

Nanoworkshop 2009

**4th International Workshop on Polymer/Metal
Nanocomposites**

**September 2 – 4, 2009
Charles University in Prague
Czech Republic**



Edited by Pavel Kudrna, Danka Slavínská and Hynek Biederman

Book of Abstracts

All rights reserved. No part of this publication may be reproduced or transmitted in any form or by any means, electronic, mechanical, photocopying or otherwise, without the prior written permission of the publisher.

© LOC, 2009

© MATFYZPRESS by publishing house of the Faculty of Mathematics and Physics, Charles University in Prague, 2009

ISBN 978-80-7378-010-4

International Organizing Committee

Hynek Biederman – Chair (Charles University Prague, Czech Republic)

Walter Caseri (ETH Zürich, Switzerland)

Franz Faupel (Christian Albrecht University of Kiel, Germany)

Detlev Fritsch (GKSS, Research Centre, Germany)

Shigehito Deki (Kobe University, Japan)

Yang Yang (UCLA, USA)

Local Organizing Committee

Hynek Biederman

Milan Tichý

Danka Slavínská

Pavel Kudrna

Ondřej Kylián

Jan Hanuš

Andrey Shukurov

Jaroslav Kousal

Martin Drábik



The building of the Faculty of Mathematics and Physics in Prague, Malostranské náměstí 25 (Malá Strana square). Next-door on the left hand side there is St. Mikuláš church.

Foreword

The 4th International Workshop on Polymer/Metal Nanocomposites (Nanoworkshop 2009) that is held from 2.9. till 4.9.2009 in Prague, Czech Republic, aims to bring together physicists, chemists, and engineers from academics and industry. The scope of the workshop ranges from advanced preparation techniques to resulting new properties and industrial applications. Theoretical work and computer simulations are also included. The nanocomposites may consist of polymer/metal in the shape of nanoclusters, nanotubes, nanofibers, and nanowires. Contributions discussing functional properties of polymer/carbon composites are also welcomed

The 1st International Workshop on Polymer/Metal Nanocomposites (Nanoworkshop 2003) was organized in 2003 at University of Kiel followed by Nanoworkshop 2005 at Geesthacht and by Nanoworkshop 2007 at Kobe.

The programme of the present **Nanoworkshop 2009** consists of 6 invited lectures, 26 short oral presentations and 11 poster contributions.

In this Book all abstracts have been reviewed and then accepted by the IOC. The abstracts were not changed only they were formatted into a uniform style.

We wish participants of the **Nanoworkshop 2009** the efficient and enjoyable time during this event.

Pavel Kudrna, Danka Slavínská and Hynek Biederman (eds.)

on behalf of

The Local Organising Committee

International Workshop on Polymer/Metal Nanocomposites - Patronages and Sponsorships

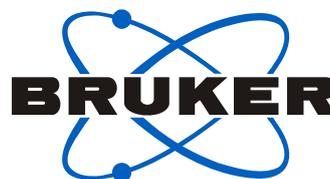
Charles University in Prague
Faculty of Mathematics and Physics
<http://www.mff.cuni.cz>



HVM PLASMA Ltd.
<http://www.hvm.cz>



Optik Instruments, Ltd.
<http://www.brukeroptics.cz>



LAO-Industrial Systems Ltd.
<http://www.lao.cz>



Vakuum Praha Ltd.
<http://www.vakuum.cz>



Vakuum servis Ltd.
<http://www.vakuum-servis.cz>



TESCAN Ltd.
<http://www.tescan.com>



Kurt J. Lesker Company
Central European Operations Hungary
<http://www.lesker.com>



Pfeiffer Vacuum
<http://www.pfeiffer-vacuum.cz>



Program Overview of the 4th International Workshop on Polymer/Metal Nanocomposites

Wednesday September 2nd 2009

8:00 – 9:30	REGISTRATION (Room S6)	
9:30 – 9:45	Opening Remarks (Hall S5)	
	Session chairman: Milan Tichý	
9:45 – 10:30	T.P. Radhakrishnan: <i>Polymer thin films embedded with in situ grown metal nanostructures</i> – Invited lecture	10
10:30 – 11:15	A. Pucci: <i>Optical properties of polymer/metal nanocomposites and application as smart materials</i> – Invited lecture	12
11:15 – 11:30	coffee break	
11:30 – 11:50	<u>Shigehito Deki</u> , Takashi Hasegawa and Minoru Mizuhata: <i>Synthesis of Metal Oxide Nanoparticles in Restricted Space of Perfluorosulfonate Ionomeric Membrane: Nafion®</i>	14
11:50 – 12:10	<u>W. L. Tan</u> , M. Abu Bakar: <i>Studies on LiCF₃SO₃-doped magnetite-ENR polymer electrolytes</i>	16
12:10 – 12:30	<u>Haybat Itani</u> , Patrick Keil, Monika Santa, Aleksander Kostka, Guido Grundmeier: <i>Spectroscopic Studies of the Structure and Stability of Silver Nanoparticles in LBL Polyelectrolyte Films</i>	18
12:30 – 12:50	<u>Dmitri Muraviev</u> , Amanda Alonso, Jordi Mas and Maria Muñoz: <i>Environmentally-safe polymer-metal nanocomposites</i>	20
13:00 – 14:00	Lunch	
14:00 – 15:00	Poster Session	
P1	<u>Z. Křižanová</u> , I. Krupa, V. Cecen, J. Prokeš, I. Vávra: <i>Structural and electrical properties of nanocomposites based on the EVA copolymer filled with nano-structuralized graphite</i>	22
P2	W. L. Tan, N.A. Mohd. Akib, N.H. Mohd. Hirmizi, <u>M. Abu Bakar</u> and J. Ismail: <i>Filtering Effect of the Polymer on Particles upon Aqueous to Organic Phase Transfer</i>	24
P3	<u>S. Novák</u> , M. Švec, R. Hrach, J. Pavlík: <i>Electrical properties of composite films</i>	26
P4	<u>P. Bartoš</u> , J. Blažek, P. Špatenka: <i>Charging of small particulates in plasma: study by computer simulations</i>	28
P5	<u>G.G. Gumarov</u> , A.I. Gumarov, V.Yu. Petukhov, N.R. Khabibullina, V.F. Valeev: <i>Magnetic properties of silicide nanoparticles ion-beam-synthesized in the external magnetic field</i>	30
P6	<u>Josef Paul</u> , Lucie Bačáková, Vladimír Starý, Ladislav Cvrček, Stanislav Daniš: <i>Structure and mechanical properties of biocompatible ZrN film on various substrates</i>	32
P7	<u>M. Vandrovcová</u> , A. Grinevich, L. Bačáková, V. Lisa, A. Shukurov, D. Slavinská, H. Biederman: <i>Effect of different concentration of Ti in hydrocarbon plasma polymer films on the adhesion, proliferation and differentiation of human osteoblast-like MG63 cells</i>	34
P8	<u>G. G. Gumarov</u> , M.M. Akhmetov, V.Yu. Petukhov, E.P. Zheglov, G.N. Konygin, R. B. Zaripov: <i>EPR study of nanodispersed calcium gluconate</i>	36
P9	<u>J. Matoušek</u> , J. Pavlík, L. Kováčik, M. Švec: <i>Tin/n-hexane nanocomposite films and their electrical properties</i>	38
P10	<u>A. Patra</u> , J. Piard, R. Métivier, K. Nakatani, T. P. Radhakrishnan: <i>Molecular nano/micro crystals: fabrication and optical properties</i>	40
P11	<u>M. Neuber</u> , J. Lucas, G. Hanke, A. Heilmann: <i>Laser Welding of Polymer Foils by using embedded Metallic Nanoparticles</i>	42
	Session chairman: Shigehito Deki	
15:00 – 15:20	<u>Stephan V. Roth</u> , Rainer Gehrke, Ulla Vainio, Kai Schlage, Ralf Röhlberger: <i>Investigating in-situ the formation of biofibre-metal nanocomposites with GISAXS</i>	44
15:20 – 15:40	<u>Darin Zimmerman</u> , Richard Bell, Joseph Filer II, Joshua Karli, Norman Wereley: <i>Percolation behavior of cobalt-nanowire-based magnetorheological fluids</i>	46
15:40 – 16:00	<u>Fanggao Chang</u> , Feng Yang, D. P. Almond, Shaoxiang Wang, Na Zhang, and Guilin Song: <i>Electrical properties of Ni-silicone rubber piezoresistive composites under uniaxial pressure</i>	48
16:20 – 18:00	Welcome party and organ concert (Refectory)	

Program Overview of the 4th International Workshop on Polymer/Metal Nanocomposites

Thursday September 3rd 2009

Session chairman: Walter Caseri

9:00 – 9:45	Luca Ravagnan: <i>Cluster beam deposition: a tool for nanoscale science and technology</i> – Invited lecture	50
9:45 – 10:30	Andreas Heilmann: <i>Laser-induced coalescence and agglomeration of noble metal nanoparticles embedded in a polymer matrix</i> – Invited lecture	52
10:30 – 10:50	<u>Vladimír Čech</u> , R. Trivedi, B. Čechalová, J. Studýnka: <i>Nanolayered composites of plasma polymer films</i>	54
10:50 – 11:10	<u>H.T. Beyene</u> , F. D. Tichelaar, M.C.M van de Sanden and M. Creatore: <i>Plasma deposition of dielectric/metal nanocomposite layers exhibiting surface plasmon resonance effects</i>	56
11:10 – 11:30	coffee break	
11:30 – 11:50	<u>Aleš Marek</u> , J. Vyskočil, J. Valter, P. Plíhal: <i>Magnetron based gas-aggregation deposition system – nanoclusters production and stability</i>	58
11:50 – 12:10	J. Hanuš, O. Kylián, A. Artemenko, J. Kousal, J. Pešička, D. Slavinská, <u>H. Biederman</u> : <i>Nanocomposite metal/plasma polymer films prepared by means of gas aggregation cluster source</i>	60
12:10 – 12:30	<u>Pavel Solář</u> , A. Choukourov, J. Hanuš, D. Slavinská, H. Biederman: <i>Magnetron Glancing Angle Deposition of Nanocomposite Thin Films</i>	62
12:30 – 12:50	<u>Vladimir Zaporojtchenko</u> , C. Pakula, H. Takele, V.S.K. Chakravadhanula, A. Kulkarni, C. Pochstein, H. Greve, T. Strunskus and F. Faupel: <i>Nanocomposite Films with Embedded Metal Nanoparticles Near the Percolation Threshold - Physico-Chemical Properties and Applications</i>	64
13:00 – 14:00	Lunch	
	Session chairman: Franz Faupel	
14:10 – 14:30	<u>Susanne Seyffarth</u> and Hans-Ulrich Krebs: <i>Preparation of PMMA/Cu-Nanocomposites by pulsed laser deposition</i>	66
14:30 – 14:50	F. Choffat, M. Fontana, J. Bremi, P. Smith, <u>Walter Caseri</u> : <i>Polymeric Metal Wires</i>	68
14:50 – 15:10	<u>Ezzeldin Metwalli</u> , K. Schlage, V. Körstgens, S. Couet, R. Meier, G. Kaune, S.V. Roth, R. Röhlberger, P. Müller-Buschbaum: <i>Real time GISAXS study of magnetic nanoparticle assemblies on polymer templates</i>	70
15:10 – 15:30	G. Kaune, M.A. Ruderer, E. Metwalli, R. Meier, W. Wang, S. Couet, K. Schlage, R. Röhlberger, S. V. Roth, <u>P. Müller-Buschbaum</u> : <i>Growth of metal thin films on conductive polymer surfaces</i>	72
15:30 – 16:00	coffee break	
16:00 – 16:20	<u>Yogendra K. Mishra</u> , S. Jebil, D. C. Agarwal, V. S. K. Chakravadhanula, V. Zaporojtchenko, D. K. Avasthi, R. Adelung and F. Faupel: <i>Noble metal-polymer nanocomposites as plasmonics and optoelectronics</i>	74
16:20 – 16:40	<u>Mathias A. Ruderer</u> , R. Meier, P. Müller-Buschbaum: <i>Enhanced light harvesting in semiconducting nanoparticle/polymer composites</i>	76
16:40 – 17:00	<u>Mottakin M. Abul Kashem</u> , Jan Perlich, Alexander Diethert, Weinan Wang, Mine Memesa, Jochen S. Gutmann, Eva Majkova, Ignác Capek, Peter Müller-Buschbaum & Stephan V. Roth: <i>Particle co-operated self-assembly in thin film of diblock copolymer</i>	78
19:00 –	Conference dinner (Restaurant "House for Professed")	

Friday September 4th 2009

Session chairman: Hynek Biederman

- 9:00 – 9:45 Bernard Despax, C. Saulou, P. Raynaud, M. Mercier-Bonin, S. Zanna and P. Marcus: *Nanocomposite films metal/plasma polymer for biomedical applications* – Invited lecture 80
- 9:45 – 10:30 Eloisa Sardella, R. Gristina, M. Altomare, D. Caruso, G. Da Ponte, C. Ingrosso: *Plasma deposited nanocomposite coatings for biomedical applications: silver and hydroxyapatite containing thin films* – Invited lecture 82
- 10:30 – 10:50 Toshifumi Takeuchi: *Molecularly Imprinted Organic/Inorganic Hybrid Materials Capable of Protein Recognition Prepared by Liquid Phase Deposition* 84
- 10:50 – 11:10 Enrico Körner, A. Ritter, P. Rupper, E. Michel, D. Hegemann: *Design of bioactive Ag-Nanocomposites with a single-step plasma process* 86
- 11:10 – 11:30 coffee break

Session chairman: Andreas Heilmann

- 11:30 – 11:50 Lucie Bačáková, Chadi Ali, Zdeněk Čejka, Martin Pařízek, Marta Vandrovcová, Lubica Grausová, Věra Lisá: *Adhesion, growth and differentiation of human osteoblast-like MG 63 cells on metallic and polymeric materials developed for artificial joint replacements* 88
- 11:50 – 12:10 S. Clémenson, Elianne Espuche, L. David: *Polymer/metal hybrid membranes : from in situ nanostructuring process to modulated functional properties* 90
- 12:10 – 12:30 Antonella Milella, E. Dilonardo, F. Palumbo, S. Martin, R. d'Agostino, F. Fracassi: *Plasma deposited platinum-containing nanocomposite films as catalysts for fuel cells* 92
- 12:30 – 12:50 Minoru Mizuhata, Katsumasa Matsumoto, Yoshikazu Miyachi, Masako Oga, Shigehito Deki: *Fabrication of Pt/Conductive Polymer Composite for Durability Improvement of Catalyst for Fuel Cells* 94
- 13:00 – 14:00 Lunch and IOC Meeting

Session chairman: Hynek Biederman

- 14:15 – 15:00 General Discussion
- 15:00 – 15:30 Closing of Workshop

List of Nanoworkshop 2009 participants	96
Full page advertisements	100

Polymer Thin Films with *In Situ* Grown Metal Nanoparticles

T. P. Radhakrishnan

School of Chemistry, University of Hyderabad, Hyderabad – 500 046, India

Email : tprsc@uohyd.ernet.in, Web : http://202.41.85.161/~tpr/

Metal – polymer nanocomposites are versatile materials which not only combine the unique characteristics of the components, but also manifest mutualistic effects. Some of the most convenient and attractive routes to the fabrication of metal nanoparticle – embedded polymer thin films involve the *in situ* generation of the nanoparticles through reduction or decomposition of appropriate precursors inside the solid film. We will describe a general and environment-friendly protocol that we have optimized for the fabrication of noble metal nanostructures inside polymer thin films, using aqueous medium for the synthesis and deploying the polymer itself as the reducing as well as stabilizing agent.^{1,2} The *in situ* growth of metal nanoparticles inside polymer films provides a unique opportunity to monitor the growth process in real time using microscopy; we will describe recent studies carried out in this direction. A variety of techniques that have been exploited by our group and other investigators to characterize the precursor to product transformation inside the polymer film will be discussed briefly.³ The unique control provided by the *in situ* fabrication route on the size, shape and homogeneous distribution of the nanostructures and chemical transformation within the polymer film will be highlighted. Following a brief overview of the range of applications of the polymer thin films with *in situ* generated metal nanoparticles, reported by us and others in areas such as nonlinear optics, microwave absorption, random lasers and e-beam lithography,⁴ some new directions of explorations will be noted.

References

1. S. Porel, S. Singh, S. S. Harsha, D. N. Rao, T. P. Radhakrishnan, *Chem. Mater.* **2005**, *17*, 9.
2. S. Porel, S. Singh, T. P. Radhakrishnan, *Chem. Commun.* **2005**, 2387.
3. (a) S. Porel, N. Hebalkar, B. Sreedhar, T. P. Radhakrishnan, *Adv. Funct. Mater.* **2007**, *17*, 2550; (b) S. Clémenson, L. David, E. Espuche, *J. Polym. Sci. A.* **2007**, *45*, 2657.
4. (a) S. Porel, N. Venkatram, D. N. Rao, T. P. Radhakrishnan, *J. Appl. Phys.* **2007**, *102*, 033107; (b) X. Meng, K. Fujita, Y. Zong, S. Murai, K. Tanaka, *Appl. Phys. Lett.* **2008**, *92*, 20112; (c) R. Abargues, J. Marqués-Hueso, J. Canet-Ferrer, E. Pedrueza, J. L. Valdés, E. Jiménez, J. P. Martínez-Pastor, *Nanotechnology* **2008**, *19*, 355308; (d) G. V. Ramesh, K. Sudheendran, K. C. J. Raju, B. Sreedhar, T. P. Radhakrishnan, *J. Nanosci. Nanotech.* **2009**, *9*, 261.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Optical Properties of Polymer/Metal Nanocomposites and Application as Smart Materials

Andrea Pucci^{1,2}, Marco Bernabò¹, Giacomo Ruggeri^{1,2}

¹ Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa (Italy); E-mail: apucci@ns.dcci.unipi.it; phone: +39 0502219270; fax: +39 0502219320

² INSTM, c/o DCCI, University of Pisa, via Risorgimento 35, I-56126 Pisa, Italy

Since the born of nanotechnology it was evident that the optical properties of nanostructured metal particles strongly depend on their dimensions and shape. In particular, noble metal nanoparticles or semiconducting nanocrystals embedded in bulk polymer matrices show enhanced optical and magnetic properties due to the stabilizing effects to size and aggregation provided by the macromolecular support. For example, clusters of noble metals, such as gold, silver or copper, assume a real and natural colour due to the absorption of visible light at the surface plasmon resonance frequency. The application of composites containing noble metal nanoparticles strictly depends on the ability to control and to modulate their size, shape and aggregation extent. In the last years a lot of efforts were focused in our laboratory on the preparation of metal “nanodispersion” in the polymer matrix by mixing the components in solution or by a one-step method based on the thermally- or UV-induced reduction of the inorganic precursor through a solid state synthesis.^[1-3]

All the nanocomposites containing moderate amounts of the nanostructured filler (from 0.5 to 4% by weight) showed modulable optical properties, which are responsive to the local environment due to the interactions between stabilizing layers and polymeric matrices. Thus these hybrid materials can be regarded as very important for future advanced applications including the possibility of inducing nanophase organization through external stimuli.

