Nanostructured Materials and Nanotechnology IV

A Collection of Papers Presented at the 34th International Conference on Advanced Ceramics and Composites
January 24–29, 2010
Daytona Beach, Florida

Edited by
Sanjay Mathur
Suprakas Sinha Ray

Volume Editors
Sanjay Mathur
Tatsuki Ohji

The American Ceramic Society

WILEY
A John Wiley & Sons, Inc., Publication
This page intentionally left blank
Nanostructured Materials and Nanotechnology IV
Contents

Preface vii

Introduction ix

Core-Shell Nanostructures: Scalable, One-Step Aerosol Synthesis and In-Situ SiO₂ Coating and Functionalization of TiO₂ and Fe₂O₃ Nanoparticles
J. T. N. Knijnenburg, A. Teleki, B. Buesser, and S. E. Pratsinis 1

Self-Assembly of Metal Oxides—Liquid Phase Crystal Deposition of Anatase TiO₂ Particles and Their Change in Surface Area
Yoshitake Masuda 13

Single Step Synthesis and Self-Assembly of Magnetite Nanoparticles
M. Hoffmann, R. von Hagen, H. Shen, and S. Mathur 21

Printable Silver Nanostructures: Fabrication and Plasma-Chemical Modification

Nanostructured Tin Dioxide and Tungsten Trioxide Gas Sensors Prepared by Glancing Angle Deposition
Derya Deniz, Aravind Reghu, and Robert J. Lad 37

Hydrothermal Synthesis of TiO₂ Nanotubes: Microwave Heating Versus Conventional Heating
Lucky M. Sikhwivhilu, Siyasanga Mpelmane, Nosipho Moloto, and Suprakas Sinha Ray 45
Fabrication and Properties of Core-Shell Type SiC/SiO₂ Nanowires through Low-Cost Production Technique
Wasana Khongwong, Katsumi Yoshida, and Toyohiko Yano

Fabrication and Characterization of Multifunctional ZnO-Polymer Nanocomposites
Hongbin Cheng, Qian Chen, and Qing-Ming Wang

Hybrid Nanostructured Organic/Inorganic Photovoltaic Cells
S. Antohe, I. Enculescu, Cristina Besteaga, Iulia Arghir, V. A. Antohe, V. Covlea, A. Radu, and L. Ion

Enhanced Photovoltaic Effect Using Nanostructured Multi-Layered Photoelectrode
M. Ramrakhiani and J.K. Dongre

Evaluation of Nanoparticles as Contrast Agent for Photoacoustic Imaging in Living Cells
Yvonne Kohl, Hagen Thielecke, Wolfgang Bost, Robert Lemor, Frank Stracke, Christian Kaiser, Michael Schroeter, Karl Kratz, Andreas Henkel, and Carsten Sönrichsen

The Use of CaCO₃ and Ca₃(PO₄)₂ as Supports for Fe-Co Catalysts for Carbon Nanotube Synthesis: A Comparative Study
Sabelo D. Mhlanga, Suprakas Sinha Ray, and Neil J. Coville

Nano-Microcomposite and Combined Coatings on Ti-Si-N/WC-Co-Cr/Steel and Ti-Si-N/(Cr₃C₂)₇₅-(NiCr)₂₅ Base: Their Structure and Properties

Phase Composition, Thermal Stability, Physical and Mechanical Properties of Superhard On Base Zr-Ti-Si-N Nanocomposite Coatings
A. D. Pogrebniak, O. V. Sobol, V. M. Beresnev, P. V. Turbin, G. V. Kirik, N. A. Makhmudov, M. V II'yashenko, A. P. Shypylenko, M. V. Kaverin, M.Yu. Tashmetov, and A. V. Pshyk

Characterization of Nanocrystalline Surface Layer in Low Carbon Steel Induced by Surface Rapid Multi-Rolling Treatment
Chang Sun, Kangning Sun, Jingde Zhang, Pengfei Chuan, Xiaoxin Wang, and Nan Wang

Properties of Nano-Metal Carbide Contained Mg-TiC (SiC) Composites
Mustafa Aydin and Rasit Koc

Author Index
The 4th International Symposium on Nanostructured Materials and Nanotechnology was held during the 34th International Conference and Exposition on Advanced Ceramics and Composites, in Daytona Beach, Florida during January 24–29, 2010. This symposium provided, for the fourth consecutive year, an international forum for scientists, engineers, and technologists to discuss new developments in the field of nanotechnology. This year’s symposium had a special focus on the large-scale production and potential of nanomaterials in energy applications. The symposium covered a broad perspective including synthesis, processing, modeling and structure-property correlations in Nanomaterials and nanocomposites. More than 90 contributions (invited talks, oral presentations, and posters) were presented by participants from universities, research institutions, and industry, which offered interdisciplinary discussions indicating strong scientific and technological interest in the field of nanostructured systems. The geographical spread of the symposium was impressive with participants coming from 16 nations.

