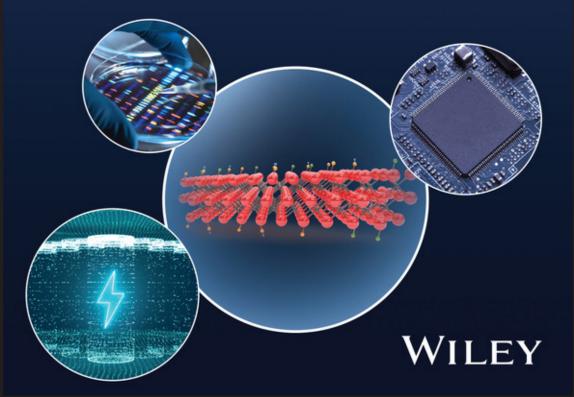
# Transition Metal Carbides and Nitrides (MXenes) Handbook

Synthesis, Processing, Properties and Applications

Edited by Chuanfang Zhang • Michael Naguib



Transition Metal Carbides and Nitrides (MXenes) Handbook

# **Transition Metal Carbides and Nitrides (MXenes) Handbook**

Synthesis, Processing, Properties and Applications

Edited by

Chuanfang Zhang Sichuan University Chengdu, China

Michael Naguib Tulane University New Orleans, LA, US

# WILEY

Copyright © 2024 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Trademarks: Wiley and the Wiley logo are trademarks or registered trademarks of John Wiley & Sons, Inc. and/or its affiliates in the United States and other countries and may not be used without written permission. All other trademarks are the property of their respective owners. John Wiley & Sons, Inc. is not associated with any product or vendor mentioned in this book.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

#### Library of Congress Cataloging-in-Publication Data

Names: Zhang, Chuanfang, author. | Naguib, Michael, author.
Title: Transition metal carbides and nitrides (MXenes) handbook : synthesis, processing, properties and applications / Chuanfang Zhang, Michael Naguib.
Description: Hoboken, New Jersey : Wiley, [2024] | Includes index.
Identifiers: LCCN 2024007590 (print) | LCCN 2024007591 (ebook) | ISBN 9781119869498 (hardback) | ISBN 9781119869504 (adobe pdf) | ISBN 9781119869511 (epub)
Subjects: LCSH: MXenes.
Classification: LCC QD172.T6 Z46 2024 (print) | LCC QD172.T6 (ebook) | DDC 546/.3-dc23/eng/20240324
LC record available at https://lccn.loc.gov/2024007591

Cover Design: Wiley

Cover Images: © Westend61/Getty Images, Wentao Zhang from Prof. Chuanfang Zhang group, College of Materials Science and Engineering, Sichuan University, Chengdu, China, © Black\_Kira/Shutterstock, © angelo gilardelli/Shutterstock.

Set in 9.5/12.5pt STIXTwoText by Straive, Pondicherry, India

### Contents

List of Contributors xvii Preface xxiv

#### Part I The Introduction 1

1 Introduction to the MXene Handbook 3 Michael Naguib and Chuanfang Zhang References 7

Part II Guidelines on MXenes Synthesis, Characterizations and Processing 11

#### 2 Synthesis of MXene Precursors – Tips and Tricks 13

Joseph Halim, Jie Zhou, Martin Dahlqvist, and Johanna Rosen

- 2.1 Structure and Composition of MXene Precursors 13
- 2.1.1 MAX Phases (Nitrides/Carbides/Alloys) and o-MAX Phases 15
- 2.1.2 *i*-MAX Phases 18
- 2.1.3 Mo<sub>2</sub>Ga<sub>2</sub>C and Zr/Hf-based Carbides 18
- 2.2 Synthesis of MXene Precursors Including Good "Tips" and Guidelines *18*
- 2.2.1 MAX Phases (Nitrides/Carbides/Alloys) and o-MAX Phases 18
- 2.2.1.1 Preparation for Synthesis 19
- 2.2.1.2 Synthesis, Techniques, and Conditions 21
- 2.2.1.3 Preparation of Powders for MXene Synthesis 25
- 2.2.2 *i*-MAX Phases 27
- 2.2.3 Mo<sub>2</sub>Ga<sub>2</sub>C and Zr/Hf-based Carbides 28 References 28

v

- vi Contents
  - 3 Guidelines on Fluorine-based Synthesis of MXenes 34

Annabelle Bedford, Brian C. Wyatt, Wyatt J. Highland, Srinivasa Kartik Nemani, Krista K. Pulley, Jonah Jordan, and Babak Anasori

- 3.1 Introduction 34
- 3.2 M–A vs. M–X Bonding Roles in Fluorine-based Synthesis 36
- 3.3 Interactions of Fluorine with A-group Elements within Precursor Phases *37*
- 3.4 Effect of Precursor Structure on Fluorine-based MXene Synthesis 43
- 3.5 Diversity of Fluorine-based Etchants in MXene Synthesis 46
- 3.6 Safety Considerations and Protocols 51
- 3.7 Conclusion 52 Acknowledgments 52 References 52