[1] A. Pucci, M. Boccia, F. Galembeck, C. A. d. P. Leite, N. Tirelli, G. Ruggeri, *React Funct Polym* **2008**, *68*, 1144-1151.

[2] A. Pucci, M. Bernabò, P. Elvati, L. I. Meza, F. Galembeck, C. A. de Paula Leite, N. Tirelli, G. Ruggeri, *J. Mater. Chem.* **2006**, *16*, 1058-1066.

[3] A. Pucci, N. Tirelli, E. A. Willneff, S. L. M. Schroeder, F. Galembeck, G. Ruggeri, *J. Mater. Chem.* **2004**, *14*, 3495-3502.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Synthesis of Metal Oxide Nanoparticles in Restricted Space of Perfluorosulfonate Ionomeric Membrane: Nafion®

Shigehito DEKI¹, Takashi HASEGAWA² and Minoru MIZUHATA²

¹ Professor Emeritus, Kobe University

² Dept. of Chemical Science and Engineering, Graduate School of Engineering, Kobe University.

1-1, Rokkodai-cho, Nada, Kobe 657-8501, Japan

E-mail: deki@kobe-u.ac.jp, hasegawa@cx2.scitec.kobe-u.ac.jp, mizuhata@kobe-u.ac.jp

It is well-known that metal oxide dispersed Nafion membrane is utilized for the non-humidified fuel cell by the improvement of water uptake performance¹⁾. Several research has been attempted for the improvement of the fuel cell performance. However, casted membrane has used in most studies because the metal oxide cannot be mixed with the nafion membrane and used Nafion solution for mixing with the oxide particle and ion-exchange polymer. On the other hand, it is known that the ion channel exists for ionic conduction in the Nafion membrane, so-called "cluster structure" named by Yeager²⁾ and Gierke³⁾ for Nafion membrane. The Nafion membrane in water media with large ion exchanging capacity (ca. 1.0 meq/g) is known the existence of ionic cluster contributed from nanophase segregation of hydrophobic-hydrophilic region. In order to discuss the structural properties of the nafion/ metal oxide composite, it is better to use the uniform membrane containing the metal oxide. We have been studied the fabrication of metal oxide/ organic compound composite using the Liquid Phase Deposition which is one of the preparation method of metal oxide called *soft solution process*⁴⁾⁻⁶⁾. The dye/TiO₂ composite⁴⁾ and protein templated hybrid materials for biosensing⁵⁾ has been obtained. The mechanism is considered ligand exchanging hydrolysis of metalfluoro complex and F⁻ consumption reaction for accelerate of metal oxide's supersaturation. In this study, we prepare the TiO₂ nanoparticles in perfluorosulfonate ionomeric membrane (Nafion® by DuPont) using the LPD method. Using this method, we also fabricated the TiO₂:Eu³⁺ nanoparticle dispersed in Nafion membrane. In this system, we measure the photo luminescence of Eu³⁺ doped in metal oxide nanopartilces for evaluating an enhancement of photo luminescence intensity.

We confirmed the deposition of TiO₂ nanoparticles in Nafion membrane after immersion into the mixed aqueous solution of metalfluoro complex and boric acid. The size of nanoparticles is narrow distribution and the particles is TiO₂ anatase assigned from SAED pattern and lattice space of (101) 3.5 Å. From depth profile of Ti XPS spectra, the existence of Ti can be confirmed in ca. 10 μm depth.

Photo luminescence (PL) spectrum of Nafion / TiO₂:Eu³⁺ is an effective way to investigate the electronic structure and optic characteristics of semiconductor nano-materials, by which the information such as surface oxygen vacancies and defects as well as separation and recombination of charge carriers can be obtained. Figure is TEM image of nanoparticles in Eu³⁺ Nafion and inset shows the PL excited by 398 nm (Eu³⁺ : ⁷F₀→⁵D₄). Nanoparticles are TiO₂ anatase assigned from SAED. From the emission spectra, it can be observed that the most intense peak around 595 nm, which corresponds to the magnetic dipole transition between the ⁵D₀ and ⁷F₁ levels and is much stronger than that of the ⁵D₀→⁷F₂ transition. It is well-known that the selection rules and transition probabilities between states strongly depend on the crystal field^{7, 8)}. If the Eu³⁺ ions embedded in a site with inversion symmetry, the ⁵D₀→⁷F₁ magnetic dipole transition is dominating, while in a site without inversion symmetry the ⁵D₀→⁷F₂ electric dipole transition is the strongest contributed from their parity. In this spectra, The emission intensity at 617 nm (⁵D₀→⁷F₂) is enhanced by inducing TiO₂. Inducing TiO₂ nanoparticles cause changing the symmetry of Eu³⁺ crystal field.

This study was partly supported by Grant-in-Aid for Scientific Research (A) (No. 19205029), by Grant-in-Aid from MEXT, Japan.

References

- 1) M. Watanabe, H. Uchida, Y. Seki, M. Emori, *J. Electrochem. Soc.*, **143**, 3847 (1996).
- 2) H.L. Yeager and A. Steck, *J. Electrochem. Soc.*, **128**, 1880, 1981.
- 3) T.D. Gierke, G. E. Munn, F. C. Wilson, *J. Poly. Sci; Poly. Phys. Edit.* **19**, 1687 (1981).
- 4) S. Deki, Y. Kodama, M. Mizuhata, *J. Ceram. Soc. Jpn*, **117**, 326 (2009).
- 5) M. Tatemichi, M. Sakamoto, M. Mizuhata, S. Deki, T. Takeuchi, *J. Am. Chem. Soc.*, **129**, 10906 (2007).
- 6) L. Li, M. Mizuhata, A. Kajinami, S. Deki, *Synthetic Metals*, **146**, (14), 17, (2004).
- 7) B.R. Judd, *Phys. Rev.* **127**, 750 (1962).
- 8) G.S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).

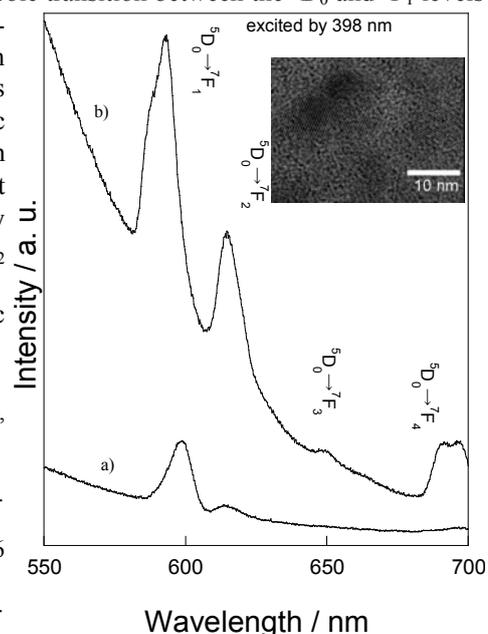


Fig.1. Emission spectra excited by 396 nm (⁷F₀ → ⁵D₄) of Eu³⁺-Nafion before^{a)} / after^{b)} deposition of TiO₂. Inset shows TEM image of nanoparticle in Eu³⁺Nafion. The lattice space TiO₂ anatase (101) was visible.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Studies on LiCF₃SO₃-doped magnetite-ENR polymer electrolytes

W. L. Tan and M. Abu Bakar*

Nanoscience Research Laboratory
School of Chemical Sciences, Universiti Sains Malaysia
11800 Penang, Malaysia

* Corresponding Author

E-mail: bmohamad@usm.my; Fax: 04-6574854

Abstract

Magnetite-ENR polymer electrolytes doped with various % wt of LiCF₃SO₃ salt were synthesized *in-situ* in the presence of ENR and cast into film doped with LiCF₃SO₃. XRD results confirmed the purity of the as-formed magnetite particles. The diffraction peaks assigned for LiCF₃SO₃ become more intense as the concentration of salt is increased. FTIR analyses showed that both “free” (dissociation) and ion pairs (association) of LiCF₃SO₃ were present in the electrolytes system. Nevertheless, the degree of LiCF₃SO₃ dissociation was enhanced by the presence of magnetite particles. Magnetite particles as small as ~4 nm were successfully synthesized and dispersed in the ENR as revealed by TEM micrographs. The homogeneity and distribution of magnetite particles and LiCF₃SO₃ salt in the polymer electrolytes system was confirmed by the SEM and x-mapping techniques. Thermal behavior of the polymer electrolytes was evaluated using DSC and TGA. Glass transition temperature (T_g) increased with increasing of %wt LiCF₃SO₃. This implies the plausible formation of Li⁺-ENR complexation. LiCF₃SO₃-doped magnetite-ENR polymer electrolytes were thermally less stable as compared to that of neat ENR. Even so, they still offer good thermal stability to meet the requirement for battery applications where the initial degradation temperature (T_i) is >300 °C.

Keywords: magnetite, polymer electrolytes, LiCF₃SO₃, ENR

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Spectroscopic Studies of the Structure and Stability of Silver Nanoparticles in LBL Polyelectrolyte Films

Haybat Itani^{1*}, Patrick Keil¹, Monika Santa¹, Aleksander Kostka¹, Guido Grundmeier²

¹ Max-Planck Institut für Eisenforschung GmbH, Max-Planck Straße 1, D-40237, Düsseldorf - Germany

² Department of Technical and Macromolecular Chemistry, University of Paderborn, Warburger Straße 100, D-33098 Paderborn - Germany

* IMPRS-SurMat: International Max-Planck Research School for Surface and Interface Engineering in Advanced Materials

Abstract

The system under-study is consisting of embedded Ag-nanoparticles inside a layer-by-layer polyelectrolyte film composed of polyacrylic acid and polyallylamine hydrochloride. Incorporation of the nanoparticles is achieved by diffusion of Ag⁺ inside the matrix at different pH-values and various numbers of adsorbed bi-layers [1], [2], [3]. The formation of metallic Ag nanoparticles is realized by reduction in dilute NaBH₄ aqueous solution [4]. The structure of Ag nanoparticles characterised by local distances and coordination shells around the absorbing atom was investigated by means of X-ray Absorption Spectroscopy (XAS). The analysis of the near edge structure reflects the fraction composition of the embedded Ag before, during and after the reduction process and highlights the nanoparticle formation at the carboxylate sites. The size and the crystallographic properties of the formed nanoparticles were investigated by means of HR-TEM while the optical properties were monitored in-situ by means of UV-Vis Spectroscopy. Kinetic exchange at the interface of the Ag-nanoparticles and the polymer matrix was examined by means of Surface Enhanced Raman Scattering (SERS).

Keywords: Ag nanoparticles, LbL, XAS, HR-TEM, in-situ UV-Vis spectroscopy, SERS.

[1] Radeva, T.; Grozeva, M. *Journal of Colloid and Interface Science*, **2005**, 287, 415-421.

[2] Fujita, S.; Shiratori, S. *Thin Solid films* 499, **2006**, 54-60.

[3] Grunlan, J. C.; Choi, J. K.; Lin, A. *Biomacromolecules*, **2005**, 6, 1149-1153.

[4] Pal, T.; Sau, T. K.; Jana, N. R. *Langmuir*, **1997**, 13, 1481-1485.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Environmentally-safe polymer-metal nanocomposites

Dmitri Muraviev^{a)}, Amanda Alonso^{a)}, Jordi Mas^{b)} and Maria Muñoz^{a)}

^{a)} Unitat de Química Analítica, ^{b)} Grup de Microbiologia Ambiental,
Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

The environmental safety of nanocomposite materials (which consist of or contain nanosize components) is one of the hottest topics of the modern Nanotechnology within the last few years. The main concerns dealing with the rapid development and commercialization of various nanomaterials (NM) are associated with 1) the approved higher toxicity of many nanomaterials (NM) in comparison with their larger counterparts, 2) the absence of the adequate analytical techniques for detection of NM in the environment, and 3) the absence of the legislation normative for permitted levels of various NM in water and air. In this regard the increase of the safety of NM is of particular importance.

In our presentation we report the results obtained by the development of the environmentally-safe polymer-metal nanocomposite materials, which can be applied in various fields, such as catalysis, water treatment and others. The material represents a functional polymer with immobilized metal nanoparticles (MNPs) distributed mainly by the surface of polymer that makes them maximally accessible for the substrate to be catalyzed or eliminated. MNPs have a core-shell structure and consist of a superparamagnetic core coated with the functional metal shell of the minimal thickness, which provides the desired activity of nanocomposite material. The MNPs are strongly captured inside polymer matrix that prevents their escape into the medium under treatment. The superparamagnetic nature of MNPs provides an additional level of the material safety as MNPs leached from the polymer matrix can be easily captured by the magnetic traps that permits either to completely prevent any post-contamination of the treated medium or recycle MNPs what is particularly important when they contain precious metals. The presence of MNPs does not block the functional groups of the polymer so that the polymer-metal nanocomposite can also function as the dual function material.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Structural and electrical properties of nanocomposites based on the EVA copolymer filled with nano-structuralized graphite

Z. Križanová¹, I. Krupa², V. Cecen³, J. Prokeš⁴, I. Vávra¹

¹*Institute of Electrical Engineering, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, SLOVAKIA*

²*Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 8242 36 Bratislava, SLOVAKIA*

³*Dokuz Eylul University Mechanical Eng. Department 35100 Bornova/Izmir, TURKEY*

⁴*Charles University Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, 182 00 Prague 8, CZECH REPUBLIC*

Polymer nanocomposites prepared from high aspect ratio layered graphite nanofillers achieve significant improvements in mechanical, thermal, electrical and barrier properties at very low filler concentrations, compared to conventional composites, without a significant increase in density. This is caused by the sheet-like structure of natural graphite where the atoms are strongly bonded on a hexagonal plane but weakly bonded normal to that plane. If these graphene layers could be separated down to a nanometer thickness through intercalation and exfoliation, they would form graphite nanosheets, which possess a huge surface area and satisfy the high aspect ratio (200-1500) criterion needed for high strength composites.

Structural and electrical properties of nanocomposites based on the ethylene-vinylacetate (EVA) matrix filled with graphite micro and nanofiller will be discussed in this contribution. It was found that electrical conductivity of composites strongly depends on the graphite structure. The polymer structure was investigated by transmission electron microscopy. In the case of micro-sized graphite, the percolation concentration of the filler is at about 15-17 vol.%, whereas when nano-sized the percolation concentration in composites was significantly lower – its value was at about 5-6 vol.%. Electrical conductivity of graphite-based nanocomposites was found to be much higher than electrical conductivity of graphite based microcomposites at comparable concentrations.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Filtering Effect of the Polymer on Particles upon Aqueous to Organic Phase Transfer

W. L. Tan, N.A. Mohd. Akib, N.H. Mohd. Hirmizi, M. Abu Bakar* and J. Ismail

Nanoscience Research Laboratory
School of Chemical Sciences, Universiti Sains Malaysia
11800 Penang, Malaysia

* Corresponding Author

E-mail: bmohamad@usm.my; Fax: 04-6574854

Abstract

Size exclusion of coinage metal particles (copper, silver and gold) via aqueous to organic phase transfer is described. Metal particles were synthesized in the aqueous phase via simple borohydride reduction in the presence of CTAB as stabilizer. These particles were then transferred into the organic phase with the aid of 2-propanol as the transferring agent. Various organic environments were studied *viz.* toluene with or without epoxy polymer. The particles size and size distribution of the metal particles in various environments were deduced from TEM. Generally, particles size and size distribution increase from aqueous to organic. The increment of size from the aqueous to organic phase is due to the destruction of CTAB bilayers that stabilized the metal particles in aqueous phase. The destruction is probably induced during the stirring process. However, the particles size and size distribution decrease upon addition of epoxy into the organic phase and further decrease when more of epoxy is added. This implies a phenomenon where the polymer acts as a filter whereby only the finer particles are able to cross from the aqueous to organic phase boundary as compared to neat organic solvent. The nature of the resultant conformation of the polymer in the organic solvent is believed to be responsible for this filtering phenomenon.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Electrical properties of composite films

S. Novák¹, M. Švec¹, R. Hrach^{1,2}, J. Pavlík¹

¹ Department of Physics, Faculty of Science, J. E. Purkinje University,
České mládeže 8, 400 96 Ústí nad Labem, Czech Republic

² Department of Surface and Plasma Science, Faculty of Mathematics and Physics,
Charles University, V Holešovičkách 2, 180 00 Prague 8, Czech Republic

Composite films belong to very interesting materials with a huge scale of applications for their mechanical, optical and electrical properties. In our contribution we present a study of their electrical properties by the help of self-made software analytical tools. We concentrate on connection of these properties with structure parameters of the films.

Several models of composite films were prepared at first. We used the molecular dynamics and Monte Carlo method in this part of the computer experiment, including hard-sphere and soft-sphere models [1]. Then the structures were studied to obtain structural parameters, so methods of mathematical morphology [2] were used here. The electrical properties are studied especially below and close to so-called percolation threshold [3] of the structure. When the structure reaches the percolation threshold it assigns interesting behaviour. The Monte Carlo method and the theory of percolation were used for the study of electrical properties. The electric transport is carried out through individual channels with tunnel or ohmic conductivity mechanisms [4]. These channels can be described in terms similar to standard ohmic conductivity, e.g. infinite cluster, its backbone, dead-ends, etc., however the tunnel conductivity channels have a fuzzy characters, so the usual terms of the percolation theory must be redefined and some new parameters added.

As main results of our contribution we show both correlations of electrical properties with morphology of the structures and analysis of current noise in composite films.

