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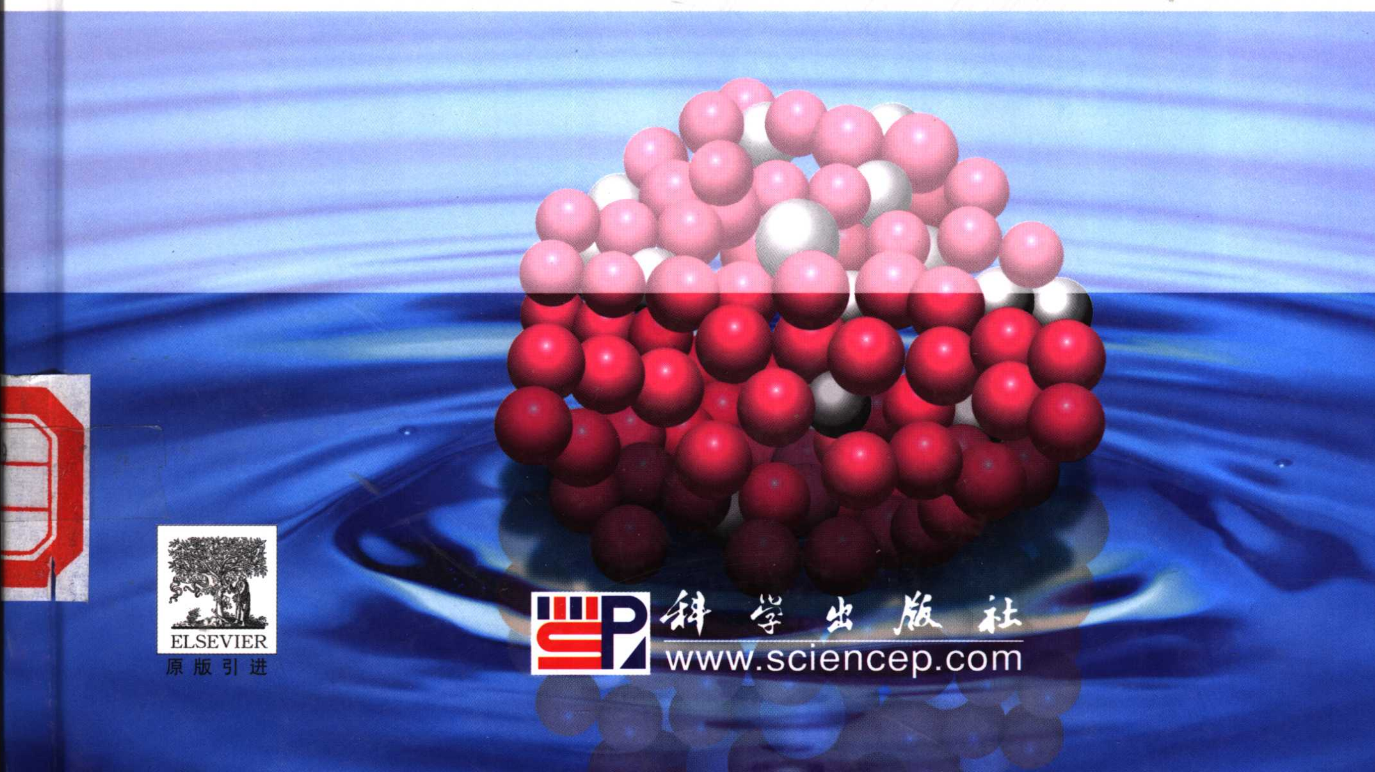
Nanochemistry

纳米化学

G.B. Sergeev



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序　言

在世纪之交，当人们认为他们已经发现和理解化学中的一切，并等待将其造福于人类时，一个新的交叉领域——纳米科学诞生了。这本书主要介绍这个领域的一个方向——纳米化学。

化学家一直都知道并清楚理解在化学的巨大基石中，原子和分子作为主要板块的重要意义。与此同时，随着高分辨电镜，扫描探针显微镜以及高选择性质谱的发展，并结合特殊的制样技术，使得我们能够洞悉诸如只包含 100 个原子的金属颗粒的性质。这些尺寸为 1nm（10^{-9}m）的颗粒呈现出非同寻常并难以预测的化学性质。由于这些颗粒或团簇有着很高的活性，使得那些在宏观颗粒下无法发生的反应，能够在很宽的温度范围内得以进行。纳米化学就是关于这些小颗粒的科学。

