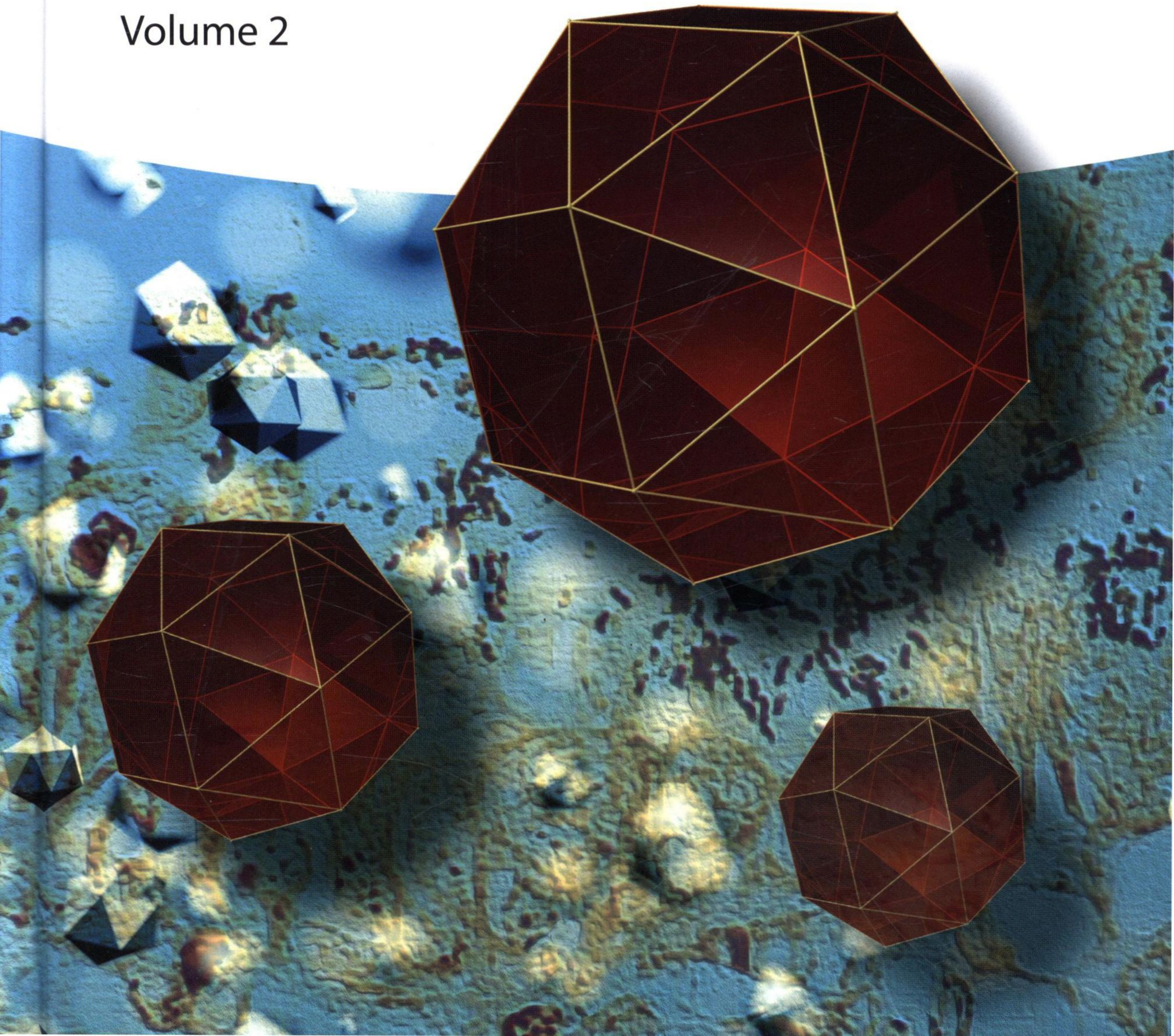
WILEY-VCH

Edited by
Marie-Helene Delville and Andreas Taubert

Hybrid Organic–Inorganic Interfaces

Towards Advanced Functional Materials

Volume 2



WILEY-VCH

Hybrid organic–inorganic materials and the rational design of their interfaces open up the access to a wide spectrum of functionalities not achievable with traditional concepts of materials science. This innovative class of materials has a major impact in many application domains such as optics, electronics, mechanics, energy storage and conversion, protective coatings, catalysis, sensing and nanomedicine. The properties of these materials do not only depend on the chemical structure, and the mutual interaction between their nano-scale building blocks, but are also strongly influenced by the interfaces they share.

This handbook focuses on the most recent investigations concerning the design, control, and dynamics of hybrid organic-inorganic interfaces, covering: (i) characterization methods of interfaces, (ii) innovative computational approaches and simulation of interaction processes, (iii) in-situ studies of dynamic aspects controlling the formation of these interfaces, and (iv) the role of the interface for process optimization, devices, and applications in such areas as optics, electronics, energy and medicine.

Marie-Helene Delville *is a Senior Researcher at French National Centre for Scientific Research CNRS since 1985 and in the Institute of Condensed Matter of Bordeaux since 1997. Her research interests are focused on the fundamental and practical aspects involved in the synthesis of organic-inorganic colloidal nano-objects as well as the role of interfaces. She has been from 2012 to 2016, the chair of a European COST action (Action No MP1202, section Materials, Physics, and Nanosciences) concerning the "Rational design of hybrid organic-inorganic interfaces: the next step towards advanced functional materials".*

Andreas Taubert *is Professor of Supramolecular Chemistry at the University of Potsdam, Germany. After his PhD at the Max-Planck-Institute for Polymer Research in Mainz he was a postdoc at the University of Pennsylvania, USA, and then a group leader at the University of Basel, Switzerland. His research interests are bioinspired hybrid materials and materials chemistry with ionic liquids. Since 2010 he has been one of the organizers of a series of symposia on hybrid materials at the E-MRS Spring Meetings.*