References

- [1] Rapaport D.C.: The Art of Molecular Dynamics Simulation, Cambridge University Press, Cambridge, 1995.
- [2] Serra J., Image Analysis and Mathematical Morphology, Academic Press, London, 1982.
- [3] Stauffer D., Aharony A., Introduction to Percolation Theory, Taylor and Francis, London, 2003.
- [4] Hrach R., Novák S., Švec M., Škvor J.: Study of Electron Transport in Composite Films below Percolation Threshold, LNCS 3991, 806 (2006).

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Charging of small particulates in plasma: study by computer simulations

P. Bartoš*, J. Blažek, P. Špatenka

*University of South Bohemia, Faculty of Pedagogy, Department of Physics, Jeronýmova 10,
371 15 České Budějovice, Czech Republic*

Computer simulations are in recent years a powerful and frequently used tool in science and industry. With the increasing of the computer performance they can be used also for the study of dusty plasma behaviour, that is a complex problem involving many physical phenomena. The complexity of these models necessitates the usage of effective numerical methods.

Our contribution is aimed on the theoretical aspects of electrical charging of small particulates immersed into plasma. When a dust particulate is immersed into plasma, it charges electrically due to different velocities of different kinds of charged species contained in plasma. In laboratory facilities the light electrons are usually much faster than much heavier ions, and, therefore, the particulate charges negatively. This behaviour can be well used for plasma diagnostics and in many technical applications.

In the presented computer model the plasma is considered to be a fluid of electrons, positively charged ions and neutral particles. Plasma is described by continuity equations for charged particles and the Poisson's equation. The particle flux is expressed by the drift-diffusion approximation, the convective term in the equation of motion is neglected. Reaction rates are determined by the non self-consistent particle model. The surface charge is determined by the integration of total particle flux over the given boundary. Computer models are conceived as time-dependent problems.

The work is supported by the grant project KAN 101 120 701 - Nanocomposite films and nanoparticles prepared in low pressure plasma for surface modifications.

Email adress: bartos-petr@seznam.cz

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Magnetic properties of silicide nanoparticles ion-beam-synthesized in the external magnetic field

G.G. Gumarov¹, A.I. Gumarov², V.Yu. Petukhov¹, N.R. Khabibullina¹,
V.F. Valeev¹

¹*Zavoisky Physical-Technical Institute, Kazan, 420029, Russia*

²*Kazan State University, 420008, Russia*

gumarov@kfti.knc.ru

It has been shown that ion-beam synthesis in the external magnetic field leads to the formation of anisotropic ferromagnetic silicide films [1]. The synthesized films exhibit a high value of the effective saturation magnetization and the pronounced in-plane anisotropy. Earlier [2], the anisotropy of these films has been investigated by radio-frequency autodyne method. The goal of this work is to study the nature of magnetic anisotropy in the films ion-beam-synthesized in the applied magnetic field.

Iron ions with energy of 40 keV were implanted into the (111) single-crystal silicon wafers at room temperature. The implantation dose was $3 \cdot 10^{17}$ cm⁻², the ion current density being 5 μ A/cm². During implantation a magnetic field H_i of 500 Oe was applied parallel to the plane of the substrate. Samples were investigated by X-ray diffraction (XRD), fluxgate magnetometry, L-band ferromagnetic resonance (FMR) and conversion electron Moessbauer spectroscopy (CEMS).

XRD at grazing angles and CEMS indicate that the synthesized films contain two phases: FeSi and ferromagnetic Fe₃Si. Easy magnetization axes in the plane of the films were observed depending on the orientation of the field H_i regarding to the crystal axes of the substrate. FMR and fluxgate magnetometry measurements also confirm the appearance of in-plane anisotropy. Using the three-dimensional Stoner-Wohlfarth model we showed that the observed in-plane magnetic anisotropy is the result of superposition of the threefold magnetocrystalline and the induced uniaxial anisotropies. The mechanisms of the induced anisotropy appearance are discussed.

Acknowledgements: The work was supported by the Grant of Presidium of RAS № 01/09.

References:

- [1] G. G. Gumarov, V.Yu. Petukhov, I.B. Khaibullin, E.P. Zheglov, E.N. Dulov, N.G. Ivoilov. Abstracts of the International Conference “Modern development of magnetic resonance” Kazan, Russia, 2004.- P.247.
- [2] Gumarov G.G., Petukhov V.Yu., Zhikharev V.A., Valeev V.F., Khaibullin R.I. Nuclear Instruments and Methods in Physics Research B 267 (2009) 1600–1603.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

STRUCTURE AND MECHANICAL PROPERTIES OF BIOCOMPATIBLE ZrN FILM ON VARIOUS SUBSTRATES

Josef Paul^{a),b)}, Lucie Bačáková^{b)}, Vladimír Starý^{a)}, Ladislav Cvrček^{c)}, Stanislav Daniš^{d)}

- a) DEPARTMENT OF MATERIALS ENGINEERING, FACULTY OF MECHANICAL ENGINEERING, CZECH TECHNICAL UNIVERSITY IN PRAGUE, KARLOVO SQ. 13, 121 35 PRAGUE 2, CZECH REPUBLIC
- b) DEPT. OF GROWTH AND DIFFERENTIATION OF CELL POPULATIONS, INSTITUTE OF PHYSIOLOGY, ACADEMY OF SCIENCES OF THE CZECH REPUBLIC, VIDENSKA 1083, 142 20 PRAGUE 4 – KRC, CZECH REPUBLIC
- c) HVM PLASMA, NA HUTMANCE 2, 158 00 PRAGUE 5, CZECH REPUBLIC
- d) DEPARTMENT OF CONDENSED MATTER PHYSICS, FACULTY OF MATHEMATICS AND PHYSICS, CHARLES UNIVERSITY, KE KARLOVU 5, 121 16 PRAGUE 2, CZECH REPUBLIC

ABSTRACT

Zirconium nitride is considered as a promising material for strengthening the surface of various materials, especially those designed for hard tissue surgery. In this study, two kinds of ZrN films were prepared by PVD methods: magnetron sputtering and cathodic arc evaporation. ZrN films were deposited on various substrates: non-modified and ground CFRC (carbon reinforced carbon composites), Ti Gr. 2 and high-alloy steel X153CrMoV12. Structure of ZrN films was measured by rtg. diffraction (Parallel Beam and Bragg Brentano configuration), as well as, mechanical properties (hardness, elastic modulus and adhesion) were measured.

There were found significant differences in structure ZrN films prepared by various methods and differences in mechanical properties. We found that all samples gave good support for the adhesion and growth of human-osteoblast-like MG 63 cells, though the cell numbers on these materials were often lower than on standard cell culture polystyrene dishes and microscopic glass coverslips. Nevertheless, ZrN films can be considered as suitable materials for surface modification of bone implants in order to improve their mechanical properties and their integration with the surrounding tissue.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Effect of different concentration of Ti in hydrocarbon plasma polymer films on the adhesion, proliferation and differentiation of human osteoblast-like MG63 cells

Vandrovcova M¹, Grinevich A², Bacakova L¹, Lisa V¹, Shukurov A², Slavinska D², Biederman H²

¹ Department of Cell Growth and Differentiation, Institute of Physiology, Academy of Sciences of the Czech Republic, 142 20 Prague 4-Krc, Czech Republic

² Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, 182 20 Prague 8, Czech Republic

Titanium improves adhesion, growth, proliferation and differentiation of bone cells, but there is only little information about influence of different titanium content on cell behaviour. The aim of this investigation was to study effect of different titanium content on osteoblast-like MG63 cells. Titanium/hydrocarbon plasma polymer films were prepared by DC magnetron sputtering of titanium target in a mixture of two gases: *n*-hexane and argon. Concentration on titanium was controlled by adjusting the argon/*n*-hexane ratio in the working gas. This determines the emission of Ti from the target partially covered with carbonaceous C:H deposit (target poisoning). Samples with Ti concentrations ranging from zero to 24 at.% were prepared. Samples were sterilized with 70% ethanol, inserted into 12-well cell culture polystyrene plates and seeded with human osteoblast-like MG 63 cells (European Collection of Cell Cultures, Salisbury, UK). Each well contained 30,000 cells (i.e., approximately 8,000 cells/cm²) and 3 ml of a medium DMEM, supplemented with 10% of fetal bovine serum and gentamicin. The cells were cultured at 37 °C in a humidified air atmosphere containing 5% CO₂. The cell population densities on days 1, 3 and 7 after seeding, cell spreading area on day 1, formation of focal adhesion plaques, and concentration of talin, osteocalcin and ICAM-1 were compared with the reference cell culture materials (i.e., microscopic coverslips and polystyrene dishes). Samples with 10 at.% of Ti had the most pronounced influence on the cell behaviour. On day 1 after seeding, the highest number of cells was found on this surface in comparison with other samples and controls. On the contrary, on day 7 after seeding the cell number on the sample with 10 at.% of titanium was significantly lower in comparison with the control and other tested samples. It is probable that the cells cultured on the samples with 10 at.% of Ti adhered better and entered the differentiation program earlier than the cells cultured on the other samples. This assumption is supported by an enzyme-linked immunosorbent assay (ELISA) which revealed that the concentration of talin, a focal adhesion protein associated with integrin adhesion receptors, tended to be higher in cells on samples with 10at% of Ti (as well as other samples with lower Ti concentrations up to 12 at%) in comparison with the samples with higher Ti content (15-24 at.%) and control materials, although this difference was not statistically significant. The production of **osteocalcin**, a marker of osteogenic cell differentiation, showed an opposite tendency – higher concentrations of this glycoprotein were obtained on samples with a higher Ti content (12, 15 and 18 at.%). The concentration of **ICAM-1**, a marker of cell immune activation, was similar on all tested groups.

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic under contract KAN101120701.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

EPR STUDY OF NANODISPERSED CALCIUM GLUCONATE

G. G. Gumarov¹, M.M. Akhmetov¹, V.Yu. Petukhov¹, E.P. Zheglov¹,
G.N. Konygin², R. B. Zaripov¹

¹*Zavoisky Physical-Technical Institute, Kazan, Russia*

²*Physical-Technical Institute UrB, Izhevsk, Russia*

gumarov@kfti.knc.ru

Calcium gluconate is widely used as a medicine for hypocalcemia therapy. However, the effectiveness of this drug is very low. Earlier, the modified nanodispersed form of calcium gluconate has been produced by mechanical activation that led to the improvement of its bioavailability and pharmacokinetic properties [1]. The Lorenz-shaped EPR signal with $g=2.005$ and a line width of 8.5 Oe has been revealed after the mechanochemical treatment [2]. The goal of this work was to elucidate the physical-chemical transformation of calcium gluconate under mechanical activation and to establish the nature of a paramagnetic center.

The paramagnetic center responsible for appearance of the EPR signal is a long-lived one. The integral intensity of the signal from paramagnetic centers depends on the time of mechanical milling and has remained unchanged within several months. Additional EPR investigation of ingredients of officinal calcium gluconate has shown that the observed line is due to the transformation of the calcium gluconate molecule.

To identify the nature of a radical center the method of electron spin echo envelope modulation was used. The results showed that paramagnetic centers are localized in the vicinity of the calcium atom.

To specify the structure of radicals further investigations are needed.

Acknowledgements

The work was supported by the Grant of RFBR 07-03-96005.

- [1] G. N. Konygin et al.: Method of treatment of hypocalcemia, osteoporosis, fractures, Patent of Russia № 2268053 (2004).
- [2] G. G. Gumarov et al. Abstr. of Int. Conf. "Modern Development of Magnetic Resonance", Kazan, September 24-29, 2007, P. 170.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Tin/n-hexane nanocomposite films and their electrical properties

J. Matoušek¹, J. Pavlík¹, L. Kováčik^{2,3}, M. Švec¹

¹ Department of Physics, Faculty of Science, J. E. Purkinje University, České mládeže 8, 400 96 Ústí nad Labem, Czech Republic

² Institute of Cellular Biology and Pathology, First Faculty of Medicine, Charles University in Prague, Albertov 4, 128 01 Prague, Czech Republic

³ Institute of Physiology, Academy of Sciences of the Czech Republic, v.v.i., Vídeňská 1083, 142 20 Prague, Czech Republic

Introduction

Nanocomposite films metal/dielectric were studied in the second half of the 20th century. Later metal/polymer and metal/hard carbon (C:H or a-C:H) composite films were also considered. In recent time, magnetron DC and RF sputtering from a metallic target in a working gas mixture of argon and active (hydrocarbon) gas were used to deposit metal/hydrocarbon nanocomposite films.

Nanocomposite films of metal (or metal oxide) embedded in plasma polymer matrix represent a class of promising materials. The main research attention has been paid to their attractive electrical and optical properties.

We investigated the relationship between electrical properties of tin/plasma polymer nanocomposite films and the deposition parameters and structure. Experimental results are compared with the computer simulation.

Experimental

The nanocomposite layers (tin in plasma polymer matrix) were prepared in a stainless steel vacuum chamber. RF powered magnetron with tin target was used to excite the discharge and to activate the monomer species. Working gas mixture was consisting of Ar and n-hexane vapours. The deposited films were characterized by several methods: AFM, TEM, Electron tomography and XPS. Current-voltage characteristics were measured to examine the electrical properties of the layers and their dependence on the deposition parameters.

The TEM and Electron tomography was employed to allow comparison of the layers with models. The computer experiments were done by self-made software analytical tools.

References

- [1] Abeles B. Appl. Solid State Sci. 1976;6:1.
- [2] Biederman H, Martinu L. Plasma deposition, treatment and etching of polymers, New York: Academic Press; 1990:269.
- [3] Heilmann A, Hamann C. Progr. Colloid Polym. Sci. 1991;85:102 – 110.
- [4] Reinhardt C, Heilmann A, Grunewald W, Hamann C. Thin Solid Films 1993;235:57 – 61.
- [5] Biederman H, Hlidek P, Pesicka J, Slavinska D and Stundzia V. Vacuum 1996;47:1385 – 1389.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Molecular Nano/micro Crystals: Fabrication and Optical Properties

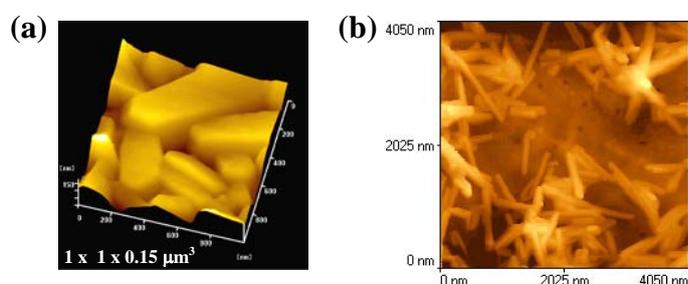
A. Patra,^{†,‡} J. Piard,[†] R. Métivier,[†] K. Nakatani[†] and T. P. Radhakrishnan[‡]

[†] PPSM, IFR d'Alembert, ENS Cachan, CNRS, UniverSud, 94230 Cachan, France

[‡] School of Chemistry, University of Hyderabad, Hyderabad – 500 046, India

Email: apatra@ppsm.ens-cachan.fr

Molecular nano/micro crystals have emerged as a contemporary area of research because of the flexibility and versatility inherent in their assembly, novel size-dependent attributes they manifest, and the promise of several optical, nonlinear optical and biological applications.¹ In the context of the rapidly growing field of molecular mesoscopic materials, we have developed a simple reprecipitation-digestion protocol to fabricate nano/micro crystals (with sizes varying from ~ 50 nm to ~ 1-2 μm) of a series of novel zwitterionic diaminodicyanoquinodimethane molecules which show a range of interesting size-dependent photophysical properties. We have focused attention mainly on 7,7-bis(4-chloroanilino)-8,8-dicyanoquinodimethane (BCADQ),² and its bromo analogue (BBADQ).³ A simple approach



was developed to arrest the growth of nanocrystals to achieve stable particle size and optical responses in the colloidal dispersions. Crystal structure and microscopy characterizations (Fig. 1a), spectroscopic investigations and semiempirical quantum chemical studies lead to a viable model which espouses the progressive manifestation of hierarchical intermolecular interactions in these molecules.²

Figure 1. Morphology of (a) BCADQ and (b) DBAP crystals revealed through AFM.

Recently the photochromic properties of nanoparticles of *N*-(3,5-di-*tert*-butylsalicylidene)-4-aminopyridine (DBAP) have also been investigated. Nano/microcrystals of DBAP with rod-like morphology (Fig. 1b) were fabricated by laser ablation (355 nm) of microcrystalline powder suspensions of DBAP in water-surfactant (triton X) medium. Particle size and distribution can be varied by changing the laser fluence and ablation time. These nano/microcrystals exhibit reversible photoswitching through the intramolecular keto(-amine) – enol(-imine) tautomerism⁴ induced by UV and visible light respectively. It was observed that the nanoparticle dispersions show slower rate of photochromism (keto to enol) compared to organic solution but greater than that of bulk solid.

Acknowledgements

We thank A. Brosseau, Dr. B. Sridhar, Dr. N. Hebalkar, Dr. M. Sliwa and Prof. A. Samanta for fruitful help and UGC, CSIR, DST, India and PRES UniverSud for financial support.

