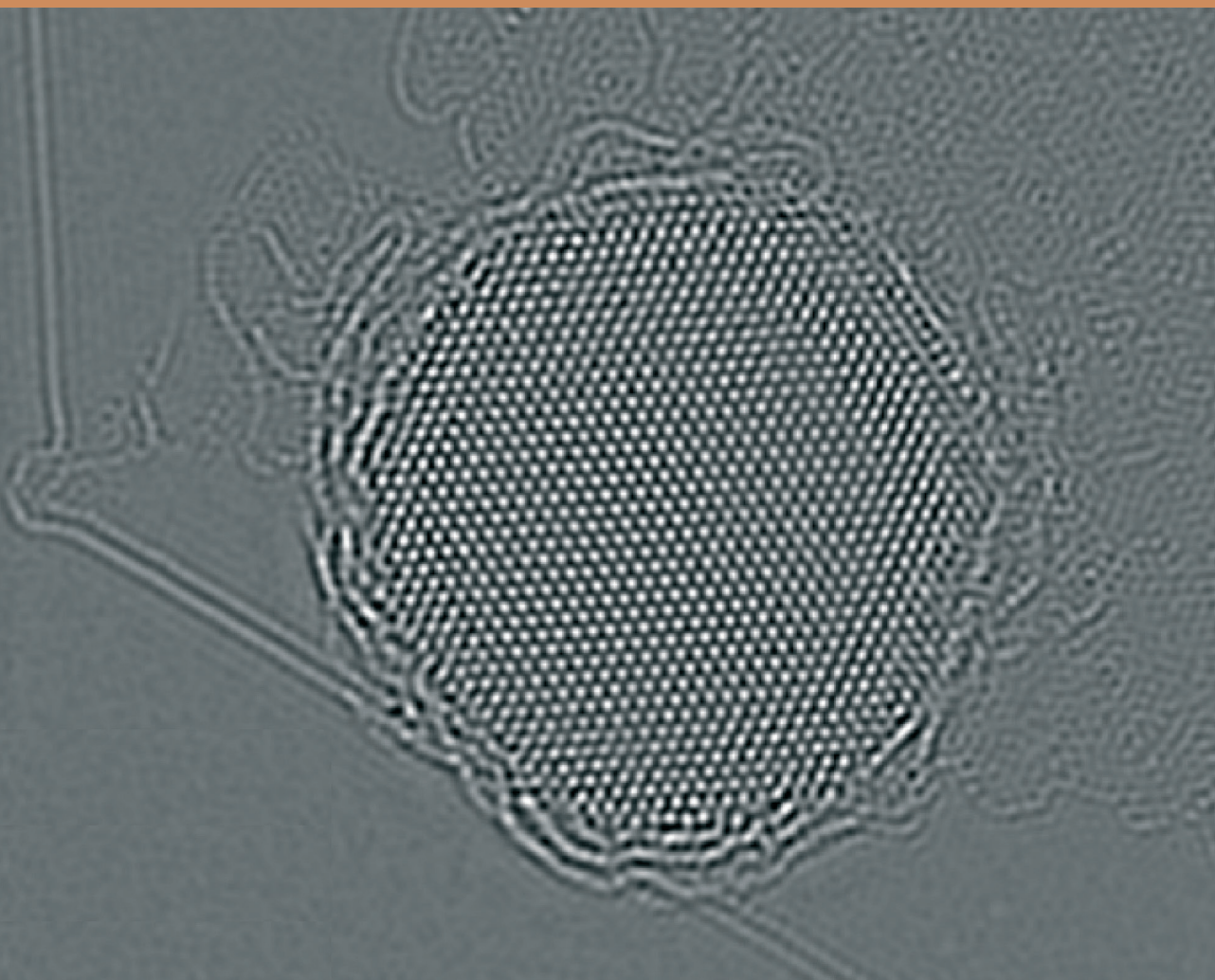


SERBIAN ACADEMY OF SCIENCES AND ARTS
СРПСКА АКАДЕМИЈА НАУКА И УМЕТНОСТИ



FASCINATING WORLD OF NANOSCIENCES
AND NANOTECHNOLOGIES
ФАСЦИНАНТНИ СВЕТ НАНОНАУКА
И НАНОТЕХНОЛОГИЈА

FASCINATING WORLD OF NANOSCIENCES
AND NANOTECHNOLOGIES

ФАСЦИНАНТНИ СВЕТ НАНОНАУКА
И НАНОТЕХНОЛОГИЈА

СРПСКА АКАДЕМИЈА НАУКА И УМЕТНОСТИ

ЦИКЛУС ПРЕДАВАЊА

Књига 6

ФАСЦИНАНТНИ СВЕТ НАНОНАУКА И НАНОТЕХНОЛОГИЈА

Примљено на I скупу Одељења техничких наука,
одржаном 22. јануара 2020. године

Уредници

ВЕЛИМИР Р. РАДМИЛОВИЋ

Српска академија наука и уметности

и

ЏЕФ Т. М. ДЕХОСОН

Холандска краљевска академија наука и уметности

БЕОГРАД 2020

SERBIAN ACADEMY OF SCIENCES AND ARTS

LECTURE SERIES

Book 6

FASCINATING WORLD OF NANOSCIENCE
AND NANOTECHNOLOGY

Accepted at the 1st meeting of the Department of Technical Sciences
held on January 22, 2020

Editors

VELIMIR R. RADMILOVIĆ

Serbian Academy of Sciences and Arts

and

JEFF TH. M. DEHOSSON

Royal Netherlands Academy of Arts and Sciences

BELGRADE 2020

Published by
Serbian Academy of Sciences and Arts
Belgrade, 35 Kneza Mihaila St.

Издаје
Српска академија наука и уметности
Београд, Кнеза Михаила 35

Reviewers
Prof. Dr. Dragan Uskoković
Prof. Dr. Djordje Janačković

Рецензенти
Проф. др Драган Ускоковић
Проф. др Ђорђе Јанаћковић

Copy editing for English
Jelena Mitrić and Vuk V. Radmilović

Лектура
Јелена Мићрић и Вук В. Радмиловић

Proofreader
Nevena Đurđević

Коректура
Невена Ђурђевић

Translation of Summaries
Vuk V. Radmilović

Превод резимеа
Вук В. Радмиловић

Technical editor
Nikola Stevanović

Технички уредник
Никола Стевановић

Print run
400 copies

Тираж
400 примерака

Printed by
Planeta print

Штампа
Планета ѝриниј

ISBN 978-86-7025-859-4

ISBN 978-86-7025-859-4

CONTENTS

<i>Velimir R. Radmilović, Jeff Th. M. DeHosson</i> Fascinating world of nanosciences and nanotechnologies	7
<i>Велимир Р. Радмиловић, Џеф ДеХосон</i> Фасцинантни свет нано наука и нанотехнологија	11
<i>Jeff Th. M. DeHosson, Eric Detsi</i> Metallic muscles: nanostructures at work	15
<i>Џеф ДеХосон, Ерик Дејиси</i> Метални мишићи: наноструктуре у акцији	45
<i>Alexandra E. Porter, Ioannis G. Theodorou</i> Emerging risks and opportunities for zinc oxide-engineered nanomaterials	47
<i>Александра Е. Портер, Јоанис Г. Теодору</i> Сагледавање ризика и могућности за цинк-оксидне наноматеријале	69
<i>Miodrag Čolić, Sergej Tomić</i> Toxicity of nanostructures	71
<i>Миодраг Чолић, Сергеј Томић</i> Токсичност наноструктура	121
<i>Gordana Ćirić-Marjanović</i> Nanostructures of electro-conducting polymers and carbon nanomaterials produced by their carbonization	123
<i>Гордана Ђирић-Марјановић</i> Наноструктуре електропроводних полимера и угљенични материјали произведени њиховом карбонизацијом	154
<i>Marija Radoičić, Mila Vranješ, Jadranka Kuljanin Jakovljević, Gordana Ćirić-Marjanović, Zoran Šaponjić</i> Probing the optical, magnetic and photocatalytic properties of doped TiO ₂ nanocrystals and polymer based nanocomposites for various applications	155
<i>Марија Радоичић, Мила Врањеш, Јадранка Куљанин Јаковљевић, Гордана Ђирић Марјановић, Зоран Шайоњић</i> Испитивање оптичких, магнетних и фотокаталитичких особина допираних TiO ₂ нанокристала и нанокомпозиата на бази полимера за различите примене	181

<i>Vladimir V. Srdić, Branimir Bajac, Mirjana Vijatović Petrović, Marija Milanović, Željka Cvejić, Biljana D. Stojanović</i>	
Multiferroic BaTaO ₃ -NaFe ₂ O ₄ composites: from bulk to multilayer thin films	183
<i>Владимир В. Срдић, Бранимир Бајац, Мирјана Вијатковић Петровић, Марија Милановић, Жељка Цвејић, Биљана Д. Стојановић</i>	
Мултифероични ВаТаО ₃ -НаFe ₂ О ₄ композити: од керамике до вишеслојних танких филмова	219
<i>Tamara Radetić</i>	
Atomistic and crystallographic phenomena during nanograin island shrinkage	221
<i>Тамара Радећ</i>	
Атомистички и кристалографски феномени при контракцији нанозрна	249
<i>Igor A. Pašti, Ana S. Dobrota, Slavko V. Mentus</i>	
Modelling and simulations of nanostructures	251
<i>Игор А. Пашти, Ана С. Доброћа, Славко В. Менџус</i>	
Моделирање и симулација наноструктура	282
SUBJECT INDEX	285

FASCINATING WORLD OF NANOSCIENCE AND NANOTECHNOLOGY

Researchers whose work has led to significant discoveries, looking much further, beyond the immediate resolution of technical problems, are asking themselves important questions such as: why individual phenomena occur, how they develop, and why they work. In order to enhance our knowledge about the world around us, and to see pictures of worlds that elude the human eye, through history many experimental and theoretical methods have been developed and are still being improved, including the development of telescopes and microscopes, which enable us to see "very large" and "very small" things.

Researchers involved in the "big things" (the universe, galaxies, stars and planets) have found that a galaxy of an average size of about 100,000 light-years has, on average, around one quadrillion (10^{15}) stars. Researchers involved in the "little things" (nanostructures, molecules, clusters of atoms, individual atoms, atomic defects, etc.) have discovered that 1 cm³ of aluminum alloys also contains approximately one quadrillion (10^{15}) nanoparticles that strengthen these alloys in order to be utilized as a structural material for aircrafts, without which modern transport is unimaginable. How do we count the number of stars in a galaxy or the number of nanoparticles in an aluminum alloy? Relatively easy, because we can see the nanoparticles in aluminum alloys using electron microscopes, and stars in a galaxy using telescopes. Scientific discoveries form the basis for scientific and technological progress, and one such example are the discoveries in the fields of nanosciences and nanotechnologies.

Why is this monograph dedicated to nanosciences and nanotechnologies?

To answer this question, we must first answer the question: what are nanoscience and nanotechnology? In the inevitable *Wikipedia*, *Encyclopedia Britannica* (and any other encyclopedia), dictionaries as well as internet sources, the terms "nanoscience" and "nanotechnology" are related to the study, understanding, controlled manipulation of structures and phenomena, and the application of extremely small things, which have at least one dimension less than 100 nm. Modern aspects of nanosciences and nanotechnologies are quite new and have been developing intensively in the last twenty to thirty years, but the nanoscale substances have been used for centuries, if not millennia. Particulate pigments, for example, have been used in ancient China, Egypt, etc., several thousands of years ago. Artists have decorated windows in medieval churches using silver and gold nanoparticles of various sizes and composition, without understanding the origin of the various colors. Nanoparticles that strengthen alloys of iron, aluminum and other metals, have been used for over a hundred years, although they have not been branded with a prefix "nano", but rather called "precipitates". Scientific disci-

plines, involved in significant research activities related to nanoscience and nanotechnology, are: physical metallurgy, materials science and materials engineering, chemistry, physics, biology, electrical engineering, and so on.

Where does the prefix "nano" come from? "Nano" comes from the Greek words *vāvoç*, which means a dwarf, indicating a dimension of one nanometer (1 nm), which represents one-billionth (10^{-9}) of a meter; Similarly, "nanosecond" (ns) denotes a billionth of a second, and so on. This sounds a bit abstract to many, but to put things into context with which we are familiar, we can mention that the diameter of a human hair, for example, is on average about 100.000 nm (10^5 nm = 100 microns = 0.1 mm), which is roughly the bottom threshold of human eye detection; Thickness of newsprint on average is also about 100.000 nm = 100 μ m = 0.1 mm; Person of 2 m height is 2.000.000.000 (2×10^9) nm high. For comparison, if we assume that the diameter of a children's glass marble was 1 nm, then the diameter of the Earth would be 1 m.

When we talk about the structures of inorganic, organic and bio-nanosystems, their dimensions are as follows: Diameter of carbon atom is in the order of 0.1 nm, or one-tenth of a billionth of a meter; Single-wall carbon nanotubes have a diameter of around 2 nm, or 2 billionth of a meter; The width of the deoxyribonucleic acid (DNA) chain is also about 2 nm, or 2 billionths of a meter; Proteins, which can vary in size, depending on how many amino acids they are composed of, are in the range mainly between 2 and 10 nm, or between 2 and 10 billionths of a meter (assuming their spherical shape); Diameter of individual molecules of hemoglobin is about 5 nm, or 5 billionths of a meter.

Indeed, these are small sizes, but why should they be important, or why does size matter? When analyzing physical systems on the nanoscale, their fundamental properties change drastically. Consider the example, melting point of gold: transition temperature of solid to liquid for gold nanoparticles ~ 4 nm in size, is about 400°C, while the melting temperature of bulk (macroscopic) gold is 1063°C. The same can be said for other properties: mechanical properties, electric conductivity, magnetism, chemical reactivity, etc., also may be drastically changed, which means that nanosystems deviate from the laws of classical physics that describe the motion of the planets, the direction of movement of a rockets which carry satellites to explore space, etc. The base of this fascinating behavior of nanostructures are bonds between the atoms. As structures become smaller, more atoms are present on the surface, hence the ratio of the surface area to volume for these structures increases dramatically. It results in a dramatic change of physicochemical properties of nanostructures from the bulk, as well as possible appearance of quantum effects: nanoscale structures become stronger, less brittle, demonstrate enhanced optical and catalytic properties, and generally, are very different compared to the usual, macroscopic system dimensions to which we are accustomed to in everyday practice.

This monograph comprises a number of contributions which illustrate the sparkling and fascinating world of nanoscience and nanotechnology.

Nanoporous organometallic materials, that can mimic the properties of muscles upon outside stimuli, are ideal actuators, thereby offering a unique combination of low operating voltages, relatively large strain amplitudes, high stiffness and strength. These phenomena are discussed in the manuscript of J. Th. M. DeHosson and E. Detsi.

