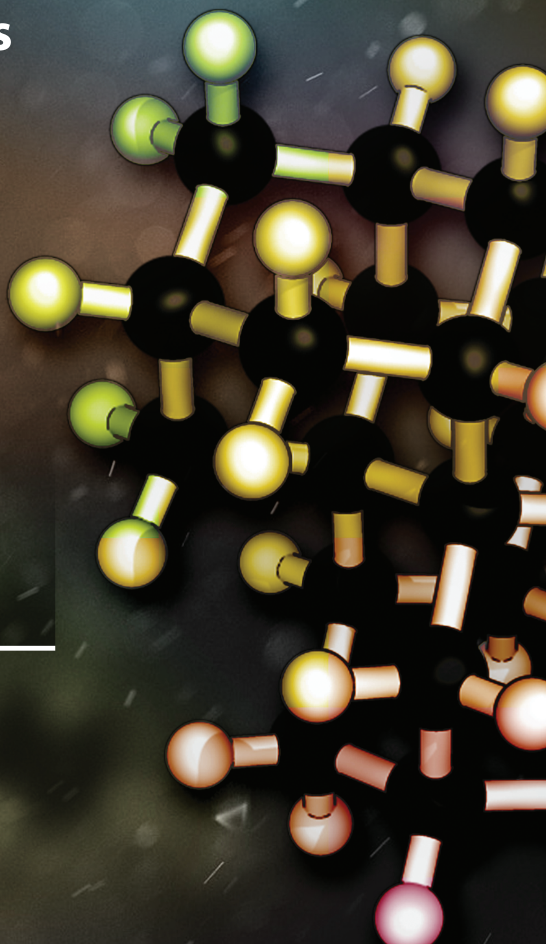
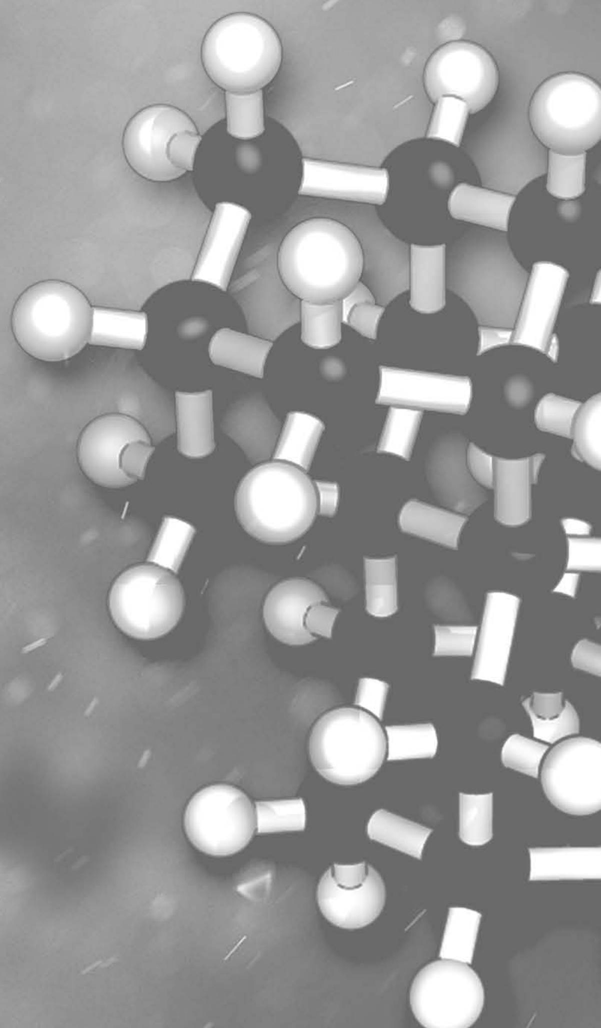
Diamondoids

Synthesis, Properties, and Applications



Sven Stauss
Kazuo Terashima

Diamondoids



Diamondoids

Synthesis, Properties, and Applications

Sven Stauss
Kazuo Terashima

Pan Stanford Publishing

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com
Web: www.panstanford.com

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

Diamondoids: Synthesis, Properties, and Applications

ISBN 978-981-4745-18-5 (Hardcover)
ISBN 978-981-4745-19-2 (eBook)

Printed in the USA

Contents

Part III Novel Approaches for the Synthesis of Diamondoids by Microplasmas

Symbols and Abbreviations

List of Symbols

C_p	Heat capacity	
E	Energy	
E_b	Binding energy	(eV)
E_{VBM}	Valence band maximum	
F_D	Density fluctuation	
M_r	Relative molecular weight	
p	Pressure	(Pa)
p_{crit}	Critical pressure	(Pa)
T	Temperature	(K)
T_{crit}	Critical temperature	(K)
V	Volume	(m^3)
V_{appl}	Applied voltage	(kV)
V_{p-p}	Peak-to-peak voltage	(kV)
β	Compressibility	
κ	Heat conductivity	

List of Abbreviations

CP	Critical point
B3LYP	Becke, three-parameter Lee–Yang–Parr exchange correlation functional used for DFT
DFT	Density functional theory
DOS	Density of electronic states
GC-MS	Gas chromatography–mass spectrometry

HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
SIM	Selected ion monitoring
SXE	Soft X-ray emission

Preface

Like a modern drama, one could consider this book to consist of three main acts: In the first act, we set the stage for the topic and expose the main actors, that is, diamondoids, and their relation to other carbon nanomaterials. In the same part, we delve more deeply into the chemical and physical properties of diamondoids and give an overview of their current and possible future applications.