References

1. *Organic Nanostructures*; Atwood, J. L.; Steed, J. W., Wiley-VCH: Weinheim, 2008.
2. Patra, A.; Hebalkar, N.; Sreedhar, B.; Sarkar, M.; Samanta, A.; Radhakrishnan, T. P. *Small* 2006, 2, 650.
3. Patra, A.; Hebalkar, N.; Sreedhar, B.; Radhakrishnan, T. P. *J. Phys. Chem. C* 2007, 111, 16184.
4. Sliwa, M.; Ltard, S.; Malfant, I.; Nierlich, M.; Lacroix, P. G.; Asahi, T.; Masuhara, H.; Yu, P.; Nakatani, K. *Chem. Mater.* 2005, 17, 4727.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Laser Welding of Polymer Foils by using embedded Metallic Nanoparticles

M. Neuber, J. Lucas, G. Hanke, A. Heilmann

Fraunhofer Institute for Mechanics of Materials,
Walter-Hülse-Str.1, 06120 Halle (Saale), Germany,
Email: Matthias.Neuber@iwmh.fraunhofer.de

The optical properties of noble metal nanoparticles which are affected by the plasmon resonance depend on the size and shape distribution as well as on the surrounding media. Due to the phonon photon coupling, laser irradiation can cause changes in particles size and shape by diffusion processes as well as melting and evaporation of the nanoparticles. For laser welding of transparent foils, nanoparticles can act absorber material. We demonstrate that one nanoparticle layer is sufficient to join transparent polymer foils e.g. ethylene tetrafluoroethylene (ETFE) copolymer foils

Gold nanoparticles were deposited on ETFE foils (200 μm thick) by magnetron sputtering or vacuum evaporation. Thereafter, thin polymer films produced by plasma polymerisation or PTFE-polymer sputtering were deposited on the gold nanoparticles to stabilize their mechanical properties. Then, a coated foil was joined with a uncoated ETFE foil. Laser irradiation was performed by a continuous wave diode laser at a wavelength of 808 nm. The laser was defocused to get welding seams with diameters of 3 mm. During the laser irradiation, the gold nanoparticle change their size and shape by coalescence and melting. Therefore, in the welding seam becomes transparent. Particles size and shape as were determined before and after laser welding by electron microscopy (SEM, TEM) and correlated with the optical spectra. Mechanical tensile tests demonstrates, that the tensile strength of the laser welding seams are comparable to conventional seams made by thermal contact welding.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Investigating in-situ the formation of biofibre-metal nanocomposites with GISAXS

Stephan V. Roth*, Rainer Gehrke, Ulla Vainio, Kai Schlage, Ralf Röhlsberger
(DESY, Notkestr. 85, D-22607 Hamburg, Germany)

Christian Riekkel, Manfred Burghammer
(ESRF, 6rue Jules Horowitz, F-38043 Grenoble)

Volker Körstgens, Ezz Metwalli, Peter Müller-Buschbaum
(Physik-Department E13, TU München, James-Franck-Str. 1, D-85748 Garching, Germany)

The reduction of structural sizes for many sensor-type devices based on nanocomposite materials creates a need for investigating the nanocomposite's structure in such a restricted geometry [1]. Typically, these devices display a flat geometry. However, e.g. nanowires, smoothed edges, channels, or wire-like connectors represent a fiber like structure and are equally important as charge-collecting components. Hence, it is important to explore routes, during which metal is deposited on curved surfaces, especially polymeric and biological fibers. In our experiments presented here we extended the investigations of metal-polymer nanocomposites thus in two ways. First we describe a way to characterize the substrate - the fiber or the channel - using a combination of nanofocused beam and grazing incidence small-angle x-ray scattering (GISAXS) [2]. We show that we are able follow the topography of the metal layer through the cross-section of a polymeric channel, without the need of special sample preparation. Secondly, we explore in-situ the self-assembly of metal nanoparticles on biopolymeric fibers using GISAXS in combination with in-situ sputter deposition [3]. This fiber-metal nanocomposite acts as a model system for many industrial applications, like anti-counterfeiting and cosmetic products, as well.

[1] M. Wolkenhauer et al., Appl. Phys. Lett 89, 054101 (2006)

[2] S. V. Roth et al., Appl. Phys. Lett. 91, 091915 (2007)

[3] E. Metwalli et al., Langmuir 24, 4265 (2008)

* presenting author:
Dr. Stephan V. Roth

Deutsches Elektronen Synchrotron
Notkestr. 85
D-22607 Hamburg
Germany

phone: +49-40-8998-2934 (office)/3992 (Lab)

fax: +49-40-8994-2934

e-mail: stephan.roth@desy.de

homepage: <http://www.desy.de/~sroth/homepage.htm>

MINAXS: http://petra3.desy.de/beamlines/beamlines/e1036/e1178/index_eng.html

BW4: http://hasylab.desy.de/facilities/doris_iii/beamlines/bw4/index_eng.html

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Percolation behavior of cobalt-nanowire-based magnetorheological fluids

Darin Zimmerman¹, Richard Bell¹, Joseph Filer II¹, Joshua Karli¹, Norman Wereley²

¹The Pennsylvania State University, Altoona College, 3000 Ivyside Park, Altoona, PA 16601, USA

²Department of Aerospace Engineering, University of Maryland, College Park, MD 20742, USA

Conventional magnetorheological (MR) fluids are composed of micron-sized ferromagnetic spherical particles suspended in a hydrocarbon or silicone carrier fluid.¹ By applying an external magnetic field (H), the initially viscous liquid/particle suspension converts to a semi-solid, with an achievable field-induced yield stress of ~ 100 kPa.² Upon application of the H-field, the particles acquire a magnetic polarization and attract one another, developing chain-like structures that join to form fibrils parallel to H . This allows for numerous applications such as variable dampers, brakes, and clutches that exploit the continuously controllable, field-dependent yield stress.³

The field-dependent shear strength of MR fluids depends on the size, composition, morphology, and volume fraction of the particles (p).⁴ Increasing p increases the achievable yield strength, but also increases the off-state viscosity.⁵ As H is increased, the shear strength of the fluid increases and then plateaus, as magnetic saturation is reached. In our work with iron-nanowire-based MR fluids, we observed a complete absence of settling and a significant enhancement of yield-stress for volume fractions as low as $p = 0.06$.⁵

To investigate further the unique rheological behavior of nanowire-based MR fluids, we generated cobalt nanowires (330 nm diam. \times 8.0 – 12 μ m) via template-based electro-deposition using commercially available, anodized alumina membranes as templates.⁵ For MR fluids synthesized with these wires, we systematically varied p and measured the dynamic yield stress at different H-fields. In doing so, we observe a percolation transition in the yield stress and find the behavior near the critical volume fraction (p_c) to depend on H (FIG 1)⁶.

Using a standard continuum percolation model, we fit the data using two critical exponents. For $p > p_c$, we find the elastic exponent (f) to be independent of H , having a value near $f = 1.3$, suggesting that these on-state MR-fluids exhibit

two-dimensional (2D) behavior,⁷ possibly due to the preferred spatial direction for fibril formation. For $p < p_c$, the superelastic exponent (c) decreases with increasing H and is smaller than that seen in 2D or 3D networks. We find p_c to increase with H , likely due to the increased alignment of the nanowires with the applied H-field.⁸ Future experiments that vary the nanowire aspect ratio, use other materials (e.g., iron and nickel), and employ quasistatic, rather than dynamic measurements, should help separate these issues from the underlying physical mechanisms.

We acknowledge support from the National Science Foundation (NSF/RUI: CBET-0755696), The Pennsylvania State University, and Altoona College.

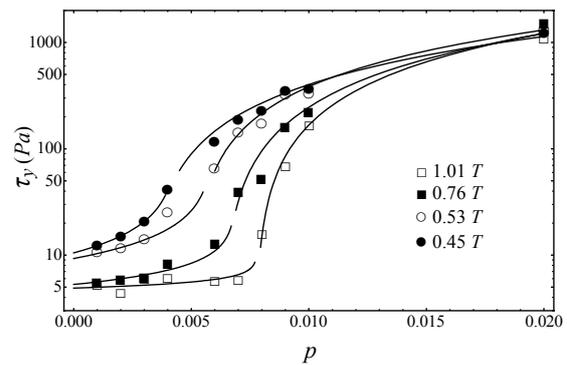


FIG. 1. Apparent yield stress (τ_y) of on-state, cobalt-nanowire MR fluids as a function of p for varying H (indicated in legend). For the sake of detail, we show the data and fit up to $p = 0.02$; both actually extend out to $p = 0.06$.

¹ D. J. Klingenberg, *AIChE J.* **47**, 246 (2001).

² S. Genç and P. P. Phulé, *Smart Mater. Struct.* **11**, 140 (2002).

³ P. P. Phulé and J. M. Ginder, *MRS Bulletin* **23**, 19 (1998).

⁴ G. T. Ngatu, N. M. Wereley, J. O. Karli, and R. C. Bell, *Smart Mater. Struct.* **17**, 045022 (2008).

⁵ R. C. Bell, J. O. Karli, A. N. Vavreck, D. T. Zimmerman, G. T. Ngatu, and N. M. Wereley, *Smart Mater. Struct.* **17**, 015028 (2008).

⁶ D. T. Zimmerman, R. C. Bell, J. A. Filer II, J. O. Karli, and N. M. Wereley, submitted to *Applied Physics Letters* (2009).

⁷ M. Zhou and P. Sheng, *Phys. Rev. Lett.* **71**, 4358 (1993), and references therein.

⁸ A. Celzard, E. McRae, C. Deleuze, M. Dufort, G. Furdin, J. F. Maréché, *Phys. Rev. B* **53**, 6209 (1996).

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Electrical properties of Ni-silicone rubber piezoresistive composites under uniaxial pressure

Fanggao Chang¹, Feng Yang¹, D. P. Almond², Shaoxiang Wang¹, Na Zhang¹, and Guilin Song¹

¹College of Physics and Information Engineering, Henan Normal University,
Xinxiang 453007, P. R. China

²Materials Research Centre, Department of Mechanical Engineering, University of Bath,
Claverton Down, Bath, BA2 7AY, United Kingdom

Abstract

The electrical characteristics of a Ni-silicone rubber composite that exhibits an extremely large piezoresistivity has been investigated. The ac conductivity and the relative permittivity have been measured as a function of frequency for a sample under selected uniaxial forces. The dc conductivity of the composite determined from the low frequency plateau of the ac conductivity is in excellent agreement with that obtained using a conventional dc technique. The dc conductivity is extremely sensitive to the applied uniaxial compression; it increases seven orders of magnitude with a uniaxial loading of 1kg. The dependence of conductivity on frequency has been discussed in terms of the predictions based on a model of microstructural networks. At high frequencies, both the ac conductivity and permittivity of the composite exhibit a power law dependence on frequency, which is consistent with the prediction of the microstructural networks model. The permittivity of the composite sample increases with uniaxial force, suggesting that the composite may be used to develop pressure tunable capacitors. A remarkable skin effect is observed in the frequency dependence of conductivity of the sample under uniaxial forces above 500 gram, which may have important ramifications in the design of radio-frequency and microwave applications and to some extent in ac electrical power transmission and distribution systems.

References

- [1] Tibrewala A, Peiner E, Bandorf R, Biehl S and L uthje H 2006 *J. MicroMech. Microeng* **16** S75
- [2] Yasuoka Tetsuo, Shimamura Yoshinobu and Todoroki Akira 2005 *Nihon Kikai Gakkai Nenji Taikai Koen Ronbunshu* **1** 395
- [3] Somani P R, Marimuthu R, Mulik U P, Sainkar S R, and Amalnerkar D P 1999 *Synthetic Metals* **106** 45
- [4] Carmona F, Canet R and Delhaes P 1987 *J. Appl. Phys.* **61**, 2550
- [5] Bloor D, Donnelly K, Hands P J, Laughlin P, and Lussey D 2005 *J. Phys. D* **38**, 2851
- [6] Martin J E, Anderson R A, Odenic J, Adolf D, and Williamson J 2003 *Phys. Rev. B* **67**, 094207
- [7] Papakostas T V and White N M 2000 *J. Phys. D* **33**, L73-L75

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Cluster beam deposition: a tool for nanoscale science and technology

L. Ravagnan^{*}, P. Piseri, P. Milani[#]

CIMAINA and Dipartimento di Fisica, Università di Milano,
Via Celoria 16, 20133 Milano, Italy

* luca.ravagnan@mi.infn.it

pmilani@mi.infn.it

Abstract

Gas phase nanoparticle production, manipulation and deposition is of primary importance for the synthesis of nanostructured and nanocomposite materials and for the development of industrial processes based on nanotechnology. In this presentation we will present and discuss this approach, introducing cluster sources, nanoparticle particle formation and growth mechanisms and the use of aerodynamic focusing methods that are coupled with supersonic expansions to obtain high intensity cluster beams with a control on nanoparticle mass and spatial distribution [1]. The implication of this technique for the synthesis of nanostructured and nanocomposite materials will be presented and applications will be highlighted [1, 2]. The recent results on the production of polymer supported Micro-Electrode Array device will be also discussed in dept.

[1] K. Wegner *et al.*, J. Phys. D: Appl. Phys. **39**, R439 (2006);

[2] L. Ravagnan *et al.*, arXiv:0902.0228 (<http://arxiv.org/abs/0902.0228>)

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Laser-induced coalescence and agglomeration of noble metal nanoparticles embedded in a polymer matrix

A. Heilmann, Fraunhofer-Institute for Mechanics of Materials
Walter-Hülse-Str. 1, 06120 Haale (Saale), Germany

During the deposition process, the size and shape of metal nanoparticles embedded in a polymer matrix is determined, and at room temperature, the polymer matrix supplies a sufficient long-time stabilization of the nanostructure. The absorption of laser light and the resulting incorporation of thermal energy can dramatically change the size and shape distribution of the embedded particles and their optical properties. Laser irradiation causes the activation of diffusion processes of metal atoms, which occurs at temperatures far below the melting point of the metals. The material transport is driven by the free surface energy of the nanoparticles and is associated with lattice defects and grain boundaries. By irradiating embedded nanoparticle assemblies with linearly polarized, ultrashort laser pulses, the diffusion processes are influenced by interferences. As a result, parallel arranged line structures of embedded gold or silver nanoparticles, and therefore anisotropic optical properties can be achieved inside the laser irradiated sample region. Otherwise, because of their high absorption, agglomeration and melting of nanoparticles can be induced locally. In this case, the incorporated energy is high enough for laser welding of polymer foils.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Nanolayered composites of plasma polymer films

V. Čech*, R. Trivedi, B. Čechalová, J. Studýnka

*Institute of Materials Chemistry, Brno University of Technology
Purkyňova 118, CZ-612 00 Brno, Czech Republic
Email: cech@fch.vutbr.cz

Well-defined nanolayered composites of plasma polymer films, deposited from tetravinylsilane monomer at different powers by plasma-enhanced chemical vapor deposition on silicon, were intensively studied by in situ spectroscopic ellipsometry, nanoindentation, and atomic force microscopy. A realistic model of the composite structure was used to analyze ellipsometric data and distinguish individual layers in the composite, evaluate their thickness and optical constants. Dispersion dependences for the refractive index were well separated for each type of individual layer, if the thickness was decreased 315 – 25 nm, and corresponded to those of the single layer. A beveled section of the nanolayered composite revealed the individual layers that were extensively investigated by atomic force microscopy (AFM) using height (Fig. 1), magnitude, phase, lateral force, and atomic force acoustic microscopy (AFAM) modes. Nanoindentation measurements were carried out in order to evaluate selected mechanical properties of the nanolayered composite in normal direction and individual layers as well.

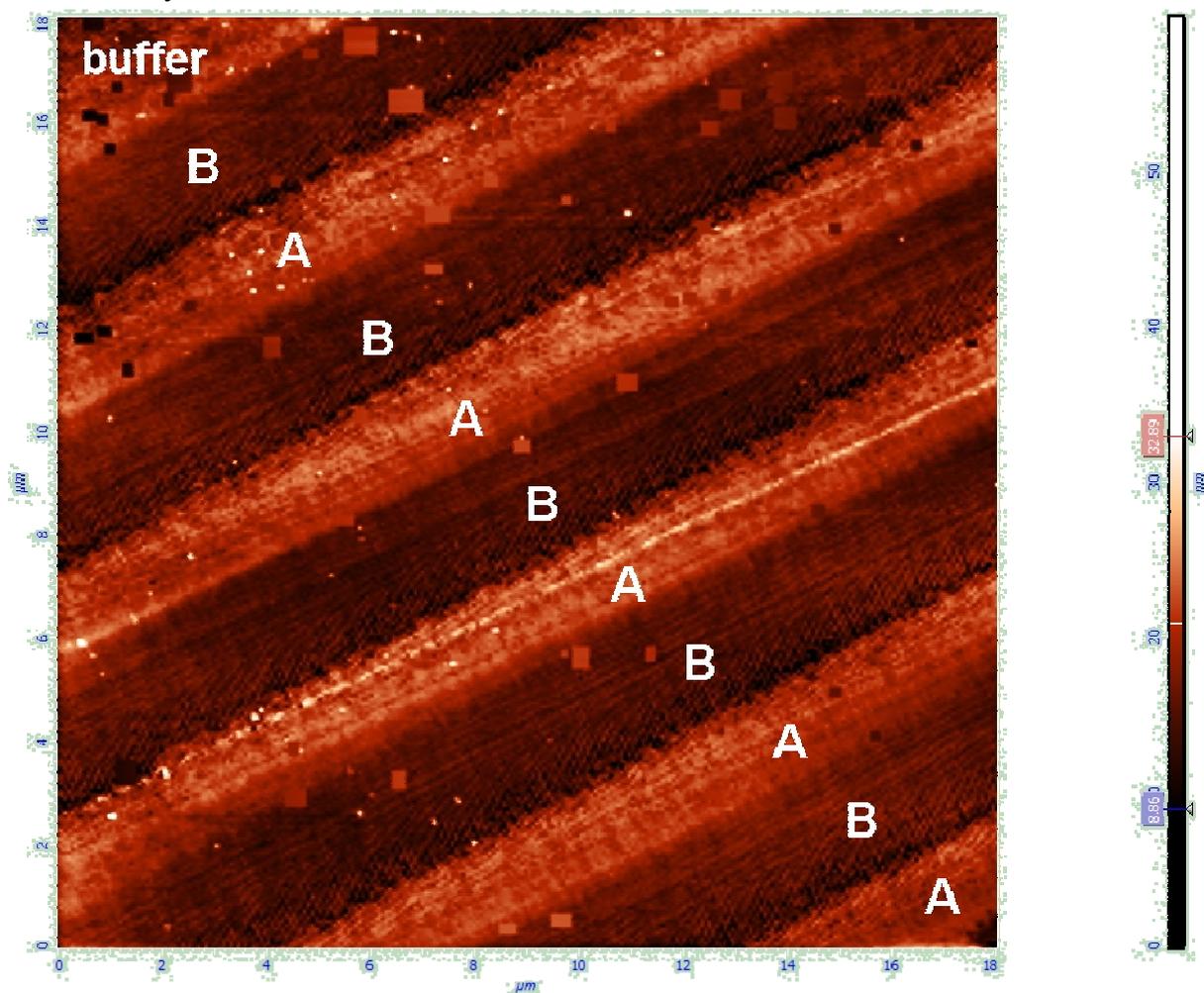


Fig. 1. AFM surface morphology (scan area: $18 \times 18 \mu\text{m}^2$) of sectioned ten-layered composite with buffer layer. Labels for layers A, B and the buffer layer are provided.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Plasma deposition of dielectric/metal nanocomposite layers exhibiting surface plasmon resonance effects.