纳米化学的一个基本问题就是要弄清，反应中颗粒的尺寸（或原子个数）是如何影响其化学性质的，而这个问题最可能在低温气相或惰性氛围中得到圆满解答。

这本专著由莫斯科州立大学化学系的 G. B. Sergeev 教授撰写。G. B. Sergeev 教授是俄罗斯低温化学的先驱者，并为这个特殊学科在俄罗斯的发展作出了巨大贡献。他曾因在低温化学理论和应用方面的成就而荣获 Lomonosov 奖。

近年来，G. B. Sergeev 教授和他的学生成功的在金属原子和纳米颗粒的低温化学中开创了一个新的方向。这本专著反映了他们的研究结果，同时也收录了大量近期发表文献中的相关信息。事实上，这是关于这一门科学的第一本书，而这门科学正在世界范围内迅速发展，它将让读者认识一个新奇且有趣的方向，名叫纳米化学。

V. A. Kabanov
俄罗斯科学院院士

前 言

这本书要献给一个了不起的人，化学博士 Rimma Vladimirovna Golovnya。R. V. Golovnya 教授是气相色谱和香料化学领域的领军人物，多年来，她在有机化学，分析化学，物理化学方面的工作可谓硕果累累。

作为学生，我们很有幸能够聆听莫斯科州立大学的 A. N. Nesmeyanov 院士，P. A. Rehbinder 院士和 V. I. Spitsin 院士的讲座。我研究生的导师 N. N. Semenov 院士是第一个获得诺贝尔奖的俄罗斯化学家，正是他在我完成毕业答辩后，立即建议我投身于低温下早期未知自发反应的研究。结果，我们发现并研究了在液氮的沸点（77K）范围内，卤化，氢卤化以及石蜡硝化的快速且爆炸性的反应；观察到具有链式和热爆炸特征的，包含解冻自由基的链反应；验证了分子，离子和自由基机制下的竞争性低温化学反应中有分子复合物的参与；确定了卤素与石蜡的低温反应中自由基的自发生成。现在，低温化学已经是一个独立并持续发展的领域。

早在二十世纪八十年代初，我们开创性的研究了在镁和有机化合物蒸汽的低温冷凝物中进行的反应。这些工作也促使低温实验室多年来致力于各种金属原子和纳米颗粒的制备，稳定及反应的研究。现在，我们在莫斯科州立大学化学系的小组仍在继续这个方向的工作。我们在金属纳米化学领域的很多研究都是开创性的，在本书中将会详细介绍这些研究的动态进展。本书的主体是作者 2003 年在俄罗斯出版的一本专著，由于这本专著出版后的两年间纳米化学的飞速发展，让我们能够在新书中增加大量的引用文献，并介绍很多近年来得到的新结果。在现今纳米化学的蓬勃发展趋势中，我们应该注意到不同形状纳米颗粒的研究，以及生物，医药领域发表文章的显著增加。过去的两年中，我在 2003 年专著中所论述的纳米化学的其他方向同样有着活跃的发展，这也使得我们能够保留原书的结构，并在很多章节中添加新的内容。从定义上来说，专著必须囊括所选学科的所有内容。然而，这对于纳米化学很难做到，因为这个学科正以指数速度快速发展着。在这种情况下，新的专著意义更加重大，因为在这些专著中能够论述系统的新观点，并重新审视已知的材料。

我要感谢以下这些人参与实验和结果的讨论，他们是：F. Z. Badaev，A. F. Batssulin，T. N. Boronina，V. E. Bochenkov，A. V. Vlasov，E. V. Vovk，M. V. Grishechkina，I. A. Gromchenko，V. V. Zagorskii，O. V. Zagorskaya，M. Yu. Efremov，M. A. Petrukhina，B. M. Sergeev，V. N. Solov'ev，I. G.. Tarkhanova，V. A. Timoshenko 和 T. I. Shabatina。同样要感谢 A. V. Nemukhin 教授为本书撰写“理论方法”部分，并给了手稿一些有价值的建议。我也很高兴 V. E. Bochenkov 帮我准备图表和参考文献目录，使得手稿准备速度得以加快。

