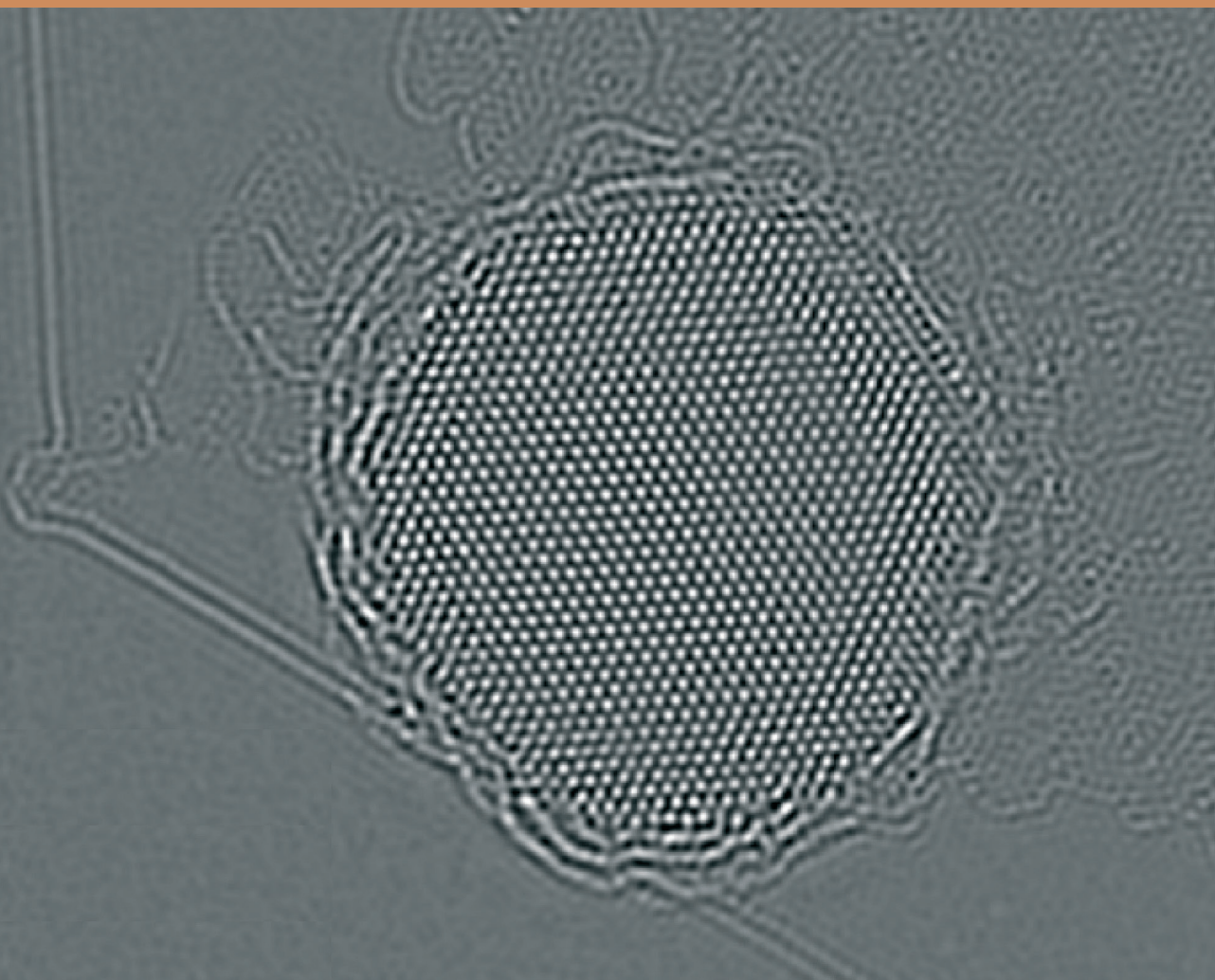


SERBIAN ACADEMY OF SCIENCES AND ARTS
СРПСКА АКАДЕМИЈА НАУКА И УМЕТНОСТИ



FASCINATING WORLD OF NANOSCIENCES
AND NANOTECHNOLOGIES
ФАСЦИНАНТНИ СВЕТ НАНОНАУКА
И НАНОТЕХНОЛОГИЈА

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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

