

Specialist Periodical Reports

Chemical Modelling

Volume 11

Edited by Michael Springborg
and Jan-Ole Joswig



Chemical Modelling

Volume 11

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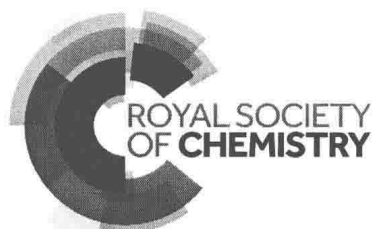
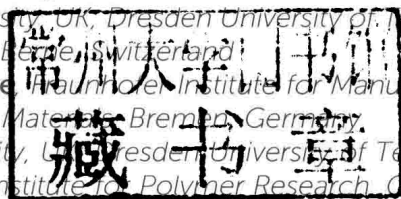
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Preface

Michael Springborg^{a,b} and Jan-Ole Joswig^c

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You are reading the 11th volume of the *Specialist Periodical Reports on Chemical Modelling: Applications and Theory*. We, the editorial team, have tried to compile a volume that keeps you, the reader, interested in the reviews from various areas of chemical modelling. As in the past years, we continue the annual appearance of the series and the wide range of topics.

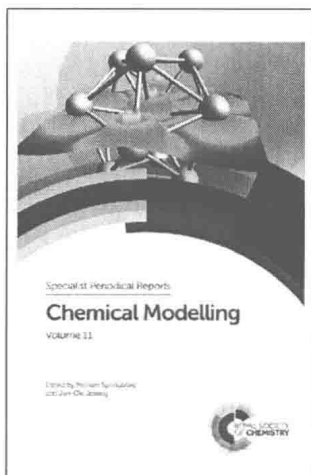
In Volume 11 we put the focus on methodological reports, considering two Nobel Prizes: the 2013 Nobel Prize in Chemistry was awarded to Martin Karplus, Michael Levitt, and Arieh Warshel “for the development of multiscale models for complex chemical systems”. Consequently, this volume contains a chapter on multi-scale modelling and one on special molecular-dynamics techniques. On the other hand, the 1998 Nobel Prize in Chemistry was given to Walter Kohn “for his development of the density-functional theory” and John A. Pople “for his development of computational methods in quantum chemistry”. Hohenberg’s and Kohn’s seminal paper on density-functional theory appeared in 1964, so that 2014 is celebrating 50 years of density-functional theory. We, the editors, took the opportunity to contribute a personal perspective on some aspects of density-functional theory, but we also managed to encourage a contribution on density-functional theory of chemical reactivity. Additionally, you will find chapters dealing with modelling solid electrolyte interphase formation, special relativity, and inorganic two-dimensional materials.

We hope that you will enjoy reading our present collection of topics contributed by scientists from different research areas. Forthcoming volumes of *SPR Chemical Modelling* are planned already, and we will be grateful for helpful suggestions with respect to authors or subjects. For now, we wish you enjoyment of Volume 11.

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Cover

The icosahedral 'golden fullerene' WAl_{12} reproduced by permission of Pekka Pyykkö, Chemistry Department, University of Helsinki, Finland.

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Michael Springborg and Jan-Ole Joswig

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Low-dimensional transition-metal dichalcogenides

Agnieszka Kuc

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1 Introduction

Nanomaterials form a field of materials science, which is devoted to the production and properties of systems with at least one dimension at the nanometre scale. If any of the dimensions is restricted, layered 2D materials are formed; if restrictions appear in two dimensions, one obtains 1D polymer-like systems; and finally, if all three dimensions are scaled down to the range of only few nanometres, 0D clusters or nanoflakes are in subject. These considerations are particularly applicable to the case of carbon, where 3D graphite can be exfoliated down to the 2D graphene monolayers (MLs), which in turn can be rolled up to form 1D nanotubes (NTs) or 0D fullerenes (see Fig. 1). Each of these sp^2 carbon allotropes exhibits very different physical properties, especially the electronic structure differs significantly between those allotropes. For example, the parabolic dispersion relation in graphite's band structure – resulting in a zero band gap – changes to linear band behaviour in graphene, where it is described by massless Dirac fermions.^{1,2} On the other hand, NTs can either be metallic or semiconducting, depending on the size and chirality. Fullerenes are always insulators with a large finite band gap, independent of size and shape. Among these carbon nanomaterials, graphene research has been developing extremely fast ever after the successful separation from bulk graphite,^{1,2} what led to the Nobel Prize for Novoselov and Geim in 2010.