很高兴我的孩子和孙子能够理解我在准备这本书时的投入。我想感谢所有同事在这本书上给予我的关心和无私的帮助。感谢所有参与这本书准备工作的人。

G. B. Sergeev

介　绍

当今化学有一种趋势，那就是，在普通条件（接近300K的温度，正常浓度，标准大气压）下进行的实验，正转移到极端条件，如超高能，超低温，超高压，超高真空以及超低浓度下进行，同时还伴随着超细或超窄颗粒的参与。

在过去的15到20年间，纳米尺度的颗粒引起了不同科学领域科学家的注意。这个研究方向较积极的发展要追溯到上世纪90年代，当时召开了第一届纳米材料的国际会议，并出现了第一本相关的学术杂志。现在，在俄罗斯和国际上召开的许多大会，讨论会，座谈会的纲要里，都包含有纳米颗粒，纳米团簇，纳米复合物，纳米工业等方面的主题，它们或单独作为一个主题，或作为分主题的一个部分在会议中出现。

这本专著首次尝试将纳米化学领域的研究系统化。纳米化学这个术语在上世纪90年代末的文献中出现，现在这个方向的发展非常迅速，但由于它的概念和定义尚未确定，所以它目前的情况也是相当复杂。这本专著中所记载的实验和理论方面的资料表明，当今的纳米科学是一门新的，活跃发展的科学领域。像任何一个其他方向一样，纳米化学有它研究的主体，客体以及实验方法，这些分析构成了这本书的主要内容。

在物理，化学和生物纳米颗粒研究领域有一个流行趋势，认为21世纪的科学和技术将会涉及纳米和埃尺度物体的研究（$1nm=10^{-9}m$；$1A=10^{-10}m$）。化学家对纳米颗粒感兴趣的原因有多种，其中主要原因是，研究元素周期表里不同元素的纳米颗粒为化学开创了一个新的领域，这个领域中的很多现象不能用已知的关系来解释。此外，尺寸小于1nm的颗粒令人非常感兴趣，这是由于这些诸如只包含大概10个原子的金属颗粒有着很大的表面积，它几乎没有体积，并呈现出增强的化学活性。而且，加入一个单原子或分子就能改变一个颗粒的化学性质和活性。现代化学最基本的问题就是要揭示颗粒尺寸对其化学物理性质和反应影响的特性。

现在，小颗粒在气相，固相及液相重的物理化学性质和反应一般通过原子或分子的个数描述，而不是用他们的尺寸。原子/分子直径的大小才具有特定的标准，包含1～100个原子/分子的颗粒才是最让人感兴趣的。只有在这样一个尺寸范围内，我们才能经常观察到化学性质和颗粒中原子数之间的不同关系。

我们可以根据目前得到的实验资料给纳米化学下一个定义，纳米化学是研究至少在一个维度尺寸小于10nm的颗粒及其组合体的制备，性质及其反应的学科。很显然，10nm这个数值比较苛刻，但却有特定的作用，因为它强调了纳米化学研究的主体。此外，10nm的尺寸和上述的定义表明，纳米化学还会研究一维，二维和三维物体，如薄膜，线和管。另一方面，它也将尺寸大于10nm颗粒排除在纳米化学之外。尺寸接近100nm的颗粒应划分到超分散颗粒的范围，由这些颗粒组成的材料可以用光学显微镜观测到。

当今纳米化学正积累实验数据并发展它的理论解释。由很少数目，如几十个原子，构成的颗粒有着不同寻常的化学性质，要想解释这些现象，就必须对那些已知的概念作出重大修正，因为这些概念是从包含千百万个原子的体系中得来的。在纳米化学这个领域的研究使得合成具有非凡的，未知性质的物质成为可能。