# 4 Guidelines Low-temperature (LT) F-free Synthesis of MXenes 58

Changda Wang, Shiqiang Wei, Pengjun Zhang, Kefu Zhu, and Li Song

- 4.1 Introduction 58
- 4.2 Electrochemical Etching Method 59
- 4.2.1 Producing Carbide-derived Carbons by Electrochemical Etching 59
- 4.2.2 Electrochemical Etching of MAX into 2D MXenes 61
- 4.3 Chloride Ion Hydrothermal Etching Method 67
- 4.4 Halogen Etching Method 70
- 4.5 Alkali Etching Method 73
- 4.5.1 Alkali Etching Under Low Concentration 73
- 4.5.2 Alkali Etching Under High Concentration 74
- 4.5.3 Organic Alkali Etching 77
- 4.6 Other F-free Etching Methods 78 References 81

#### 5 Guidelines for the Molten Salt Etching of MXenes 85

Miao Shen and Jian-Qiang Wang

- 5.1 Introduction 85
- 5.2 Reactive Molten Salt Synthesis of MXenes 86
- 5.2.1 One-Component Lewis Salt Molten Salt (LAMS) for Etching 86
- 5.2.2 Multicomponent Salts Containing Lewis Salts for Etching 87
- 5.2.3 Parameters Influencing Molten Salt Etching 92
- 5.3 Inert Molten Salt Synthesis of MXenes 95
- 5.4 Surface Terminations of MXenes Regulated by Molten Salt 97
- 5.5 Electrochemical Etching of MAX in Molten Salt 98
- 5.6 Interconversion of MXene and MAX in Molten Salt 100

- 5.6.1 From MAX to New MAX 101
- 5.6.2 From MAX to New Terminated MXene 101
- 5.6.3 From MXene to MAX 101
- 5.7 Limitations and Outlook *102* References *103*

#### **6 Guidelines on the Intercalation of Ions and Molecules in MXenes** *109 Varun Natu and Michel W. Barsoum*

- 6.1 Introduction 109
- 6.2 The 002 Peak and the Interlayer Spacing in MXenes 110
- 6.3 Ion Exchange Properties and Its Dependence on MXene Synthesis Conditions *112*
- 6.4 Why Do Cations Intercalate MXene Multilayers? 120
- 6.5 Anions and MXene 120
- 6.6 Types of Ion/Molecules that Intercalate Between MXene Layers 121
- 6.6.1 Inorganic Ions 121
- 6.6.2 Organic Molecules 121
- 6.7 Complexity of Ion Intercalation in MXenes 124
- 6.8 Cation Exchange Capacity 125
- 6.9 Hydration and Dehydration of MXene Multilayers 126
- 6.10 General Guidelines for Ion Intercalation in MXenes and Possible Pitfalls *128*
- 6.11 Summary *130* References *130*

#### **7** MXene Thermal and Chemical Stability and Degradation Mechanism *137 Shuohan Huang and Vadym N. Mochalin*

- 7.1 Introduction 137
- 7.2 Surface Chemistry and Chemical Modification of MXenes 138
- 7.3 MXene Chemical Stability and Degradation in Aqueous Solutions 141
- 7.3.1 MAX Phase Synthesis 141
- 7.3.2 Etchant 144
- 7.3.3 Storage Environment 145
- 7.3.4 Additives 148
- 7.3.5 Annealing 153
- 7.4 MXene Thermal Stability 153
- 7.4.1 Elimination of MXene Surface Functional Groups 153
- 7.4.2 Transformations of MXene Skeleton Structure 155
- 7.5 Conclusions and Outlook 157 References 158

viii Contents

8 Guidelines on MXene Handling and Storage Strategies 163

Jizhen Zhang, Dylan Hegh, Peter A. Lynch, and Joselito M. Razal

- 8.1 Introduction 163
- 8.2 The Degradation of MXene 164
- 8.2.1 Understanding the Degradation Process of MXenes 166
- 8.2.1.1 The Degradation of Wet MXene 166
- 8.2.1.2 Oxidation of Dry MXene 170
- 8.2.2 Characterizing the Oxidation of MXenes 173
- 8.2.2.1 Monitoring the Oxidation Process 173
- 8.2.2.2 Characterizing Extent of MXene Oxidation 175
- 8.2.3 Parameters Influencing Oxidation Rate 175
- 8.2.3.1 MAX Phase Quality and synthetic methods of Synthesis 175
- 8.2.3.2 Aqueous Environment 177
- 8.2.3.3 Air or Oxygen 177
- 8.2.3.4 Temperature 178
- 8.2.3.5 UV Light 178
- 8.3 Preventing the Oxidation of MXene 179
- 8.3.1 Defect Control During MXene Synthesis 179
- 8.3.2 Storing MXene in Solvents 180
- 8.3.2.1 Isolation of Water 180
- 8.3.2.2 Isolation of Oxygen or Air 181
- 8.3.2.3 Antioxidants 181
- 8.3.2.4 Low Temperature 182
- 8.3.2.5 Surface Modification 183
- 8.3.3 Coating Protection 184
- 8.4 Summary and Outlook 185 References 186