Low-dimensional nanomaterials are important in many fields of research and technology. Some examples cover silicon-based semiconductor devices, optical coatings, micro-electromechanical systems, biomedical research, lasers and electro-optics. Recently, they became extremely interesting as building blocks of next-generation devices for (opto-)electronic applications. As modern electronic devices are strongly miniaturized (nanoscale), several problems start to occur. Traditional electronics with silicon-based field-effect transistors (FETs) often suffers from heat dissipation. At this scale, also quantum effects become very important. To overcome problems of silicon-based technology at nanoscale, one could replace it with nanomaterials that perform better at atomic scale.

In the world of 2D materials, graphene has gained enormous attention, especially for its applications in nanoelectronics.^{3,4} High electron mobility, long-distance spin-transport, or exceptional mechanical properties of graphene are very attractive. Graphene has a potential as a

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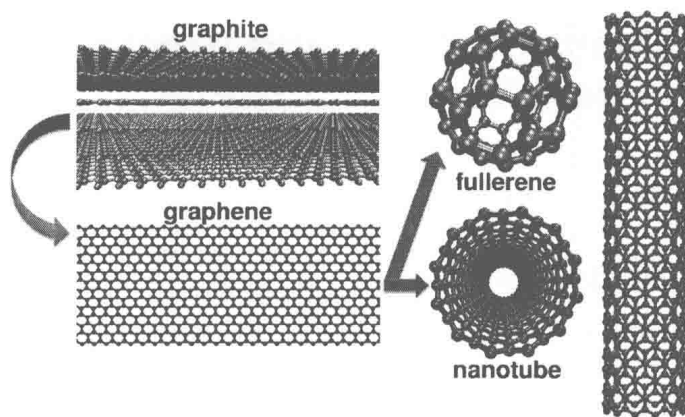


Fig. 1 Representation of sp^2 hybridized carbon allotropes: 3D graphite, 2D graphene, 1D carbon nanotubes, and 0D carbon fullerenes.

spin-conserver system and it is attractive for spintronic applications. However, weak spin-orbit coupling and zero-band gap disregard graphene as switching material in charge- and spin-based transistors.

These difficulties can be overcome in the semiconducting 2D materials. After the discoveries of CNTs⁵ and graphene,^{1,2} other layered and corresponding tubular materials have gained considerable attention. The successful methodologies and knowledge gained in the search for graphite monolayers and CNTs have been extended to other inorganic materials. Though graphene is presently a cutting-edge system, it opens up a variety of new possibilities going beyond the limits of its own properties and applications.

Many materials exist in the layered 3D bulk forms, which can be easily confined to lower dimensions resulting in single layers or tubular structures. Among them, the most known are boron nitride, transition-metal chalcogenides (TMCs), TX_2 (T-Mo, W, Nb, Re, Ti, *etc.*; X-S, Se, Te), halides (Cl, Br, I), or oxides.⁶⁻⁹ Layered 3D TMCs of TX_2 type have been extensively studied on experimental and theoretical bases for the last 50 years. There is a huge number of theoretical works on various properties of the TMC layered materials reported to date in the literature.^{6,9-76} Some of the possible elemental compositions of layered TMCs are schematically shown in Fig. 2.

Weak non-covalent interactions between the adjacent sheets and the anisotropic character of TMC structures result in easy shearing of the layers even under high pressure, leading to very good lubricant properties.⁷⁷ Other applications, such as catalysis, optoelectronics and photovoltaics, have been proposed and investigated for this family of compounds.⁷⁸⁻⁸² However, it was only in 2011, when TMCs have started their renaissance as potential materials for nano- and opto-electronics after seminal works of Nicolosi and co-workers,⁸³ and Kis and co-workers.⁸⁴ The group of Nicolosi have reported that large-area single layers of TMC can be easily produced using liquid exfoliation technique.⁸³ Using such a single layer TMC, the group of Kis have produced the first FET based on MoS_2 ML (see Fig. 3).⁸⁴ Pioneering measurements of