Drugs in nanodimension range will become much more efficient with reduced adverse effects. A typical example are drugs, carried by various types of nanoparticles which have been previously functionalized, so as to only recognize diseased cells which is a highly selective medical procedure on a molecular level. Besides drugs, functionalized nanoparticles can carry radioactive material or a magnetic structure, which in a strong magnetic field develop high temperatures, and destroy cancer cells. Some aspects of electron microscopy utilized in the study of biological nanostructures are discussed in the paper of A. E. Porter and I. G. Theodorou.

Increased production of nanomaterials raises concern about their safety, not only for humans but also for animals and the environment as well. Their toxicity depends on nanoparticle size, shape, surface area, surface chemistry, concentration, dispersion, aggregation, route of administration and many other factors. The review by M. Čolić and S. Tomić summarizes the main aspects of nano-toxicity *in vitro* and *in vivo*, points out relevant tests of demonstrating toxicity and explains the significance of reactive oxygen species, as the main mechanism of nanoparticle cytotoxicity and genotoxicity through the complex interplay between nanoparticles and cellular or genomic components.

Carbon nanomaterials are a large group of advanced materials that are in focus of extensive research, due to their interesting properties and versatile applicability, especially carbon nanostructures doped by covalently bonded heteroatoms (N, B, P, etc.) which leads to improved properties. This topic is discussed in the manuscript by G. Ćirić-Marjanović.

Combinations of optical, magnetic and photocatalytic properties of nanomaterials, especially those with large energy gaps, are of great interest for nanoscience and nanotechnology. One of such systems are TiO₂ nanostructures with different crystal lattices and shapes (spheres, nanotubes, nanorods), either pure or hybrid, in the form of nanocomposites with matrices based on conducting polymers, which is presented in the work of Z. Šaponjić and coauthors.

Design and manufacturing of multifunctional nanomaterials is one of the most important trends in materials nanoscience, where combining nanomaterials of various characteristics, such as ferroelectrics, ferromagnetics and ferroelastics can lead to achieving adequate multifunctionality, a good example of which are multiferroic nanomaterials, presented in the work of V. Srdić and coauthors.

Materials containing crystal grains of nanodimensions can demonstrate dramatically improved properties. Theoretically as well as experimentally, it has been shown that metallic nanostructures can attain a high percentage of theoretical strength, which questions the classical definition of material strength, stated

until recently by textbooks that does not depend on size of a tested sample. Some aspects of mechanisms of formation, growth and shrinking of crystal grains are discussed in the paper of T. Radetić.

Computational methods, including first principal calculations, have been proven to be a powerful tool in allowing investigations of systems of various complexities, spatial and temporal scales. This allows for screening of a large number of systems, which is not experimentally feasible, and also the understanding of general trends which is of great importance for both theoreticians and experimentalists. The use of this concept in applications of metallic and oxide nanoparticles is described in manuscript of I. A. Pašti and coauthors.

Being aware of the importance of nanosciences and nanotechnologies and their global impact on humanity, in the autumn of 2017, Serbian Academy of Sciences and Arts launched a series of lectures dedicated to these topics from which this monograph arose. We hope that this monograph will be of interest to the reader and can serve as a motivation for creating opportunity for research to those who want to find out more about these fascinating fields of sciences and technologies.

Velimir R. Radmilović
Serbian Academy of Sciences and Arts

Jeff Th. M. DeHosson
Royal Netherlands Academy of Arts and Sciences

ФАСЦИНАНТНИ СВЕТ НАНОНАУКА И НАНОТЕХНОЛОГИЈА

Истраживачи чији је рад довео до значајних открића гледају много даље, изван непосредног решавања техничких проблема, постављају себи важна питања, као што су: зашто се дешавају одређене појаве, како се оне развијају и на који начин функционишу? Кроз историју је развијен велики број експерименталних и теоријских метода, које се и дан-данас унапређују, како бисмо обогатили знање о свету који нас окружује и могли да видимо слике светова који измичу људском оку, укључујући ту и проналазак телескопа и микроскопа, који нам омогућавају да видимо „веома велике” и „веома мале” ствари.

Истраживачи који се баве „великим стварима” (универзумом, галаксијама, звездама и планетама) установили су да једна галаксија, око 100.000 светлосних година, у просеку садржи око једну билијарду (10^{15}) звезда. Истраживачи који се баве „малим стварима” (наноструктурама, молекулима, кластерима атома, појединачним атомима, атомским дефектима итд.) установили су да 1 cm^3 легуре алуминијума садржи око једну билијарду (10^{15}) наночестица које ојачавају ту легуру, како би могла да се користи као материјал за израду ваздухоплова, без којих је савремени транспорт незамислив. Како можемо пребројати звезде у једној галаксији или наночестице у једној легури алуминијума? Релативно лако, зато што уз помоћ електронских микроскопа можемо видети наночестице у легурама алуминијума, а звезде у галаксијама уз помоћ телескопа. Научна открића представљају основу научног и технолошког напретка, а један такав пример су открића у области нанонаука и нанотехнологија.

Зашто је ова монографија посвећена нанонаукама и нанотехнологијама?

Да бисмо одговорили на ово питање најпре морамо да установимо шта су то нанонауке и нанотехнологије? Према неизбежној Википедији, Енциклопедији Британици (или било којој другој енциклопедији), речницима, као и изворима са интернета, појмови „нанонаука” и „нанотехнологија” се односе на проучавање, разумевање, контролисано манипулисање структурама и појавама, као и на примену изузетно малих честица, чија је најмање једна димензија у опсегу до 100 nm. Иако су савремени аспекти нанонаука и нанотехнологија сасвим нови и интензивно се развијају у последњих двадесет до тридесет година, облици материје на нано скали користе се већ вековима, ако не и миленијумима. На пример, одређени пигменти коришћени су још у древној Кини и Египту, пре неколико хиљада година. Уметници су украшавали прозоре на средњовековним црквама користећи сребрне и златне наночестице различите величине и састава, при чему нису знали одакле потичу разне боје. Наночестице којима се ојачавају легуре гвожђа, алуминијума и других метала, користе се већ више од сто година,

иако у њиховом називу није садржан префикс „нано”, већ се обично називају „талози”. Научне дисциплине које су укључене у значајне истраживачке активности у области нанонауке и нанотехнологије су: физичка металургија, наука о материјалима и инжењерство материјала, хемија, физика, биологија, електротехника, и тако даље.

Одакле потиче префикс „нано”? Префикс „нано” потиче од грчке речи *νᾶνος*, што значи патуљак, указујући тако на димензију од једног нанометра (1 nm) која представља милијардити део метра (10^{-9} m). Слично томе, „нано-секунда” (ns) означава милијардити део секунде. Ово многим може звучати помало апстрактно, међутим, ствари можемо да поставимо у контекст који је нама познат, и да поменемо, на пример, да пречник власи људске косе у просеку износи 100.000 nm (10^5 nm = 100 микрона = 0.1 mm), што отприлике представља праг онога што може да се опази голим оком. Дебљина новинског папира у просеку такође износи око 100.000 nm = 100 μ m = 0.1 mm. Особа висине 2 m висока је 2.000.000.000 (2×10^9) nm. Поређења ради, ако претпоставимо да је пречник дечијег кликера 1 nm, онда би пречник планете Земље износио 1 m.

Када говоримо о структурама неорганских, органских и природних наносистема, њихове димензије су следеће: пречник атома угљеника је реда величине 0.1 nm, а то је једна десетина милијардитог дела метра; једнозидне угљеничне наноцеви имају пречник од око 2 nm, а то су два милијардита дела метра; ширина ланца дезоксирибонуклеинске киселине (ДНК) такође износи око 2 nm, а то су два милијардита дела метра; пречник протеина, чија величина често варира у зависности од тога од колико се аминокиселина састоје, реда је величине 2–10 nm, или између два и десет милијардитих делова метра (под претпоставком да су сферног облика); пречник појединачних молекула хемоглобина износи око 5 nm, или 5 милијардитих делова метра.

Уистину, ово су све мале димензије, али зашто би оне уопште требало да буду важне, или зашто је величина битна? Када се анализирају физички системи на нано скали, њихова основна својства се драстично мењају. Размотримо, на пример, тачку топљења злата: температура на којој наночестице злата реда величине ~ 4 nm прелазе из чврстог у течно стање износи око 400°C , док је температура топљења макроскопских узорака злата 1063°C . На исти начин мењају се и неке друге особине: механичке особине, електрична проводљивост, магнетизам, хемијска реактивност итд. могу драстично да се промене, што значи да наносистеми одступају од закона класичне физике који описују кретање планета, правац кретања ракета које носе сателите за истраживање свемира итд. Ово фасцинантно понашање наноструктура потиче од веза између атома. Што су структуре мање, то је више атома присутно на површини, услед чега се однос површине и запремине ових структура драстично повећава. Као последица јавља се драматична промена физичко-хемијских својстава наноструктура у односу на структуре макроскопских димензија, као и могућа појава квантних ефеката: структуре на нано скали

постају чвршће, мање крте, показују боља оптичка и каталитичка својства, и, уопштено, веома се разликују од структура уобичајених, макроскопских димензија, које сусрећемо у свакодневној пракси.

Ова монографија садржи низ радова који илуструју фасцинантан свет нанонаука и нанотехнологија.

Нанопорозни органометални материјали, који могу да опонашају особине мишића изложених спољашњим подстицајима, идеални су покретачи, који нуде јединствену комбинацију малих радних напона, релативно велике амплитуде напрезања, велику крутост и снагу. Ове појаве су описане у раду чији су аутори Џ. Т. М. ДеХосон и Е. Детси.

Лекови у области нанодимензија ће постати много ефикаснији и са смањеним штетним ефектима. Типичан пример су лекови које преносе различити типови наночестица, а које су претходно функционализоване тако да препознају само оболеле ћелије, што представља високо селективан поступак на молекуларном нивоу. Поред лекова, функционализоване наночестице могу да буду носачи радиоактивног материјала или магнетних структура, који у јаком магнетном пољу развијају високе температуре и тако уништавају ћелије рака. Одређени аспекти електронске микроскопије који се користе у проучавању биолошких наноструктура описани су у радовима чији су аутори А. Е. Портер и И. Г. Теодору.

Повећана производња наноматеријала изазива забринутост везану за њихову безбедност, не само по здравље људи, већ и за животиње и животну средину. Њихова токсичност зависи од величине наночестица, њиховог облика, величине и хемије површине, концентрације, дисперзије, склоности ка стварању агломерата, начина примене, као и многих других фактора. Рад чији су аутори М. Чолић и С. Томић даје преглед главних аспеката нанотоксичности ин витро и ин vivo, указује на релевантне тестове за утврђивање токсичности, појашњава значај реактивности молекула кисеоника, као главног механизма цитотоксичности и генотоксичности наночестица кроз сложено међудејство наночестица и ћелијских или генских компоненти.

Угњенични наноматеријали представљају велику групу напредних материјала, који због својих занимљивих својстава и широке примењивости заузимају централно место у опсежним истраживањима, нарочито када су у питању угњеничне наноструктуре допиране разнородним атомима, повезаних ковалентним везама (N, B, P итд.), што доводи до побољшања њихових својстава. Ову тему обрађује рад чији је аутор Г. Ћирић-Марјановић.

Комбинације оптичких, магнетских и фотокаталитичких својстава наноматеријала, нарочито оних са великим енергијским процепом, од велике су важности за нанонауке и нанотехнологије. Један од таквих система су TiO_2 наноструктуре са различитим кристалним решеткама и облицима (наносфере, наноцеви, наноштапићи), у чистом или хибридном облику, у облику нанокompозита са основама које су на бази проводних полимера, што је представљено у раду З. Шапоњића и сарадника.

Пројектовање и производња мултифункционалних наноматеријала представљају један од најважнијих трендова у наноуци о материјалима, где комбиновање наноматеријала који поседују различита својства, попут фероелектричности, феромагнетизма и фероеластичности, може довести до постизања одговарајуће мултифункционалности, чији су добар пример мултифероични наноматеријали, који су представљени у раду В. Срдића и сарадника.

Материјали који садрже кристална зрна нанодимензија показују знатно побољшане особине. Теоријски и експериментално је показано да металне наноструктуре могу да достигну висок проценат теоријске чврстоће, што доводи у питање класичну дефиницију чврстоће материјала, којом се, до скоро, у уџбеницима наводило да не зависи од величине испитиваног узорка. У раду Т. Радетић разматрани су неки аспекти механизма формирања, раста и смањивања кристалних зрна.

Показало се да рачунарске методе, укључујући ту и прорачуне на бази првог принципа, представљају моћну алатку која омогућава истраживање система различитих комплексности, како на димензионој тако и на временској скали. Оне омогућавају и преглед великог броја система, што експериментално није изводљиво, као и разумевање општих трендова који су од великог значаја, како за теоретичаре тако и за експериментаторе. Коришћење овог концепта у примени металних и оксидних наночестица описане су у раду чији су аутори И. А. Пашти и сарадници.

Свесна значаја наноука и нанотехнологија, као и њиховог глобалног утицаја на човечанство, Српска академија наука и уметности је у јесен 2017. године покренула серију предавања посвећену овим темама, на основу којих је настала и ова монографија. Надамо се да ће ова монографија бити занимљива читаоцу и да ће моћи да послужи као мотивација за стварање прилика за истраживања онима који желе да сазнају нешто више о овим фасцинантним областима наука и технологија.

Велимир Р. Радмиловић
Српска академија наука и уметности

Џеф Т. М. ДеХосон
Краљевска холандска академија наука и уметности

MODELLING AND SIMULATIONS OF NANOSTRUCTURES

IGOR A. PAŠTI*¹ ANA S. DOBROTA¹, SLAVKO V. MENTUS^{1,2}

A b s t r a c t. – Advancements in contemporary technologies require deep understanding of the link between the structure and properties of novel materials. Computational methods have been proven as a powerful tool in that quest, allowing investigation of systems of various complexity and at different spatial and temporal scales, with a desired composition and without any risk of contamination. Moreover, constant increase of computational power allowed the application of some of the most advanced computational methods at the scales which overcome sub-nanometers (small molecules and clusters of atoms), usually considered as a limit for first principles calculations. While the accuracy of such calculations reaches the experimental one, this approach also allows for the screening of a large number of systems, which is not experimentally feasible, and also the understanding of general trends which is of great importance for both theoreticians and experimentalists. This text will cover author's recent experiences in modelling and simulation of nanoscale systems of different complexity, including metal oxides, metals, carbon materials, molecular networks and complex catalytic systems.