H.T. Beyene^a, F. D. Tichelaar^b, M.C.M van de Sanden^c and M. Creatore^c

- a) Materials innovation institute (M2i), P.O. Box 5008, Mekelweg 2, 2600 GA Delft, The Netherlands.
- b) Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628CJ Delft, The Netherlands
- c) Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

Abstract:

This work addresses nanocomposite (NC) layers deposited by means of plasma- aided tools, and exhibiting a localized surface plasmon resonance (SPRs)- induced absorption in a specific wavelength range. The presence of an SPR- induced absorption allows to obtain specific colours of nanocomposite layers only dependent on the light absorption on the metal clusters. This eventually allows the development of uniformly coloured 3D geometries, therefore, eliminating the disadvantage of working on interference-based colour generation, poorly controllable on 3D geometries due to a lack of thickness uniformity. In this contribution, hybrid materials consisting of metal nanoparticles dispersed in a dielectric matrix are presented, where an Expanding Thermal Plasma CVD system is used for the deposition of the inorganic matrix (SiO₂-like layers) from hexamethyldisiloxane/oxygen mixtures, and RF magnetron sputtering is applied for the metallic clusters (gold). The optical properties of the NC layers have been investigated by UV-VIS-NIR variable angle spectroscopic ellipsometry and by optical transmission. Rutherford backscattering/ Elastic Recoil Detection and InfraRed absorption spectroscopy were used for determine the film density and chemical composition, respectively. Transmission Electron Microscope observation revealed the formation of gold nanoparticles uniformly distributed in SiO₂-like layers (Figure 1a) exhibiting deep red to blue coloured coatings with the shift of the SPRs band to higher wavelength with an increase in the size of nanoparticles and metal filling factor (Figure 1b).

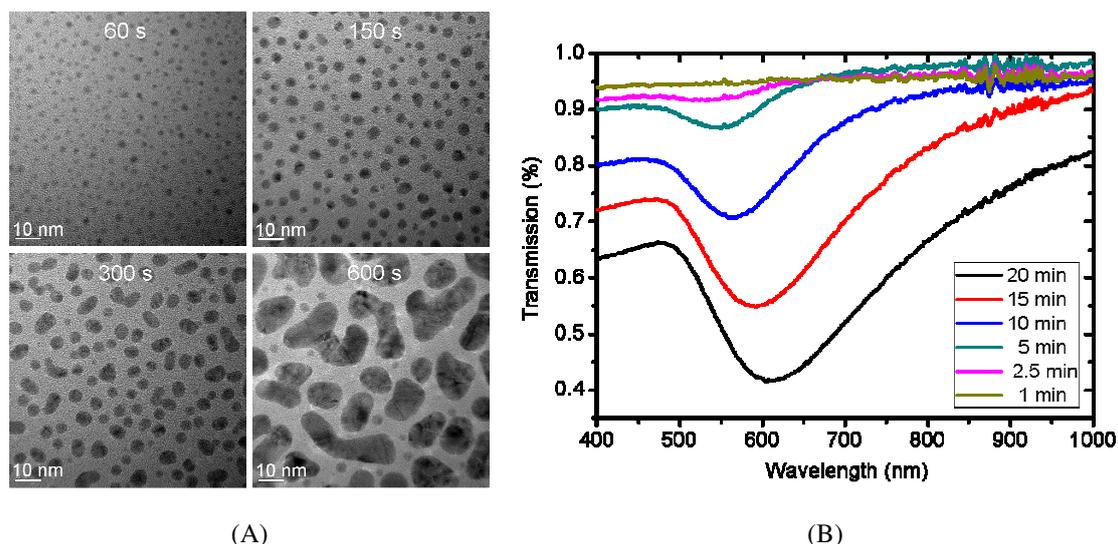


Figure 1: TEM images (A) and the transmission spectra (B) of Au/SiO₂-like nanocomposite layers deposited at various time of deposition: RF-power = 50 W, Ar flow = 30 sccs, Arc current = 25 A, P_{reactor} = 12 Pa.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Magnetron based gas-aggregation deposition system – nanoclusters production and stability

A. Marek, J. Vyskočil, J. Valter, P. Plíhal

HVM Plasma spol. s r.o., Na Hutmance 2, 158 00 Prague 5, Czech Republic

Gas-aggregation nanocluster source is one of possible sources for nanocluster production. We present gas – aggregation nanocluster deposition system of our own design based on the Haberland et al. approach [1]. The target material is sputtered by a magnetron into the medium pressure aggregation chamber with variable length where nanoclusters are formed. Then, they are blown off by the working gas through a slit. The resulting beam of nanoclusters is then scanned or filtered using a dedicated quadrupole mass filter . In our contribution we present the system, its properties and dependence of the size of copper nanoclusters on several physical parameters of the source. The efficiency of the cluster production, deposition rate, energy of nanoclusters, stability of the process and other device properties has been studied.

[1] Haberland H. et al., J. Vac. Sci. Technol. A 12 (5), 1994, 2925-2930.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Nanocomposite metal/plasma polymer films prepared by means of gas aggregation cluster source

J. Hanuš¹, O. Kylián¹, A. Artemenko¹, J. Kousal¹, J. Pešička², D. Slavínská¹
and H. Biederman¹

¹ Charles University, Faculty of Mathematics and Physics, Department of Macromolecular Physics, V Holesovickach 2, 18000 Prague 8, Czech Republic

² Charles University, Faculty of Mathematics and Physics, Department of Physics of Materials, Ke Karlovu 5, 12116 Prague 2, Czech Republic

Nanocomposite metal/plasma polymer films have been usually prepared by simultaneous plasma polymerization and co-sputtering or evaporation of metal [1]. In this case the both: activated and intact monomer molecules arrive to the substrate simultaneously with metal atoms. The former ones create plasma polymer component of the nanocomposite while metal atoms try to group into metallic inclusions with the size depending on the substrate temperature. The other way is to incorporate already fabricated clusters into the growing plasma polymer matrix. This has been achieved by a type of gas aggregation source using metal evaporation [2]. In our case we designed a gas aggregation cluster source that uses a planar magnetron in a compact and simple form. With this source we prepared Au and Ag clusters incorporated into C:H plasma polymer.

The source operates with the circular magnetron equipped with 80 mm target. Gas aggregation chamber is attached to the housing of the magnetron and is water cooled. All this set-up is mounted on ISO-K 100 mm flange. The performance of the source is described. At moderate working parameters - Ar flow 3 ccm/min, pressure 50 Pa, planar magnetron 80 mm in diameter with Ag target, Magnetron current 200 mA, magnetron voltage 300 V we received clusters up to 30 nm in diameter. Because of source simplicity we have no mass separation and therefore the cluster size distribution is broad, however, cluster flux is sufficiently intensive.

This cluster source was built in the vacuum deposition system (pumped by diffusion and rotary pumps) in opposite to another magnetron having graphite target 90 mm in DIA and with the substrates rotating in between these two. Introducing small amount of n-hexane (flow rate 0.5 ccm/min) into the vacuum chamber allowed to create a flux of plasma polymer precursors reaching the substrate. As a result a C:H plasma polymer with incorporated Ag clusters was prepared. The prepared films were characterized by TEM, SEM, XPS, FTIR and AFM. Optical properties were measured.

[1] H. Biederman, P. Kudrna and D. Slavínská, Hard plasma polymers, composites and plasma polymer films prepared by RF sputtering of conventional polymers In: Plasma Polymer Films, Ed. H. Biederman, *Imperial College Press*, London, 2004, pp. 289–324.

[2] Ryszard Lamber, Stefan Wetjen, and Ginter Schulz-Emoff, Alfred Baalman, *J. Phys. Chem.* 1995,99, 13834–13838.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Magnetron Glancing Angle Deposition of Nanocomposite Thin Films

P. Solar¹, A. Choukourov¹, J. Hanuš¹, D. Slavínská¹, H. Biederman¹

¹*Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University in Prague, Czech Republic*

1. Introduction

It has been shown recently that Glancing Angle Deposition (GLAD) can be used as a method of depositing films with tunable nano- and microstructure [1]. GLAD utilizes an effect of self-shadowing which occurs when a flux of vaporized atoms or molecules arrives at a substrate tilted at oblique angle ($>70^\circ$) to direction of the flux. In this case, the growing nuclei shadow the area opposite to incoming flux and therefore the film grows through formation of columnar structures separated from each other by voids and inclined toward the source of the flux. The choice of the material of the substrate and its temperature are of paramount importance in GLAD as they may significantly decrease the surface mobility of adatoms and hence improve the separation of columns. Furthermore, the variation of the tilt of the substrate during the deposition may produce variety of shapes from zigzag to helical pillar structures.

Majority of GLAD has been performed so far on metals and inorganic compounds by using PVD under high vacuum which ensures a directional flux of particles moving in a collisionless regime. A limited number of studies dealt with plasma sputtering technique [2]. In this case, however, higher pressure was mandatory to maintain plasma.

In this work, an attempt has been made to combine magnetron sputtering and GLAD for the deposition of the Mo and Ti films as well as Ti/CH nanocomposite films.

2. Experimental

The experiments were performed in a bell-jar reactor pumped by rotary and diffusion pumps. A DC planar magnetron was designed to produce the enhanced magnetic field of 0.2 T above the erosion track. This allowed the operation of the magnetron at reduced pressures down to 0.08 Pa. The mixture of argon and hexane was used as a working gas. The substrates (silicon and glass) were located 7 to 10 cm from the magnetron and their angle position could be varied with respect to the target normal.

3. Results and Discussion

Fig. 1 shows the cross-section of the molybdenum film deposited on glass under 0.08 Pa Ar pressure. In the middle of the deposition the substrate angle was changed from 75 to -85° for a certain period of time and then the angle was restored to its previous value. Such manipulation led to formation of zigzag

columnar structure. Obviously, magnetron sputtering in combination with GLAD may prove to be powerful technique to sculpturing the structure of thin films.

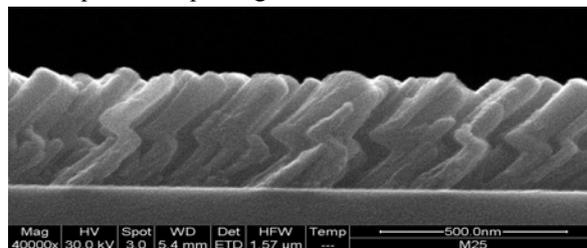


Fig. 1 Cross-section of molybdenum GLAD film.

Titanium behaved similarly to molybdenum and produced nanocolumnar films when sputtered in Ar. Ti was also sputtered in a mixture of argon and hexane. In this case, sputtering of titanium was accompanied by plasma polymerization processes which lead to increase of the C and decrease of the Ti content in the films. The columnar structure was retained at least up to 5% of hexane in the working mixture. At higher hexane concentration the discharge became unstable because of the target poisoning effects. Titanium carbide as well as titanium oxides and hydrocarbons detected in the films prove the complex chemistry involved in such deposition.

GLAD of hydrocarbon plasma polymer film was also performed by magnetron sputtering of polypropylene in the RF mode. The film deposited on glass appeared continuous without distinguishable columnar structure. However, when deposited over the structured Ti layer from the previous GLAD experiments the hydrocarbon film followed the direction and angle of the Ti columns. The direction and angle of the hydrocarbon columns could be changed by varying the tilt of the substrate.

4. Conclusions

Nanostructure of Mo and Ti films can be tuned in a wide range by using magnetron sputtering in the GLAD configuration. Plasma polymerization can be implemented with GLAD to produce composite films. The structure of the substrate may trigger the morphology of organic films deposited by GLAD from continuous to nanostructured thin films.

References

- [1] K. Robbie, M. J. Brett, *J. Vac. Sci. Technol. A* 15, 1460 (1997)
- [2] J. C. Sit, D. Vick, K. Robbie, and M. J. Brett, *J. Mater. Res.* 14, 1197 (1999)

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Nanocomposite Films with Embedded Metal Nanoparticles Near the Percolation Threshold - Physico-Chemical Properties and Applications

V. Zaporojtchenko, C. Pakula, H. Takele, V.S.K. Chakravadhanula, A. Kulkarni,
C. Pochstein, H. Greve, T. Strunskus and F. Faupel

Chair for Multicomponent Materials, Technical Faculty of the CAU Kiel,
Kaiserstrasse 2, D-24143 Kiel, Germany

The present talk reviews properties of nanocomposite films (NF) with high volume fractions (close to the percolation threshold) of metal nanoparticles embedded in polymer or ceramic matrix. In this regime, physical properties like the d.c. electrical conductivity and the permittivity are extremely sensitive on the nanoparticle concentration and separation. The morphology of the nanocomposites (particle size and distribution) which were prepared by PVD methods, depend on the host and metal properties as well as on the preparation parameters like deposition rate and substrate temperature. As a consequence, a percolation threshold in the conductivity was observed at different critical concentrations of nanoparticles ranging from 15 to 40 vol. %. It is shown also that optical, magnetic and chemical properties may be varied strongly close to percolation. Thus the index of refraction can be tuned over a wide range, and surface plasmons, occurring for noble metals in the visible range, can be shifted to the infrared regions. As potential applications of the NF near the percolation threshold electromagnetic, optical, chemical, and biosensoric devices are considered. Properties of the metal-ceramic NF will be discussed taking into account their application as electromagnetic sensors. Polymer-metal NF chemical sensors operate on the principle of swelling of the polymers in the presence of organic vapors and take advantage of the strong dependence of physical properties of the composite near the percolation threshold due to changes in the cluster separation upon swelling. Moreover, a novel approach, based on photochromic polymer-metal composites is discussed.

- [1] F. Faupel, V. Zaporojtchenko, et.al, *Contrib. Plasma Phys.* 47, 537 (2007).
- [2] V. Kochergin, V. Zaporojtchenko, H. Takele, F. Faupel, F. Foell, *J. Appl. Phys.* 101, 024302 (2007).
- [3] H. Takele, T. Strunskus, V. Zaporojtchenko, R. Adelung, F. Faupel, *Appl. Phys. A* 92, 345 (2008).
- [4] H. Takele, H. Greve, C. Pochstein, V. Zaporojtchenko, F. Faupel, *Nanotechnology*, 17, 3499 (2006).
- [5] V. Zaporojtchenko, R. Podschun, A. Kulkarni and F. Faupel, *Nanotechnology*, 17, 4904 (2006).
- [6] H. Greve, A. Biswas, U. Schurman, V. Zaporojtchenko, and F. Faupel, *APL* 88, 123103 (2006).

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Preparation of PMMA/Cu-Nanocomposites by pulsed laser deposition

Susanne Seyffarth and Hans-Ulrich Krebs
Institut für Materialphysik
University of Göttingen, 37077 Göttingen
suse@ump.gwdg.de, krebs@ump.gwdg.de

Layered polymer/metal nanocomposites consisting of poly(methyl methacrylate) PMMA and Cu were deposited by pulsed laser deposition (PLD) at room temperature by alternatively switching the target from PMMA to Cu. At this, for PMMA a laser fluence of 60 mJ/cm^2 close to the deposition threshold was used to obtain a smooth polymer film without droplets [1], while for Cu a laser fluence of 6 J/cm^2 had to be taken. On the smooth polymer layers, the metal grows in Vollmer-Weber island growth leading for thin Cu-films to layered PMMA/Cu nanostructures with spherical metallic particles as shown in Fig. 1a. The growth mechanisms of metal islands on laser deposited polymers was described earlier in [2, 3]. For larger metal layer thicknesses, the metal layers are closed and PMMA/Cu multilayers are formed (Fig. 1b).

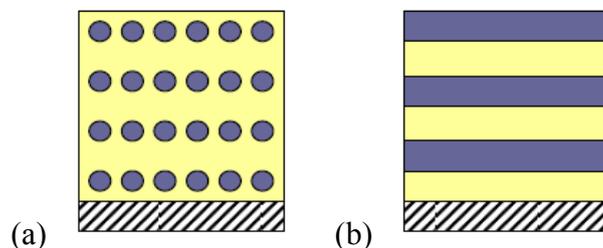


Fig. 1: Layered polymer/metal-nanocomposites as investigated (schematically)

The composition of PMMA was studied by infrared spectroscopy (FTIR). The PMMA/Cu nanostructures were analyzed by X-ray reflectometry in order to investigate the periodicity and interface roughnesses of the layered structures. Atomic force microscopy (AFM) was used to study the surface morphology. Cross section slices of the layered structures cutted by focused ion beam (FIB) were examined by electron microscopy (SEM, TEM).

It was found that indeed well layered PMMA/Cu-structures can be formed by PLD, but stress formation leads to buckles and waves of the metal layers as long as the PMMA layers are weak. Therefore, partial cross-linking of the PMMA-layers (obtained for instance by UV-radiation) is necessary to obtain polymer layers with increased hardness and smooth metal layers.

In this contribution, the properties of these periodic structures is discussed with respect to individual layer thicknesses, roughnesses and periodicities, stress formation within the Cu-layers and cross-linking of the polymer.

- [1] B. Lösekrug, A. Meschede, and H.U. Krebs, *Pulsed laser deposition of smooth poly(methyl methacrylate) films at 248 nm*, Appl. Surf. Sci., 254 (2007) 1312.
- [2] J. Röder and H.U. Krebs, *Tuning the microstructure of pulsed laser deposited polymer-metal nanocomposites*, Appl. Phys. A 85 (2006) 15.
- [3] J. Röder, J. Faupel, and H.U. Krebs, *Growth of polymer-metal nanocomposites by pulsed laser deposition*, Appl. Phys. A 93 (2008) 863.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Polymeric Metal Wires

F. Choffat, M. Fontana, J. Breimi, P. Smith, W. Caseri

ETH Zürich, Department of Materials, Wolfgang-Pauli-Str. 10, CH-8093 Zürich

The miniaturization of linear agglomerates of metallic nanoparticles embedded in a polymer matrix leads to polymeric structures resembling metal wires with atomic diameter that are stabilized by appropriate ligands. Soluble materials of this kind are rare but have been accomplished, e.g., with derivatives of Magnus' green salt (which itself is insoluble), i.e. compounds of the type $[\text{Pt}(\text{NH}_2\text{R})_4][\text{PtCl}_4]$ (R represents an alkyl group), and poly(dialkylstannane)s, i.e. compounds of the type $(\text{SnR}_2)_n$.