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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

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Technical editor
Nikola Stevanović

Технички уредник
Никола Стевановић

Print run
400 copies

Тираж
400 примерака

Printed by
Planeta print

Штампа
Планета принт

ISBN 978-86-7025-859-4

ISBN 978-86-7025-859-4

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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.

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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

METALLIC MUSCLES: NANOSTRUCTURES AT WORK

JEFF TH. M. DEHOSSON^{*1} AND ERIC DETSI²

A b s t r a c t. – Materials systems that can mimic the properties of muscles upon an outside stimulus are coined ‘artificial muscles’ in analogy to human skeletal muscles, which are ideal actuators with high energy efficiency, fast strain-rate response and high durability. The common use of existing materials as actuators like piezoceramics and electroactive polymers are limited by several factors, including low energy efficiency, low strain amplitudes, fatigue limit and high actuation voltages needed. In this contribution we will show that nanoporous organometallic materials can operate as actuators, thereby offering a unique combination of low-operating voltages, relatively large strain amplitudes, high stiffness and strength. In particular, it will be discussed that, through a smart materials design, large macroscopic strain amplitudes up to 10% and strain-rates up to 10^{-2} s^{-1} can be achieved, roughly 2 and 5 orders of magnitude larger than before in any materials system, respectively. In the summary and outlook, we introduce the concept of light-induced actuation in metallic muscle systems, i.e. the direct conversion of solar energy into mechanical work, without the need for external energy. Finally, as extension of this energy theme, we further discuss energy-related fields in which nanoporous metals may have a great impact.

Keywords: nanofoam, nanopores, actuators, sensors, muscles

INTRODUCTION TO NANOSTRUCTURED MATERIALS

Starting from the second half of the 20th century, our society has seen a great amount of attention on the development of progressively miniaturized systems in mechanical and electronic devices. In electronics, this development comes as part of the well-known Moore’s Law, where computational power is expected to double, on average, every fifteen months. Whilst this particular rate has been observed to decrease, the principle is expected to hold for the foreseeable future [1]. It then becomes a matter of maintaining parity i.e. devices used in processors – transistors, resistors, capacitors, etc., must continually be miniaturized for more of them to be able to fit in the same operating space compared to their predecessors.

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With this emphasis on miniaturization stemming from the electronics industry, the same push has been seen in mechanical systems. In medicine and biology, for example, there is a need for high-precision actuators and manipulators for work on fluid filtration and living cell manipulation [2]. The increasingly popular lab-on-a-chip technology takes advantage of highly miniaturized mechanical systems – Micro-Electronic Mechanical Systems or MEMS – to fit efficient analysis systems in a very small space. For progress in these fields there is a necessity for the continuous development of both materials with micro- and nanoscale functions and of tools that can facilitate the production and characterization of these materials.

As a rule, nanomaterials are defined as materials where one dimension of its defining feature is smaller than 100 nanometers. This dimension is then considered negligible on the macroscale, and is the material's defining property. In this way, a two-dimensional (2D) material has a single dimension that is no larger than 100 nanometers, and such materials are commonly called thin films. Arrays of thin films are commonly seen in the electric and electronic industry as transistors or components in solar cells. Thin films are also used in catalysis and protective coatings for enhanced corrosion resistance [3, 4].

Appropriately, a one-dimensional material has two dimensions under 100 nanometers. Common examples are nanowires and nanorods, the most prolific example of which is the carbon nanotube. Arrays of nanowires can form anisotropic films, where properties of the material vary depending on relative direction of influence. We see such behavior in carbon fiber weave for structural uses [5].