Volume 2 of 2

ISBN 978-3-527-34255-6

www.wiley-vch.de

Delville • Taubert (Eds.)

2

Hybrid Organic–Inorganic Interfaces

WILEY
-VCH

Hybrid Organic–Inorganic Interfaces

Towards Advanced Functional Materials

Edited by Marie-Helene Delville and Andreas Taubert

Volume 2

WILEY-VCH

Editors

Dr. Marie-Helene Delville
Universite de Bordeaux
Institut de Chimie de la Matiere
Condensee de Bordeaux (ICMCB)
CNRS UPR 9048
87 avenue du Dr. A. Schweitzer
33608 Pessac
France

Prof. Andreas Taubert
University of Potsdam
Institute of Chemistry
14476 Potsdam
Germany

Cover
fotolia/VAlex, fotolia/rafalkawa62

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-34255-6
ePDF ISBN: 978-3-527-80710-9
ePub ISBN: 978-3-527-80712-3
Mobi ISBN: 978-3-527-80711-6
oBook ISBN: 978-3-527-80713-0

Cover Design Schulz Grafik-Design, Fußgönheim, Germany
Typesetting SPi Global, Chennai, India
Printing and Binding C.O.S. Printers Pte Ltd Singapore

Printed on acid-free paper

Hybrid Organic–Inorganic Interfaces

Preface

The Interface: A Key Issue in Hybrid Materials

Marie-Helene Delville[1] *and Andreas Taubert*[2]

[1] *Universite de Bordeaux, Institut de Chimie de la Matiere Condensee de Bordeaux (ICMCB), CNRS UPR 9048, 87 avenue du Dr. A. Schweitzer, 33608 Pessac, France*
[2] *University of Potsdam, Institute of Chemistry, 14476 Potsdam, Germany*

Hybrid materials are currently among the most intensely researched topics in chemistry, physics, biology, and engineering. This stems from the fact that the proper combination of organic, polymeric, and inorganic functional components often leads to the formation of new materials with interesting and useful physical properties that are superior to those found in other materials. Two main challenges in this context, however, are (i) the proper selection of the components to obtain a specific function and (ii) the a priori (rational) design of a material with predetermined properties for a specific application.