# 9 Beyond Single-M MXenes: Synthesis, Properties, and Applications 189

- Christopher E. Shuck and Yury Gogotsi
- 9.1 Introduction 189
- 9.1.1 Synthesis of MAX 190
- 9.2 Random (Disordered) Solid Solutions 193
- 9.2.1 Properties and Applications of Random Solid Solutions 194
- 9.2.2 High-Entropy MXenes 199
- 9.3 Ordered MXenes 199
- 9.3.1 Out-of-Plane Ordered o-MXenes 199
- 9.3.2 In-Plane Ordered *i*-MXenes 202
- 9.4 Outlook 203 Acknowledgments 205 References 205

Contents ix

10.1 Summary and Outlook 226 References 227

#### 11 MXene Surface Terminations 229

Per O.Å. Persson

- 11.1 Introduction 229
- 11.2 Termination Controlled Properties 230
- 11.3 Chemical Etching 230
- 11.4 Molten Salt Etching 232
- 11.5 Termination Site Preference 234
- 11.6 MXene Surface Termination Saturation 237
- 11.7 Thermal Stability of Terminations 238
- 11.8 Post Processing of Terminations 240
- 11.9 Summary 242 References 242
- **12** Delamination and Surface Functionalization of MXenes 245 Mohammad Jafarpour, Sina Abdolhosseinzadeh, Jakob Heier, Frank Nüesch, and Chuanfang Zhang
- 12.1 Introduction 245
- 12.2 Effect of Preparation Routes on the Surface Terminations of MXenes 246
- 12.2.1 HF Etching 246
- 12.2.2 Fluoride-Containing Solution Etching 249
- 12.2.3 Fluoride-Free Etching 251
- 12.3 Intercalation and Delamination of Single and Few-Layer MXenes 253
- 12.3.1 Metal Cation and Inorganic Intercalants 255
- 12.3.2 Organic-Base Molecules 256
- 12.3.3 Ultrasonication and Physical Delamination 258
- 12.3.4 Dispersibility and Stability of Delaminated MXene Flakes 262
- 12.4 Other Methods for Delamination and Surface Engineering 263
- 12.4.1 Hydrothermal-Assisted Intercalation (HAI) 263
- 12.4.2 Microwave-Assisted Delamination 264
- 12.4.3 Freeze-and-Thaw (FAT)-Assisted Method 265
- 12.4.4 Low-Temperature Plasma Techniques 266
- 12.5 Summary and Outlooks 267 References 267

x Contents

**13 Solution Processing of MXenes for Printing, Wet Coating, and 2D Film Formation** 272 *Sina Abdolhosseinzadeh, Mohammad Jafarpour, Jakob Heier,* 

Sina Abaotnosseinzaaen, Monammaa Jajarpour, Jakob F Frank Nüesch, and Chuanfang Zhang

- 13.1 Introduction 272
- 13.2 Preparing Stable MXene Dispersions 273
- 13.3 Tuning the Rheological Properties of MXene Dispersions 277
- 13.4 Ink Formulation and Printing of MXenes 279
- 13.5 2D Printing of MXenes 280
- 13.6 Wet Coating of MXenes 285
- 13.7 Summary and Outlook 289

References 289

#### 14 Three-Dimensional (3D) Printing of MXenes 294

Elnaz Jamshidi, Mackenzie B. Woods, Virginia A. Davis, and Majid Beidaqhi

- 14.1 Introduction 294
- 14.2 MXene Inks for DIW 295
- 14.2.1 Rheological Properties of DIW Inks 297
- 14.2.2 Additive-Free MXene Inks 300
- 14.2.3 Multicomponent MXene Inks 301
- 14.3 3D Printing of MXene-based Devices 305
- 14.4 Conclusion 311 Acknowledgments 311 References 312

#### 15 Assembling of MXenes from Liquid to Solid, Including Liquid Crystals, Fibers 315

Yu Long, Zhitan Wu, Ying Tao, and Quan-Hong Yang

- 15.1 Introduction 315
- 15.2 1D Macroscopic MXene Fibers 317
- 15.2.1 Neat MXene Fibers 318
- 15.2.2 MXene Composite Fibers 321
- 15.2.2.1 Coated MXene Composite Fibers 321
- 15.2.2.2 Spun MXene Composite Fibers 323
- 15.2.2.3 Biscrolled MXene Composite Fibers 325
- 15.3 2D Macroscopic MXene Films 325
- 15.3.1 Neat MXene Films 327
- 15.3.1.1 Lamellar Structure 328
- 15.3.1.2 In-Plane Nanochannel Structure 331
- 15.3.1.3 Porous Structure 331

Contents xi

- 15.3.2 MXene-based Composite Films 335
- 15.3.2.1 MXene-Inorganics Composite Films 335
- 15.3.2.2 MXene-Organics Composite Films 341
- 15.4 3D MXene Assemblies, Including Hydrogels and Aerogels 345
- 15.4.1 3D MXene Assemblies with Crumpled Structures 345
- 15.4.2 Template-assisted 3D MXene Assemblies 348
- 15.4.3 MXene-Inorganics Hydrogels and Aerogels 354
- 15.4.3.1 Cation-Crosslinked Hydrogels 354
- 15.4.3.2 GO-assisted MXene Hydrogels and Aerogels 356
- 15.4.3.3 Other MXene-Inorganics Hybrid Assemblies 361
- 15.4.4 MXene-Organics Composite Hydrogels and Aerogels 362
- 15.4.4.1 Organic Molecule Crosslinked MXene Hydrogels 362
- 15.4.4.2 MXene-Polymer Composite Hydrogels 364
- 15.5 Summary 369 Acknowledgments 370 References 371