This issue contains 17 peer-reviewed (invited and contributed) papers covering various aspects and the latest developments related to processing, modeling and manufacturing technologies of nanoscaled materials including inorganic-organic nanocomposites, nanowire-based sensors, new generation photovoltaic cells, self-assembly of nanostructures, functional nanostructures for cell tracking and heterostructures. Each manuscript was peer-reviewed using The American Ceramic Society review process.

The editors wish to extend their gratitude and appreciation to all the authors for their cooperation and contributions, to all the participants and session chairs for their time and efforts, and to all the reviewers for their valuable comments and suggestions. Financial support from the Engineering Ceramic Division of The American Ceramic Society is gratefully acknowledged. The invaluable assistance of the ACerS’s staff of the meetings and publication departments, instrumental in the success of the symposium, is gratefully acknowledged.

We believe that this issue will serve as a useful reference for the researchers and
technologists interested in science and technology of nanostructured materials and devices.

SANJAY MATHUR
University of Cologne
Cologne, Germany

SUPRAKAS SINHA RAY
National Centre for Nano Structured Materials
CSIR, Pretoria, South Africa
Introduction

This CESP issue represents papers that were submitted and approved for the proceedings of the 34th International Conference on Advanced Ceramics and Composites (ICACC), held January 24–29, 2010 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society’s (ACerS) Engineering Ceramics Division (ECD) since 1977.

The conference was organized into the following symposia and focused sessions:

Symposium 1  Mechanical Behavior and Performance of Ceramics and Composites
Symposium 2  Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3  7th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4  Armor Ceramics
Symposium 5  Next Generation Bioceramics
Symposium 6  International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution
Symposium 7  4th International Symposium on Nanostructured Materials and Nanocomposites: Development and Applications
Symposium 8  4th International Symposium on Advanced Processing and Manufacturing Technologies (APMT) for Structural and Multifunctional Materials and Systems
Symposium 9  Porous Ceramics: Novel Developments and Applications
Symposium 10 Thermal Management Materials and Technologies
Symposium 11 Advanced Sensor Technology, Developments and Applications
Focused Session 1  Geopolymers and other Inorganic Polymers
Focused Session 2  Global Mineral Resources for Strategic and Emerging Technologies
Focused Session 3  Computational Design, Modeling, Simulation and Characterization of Ceramics and Composites
Focused Session 4  Nanolaminated Ternary Carbides and Nitrides (MAX Phases)

The conference proceedings are published into 9 issues of the 2010 Ceramic Engineering and Science Proceedings (CESP); Volume 31, Issues 2–10, 2010 as outlined below:

- Mechanical Properties and Performance of Engineering Ceramics and Composites V, CESP Volume 31, Issue 2 (includes papers from Symposium 1)
- Advanced Ceramic Coatings and Interfaces V, Volume 31, Issue 3 (includes papers from Symposium 2)
- Advances in Solid Oxide Fuel Cells VI, CESP Volume 31, Issue 4 (includes papers from Symposium 3)
- Advances in Ceramic Armor VI, CESP Volume 31, Issue 5 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics III, CESP Volume 31, Issue 6 (includes papers from Symposia 5 and 9)
- Nanostructured Materials and Nanotechnology IV, CESP Volume 31, Issue 7 (includes papers from Symposium 7)
- Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials IV, CESP Volume 31, Issue 8 (includes papers from Symposium 8)
- Advanced Materials for Sustainable Developments, CESP Volume 31, Issue 9 (includes papers from Symposia 6, 10, and 11)
- Strategic Materials and Computational Design, CESP Volume 31, Issue 10 (includes papers from Focused Sessions 1, 3 and 4)

The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD members. We would especially like to express our sincere thanks to the symposia organizers, session chairs, presenters and conference attendees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.