Magnus' green salt and its derivatives are composed of the charged coordination units $[\text{Pt}(\text{NH}_2\text{R})_4]^{2+}$ and $[\text{PtCl}_4]^{2-}$, which leads to a self-assembled quasi-one-dimensional structure comprising a linear array of platinum atoms, as a result of the electrostatic attraction of the consecutive, oppositely charged metal complexes. Poly(dialkylstannane)s contain a backbone of covalently bounded metal atoms which directly form a metal wire. Hence, in spite of their completely different chemical composition, both of these structure types can therefore be regarded as molecular metal wires surrounded by a jacket of organic matter.

The Magnus' salt derivatives and the poly(dialkylstannane)s can be processed with common techniques applied for polymers into oriented films or fibers. Depending on their exact nature, these compounds show semiconductivity, dichroism or liquid crystallinity even below room temperature. One of these compounds was applied as active semiconducting layer in field-effect transistors which showed remarkable stability towards air and water.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Real time GISAXS study of magnetic nanoparticle assemblies on polymer templates

E. Metwalli¹, K. Schlage², V. Körstgens¹, S. Couet², R. Meier¹, G. Kaune¹, S.V. Roth²,
R. Röhlberger², P. Müller-Buschbaum¹

¹Physikdepartment E13, Technische Universität München, James-Franck-Str. 1, 85747 Garching, Germany

²HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany.

Abstract

Hybrid materials consisting of metal nanoparticles dispersed in a polymer matrix open pathways for engineering composites that exhibit advantageous electrical, optical, or magnetic properties. Using a portable DC magnetron sputtering deposition system [1-2], the incorporation of cobalt atoms into a microphase-separated polystyrene-block-polyethylene oxide *P(S-b-EO)* diblock copolymer film with parallel cylinder morphology is achieved. Time-resolved in situ grazing incidence small angle X-ray scattering (GISAXS) allows successfully to investigate the systematic formation and growth of Co nanoparticles into the polymer template. Cobalt atoms were found to wet selectively the polystyrene domains of the microphase-separated polymer film and then aggregates to form surface metal nanopatterns. Upon increasing the amount of metal content, the selectivity nature of the sputtering process was found to diminish with the formation of a pseudo-uniform metal layer. This study utilizes the real time GISAXS method to gain a better understanding of how the self-assembly process correlate with the structure of the copolymer domains in the polymer film.

[1] E. Metwalli, S. Couet, K. Schlag, R. Röhlberger, V. Körstgens, M. Ruderer, W. Wang, G. Kaune, S.V. Roth, P. Müller-Buschbaum; *Langmuir* **24**, 4265 (2008)

[2] G.Kaune, M.Ruderer, E.Metwalli, W.Wang, S.Couet, K.Schlage, R.Röhlberger, S.V.Roth, P.Müller-Buschbaum *ACS Appl. Mater. Interfaces* **1**, 353 (2009)

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Growth of metal thin films on conductive polymer surfaces

G. Kaune¹, M.A. Ruderer¹, E. Metwalli¹, R. Meier¹, W. Wang¹, S. Couet², K. Schlage², R. Röhlberger², S. V. Roth², P. Müller-Buschbaum¹

¹ TU München, Physik-Department LS E13, James-Franck-Str. 1, 85747 Garching, Germany

² HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany

Type and structure of the metal electrode deposited on top of the active layer of an organic photovoltaic cell have a strong influence on the performance of the corresponding device. Therefore understanding of the structural growth of the metal layer and the interaction with the photoactive polymer layer is necessary.

We investigate the formation of a metal/polymer interface in-situ with grazing incidence small angle x-ray scattering (GISAXS) [1] during DC magnetron sputtering. Two model systems with completely different growth behaviour are focussed: 1) The deposition of gold on a poly(N-vinylcarbazole) surface [2] and 2) the growth of an aluminium layer on a poly(3-hexylthiophene) surface [3]. These in-situ GISAXS experiments allow us to follow the spatial growth of the metal clusters from the initial stage to the formation of a continuous layer and to determine the temporal evolution of the cluster morphology and layer growth. From these observations a growth model is derived, explaining the cluster growth within individual steps. Moreover, metal incorporation inside the semi-conducting polymer film is revealed with x-ray reflectivity measurements [2]. Atomic force microscopy measurements picturing the surface structure complement the investigation.

[1] **P. Müller-Buschbaum:** *A basic introduction to grazing incidence small angle X-ray scattering*; in Special issue of Lecture Notes in Physics on "Applications of Synchrotron Light to Noncrystalline Diffraction in Materials and Life Sciences", Vol. 776, ed. Ezquerra, T.A.; Garcia-Gutierrez, M.; Nogales, A.; Gomez, p.61-90 Springer Berlin, ISBN-13: 978-3-540-95967-0 (2009)

[2] **G. Kaune, M.A. Ruderer, E. Metwalli, W. Wang, S. Couet, K. Schlage, R. Röhlberger, S.V. Roth, P. Müller-Buschbaum:** *In-situ GISAXS study of gold film growth on conducting polymer films*; ACS Appl. Mater. Interfaces **1**, 353-360 (2009)

[3] **G. Kaune, M.A. Ruderer, E. Metwalli, R. Meier, S. Couet, K. Schlage, R. Röhlberger, S.V. Roth, P. Müller-Buschbaum;** *to be published*

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Noble metal-polymer nanocomposites as plasmonics and optoelectronics

Y. K. Mishra,^{1*} S. Jebiril,¹ D. C. Agarwal,² V. S. K. Chakravadhanula,³ V. Zaporozhchenko,³ D. K. Avasthi,² R. Adelung¹ and F. Faupel³

¹Functional Nanomaterials, Institute for Materials Science, Faculty of Engineering, Christian-Albrechts-University, Kaiserstraße 2, 24143 Kiel, Germany.

²Inter University Accelerator Centre, Post Box -10502, New Delhi -110067, India

³Chair for Multicomponent Materials, Institute for Materials Science, Faculty of Engineering, Christian-Albrechts-University, Kaiserstraße 2, 24143 Kiel, Germany.

ABSTRACT

Dielectric matrices embedded with noble metal nanoparticles/nanostructures have attracted immense research interest due to their functional applications ranging from biomedical to optoelectronics. Polymer matrices are particularly suitable because of their low dielectric constants and high flexibility. In this work we report the synthesis of Ag and Au nanoparticles in different polymer matrices (polyethylene terephthalate and polyimide) using atom beam co-sputtering technique. The nanocomposites with varying metal fractions were characterized by optical absorption, transmission electron microscopy (TEM) and I-V measurements. Optical absorption studies revealed tunable and broad surface plasmonic resonant absorption with varying metal fractions. Microstructural evolutions of nanocomposite films using TEM, confirmed the formation of spherical and irregular shaped nanoparticles and adjoined network of nanostructures. The chemical composition of sputtered polymer and nanocomposite films were investigated by X-ray photoelectron spectroscopy. Nanocomposites exhibit narrow transmission of UV light which could be of interest in designing filters whereas the extended broad plasmonic absorption make them to be the suitable candidates for solar absorbers. The current-voltage measurement shows that the gold-polymer nanocomposite exhibits photoswitching response with respect to UV-light.

*Corresponding Author

Dr. Y. K. Mishra
Humboldt Research Fellow
Functional Nanomaterials
Institute for Materials Science
Faculty of Engineering, CAU Kiel
Kaiserstraße 2, 24143 Kiel, Germany
Email: ykm@tf.uni-kiel.de
Tele-Ph: +49-431 880 6195
Tele-Fax: +49-431-880-6229

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Enhanced light harvesting in semiconducting nanoparticle/polymer composites

M. A. Ruderer, R. Meier, P. Müller-Buschbaum

TU München, Physik-Department LS E13, James-Franck-Str. 1, 85747 Garching, Germany

Photoactive semi-conducting polymers have shown to be interesting candidates for photovoltaics due to their high absorption coefficient, easy processibility, mechanical flexibility and low costs. Nevertheless there are stringent constraints in device fabrication due to the short exciton diffusion length, i.e. the charge carrier separation has to occur in this length scale (on order of 10 nm). Therefore the structure of the polymer film is crucial. It was shown that the photophysical performance can be improved by increasing the interface area between electron acceptor and conjugated polymer as well as the lateral dimensions of the domains. One promising approach is the incorporation of conjugated polymers into block copolymers with conventional coil-like polymers. Block copolymers form highly ordered nanostructures due to micro-phase separation. These polymer nano-structures, acting as a template, enable a completely new arrangement of semiconducting nanoparticles which are embedded via a chemically controlled surface [1, 2]. From the presence of the semiconducting nanoparticles new optical properties arise.

The spatial arrangement in lateral and perpendicular direction of the nanoparticles in the polymer film is monitored by X-ray and neutron scattering techniques such as grazing incidence small angle scattering (GISAS) and reflectivity. The surface topography is imaged with atomic forces microscopy (AFM) and a structural model of the film is obtained. The absorption and conductivity are determined depending on the arrangement of the nanoparticles in the polymer matrix and compared to the pure polymer film.

1. M.M.Abul Kashem, J.Perlich, L.Schulz, S.V.Roth, W.Petry, P.Müller-Buschbaum; *Macromolecules* **40**, 5075 (2007)
2. M.M.Abul Kashem, J.Perlich, L.Schulz, S.V.Roth, P.Müller-Buschbaum; *Macromolecules* **41**, 2186-2194 (2008)

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Particle co-operated self-assembly in thin film of diblock copolymer

Mottakin M. Abul Kashem¹, Jan Perlich², Alexander Diethert², Weinan Wang², Mine Memesa³, Jochen S. Gutmann³, Eva Majkova⁴, Ignác Capek⁵, Peter Müller-Buschbaum² & Stephan V. Roth¹

¹HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany

²Technische Universität München, Physik-Department LS E13,
James-Franck-Str.1, 85748 Garching, Germany

³Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

⁴Institute of Physics SAS, Dúbravská 9, SK 84511 Bratislava, Slovakia

⁵Polymer Institute, SAS, Dúbravská 9, SK 84236 Bratislava, Slovakia

Microphase separated mesoscopic lattice structures in a thin film of a block copolymer can be used as a template to achieve an ordered arrangement of nanoparticles [1-3] in order to produce new generation hybrid materials toward potential applications such as chemical sensor, biosensor, catalysts, chemical separation, photonic materials and high-density data storage. During the self-assembly process in a block copolymer film, van der Waals forces and balance of surface free energies lead to a spatial arrangement of the nanoparticles inside the domain-structures of the film. We have investigated the role of nanoparticles in such a kind of particle co-operated self-assembly process and the domain orientation in asymmetric block copolymer films with grazing incidence small-angle X-ray scattering (GISAXS) [4]. Thin films of polystyrene-*block*-polymethylmethacrylate P(S-*b*-MMA) containing varying amount of iron oxide nanoparticles are prepared on top of silicon substrates by spin-coating. During annealing at above the glass transition temperature of the P(S-*b*-MMA) block copolymer, the nanoparticles migrate to the cylindrical domains of PMMA. This results in an increase of diameter of the cylindrical domains and cylinder-to-cylinder distances. Besides, an addition of a small amount of nanoparticles orients PMMA domains perpendicular to the substrate. Thus, an ordered array of magnetic nanoparticles hosted by perpendicularly oriented PMMA domains is prepared. GISAXS experiments have been carried out at the beam line BW4 [5] of the DORIS III storage ring of HASYLAB at DESY in Hamburg. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) have been used to image the spatial arrangement of the nanoparticles.

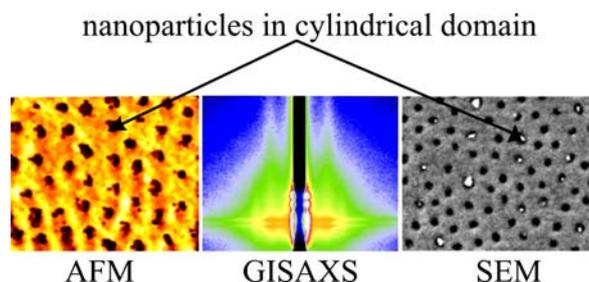


Figure 1. Spatial arrangement of iron oxide nanoparticles inside the PMMA domains investigated by AFM, SEM and GISAXS

References

- [1] M.M. Abul Kashem, J. Perlich, L. Schulz, S.V. Roth, W. Petry, P. Müller-Buschbaum. 2007 *Macromolecules* **40** 5075.
- [2] M.M. Abul Kashem, J. Perlich, L. Schulz, S.V. Roth, P. Müller-Buschbaum. 2008 *Macromolecules* **41** 2186.
- [3] V. Lauter-Pasyuk, H.J. Lauter, G.P. Gordeev, P. Müller-Buschbaum, B.P. Toperverg, M. Jernenkov, W. Petry. 2003 *Langmuir* **19** 7783.
- [4] P. Müller-Buschbaum. 2003 *Anal. Bioanal. Chem.* **376** 3.
- [5] S.V. Roth, R. Döhrmann, M. Dommach, M. Kuhlmann, I. Kröger, R. Gehrke, H. Walter, C. Schroer, B. Lengeler, P. Müller-Buschbaum. 2006 *Rev. Sci. Instrum.* **77** 085106.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Prevention of biological surface contamination by deposition of silver nanoparticle-containing plasma SiC_xO_yH_z thin films.

B. Despax¹, C. Saulou², M. Mercier-Bonin², P. Raynaud¹, S. Zanna³, P. Marcus³

¹LAPLACE Université Paul Sabatier, 118 route de Narbonne 31062 Toulouse Cedex 09, France

²LISPB INSA (UMR CNRS 5504) 135 Avenue de Rangueil 31077 Toulouse Cedex 04, France

³LPCS, UMR CNRS/ENSCP 7045, 11 rue P. et M. Curie, 75005 Paris, France

The growing interest in the dispersion of metallic particles in polymers or ceramic matrices is motivated by the prospect of developing new materials with technological applications. Recently, a large field of applications has been opened to prevent microbial colonization and biofilm formation. One possible strategy for the prevention of biofilm formation on surfaces is to coat the material with an antibacterial agent. The surface treatment can prevent bacterial adhesion to the surface or can kill bacteria as they come in contact with the surface.

The combination of silver particles as an inhibitor agent of biological colonization and silicon-based materials as an antifouling matrix seems to be of particular interest for biological and medical applications. In order to synthesize this kind of deposit, we used a process combining the silver sputtering and the plasma polymerization of hexamethyldisiloxane (HMDSO).

In gas mixtures such as argon and HMDSO, it is difficult to adjust the metal sputtering because of the large amount of organic fragments which contribute to a rapid polymer covering on the metal target. In order to control the target poisoning, we utilized a pulsed injection of HMDSO. In fact, at the same rf power input, the time duration choice of pulsed HMDSO injection adjusts the covering rate on the target and consequently the Ag sputtering¹. The competition between Ag sputtering and plasma polymerization was monitored by optical emission spectroscopy. The silver lines (546.55 and 520.91 nm), the H β transition (486.00 nm) and the Ar transition (549.59 nm) were easily detected and identified. The Ag lines and H β transition were assumed to be related respectively to the silver atom presence and the HMDSO dissociation in the plasma phase. Physicochemical analyses of deposits revealed the presence of silver-containing SiCO films. Infrared, Raman and XPS studies showed that the SiCO network was mainly constituted of Si-O bonds, Si-C bonds and C=C bonds. Moreover XPS and Energy dispersive X-ray analysis with electron probe (EDX) measured the film silver content.

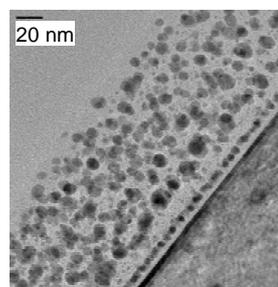


Figure 1: TEM cross section of Ag-SiCO films

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) (Fig.1) revealed the presence of well distributed silver nanoparticles from the surface into the material bulk. Their shape and size distribution depend on the competition between the sputtering and the plasma polymerisation. In Fig.1, the mean particle size is around 7 nm. By decreasing the duration of HMDSO pulsed injection, the mean size of Ag grains can be varied between 4nm and 100 nm. This is mainly a consequence of the increase in silver sputtering due to the decrease in target poisoning.

Ageing tests on Ag-SiCO films in saline solution (NaCl 150 mM) during 2 weeks showed a partial oxidation of matrix and a partial release of silver from the surface and the subsurface into aqueous solution. Besides, TEM coupled with EDX revealed that the whole layer was affected by the saline solution. Indeed, the presence of chlorine was detected at the interface between the matrix and the nanoparticles in the deposit bulk.

Finally, some Ag-SiCO layers deposited on stainless steel were tested on the bacteria *Escherichia coli* ATCC 10536 as gram-negative microbial model and on the yeast *Saccharomyces cerevisiae*. The viable bacterial survival number was determined after 24h-exposure to different silver-coated surfaces. A significant drop in viable bacterial count (>5log reduction) was observed, whatever the Ag content, thus showing the high antimicrobial activity. Besides, the silver penetration were studied on *Saccharomyces cerevisiae* by TEM and EDX

1-B. Despax, P. Raynaud, Plasma Process. Polym., 4, 127, (2007)

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Plasma deposited nanocomposite coatings for biomedical applications: silver and hydroxyapatite containing thin films

E. Sardella¹, R. Gristina¹, M. Altomare², D. Caruso², G. Da Ponte², C. Ingrosso²,
P. Favia^{1,2,3}, R. d'Agostino^{1,2,3}

¹ Institute of Inorganic Methodologies and Plasma (IMIP) CNR, via Orabona 4, Bari 70126, Italy

² Department of Chemistry, University of Bari, via Orabona 4, Bari 70126, Italy

³ Plasma Solution Srl, Spin off of the University of Bari, via Orabona 4, 70126, Italy

Nanocomposite materials are characterized by unique properties, different from separate phases and represent new challenges of great technological and economical impact.