#### Part III Guidelines on Obtaining MXenes Properties 385

16 Insights into the Properties of MXenes and MXene Analogs from Atomistic Simulation 387 Murali Gopal Muraleedharan, Rabi Khanal, Stephan Irle, and Paul R. C. Kent 16.1 Introduction 387 16.2 Computational Methods 388 Structures of MXenes and MXene Analogs 389 16.3 16.4 Predicted Structures and Thermodynamic Stabilities 391 16.4.1 Structure Prediction 391 16.4.2 Stability Prediction 394 16.5 Electronic Properties 397 16.6 Energy Storage Properties 401 16.6.1 Rechargeable Metal-Ion Batteries 401 16.6.2 Supercapacitors 405 16.6.3 Ion Mobility 409 16.7 Insights from Molecular Dynamics 412 16.7.1 Ab initio Molecular Dynamics and Approximate Quantum Chemical Simulations 413 16.7.2 Reactive and Classical Force Field Simulations 417 16.8 Summary and Future Opportunities 420 Acknowledgments 421 References 421

- xii Contents
  - 17 MXenes' Optical and Optoelectronic Properties and Related Applications 429

Danzhen Zhang, Kanit Hantanasirisakul, and Yury Gogotsi

- 17.1 Introduction 429
- 17.2 Plasmonic Properties 431
- 17.3 Plasmonic Applications 433
- 17.4 Ultrafast Carrier Dynamics 435
- 17.5 Nonlinear Optical Properties 438
- 17.6 Nonlinear Optical Applications 440
- 17.7 Optoelectronic Properties 442
- 17.8 Optoelectronic Applications 444
- 17.9 Conclusions and Outlook 447 Acknowledgments 448 References 448

#### 18 Mechanical Properties and Reinforcement Effect of Single MXene Flakes and MXene Composites 453

Qunfeng Cheng and Alexander Sinitskii

- 18.1 Introduction 453
- 18.2 Mechanical Measurements of Individual  $Ti_3C_2T_x$  Flakes 454
- 18.3 Mechanical Properties of MXene Composites 462
- 18.3.1 1D Fiber MXene Composites 464
- 18.3.2 2D Film MXene Composites 466
- 18.3.3 3D Bulk MXene Composites 469
- 18.4 Effective Strategy to Reduce Voids and Strengthening Interface Interactions 471
- 18.4.1 Sequential Bridging of Hydrogen and Ionic Bonding 471
- 18.4.2 Sequential Bridging of Hydrogen and Covalent Bonding 475
- 18.5 Outlook and Perspectives 477 Acknowledgments 478 References 478

#### Part IV MXene Applications 485

- **19 MXene Capacitive Behaviors and Supercapacitor Devices** 487 *Zifeng Lin, Liyuan Liu, and Patrice Simon*
- 19.1 Capacitive Behaviors of MXenes Electrodes in Aqueous Electrolytes 487
- 19.2 MXenes as Capacitive Electrodes in Non-Aqueous Electrolytes 492
- 19.3 Achieving High Electrochemical Properties by MXene Electrode Construction 497

Contents xiii

- 19.4 Tuning of MXene Surface Chemistry 500
- 19.5 MXene-based Supercapacitor Devices 502
- 19.5.1 MXene-based Asymmetric Supercapacitors 502
- 19.5.2 MXene-based Micro-Supercapacitors (MSCs) 504
- 19.6Conclusion508References510

#### 20 MXene Application in Lithium-Ion Batteries 514

Majid Farahmandjou, Xin Guo, Zefu Huang, Bijay Janardhanan, A. M. Ruhul, and Guoxiu Wang

- 20.1 Introduction 514
- 20.2 MXenes as Electrode Active Materials 516
- 20.2.1 MXenes with Various Formula 517
- 20.2.2 Functionalized MXenes 519
- 20.2.2.1 Modification of Functional Surface Groups 519
- 20.2.2.2 Defect Engineering 520
- 20.2.2.3 Intercalation-Interlayer Space Engineering 520
- 20.2.2.4 Three-Dimensional (3D) MXene Engineering 521
- 20.2.2.5 Doping/Heteroatom Doping 523
- 20.3 MXenes-based Composites 524
- 20.3.1 MXene Derivatives 524
- 20.3.1.1 Completely Oxidized MXenes 525
- 20.3.1.2 Partially Oxidized MXenes 526
- 20.3.1.3 Other MXene Derivatives 528
- 20.3.2 MXene/Metal Chalcogenides 529
- 20.3.3 MXene/Alloy-type Materials 530
- 20.3.4 Other Composites 533
- 20.4 Conclusions 535 Acknowledgment 536 References 537

#### 21 MXenes in Rechargeable Batteries Beyond Li-Ion Battery 541

- Zhuoqi Cen, Qing Huang, and Kun Liang
- 21.1 Introduction 541
- 21.2 Metal-Ion Batteries 542
- 21.2.1 Sodium-Ion Batteries 542
- 21.2.1.1 Multilayer MXenes 557
- 21.2.1.2 Single/Few-Layer MXenes 557
- 21.2.1.3 MXenes with an Expanded Interlayer Spacing 559
- 21.2.1.4 MXenes with Porous Structure 559
- 21.2.1.5 MXene-based Composites 560
- 21.2.2 Potassium-Ion Batteries 564