Keywords: nanostructure, materials modelling, electronic structure calculations, reactivity trends, multiscale modelling

INTRODUCTION

A macroscopic physical system can be characterized with a number of well-defined physical properties which change drastically at the system boundary. If the system is macroscopic, its surface has little effect on these properties and the edge effects diminish rather quickly with the distance from the system boundary. However, if one starts to reduce the system size, its surface-to-volume ratio increases, its physical properties change, and new ones come into sight. With the reduction of system dimensions down to nanometers, every atom, being constituent of the system, starts to make a difference, opening a range of possibilities for applying such a system in various contemporary technologies. However, with new possibilities new problems also appear. This relates to the understanding how

*Corresponding author: <igor@ffh.bg.ac.rs>; ¹University of Belgrade – Faculty of Physical Chemistry, Studentski trg 12-16, 11158 Belgrade, Serbia; ²Serbian Academy of Sciences and Arts, Kneza Mihaila 35, 11000 Belgrade, Serbia

such small systems exert their properties under different conditions, how these properties can be controlled and tailored for a given application. For this reason, a great deal of today's materials science is focused on materials which have constituents of internal structure in the nanometer range. These materials are called nanomaterials and present the core of modern nanotechnology.

By definition, *nanoscale* is the "length range approximately from 1 nm to 100 nm" [1]. Following this definition, a *nanomaterial* is a "material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale" [1]. This means that nanomaterials are comprised either of a *nanobject*, having at least one external dimension in the nanoscale or can be considered as nanostructured materials. The latter class of nanomaterials has internal or surface structure on the nanoscale. Nanoobjects could be classified as *nanoparticles*, *nanofibers* and *nanoplates* [2]. While nanoparticles have all three external dimensions in the nanoscale, nanofibers have only two, while nanoplates have only one external dimension in the nanoscale. In principle, any class of materials can be reduced to nanoscale, at least in one dimension. If one speaks of nanomaterials intentionally produced to have selected properties or composition, such material is called a *manufactured nanomaterial* [2]. However, if a nanomaterial is designed for a specific purpose or function it is called an *engineered nanomaterial* [2]. While these two classes of nanomaterials are formed by intentional human action, nature itself provides a wide variety of *natural nanomaterials*.

Our focus will be on manufactured as well as engineered nanomaterials. A good example of a nanomaterial is nanosized platinum. This material is routinely made in form of nanoparticles and their dimensions are usually tuned to be below 10 nm. As platinum has a wide range of applications in modern (nano)technologies, primarily as a catalyst, reduction of the size of platinum particles is extremely important due its high price. By reducing the size of particles, surface-to-volume ratio increases, providing more surface sites for catalytic processes to take place. Nevertheless, properties of platinum atoms located on nanoparticle surface differ from those located in bulk Pt. Low coordination of surface atoms, combined with the effects of edges inevitably lead to altered surface stability and reactivity. One example of such behavior is platinum dissolution. While bulk Pt is very stable and has high standard electrode potential, dissolution of nanosized platinum is experimentally observed and presents a great problem for practical, long-term applications [3–7]. Platinum nanoparticles applied as electrocatalysts in fuel cells are usually deposited on some inert, electronically conductive support, as carbon. Optimal size of such nanocatalyst is around 4 nm. Simple calculation shows that such nanoparticle contains around 2000 Pt atoms which can be distributed within the nanoparticle in various ways, depending its shape. Properties of these nanoparticles can be probed using a range of experimental techniques, as listed in Table 1.

Table 1. Main experimental techniques used to probe nanomaterial properties

Property	Main techniques
Size	Atomic force microscopy (AFM); Dynamic light scattering (DLS); Transmission electron microscopy (TEM); Scanning electron microscopy (SEM)
Shape	Atomic force microscopy (AFM); Transmission electron microscopy (TEM); Scanning electron microscopy (SEM)
External surface (including pore surface and pore distribution)	Gas adsorption measurement (based on Brunauer–Emmett–Teller (BET) theory)
Crystal structure	X-ray diffraction measurement (XRD)
Surface composition and chemistry	X-ray photoelectron spectroscopy (XPS)
Bulk composition and chemistry	Inductively coupled plasma-mass spectrometry (ICP-MS); Nuclear magnetic resonance (NMR)

If we take look at a nanoparticle, it is clear that its atomic structure must not be disregarded. Moreover, due to a small number of atoms constituting a nanoparticle, its surface atoms have a different chemical environment, making every atom essentially different. If platinum nanocatalyst is applied in a realistic system, one will see the average response of the system in terms of performance. However, in order to improve the properties of the nanocatalyst the main question is how differently the surface atoms actually behave in a realistic system. If this question is to be properly answered, one could optimize engineered nanocatalysts in order to maximize their performance. Of course, it is possible to search for the solution using a whole army of experimental techniques, but these techniques must fulfil the requirement of atomic resolution with the possibility of differentiating the states of the catalyst at timescales which correspond to reaction rates. Even though a limited number of such studies can be found in modern scientific literature, their routine application is not foreseen, and it is further de-stimulated by the price of the required experimental facilities.

Considering that, in the case of nanoobjects and nanostructures, one must not disregard their atomistic (and consequently electronic) structure, it is expected that the solution of the aforementioned problems can be sought in the application of computational methods. These methods have their origin in computational solid-state physics and quantum chemistry. Historically speaking, theoretical treatment of a nanoobject would require the solution of the Schrödinger equation [8] which would allow determination of desirable physical observables. Nevertheless, it can be said without making a large mistake, that this task is impossible to accomplish for any realistic system of interest unless a number of approximations is made. A breakthrough in the application of computational techniques in the studies of electronic and crystal structure of materials was achieved with the de-

velopment of Density Functional Theory (DFT) by Hohenberg and Kohn [9, 10]. For this accomplishment Kohn was awarded the Nobel Prize in Chemistry in 1998 [11].

As the computational treatment of nanoobject actually corresponds to the description of its electronic structure, DFT is a natural choice for this task. DFT stands on two pillar theorems, given by Hohenberg and Kohn for the case of an arbitrary number of electrons in a box, subjected to external potential $\mathbf{v}(\mathbf{r})$ [9,10]. The first one states that the system is Hamiltonian and its ground state is uniquely determined by the electron density $n(\mathbf{r})$. The other one recognizes that the total energy of the system is determined by a universal functional $F[n]$. Energy is given as $E[n] = \int \mathbf{v}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n]$ and takes on a minimal value for the ground state $n(\mathbf{r})$. Using the scalar electron density, instead of the many-body wavefunction, simplifies the problem significantly [12]. However, the exact form of the universal functional $F[n]$ is not known. It consists of the kinetic energy of non-interacting electrons, the energy of electron-electron interactions, and the exchange-correlation energy (E_{xc}). This way, uncertainty is reduced to E_{xc} , which makes DFT somewhat approximate, and not first-principles in its full sense. Kohn and Sham [10] derived the self-consistent equations which can be solved iteratively, starting from a estimated $n(\mathbf{r})$. After the convergence, the total energy of the system can be deduced. A proper choice of E_{xc} is of great importance for accurate description of the system [13]. To account for the unknown E_{xc} , various approximations which have proven successful in practice are used, the simplest one being the local density approximation (LDA), employing E_{xc} of a uniform electron gas [14]. Somewhat more complex are the generalized gradient approximation (GGA), in which E_{xc} depends both, on the electron density and its gradient [15], and meta-GGA, in which the second derivatives are also included [16]. Hybrid functionals, which include a certain amount of Hartree-Fock exchange, are also widely used today [17]. Problems associated with the use of DFT approach are also connected with the proper treatment of dispersion interactions [18, 19] which can be alleviated using different semi-empirical terms, or modification of E_{xc} to explicitly treat dispersion interaction. Another problem, which essentially lies in the foundations of DFT, is self-interaction error which is especially severe in the systems with localized d and f states and it is most commonly resolved using the ideas of the Hubbard model [20], adding an extra on-site Coulombic interaction term to the d and/or f states [21–23].

Nowadays, DFT has reached an excellent balance between accuracy and the computational cost [24, 25]. When the DFT-based electronic structure calculations are combined with the use of transition-state theory, which enables formulation of microkinetic models [24, 26] and the incorporation of obtained parameters in kinetic Monte Carlo codes [27, 28], DFT-based studies stand on par with the experimental research, mutually complementing each other. Moreover, computational codes which employ DFT calculations are nowadays stable and benchmarked [29]. To illustrate the importance of accuracy, a simple calculation can be performed. As the kinetics of elementary steps can be described by the Arrhenius equation, an

error in the activation energy of only 0.06 eV changes the reaction rate by a factor of 10 at room temperature (the error in the reaction rate, however, vanishes as the temperature increases). Once the adequate equations are solved, depending on the level of theory used, one can determine crystal and electronic structure, spectral, magnetic and electrical properties of the system, time evolution, complete thermodynamics and so on. Moreover, as recently emphasized by our group [30], its accuracy is high enough to explain and predict reactivity trends. Finally, although direct application of the available codes seems rather tempting, these must not be considered as black boxes. The use of DFT without the appropriate background is, if nothing else, a brave deed.

MODELS

In order to reach ground state electronic structure of the investigated physical system, an appropriate model is needed. In principle, solving the equations underlying both, DFT and wave-function methods will give the electron density of wave function in a self-consistent manner, so the initial configuration of atomic nuclei which span the system is needed. For finite size systems it is natural to define initial position of atomic nuclei (to which inner electron cores can be added, following pseudopotential philosophy). This leads to a cluster model which is typical for quantum chemical calculations of (relatively) small molecules, combined with the wave-function based methods employing localized basis sets. If an extended system is modelled using cluster model, it is set in such a way that atoms are extracted from the system of interest in an arrangement which corresponds to the intact system. This must be done in such a way that the main physical and chemical properties of the modelled system are not affected by cluster size. If one considers a crystalline material, it is natural to use periodic boundary conditions in combination with plane waves which span basis set. This leads to the slab model which is most frequently applied for modelling (nano)materials. The choice of the slab model is similar to the definition of cluster model, but periodic boundary conditions allow simulation of extended (infinite) crystals. In fact, most of the DFT codes which employ periodic boundary conditions (like Quantum ESPRESSO [31, 32] or VASP [33–36]) are also suitable for modelling isolated clusters. This is possible by adding a series of corrections which remove interactions of the model with periodically repeated images. Once the model is set up, the simulation can be done. This includes a range from the evaluation of static properties, like the ground state geometric and electronic structure, to time evolution of nanoscale systems.

Generally speaking, the size of the model used to address desired physical and chemical properties will determine the accuracy and the quality of the obtained data, but also the computational costs. Today, DFT is widely used as a numerical simulation tool for investigating systems consisting of up to 10^2 - 10^3 at-

oms, which is sufficient for the analysis of large molecules (DNA, polymers), solid bulk materials (oxides, metals) and (complex) interfaces. Considering the number of atoms which can be incorporated in DFT models, computational modelling is *de facto* performed at the nanoscale.

As anticipated, the exactness of the model is crucial for the simulation of nanomaterials properties or processes at the nanoscale. Nevertheless, some simplifications have to be made. An excellent example for the limitations of theoretical modelling are electrochemical reactions. In electrochemistry, a wide variety of processes can take place at the electronic conductor/ionic conductor interface (electrode), and these range from electrocatalytic reactions and pseudo-faradaic processes to purely adsorptive processes. Considering 'true' electrochemical reactions, i.e. Faradaic processes which involve charge transfer, virtually every electrochemical reaction can be thought of as an electrocatalytic one [37] as electrode reaction rates commonly depend on the physical and chemical properties of the electrode material. As reviewed recently [30], computational methods have proved to be powerful tools for investigating elementary steps of chemical reactions and catalytic cycles and reveal the key properties of a catalyst while providing valuable insights for the design of novel materials with improved catalytic performances. Moreover, the use of computational methods for the analysis of adsorption processes can be considered as a routine task, excepting some complicated cases where special treatments are necessary. Considering the fact that the electrocatalytic activity of various materials can be analyzed in terms of adsorption properties of reaction intermediates, it all comes down to the analysis of the interaction of electrode materials with various species present at the electrode. However, the electrochemical interface is extremely complex. There is a number of factors that determine kinetics and thermodynamics of an electrode process. These factors include: the coverage of the electrode surface, electrode potential, the presence and the nature of solvent, pH value of the electrolytic solution and others. The inclusion of all these effects into a computational model is rather demanding, if not impossible. According to Santos *et al.* [38], this could present a major problem for first principle modelling of the electrochemical processes in energy conversion systems, as there is no proper way to account for the electrode potential in the calculations [38]. Nevertheless, it appears that at least the treatment of the electrocatalytic process does not require any explicit inclusion of the electrode potential as the trends are usually captured correctly without the inclusion of the electrode potential [39, 40]. Moreover, the presence of solvent can usually be disregarded, while sometimes it can be included implicitly by *a posteriori* correcting of the adsorption energies of reaction intermediates [39, 40]. Hence, by disregarding the effects of the electrode potential and the presence of solvent (in the first approximation) electrochemical processes are treated theoretically as the processes at the solid/gas interface (Fig. 1).

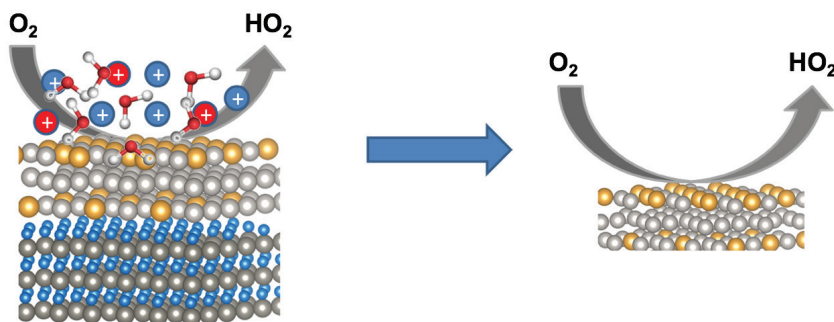


Figure 1. Simplification of an electrode interface on which oxygen reduction reaction (ORR) takes place on thin film catalyst: ORR can be simulated as the reaction taking place at gas/solid interface where the catalyst is modelled only by the thin film phase (thin film support can be disregarded if the film is thick enough, see further).

In the continuation of this text we shall address examples of DFT modelling of nanostructures of various sizes and complexity, emphasizing the possibilities of DFT addressing physical problems at various spatial scales. The results which will be presented have been obtained using slab models combined with the plane-waves approach. Two DFT codes were used, Quantum ESPRESSO and VASP. It should be noted that this is a selective review, and the examples shown from this point on are results of the authors' group.

SMALL SYSTEMS

Lateral dimensions of 1-2 nm

If one takes into account an average chemical bond length, which is approx. 0.15 nm, physical systems spanning up to 1 or 2 nm, consist of a relatively small number of atoms which can be easily treated with moderate computational costs. If the system is 1D (atomic array) there will be 100 atoms, while for 2D systems the number of atoms is 10 to 100. In these cases, direct application of DFT is possible, providing exceptional accuracy. The results can be used to explain experimental observations, or to predict and design new materials, enabling development of engineered nanomaterials.

Oxide-based materials

All elements in the Periodic Table form oxides. Their properties can be rather different and in terms of conductivity they range from insulators to semi-conductors and electronic conductors (possessing metallic properties). For this reason, these materials are widely used in modern technologies. One of the most vibrant fields of application is energy conversion, where oxide materials are im-

plemented in metal-ion batteries, electrochemical capacitors, catalysis, electrocatalysis, and so on.