At the lowest end of the scale are zero-dimensional materials, often called nanodots. Of great interest to the electronics industry, they have unique photonic and spin properties for use in the expected next generation of electronic devices: molecular transistors, quantum bits etc. [6].

By appropriately expanding the dimensions of a nanostructured material it is possible to make a material with very specific ordering tailored to suit the needs of a particular function. As mentioned above, stacked thin films form a three-dimensional structure with one-dimensional ordering. This principle can be applied to a zero-dimensional material: by stacking the zero-dimensional unit cell into three dimensions a three-dimensionally-ordered material can be made.

Mechanical displacement that comes as a result of an electric signal passing through a material is called actuation. In materials that produce an actuation response, the reverse is often possible as well – an electric current can be induced to flow if the material is deformed. The most common type of material that shows such properties is described as piezoelectric, and of this class of materials quartz is the best-known. Indeed, it is the piezoelectric property of quartz that allows it to be used as an oscillating pace mechanism in the common wristwatch [7]. The typical piezoactuator delivers a $\sim 0.2\%$ strain at a high potential of 150V. Considering that it is desirable to see the use of actuation in low-voltage devices,

such as MEMS, much lower operational parameters are required for the modern actuating material [8].

Polymer-based actuation materials have been developed that offer extraordinary capacity for induced deformation, but have the drawback of being weak and compliant [8]. Extensive investigations by Gleiter, Kramer Weissmuller, Detsi and DeHosson [9–12] have demonstrated the potential of nanostructured metals to act as actuators, creating so-called “metallic muscles,” with the ability to demonstrate the properties required of the modern actuator: low throughput voltage requirements, high extension yield, strength and stiffness.

METAL FOAMS AND NANOFOAMS

The principle of metallic composites has existed since the discovery that alloying metals yield a material with the properties of both of its parts. Indeed, a well-known alloy of copper and tin was the centerpoint of human civilization during the aptly-named Bronze Age, where tools, coin and weapons were all forged from the highly versatile metal [13]. Modern materials science is almost entirely focused on the development of multi-component alloys with properties tailored to fulfill specific functions [14, 15]. Taken from a wider point of view, a metal alloy is a type of composite material, where a composite material is, in general, described as a material composed of two or more different components.

When one of the components in a composite system is air, the system is described as being porous. Porous systems come in two types – interconnected and non-interconnected (alternatively, open-cell and closed-cell, respectively), describing the relationship of the material’s pores: in the former, there exists a continuous pathway between every single pore in the material and in the latter the pores exist independently as separated islands. A porous system is typically characterized by a high surface area-to-volume ratio due to the high amount of air-to-solid interface area, as well as by a lower density and, by connection, by a lower weight compared to its solid bulk counterpart.

To briefly mention terminology, a porous material is made up of pores, struts and nodes. Pores are the encompassing term for the volume of air within a foam and struts are solid material that merge at nodes and connect nodes together.

The popularity of macrofoams i.e. porous materials where pore size is above the scale of tens of microns, stems from the intersection of a variety of desirable properties in industry, see Fig.1 [16].

For example, aluminum macrofoam boasts a high stiffness-to-density ratio, high capacity for energy absorption during compression, high temperature resistance, electrical and thermal conductivity, good machinability and cheap production costs [17]. Such properties make macrofoams attractive in the construction and automotive industries, for example [18–22].