#### **xiv** Contents

- 21.2.3 Magnesium-Ion Batteries 568
- 21.2.4 Aluminum-Ion Batteries 571
- 21.3 Metal-Sulfur Batteries 572
- 21.3.1 Lithium-Sulfur Batteries 575
- 21.3.1.1 MXene on the Sulfur Cathode in LSBs 577
- 21.3.1.2 MXene as Separator in LSBs 581
- 21.3.1.3 MXene on Alkali-Metal (Li, Na, and K) Anodes 582
- 21.3.2 Sodium-Sulfur Batteries 584
- 21.3.3 Magnesium-Sulfur Batteries 584
- 21.4 Conclusions and Perspectives 587 References 590

#### 22 Electromagnetic Interference Shielding of MXene/Polymer Composites 602

Hao-Bin Zhang and Xinfeng Zhou

- 22.1 Introduction 602
- 22.2 MXene as EMI Shielding Materials 607
- 22.3 MXene/Polymer Composites as EMI Shielding Materials 609
- 22.3.1 The Modulation of MXene-Polymer Interfaces 609
- 22.3.1.1 Hydrogen Bonding Interactions 610
- 22.3.1.2 Covalent Bonding Interaction 611
- 22.3.1.3 Electrostatic Interactions 612
- 22.3.2 Preformed of 3D Conductive Architectures 616
- 22.4 Outlook 618 References 618
- 23 MXenes in Electronics and Communication Devices 621

Xiangming Xu and Husam N. Alshareef

- 23.1 Introduction 621
- 23.2 MXene in Oxide Electronics 622
- 23.3 MXene in 2D Electronics 625
- 23.4 MXene in Flexible and Wearable Electronics 629
- 23.5 MXene in Iontronics and Neuromorphic Devices 635
- 23.6 MXene in Wireless Communication Devices 640
- 23.7 Conclusion and Outlook 643 References 645
- 24 MXene in Sensing Devices 651

Seon Joon Kim

- 24.1 Increasing Demand of Sensors 651
- 24.2 Use of 2D Nanomaterials for Sensors 652
- 24.2.1 Merits of 2D Nanomaterials 652

Contents xv

- 24.3 MXenes for Sensors 653
- 24.3.1 Sensing Mechanism of MXenes 653
- 24.3.2 Factors of MXene Nanomaterials That Can Influence Sensing Properties 654
- 24.3.2.1 MXene Flake Morphology 654
- 24.3.2.2 Surface Functional Groups and Defects 655
- 24.3.2.3 Adsorbents and Intercalants 655
- 24.3.2.4 Oxidation 656
- 24.4 MXenes for Chemical Sensors 656
- 24.4.1 Important Factors in Chemical Sensors 656
- 24.4.2 Theoretical Estimations 658
- 24.4.2.1 DFT Calculations 658
- 24.4.2.2 Gaps Between Theory and Experiment 658
- 24.4.3 Guidelines and Considerations for Chemical Sensors 659
- 24.4.3.1 Guidelines and Considerations for MXene Synthesis in Chemical Sensors 659
- 24.4.3.2 Guidelines and Considerations for MXene Processing in Chemical Sensors 664
- 24.4.3.3 Guidelines for Sensor Fabrication and Testing Conditions 666
- 24.4.4 Considerations in the Interpretation of Sensing Data 667
- 24.4.5 Summary 667
- 24.5 MXenes for Mechanical (or Tactile) Sensors 668
- 24.5.1 Important Factors in Mechanical Sensors 668
- 24.5.2 Comparisons with Other 2D Materials 669
- 24.5.3 Guidelines and Considerations for Mechanical Sensors 670
- 24.5.3.1 Guidelines and Considerations for MXene Synthesis in Mechanical Sensors 670
- 24.5.3.2 Guidelines and Considerations for Sensor Fabrication 670
- 24.5.4 Summary 671
- 24.6 Conclusions and Outlook 675 References 675
- 25 MXenes for Environmental Treatments 678

Jie Wang, Zhenjun Wu, Xiuqiang Xie, and Nan Zhang

- 25.1 Introduction 678
- 25.2 MXenes for Adsorption Toward Water Purification 679
- 25.3 MXenes Membranes Toward Separation of Pollutants 682
- 25.4 MXenes for Water Desalination 683
- 25.5 MXenes for Photocatalytic Degradation 686
- 25.6 MXenes for Anti-biofouling Applications 691
- 25.7 MXenes for Contaminants Detection 692

- xvi Contents
  - 25.8 Sustainability of MXenes 694
  - 25.9 Conclusions and Outlook 697 References 698

#### 26 MXenes in Healthcare Technologies 706 Natalia Noriega, Tochukwu Ozulumba, Grace Cooksley, Emma J. Ward, and Susan Sandeman