One of the key parameters in these complex advanced materials is the interface. Modern hybrid materials often contain more than one interface, and the physical properties (and hence the performance of a material) strongly depend on how processes at these interfaces take place. For example, the behavior of charge carriers in an electrochemical device such as a solar cell or a battery will directly influence the performance of this device. Control over the structure, the properties, and the dynamics of these interfaces is therefore of utmost importance for proper device operation. Poorly defined interfaces will lead to rapid degradation of a device or even its complete destruction.

As a result, understanding the structure and physical properties of hybrid materials and the ability to rationally design these parameters is one of the key requirements for successful materials development. This particularly applies to interfaces; they are the decisive factor controlling whether a device will function properly and efficiently or not.

Interfaces, however, are very difficult to fabricate, to design in detail, and to characterize. Consequently, the rational design of interface-based materials with preprogrammed interface chemistry and physics is not easily accessible, and often, the design of interfaces for specific applications relies on trial-and-error approaches. In light of the ever-growing need for such materials with ever-improved properties, trial-and-error methods toward hybrid materials with defined interfaces are not ideal. Rather, there is a need for rational approaches based on established fundamental and quantitative principles of solid-state materials formation, interface engineering, and interface design. Moreover, there is a need to understand the correlation between the structure and composition of the interface in relation to the rest of the material to achieve a synthesis-by-design approach toward specifically tailored hybrid materials with specifically tailored interfaces for every application necessary.

As the correlation of structure and properties in hybrid materials and interfaces is a complex and challenging task, there have been multiple attempts of providing platforms for the exchange of information on this topic on a larger scale. For example, the European Union has set up a highly successful COST Action, COST MP1202 coordinated by one of the editors of this book, to enhance and accelerate the development of hybrid materials and interfaces for essentially every application possible – from energy and environment to healthcare and beyond. A series of symposia on advanced hybrid materials at the E-MRS Spring Meetings in operation since 2010, again co-organized by one of the editors of this book, has been another successful outlet for research on hybrid materials and interfaces. There is, however, still a need to better connect individual research findings and groups and to compile the necessary information available on how functional hybrid interfaces can be designed for perfect performance such that researchers from all fields have direct and easy access to all necessary information on the topic.

The current book for the first time assembles contributions from experts in all fields of hybrid materials and interface synthesis, design, characterization, computation, and application to provide a compact yet informative and thorough overview over the field and its future perspectives. A major focus is on interfaces in 2D and 3D hybrid materials, their structure, properties, adaptation to different requirements, their analysis, and their application. Applications cover the most important fields such as energy, catalysis, gas separation, or healthcare.

The second section focuses on special aspects of the material–biology interface, largely with the challenges of modern healthcare in an aging society in mind. These chapters again provide an in-depth overview over recent developments, the state of the art, and future perspectives.

Finally, the third section focuses on computation and analysis of hybrid interfaces. Although the importance of this subject has long been recognized, the details of interface analysis are still challenging and new and interesting developments are to be expected in the future. Again, this section provides a detailed overview over the state of the art, and the entire book will provide an invaluable source of information both for the experts in the field and the newcomer interested in developing his or her own powerful research profile in the general area of hybrid materials and interfaces.

The editors of this book would like to express their gratitude not only to the team at Wiley-VCH for making this book possible but also to the numerous authors for their excellent and diverse contributions. It has been a pleasure working with everyone, and the editors hope that this book will foster further collaborations and projects, old and new, in this fascinating research field at the interface of chemistry, physics, biology, engineering, and everyday life.