Several classes of transition metal oxides, which have adequate crystal structure, are able to accommodate metal ions of interest (Li, Na, K, Mg) and are thus used as electrodes in rechargeable batteries. One of these materials is V_2O_5 . Its layered structure enables intercalation of Li (and other small) ions, so it can be used as a cathode in metal-ion batteries. Li intercalation into V_2O_5 is followed by a series of first-order phase transitions, and reversible capacity corresponds to the phase LiV_2O_5 . Further intercalation leads to irreversible transformations [41]. With the theoretical capacity of approx. 294 mA h g^{-1} , V_2O_5 outperforms commonly used cathode materials, making it a very promising cathode material for the next-generation of lithium-ion batteries (LIBs). In fact, the interest in V_2O_5 as an electrode material for LIBs and other types of metal-ion batteries has been revitalized due to the use of lithium metal as anode [42] interest in complementary alkali-ion battery technologies has seen a tremendous resurgence. Out of the set of alternative chemistries, V_2O_5 has seen the most considerable and promising gains as a cathode for Na-ion battery (NIB and extensive search for cathode materials beyond LIBs [42–46] interest in complementary alkali-ion battery technologies has seen a tremendous resurgence. Out of the set of alternative chemistries, V_2O_5 has seen the most considerable and promising gains as a cathode for Na-ion battery (NIB. The layered structure of V_2O_5 allows metal ion intercalation in-between V_2O_5 layers, causing the texture and morphology changes when metal ions are introduced into the structure [41]. While the electrode materials obtained from V_2O_5 show higher energy and power density, and are generally easier to prepare than conventional materials, the main drawback is the decrease in capacity during cycling, which is assumed to arise from the issues associated with low conductivity and material degradation [47]. One of the strategies to overcome the problems related to stability and to improve the electrode performance of V_2O_5 is doping by various transition metals, including Ag, Cu, Zn, Fe, Cr and Mn [48, 49], all of which contribute to an improved stability and better intercalation behavior of metal ions compared to pure V_2O_5 . Experimental studies confirmed an increase of conductivity of V_2O_5 upon doping without significant alteration of its crystal structure. Without detailed insights provided from the experimental data, the effects of doping have to be addressed using computational approach. However, V_2O_5 combines two properties which make “standard” DFT fail. First, the interactions between the layers are dispersive in nature, while the system is highly correlated, leading to inaccurate description of the electronic structure within DFT. For this reason, we have combined classical DFT, in the formulation of Perdew, Burke and Ernzerhof, PBE [15], with D2 correction of Grimme [18] and DFT+ U scheme [23]. This first correction accounts for the dispersion interactions, while the second approach allows correcting for the self-interaction error, as mentioned before. We have shown that within the PBE+D2+ U approach [50] one can accurately describe both crystal (Fig. 2) and electronic structure of pristine V_2O_5 (Fig. 3). As can be seen from Fig.

2, the error in prediction of crystal structure is most severe along the vector c of unit cell which corresponds to interlayer stacking. When dispersion correction is not present, the error is around 15%, while addition of D2 correction reduces the error to 3.5%, which is acceptable within DFT.

Considering the description of the electronic structure, PBE and PBE+D2 lead to significantly underestimated band gap. Upon the inclusion of the on-site Coulombic U term gap opens progressively with the value of U . Using $U = 6$ eV it was possible to fully reproduce experimentally measured band gap, which is close to 2.2 eV [51].

Once the theoretical approach was set, we investigated the effects of doping of V_2O_5 with all 3D metals, from Sc to Zn, taking into consideration both, interstitially and substitutionally doped V_2O_5 . Using rigorous theoretical treatment, we have predicted the appearance of magnetism upon doping and the changes of the electronic structure of parental V_2O_5 . To be precise, we observed that, upon doping band gap narrowing of V_2O_5 occurs which is in line with the experimentally observed conductivity increase. Such changes can be clearly seen in Fig. 4, where Density of States (DOS plots) of doped V_2O_5 are shown. Narrowing of the band gap is due to dopant states which are hybridized with the states of parental V_2O_5 lattice.

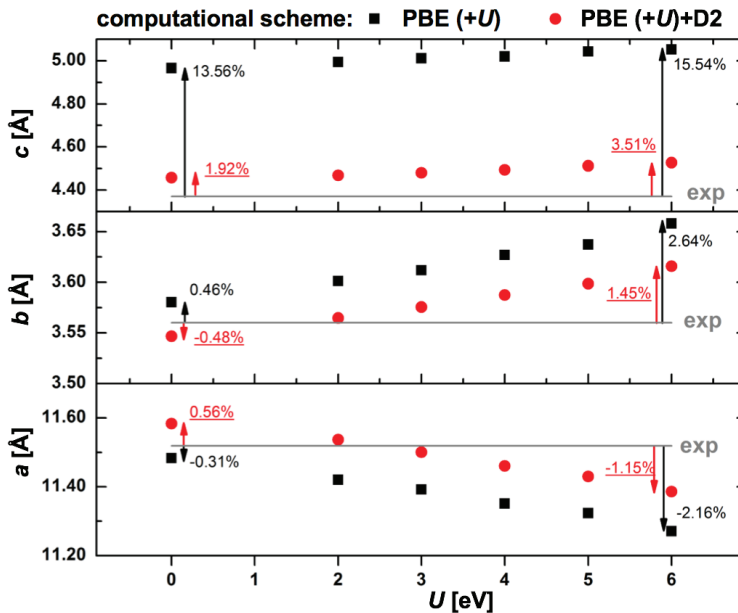


Figure 2. Dependence of the unit cell parameters of pristine V_2O_5 on the applied value of U , depending whether D2 correction was applied (circles) or not (squares). $U = 0$ is equivalent to plain PBE or PBE+D2. Indicated numbers note the relative errors (given in %) of calculated lattice parameters with respect to the experimental values (underlined numbers are for PBE+ U +D2 scheme). Reproduced from ref. [50] with permission from the PCCP Owner Societies.

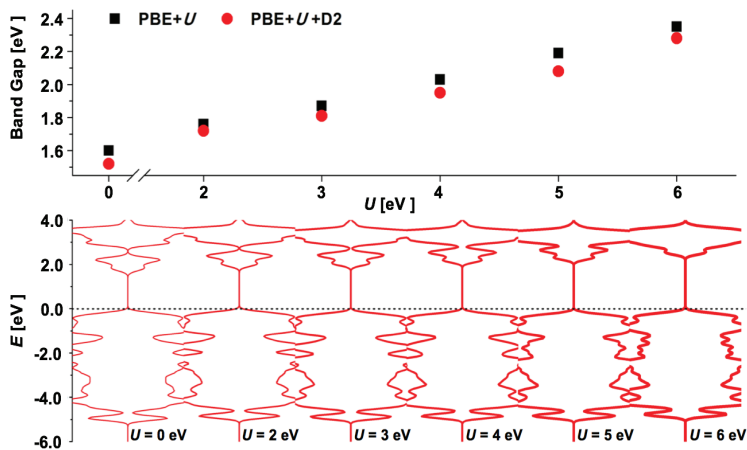


Figure 3. Calculated band gaps of pristine bulk V_2O_5 using PBE+ U (squares) and PBE+ U +D2 (circles), top, and density of states (DOS) obtained using PBE+ U +D2 approach, bottom. Top of the valence band is set to 0 eV. Reproduced from ref. [50] with permission from the PCCP Owner Societies.

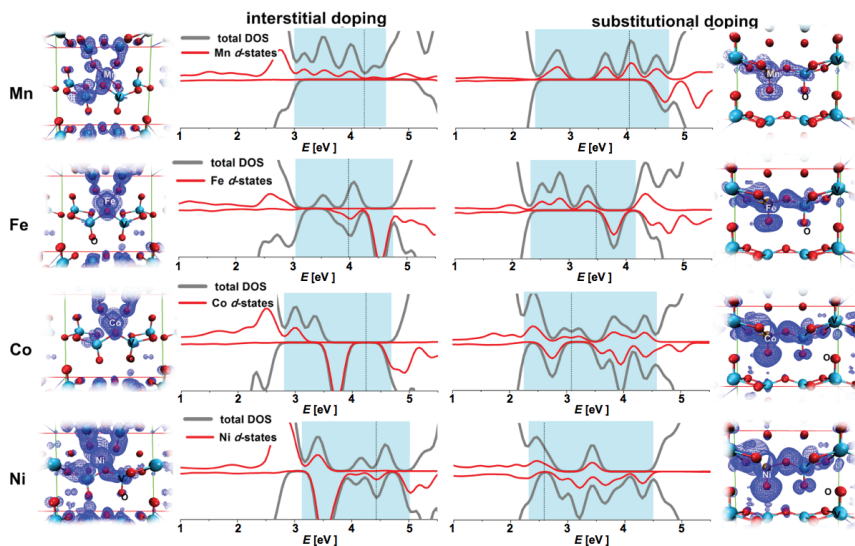


Figure 4. Projected density of states and the corresponding 3D charge density distribution maps of the states within the shaded energy window in the DOS plot.

The results are presented for the case of V_2O_5 doping with Mn, Fe, Co and Ni (left side – interstitial doping, right side – substitutional doping). Vertical dashed lines in the DOS plots indicate Fermi levels. Reproduced from ref. [50] with permission from the PCCP Owner Societies.

This example shows how DFT calculations can be used to address a large number of systems, providing valuable information for practical applications, and also to acquire a deep insight which was not possible to obtain using an experimental approach.

In addition to batteries, oxides are also frequently applied as catalyst supports. For this purpose, chemically inert oxides are used, like MgO. By combining proper surface chemistry of oxides with high dispersion of the catalyst, performance can be significantly boosted. Upon the increase of catalyst dispersion one can reach monoatomic limit entering the field of single atom catalysts. In this limit each atom bears catalytic function which maximizes catalyst utilization. The choice of proper support-catalyst combination can be difficult to achieve and computational tools can be very valuable in this sense. As an example, we show the results of a computational DFT study which analyzes the reactivity of transition dimers supported by MgO in a combinatorial fashion [52]. Not only that the preferred surface structures could be identified in this way (Fig. 5), but also the reactivity of low coordinated atoms can be directly probed.

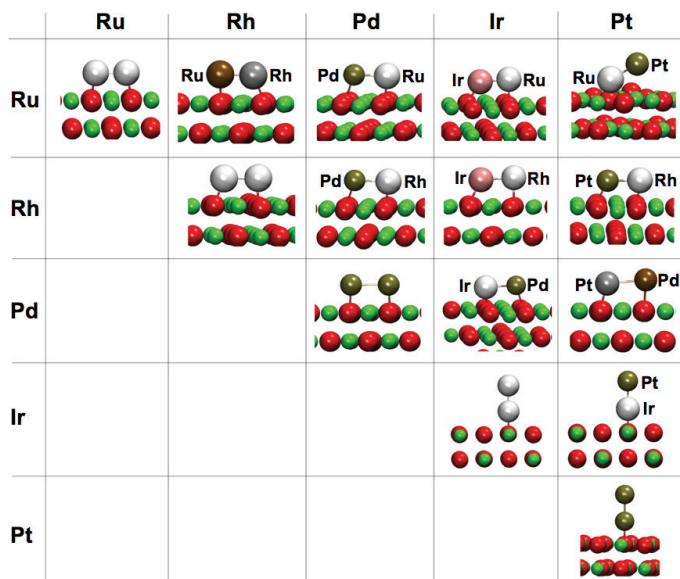


Figure 5. Optimized geometries of the ground state configurations of M1M2 bimetallic dimers on defect-free Mg(001). Reproduced from ref. [52] with permission from the PCCP Owner Societies.

Using the CO molecule as a reactivity probe, we have shown that the chemisorption properties of low coordinated metal atoms on MgO, which are associated with catalyst performance, can be directly linked to the electronic structure of supported atoms in dimers (Fig. 6).

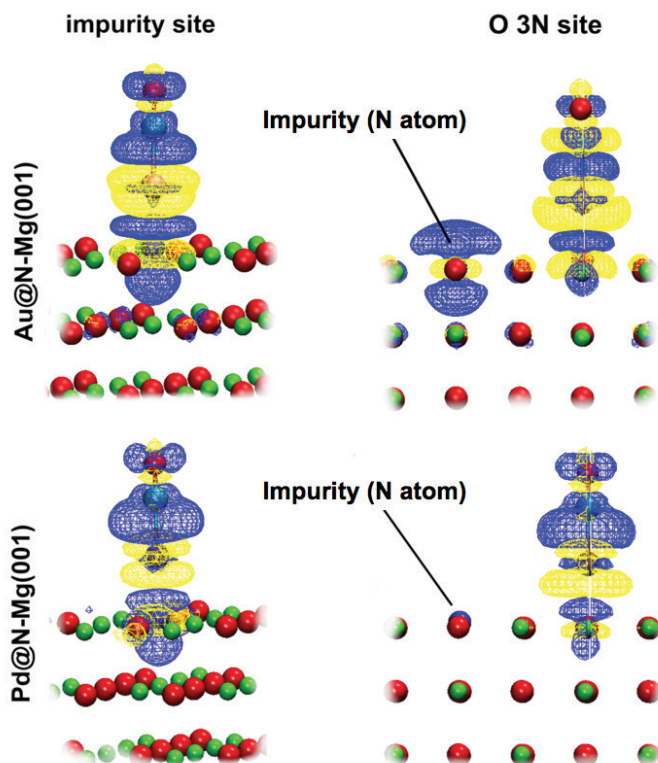


Figure 7. Charge difference plot for the case of CO adsorption on Au (top row) and Pd (bottom row) supported on N-doped MgO(001). Left column depicts the case of metal adsorbed on impurity site while right column is for the case of metal on O 3N site. The isosurface values are $\pm 0.0008 \text{ e \AA}^{-3}$ (blue – build up of charge density, yellow – depletion of charge density). Reproduced from ref. [54] with permission from the PCCP Owner Societies.

Modelling of metals and metallic systems

In these systems, the expensive core of a nanoparticle (which does not have any catalytic function) is replaced with a less expensive metal or alloy. Hence, only the shell contains expensive platinum group metals, which reduces the price of the catalyst. As such, the core should be selected in such a way to provide good adherence to the shell and not to affect the catalytic performance of the shell. One can also ask the question concerning the thickness of the shell: how thick does the shell have to be so that the effects of chemical composition of the core are no longer relevant? Moreover, if the effects of chemical composition of the core are not seen, there is another effect which relates to the lattice mismatch between the core and the shell. Namely, as the shell grows over the core, interfacial layers of the shell adjust to the lattice parameter of the core. This inevitably results with the

surface strain of the shell, which can further affect its surface layers' composition, electronic structure, dissolution tendency and ultimately reactivity.