- 26.1 Introduction 706
- 26.2 The Biocompatibility of MXenes 706
- 26.3 MXenes, Inflammation, Infection, and the Wound Healing Response 711
- 26.4 MXenes Sensors and Biosensors in Diagnostics 713
- 26.4.1 MXene-based Mechanical Sensors 715
- 26.4.2 MXene-based Electrical Sensors 715
- 26.4.3 MXene-based Electrochemical Sensors and Biosensors 716
- 26.4.4 MXene-based Optical Sensors and Biosensors 717
- 26.5 MXenes in Photothermal Therapy 719
- 26.6 MXenes in Theranostics 722
- 26.7 Perspective on Future Outlook 723 Acknowledgments 725 References 725

#### Part V Conclusions and Perspectives 735

#### 27 Summary and Outlook 737

Chuanfang Zhang and Michael Naguib References 740

Index 742

## List of Contributors

#### Sina Abdolhosseinzadeh

Department of Advanced Materials and Surfaces, Laboratory for Functional Polymers, Swiss Federal Laboratories for Materials Science and Technology (Empa), ETH Domain, Dübendorf, Switzerland

#### Husam N. Alshareef

Materials Science and Engineering, Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi Arabia

#### Babak Anasori

School of Materials Engineering, Purdue University, West Lafayette, IN, USA; Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development Institute (INDI), Indiana University-Purdue University, Indianapolis, IN, USA; School of Mechanical Engineering, Purdue University, West Lafayette, IN, USA

#### Michel W. Barsoum

Department of Materials Science and Engineering, Drexel University, Philadelphia, PA, USA

#### Annabelle Bedford

School of Materials Engineering, Purdue University, West Lafayette, IN, USA; Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development Institute (INDI), Indiana University-Purdue University, Indianapolis, IN, USA

#### Majid Beidaghi

Department of Mechanical and Materials Engineering, Auburn University, Auburn, AL, USA; Department of Aerospace and Mechanical Engineering University of Arizona, Tucson, AZ, USA

#### Zhuoqi Cen

Zhejiang Key Laboratory of Data-Driven High-Safety Energy Materials and Applications, Ningbo Key Laboratory of Special Energy Materials and Chemistry, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang, China; Qianwan Institute of CNITECH, Ningbo, Zhejiang, China

#### xviii List of Contributors

#### Qunfeng Cheng

School of Chemistry, Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, Beihang University, Beijing, China

#### Grace Cooksley

Centre for Regenerative Medicine and Devices (CRMD), Centre for Life long Health, School of Applied Sciences, University of Brighton, Brighton, East Sussex, UK

#### Martin Dahlqvist

Materials Design division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden

#### Virginia A. Davis

Department of Chemical Engineering, Auburn University, Auburn, AL, USA

#### Majid Farahmandjou

Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, New South Wales, Australia

#### Yury Gogotsi

Department of Materials Science and Engineering, A. J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA, USA

#### Xin Guo

Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, New South Wales, Australia

#### Joseph Halim

Materials Design division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden

#### Kanit Hantanasirisakul

Department of Materials Science and Engineering, A. J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA, USA

#### Dylan Hegh

Institute for Frontier Materials, Deakin University, Geelong, Victoria, Australia

#### Jakob Heier

Department of Advanced Materials and Surfaces, Laboratory for Functional Polymers, Swiss Federal Laboratories for Materials Science and Technology (Empa), ETH Domain, Dübendorf, Switzerland

#### Wyatt J. Highland

Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development Institute (INDI), Indiana University-Purdue University, Indianapolis, IN, USA

#### Qing Huang

Zhejiang Key Laboratory of Data-Driven High-Safety Energy Materials and Applications, Ningbo Key Laboratory of Special Energy Materials and Chemistry, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang, China; Qianwan Institute of CNITECH, Ningbo, Zhejiang, China

#### Shuohan Huang

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, China

#### Zefu Huang

Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, New South Wales, Australia

#### Stephan Irle

Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

#### Mohammad Jafarpour

Department of Advanced Materials and Surfaces, Laboratory for Functional Polymers, Swiss Federal Laboratories for Materials Science and Technology (Empa), ETH Domain, Dübendorf, Switzerland; Institute of Materials Science and Engineering, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland

#### Elnaz Jamshidi

Department of Mechanical and Materials Engineering, Auburn University, Auburn, AL, USA

#### Bijay Janardhanan

Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, New South Wales, Australia

#### Jonah Jordan

Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development Institute (INDI), Indiana University-Purdue University, Indianapolis, IN, USA

#### Paul R. C. Kent

Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

#### Rabi Khanal

Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

#### Seon Joon Kim

Materials Architecturing Research Center, Korea Institute of Science and Technology, Seoul, Republic of Korea

#### Kun Liang

Zhejiang Key Laboratory of Data-Driven High-Safety Energy Materials and Applications, Ningbo Key Laboratory of Special Energy Materials and Chemistry, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang, China; Qianwan Institute of CNITECH, Ningbo, Zhejiang, China

#### Zifeng Lin

College of Materials Science and Engineering, Sichuan University, Chengdu, China

#### Liyuan Liu

CIRIMAT UMR CNRS 5085, Université Toulouse III Paul Sabatier, Toulouse, France

#### xx List of Contributors

#### Yu Long

Nanoyang Group, State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin, China

#### Peter A. Lynch

Institute for Frontier Materials, Deakin University, Geelong, Victoria, Australia; Manufacturing BU, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Waurn Ponds, Geelong, Victoria, Australia