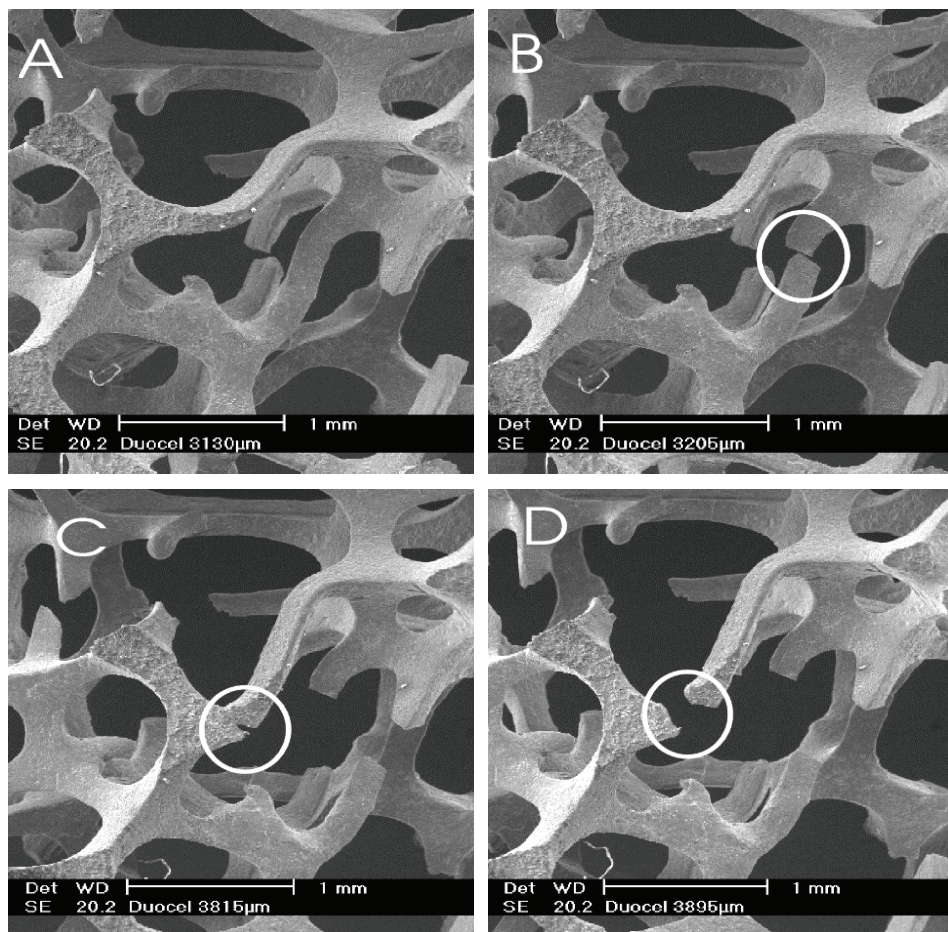


Figure 1. *In-situ* deformation in a FEI-Philips XL30-FEG-ESEM of Duocel 40 PPI macrofoam with a relative density of approximately 7%

While macrofoams are common materials with known applications in industry, the class of materials known as nanofoams is more exotic. Operating under the same concepts as macrofoams in principle, nanofoams are characterized by pore and strut sizes being at the nanoscale, in other words the greatest diameter of a pore or strut must be considered a nanoscale dimension. For a more precise definition, the International Union of Pure and Applied Chemistry has categorized nanoporous metals into three groups, depending on the pore size: microporous metals have pore size under 2 nm, mesoporous metals have pore sizes between 2 and 50 nm and macroporous metals have pore size above 50 nm.

Nanofoams share many properties with their macrofoam counterparts, such as the high surface-area-to-volume ratio, as well as the capacity for cheap produc-

tion and easy machinability. However, nanoporous foams have seen usage in many applications beyond those of macrofoams, including nanofiltration systems, drug delivery platforms, catalysis, sensing and actuation [23–28]. A major advantage that nanoporous metals have is the ability to hold a lattice of nanoscale features whilst being able to be easily handled and transported, something metallic nanoparticles, for example, cannot provide.

Production of disordered metal nanofoams

In the majority of cases, metal nanofoams are produced through dealloying using leaching. For this process to work, an alloy must be produced between the required metal and another that can be etched away in some manner. It is also required that the two metals be able to form a solid solution, as any other morphology will not allow for the eventual formation of an isotropic structure of pores and ligaments. This is often the limiting factor for the dealloying process of nanofoam manufacture, as many metals do not easily form solid solutions, and if they do, it may not be possible to selectively etch one of the components of the alloy system whilst leaving the other intact.