在这本专著中，作者主要介绍周期表中不同族的金属原子，团簇和纳米颗粒的合成和化学反应，并用独立的一章专门介绍碳族纳米颗粒。金属核，团簇和纳米颗粒的形成通常从原子开始。为了正确理解这个过程，就必须了解原子化学性质的本原。因此，在这本书中会涉及某些特定的反应。纳米颗粒的合成，稳定及研究的方法只作简要论述。对多组分系统及具有不同化学性质的杂化物和薄膜材料也进行了分析。本书将会关注化学中的尺寸效应。尺寸效应只在小于 10nm 的体系中发生，它与体系的物理化学性质和反应的定性变化密切相关，并且这种定性变化取决于颗粒中物种的定量变化。书中简要概括了用半经验和量子化学从头计算来描述纳米颗粒性质的理论方法，并单独用一个章节介绍金属原子和纳米颗粒的低温化学研究。这本专著的作者和他的学生，以及和他合作过的俄罗斯和国外的科学家们，在纳米化学领域的研究成果显著。本书专门用一个章节收录纳米颗粒和相关材料在科技上的各种应用前景，并讨论了纳米化学和纳米工业发展面临的问题和前景展望，以及纳米颗粒在生物和医学上的应用。

这本专著一方面可以作为化学的一个新领域的介绍，另一方面也类似一本指导书，借助它来研究纳米颗粒化学的相关大量文献。书中的大量内容是最近 3～4 年发表的研究成果。除了原始文献，书中还用到了作者在莫斯科州立大学化学和材料科学系的授课讲义，这也为本书的几个章节引入了教科书的特定元素。

总之，对想要了解这个物理，化学和材料科学相互交叉的新兴科学领域的读者而言，这本书是很有意思的。同样，对于那些从事纳米科学不同方向研究的科学家和教师，以及准备投身这个新奇且充满挑战的领域的学生和研究生们，这本书也是有所帮助的。

（邹凯　译）

Foreword

At the turn of the century when it seemed that everything in chemistry had already been discovered, understood, and just waiting to be applied to the benefit of mankind, a new interdisciplinary field—nanoscience—was born. This book is devoted to one of its directions, nanochemistry.

Chemists always knew and well understood the significance of atoms and molecules as the main 'blocks' in the huge foundation of chemistry. At the same time, the development of new precision, 'custom-made' instrumentation, such as high-resolution electron microscopy, probe scanning microscopy, highly selective mass spectrometry, in combination with special procedures for synthesizing samples provided insight into the behavior of particles of, e.g., metals that contain few, i.e., less than 100 atoms. Such particles measuring about 1 nm (10^{-9} m) exhibited unusual, hardly predictable chemical properties. It turned out that such nanoparticles or clusters display a high activity and provide an opportunity for carrying out reactions, which never occurred with macroscopic particles, in a wide temperature range. Nanochemistry concerns itself precisely with such fine particles.

One of the basic problems of nanochemistry is associated with finding out how the chemical properties depend on the size (or the number of atoms) of particles involved in the reaction. This problem can be solved most successfully in the gas phase at low temperatures or in inert matrices.

This monograph is written by Professor G.B. Sergeev of the Faculty of Chemistry, Moscow State University. He is a pioneer and the greatest contributor to the development in our country of such a unique direction as cryochemistry. His studies in theoretical and applied aspects of cryochemistry were acknowledged by awarding him the Lomonosov Prize.

In recent years, he and his pupils successfully elaborated a new direction in cryochemistry of metal atoms and nanoparticles. This monograph reflects the results of these studies together with a large body of literature information published in recent years. In fact, this is the first book on this science, which is rapidly developing all over the world, and it will allow the reader to acquaint with a new and interesting direction, named nanochemistry.

V.A. Kabanov, Member of the Russian Academy of Sciences

Dedication

In memory of Rimma, my beloved wife and friend.

Preface

This book is dedicated to a wonderful person, Rimma Vladimirovna Golovnya, Doctor of Chemistry. Professor R.V. Golovnya was a leading scientist in the field of gas chromatography and flavochemistry and worked fruitfully for many years in organic, analytical, and physical chemistry.

Being students, we were fortunate to enjoy lectures by academicians A.N. Nesmeyanov, P.A. Rehbinder, and V.I. Spitsin, professors of the Faculty of Chemistry at Moscow State University. The supervisor of my post-graduate training, academician N.N. Semenov, was the first among Russian chemists to win the Nobel Prize. It was he who suggested, immediately after I defended my Candidate of Chemistry Dissertation, that I should direct my efforts at studying the earlier unknown spontaneous reactions at low temperatures. Thus, the fast, virtually explosive reactions of halogenation, hydrohalogenation, and nitration of olefins in the vicinity of the boiling point of liquid nitrogen (77 K) were discovered and studied; chain reactions that involved frozen-out radicals and combined the features of chain and thermal explosions were observed; the participation of molecular complexes in competitive cryochemical reactions that proceeded via molecular, ionic, and radical mechanisms was proved; and the spontaneous formation of free radicals in low-temperature reactions of halogens with olefins was established. Currently, cryochemistry represents an independent and constantly developing field.