#### Vadym N. Mochalin

Department of Chemistry, Missouri University of Science & Technology, Rolla, MO, USA; Department of Materials Science & Engineering, Missouri University of Science & Technology, Rolla, MO, USA

#### Murali Gopal Muraleedharan

Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

#### Michael Naguib

Department of Physics and Engineering Physics, Tulane University, New Orleans, LA, USA

#### Varun Natu

Physical and Materials Chemistry Division, National Chemical Laboratory, Pune, Maharashtra, India

#### Srinivasa Kartik Nemani

Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development Institute (INDI), Indiana University-Purdue University, Indianapolis, IN, USA

#### Natalia Noriega

Centre for Regenerative Medicine and Devices (CRMD), Centre for Life long Health, School of Applied Sciences, University of Brighton, Brighton, East Sussex, UK

#### Frank Nüesch

Department of Advanced Materials and Surfaces, Laboratory for Functional Polymers, Swiss Federal Laboratories for Materials Science and Technology (Empa), ETH Domain, Dübendorf, Switzerland; Institute of Materials Science and Engineering, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland

#### Tochukwu Ozulumba

Centre for Regenerative Medicine and Devices (CRMD), Centre for Life long Health, School of Applied Sciences, University of Brighton, Brighton, East Sussex, UK; Department of Chemistry, University of Virginia, Charlottesville, VA, USA

#### Per O.Å. Persson

Thin Film Physics Division, Department of Physics, Chemistry and Biology, Linköping University, Linköping, Sweden

#### Kaitlyn Prenger

Department of Physics and Engineering Physics, Tulane University, New Orleans, LA, USA

#### Krista K. Pulley

Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development Institute (INDI), Indiana University-Purdue University, Indianapolis, IN, USA

#### Joselito M. Razal

Institute for Frontier Materials, Deakin University, Geelong, Victoria, Australia

#### Johanna Rosen

Materials Design division, Department of Physics, Chemistry, and Biology (IFM), Linköping University Linköping, Sweden

#### A. M. Ruhul

Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, New South Wales, Australia

#### Susan Sandeman

Centre for Regenerative Medicine and Devices (CRMD), Centre for Life long Health, School of Applied Sciences, University of Brighton, Brighton, East Sussex, UK

#### Miao Shen

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, China; University of Chinese Academy of Sciences, Beijing, China

#### Christopher E. Shuck

Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ, USA

#### Patrice Simon

CIRIMAT UMR CNRS 5085, Université Toulouse III Paul Sabatier, Toulouse, France

#### Alexander Sinitskii

Department of Chemistry and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, NE, USA

#### Li Song

National Synchrotron Radiation Laboratory, CAS Center for Excellence in Nanoscience, Key Laboratory of Precision and Intelligent Chemistry, School of Nuclear Science and Technology, University of Science and Technology of China, Hefei, China

#### Anika Tabassum

Department of Physics and Engineering Physics, Tulane University, New Orleans, LA, USA

#### Ying Tao

Nanoyang Group, State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin, China

#### xxii List of Contributors

#### Changda Wang

National Synchrotron Radiation Laboratory, CAS Center for Excellence in Nanoscience, Key Laboratory of Precision and Intelligent Chemistry, School of Nuclear Science and Technology, University of Science and Technology of China, Hefei, China

#### Guoxiu Wang

Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, New South Wales, Australia

#### Jian-Qiang Wang

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, China; University of Chinese Academy of Sciences, Beijing, China

#### Jie Wang

College of Materials Science and Engineering, Hunan University Changsha, PR China

#### Emma J. Ward

Centre for Regenerative Medicine and Devices (CRMD), Centre for Life long Health, School of Applied Sciences, University of Brighton, Brighton, East Sussex, UK

#### Shiqiang Wei

National Synchrotron Radiation Laboratory, CAS Center for Excellence in Nanoscience, Key Laboratory of Precision and Intelligent Chemistry, School of Nuclear Science and Technology, University of Science and Technology of China, Hefei, China

#### Mackenzie B. Woods

Department of Chemical Engineering, Auburn University, Auburn, AL, USA

#### Zhenjun Wu

College of Chemistry and Chemical Engineering, Hunan University Changsha, PR China

#### Zhitan Wu

Nanoyang Group, State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin, China

#### Brian C. Wyatt

Department of Mechanical and Energy Engineering, and Integrated Nanosystems Development Institute (INDI), Indiana University-Purdue University, Indianapolis, IN, USA

#### Xiuqiang Xie

College of Materials Science and Engineering, Hunan University Changsha, PR China

#### Xiangming Xu

Materials Science and Engineering, Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi Arabia

#### Quan-Hong Yang

Nanoyang Group, State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin, China

#### Chuanfang Zhang

College of Materials Science and Engineering, Sichuan University, Chengdu, Sichuan, China

#### Danzhen Zhang

Department of Materials Science and Engineering, A. J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA, USA

#### Hao-Bin Zhang

State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, China

#### Jizhen Zhang

Institute for Frontier Materials, Deakin University, Geelong, Victoria, Australia; Manufacturing BU, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Waurn Ponds, Geelong, Victoria, Australia

#### Nan Zhang

College of Materials Science and Engineering, Hunan University Changsha, PR China