Marie-Helene Delville and Andreas Taubert

Contents to Volume 1

Preface *xv*

1 **Clay–Organic Interfaces for Design of Functional Hybrid Materials** *1*
Pilar Aranda, Margarita Darder, Bernd Wicklein, Giora Rytwo, and Eduardo Ruiz-Hitzky

2 **Hybrid Nanocomposites Based on Prussian Blue-Type Nanoparticles Included into Polysaccharides Matrices** *85*
Jérôme Long, Françoise Quignard, Yannick Guari, Eric Guibal, Thierry Vincent, Christian Guérin, Luís D. Carlos, and Joulia Larionova

3 **Self-Healing Thermosetting Composites: Concepts, Chemistry, and Future Advances** *121*
Jamal Seyyed Monfared Zanjani, Burcu Saner Okan, Yusuf Menceloglu, and Mehmet Yildiz

4 **Silica–Polymer Interface and Mechanical Reinforcement in Rubber Nanocomposites** *151*
Roberto Scotti, Massimiliano D'Arienzo, Barbara Di Credico, Luca Giannini, and Franca Morazzoni

5 **Sustainable Organic–Inorganic Interfaces in Energy Applications** *199*
Ryan Guterman, Jiayin Yuan, Liji Sobhana, Pedro Fardim, Susana García-Mayo, and German Salazar-Alvarez

6 **Hybrid Conjugated Polymer–Inorganic Objects: Elaboration of Novel Organic Electronic Materials** *241*
Antoine Bousquet, Roger C. Hiorns, Christine Dagron-Lartigau, and Laurent Billon

7 **Hybrid Organic–Inorganic Nanostructures for Spin Switching and Spintronic Applications** *301*
Sayani Majumdar, Gerard Śliwiński, and Yann Garcia

8 **Application of Sol–Gel Method to Synthesize Organic–Inorganic Hybrid Coatings to Minimize Corrosion in Metallic Substrates** *355*
Rita B. Figueira and Carlos J. R. Silva

9 **Gas-Organic and Gas-Inorganic Interfacial Effects in Gas/Adsorbent Interactions: The Case of CO_2/CH_4 Separation** *413*
Mirtha A. O. Lourenço, José R. B. Gomes, and Paula Ferreira

10 **Design and Characterization of MOFs (Metal–Organic Frameworks) for Innovative Applications** *459*
Jenny G. Vitillo, Cesare Atzori, Bartolomeo Civalleri, Nadia Barbero, Claudia Barolo, and Francesca Bonino

Contents to Volume 2

Preface *xv*

11 **Nanocarbon–Ionic Liquid Hybrid Materials for Heterogeneous Catalysis** *497*
Bao-Bing Huang and Zai-Lai Xie
11.1 Introduction *497*
11.2 Ionic Liquids *499*
11.3 Nanocarbon–Ionic Liquids Formation by Physical Confinement *501*
11.4 Nanocarbon–Ionic Liquids Formation by Covalent Anchoring *507*
11.5 Ionic Liquids as Precursor-Derived Carbon Materials *509*
11.6 Nanocarbon–Ionic Liquid Hybrid-Derived Carbon Materials *514*
11.7 Applications of Nanocarbon–Ionic Liquid Hybrids *515*
11.8 Conclusions *523*
Acknowledgment *524*
List of Abbreviations *524*
References *525*

12 **Tough Hydrogels: Toughening Mechanisms and Their Utilization in Stretchable Electronics and in Regenerative Medicines** *535*
Hyun-Joong Chung, Hemant Charaya, Li Liu, and Xinda Li
12.1 Introduction *535*
12.2 A Review of Fracture Toughness *536*
12.2.1 Fracture Energy *536*
12.2.2 Fracture Energy of Hyperelastic Materials *537*
12.2.2.1 Intrinsic Fracture Energy *538*
12.2.2.2 Fracture Energy Dissipation *539*
12.2.2.3 Experimental Measurement of Fracture Energy *540*
12.3 Designing Tough Hydrogels *540*

