. In systems with incorporated fluorosilanes, leading to low surface free energy coatings, nanoparticles were used to tailor the fluorine depth profile in self-aligning transparent easy-to-clean coatings by influencing the critical micelle concentration.

The commonly used TCO (transparent conducting oxide) materials are wide band gap ($E_g \geq 3$ eV) n-type semiconductors, mostly employing pure or doped indium oxide (In_2O_3), tin oxide (SnO_2) or zinc oxide (ZnO). The doping materials in the case of wet chemically deposited thin films, however, differ from those known from PVD and CVD, as for example an anionic fluorine doping is difficult to realize in wet chemical processing.

The most frequently used sol-gel TCO systems are reported in reference [7].

Due to the excellent electrical properties of the Indium Tin Oxide (ITO), the Sn-doped indium oxide (In_2O_3:Sn), attracts the greatest attention, but the high costs limit its application. The carrier concentration in the ITO coating can be adjusted by the number of the oxygen vacancies induced using a post thermal treatment under inert or reducing conditions.

The principle properties of ATO, the Antimony-doped Tin Oxide (SnO_2:Sb) are mainly its chemical and mechanical stability and its low number of processing steps. The smaller influence of oxygen vacancies makes it more thermally stable compared to ITO. On the other side, the resistivity of ATO coatings is typically at least one order of magnitude higher than that of ITO.

The AZO Aluminium-doped Zinc Oxide (ZnO:Al) is the material of choice for most of the solar applications, as it exhibits a very high optical transmission and can easily be patterned by chemical etching. Highly conductive films, however, can only be obtained by a multiple deposition of thin layers leading to an orientation of the crystallites, and a subsequent post treatment under reducing atmosphere.

A representative of the group of ternary oxides is cadmium stannate (CTO - Cd_2SnO_4), which is investigated for its high carrier mobility. In addition, some ternary oxides like zinc stannate (ZTO - Zn_2SnO_4) have attracted attention as promising candidates for coatings with a higher work function, especially in view of future display developments.

Some sol-gel activities have been done in the area of TCO transparent conductors based on Nb-doped TiO_2 (TNO) [8,9]. In 2006 the Furubayashi group published [10] a fabrication method of single crystal $Ti_xNb_xO_2$ films with x = 0.002 – 0.2 deposited onto $SrTiO_3$ substrates by pulsed laser deposition (PLD). The resistivities of films with $x \geq 0.03$ are 2 to 3 $x10^{-4}$ Ω . cm at room temperature and the transmittances of films reach up to 97%. Sol-gel method has been used to produce $Ti_{0.94}Nb_{0.06}O_2$ (TNO). The films have been formed by dip coating and a subsequent two step annealing treatment. They exhibit a minimum resistivity of 19.3 Ω . cm and an average optical transmittance of about 75% in the visible range, indicating that the sol–gel method could be a feasible and promising method to fabricate TNO films.

The strategy to use opaque conducting nanowires like silver, gold or palladium to produce transparent and conductive coatings has been early used. But the aspect ratio of the fibers are not high enough to obtain a percolation of the fibers in a solid concentration below 10%. With the entrance of carbon nanotubes (CNT) in the field a new high conductive fiber with a high aspect ratio has been produced. Kaiser et al. [11] have used conductive CNTs as fillers in a polymer matrix to enhance conductivity, but the resulting nanocomposites exhibited little or no transparency in the visible range (400-800 nm). Coleman et al. [12] and Curran et al. [13] reported conjugated polymer-CNT composites using multi-walled CNTs, which showed percolation concentration of the CNTs exceeding 5 wt.%. The resulting nanocomposites were black with no transparency in the visible region. Shaffer and Windle [14] reported conductivities of a multi-walled CNT/poly(vinyl alcohol) composite, which also showed percolation above 5 wt.% nanotube loading and led to a black nanocomposite. The same group [15] reported another multi-walled CNT composite in an epoxy resin, which achieved percolation below 0.04 wt.%. An optical micrograph of the CNT/epoxy resin composite was reported, which revealed that the CNT phase was separated from the epoxy resin, showing several millimeters of resin-rich domains. The dispersion of CNTs in this material was very poor. This agglomeration of CNTs in selected areas of the composite could explain the high conductivity observed since this provides the "shortest path" for the current to travel.