While it is rather difficult to answer all these questions using an experimental approach, the use of DFT calculations can provide valuable insights into strategies for the design of novel core-shell catalysts. In our recent contribution, we have addressed the effects of strain on the surface composition, dissolution and electronic structure of thin Pd₃M and Pt₃M films (M = Cu, Ag, Au) over various supports, as a model of core-shell (electro)catalysts [62]. A part of the surface of a core-shell nanocatalyst was modelled using various supports (WC, Cu, Ag, Au, Pd or Pt), with (111) orientation for the case of FCC metals and (0001) for the case of WC. The latter substrate was of particular interest as we have shown previously that WC support has very strong influence on the overlayer structure and reactivity [63–65]. In order to estimate segregation tendencies in Pd₃M and Pt₃M shells, DFT calculated total energies of pristine and segregated surfaces which were compared in order to evaluate segregation energies (E_{seg}) [66], as:

$$E_{\text{seg}} = E_{\text{X-seg}} - E_{\text{stoich}} \quad (1)$$

In the equation above, $E_{\text{X-seg}}$ and E_{stoich} stand for the total energy of the segregated slab and the total energy of the stoichiometric slab, respectively. Moreover, dissolution energies of Pd, Pt, Cu, Ag and Au were evaluated for stoichiometric and segregated surfaces, while electronic structure was described using *d*-band centers, which are known as very good descriptors for surface reactivity [67] (see also Fig. 6). As the film is grown on the support in an epitaxial manner, the effects of support were tested by varying the thickness of the film (overlayer). The results of the set of the exact calculations on support/overlayer systems were compared with the results of the calculations for the strained overlayers. Strain in the overlayers was introduced in the range $\pm 6\%$ (in lateral directions). Once the strain dependence of aforementioned properties was known, it was possible to evaluate them for any strain within a given range. Subsequently, the segregation and dissolution energies were estimated for the lattice parameter corresponding to the lattice parameter of the support. We observed that the properties of overlayers approach those of pure strained overlayer surfaces as the thickness of the overlayer approaches three atomic layers (Fig. 8).

The obtained results allowed us to conclude that the properties of the shell in a core-shell catalyst can be reliably estimated using the lattice mismatch between the core and the shell. In other words, if the shell is thick enough (more than three atomic layers), electronic structure, composition, stability and reactivity will be dominated by surface strain. This allows for the screening of desirable core-shell combinations based on the lattice mismatch in order to rationalize the number of candidates which can be tested experimentally.

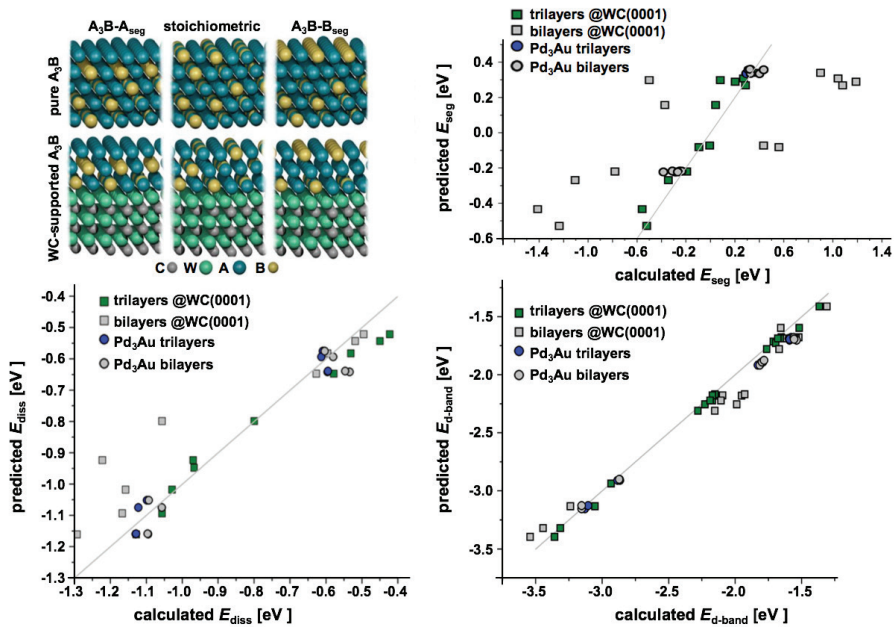


Figure 8. Top left: slab models of segregated and stoichiometric surface both, with and without support; top right: correlation between calculated and estimated dissolution energies for studied core-shell model systems; at the bottom the same correlations are given for dissolution energies and d-band centers. Adapted from ref. [62] with permission from the PCCP Owner Societies.

Modelling of carbon nanostructures

Carbon forms a wide variety of nanostructures, but the most investigated is graphene. It is a two-dimensional sheet of carbon atoms arranged in a honeycomb lattice [68]. Unique electronic structure, combined with high surface area, exceptional thermal and mechanical properties made graphene attractive for many applications [69, 70]. It is also known to be chemically inert, only weakly interacting with other chemical species [71, 72]. However, a better understanding of graphene reactivity would be useful for a variety of applications, where graphene or other carbon materials are the key elements. In order to investigate the reactivity of pristine graphene we have conducted an extensive computational study which addressed atomic adsorption on pristine graphene [73]. In this study, we have included all the elements of the PTE located in rows 1 to 6, excluding lanthanides. Due to inertness of the π electron cloud of pristine graphene it was clear that the treatment of dispersion interactions must be considered, so we have applied different computational schemes, including PBE, PBE+D2, PBE+D3 [19] broader range of applicability, and less empiricism. The main new ingredients are

atom-pairwise specific dispersion coefficients and cutoff radii that are both computed from first principles. The coefficients for new eighth-order dispersion terms are computed using established recursion relations. System (geometry and vdW-DF2 calculations [74, 75]. Pristine graphene was modeled using a one atom thick sheet corresponding to 4×4 cell of graphene, containing 32 atoms. In spite of the fact that single atoms are very reactive species, calculated adsorption energies were rather small, typically under 2 eV (Fig. 9).

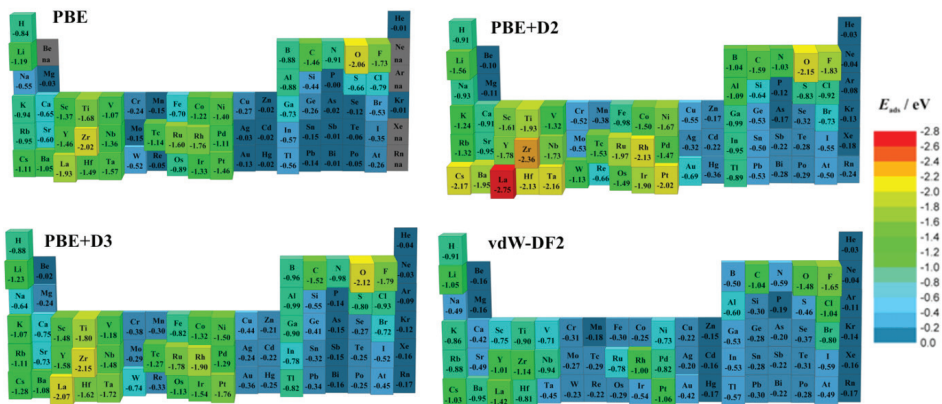


Figure 9. Calculated adsorption energies of the elements located in rows 1-6 of the PTE on pristine graphene. Four different computational schemes are applied, as indicated in the figure. Adapted from ref. [73], ©Elsevier 2018.

Once the adsorption energies were calculated it was obvious that a clear trend along the rows of PTE can be observed. Adsorption energies were found to have minima for the elements with filled electronic shells (Fig. 9). The inclusion of dispersion interactions led to more exothermic adsorption for all the investigated elements. Dispersion interactions were found to be of particular importance for the adsorption of low atomic weight earth alkaline metals, coinage and s-metals (11th and 12th groups), high atomic weight p-elements and noble gases.

Due to demonstrated low reactivity, practical applications of graphene in the fields of energy conversion or catalysis require its appropriate functionalization. In other words, graphene has to be made less ideal. The simplest way to accomplish this is to make a vacancy in the carbon lattice. A vacancy contains three dangling bonds and presents the center of altered reactivity [76–78]. In the existing literature it was not possible to find a comprehensive overview of the interaction of a wide variety of chemical elements with a single vacancy (SV) in graphene. For this reason, we have performed another systematic study covering chemical elements in rows 1-6, interacting with a single vacancy in graphene [79]. In contrast to pristine graphene, we found very strong binding of, basically, all the studied elements (Fig. 10) with graphene single vacancy.

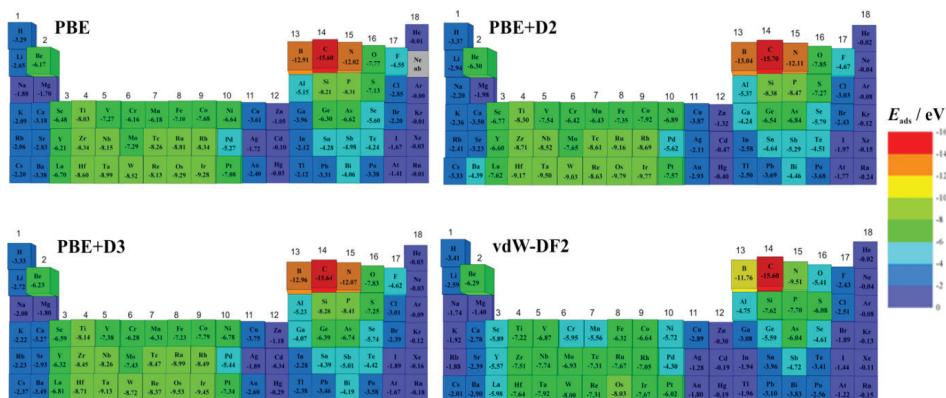


Figure 10. Calculated adsorption energies of the elements located in rows 1-6 of the PTE on pristine graphene. Four different computational schemes are applied, as indicated in the figure. Adapted from ref. [79] with permission from the PCCP Owner Societies.

Once again, when adsorption energies were known with high accuracy it was possible to observe some general trends. It was observed that the adsorption energy scale with the cohesive energies of pure elements follow a simple rule-of-thumb: the higher is the cohesive energy, the element will interact more strongly with the SV site in graphene (Fig. 11). Besides, as thermodynamics are known from the DFT calculations, it was possible to calculate the dissolution potentials of single metal atoms embedded in graphene single vacancy site (Fig. 11). When looking over the entire Periodic Table it was clear that most of the metals entrapped in graphene vacancy behave “more noble” than their pure phases. This means that such systems can potentially be used as single atom catalysts with a wide range of thermodynamic stability.

From Fig. 11 it is interesting to observe very high stability of, for example, Fe, Co and Ni embedded in single vacancy, as these elements easily dissolve in acidic media. One could ask the questions whether these elements (in the form of single atoms) can be used as electrocatalysts as they have very high thermodynamic stability and whether the use of such systems ($M@SV$ -graphene) could provide catalytic action. Taking, for example, the oxygen reduction reaction (ORR), one can use DFT modelling to investigate its steps on $M@SV$ -graphene catalysts. We have performed such analysis and observed that Ni and Co embedded in graphene single vacancy site can easily cleave O-O bonds in O_2 molecule, upon protonation during ORR process (Fig. 12). These results enabled us to explain improved ORR activity of mesoporous carbons containing traces of Ni and Co [80].

Besides the formation of vacancies in graphene, attachment of various functional groups on its surface can also play a significant role in alteration of its properties. Oxygen functional groups are inevitably present on graphene surface and this can have a very important role in charge storage applications of graphene [81].

We have used DFT modelling to investigate the alteration of structural, electronic, and chemical properties of oxygen-functionalized graphene [72], its ability to store alkali metals [82], the interactions between oxygen functional groups over graphene basal plane [83], the interactions of oxygen functional groups with heteroatoms incorporated in graphene basal plane [76], and so on.

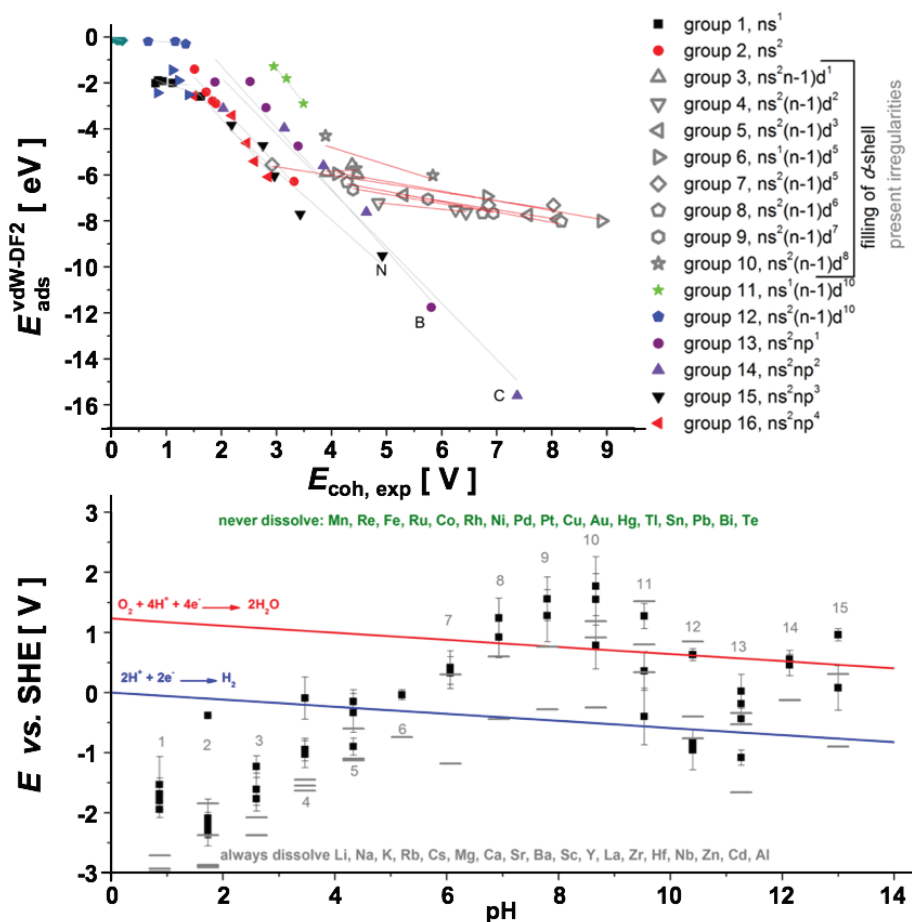


Figure 11. Top: Correlation between the cohesive energy and the adsorption energy calculated using vdW-DF2 scheme, bottom: Average electrode potentials for the dissolution of metal adsorbed at the SV site of graphene. Numbers next to symbols denote the PTE group. Data points give the average electrode potential obtained using four computational schemes while the error bars indicate their variation among the used methods. Note that the data points for the electrode potentials of the considered metals are not linked to pH scale. Horizontal lines give electrode potentials for the pure metallic phases of given elements. Reproduced from ref. [79] with permission from the PCCP Owner Societies.