12.3.1 Fundamentals of Designing Tough Hydrogels *540*
12.3.2 Tough Hydrogels Based on Homogeneous Network *542*
12.3.2.1 Practicing Radiation Cross-Linking over Chemical Cross-Linking *542*
12.3.2.2 "Click" Hydrogels *543*
12.3.2.3 Tetra-PEG Hydrogels *543*
12.3.2.4 Slide/Slip-Ring Hydrogels *544*
12.3.3 Tough Hydrogels Based on Mechanical Energy Dissipation *544*
12.3.3.1 Double-Network Hydrogels *545*
12.3.3.2 Synthesis and Basic Features of DN Hydrogels *545*
12.3.3.3 Mechanical Behavior of DN Hydrogels *546*
12.3.3.4 Toughening Mechanism of DN Hydrogels *547*
12.3.3.5 Fiber/Filler-Reinforced Tough Hydrogels *548*
12.3.4 Multifunctional Cross-Linked Tough Hydrogels *548*
12.3.4.1 Nanocomposite Tough Hydrogels *548*
12.3.4.2 Microsphere-Reinforced Tough Hydrogels *550*
12.4 Sticky Hydrogels *552*
12.4.1 Polysaccharide-Based Hydrogel Adhesives *552*
12.4.2 Protein-Based Hydrogel Adhesives *554*
12.4.3 Synthetic Polymer-Based Hydrogel Adhesives *555*
12.5 Integrating Hard Materials and Devices in Tough Hydrogels *556*
12.5.1 Hydrogel Composite *556*
12.5.1.1 Clay–Hydrogel Nanocomposite *557*
12.5.1.2 Carbon Nanotube (CNT) Hydrogel *559*
12.5.1.3 Graphene (or Graphene Oxide) Hydrogel Nanocomposite *560*
12.5.1.4 Metallic Nanoparticles *560*
12.5.1.5 Semiconductor Nanoparticles *561*
12.5.2 Integrating Devices in Tough Hydrogels *561*
12.6 Application of Tough Hydrogels in Stretchable Electronics, Energy Devices, and Soft Machines *563*
12.6.1 Stretchable Electronics *563*
12.6.2 Energy Storage Devices *563*
12.6.3 Soft Machines *564*
12.7 Application of Tough Hydrogels in Biomedical Applications *565*
12.7.1 General Hydrogels in Tissue Engineering and Regenerative Medicine *566*
12.7.1.1 Hydrogels as Scaffold Materials *566*
12.7.1.2 Hydrogels as Barriers *566*
12.7.1.3 Hydrogels for Drug Delivery *567*
12.7.1.4 Hydrogels for Cell Encapsulation *567*
12.7.2 Tough Hydrogels in Tissue Engineering and Regenerative Medicine *568*
12.7.2.1 Tough Hydrogels as Artificial Cartilage Materials *568*
12.7.2.2 Tough Hydrogels as Cornea Repair Materials *568*
12.8 Conclusion *569*
List of Abbreviations *569*
References *571*