Sanjay Mathur and Tatsuki Ohji, Volume Editors
July 2010
CORE - SHELL NANOSTRUCTURES: SCALABLE, ONE-STEP AEROSOL SYNTHESIS AND IN-SITU SiO$_2$ COATING AND FUNCTIONALIZATION OF TiO$_2$ AND Fe$_3$O$_3$ NANOPARTICLES

J.T.N. Knijnenburg, A. Teleki, B. Buesser, S.E. Pratsinis
Particle Technology Laboratory, Institute of Process Engineering
Department of Mechanical and Process Engineering
Swiss Federal Institute of Technology, ETH Zurich
Sonnergasse 3, CH-8092 Zurich, Switzerland

ABSTRACT
Scalable flame aerosol synthesis of surface-functionalized and coated nanoparticles in one-step is presented. These composite materials provide the functionality of nanoparticles and even "cure" any deleterious effects that might have. So they can be incorporated readily in a liquid or polymer matrix. Magnetic maghemite core nanoparticles are made by a spray flame and coated in-situ by judiciously positioning (as guided by computational fluid dynamics simulations) a hollow ring that delivers in swirling mode precursor coating vapor for the SiO$_2$ shell through 1 to 16 jets. This results in hermetically-coated superparamagnetic particles (15-20 nm) with a 1-3 nm thin silica film as determined by microscopy and thermal conductivity measurements. Furthermore, the extent of surface functionalization by organic coatings is evaluated by infrared spectroscopy and dynamic light scattering of particle suspensions in organic solvents.

INTRODUCTION
The need for coating or surface modification of nanostructured particles comes from the fact that typically the surface properties of as-prepared particles are different than the desired ones for the final applications. In such systems, the core particle possesses functionality while the shell enhances or facilitates the interaction with the host liquid or solid matrix. A classic example of functional core particles is the coating of TiO$_2$ pigment particles with SiO$_2$. Light scattering by the TiO$_2$ core gives the desired white color whereas the SiO$_2$ shell allows incorporating the particles in paints or polymers by blocking the reactivity of TiO$_2$ which would otherwise degrade the surrounding material. In other applications (e.g. V$_2$O$_5$-TiO$_2$ catalysts) the core provides the support (TiO$_2$) of the catalytically active V$_2$O$_5$ for deNO$_x$ selective catalytic reduction or for synthesis of phthalic anhydride.

Also magnetic nanoparticles can bind to drugs and proteins that can be guided in the human body using external magnetic fields. Although metal oxides have a lower magnetization than metallic nanoparticles, the latter are highly reactive and toxic and therefore less suitable for biomedical applications. Iron oxide nanoparticles have been widely investigated for in vivo applications (e.g. magnetic resonance imaging (MRI) contrast enhancement and drug delivery). Such magnetic iron oxide nanoparticles are frequently coated with silica to improve their functionality and biocompatibility. The silica coating makes the nanoparticles stable in aqueous conditions and limits magnetically induced self-agglomeration of magnetic cores. Furthermore, the silanol groups on the silica surface are able to react further with alcohols and silanes to make stable nonaqueous suspensions and can be further modified by covalent bonding of specific ligands. Moreover, silica-coated or embedded maghemite (γ-Fe$_3$O$_4$) nanoparticles exhibit improved thermal stability. Pure or uncoated γ-Fe$_3$O$_4$ is thermally unstable and is transformed to hematite (α-Fe$_2$O$_3$), the most stable form at high temperatures. Silica inhibits such transformations of γ-Fe$_2$O$_3$ in O$_2$ or in air. Various studies have been done on the incorporation of Fe$_3$O$_4$ nanoparticles in polymers to obtain superparamagnetic, transparent nanocomposites. Coating maghemite with silica facilitates homogeneous distribution of nanoparticles in a polymer matrix. Typically such coatings are made by a sol-gel process involving several steps, as Fe$_3$O$_4$ core formation and its SiO$_2$ coating are two separate unit operations.
Nanocomposites combine the advantages of the inorganic filler material (e.g. thermal stability, rigidity) and the organic host polymer (e.g. flexibility, processability), having enhanced electrical, optical or mechanical properties over the individual components. Surface functionalization of hydrophilic nanoparticles increases their hydrophobicity and can also include reactive groups (e.g. vinyl groups) that can cause further crosslinking between particles and host polymer. For example, silica dispersibility into an acrylic-based polyurethane is improved by surface functionalization of hydrophilic silica with long chain coupling agents like octyltriethoxysilane (OTES) while the non-functionalized silica showed inhomogeneous dispersion that reduces strength and transparency of the nanocomposite.