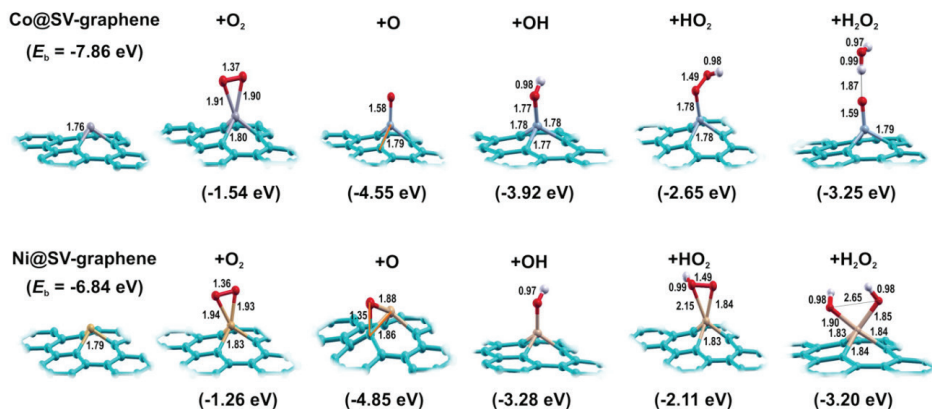


Figure 12. Optimized structures of Co@SV-graphene and Ni@SV-graphene with O₂ and ORR intermediates. Bond lengths are given in angstroms. Adsorption energies of O₂ and ORR intermediates are given in parentheses below the presented structures and are in eV units. Reproduced from ref. [80].

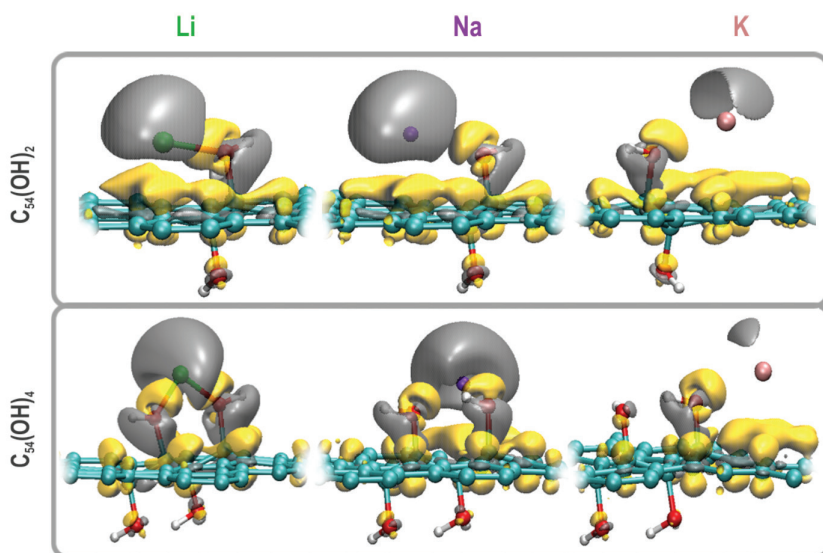


Figure 13. Charge difference plots for alkali metal adsorption on OH-dimer and tetramer on graphene. Yellow surfaces indicate charge gain, while grey surfaces indicate charge depletion (compared to non-interacting metal and n OH-graphene).

Isosurface values are ± 0.0015 e Å⁻³. Reproduced from ref. [83] with permission from the Royal Society of Chemistry.

Considering the storage of alkali metals on oxygen functionalized graphene, DFT calculations have been particularly useful for the identification of redox-active domains of functionalized graphene basal plane. One of the main conclusions in the mentioned studies is that the redox activity cannot be limited to one oxygen functional group. Rather a whole assembly of these groups, and a certain domain of the basal plane, are involved together in the localization of an electron provided through the external circuit and the stabilizing interaction with M^+ ion coming from the electrolyte, so that the process of alkali metal ion storage on oxygen functionalized graphene can be presented (under electrochemical conditions) as [83]:



Such behavior can be depicted using charge difference analysis. In this approach, ground state charge densities before and after M^+ interaction with graphene sheet, obtained in DFT calculations, are compared. Fig. 13 shows how OH dimers and tetramers localize charge upon the interaction with Li, Na and K.

MODELLING OF MEDIUM SIZE SYSTEMS

Lateral dimensions up to 10 nm

The systems with lateral dimensions up to 10 nm contain from a couple of hundreds to couple of thousands of atoms. There are examples of direct use of DFT calculations for systems of this size, but these cases are rather rare [84]. However, increasing strength of today's computers and existing large scale computational infrastructure make such calculations possible. In contrast to the cases demonstrated in Section 3, the size and complexity of these systems make systematic studies rather demanding and computationally expensive. Hence, the use of DFT calculations is, in this case, primarily for explanatory purposes.

Here, we shall show an example of the application of DFT calculations for the systems containing hundreds of atoms in the case of ordered molecular networks on metallic surface. Individual adsorbates on metallic surfaces exhibiting a Shockley surface state are known to scatter this electronic state [85]. Thus, with the help of artificially fabricated on-surface structures, the surface state can be confined and thereby, quantum units can be generated [86–88]. A practical way to fabricate arrays consisting of hundreds of quantum units is provided by on-surface self-assembly, ultimately assuring high precision concerning the individual quantum unit, the periodicity of the array and the coupling with the surrounding units [89]. The coupling strength depends on the properties of the confining barrier, especially on its interaction with the surface. Recently, it was observed that the

coupling strength can also be tuned by dosing different adsorbates on confining barrier which form a network over Ag(111) surface [90]. Taking C_{60} and Xe atoms as adsorbates, it was observed that the C_{60} adsorbs inside the pore and affects inter-pore coupling, while Xe adsorbs on confining barrier (molecule on Ag(111) surface) (Fig. 14).

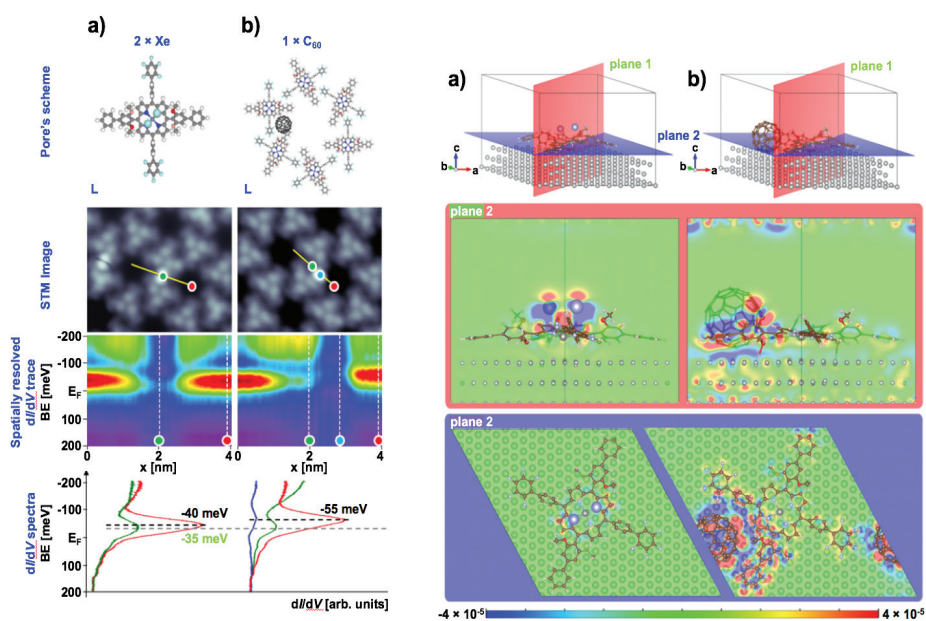


Figure 14. Left: STM images and STS spectra of adsorbate-modified confining barriers; right: charge difference analysis of C_{60} and Xe adsorption on confining barrier + Ag(111) surface system. Reprinted with permission from ref. [90]. Copyright 2018 ACS Publications.

The use of DFT calculations for this system required certain simplification in order to derive an adequate model. It was not possible to reproduce an entire pore, so, as a model a 10×10 cell of Ag(111) was taken with one confining barrier molecule on top of it. When adsorbates were added it was confirmed that C_{60} tends to bind to Ag(111) next to the confining barrier, while Xe atoms adsorb on top of the confining barrier molecule. Moreover, it was shown that Xe does not affect electron density distribution of confining barrier + Ag(111) surface system, which is not the case for C_{60} (Fig. 14) where it was found to affect the charge distribution significantly, which allowed to explain experimentally observed changes in scanning tunnelling spectroscopy (STS) spectra (Fig. 14).

MODELLING OF LARGE SYSTEMS

Lateral dimensions – tens of nm

When a nanostructure or nanoobject spans over tens of nanometers, it consists of thousands of atoms. Direct application of DFT, or any electronic structure calculations, is not feasible in this case. Thus, modelling requires significant simplification and various strategies can be used for this purpose. One of the possibilities is to model parts of a large nanostructure, as described in Section 3. Modelling of core-shell nanocatalysts described previously is also an example of “local modelling” of a large nanosystem. Another option, particularly when the system is complex, is to address thermodynamic properties of building units in order to rationalize experimentally observed behavior.

An example of decomposition approach can be found in Ref. [91] where reduced graphene oxide/Ni foam composite (rGO@Ni) was used as an electrocatalyst for hydrogen evolution reaction (HER) (Fig. 15). The catalyst was made by electrochemical reduction and deposition of graphene oxide (GO) onto the Ni foam substrate.

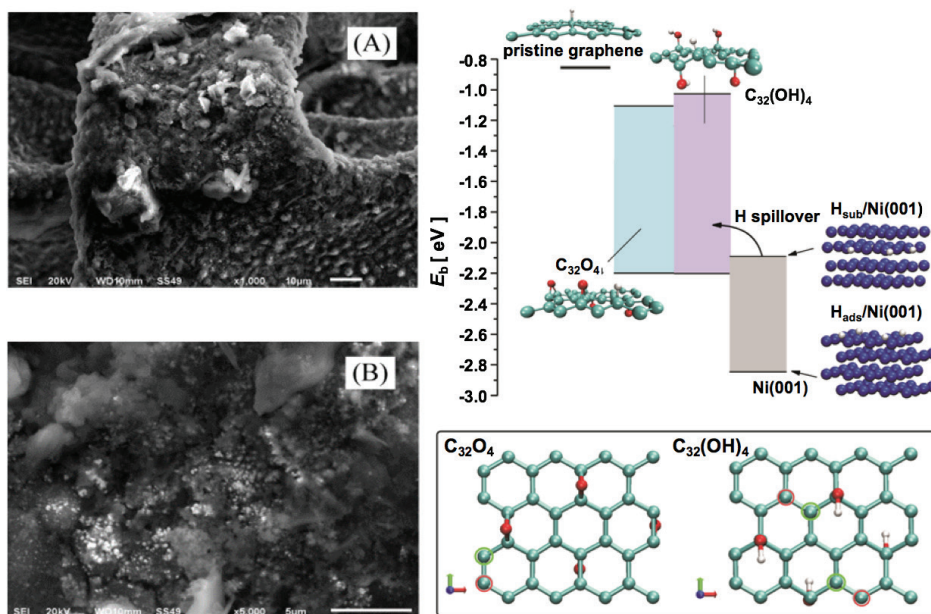


Figure 15. Left: SEM micrographs of rGO/Ni foam electrocatalysts (A and B); right: thermodynamic consideration of H interaction with constituents of the system. Bottom right: models of rGO used in the work. Adapted from ref. [91] with permission from the PCCP Owner Societies.

Due to the complexity of rGO@Ni electrocatalyst it was not possible to model it as such. However, by analyzing the interactions of H, formed upon water discharge, with Ni surface, the possibility of formation of Ni-hydride and the interaction of H with rGO, it was possible to propose the mechanism of the improved HER activity of such catalyst. Namely, H transfer (spillover) from Ni surface to rGO is energetically more favorable than Ni-hydride formation, so H atoms during HER get transferred to rGO. In this way, Ni surface gets cleaned and active sites for H₂O discharge are recovered without activity losses due to hydride formation. Once H atoms are on rGO, they recombine quickly and H₂ is produced. As a result, rGO@Ni catalyst outperforms Pt/C nanocatalyst in terms of activity and stability under operating conditions [91]. The described study led us to ask a question if the strategy for making metal/rGO composites can be generalized. In principle, if the catalyst formed by rGO deposition on Ni shows improved HER performance due to H spillover, then Ni deposited on rGO (Ni@rGO) should also show better HER performance than rGO or Ni.

These Ni@rGO catalysts were further produced by electrochemical deposition on rGO (formed during Ni deposition by GO reduction) and their HER performance was confirmed to be better than HER performance of Ni catalyst [92]. DFT modelling of such a complex was, again, impossible, although DFT was used to understand initial steps of Ni deposition on rGO, using “local approach”. However, in order to explain high HER activity, which also depended on the electrodeposition time in a non-monotonous way, another modelling approach was used. Namely, Kinetic Monte Carlo (KMC) simulations were employed [28, 93, 94]. This approach allows following the evolution of the system looking only at the slow processes which are defined before simulation. In this sense, KMC cannot provide new physics and chemistry but can deal from tens to hundreds of thousands of atoms, addressing temporal and spatial scales which are well beyond the limits of DFT methods. A general scheme for modelling HER on supported nanocatalyst was previously established [95] and employed for this purpose. The effects of H spillover, previously proposed for rGO@Ni catalyst, were tested by changing support (rGO) coverage by Ni particles (catalyst) and simultaneous variation of H spillover rate from the catalyst to the support (Fig. 16).

By changing surface coverage, the effects of deposition time were addressed. When the results of KMC simulations were compared with the experimental ones, it was concluded that there is optimum electrodeposition time, i.e. support coverage by catalyst, which maximized catalytic activity. This is the case only if the spillover rate is sufficiently high (Fig. 16), otherwise catalytic activity increases monotonically with the number of catalytically active sites (i.e. Ni coverage). The knowledge accumulated using KMC simulations was applied to further improve HER activity of Ni@rGO by electrochemical formation of Ni-Mo@rGO catalysts [96].