13 Ionic Liquids for the Synthesis and Design of Hybrid Biomaterials and Interfaces *581*
Rui F. P. Pereira, Kerstin Zehbe, Stefanie Krüger, Maria M. Silva, Ahmed Salama, Peter Hesemann, Veronica de Zea Bermudez, and Andreas Taubert
13.1 Introduction *581*
13.2 Dissolution of Biopolymers in ILs *585*
13.2.1 Carbohydrates *585*
13.2.1.1 Cellulose *585*
13.2.1.2 Chitin and Chitosan *590*
13.2.2 Proteins *592*
13.2.2.1 Silk *592*
13.2.2.2 Keratin *597*
13.2.2.3 Collagen *599*
13.3 Ionic Liquid-Assisted Synthesis of Functionalized Polysaccharides and Polysaccharide Composites *600*
13.3.1 Background *600*
13.3.2 IL-Assisted Chemical Modification of Polysaccharides *602*
13.3.3 IL-Assisted Synthesis of Polysaccharide-Based Nanocomposites and Blends *605*
13.3.3.1 Multiwalled Carbon Nanotubes and Graphene Nanosheets *605*
13.3.3.2 Mineral Nanofillers *606*
13.3.3.3 Ionic Liquid-Assisted *In Situ* Mineralization *608*
13.3.3.4 Cellulose/Polymer Blends *609*
13.4 Applications of ILs in the Biomaterials Field *611*
13.4.1 IL-Based Biosensors *611*
13.4.2 IL-Based Biomaterials for Photothermal Therapy *616*
13.4.3 IL-Based Biomaterials for the Pharmaceutical Industry *617*
13.4.4 IL-Based Biomaterials with Antimicrobial Activity *618*
13.4.5 IL-Based Biomaterials for Drug Delivery *619*
13.4.6 IL-Based Ink-Jet Biomaterials *619*
List of Abbreviations *619*
References *621*

14 Interface Engineering with Self-Assembled Monolayers in Biosensors *637*
Cihat Taşaltín, İlke Gürol, Hatice Duran, Yíldíz Uludağ, Umran Aydemir Sezer, Zuhal Taşdemir, and Fevzihan Başarír
14.1 Introduction *637*
14.2 Fabrication of Biosensors Based on Metallic Transducers *639*
14.2.1 SAM Formation on Metallic Transducers *639*
14.2.1.1 Assembly and Structure *639*
14.2.1.2 Characterization *640*
14.2.1.3 Deposition of SAM *640*
14.2.1.4 Immobilization of Biomolecules on SAM *640*
14.2.2 Applications in Biosensors *640*
14.2.2.1 Electrochemical Biosensors *640*
14.2.2.2 Mass-Sensitive Biosensors *643*

14.2.2.3 Optical Biosensor *644*
14.3 Preparation of Biosensors Based on Nonmetallic Transducers *648*
14.3.1 SAM Formation on Nonmetallic Transducer *648*
14.3.1.1 Assembly and Structure *649*
14.3.1.2 Characterization *649*
14.3.1.3 Deposition of SAM *649*
14.3.1.4 Immobilization of Biomolecules on SAM *649*
14.3.2 Applications of Nonmetallic Biosensors *650*
14.3.2.1 Resistive Biosensors *650*
14.3.2.2 Acoustic Biosensors *651*
14.4 Conclusion *653*
List of Abbreviations *653*
References *654*

15 Coordination Polymers for Medical Applications: Amorphous versus Crystalline Materials *661*
Fernando Novio and Daniel Ruiz-Molina
15.1 Introduction *661*
15.2 Synthesis of Coordination Polymer Nanomaterials *663*
15.2.1 Nanoscale Metal–Organic Frameworks (NMOFs) *663*
15.2.2 Nanoscale Coordination Polymers (NCPs) *665*
15.3 Loading of Active Species *667*
15.3.1 Loading of Active Species in NMOF *668*
15.3.2 Loading of Active Species in NCPs *669*
15.4 Adequacy of NMOFs/NCPs for Theranostic Applications *673*
15.4.1 NMOFs/NCPs Toxicity *674*
15.4.2 NMOFs/NCPs for Cancer Therapy *675*
15.4.2.1 Drug Delivery *675*
15.4.2.2 Photodynamic (PDT) and Photothermal (PTT) Therapy *677*
15.4.3 Biomedical Imaging *678*
15.4.3.1 Magnetic Resonance Imaging (MRI) *678*
15.4.4 Optical Imaging (OI) *679*
15.4.5 Other Bioimaging Modalities *680*
15.5 Conclusions and Perspectives *681*
List of Abbreviations *682*
References *683*