Wet phase functionalization of flame-made particles has been studied in some detail. For example, flame-made radiopaque and amorphous Ta2O5/SiO2 nanoparticles were functionalized and subsequently incorporated into a polyacrylate matrix. Functionalization of these powders facilitated dispersion into the polymer matrix.

Particle suspensions are generally sterically stabilized with an organic adlayer that acts as a steric barrier counteracting the attractive forces causing agglomeration. Long shelf-life suspensions have direct applications as electronic ink displays, where the image quality is affected by the uniformity and stability of particle dispersions inside an organic medium. Dilute suspensions are used for biomedical applications, while the more concentrated ones (30-40 vol%) find their application in further processing into organic films on devices (i.e. sensors or solar cells) by screen-printing or tape casting.

Typically surface functionalization processes have multiple steps (ex-situ synthesis) where the core material is formed first, followed by a second operation where coating is done (Figure 1: wet phase coating). In-situ processes are available as well in the wet phase, where the coating is done at
the same time as core particle is formed. There is, however, an increasing interest in rapid gas phase processes. Aerosol routes are attractive as they offer fewer process steps than conventional wet chemistry, easier particle collection from gaseous rather than liquid streams and no liquid by-products that require costly cleaning. In addition, aerosol-made particles and films have unique morphology and high purity (e.g. optical fibers) and sometimes even metastable phases (e.g. low temperature BaCO₃ for NOx storage-reduction or ε-WO₃ for ultrasensitive sensing of acetone, a tracer of diabetes) leading to synthesis of mixed oxides, metal salts and pure metals as well as layered particles and solid or highly porous films with unique functionality resulting in novel catalysts, micropatterned sensors, phosphors, battery, solar and fuel cell electrodes, dental prosthetics, nutritional supplements and even durable sorbents for CO₂ sequestration.

Many metal oxides (e.g. TiO₂, SiO₂) are made today on a large scale in flame aerosol reactors. However for the coating of these products often costly and extensive wet-phase processes are required. In fact, the cost of coating pigmentary TiO₂ particles is comparable to their coating and functionalization cost. As a result, there is a need for continuous gas phase coating or functionalization processes and in particular to simplify and improve such processes by combining both particle synthesis and coating in a one-step gas phase process (Figure 1: gas phase coating). Coherent and homogeneous coating on all particles is essential for optimal performance. A “coherent coating” in this context means that the core particle and the coating material stick (cohere) together. A “homogeneous coating” signifies that the coating has the same thickness around the core particle, i.e. the silica is distributed evenly over the core surface without any “patches”. Furthermore, optimization of coating thickness is desired, as silica decreases the UV absorbance of TiO₂ (e.g. in sunscreens) and increases production costs. Scalable production of pure and mixed oxides up to 1 kg/h can be achieved using flame spray aerosol processes even in academic laboratories. At industrial facilities this is in the order of 25 tons/h.

In-Situ Coating of Flame-Made Titania

An alternative process for the scalable manufacture of silica-coated nanoparticles in one step is flame spray pyrolysis (FSP). Various studies have been performed on coating of freshly-made TiO₂ with silica. Teleki et al. coated rutile TiO₂ particles by injection of hexamethyldisiloxane (HMDSO), a Si precursor, downstream of the TiO₂ formation zone in an enclosed FSP reactor. Figure 2a shows the experimental setup, where the FSP reactor is enclosed by a 5-30 cm long quartz glass tube (4.5 cm ID). There Al-doped (4 wt% Al₂O₃) rutile TiO₂ particles were produced by FSP of a 1 M solution of aluminum sec-butoxide and titanium-tetra-isopropoxide in xylene. The precursor solution was injected through the inner capillary with a flow rate of 5 mL/min, dispersed with 5 L/min O₂ (pressure drop 1.5 bar) and sheathed by another 40 L/min O₂. The solution spray was ignited by a ring shaped methane/oxygen (1.5/3.2 L/min) premixed flame. At the top of the lower glass tube, a stainless steel metal torus pipe (0.38 cm ID) ring (4.5 cm ID) with 1, 2, 4, 8 or 16 radial outlets (0.06 cm each in diameter) was placed. The outlets are directed 10° away from the ring radius and pointed 20° downstream to enable judicious swirl mixing of the coating precursor vapor with the titania-containing aerosol stream. Above the ring, another 30 cm long quartz glass tube (4.5 cm ID) was placed. Through the torus ring outlets, a gas flow of 0.8 L/min N₂ carrying HMDSO vapor (the Si coating precursor) was injected with an additional 15 L/min N₂. The product particles are collected on a glass fiber filter using a vacuum pump.