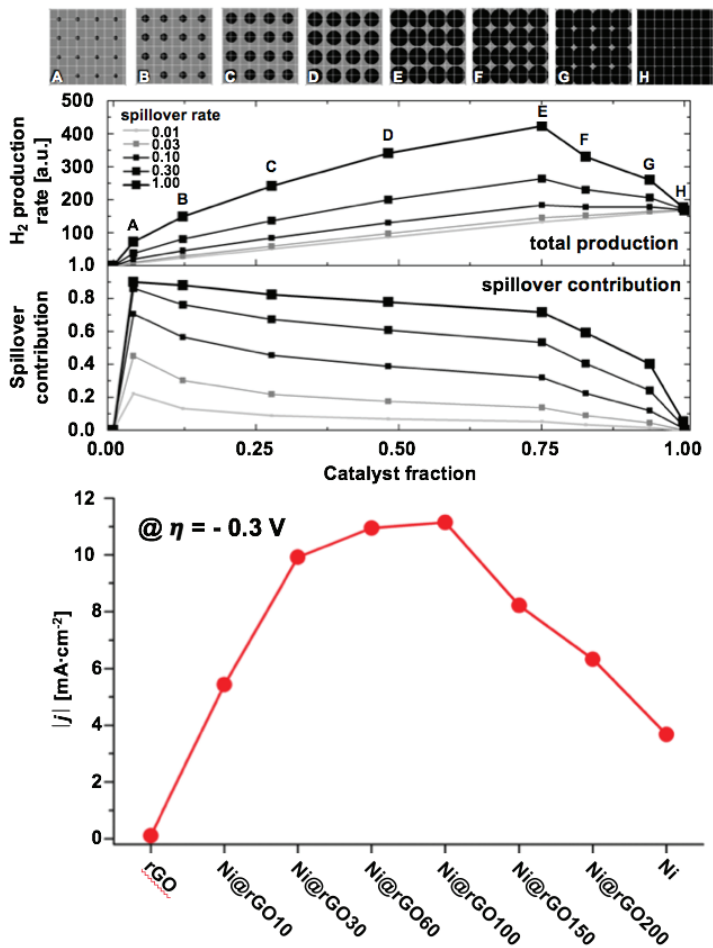


Figure 16. Model of Ni@rGO catalyst with various surface coverage by Ni particles. Lateral dimensions are approx. 50 nm × 50 nm (top), the results of KMC simulations for different catalyst/support configurations and H spillover rates (middle) compared with experimentally measured HER currents for the catalyst obtained by changing Ni electrodeposition time (HER overvoltage -0.3 V). Reproduced from ref. [96] with permission from the PCCP Owner Societies.

CONCLUSION AND OUTLOOK

Computational modelling of nanoobjects and nanostructures provides valuable atomic-level information necessary to understand the physics and chemistry at nanoscale. In authors' opinion, Density Functional Theory provides an optimal balance between the accuracy, computational cost and the possibility to address

the objects at various spatial scales. While modelling of small nanoscale systems, up to a hundred atoms is rather simple, treatment of larger systems, with thousands of atoms is still difficult and requires large scale computational facilities. Further integration of computational modelling in modern nanoscience is anticipated in the coming years due to the constant growth of computational power, development of novel theoretical methods and improved algorithms for solving equations which describe physical systems at various levels of complexity. The impact of multiscale modelling by combination of DFT and other approaches, like Monte Carlo simulations, will grow over time and will allow addressing local physical and chemical properties with the accuracy which approaches the experimental one as well as the possibility to analyze spatial and temporal scales which are far beyond the limits of advanced electronic structure methods.

Acknowledgements. This work was supported by the Serbian Ministry of Education, Science, and Technological Development through the projects III45014 and NATO Project EAP.SFPP 984925 - "DURAPEM - Novel Materials for Durable Proton Exchange Membrane Fuel Cells". S.V.M. is indebted to Serbian Academy of Sciences and Arts for funding the research through the project No F-190. I.A.P. acknowledges the support from Carl Tryggers Foundation for Scientific Research. I.A.P. would like to thank to Prof. Natalia Skorodumova and Prof. Börje Johansson for helpful discussions.

REFERENCES

- [1] *International Organization for Standardization, Nanotechnologies–Vocabulary–Part 1: Core Terms*, (2015) ISO/TS 80004-1:2015(en).
- [2] *International Organization for Standardization, Nanotechnologies - Vocabulary - Part 2: Nano-objects*, (2015) ISO/TS 80004-2:2015(en).
- [3] N. Hodnik, C. Jeyabharathi, J. C. Meier, A. Kostka, K. L. Phani, A. Rečnik, M. Bele, S. Hočevar, M. Gaberšček, K. J. J. Mayrhofer, Effect of ordering of PtCu₃ nanoparticle structure on the activity and stability for the oxygen reduction reaction, *Phys. Chem. Chem. Phys.* 16 (2014) 13610–13615.
- [4] S. Cherevko, G. P. Keeley, S. Geiger, A. R. Zeradjanin, N. Hodnik, N. Kulyk, K. J. J. Mayrhofer, Dissolution of Platinum in the Operational Range of Fuel Cells, *Chem. Electro.Chem.* 2 (2015) 1471–1478.
- [5] P. Jovanovič, A. Pavlišič, V. S. Šelih, M. Šala, N. Hodnik, M. Bele, S. Hočevar, M. Gaberšček, New Insight into Platinum Dissolution from Nanoparticulate Platinum-Based Electrocatalysts Using Highly Sensitive In Situ Concentration Measurements, *Chem. Cat. Chem.* 6 (2014) 449–453.
- [6] A. Pavlišič, P. Jovanovič, V. S. Šelih, M. Šala, M. Bele, G. Dražič, I. Arčon, S. Hočevar, A. Kokalj, N. Hodnik, M. Gaberšček, Atomically Resolved Dealloying of Structurally Ordered Pt Nanoalloy as an Oxygen Reduction Reaction Electrocatalyst, *ACS Catal.* 6 (2016) 5530–5534.

- [7] V. E. Guterman, S. V. Belenov, A. A. Alekseenko, R. Lin, N. Y. Tabachkova, O. I. Safronenko, Activity and Stability of Pt/C and Pt-Cu/C Electrocatalysts, *Electrocatalysis*. (2018) 1–13.
- [8] E. Schrödinger, A Method of Determining Quantum-Mechanical Eigenvalues and Eigenfunctions, *Proc. R. Irish Acad. Sect. A Math. Phys. Sci.* 46 (1940/1941) 9–16.
- [9] P. Hohenberg, W. Kohn, Inhomogeneous Electron Gas, *Phys. Rev.* 136 (1964) B864–B871.
- [10] W. Kohn, L. J. Sham, Self Consistent Equations Including Exchange and Correlation effects, *Phys. Rev.* 140 (1965) A1133–A1138.
- [11] W. Kohn, Nobel Lecture: Electronic structure of matter—wave functions and density functionals, *Rev. Mod. Phys.* 71 (1999) 1253–1266.
- [12] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, First-principles simulation: ideas, illustrations and the CASTEP code, *J. Phys. Condens. Matter.* 14 (2002) 2717–2744.
- [13] D. W. Boukhvalov, Y. Wu, Y. Hao, J. Geng, M. Charlton, S. Chen, Y. Ren, H. Ji, H. Li, D. W. Boukhvalov, R. D. Piner, C. W. Bielawski, R. S. Ruoff, K. S. Novoselov, L. A. Ponomarenko, DFT modeling of the covalent functionalization of graphene: from ideal to realistic models, *RSC Adv.* 3 (2013) 7150.
- [14] J. P. Perdew, Density-functional approximation for the correlation energy of the inhomogeneous electron gas, *Phys. Rev. B.* 33 (1986) 8822–8824.
- [15] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868.
- [16] J. P. Perdew, S. Kurth, A. Zupan, P. Blaha, Accurate Density Functional with Correct Formal Properties: A Step Beyond the Generalized Gradient Approximation, *Phys. Rev. Lett.* 82 (1999) 2544–2547.
- [17] M. Marsman, J. Paier, A. Stroppa, G. Kresse, Hybrid functionals applied to extended systems, *J. Phys. Condens. Matter.* 20 (2008) 64201.
- [18] S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *J. Comput. Chem.* 27 (2006) 1787–1799.
- [19] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* 132 (2010) 154104.
- [20] A. Georges, G. Kotliar, Hubbard model in infinite dimensions, *Phys. Rev. B.* 45 (1992) 6479–6483.
- [21] A. I. Liechtenstein, V. I. Anisimov, J. Zaanen, Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators, *Phys. Rev. B.* 52 (1995) R5467–R5470.
- [22] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study, *Phys. Rev. B.* 57 (1998) 1505–1509.
- [23] M. Cococcioni, S. de Gironcoli, Linear response approach to the calculation of the effective interaction parameters in the LDA + U method, *Phys. Rev. B.* 71 (2005) 35105.
- [24] J. E. Sutton, W. Guo, M. A. Katsoulakis, D. G. Vlachos, Effects of correlated parameters and uncertainty in electronic-structure-based chemical kinetic modelling, *Nat. Chem.* 8 (2016) 331–337.

- [25] J. K. Nørskov, T. Bligaard, J. Rossmeisl, C. H. Christensen, Towards the computational design of solid catalysts, *Nat. Chem.* 1 (2009) 37–46.
- [26] D. Teschner, G. Novell-Leruth, R. Farra, A. Knop-Gericke, R. Schlögl, L. Szentmiklósi, M. G. Hevia, H. Soerijanto, R. Schomäcker, J. Pérez-Ramírez, N. López, In situ surface coverage analysis of RuO₂-catalysed HCl oxidation reveals the entropic origin of compensation in heterogeneous catalysis, *Nat. Chem.* 4 (2012) 739–745.
- [27] S. Pogodin, N. López, A More Accurate Kinetic Monte Carlo Approach to a Monodimensional Surface Reaction: The Interaction of Oxygen with the RuO₂ (110) Surface, *ACS Catal.* 4 (2014) 2328–2332.
- [28] M. Stamatakis, D. G. Vlachos, A graph-theoretical kinetic Monte Carlo framework for on-lattice chemical kinetics, *J. Chem. Phys.* 134 (2011) 214115.
- [29] K. Lejaeghere, G. Bihlmayer, T. Björkman, P. Blaha, S. Blügel, V. Blum, D. Caliste, I. E. Castelli, S. J. Clark, A. Dal Corso, S. De Gironcoli, T. Deutsch, J. K. Dewhurst, I. Di Marco, C. Draxl, M. Duřák, O. Eriksson, J. A. Flores-Livas, K. F. Garrity, L. Genovese, P. Giannozzi, M. Giantomassi, S. Goedecker, X. Gonze, O. Grånäs, E. K. U. Gross, A. Gulans, F. Gygi, D. R. Hamann, P. J. Hasnip, N. A. W. Holzwarth, D. Iuřan, D. B. Jochym, F. Jollet, D. Jones, G. Kresse, K. Koepnik, E. Küçükbenli, Y. O. Kvashnin, I. L. M. Locht, S. Lubeck, M. Marsman, N. Marzari, U. Nitzsche, L. Nordström, T. Ozaki, L. Paulatto, C. J. Pickard, W. Poelmans, M. I. J. Probert, K. Refson, M. Richter, G. M. Rignanese, S. Saha, M. Scheffler, M. Schlipf, K. Schwarz, S. Sharma, F. Tavazza, P. Thunström, A. Tkatchenko, M. Torrent, D. Vanderbilt, M. J. Van Setten, V. Van Speybroeck, J. M. Wills, J. R. Yates, G. X. Zhang, S. Cottenier, Reproducibility in density functional theory calculations of solids, *Science* (80-.). 351 (2016) aad3000.
- [30] I. A. Pašti, N. V. Skorodumova, S. V. Mentus, Theoretical studies in catalysis and electrocatalysis: From fundamental knowledge to catalyst design, *React. Kinet. Mech. Catal.* 115 (2015) 5–32.
- [31] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, *J. Phys. Condens. Matter.* 21 (2009) 395502.
- [32] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. De Gironcoli, P. Delugas, R. A. Distasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H. Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H. V. Nguyen, A. Otero-De-La-Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, S. Baroni, Advanced capabilities for materials modelling with Quantum ESPRESSO, *J. Phys. Condens. Matter.* 29 (2017) 465901.

- [33] G. Kresse, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B.* 59 (1999).
- [34] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* 6 (1996) 15–50.
- [35] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, *Phys. Rev. B.* 47 (1993) 558–561.
- [36] G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metal-amorphous- semiconductor transition in germanium, *Phys. Rev. B.* 49 (1994) 14251–14269.
- [37] J. Cheng, P. Hu, Utilization of the Three-Dimensional Volcano Surface To Understand the Chemistry of Multiphase Systems in Heterogeneous Catalysis, *J. Am. Chem. Soc.* 130 (2008) 10868–10869.
- [38] E. Santos, P. Quaino, W. Schmickler, Theory of electrocatalysis: hydrogen evolution and more, *Phys. Chem. Chem. Phys.* 14 (2012) 11224–11233.
- [39] J. Greeley, J. Rossmeisl, Theoretical trends in particle size effects for the oxygen reduction reaction, *Zeitschrift Für Phys. Chemie.* 221 (2007) 1209–1220.
- [40] L. Yu, X. Pan, X. Cao, P. Hu, X. Bao, Oxygen reduction reaction mechanism on nitrogen-doped graphene: A density functional theory study, *J. Catal.* 282 (2011) 183–190.
- [41] C. Delmas, H. Cognac-Auradou, J. Cocciantelli, The $\text{Li}_x\text{V}_2\text{O}_5$ system: An overview of the structure modifications induced by the lithium intercalation, *Solid State Ionics.* 69 (1994) 257–264.
- [42] J. Yao, Y. Li, R. C. Massé, E. Uchaker, G. Cao, Revitalized interest in vanadium pentoxide as cathode material for lithium-ion batteries and beyond, *Energy Storage Mater.* 11 (2018) 205–259.
- [43] I. Stojković, N. Cvjetičanin, S. Marković, M. Mitrić, S. Mentus, Electrochemical behaviour of V_2O_5 xerogel and V_2O_5 xerogel/C composite in an aqueous LiNO_3 and $\text{Mg}(\text{NO}_3)_2$ solutions, *Acta Phys. Pol. A.* 117 (2010) 838–840.
- [44] S. H. Lee, R. A. DiLeo, A. C. Marschilok, K. J. Takeuchi, E. S. Takeuchi, Sol Gel Based Synthesis and Electrochemistry of Magnesium Vanadium Oxide: A Promising Cathode Material for Secondary Magnesium Ion Batteries, *ECS Electrochem. Lett.* 3 (2014) A87–A90.
- [45] M. Vujković, I. Pašti, I. Simatović, B. Šljukić, M. Milenkovic, S. Mentus, The influence of intercalated ions on cyclic stability of V_2O_5 /graphite composite in aqueous electrolytic solutions: experimental and theoretical approach, *Electrochim. Acta.* 176 (2015) 130–140.
- [46] R. C. Massé, E. Uchaker, G. Cao, Beyond Li-ion: electrode materials for sodium- and magnesium-ion batteries, *Sci. China Mater.* 58 (2015) 715–766.
- [47] B. Owens, S. Passerini, W. Smyrl, Lithium ion insertion in porous metal oxides, *Electrochim. Acta.* 45 (1999) 215–224.
- [48] Y. Wei, C. W. Ryu, K. B. Kim, Cu-doped V_2O_5 as a high-energy density cathode material for rechargeable lithium batteries, *J. Alloys Compd.* 459 (2008) L13–L17.
- [49] D. Liu, S. Zhan, G. Chen, W. Pan, C. Wang, Y. Wei, High energy density lithium ion batteries using $\text{Li}_{2.6}\text{Co}_{0.4-x}\text{Cu}_x\text{N}$ (anode) and $\text{Cu}_{0.04}\text{V}_2\text{O}_5$ (cathode) electrode materials, *Mater. Lett.* 62 (2008) 4210–4212.