Nanocomposite coatings find applications in biomedical field showing favourable effects in biomedical applications to manufacture materials for tissue engineering, drug delivery devices or as a strategy to improve mechanical properties or chemical inertness of materials. In this work two kind of nanocomposite coatings deposited by means of plasma assisted technology will be presented like silver containing and hydroxyapatite (HA) containing plasma deposited nanocomposite coatings. The former aimed to produce antibacterial surfaces and the latter intended for application in bone and cartilage generation on properly designed scaffolds. Bacteria responsible for nosocomial infections are often multi-resistant to antibiotics and represent a special therapeutic challenge. Antibacterial surfaces are of fundamental importance for many health and consumer products (e.g. catheters) [1,3]. In this study plasma deposition of nano-composite coatings (*i.e.* dispersions of silver clusters embedded into an organic matrix) are presented as silver delivery systems. The aim of this work is to improve the performance and reliability of existing products and to extend the use of silver to new value-added products, by applying PE-CVD of silver containing nano-composite coatings directly on biomaterial surfaces. The coatings were deposited in RF (13.56 MHz) Glow Discharges fed by a mixture of Diethyleneglycol di-methyl ether (DEGDME) and Ar. A simultaneous sputtering process occurred when a silver coated sputter target was used, to obtain a dispersion of silver clusters into an organic matrix [2]. A similar strategy was applied to produce HA containing coatings replacing the Ag target with one of HA. XPS characterization demonstrates that the higher the amount of silver embedded, the higher the crosslinking of organic matrix: the retention of the monomer structure is lost due to experimental conditions used during glow discharge. Water contact angle (WCA) measured on such surfaces increases as a function of surface roughness. A deep FT-IR characterization of coatings deposited in this work shows characteristic vibrations of structural groups placed tightly on surfaces of small silver inclusions. Such kind of absorption peaks is not present on coatings that do not include Ag. The enhancement of such absorptions greatly depends on the morphology, dimension and density of metal clusters. It can be used to estimate ageing of coatings and possible amount of released silver. Investigation of the influence of Ag-nanocomposite coatings, containing the highest amount of Ag, on bacterial (*S. epidermidis*, ATCC 35984, slime-positive) adhesion, under static and flow conditions, shows that these coatings not only significantly reduce bacterial adhesion, in comparison to the native PET, but cause bacterial death as well. HA-nanocomposite coatings with variable HA content have been deposited from allyl alcohol vapours (fixed flow rate 0.1 sccm) in Ar carrier (20sccm). A HA-sputter coated cathode has been used, RF power (10–100 W) and pressure (10–50 mTorr) have been changed. The HA content in the coatings increases as the input power increases and a clear evidence of the characteristic feature of HA in the FT-IR spectra has been shown. By comparing the behaviour of Saos-2 osteoblasts grown on plasma deposited coatings it has been shown that nano-composite coatings containing HA are much more effective in promoting cell spreading with respect organic coatings with similar chemical composition but non containing HA and coatings of only HA sputtered on glass substrates.

References:

- [1] Elliot, T. S. J., *et al.* Journal of Hospital Infection 30, 181, 1995.
- [2] Sardella E., *et al.* Plasma Processes and Polym. 3, 456, 2006 and references therein.
- [3] Silver S., FEMS Microbiol Rev 27, 341, 2003

Acknowledgements:

M. Katsikogianni, Y.F. Missirlis are gratefully acknowledged for their contribution and MIUR-FIRB RBNE01458S_006 and INTERREG (No. I 2101003) Italy-Greece projects for funding.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Molecularly Imprinted Organic/Inorganic Hybrid Materials Capable of Protein Recognition Prepared by Liquid Phase Deposition

Toshifumi Takeuchi

Graduate School of Engineering, Kobe University

Nada-ku, Kobe 657-8501, Japan.

E-mail: takeuchi@gold.kobe-u.ac.jp

Molecularly imprinted organic/inorganic hybrid materials have been prepared for the recognition of proteins by using liquid-phase-deposition (LPD), a wet process for the preparation of metal oxide films. Therein, protein-polyion compound adducts were formed electrostatically in the titanium oxide-LPD treatment solution and were co-deposited with titanium oxide onto a gold substrate during the LPD process. After the removal of the proteins, protein-imprinted organic/inorganic hybrid thin films were obtained. As a reference, a non-imprinted film was also prepared without the addition of proteins. In addition, the chips prepared without polyion compounds were prepared in the presence and absence of proteins.

The binding studies were conducted to measure the binding activity for proteins by surface plasmon resonance measurements. Only when both polyion compounds and proteins were added to the LPD, the obtained imprinted films showed high selectivity for the template proteins. It is also found that appropriate ratio of the polyion compounds in the complexation process could keep native structure of the proteins, under which LPD process was employed. These results reveal that molecularly imprinted organic/inorganic hybrid materials prepared by LPD is a new versatile technology, where various molecularly imprinted organic/inorganic hybrid materials can be prepared by simply mixing diverse range of organic polyion compounds with the LPD treatment solution capable of interacting with target proteins.

References

1. Tatemichi, M., Sakamoto, M., Mizuhata, M., Deki, S., Takeuchi, T., Protein-templated Organic/inorganic Hybrid Materials Prepared by Liquid-phase Deposition, *J. Am. Chem. Soc.* 2007, 129, 10906 -10910.
2. Takeuchi, T., Hishiya, T. Molecular Imprinting of Proteins Emerging as a Tool for Protein Recognition, *Org. Biomol. Chem.* 2008, 6, 2459-2467 (review).

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Design of bioactive Ag-Nanocomposites with a single-step plasma process

E. Körner, A. Ritter, P. Rupper, E. Michel, D. Hegemann

Empa, Swiss Federal Laboratories for Materials Testing and Research
e-mail: enrico.koerner@empa.ch

Producing materials that are efficient for reducing and killing bacteria and harmless for humans and the environment is still a big challenge in research and science. Different materials are under investigation, including silver. Ag is proven to be effective against several bacteria strains^[1] and does not promote bacterial resistance. Plasma-deposited nanocomposites enable products with very low raw material input.

The combination of plasma polymerization and etching within a co-sputtering process was found to result in the incorporation of metal nanoparticles^[2] in a hydrocarbon matrix. In addition, the plasma polymer matrix can be designed in a way that accessible functional groups are exposed within a nanoporous structure. These structures possess a high specific surface area and may thus provide a high density of functional groups^[3]. The deposition of nanostructured coatings depends on reactor design parameters and operating conditions such as power input, gas flow, and gas composition.

A capacitively coupled radiofrequency batch reactor (asymmetric geometry) was used to produce the multifunctional coatings in a one-step process. The polymer matrix is built-up by using ethylene (C₂H₄) as a monomer gas. In addition, carbon dioxide (CO₂) is used as the reactive gas in order to structure the matrix and add functional groups to the a-C:H network^[4]. An excess of argon is used in the gas mixture for co-sputtering from a Ag cathode.

The size and the growing behavior of the Ag nanoparticles show a clear dependence on the process parameters gas ratio and power input. The particle distribution could be classified in different sections with TEM measurements. The total Ag content in the films is determined with ICP-OES. This method is also used to quantify the Ag release of the nanocomposite coatings. Figure 1 shows that the Ag release (after 14 days) is proportional to the Ag content which is available in the nanocomposite.

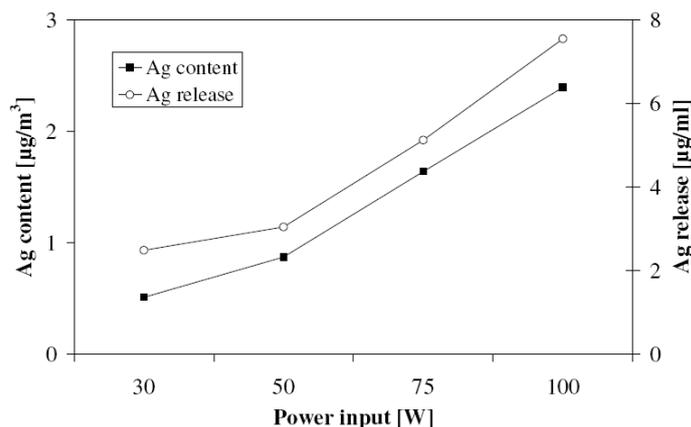


Fig. 1: Dependence of Ag release on the Ag content of Ag/a-C:H:O coatings

- [1] A. D. Russell, W. B. Hugo, Prog. Med. Chem. 1994, 31, 351.
- [2] H. Biederman, L. Martinu, D. Slavinska, I. Chudacek, Pure Appl. Chem. 1988, 60, 607.
- [3] D. Hegemann, M. M. Hossain, D. J. Balazs, Prog. Org. Coat. 2007, 58, 237.
- [4] E. Körner, G. Fortunato, D. Hegemann, Plasma Process. Polym. 2009, 6, 119.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Adhesion, growth and differentiation of human osteoblast-like MG 63 cells on metallic and polymeric materials developed for artificial joint replacements

Lucie Bačáková¹, Chadi Ali², Zdeněk Čejka³, Martin Pařízek¹, Marta Vandrovcová¹, Lubica Grausová¹, Věra Lisá¹

¹ Institute of Physiology, Academy of Sciences of the Czech Republic, Vídeňská 1083, Prague 4-Krč, Czech Republic; E-mail: lucy@biomed.cas.cz

² Orthopaedic Clinic, Faculty Hospital Bulovka, 1st Medical School, Charles University, Prague, Czech Republic; ³Prospon Ltd., Kladno, Czech Republic

Recently, there is an increasing demand for artificial replacements of damaged tissues and organs. Therefore, the search for adequate artificial materials or innovation of materials currently used in the clinical practice is always reasonable. In this study, we investigated the adhesion, growth and osteogenic differentiation of human osteoblast-like cells of the line MG 63 in cultures on the following surface-modified metallic and polymeric materials, developed for construction of artificial hip joint replacements: Ti-6Al-4V alloy modified by plasma-spraying, polishing, plasma-spraying and coating with amorphous hydrogenated carbon (a-C:H) or polishing and coating with a-C:H; stainless steel AISI 316 LWM modified with plasma-spraying or polishing; non-modified or polished polyetheretherketon (PEEK) Optima, and non-modified or polished ultra-high molecular weight polyethylene (UHMWPE). Standard cell culture polystyrene dishes (TPP, Switzerland) served as a reference material.

On day 1 after seeding, the cells on all investigated materials adhered in lower numbers than on control polystyrene dishes (from 19,000±6,300 to 49,000±12,000 cells/cm² vs. 61,000±17,000 cells/cm²), except Ti-6Al-4V treated by plasma-spraying and coating with a-C:H, where the cell number, as well as the size of the cell adhesion area, were comparable with the values obtained on the reference material. As revealed by an enzyme-linked immunosorbent assay (ELISA) the cells on plasma-sprayed and a-C:H-coated Ti-6Al-4V contained the highest concentration of integrin adhesion receptors with beta 1 chain (by 132% compared to the value on polystyrene), i.e., receptors for collagen, fibronectin and vitronectin, extracellular matrix molecules which are known to be spontaneously adsorbed on the materials from the serum supplement of the culture medium or deposited by the cells themselves.

On day 3 after seeding, also the cell number on Ti-6Al-4V treated by polishing and coating with a-C:H (126,000±4,700 cells/cm²) equaled with the value on the control polystyrene (124,000±3,100 cells/cm²). A relatively high cell number (121,000±4,500 cells/cm²) was also obtained on polished stainless steel AISI 316 LWM. The cells on these samples contained the highest concentrations of integrins alpha v (i.e., receptors for vitronectin), vinculin (an integrin-associated protein) and osteocalcin (a calcium-binding extracellular matrix glycoprotein and important marker of osteogenic cell differentiation).

On day 8 after seeding, the cell numbers on almost all samples equaled with the values on control polystyrene, except the numbers on polished and relatively highly hydrophobic UHMWPE. On plasma-sprayed and a-C:H-coated Ti-6Al-4V, and also non-modified PEEK, the cell numbers even exceeded the values on polystyrene dishes. In addition, the cells on non-modified PEEK contained one of the highest concentrations of talin, another integrin-associated protein, and on polished PEEK, the highest concentration of osteopontin, another marker of osteogenic cell differentiation.

Therefore, it can be concluded that plasma-sprayed and a-C:H-coated Ti-6Al-4V, polished stainless steel AISI 316 LWM and PEEK seem to be the most appropriate materials for constructing bone-anchoring parts of joint prostheses, while polished UHMWPE can be used for creation of articular surfaces, where the cell adhesion and growth is not desirable.

Supported by the Academy of Sciences of the Czech Republic (Grant No. KAN101120701)

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Polymer/metal hybrid membranes : from in situ nanostructuration process to modulated functional properties

S. Clémenson, E. Espuche, L. David

Université de Lyon, F-69003, Lyon, Université Lyon 1, F-69622 Villeurbanne, France; CNRS, UMR5223, Ingénierie des Matériaux Polymères, Laboratoire des Matériaux Polymères et des Biomatériaux

eliane.espuche@univ-lyon1.fr - Tel : +33 (0)4 72 43 27 01 - Fax : +33 (0)4 72 43 12 49

During the last few years, the preparation of hybrid organic-inorganic nanocomposite membranes by in situ methods has been a subject of growing interest. Indeed it generally allows to obtain homogeneous dispersions of nanometer size fillers within the membrane and to achieve functional properties [1, 2, 3]. The aim of this work is to prepare palladium/polymer nanocomposites membranes with different morphologies and modulated functional properties.

Dense films were prepared by cast process from palladium acetate and polyetherimide. The films were annealed according to different cure cycles. A nanostructuration process leading to the formation of crystalline palladium nanoparticles within the film occurred during the thermal treatments. The particles were homogeneously dispersed for Pd amount lower than 15 wt%. For higher palladium content, a surface layer composed of Pd particles was obtained in addition to an homogeneous dispersion of nanoparticles in the bulk for some curing conditions. The effects of the nanoparticle dispersion state were studied on gas permeation. Specific interactions with hydrogen were evidenced. Enhanced effects were observed as the total amount of particles increased and particularly as the particles were mainly located at the film surface.

In order to promote the palladium particles accessibility, asymmetric porous hybrid films were prepared. As for dense films, palladium crystalline nanoparticles were formed after thermal annealing. These particles were mainly located at the film surface of the dense polymer layer and on the walls of the pores (Figure 1).

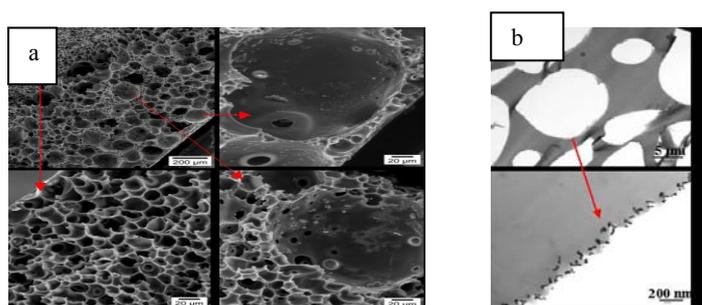


Figure 1: porous nanocomposite films
a) at the SEM scale and
b) at the TEM scale on an ultra-microtomed slice.

- [1] S.S. Ozdemir, M.G. Buonomenna, E. Drioli, Catalytic polymeric membranes: preparation and application, *Applied Catalysis A: General*, 2006, 307, 167-183
- [2] K. Ebert, G. Bengtson, R. Just, M. Oehring, D. Fritsch, Catalytically active poly(amideimide) nanofibre mats with high activity tested in the hydrogenation of methyl-cis-9-octadecenoate, *Applied Catalysis A: General*, 2008, 346, 72-78
- [3] J.M. Compton, D.W. Thompson, D.E. Kranbuehl, S. Ohl, O. Gain, L. David, E. Espuche, Hybrid films of polyimide containing in situ generated silver or palladium nanoparticles: effect of the particle precursor and of the processing conditions on the morphology and the gas permeability, *Polymer*, 2006, 47(15), 5303-5313

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Plasma deposited platinum-containing nanocomposite films as catalysts for fuel cells

A. Milella¹, E. Dilonardo¹, F. Palumbo², S. Martin³, R. d'Agostino¹, F. Fracassi¹

¹ University of Bari, Department of Chemistry, Via Orabona 4, 70126 Bari (Italy)

² Institute for Inorganic Methodologies and Plasmas (IMIP)- CNR; Department of Chemistry

³ CEA-G/ Leti, Grenoble (France)

In Proton Exchange Membrane Fuel Cells (PEMFC) the electrode reactions rely heavily on the use of platinum catalysts. Since cost of this precious metal is one of the main barriers for commercialization of fuel cells, many research efforts are addressed to obtaining higher catalytic activity than the standard carbon-supported platinum particle catalysts used in current PEM fuel cells, but using a reduced amount of catalyst. One strategy to increase the performance of platinum catalysts is to disperse it in form of nanoparticles, eventually embedded in a polymeric matrix. In the framework of limiting the amount of precious metal in the fuel cell assembly, plasma processes are particularly appealing since they allow control of the film thickness to the nanometer scale.

In this contribution we report on the deposition of nanocomposite thin films containing platinum nanoclusters (high specific area) with definite concentration and uniform in size. Thin films are obtained from a simultaneous plasma-enhanced chemical vapour deposition of ethylene (C₂H₄) / argon gas mixtures and RF sputtering of a platinum target. The main advantages of this approach consist in the reduced thickness (less than 1 micron), the possibility to coat complex shapes, and the easy scale up in a continuous process. Chemical and morphological characterization show that the platinum content in the coating can be finely controlled by varying the RF power and the monomer flow rate. Furthermore platinum is organized in crystalline nanoclusters uniformly distributed in the material. Cyclic voltammetry indicates that the catalytic activity of deposited films reaches a maximum correspondingly to a platinum load of about 60%. Preliminary results on device testing will be also presented.

Acknowledgments

This work was funded by the European Project *NAPOLYDE* (NMP2-CT-2005-515846).

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

Fabrication of Pt/Conductive Polymer Composite for Durability Improvement of Catalyst for Fuel Cells

Minoru MIZUHATA¹, Katsumasa MATSUMOTO¹, Yoshikazu MIYACHI¹, Masako OGA¹ and Shigehito DEKI²

¹ Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University

² Professor Emeritus, Kobe University

1-1, Rokkodai-cho, Nada, Kobe 657-8501, Japan

E-mail : mizuhata@kobe-u.ac.jp

In the viewpoint of the electrode durability of polymer electrolyte fuel cells (PEFCs), some studies intended that the platinum catalyst diffuse into the ion-exchange membrane by oxidation during the oxygen reduction at the open circuit voltage. It is necessary to prevent the coagulation and diffusion of the platinum catalyst and its shortage of the durability. In this study, we carried out the quantitative analysis of Pt surface area using CO stripping method and the durability of Pt catalytic activity was discussed. According to cyclic voltammetry of Pt/PPy/C composite, we found the Pt oxidation and reduction peak from original stage to after 10000 cycles. At the original state, the specific surface area of platinum is 92 m²/g, which corresponds to more than 85% of the surface area of Pt/C system (105 m²/g). which is much more than our target (25%). After 10000 cycles of potential sweeps, the measured surface area was ca.18 m²/g for Pt/PPy/C systems, which was 4 times of the value for the Pt/C systems (ca.4 m²/g) after 10000 cycles. The mean diameter of platinum particles was ca 5.5 nm after 10000 cycles for Pt/PPy/C composites, whereas the Pt for Pt/C system aggregated in catalytic layer. These results indicated that Pt/PPy on carbon composite has higher durability than Pt/C. Coagulation condition for Pt/PPy/C during PEFC operation with the redox operation of Pt catalyst is shown in Fig.1. PPy acts a role as a blocking layer for dissolution and an inhibitor for agglomeration of platinum catalyst.