The effect of burner-ring-distance (BRD) on the coating quality was determined experimentally. Injection of HMDSO vapor at low BRD (where high temperature and TiO₂ formation still takes place) leads to fast oxidation of HMDSO, resulting in separate SiO₂ and TiO₂ particles or domains. In contrast, all particles were coated homogeneously with 2-3 nm thick SiO₂ films and no
separate domains or particles were obtained when HMDSO was injected at BRD ≥ 20 cm. The coating quality was verified by photooxidation of isopropyl alcohol (IPA).\textsuperscript{38} Titania is photocatalytically active converting IPA to acetone. So the released acetone concentration by photooxidation of IPA slurries containing SiO₂-coated TiO₂ made at various BRD was determined by gas conductivity measurements. This confirmed the formation of hermetic SiO₂ coatings onto the TiO₂ particles.\textsuperscript{35}

The influence of silica content on the coating morphology was studied at a BRD of 20 cm.\textsuperscript{34} For 5 wt% SiO₂ no coating film was visible by TEM due to the low theoretical coating thickness (< 1 nm for a 40 nm particle). The existence of such SiO₂ shells was confirmed\textsuperscript{34} as it had reduced the photooxidation of IPA to acetone to 50%. Increasing to 10 or 20 wt% SiO₂ yielded homogeneous hermetic coatings of 2-4 nm thick in agreement with the expected theoretical coating thickness. For these concentrations, no separate silica particles were observed by TEM while the quality of the coating was confirmed by photocatalytic evaluation of such particle slurries containing IPA.

![Figure 2: Experimental setup for (a) in-situ SiO₂ coating\textsuperscript{34,39} and (b) in-situ surface functionalization\textsuperscript{40} of flame-made TiO₂ or Fe₂O₃ particles.](image)

The mixing of aerosol with vapor during TiO₂ coating by SiO₂ was studied also by varying N₂ flow rate and the number of coating jets. Such coating was optimized by systematic design using computational fluid dynamics (CFD) where the mixing of the incoming HDMSO-containing N₂ flow...
with the product TiO₂ aerosol was visualized. The volume fraction of the carrier N₂ in the stream is an indication for the mixing efficiency of HMDSO as N₂ is the main component of the coating precursor stream. Figure 3 shows the N₂ volume fraction distribution along the tube axis above the ring for various N₂ volume flow rates. The flows at the jet outlets are red as they contain 100 vol% N₂. At a low overall jet flow rate of 5 L/min (Figure 3a) the N₂ flow remains largely near the tube wall while N₂-poor regions remain along the centerline of the tube. Increasing the flow rate to 10 L/min (Figure 3b) improves homogeneity along and across the tube, however still rather limited mixing of the HMDSO-laden vapor stream with the TiO₂ particle-containing aerosol takes place. For high flow rates (15 L/min), some N₂ lean regions (blue) are still present above the torus ring along the reactor walls by the high jet exit velocity, but there is already improved mixing at 3 cm above the injection point, shown by the rather homogeneous concentration of 15-30 vol% N₂ (green). With increasing height above the torus ring, however, the flow becomes more homogeneous throughout the tube, in stark contrast to the lower jet flow rates (Figure 3a,b).

The homogeneity of the SiO₂ coating on the rutile TiO₂ nanoparticles was verified experimentally at different HMDSO-laden N₂ injection flow rates: Figure 4 displays TEM images of rutile TiO₂ nanoparticles coated with 20 wt% SiO₂ at various N₂ flow rates. At 5 (Figure 4a) and 10 (Figure 4b) L/min, the coating is rather inhomogeneous and large domains of separate amorphous SiO₂ particles are clearly visible. For 20 (Figure 4c) and 30 (Figure 4d) L/min N₂, all titania particles appear to be coated without any separate SiO₂ particles. This is attributed to the improved mixing and the decreased silica precursor concentration which forms smaller silica particles that can deposit and sinter faster on the titania rather than collide with other SiO₂ coating particles and form larger ones. As a result, smooth coating films are formed.

Teleki et al. have visualized by CFD the effect of the number of jets issuing from the torus pipe. This plays a large role in the homogeneity of the flow. For increasing number of jet outlets, the N₂ concentration is more homogeneous and the mixing quality increases. For only 1 jet, the N₂ concentration was enriched at the walls opposite of the coating precursor inlet. With 2 or 4 inlets still