Silver is alloyed with gold to form so-called “white gold,” an alloy commonly used in jewelry. The versatility of the alloy stems from its ability to form a solid solution at any ratio of gold to silver, allowing for fine control of porosity of a resultant pure gold system, see Fig. 2.

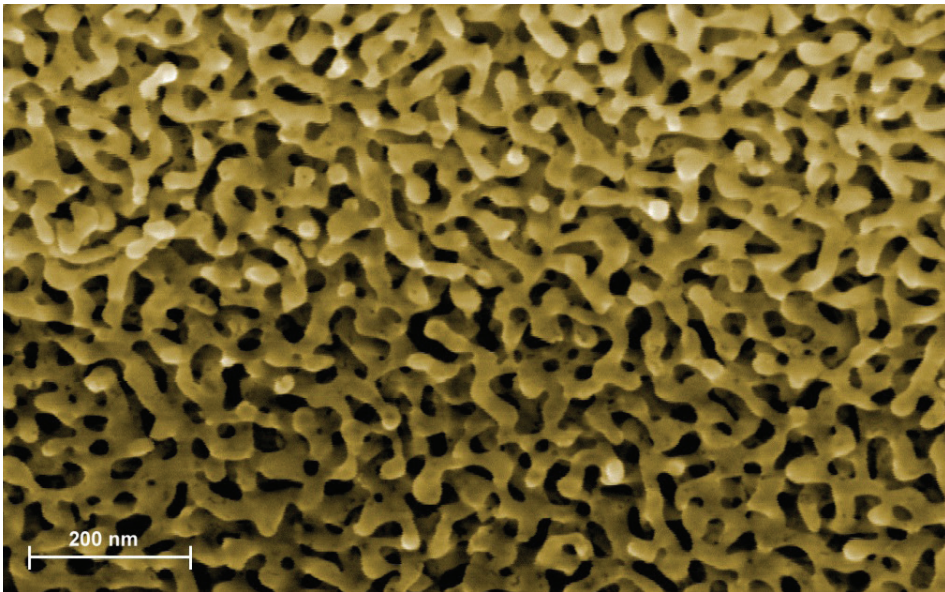


Figure 2. Typical nanoporous Au

While copper does not have alloy systems as simple as gold's with silver, copper-manganese forms a reliable solid solution across a wide range of compositions. Unfortunately, except at very low percentages, Mn tends to segregate out of the solid solution and form a phase of pure Mn at low temperatures. This issue is solved through rapid quenching from solid solution temperature. This process prevents the formation of the pure Mn phase and, provided that the quenching had occurred successfully, yields an ingot with a microstructure comparable to that of Ag-Au alloy.

While the production of nanoporous metallic structures is well-documented, up until recently very little was known about their mechanical properties – at submicron scales, sample size has the possibility to produce a large effect on mechanical properties, where in macroporous foams cell size specifically does not have an influence on material strength [29]. Indeed, it is highly uncertain that the behaviors of macroscopic and microscopic foams will be at all similar in principle and nature. Li and Sieradzki reported that porous Au undergoes a ductile-brittle transition that seemed to be influenced by the microstructural length scale of the material [30]. Biener *et al.* have continued this investigation into the mechanical properties of nanoporous Au through nanoindentation [31]. They report the main deformation mechanism during nanoindentation as a ductile, plastic densification. Strong long-range stress fields, brittle fracture and crack emission were not observed. They note that the scaling laws that are typically applied to macroporous foams apply poorly to nanoporous metals, as they observe an experimental yield strength of 145MPa instead of the expected 16MPa.

Volkert *et al.* performed microcompression experiments on FIB-milled micron-sized pillars of nanoporous Au with 15 nm diameter ligaments [32]. They found that, while Young's modulus values, as determined experimentally and as predicted by scaling laws, do not show significant difference, there is a major increase in yield strength as sample size decreases below 50um length scales. A yield strength of 1.5GPa is predicted, which is several orders of magnitude above that of typical bulk of Au. They interpret this effect as influenced by the increased stress required to activate dislocation sources as ligament size decreases, until theoretical shear strength is reached.