16 High Pressure Hydrothermal Procedure: A Tool for Surface Modification of Superparamagnetic Nanostructured Materials for Medical Applications *695*
Laura M. Popescu, Roxana M. Piticescu, Dietmar Appelhans, Michael Schöneich, Markus Meyer, Alexandrina Burlacu, Bogdan Preda, Gabriel Schinteie, Victor Kuncser, and Eugeniu Vasile
16.1 Introduction *695*
16.1.1 Hybrid Materials Based on Dendritic Polymers and Superparamagnetic Iron Oxides *695*

16.1.2 Hydrothermal Synthesis as a New Tool for Surface Modification of Superparamagnetic Nanostructured Materials with Dendritic Polymers *697*
16.2 Synthesis *697*
16.2.1 Preparation of Poly(ethylene imine) (PEI) and Poly(propylene imine) (PPI) Decorated with Maltose Groups *697*
16.2.2 High Pressure Synthesis of Nanocomposites *698*
16.2.2.1 Hydrothermal Synthesis at 100 Bar Using Ar Gas *698*
16.2.2.2 Hydrothermal Synthesis at 1000 Bar Isostatic Pressure *699*
16.2.3 Hybrid Material Characterization *699*
16.2.3.1 Chemical Analysis *700*
16.2.3.2 FT-IR Analysis *701*
16.2.3.3 Thermal Analysis (DSC–TG) *702*
16.2.3.4 Thermoanalytical Analysis, Mass Changes, Energetic Effects, and Evolved Gas Analysis *703*
16.2.3.5 Particle Size Measurements *710*
16.2.3.6 HRTEM Analysis *710*
16.2.4 Magnetic Properties *711*
16.3 Biocompatible Properties *720*
16.4 Conclusions *723*
Acknowledgments *723*
List of Abbreviations *724*
References *724*

17 Silica-Based Organic–Inorganic Hybrid Nanomaterials for Optical Bioimaging *729*
Ivana Miletto, Enrica Gianotti, Marie-Helene Delville, and Gloria Berlier
17.1 Introduction to Hybrid Nanomaterials for Bioimaging *729*
17.2 Fluorescent Silica Nanoparticles *731*
17.2.1 Non-covalent Entrapment of Fluorophores *732*
17.2.2 Covalent Immobilization of Alkoxysilane-Derivatized Fluorophores *733*
17.3 Mesoporous Silica-Based Nanoparticles *739*
17.3.1 Mesoporous Silica Nanoparticles *739*
17.3.2 Fluorescent Organosilicas *743*
17.4 Zeolites *748*
List of Abbreviations *751*
References *753*

18 Design of Biohybrid Structures for Enzyme–Electrode Interfaces *767*
Bruce Dunn and Esther Lan
18.1 Introduction and Background *767*
18.2 Sol–Gel Synthesis *772*
18.3 Sol–Gel Materials in Biofuel Cells *774*
18.4 Mediated Transfer in EFCs *777*

18.5 Direct Electron Transfer in EFCs *779*
18.6 Direct Electron Transfer in GOx–NanoAu–M13 Bacteriophage for EFCs *781*
18.7 Summary and Future Outlook *787*
Acknowledgments *787*
References *788*