In the second part of the book, we, little by little, approach the main complications related to the application of especially larger diamondoids: the current approaches for obtaining diamondoids and the current attempts to obtain them by conventional chemical synthesis. In particular, we aim at demonstrating the different problems associated with the various conventional approaches.

Finally, in the third part, we present possible alternative solutions for synthesizing diamondoids from the smallest member, adamantane, using plasmas generated in supercritical fluids. Because the field of plasmas generated in such high-density fluids is still not known to a wide audience, we are first briefly presenting the properties and applications of supercritical fluids before discussing the properties of electric discharge and pulsed laser plasmas generated in supercritical fluids.

The last part of the book deals with the application of such plasmas for diamondoids in more detail before giving a final assessment of the current state of the research on diamondoids.

Molecular diamonds, commonly called diamondoids, are a very interesting class of carbon nanomaterials that can be considered the archetypical molecular building block. While still not as widely known as other carbon nanomaterials, such as carbon nanotubes and graphene, previous and current research shows that this class of materials holds a lot of promise for many different fields of science and nanotechnology.

One of the goals in preparing this book was to introduce interested readers to the field of diamondoids; their structure, chemical, and physical properties; and the different isolation and synthesis approaches that currently exist. In addition to conventional isolation and synthesis approaches, we also introduce new ones, especially those based on electric discharge and pulsed laser plasmas generated inside supercritical fluids and at atmospheric pressure.

We hope that the present book will be useful not only as both an introductory and a reference text on diamondoids but also as an inspiration for further research on this remarkable class of nanomaterials.

This book is mainly aimed at researchers and graduate students who are curious about the field of diamondoids, that is, materials science, physics, and chemistry, but we hope that it will also be interesting for persons from other fields of science and technology.

One of our goals in writing this book was to make it an introductory text on diamondoids aimed at researchers and graduate students active in the field and at the same time to make it also a stand-alone text so that people who are not familiar with certain topics do not have to refer to the scientific literature themselves.

Special care was given to the figures and graphs. Whenever possible, we remade both graphs and figures in this book in order to avoid raster images as much as possible. In the cases where we have relied on data from other publications, we have indicated all the original data sources and references. We also tried to make the figure and table captions as self-explanatory as possible so that people who just want to flip through the book can understand the main points of an illustration or graph without having to resort to the main text.

For those readers who wish to delve more deeply into the field of diamondoids, we have compiled a comprehensive list of the current scientific literature. Especially the field of organic synthesis of diamondoids is very vast. However, for the convenience of the readers, we have limited ourselves to those references that can currently be accessed electronically.

In writing this book, we have tried to remain as general and make the contents as enduring as possible, but at the same time we also wanted to provide the reader with the latest results of the research on diamondoids. However, we are fully aware that with todays rapid pace with which science and technology advance, the contents of this book might become outdated quite rapidly. Nevertheless, we hope that this will not happen too soon and that it can serve researchers from many different backgrounds as a reference and hopefully also as an inspiration for their own research.

A very special thank-you goes to Stanford Chong for suggesting this book project and his patience and encouragement during the writing process. We are also indebted to all the staff at Pan Stanford Publishing for their efforts in bringing this book to print.

We would like to thank the following persons for their support in the work related to this book:

- Prof. Takehiko Sasaki for his help with mass spectrometry measurements and comments concerning the interpretation of the results
- Prof. Hiroshi Kataoka and Dr. Minoru Suzuki (now at Shimadzu Corp.) for their support with gas chromatography–mass spectrometry measurements and helpful discussions
- Prof. Tohru Suemoto and Prof. Motoyoshi Baba (now at Saitama University) for their help with pulsed laser ablation
- Dr. Keiichiro Urabe (now at Air Liquide) for commenting on one of the very early drafts of the manuscript
- All present and former students of the Terashima Lab for the work presented in this text

Concerning the experiments on diamondoid synthesis, we would like to thank Dr. Takaaki Tomai (now at Tohoku University), Dr. Hiroyuki Miyazoe (now at IBM Thomas J. Watson Research Center), Hirokazu Kikuchi, Sho Nakahara, Tomoki Shizuno, Fumita Oshima, Chikako Ishii, Satoshi Kato, and Koichi Kuribara. We would also like to thank Dr. David Z. Pai (Université de Poitiers) for his contribution to atmospheric-pressure diamondoid synthesis.

Since the topic of diamondoids encompasses various branches of science and readers are most probably from many different fields of science, we have tried to keep the text as self-explanatory as possible. Especially organic chemists might find our treatment of organic synthesis too basic; however, as some of the readers (and the authors) do not have a background in organic chemistry, we hope that they can bear with us.

As any book, probably this one also contains many errors and oversights, and any mistakes in the text are entirely the responsibility of the authors. We are grateful for any feedback from the readers, and we are grateful for any feedback from the readers to point us to these.

Finally, we hope that the book can serve both as a reference text and an inspiration, both for seasoned researchers and new students, and that the field of diamondoids can grow more in the future.

This work was supported financially in part by a Grant-in-Aid for Scientific Research on Innovative Areas (Frontier Science of Interactions between Plasmas and Nano-interfaces, Grant No. 21110002) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. The authors thank the Materials Design and Characterization Laboratory, Institute for Solid State Physics, University of Tokyo, for providing access to the pulsed laser facility.

Sven Stauss
Kazuo Terashima
Kashiwa and Tokyo, Japan