Further work by Biener *et al.* investigated this elevated yield strength and whether its origin was the microstructure of disordered nanoporous Au ligaments or the specific size-dependent mechanical properties of Au [29]. This was performed by preparing multiple samples with varying ligament sizes. It is established that in the production of a nanoporous material it is possible to tune ligament and pore size through varying dealloying conditions [33]. They observed a clear influence of ligament size, such that the strength of nanoporous Au increases with decreasing ligament diameter, and thus propose that the Gibson and Ashby scaling model of foam plasticity needs to be adjusted to take into account ligament size for nanoporous systems [34].

Ordered metal foams and nanofoams

As is often the case for many novel materials, interest in producing a nanoporous structure with an ordered, anisotropic pore structure came from observing nature. Specifically, the opalescence effect – variation in color based on direction of observation – seen in butterfly wings and mother-of-pearl stems from the ordered chitinous scales for the former or calcium plates for the latter serving as photonic diffraction gratings.

The brilliant color variation seen in Fig. 3 is a light effect described as opalescence and is a result of an ordered nanoporous lattice acting as a series of waveguides, only permitting through light of a particular frequency, depending on viewing direction. The use of waveguide materials such as these has been proposed for use in optical circuitry [35].

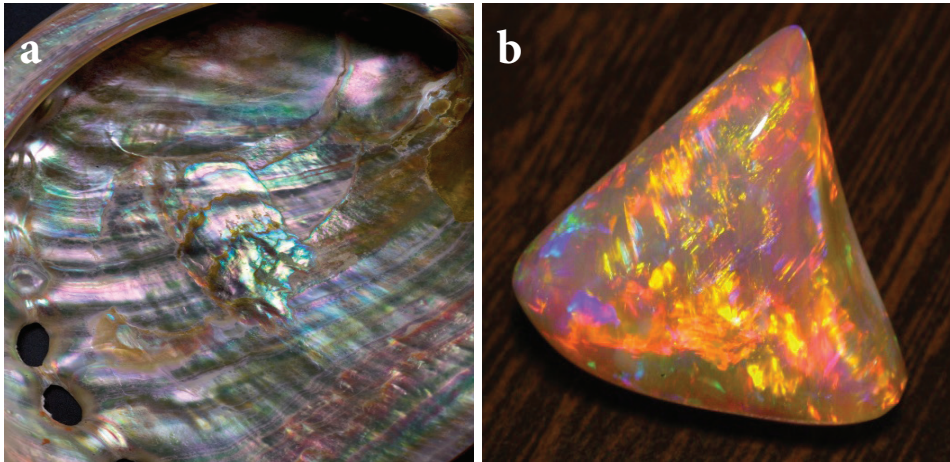


Figure 3. Mother-of-pearl, photo by Roy Kaltschmidt, Berkeley Lab (a) and natural opal, Department for Manufacturing, Innovation, Trade, Resources and Energy, Government of South Australia (b)

With clear applications across many industries [36–38], three-dimensionally-ordered materials have garnered much attention [39]. As with all nanostructured materials, two methods of approach are viable for their production: top-down and bottom-up. Top-down production focuses on reducing a bulk source sample down to the correct size, shape and morphology through a variety of destructive production methods. Whilst the top-down method boasts a very logical application with easy potential for iterative improvement, its greatest limitation is the scale down threshold to which its production methods can reach – detail at the nanometer scale is beyond the capabilities of the typical top-down method [40–42]. The alternative is the bottom-up approach, where nanoscale features are

assembled piece by piece into a full structure. This method allows for far finer detail control and overall quality of the assembled structure, but is typically challenging to implement due to it often being a multi-stage process.