- [50] A. Jovanovic, A. Dobrota, L. D. Rafailovic, S. V. Mentus, I. A. Pašti, B. Johansson, N. V. Skorodumova, Structural and electronic properties of V_2O_5 and their tuning by doping with 3d elements – Modelling with DFT+ U method and dispersion correction, *Phys. Chem. Chem. Phys.* 20 (2018) 13934–13943.
- [51] E. E. Chain, Optical properties of vanadium dioxide and vanadium pentoxide thin films, *Appl. Opt.* 30 (1991) 2782–2787.
- [52] I. A. Pašti, M. R. Baljzović, L. P. Granda-Marulanda, N. V. Skorodumova, Bimetallic dimers adsorbed on a defect-free MgO(001) surface: bonding, structure and reactivity, *Phys. Chem. Chem. Phys.* 17 (2015) 9666–9679.
- [53] I. A. Pašti, N. V. Skorodumova, Structural, electronic, magnetic and chemical properties of B-, C- and N-doped MgO(001) surfaces, *Phys. Chem. Chem. Phys.* 18 (2016) 426–435.
- [54] I. A. Pašti, B. Johansson, N. V. Skorodumova, Tunable reactivity of supported single metal atoms by impurity engineering of the MgO(001) support, *Phys. Chem. Chem. Phys.* 20 (2018) 6337–6346.
- [55] J. Y. Cheon, T. Kim, Y. Choi, H. Y. Jeong, M. G. Kim, Y. J. Sa, J. Kim, Z. Lee, T. H. Yang, K. Kwon, O. Terasaki, G. G. Park, R. R. Adzic, S. H. Joo, Ordered mesoporous porphyrinic carbons with very high electrocatalytic activity for the oxygen reduction reaction, *Sci. Rep.* 3 (2013) 2715.
- [56] C. Koenigsmann, A. C. Santulli, K. Gong, M. B. Vukmirovic, W. Zhou, E. Sutter, S. S. Wong, R. R. Adzic, Enhanced Electrocatalytic Performance of Processed, Ultrathin, Supported Pd–Pt Core–Shell Nanowire Catalysts for the Oxygen Reduction Reaction, *J. Am. Chem. Soc.* 133 (2011) 9783–9795.
- [57] J. Zhang, F. H. B. Lima, M. H. Shao, K. Sasaki, J. X. Wang, and J. Hanson, R. R. Adzic, Platinum Monolayer on Nonnoble Metal–Noble Metal Core–Shell Nanoparticle Electrocatalysts for O₂ Reduction, 109 (2005) 22701–22704.
- [58] K. Sasaki, H. Naohara, Y. Cai, Y. M. Choi, P. Liu, M. B. Vukmirovic, J. X. Wang, R. R. Adzic, Core-Protected Platinum Monolayer Shell High-Stability Electrocatalysts for Fuel-Cell Cathodes, *Angew. Chemie Int. Ed.* 49 (2010) 8602–8607.
- [59] J. X. Wang, H. Inada, L. Wu, Y. Zhu, Y. Choi, P. Liu, W. P. Zhou, R. R. Adzic, Oxygen Reduction on Well-Defined Core–Shell Nanocatalysts: Particle Size, Facet, and Pt Shell Thickness Effects, *J. Am. Chem. Soc.* 131 (2009) 17298–17302.
- [60] J. Zhang, M. B. Vukmirovic, Y. Xu, M. Mavrikakis, R. R. Adzic, Controlling the Catalytic Activity of Platinum-Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates, *Angew. Chemie Int. Ed.* 44 (2005) 2132–2135.
- [61] Y. C. Hsieh, Y. Zhang, D. Su, V. Volkov, R. Si, L. Wu, Y. Zhu, W. An, P. Liu, P. He, S. Ye, R. R. Adzic, J. X. Wang, Ordered bilayer ruthenium–platinum core-shell nanoparticles as carbon monoxide-tolerant fuel cell catalysts, *Nat. Commun.* 4 (2013) 2466.
- [62] E. Fako, A. S. Dobrota, I. A. Pašti, N. López, S. V. Mentus, N. V. Skorodumova, Lattice mismatch as the descriptor of segregation, stability and reactivity of supported thin catalyst films, *Phys. Chem. Chem. Phys.* 20 (2018) 1524–1530.
- [63] D. D. Vasić, I. A. Pašti, S. V. Mentus, DFT study of platinum and palladium overlayers on tungsten carbide: structure and electrocatalytic activity toward hydrogen oxidation/evolution reaction, *Int. J. Hydrogen Energy.* 38 (2013) 5009–5018.

- [64] D. D. Vasić Anićijević, V. M. Nikolić, M. P. Marčeta-Kaninski, I. A. Pašti, Is platinum necessary for efficient hydrogen evolution?—DFT study of metal monolayers on tungsten carbide, *Int. J. Hydrogen Energy*. 38 (2013) 16071–16079.
- [65] D. D. Vasić Anićijević, V. M. Nikolić, M. P. Marčeta Kaninski, I. A. Pašti, Structure, chemisorption properties and electrocatalysis by Pd₃Au overlayers on tungsten carbide - A DFT study, *Int. J. Hydrogen Energy*. 40 (2015) 6085–6096.
- [66] A. V. Ruban, H. L. Skriver, J. K. Nørskov, Surface segregation energies in transition-metal alloys, *Phys. Rev. B*. 59 (1999) 15990–16000.
- [67] B. Hammer, J. Nørskov, Theoretical surface science and catalysis—calculations and concepts, *Adv. Catal.* 45 (2000) 71–129.
- [68] A. K. Geim, K. S. Novoselov, The rise of graphene, *Nat. Mater.* 6 (2007) 183–191.
- [69] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, A roadmap for graphene, *Nature*. 490 (2012) 192–200.
- [70] C. N. R. R. Swapan K. Pati, Toshiaki Enoki, *Graphene and Its Fascinating Attributes*, World Scientific Publishing Co. Pte. Ltd. Singapore, 2011.
- [71] V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril, K. S. Kim, Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications, *Chem. Rev.* 112 (2012) 6156–6214.
- [72] A. S. Dobrota, I. A. Pašti, S. V. Mentus, N. V. Skorodumova, A general view on the reactivity of the oxygen-functionalized graphene basal plane, *Phys. Chem. Chem. Phys.* 18 (2016) 6580–6586.
- [73] I. A. Pašti, A. Jovanović, A. S. Dobrota, S. V. Mentus, B. Johansson, N. V. Skorodumova, Atomic adsorption on pristine graphene along the Periodic Table of Elements – From PBE to non-local functionals, *Appl. Surf. Sci.* 436 (2018) 433–440.
- [74] K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, D. C. Langreth, Higher-accuracy van der Waals density functional, *Phys. Rev. B*. 82 (2010) 81101.
- [75] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, B. I. Lundqvist, Van der Waals Density Functional for General Geometries, *Phys. Rev. Lett.* 92 (2004) 246401.
- [76] A. S. Dobrota, I. A. Pašti, S. V. Mentus, N. V. Skorodumova, A DFT study of the interplay between dopants and oxygen functional groups over the graphene basal plane – implications in energy-related applications, *Phys. Chem. Chem. Phys.* 19 (2017) 8530–8540.
- [77] A. S. Dobrota, I. A. Pašti, S. V. Mentus, B. Johansson, N. V. Skorodumova, Functionalized graphene for sodium battery applications: the DFT insights, *Electrochim. Acta*. 250 (2017) 185–195.
- [78] F. Banhart, J. Kotakoski, A. V. Krasheninnikov, Structural Defects in Graphene, *ACS Nano*. 5 (2011) 26–41.
- [79] I. A. Pašti, A. Jovanović, A. S. Dobrota, S. V. Mentus, B. Johansson, N. V. Skorodumova, Atomic adsorption on graphene with a single vacancy: systematic DFT study through the periodic table of elements, *Phys. Chem. Chem. Phys.* 20 (2018) 858–865.
- [80] N. Gavrilov, M. Momčilović, A. S. Dobrota, D. M. Stanković, B. Jokić, B. Babić, N. V. Skorodumova, S. V. Mentus, I. A. Pašti, A study of ordered mesoporous carbon doped with Co and Ni as a catalyst of oxygen reduction reaction in both alkaline and acidic media, *Surf. Coatings Technol.* 349 (2018) 511–521.

- [81] A. Ganguly, S. Sharma, P. Papakonstantinou, J. Hamilton, Probing the Thermal Deoxygenation of Graphene Oxide Using High-Resolution In Situ X-ray-Based Spectroscopies, *J. Phys. Chem. C*. 115 (2011) 17009–17019.
- [82] A. S. Dobrota, I. A. Pašti, N. V. Skorodumova, Oxidized graphene as an electrode material for rechargeable metal-ion batteries - a DFT point of view, *Electrochim. Acta*. 176 (2015) 1092–1099.
- [83] A. S. Dobrota, S. Gutić, A. Kalijadis, M. Baljović, S. V. Mentus, N. V. Skorodumova, I. A. Pašti, Stabilization of alkali metal ions interaction with OH-functionalized graphene: Via clustering of OH groups-implications in charge storage applications, *RSC Adv.* 6 (2016) 57910–51919.
- [84] Y. Yang, C. C. Chen, M. C. Scott, C. Ophus, R. Xu, A. Pryor, L. Wu, F. Sun, W. Theis, J. Zhou, M. Eisenbach, P. R. C. Kent, R. F. Sabirianov, H. Zeng, P. Ercius, J. Miao, Deciphering chemical order/disorder and material properties at the single-atom level, *Nature*. 542 (2017) 75–79.
- [85] L. Gross, F. Moresco, L. Savio, A. Gourdon, C. Joachim, K. H. Rieder, Scattering of Surface State Electrons at Large Organic Molecules, *Phys. Rev. Lett.* 93 (2004) 56103.
- [86] M. F. Crommie, C. P. Lutz, D. M. Eigler, Confinement of Electrons to Quantum Corrals on a Metal Surface, *Science*. 262 (1993) 218–220.
- [87] N. Nilus, T. H. Wallis, W. Ho, Development of one-dimensional band structure in artificial gold chains, *Science*. 297 (2002) 1853–1856.
- [88] Y. Pennec, W. Auwärter, A. Schiffrin, A. Weber-Bargioni, A. Riemann, J. V. Barth, Supramolecular gratings for tuneable confinement of electrons on metal surfaces, *Nat. Nanotechnol.* 2 (2007) 99–103.
- [89] I. Piquero-Zulaica, J. Lobo-Checa, A. Sadeghi, Z. M. A. El-Fattah, C. Mitsui, T. Okamoto, R. Pawlak, T. Meier, A. Arnau, J. E. Ortega, J. Takeya, S. Goedecker, E. Meyer, S. Kawai, Precise engineering of quantum dot array coupling through their barrier widths, *Nat. Commun.* 8 (2017) 787.
- [90] S. Nowakowska, F. Mazzola, M. N. Alberti, F. Song, T. Voigt, J. Nowakowski, A. Wäckerlin, C. Wäckerlin, J. Wiss, W. B. Schweizer, M. Broszio, C. Polley, M. Leandersson, S. Fatayer, T. Ivas, M. Baljović, S. F. Mousavi, A. Ahsan, T. Nijs, O. Popova, J. Zhang, M. Muntwiler, C. Thilgen, M. Stöhr, I. A. Pašti, N. V. Skorodumova, F. Diederich, J. Wells, T. A. Jung, Adsorbate-Induced Modification of the Confining Barriers in a Quantum Box Array, *ACS Nano*. 12 (2018) 768–778.
- [91] D. Chanda, J. Hnát, A. S. Dobrota, I. A. Pašti, M. Paidar, K. Bouzek, The effect of surface modification by reduced graphene oxide on the electrocatalytic activity of nickel towards the hydrogen evolution reaction, *Phys. Chem. Chem. Phys.* 17 (2015) 26864–26874.
- [92] S. J. Gutić, A. S. Dobrota, M. Leetmaa, N. V. Skorodumova, S. V. Mentus, I. A. Pašti, Improved catalysts for hydrogen evolution reaction in alkaline solutions through the electrochemical formation of nickel-reduced graphene oxide interface, *Phys. Chem. Chem. Phys.* 19 (2017) 13281–13293.
- [93] M. Leetmaa, N. V. Skorodumova, KMCLib: A general framework for lattice kinetic Monte Carlo (KMC) simulations, *Comput. Phys. Commun.* 185 (2014) 2340–2349.
- [94] M. Leetmaa, N. V. Skorodumova, KMCLib 1.1: Extended random number support and technical updates to the KMCLib general framework for kinetic Monte-Carlo simulations, *Comput. Phys. Commun.* 196 (2015) 611–613.

- [95] I. A. Pašti, M. Leetmaa, N. V. Skorodumova, General principles for designing supported catalysts for hydrogen evolution reaction based on conceptual Kinetic Monte Carlo modeling, *Int. J. Hydrogen Energy*. 41 (2016) 2626–2538.
- [96] S. J. Gutić, A. Z. Jovanović, A. S. Dobrota, D. Metarapi, L. D. Rafailović, I. A. Pašti, S. V. Mentus, Simple routes for the improvement of hydrogen evolution activity of Ni-Mo catalysts: From sol-gel derived powder catalysts to graphene supported co-electrodeposits, *Int. J. Hydrogen Energy*. 43 (2018) 16846–16858.

Игор А. Пашти, Ана С. Доброћа, Славко В. Менџус

МОДЕЛИРАЊЕ И СИМУЛАЦИЈА НАНОСТРУКТУРА

Резиме

Напредак савремених технологија захтева фундаментално разумевање везе између структуре и својстава нових материјала. Методе прорачуна и симулације показале су се као моћно средство у испитивању ових веза, омогућавајући анализу система различитих нивоа сложености, на различитим просторним и временским скалама, са жељеним саставом и без икаквог ризика од контаминације. Штавише, константно повећање рачунарских ресурса омогућило је примену неких од најнапреднијих метода прорачуна на скали која превазилази суб-нанометарску (мали молекули и кластери атома), која се обично сматра границом за *ab initio* прорачуне. Иако се тачност таквих израчунавања приближава грешкама експеримента, овај приступ такође омогућава (теоријску) претрагу великог броја система, што није експериментално изводљиво, као и разумевање општих трендова који су од великог значаја, како за теоретичаре тако и за експериментаторе. Ово поглавље приказује искуства аутора у моделирању и симулацијама система нанометарских димензија различите сложености, укључујући оксиде метала, метале, угљеничне материјале, молекулске мреже и сложене каталитичке системе.