#### Pengjun Zhang

National Synchrotron Radiation Laboratory, CAS Center for Excellence in Nanoscience, Key Laboratory of Precision and Intelligent Chemistry, School of Nuclear Science and Technology, University of Science and Technology of China, Hefei, China

#### Jie Zhou

Materials Design division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden

#### Xinfeng Zhou

State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, China

#### Kefu Zhu

National Synchrotron Radiation Laboratory, CAS Center for Excellence in Nanoscience, Key Laboratory of Precision and Intelligent Chemistry, School of Nuclear Science and Technology, University of Science and Technology of China, Hefei, China

#### Preface

In 2011 came the first report telling a story of the discovery of MXenes, a twodimensional (2D) transition metal carbide,  $Ti_3C_2T_x$ , obtained from selective removal of aluminum layers from a 3D-layered  $Ti_3AlC_2$  MAX phase. This discovery was within a year followed by the realization of more MXenes, including  $Ti_2CT_x$ ,  $Ta_4C_3T_x$ , and  $Ti_3CNT_x$ , and since then, the family of 2D carbides and nitrides has been growing at an unprecedented rate. There are currently more than 50 MXenes reported, including those with out-of-plane and in-plane ordering, solid solutions on both the M and X sites, and high-entropy compositions. Considering the possibility of having both single (Cl, Br, S, etc.) and multiple (O, OH, F, etc.) terminations on these laminates, this family is by far the largest and most diverse family of 2D materials.

Since 2011, more than 20000 papers have been published by groups from more than 100 countries all over the world (six continents), and the number of publications appearing every year continues to increase. By the most conservative count (Web of Science), more than 70 000 researchers have co-authored MXene papers, following the initial discovery and exploring the enormously rich chemistry and large variety of MXene structures. The fast growth observed in the past five to six years is caused not only by an almost infinite number of new materials that can be synthesized but first and foremost by the unique properties of MXenes. Those include the very high electrical conductivity of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, a wide range of optical properties depending on the composition with absorption peaks from UV to IR wavelength ranges, etc. Biocompatibility and easy processability from aqueous colloids add another advantage. Over the past decade, a major progress has been achieved in increasing the environmental stability of MXenes, with  $M_3C_2$  and  $M_4C_3$  MXenes staying for a year or longer in aqueous solution without degradation, MXene supercapacitor electrodes lasting for 500000 cycles in acidic electrolytes, and micron-thin films maintaining their conductivity after several years of storage in the ambient environment.

We stand at the crossroads of discovery and applications. While new MXenes are reported regularly and their fundamental properties are being explored, they are also tested for a vast array of potential applications. More than 4200 patent applications were known to be published at the end of 2022, according to Patsnap. Taking into account the 18-month gap between patent filing and publishing by patent offices, this number is much higher today. The initially explored area of application was energy storage, and the largest

number of patents filed address energy, electrochemistry, and separation membranes. However, applications in optics and optoelectronics, as well as biomedical applications, are the fastest areas of growth nowadays. The area closest to commercialization may be electromagnetic interference shielding, where MXenes not only outperform all other materials in performance but also allow controlled reflection or absorption, depending on the choice of MXene and the film architecture, as well as modulation of shielding effectiveness. However, with many other applications being explored, it is difficult to predict where the first large commercial breakthrough will occur. What matters is that, due to their extreme properties, MXenes have already outperformed all known materials in a multitude of applications, from electromagnetic shielding to epidermal electronics and thermal management. By adding their simple processing from colloidal solution in water with no surfactant or additives needed, the chances are high for fast commercialization.

With properties outperforming many of those for currently applied materials, it is crucial to put extra emphasis on how the MXenes, and their precursors, are synthesized. This handbook contains 27 chapters covering synthesis and processing (14 chapters), properties (3 chapters), and applications (8 chapters). A clear emphasis is placed on the synthesis, chemistry, and processing of MXenes. In light of current challenges and demand for cost-efficient, scalable, and not the least sustainable synthesis procedures, the topic of this book *Transition Metal Carbides and Nitrides (MXenes) Handbook: Guidelines for the Synthesis, Processing, Properties, and Applications*, is timely. A comprehensive book that summarizes the current state-of-the-art of MAX and MXene synthesis, also providing details that may sometimes be overlooked in scientific publications, can provide a platform from which we develop MXene synthesis and processing further.

The potential of MXenes will be fully utilized once we have sustainable synthesis methods. While sustainability and materials are often discussed in terms of achieving desired material properties for specific energy and environmental applications, the technology to process the materials is sometimes overlooked. Sustainable MXene synthesis requires minimizing the environmental impact and consumption of resources. It entails principles such as reducing the use of hazardous chemicals (e.g. hydrofluoric acid), optimizing energy efficiency, and recycling raw materials and waste products (salt solutions). Moreover, this approach should also be used to manufacture MAX phases or other MXene precursors. By embracing this way of thinking and with more efforts invested in research on the processing of MXenes, they can play a key role in addressing pressing global challenges, from purification of water, air, and soil to clean energy and beyond.

Johanna Rosen

Johanna Rosen Linköping University, Sweden

Junglepogoti

Yury Gogotsi Drexel University, USA (signed using  $Ti_3C_2T_x$  MXene ink)

Part I

The Introduction