The top-down process of production of nanostructured materials typically involves a starting bulk macroscale solid and then the use of one of several techniques to achieve a nanostructure through size reduction. In medical applications, a top-down method for the production of nanoparticle suspensions is high-pressure homogenization, consisting of repeated forcing of a suspension through a very thin gap at high velocity or media milling, which is the mechanical attrition of suspended particles using glass or zirconium oxide [43]. Mechanical attrition in general is a common procedure for the production of nanostructured materials, and one example of such a procedure is the method of ball milling, where powders are sealed in a strengthened container with a set of hard metal spheres and treated in a vibratory mill to elicit potential phase changes and the formation of nanostructured grains in the processed particles [44]. More non-standard procedures are also known: Yan *et al.* have proposed that, considering its simplicity and capacity for high-resolution spatial imaging, an atomic force microscopy (AFM) apparatus can be used to machine nanoscale features, and have demonstrated this capability in aluminum [45].

N a n o s p h e r e t e m p l a t i n g. – As a whole, lithography is considered a top-down method, and is common in the electronics industry for the production of microchips. However, it can be converted into a bottom-up method by reducing the size of the initial template. This idea can be applied for 3D nanostructures: a porous 3D template is constructed that allows for the introduction of a particular material into the pore spaces within the template. After the template is removed the result is a 3D “image” of the template’s pore network. This is called inverse templating, and is the principal bottom-up method that allows for repeatable batch production in moderately large quantities, provided that the template is easily constructed. For this purpose, self-assembling templates are highly valued – templates whose component parts can, over time, arrange themselves into a desired 3D pattern with no further intervention aside from the initial process setup.

Nanosphere templating uses the natural ability of silica or polymer (PMMA, polystyrene, latex) nanospheres to reliably self-assemble into a template on a large scale. The nanospheres are suspended in a solution and are allowed to naturally settle over time, although centrifugation can be used to accelerate the process at the expense of quality of ordering. An alternative method is to allow the spheres to settle across a meniscus to improve ordering with the downside of the resultant template film being very thin. The spheres will preferentially settle into their most low-energy configuration, which is a crystalline face-centered cubic (FCC) arrangement. As the nanospheres settle, the solution evaporates and eventually a dry nanosphere template remains, see Fig. 4.

A settled nanosphere template is typically weak, brittle solid, as the spheres are held together only through van der Waals forces. Thermal processing can be

applied to strengthen a finished template by furnace-treating the template to allow necks to form between adjacent spheres.

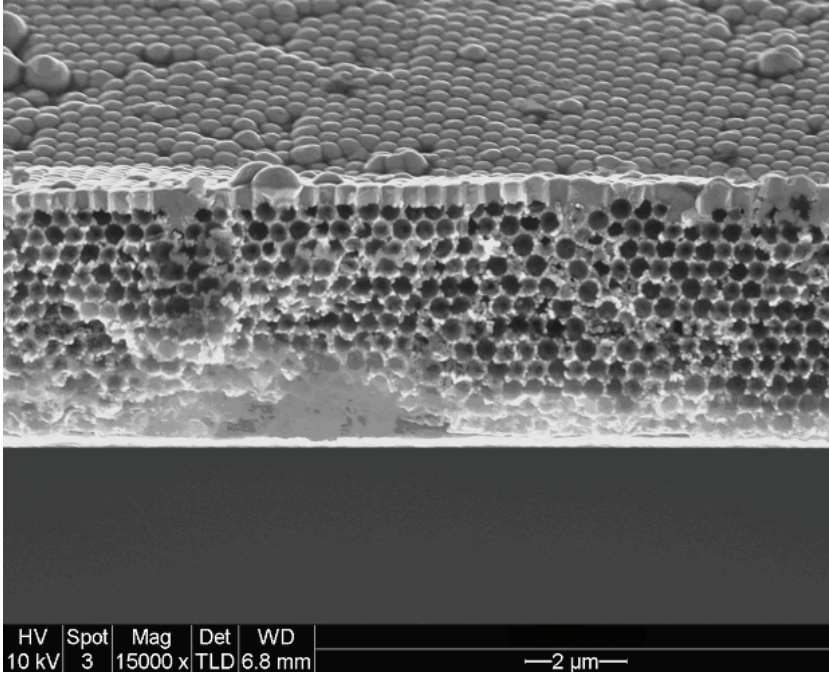


Figure 4. Cross-sectional SEM micrograph of electroless Ni plated nanosphere template on gold-plated silicon wafer after template removal