The promising use of TMC low-dimensional materials as building blocks in nanoelectronic devices calls for detailed investigations of their physical properties. Therefore, in the following, we will try to summarize what is presently known in the field of TMCs. We will review the recent theoretical developments on the properties of low-dimensional TMCs for applications in nano- and opto-electronics. We will compare physical properties, such as electronic structure or lattice dynamics, and show that quantum confinement to single layers or nanotubes causes significant changes in the properties and opens up the possibility for new applications. Further, we will show that these electronic properties could be tuned by external modulators, such as tensile strain or electric fields. Although TMC materials have been widely investigated for about five decades, their role as single-layer systems is new. We will focus on the electronic properties of TMCs from groups 5–7 with the 2H polytype. 0D through 2D systems will be considered as platelets, nanotubes and layers, respectively. Theoretical findings will be compared to the available experimental data. This chapter is organized as follows: in Section 2, the state-of-the-art synthesis methods of 1D and 2D materials are summarized, Section 3 discusses the structural and mechanical properties of TMCs, and Section 4 reports the electronic properties of TMCs and the possibility to tune them in a desired manner.

2 Synthesis methods

2.1 2D Transition-metal dichalcogenide nano-layers and -platelets

2D TMC materials can be presently synthesized using two types of methods: the top-down technique, where the bulk forms are exfoliated into monolayers (MLs), and the bottom-up approach using substrate materials.

The *top-down technique* includes micromechanical cleavage, also known as the Scotch-tape technique, liquid and chemical exfoliation, intercalation by ionic species, ultrasonication, and others.^{67,83,84,88,96–115} After successful application to graphite,² the micromechanical cleavage has been extended to other inorganic materials, such as MoS₂, BN, or perovskites. Thin TMC flakes can be peeled from their bulk crystal structures, attached to the substrates, and identified using similar methods as those developed for graphene (*e.g.* by optical microscopy).^{67,84,115–117} This method produces single-crystal flakes of high-purity and macroscopic continuity, as in the case of graphene. Such flakes can be characterized and utilized for fabrication of individual devices. The size and the thickness of the flakes produced by the Scotch-tape technique cannot, however, be easily controlled and monolayers are in great minority among much thicker flakes. Therefore, this technique is not feasible for large-scale production of TMC-MLs for technological applications.

In order to produce large-area TMC-MLs in more controlled way, liquid exfoliation was proven to be very efficient and promising.^{83,107,118} In 2011, Coleman *et al.*⁸³ reported that liquid exfoliation produces few-layer TMC materials. This method is highly scalable, insensitive to air and

water, and can be applied generally to other materials, including boron nitride or graphene.⁸ It allows production of hybrid dispersion or composites by blending dispersions of different materials.

Ion intercalation, like *e.g.* ultrasound-promoted hydration of lithium-intercalated compounds, is another effective method, allowing production of single-layer materials. Zeng *et al.*^{108,109} have recently shown that TMC-MLs can be produced with high yield through a complex lithiation processes. These intercalation methods are known since 1970s⁹⁶ and they have been re-discovered in the past few years.^{102,108,109,111,112} The exfoliation by ionic intercalation was advanced in 1980s by Morrison and co-workers,¹⁰⁴ and it typical involves merging of TMC bulk with Li-containing compounds and subsequent exposure to water. Water interacts with lithium to release H₂, which in turn separates the layers. This method was successfully used for various TMC materials, including MoS₂, SnS₂, TiS₂, or MoSe₂.^{103,108,109} The main disadvantage of the method is the structural deformation that may affect the electronic or optical properties of the TMC-MLs.

TMCs can also be exfoliated from the parental bulk materials using ultrasonication in selected liquids, such as organic solvents, polymer or surfactant solutions.^{83,97,105,107,110,119} Several layered crystals were also successfully exfoliated in aqueous solutions of the surfactant sodium cholate using sonication. This procedure results in flakes of few-hundred nanometres in size and can be stabilized against re-aggregation by solvation or steric repulsion of molecules adsorbed from the solvent.

Taking into account the advantages and disadvantages of the above methods, for electronic and photonic applications, the ion-exfoliation is favoured, while the liquid exfoliation technique is preferred for production of composite materials. Application of 2D TMC materials in fields of nano- and opto-electronics requires control over the size and thickness of the nanolayers.