Preliminary measurements of the conductivity of a CNT/poly(methyl methacrylate) (PMMA) composite were measured on a fiber [16]. The level of conductivity was relatively high (1.18 x 10^{-3} Scm^{-1}) at 1.3 wt.% SWNT loading. However, the optical transparency in the visible range was not determined for the fiber sample. The mechanical properties of these fibers were much lower than the predicted value, which implies that the CNTs were not fully dispersed as Connel et al. [17] reported. New results concerning the applicability of the CNTs for conductive transparent coatings has been published by Pimenta showing a big potential of the CNTs to be used as electrodes for solar cell technology [18].

Optical devices

The industrial fabrication of active and passive microoptical devices as gratings, micro lenses, micro lens arrays, Y-couplers lead to the development of new materials and technologies. This was limited in the last 10 years by high development costs and small market volumes for these elements. The market of micro optical elements has grown and requires new holographic techniques and new photosensitive coatings. The organic photopolymers have contributed significantly to the recent growth of holographic and lithographic applications, but the photoresists and photopolymers have shown limitations like non linear response in the deep UV, decrease of the diffraction efficiency (after wet development and subsequent UV-irradiation) and only very small modulation of the refractive index as well as the instability against wheathering agents.

Micro optic elements are applied in a wide branch of optical products, like holograms, gratings, micro lens arrays, light guiding elements (waveguides, diffusers, reflectors), and optical data storage (CD-ROM). The structures of microoptical elements are based on the layers with surface relief patterns in the range of one µm to one hundred nm. The commonly used method to produce these microoptical elements are etching and photolithography, ion exchange, laser beam writing, or embossing.

The embossing process consists of a stamper (planar or roll) with a negative surface relief. The desired micro pattern can be produced by pressing the stamper into the material which is being fixed by curing or cooling and removing the stamper.

The embossing process, compared to the photolithography has at least two advantages: low production costs because of manifold replication of the master pattern. Also micro patterns with complicated cross sections can be obtained in a single step, whereas photolithography requires several cycles of coating, illumination and developing or etching.

One can distinguish between two different embossing techniques: hot embossing and reactive embossing. In the hot embossing process, a heated stamper is pressed onto a thermoplastic material and is removed after cooling. There is a time wasting at every cycle between 25 to 60 min for processing temperatures of 100 to 180 °C, which limits the speed of mass production of micro patterns. For the reactive embossing process a UV curable lacquer with a very low viscosity is used. To obtain a copy of the micro pattern the curing step has to be carried out underneath of the embossing stamper, which causes a low speed mass production. A disadvantage for organic monomers is their high shrinkage up to 16 vol. % during polymerisation process. Another problem for these organic nanomers is their poor thermal and mechanical stability.

The first generation of nano composite materials for the embossing process are synthesized by sol-gel route at INM. An inorganic component formed by the hydrolysis and condensation process included in the polymerization of organic component leading to an organic-inorganic network. This nano composite material with overall low shrinkage character (less than 5 vol. %) allows to accomplish the embossing with a near net shaping quality [19]. By adding a proper photo initiator to the nano composite material the curing by light irradiation (UV-VIS) is made possible. The inorganic component improves the thermal and mechanical stability in comparison to the pure organic polymers. The organic component allows the decrease of the densification temperature to less than 150 °C [19]. The nano composite material is based on methacryl oxypropyl trimethoxy silane and zirconium n-proxpoxide with methacrylic acid for starting the reaction. In Fig. 1 the thixotropic embossing process is shown.