In the early 1980s, we pioneered the studies of reactions in joint low-temperature condensates of vapors of magnesium and organic compounds. It is these studies that initiated the many year cycle of studies carried out at the Laboratory of Low Temperatures devoted to the synthesis, stabilization, and reactions of atoms and nanoparticles of different metals. At present, our group at the Faculty of Chemistry of Moscow State University is continuing the research in this direction. A number of our studies on the nanochemistry of metals were accomplished for the first time, and the dynamics of their development is described in detail in this monograph. A monograph written by the author and published in Russian in 2003 forms the basis of this book. The development of nanochemistry is so fast that the two years since the monograph's publication have allowed us to substantially increase the number of cited papers and to introduce a large number of new results obtained in recent years. Among the trends most actively developed at present, mention should be made of the great attention devoted to nanoparticles of various shapes and the impressive growth of publications in the fields of biology and medicine. In the past two years, the other directions of nanochemistry covered in the 2003 monograph were also actively developed, which allowed us to retain the original structure of the book and to add new material to many chapters. By definition, a monograph should reflect most comprehensively the subject chosen. However, this condition is difficult to fulfill for nanochemistry, because its development proceeds exponentially. In such cases, new monographs are of the greatest importance, as they make it possible to describe newly formulated ideas and take a new look at the known material.

I am grateful to F.Z. Badaev, A.F. Batsulin, T.N. Boronina, V.E. Bochenkov, A.V. Vlasov, E.V. Vovk, M.V. Grishechkina, I.A. Gromchenko, V.V. Zagorskii, O.V. Zagorskaya, M.Yu. Efremov, M.V. Kiryukhin, V.S. Komarov, A.M. Kosolapov, I.A. Leenson, Yu.N. Morozov, S.P. Mikhalev, M.A. Petrukhina, B.M. Sergeev, V.N. Solov'ev, I.G. Tarkhanova, V.A. Timoshenko, and T.I. Shabatina for their participation in the experiments and discussions of the results obtained. I would also like to thank Professor A.V. Nemukhin, who wrote the Section "Theoretical Methods" and made certain valuable remarks concerning the manuscript. I am also grateful to V.E. Bochenkov for help in preparing the figures and the reference list, which accelerated the preparation of the manuscript.

I am also grateful to my children and grandchildren, who kindly understood my preoccupation with the preparation of this book. I would like to thank all my colleagues for their attention to my concerns with this book and their valuable help. I am grateful to all those who took part in the preparation of this edition.

G.B. Sergeev

Introduction

Contemporary chemistry demonstrates a trend for a transition from carrying out experiments under 'ordinary' conditions (temperatures close to 300 K, normal concentrations, and atmospheric pressure) to conducting syntheses at superhigh energies and superlow temperatures, superhigh pressures and superhigh vacuum, superlow concentrations and with participation of supersmall or small-scale particles.

Particles of nanometer sizes began to attract the attention of scientists in different fields of science in the last 15–20 years. More active development in this direction dates back to the 1990s, when the first international conferences on nanomaterials were held and the first relevant scientific journals appeared. At present, the programs of many Russian and international congresses, conferences, and symposia include the subjects Nanoparticles, Nanoclusters, Nanocomposites, Nanotechnology, either as such or as constituents of the section subject.

This monograph is one of the first attempts to consider and systemize the studies in the field of nanochemistry. The term 'nanochemistry' appeared in the cited literature at the end of the 1990s. This direction is being explored very rapidly, and the situation is additionally complicated by its yet unsettled concepts and definitions. The experimental and theoretical material described in this monograph show that contemporary nanochemistry is a new, actively developing scientific direction. Like any other direction, nanochemistry has its own subject, objects for studying, and experimental methods, the analysis of which forms the major subject of this book.