The second type of synthesis methods is the so-called *bottom-up technique*. Large-scale device fabrication was demonstrated for graphene¹²⁰ through chemical vapour deposition (CVD) on metal substrates¹²¹ or epitaxial growth on SiC substrates.¹²² Recently, the CVD methods were applied to grow MoS₂ thin films on insulating substrates.^{123–129} 3D MoS₂ materials can be produced by chemical reactions,^{130–133} CVD,¹³⁴ thermal evaporation,^{135,136} *etc.* These techniques could be easily explored to produce thin-film TMCs. Zhan *et al.*¹²⁹ have produced MLs and few-layer MoS₂ by vapour-phase growth of elemental molybdenum on the SiO₂ substrate using electron-beam in presence of pure sulphur. Lee *et al.*¹²⁷ have obtained MoS₂ MLs using MoO₃ and sulphur reactants on reduced graphene oxide or modified SiO₂ substrates. The authors have shown that the MoS₂ growth was promoted by surface treatment. Furthermore, using sapphire or SiO₂/Si substrates, Liu *et al.*¹²⁵ have produced large-area MoS₂ MLs through thermolysis of (NH₄)₂MoS₄ and subsequent annealing in sulphur vapour. In many CVD methods, the thickness of the MoS₂ sheets depends strongly on the concentration and thickness of the precursors. Different CVD methods are still at relatively early stage of TMC-MLs production, but are also promising to be leading synthesis of

thin films of materials other than MoS₂. As a matter of fact, first attempts to produce WS₂ nanosheets down to 2–3 layers have been performed through the chemical reaction of W₁₈O₄₉ nanorods with CS₂ in hexadecylamine solution.¹³⁷

Hydrothermal synthesis at high temperature and pressure from aqua solutions lead to chemical production of MoS₂ and MoSe₂.^{138,139} Layered transition-metal sulphides or selenides have also been produced at high temperature from reactions of MoO₃ or WO₃ with SC(NH₂)₂ or SeC(NH₂)₂.¹⁴⁰ In this way, good-quality flakes with sizes in nano- and micrometres range are produced, however, not restricted to the ML thickness. Other TMC thin films have been produced through CVD methods,^{141–147} however, the procedures remain challenging.

Planar small MoS₂ clusters (platelets/flakes) of single- or few-layers have been produced by Besenbacher and co-workers^{148–151} in standard ultrahigh vacuum chamber using high-resolution scanning tunnelling microscopy (HRSTM). In this procedure, two types of substrates have been used, namely Au(111) and the highly-oriented pyrolytic graphite (HOPG). When molybdenum was deposited on Au(111) surface, a self-assembled regular array of Mo islands was formed, which were transformed into MoS₂ nanoclusters after the subsequent sulphidation. Therefore, the gold surface acts as a template that allows dispersion of Mo into islands. Following this procedure, the majority of Mo islands can be changed into crystalline MoS₂. The HOPG substrate does not support dispersion of Mo, unless defects were formed due to the ion bombardment. Depending on the substrate, different shapes of MoS₂ platelets were formed with single-layer triangular clusters favoured in the case of Au(111), while HOPG supported rather hexagon-like truncated shapes of MLs or few-layers stackings.

2.2 1D Transition-metal dichalcogenide nanotubes

Transition-metal dichalcogenides can form structures that resemble nested carbon nanotubes (1D) or fullerenes (0D). TMC inorganic nanotubes (TMC-NTs) are highly regular and almost defect-free, as opposed to the inorganic fullerenes (TMC-IFs). In this section, we will focus solely on the synthesis methods of tubular forms of TMCs.

Folding the TMC layers into tubular or IF-like forms comes back as early as 1979, when Chianelli and co-workers reported the formation of tubular MoS₂ structures and their possible applications in catalysis.¹⁵² At the same time, Sanders observed that MoS₂ ML could close-up and encapsulate NiO nanoparticles. This was obtained, when the authors were studying the reactivity of the oxide particles in hydro-desulphurization of petroleum.¹⁵³

NTs and IFs of transition-metal dichalcogenides have been first synthesized and characterized by Tenne and co-workers in early 1990s,^{89,90} shortly after the identification of carbon nanotubes (CNTs) by Iijima *et al.*⁵ Over the past two decades, significant progress has been achieved in the synthesis of NTs from layered materials.^{154–172} The synthesis of TMC-NTs is, most commonly, performed at elevated temperatures. High temperatures help to accelerate the kinetics of the process and induce fluctuations of the planar layers, leading to folding into tubular forms.