19 *In Situ* and *Ex Situ* Electrochemical Measurements: Spectroelectrochemistry and Atomic Force Microscopy *793*
Angelja Kjara Surca, Mirjana Rodošek, Ahmed Kreta, Mohor Mihelčič, and Miran Gaberšček
19.1 Introduction *793*
19.2 Spectroelectrochemistry *795*
19.2.1 IR Reflection–Absorption Spectroelectrochemistry *796*
19.2.1.1 *In Situ* IR Internal and External Reflection *796*
19.2.1.2 Background of NGIA–IR–RA *797*
19.2.1.3 *Ex Situ* NGIA–IR–RA Spectroelectrochemistry of Sol–Gel Protective Coatings Against Corrosion *801*
19.2.1.4 Combined *Ex Situ* and *In Situ* NGIA–IR–RA and IR Absorbance Spectroelectrochemical Approach in the Study of Films with Intercalation Properties *803*
19.2.1.5 *In Situ* NGIA–IR–RA Approach in the Literature *810*
19.2.2 *In Situ* Raman Spectroelectrochemistry *811*
19.2.2.1 Background of Raman Spectroscopy *811*
19.2.2.2 *In Situ* Raman Spectroelectrochemistry of Mixed Sol–Gel/Epoxy Protective Coatings against Corrosion *812*
19.2.2.3 *In Situ* Raman Spectroelectrochemical Approach in the Literature *816*
19.3 *In Situ* Electrochemical AFM Technique *818*
19.3.1 Background of *In Situ* Electrochemical AFM Approach *818*
19.3.2 *In Situ* Electrochemical AFM Measurement of Sol–Gel Protective Coating against Corrosion *819*
19.4 Geometry Aspects of *In Situ* Cells *822*
19.5 Conclusions *826*
Acknowledgment *827*
List of Abbreviations *827*
References *828*

20 Nuclear Magnetic Resonance as a Tool for the Investigation of Interfaces and Textures in Nanostructured Hybrid Materials *839*
Bruno Alonso, Christian Bonhomme, Christel Gervais, Flavien Guenneau, Danielle Laurencin, and François Ribot
20.1 Introduction *839*
20.2 Study of the Functionalization of Nano-objects in Solution with DOSY NMR *840*

20.3 Solid-State NMR as a Tool of Analysis of Organic–Inorganic Interfaces *843*
20.3.1 Characterizations of the Interface of Grafted Nanoparticles *843*
20.3.1.1 Structural Information Accessible Using Solid-State NMR *843*
20.3.1.2 Novel NMR Methodologies for the Characterization of Nano-objects *844*
20.3.2 Characterizations of Nanostructured Hybrid Materials Involving Strongly Interconnected Organic and Inorganic Components *847*
20.3.2.1 Hybrid Materials Developed for Energy Applications *847*
20.3.2.2 Natural and Synthetic Hybrid Biomaterials *848*
20.3.2.3 Porous Coordination Networks: The Case Study of MOFs *849*
20.4 NMR Studies of the Texture and Porosity of Hybrid Materials *849*
20.4.1 Organic–Inorganic Interfaces between Organic Porogens and Porous Skeletons *849*
20.4.1.1 Zeolites *850*
20.4.1.2 Templated Mesoporous Materials *851*
20.4.2 ^{129}Xe NMR Studies of Porous Materials *852*
20.4.2.1 Functionalization of Mesoporous Silicas *853*
20.4.2.2 Mobility of Encapsulated Drug-Model Molecules *855*
20.5 Combined Experimental: Computational Approaches for the Study of Hybrid Interfaces *855*
20.6 Conclusion *859*
List of Abbreviations *859*
References *860*

21 Electrostatic Force Microscopy Techniques for Interphase Characterization *867*
Massimiliano Labardi, Daniele Prevosto, and Simone Capaccioli
21.1 Introduction *867*
21.2 Atomic Force Microscopy *868*
21.3 Electrostatic Force Microscopy *868*
21.4 Characterization of Hybrid Interface *869*
List of Abbreviations *877*
References *877*

22 The Use of EPR Spectroscopy for the Study of Hybrid Materials and Interphases *879*
Franca Morazzoni, Massimiliano D'Arienzo, Barbara Di Credico, Roberto Scotti, Michela Cangiotti, Alberto Fattori, and Maria Francesca Ottaviani
22.1 Introduction *879*
22.2 Fundamentals of EPR Spectroscopy *880*
22.2.1 The Origin of the Resonance Condition *880*
22.2.2 EPR Experiment and g Measurement *882*
22.2.3 Hyperfine Nuclear Interaction *882*
22.2.4 Measure of the Electron–Nucleus Interaction *883*