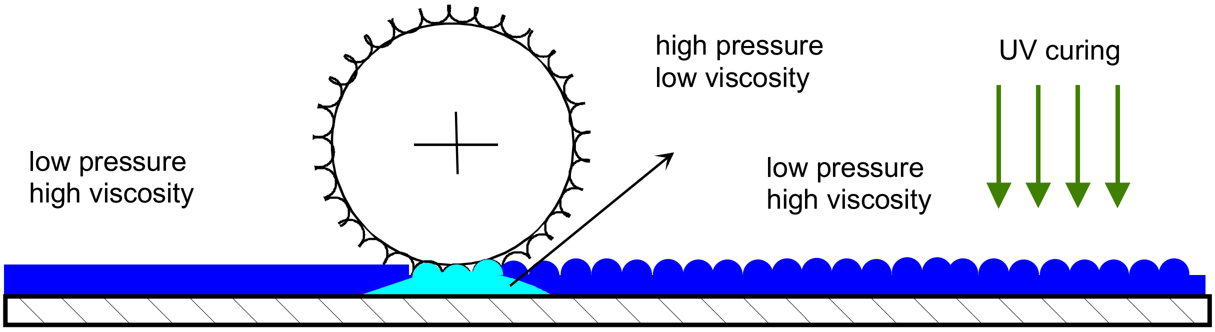

Fig. 1 Schematic diagram of thixotropic embossing.

The thixotropic embossing process has three different steps. First, a coated substrate foil with a high viscose thixotropic material is introduced in the embossing cylinder. Under high pressure the viscosity of the thixotropic coating will be drastically reduced. The last step (after the film has left the high pressure region) the gain in of the caused by the absence of the shear force. With this process the curing area can be extend to some meters, which will increase the production speed.

The relief hologram is a mass product with very low contrast and diffraction efficiency. Optical elements for display and security need to have volume and phase structures in order to fulfil the iniquity required for security labels.

For the production of passive optical elements conventional photoresists, sensitive to near UV light based on an aromatic polymer containing benzene rings, are largely used, but the mechanical properties and low aging agents stability have been limited for the application in displays or architecture. Chalcogenide films have high holographic energy sensitivity only in the visible region of the spectrum, which limits the periodicity of the gratings (min. periodicity about 300 nm) and the coating is therefore made by vacuum deposition or sputtering. Roxan (PMMA und cyanine dye films) can be used for three dimensional phase recording. The substrates can be coated by spin or dip coating techniques but the holographic energy sensitivity is only present in the visible range (min periodicity about 250 nm). Silver halide materials have a very high sensitivity (about 10^{-7} j/cm^2) and a high refractive index modulation (Δn=0.8). However the maximum diffraction efficiency is controlled by the development step and contact with humidity produces a decrease of the amplitude of the refractive index modulation. The organic photopolymers show non-linear response in deep-UV and produce a very low signal/noise ratio (150:1) They also shown small variation in the intensity of the light resulting in a drastic overexposure of the resist (SNR 200 Deep-UV from Shipley). Some photopolymers show better irradiation response linearity at λ=257 nm, but the absorption is more than 75% measured on a film of 400 nm of thickness (ex. SPR 505 from Shipley, or UV-resists from Du Pont). The holographic structure in organic photopolymers shows a decrease of the diffraction efficiencies by up to 50% in the case the holograms are read with deep ultraviolet. This is because the ultraviolet irradiation produces organic network formation and subsequent shrinkage of the unpolymerized part of the hologram. None of the materials currently used for the recording of relief or phase holograms fulfill all of the requirements with respect to applications in integrated optics and to efficient processing. On the other hand a new class of holographic nanocomposites has shown great potential to produce holograms with a very high signal/noise value (450:1), a high refractive index modulation of 1.5 x 10^{-2} and the factor Gamma (linearity of the holographic sensitivity) can be adjusted by the type and concentration of the photoinitiator.

New photo polymerizable organic-inorganic hybrid materials based on methacryl silane and functionalized zirconium nano particles have shown advantages (like high refractive index modulation and a good signal/noise ratio) as holographic recording materials compared to photoresists or photopolymers. Thick films of this composite system were prepared and volume diffractive gratings were fabricated by holographic copy technique developed at INM. The formation of the phase gratings by irradiation of a photosensitive material with a UV pattern is based 1) on the diffusion of high refractive index functionalized nanoparticles to areas with high irradiation intensity with 2) subsequent immobilization by full irradiation of the film. The relief grating can be formed by production of three-dimensional relief structures using a wet development step of the unpolymerized region or by a heat treatment to produce an inorganic network.