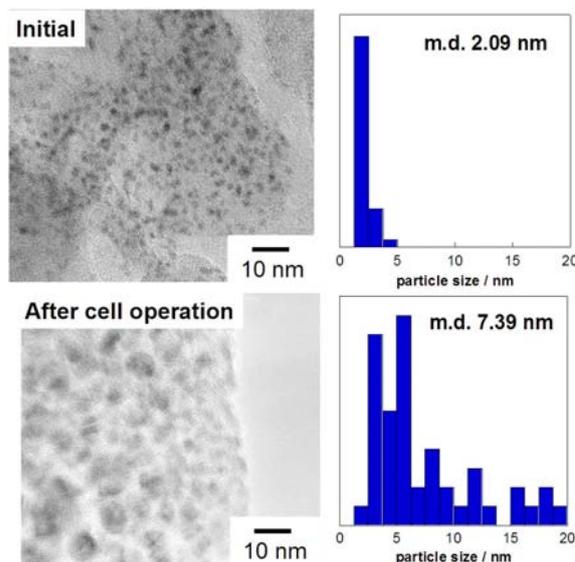


Fig. 1. Coagulation condition of Pt catalyst and the variation of Pt catalyst for Pt/PPy/C during PEFC operation.

MEA with Pt/Polypyrrole (PPy) on C as gas diffusion electrode of cathode was prepared. The durability test of the MEA was performed with CV in PEFC operating temperature. It was observed that aggregation and dissolution of platinum in Pt/PPy on C is inhibited comparing with Pt/C. Besides, durability test of Pt/PANI on C with CV was performed in H₂SO₄ aqueous solution. The electrochemical surface area is maintained in Pt/PANI on C than Pt/C because their degradation of Pt is repressed in Pt/PANI on C. The gas diffusion electrode as the PEFC cathode with the conducting polymers has improved its durability.

We also attempt to prepare the Pt alloy catalytic composite with PPy. PtRu alloy particles were composed by ion-exchange reaction using RuCl₃ aqueous solution after platinum reduction with pyrrole polymerization. Ru content in PtRu alloy was controlled by the Ru/Pt content in the preparation reaction.

This study was supported by the NEDO, Japan and Grant-in-aid from JSPS, Japan.

References

- 1) S. Deki, H. Nishikawa, M. Mizuhata, *Electrochemistry*, 72, 415 (2004).
- 2) M. Mizuhata, M. Oga, S. Deki, *ECS Transactions*, 2 (8) 63-72 (2007).

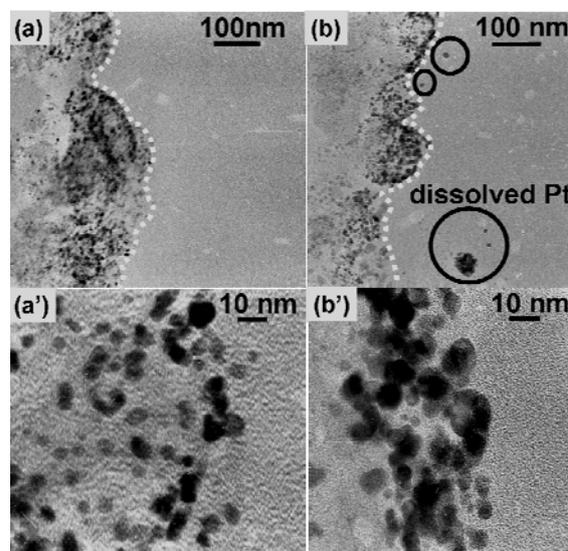


Fig. 2 Cross-sectional TEM images of MEA after CV measurement for (a)Pt/PPy on C, (b)Pt on C, and high resolution images are shown below (a') Pt/PPy on C, (b') Pt on C.

Nanoworkshop 2009

4th International Workshop on Polymer/Metal Nanocomposites
September 2 – 4, 2009, Prague, Czech Republic



Notes

List of Nanoworkshop 2009 participants

Lucie Bačáková
Institute of Physiology
Academy of Sciences of the Czech Republic
Václavská 1083, 142 20 Praha 4-Krč
Czech Republic
e-mail: lucy@biomed.cas.cz

Petr Bartoš
Department of Physics, Faculty of Pedagogy
University of South Bohemia
Jeronýmova 10, 37115 České Budějovice
Czech Republic
e-mail: bartos-petr@seznam.cz

Hynek Biederman
Department of Macromolecular Physics
Faculty of Mathematics and Physics
Charles University in Prague
V Holešovičkách 2, 180 00 Praha 8
Czech Republic
e-mail: bieder@kmf.troja.mff.cuni.cz

Walter Caseri
Department of Materials
Swiss Federal Institute of Technology Zurich
Wolfgang-Pauli-Strasse 10, 8093 Zürich
Switzerland
e-mail: wcaseri@mat.ethz.ch

Shigehito Deki
Kobe University
1-1 Rokkodai-cho, Nada-ku, 657-8501 Kobe
Japan
e-mail: deki@kobe-u.ac.jp

Martin Drábik
Department of Macromolecular Physics
Faculty of Mathematics and Physics
Charles University in Prague
V Holešovičkách 2, 180 00 Praha 8
Czech Republic
e-mail: martin.drabik@gmail.com

Franz Faupel
Institute for Materials Science Faculty of Engineering
Christian-Albrechts University at Kiel
Kaiserstr. 2, 24143 Kiel
Germany
e-mail: ff@tf.uni-kiel.de

Gabrauf Gumarov
Zavoisky Physical -Technical Institute
Sibirsky tract 10/7, 420029 Kazan
Russian Federation
e-mail: graufg@mail.ru

Mohamad Abu Bakar
School of Chemical Sciences
Universiti Sains Malaysia
Minden, 11800 Pulau Pinang
Malaysia
e-mail: bmohamad@usm.my

Haile Takele Beyene
Materials innovation institute (M2i)
P.O.Box 5008 Mekelweg 2, 2600 GA Delft
Netherlands
e-mail: h.takele.beyene@tue.nl

Fanggao Chang
College of Physics & Information Engineering
Henan Normal University
Jianshe Road 46, 453007 Xixiang
China
e-mail: chfg@henannu.edu.cn

Vladimír Čech
Institute of Materials Chemistry
Brno University of Technology
Purkynova 118, 612 00 Brno
Czech Republic
e-mail: cech@fch.vutbr.cz

Bernard Despax
Univ Toulouse 3, Lab Plasma & Convers Energie
UMR CNRS 5213
F-31062 Toulouse 9
France
e-mail: bernard.despax@laplace.univ-tlse.fr

Eliane Espuche
Université de Lyon, Université Lyon 1
A. Latarjet
69622 Villeurbanne
France
e-mail: eliane.espuche@univ-lyon1.fr

Amir Gumarov
Physics faculty Kazan State University
Kremlyovskaya 18, 420008 Kazan
Russian Federation
e-mail: amirgumarov@rambler.ru

Haybat Itani
Max Planck Institute for Iron Research
Max-Planck-Str. 1, 40237 Düsseldorf
Germany
e-mail: h.itani@mpie.de

List of Nanoworkshop 2009 participants

Andreas Heilmann
Fraunhofer-Institute for Mechanics of Materials
Walter-Hülse-Str. 1, 06120 Haale (Saale)
Germany
e-mail: Andreas.Heilmann@iwmh.fraunhofer.de

Lukáš Hoferek
Institute of Materials Chemistry
Brno University of Technology
Purkynova 118, 612 00 Brno
Czech Republic
e-mail: xhoferek@fch.vutbr.cz

Mottakin M. Abul Kashem
HASYLAB @ DESY
Notkestr. 85
22607 Hamburg
Germany
e-mail: mottakin.abul.kashem@desy.de

Eva Kolíbalová
TESCAN, s.r.o.
Libušina třída 21, 623 00 Brno
Czech Republic
e-mail: eva.kolibalova@tescan.cz

Martin Kormunda
Department of Physics, Faculty of Science
J.E. Purkinje University
České mládeže 8, 400 96 Ústí nad Labem
Czech Republic
e-mail: martin.kormunda@ujep.cz

Enrico Körner
Empa
Lerchenfeldstrasse 5, CH-9000 St. Gallen
Switzerland
e-mail: enrico.koerner@empa.ch

Jaroslav Kousal
Department of Macromolecular Physics
Faculty of Mathematics and Physics
Charles University in Prague
V Holešovičkách 2, 180 00 Praha 8
Czech Republic
e-mail: Jaroslav.Kousal@mff.cuni.cz

Hans-Ulrich Krebs
Institut für Materialphysik
University of Göttingen
Friedrich-Hund-Platz 1, 37077 Göttingen
Germany
e-mail: krebs@ump.gwdg.de

Zuzana Križanová
Department of Superlattices Institute of Electrical
Engineering, Slovak Academy of Science
Dúbravská cesta 9, 841 04 Bratislava
Slovakia
e-mail: z.krizanova@gmail.com

Pavel Kudrna
Department of Surface and Plasma Science
Faculty of Mathematics and Physics
Charles University in Prague
V Holešovičkách 2, 180 00 Praha 8
Czech Republic
e-mail: Pavel.Kudrna@mff.cuni.cz

Ondřej Kylián
Department of Macromolecular Physics
Faculty of Mathematics and Physics
Charles University in Prague
V Holešovičkách 2, 180 00 Praha 8
Czech Republic
e-mail: Ondrej.Kylian@mff.cuni.cz

Aleš Marek
HVM Plasma spol. s r. o.
Na Hutmance 2, 158 00 Praha 5
Czech Republic
e-mail: ales.marek@hvm.cz

Jindřich Matoušek
Department of Physics, Faculty of Science
J.E. Purkinje University
České mládeže 8, 400 96 Ústí nad Labem
Czech Republic
e-mail: jindrich.matousek@ujep.cz

Ezzeldin Metwalli
TUM, Physikdepartment
James-Franck-str. 1, 85747 Garching bei Muenchen
Germany
e-mail: ezzmet@ph.tum.de

Antonella Milella
Department of Chemistry
University of Bari
Via Orabona 4, 70126 Bari
Italy
e-mail: milella@chimica.uniba.it

Yogendra Kumar Mishra
Institute for Materials Science, Faculty of Engineering
Christian-Albrechts University at Kiel
Kaiserstr. 2, 24143 Kiel
Germany
e-mail: ykm@tf.uni-kiel.de

List of Nanoworkshop 2009 participants

Minoru Mizuhata
Department of Chemical Engineering
Graduate School of Engineering
Kobe University
1-2 Rokkodai-cho, Nada-ku, 657-8501 Kobe
Japan
e-mail: mizuhata@kobe-u.ac.jp

Dmitri Muraviev
Chemical Department of the Autonomous University
of Barcelona
08193 Bellaterra, Barcelona
Spain
e-mail: Dimitri.Muraviev@uab.es

Abhijit Patra
PPSM, ENS Cachan
Avenue du President Wilson 61, 94235 Cachan
France
e-mail: patraabhi@yahoo.co.in

Jaroslav Pavlík
Department of Physics, Faculty of Science
J.E. Purkinje University
České mládeže 8, 400 96 Ústí nad Labem
Czech Republic
e-mail: pavlikj@sci.ujep.cz

Andrea Pucci
Department of Chemistry and Industrial Chemistry
University of Pisa
Via Risorgimento 35, 56126 Pisa
Italy
e-mail: apucci@ns.dcci.unipi.it

Luca Ravagnan
Department of Physics and CIMAINA
University of Milano
Via Celoria 16, 20133 Milano
Italy
e-mail: luca.ravagnan@mi.infn.it

Stephan Volkher Roth
HASLAB @ DESY
Notkestr. 85, 22607 Hamburg
Germany
e-mail: stephan.roth@desy.de

Eloisa Sardella
Institute of Inorganic Methodologies and Plasma CNR
Via Orabona 4, 70126 Bari
Italy
e-mail: eloisa.sardella@cnr.it

Peter Müller-Buschbaum
TUM, Physikdepartment
James-Franck-str. 1, 85747 Garching bei Muenchen
Germany
e-mail: muellerb@ph.tum.de

Stanislav Novák
Department of Physics, Faculty of Science
J.E. Purkinje University
České mládeže 8, 400 96 Ústí nad Labem
Czech Republic
e-mail: novaks@sci.ujep.cz

Josef Paul
Department of Materials Engineering Faculty of
Mechanical Engineering
Czech Technical University in Prague
Karlovo náměstí 13, 121 35 Praha 2
Czech Republic
e-mail: Josef.Paul@fs.cvut.cz

Petr Plíhal
HVM Plasma spol. s r. o.
Na Hutmance 2, 158 00 Praha 5
Czech Republic
e-mail: petr.plihal@hvm.cz

T. P. Radhakrishnan
School of Chemistry
University of Hyderabad
Hyderabad – 500 046
India
e-mail: tprsc@uohyd.ernet.in

Sara Rebasti
University of Milano
Via Celoria 16, 20133 Milano
Italy
e-mail: sara.rebasti@gmail.com

Matthias Ruderer
Technische Universität München
James-Franck-Str. 1, 85747 Garching
Germany
e-mail: matthias.ruderer@ph.tum.de

Susanne Seyffarth
Institut für Materialphysik
University of Göttingen
Friedrich-Hund-Platz 1, 37077 Göttingen
Germany
e-mail: suse@ump.gwdg.de

List of Nanoworkshop 2009 participants

Andrey Shukurov
Department of Macromolecular Physics
Faculty of Mathematics and Physics
Charles University in Prague
V Holešovičkách 2, 180 00 Praha 8
Czech Republic
e-mail: Andrey.Shukurov@mff.cuni.cz

Pavel Solař
Department of Macromolecular Physics
Faculty of Mathematics and Physics
Charles University in Prague
V Holešovičkách 2, 180 00 Praha 8
Czech Republic
e-mail: pawell.solar@seznam.cz

Martin Švec
Department of Physics, Faculty of Science
J.E. Purkinje University
České mládeže 8, 400 96 Ústí nad Labem
Czech Republic
e-mail: martin.svec@ujep.cz

Wei Leng Tan
School of Chemical Sciences
Universiti Sains Malaysia
Minden, 11800 Pulau Pinang
Malaysia
e-mail: weileng80@hotmail.com

Jan Valtr
HVM Plasma spol. s r. o.
Na Hutmance 2, 158 00 Praha 5
Czech Republic
e-mail: jan.valtr@hvm.cz

Jiří Vyskočil
HVM Plasma spol. s r. o.
Na Hutmance 2, 158 00 Praha 5
Czech Republic
e-mail: jiri.vyskocil@hvm.cz

Darin Zimmerman
The Pennsylvania State University
Altoona College
3000 Ivyside Park, 16601-3760 Altoona
USA
e-mail: dtz1@psu.edu

Danka Slavínská
Department of Macromolecular Physics
Faculty of Mathematics and Physics
Charles University in Prague
V Holešovičkách 2, 180 00 Praha 8
Czech Republic
e-mail: slavinsk@mbox.troja.mff.cuni.cz

Petr Špatenka
Department of Physics Faculty of Pedagogy
University of South Bohemia
Jeronýmova 10, 37115 České Budějovice
Czech Republic
e-mail: spatap@pf.jcu.cz

Toshifumi Takeuchi
Graduate School of Engineering Kobe University
1-3 Rokkodai-cho, Nada-ku, 657-8501 Kobe
Japan
e-mail: takeuchi@gold.kobe-u.ac.jp

Milan Tichý
Department of Surface and Plasma Science
Faculty of Mathematics and Physics
Charles University in Prague
V Holešovičkách 2, 180 00 Praha 8
Czech Republic
e-mail: Milan.Tichy@mff.cuni.cz

Marta Vandrovcová
Institute of Physiology
Academy of Sciences of the Czech Republic
Václavská 1083, 142 20 Praha 4-Krč
Czech Republic
e-mail: vandrovcova@biomed.cas.cz

Vladimir Zaporozhchenko
Institute for Materials Science Faculty of Engineering
Christian-Albrechts University at Kiel
Kaiserstr. 2, 24143 Kiel
Germany
e-mail: vz@tf.uni-kiel.de

LYRA_{FEG}

The Formula 1 for Nanotechnology



- A favorable setup of a high resolution Schottky FE-SEM, FIB, GIS
- SEM / FIB / GIS integrated controlling and imaging software
- Pattern programming for milling, deposition and lithography
- Optimal geometry for EDX, EBSD, nanomanipulators etc.
- All excellent features of the TESCAN SEMs preserved

 **TESCAN**
PERFORMANCE IN NANOSPACE

TESCAN, s.r.o.

Libušina třída 21, 623 00 Brno, CZ, Phone: +420 547 130 411, e-mail: info@tescan.cz, www.tescan.com



Vakuum servis s.r.o.

Nabízíme komplexní řešení v oblasti vakuových systémů a servis vakuových zařízení.

Obchodní a servisní zastoupení firem:

Oficiální servisní centrum firmy:



Vakuum servis s.r.o. : Hasičská 2643, 756 61 Rožnov pod Radhoštěm
www.vakuum-servis.cz, office@vakuum-servis.cz

4th International Workshop on Polymer/Metal Nanocomposites, Book of Abstracts

Edited by

Pavel Kudrna, Danka Slavínská and Hynek Biederman

Published by

MATFYZPRESS

publishing house of the Faculty of Mathematics and Physics

Charles University in Prague

Sokolovská 83, CZ - 186 75 Praha 8

as the 204th publication

Printed by Reproduction center UK MFF

Sokolovská 83, CZ - 186 75 Praha 8

First edition

Prague 2009

ISBN 978-80-7378-010-4