A modern trend in the research of nanosized particles in physics, chemistry, and biology allows one to assert that in the 21st century both science and technology will deal with nanosized, angström objects ($2\,\text{nm} = 10^{-9}\,\text{m}$; $1\,\text{Å} = 10^{-10}\,\text{m}$). The interest of chemists in nanoparticles is explained as being due to several reasons. The chief reason is the fact that studying nanoparticles of various elements in the Periodic Table opens up new directions in chemistry that cannot be described in terms of already known relationships. Moreover, particles measuring less than 1 nm are of the greatest interest. This is explained by the fact that such formations of, e.g., metals contain approximately 10 atoms that form a superficial particle that has no volume and displays an enhanced chemical activity. At the same time, it is known that chemical properties and activity of a particle can be changed by the addition of just a single atom or molecule. The most fundamental problem of modern chemistry is to reveal the peculiarities of the effect of the particle size (or the number of atoms) on its physicochemical properties and reactivity.

Nowadays, the physicochemical properties and reactions of small particles in the gas phase and, recently, in solid and liquid phases are often described by the number of atoms or molecules rather than by their sizes in nanometers. Of certain value can be the scale of atomic/molecular diameters, where the particles comprising 1–100 atomic/molecular diameters are most interesting. In such a range of sizes, the different relationships between the chemical properties and the number of atoms in a particle are observed most frequently.

The experimental material obtained to date makes it possible to define nanochemistry as a field that studies synthesis, properties, and reactivity of particles and assemblies they form, which measure less than 10 nm at least in one direction. Apparently, the value 10 nm is arbitrary; however, its introduction plays a certain role, stressing the subject of nanochemistry. Moreover, a size of 10 nm and the aforementioned definition show that nanochemistry deals with one-, two-, and three-dimensional objects such as films, wires, and tubes. On the other hand, this rules out the assignment of particles larger than 10 nm to nanochemistry. Particles with sizes approaching 100nm would be more correctly classified as ultradispersed, and materials on their basis as microscopic.

Contemporary nanochemistry accumulates experimental material and develops its theoretical interpretation. Unusual chemical properties of particles consisting of a small number of atoms, i.e., several tens of atoms, require a serious modification of concepts developed for systems that involve thousands and millions of atoms. Studies in the field of nanochemistry open up possibilities for the formation of new paradigms of synthesizing substances with remarkable, earlier unknown properties.

In this monograph, attention is focused on synthesis and chemical reactions of atoms, clusters, and nanoparticles based on metals of different groups in the Periodic Table. A separate chapter is devoted to nanoparticles based on carbon. The formation of metal cores, clusters, and nanoparticles begins as a rule with atoms. To correctly understand such processes, it is vital to get to the bottom of chemical properties of atoms; thus, the participation of certain reactions are reflected upon in this book. Methods for synthesizing, stabilizing, and studying nanoparticles are discussed relatively briefly. Multicomponent systems, hybrid and film materials with various chemical properties are analyzed. Great attention is devoted to size effects in chemistry, which are associated with the *qualitative* changes in physicochemical properties and reactivity depending on the *quantity* of species in a particle and proceed in a range smaller than 10 nm. Semiempiric and *ab initio* quantum-chemical approaches to theoretical description of nanoparticle properties are briefly outlined. A separate chapter is devoted to studies on cryochemistry of metal atoms and nanoparticles. This field of nanochemistry is actively explored by the author of this monograph and his pupils and colleagues in cooperation with Russian and foreign scientists. The sections providing an outlook on various applications of nanoparticles and relevant materials in science and technology are collected in a special chapter. Problems and prospects in the development of nanochemistry and nanotechnology as well as the use of nanoparticles in biology and medicine are discussed.

The monograph can be considered, on the one hand, as an introduction to a new field of chemistry and, on the other, as a sort of a guidebook to the extensive literature devoted to the chemistry of nanoparticles. For the most part, it comprises the studies published in the past 3–4 years. In addition to original literature, the materials of lecture courses held by the author at the Faculties of Chemistry and Material Sciences of the Moscow State University were used. This fact introduces certain elements of a study-book into the material of several sections.

First of all, this book should be interesting for those who wish to get acquainted with this new scientific field, in which the concepts of physics, chemistry, and material science are closely interlinked. The book will also be helpful for those scientists and pedagogues who develop different concrete aspects of nanoscience as well as for students and post-graduate students who want to direct their efforts to studying this new and challenging field.

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