Holographic diffusers are key optical elements in liquid crystal displays (LCDs) used to manage incident light from sources over a defined angle to, keep the brightness uniform over the entire display area. Generally, the diffusers can be classified into three types: the particle-diffusing, the surface-relief type and the phase or volume diffuser. Particle diffusers rely on the transparent beads inside the plastic films of plates to scatter light [20]. The surface-relief diffusers scatter the light by the microstructures thereon, (e.g. micro lens, random phase [21], deterministic diffractive).[22] The surface relief diffuser is normally produced by embossing. Much research has been focused on volume phase diffusers owing to their unique properties, such as controllable diffusion angle, directional property, volume refractive index variation, and high transmittance or high efficiency. Hologram materials such as silver-halide sensitized gelatine, dichromated gelatine, photopolymers [23], and azobenzene polymers [24] have been used to fabricate the diffusers (see Fig. 2).

Ionic liquids are organic salts that are liquid at ambient temperature, preferably at room temperature. They often possess unusual properties such as non volatility, non flammability and may be considered as highly polar liquids. Ionic liquids may be seen as a tool with potential for use in sustainable processes such as solvent replacement, in catalytic reactions, in electrochemical devices and in synthesis of nano particles. Ionic liquids as “green solvents” have attracted increasing interests in polymerizations. Many types of polymerization have been studied using ionic liquids as media in common reactions including olefin polymerization, oxidative polymerization, condensation polymerization, enzymatic polymerization, conventional free radical polymerization, transition-metal-mediated radical polymerization and reverse atom transfer radical polymerization. In these radical polymerization processes, significantly enhanced polymerization rates and high molecular weights are usually observed due to the diffusion-controlled polymerization [25,26].

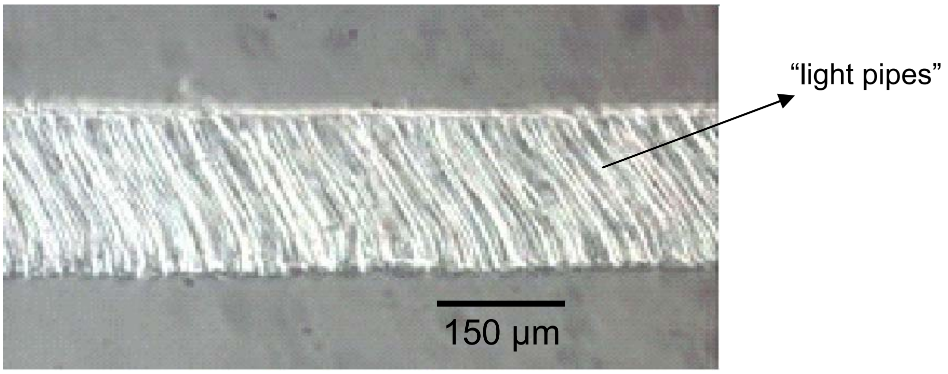

Fig.2 Cross Section optical phase microscopy of an optical diffuser made by continuous roll-to-roll lithographic process.

The formation of the light pipes (as in Figure 2) is attributed to the diffusion of the ZrO_2 nanoparticles along the concentration gradient of their photopolymerizable bounds (Colburn-Haines effect) [27]. By local irradiation (holographic writing) ZrO_2 nanoparticles are diffusing towards the irradiated region and their ligands are photopolymerized, leading to an up-concentration of high refractive index particles. Finally the structure is fixed by subsequent complete UV irradiation (350 nm to 450 nm) with 250 mJ/cm^2 of intensity. The material provides thick phase gratings with the diffraction efficiency up to the theoretical maximum of 100%.

The next step to adjust the new diffuser to the commercialization will be the scaling up process, which will be done in the application centre of INM. The “up scaling” works will be divided in three phases: 1) the up scaling of the photosensitive material, 2) the coating of the photosensitive material in a roll-to-roll process and 3) the production of the volume phase diffuser using a continuous lithographic process.

In this paper we have shown only a few practical examples of the production of optical coatings and devices using wet chemical processes. One of the usually used coating techniques for the wet chemical processing of foils is the roll-to-roll process integrated with offset, doctor blade or reverse roll-coating setups. A typical machine developed for the wet coating process is shown in Figure 3.

a) b)

Fig.3 Roll-to-Roll coating machinery at INM application center. This machinery with 1.6 meters web is installed in a clean room with special illumination and explosion safety areas, which enable the work with high pressure vapor solvents types. a) coating setup and b) area for the optical and mechanical structuring of the films.

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