The appropriate temperature and time vary significantly by material, where several minutes at 120°C is enough for polymers like polystyrene, and several hours' processing at over 900°C is required for silica. The result is a much more robust template that can withstand mechanical rigor, but may be more challenging to remove.

D i b l o c k c o p o l y m e r t e m p l a t i n g . – In principle, any sort of material with submicron-scale features that exhibits ordering can be used as a template, provided that interconnected voids exist between the features. One such material is the so-called “block copolymer”. In such a material, two covalently-linked polymers, or blocks, undergo a process called microphase separation, i.e. attempt to separate as oil and water would, but are limited in their capacity to do so due to cross-linking. An enthalpy-entropy balance governs the specific manner in which this separation occurs. By controlling the compositions of the component block, it is possible to influence the phase behavior of the copolymer and thus form a variety of phases: lamellar, cylindrical and spherical phases are common, classical phases, with the perforated lamellar, gyroidal and ordered bicontinuous double diamond phases are seen more rarely. In all cases, depending on the com-

position, one block forms the specific feature that the morphology is named after and the other forms a matrix around the feature.

Remarkably, all resultant structures show a high degree of ordering of their characteristic unit cell. As such, if, once a particular phase has been formed, one of the blocks of the copolymer could be removed whilst leaving the other preserved, the resultant polymer matrix could be used as an organic template. Of the possible phases formed by diblock copolymers, the gyroid phase is most interesting due to its repeating, long-ranged ordering of a three-dimensional feature. See Fig. 5 [46–49].

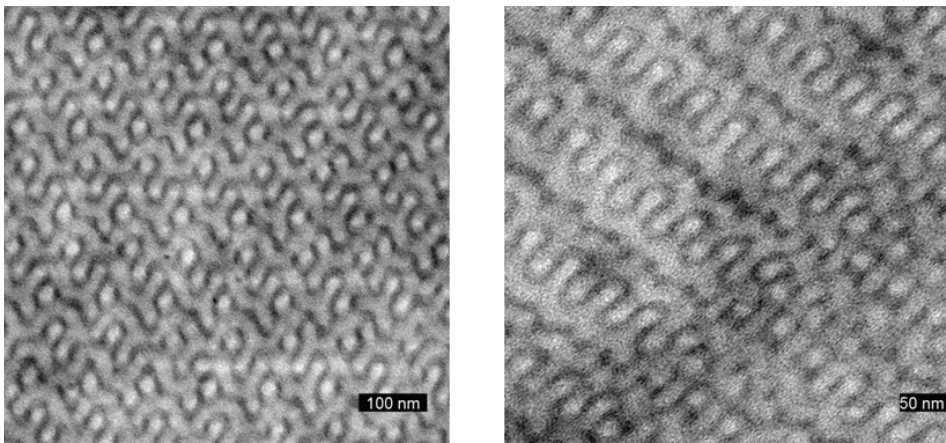


Figure 5. TEM observation of ordered block co-polymer + electroless Ni plating

In other words, the gyroid morphology offers the strongest potential for use as a template to produce a three-dimensionally-ordered nanofoam [50].

METALLIC MUSCLES: HOW DOES IT WORK?

The actuation mechanism in metallic muscles based on nanoporous metals with high surface-to-volume ratios is different to piezoceramics [51]. As a starting point, note that in crystalline materials, surface atoms have fewer neighbors than those in the bulk. This results in unbalanced interatomic surface bonds, which in turn gives rise to an excess negative surface charge. The unbalanced surface bonds will redistribute at the surface so as to strengthen the surface atoms by shortening the interatomic distance with respect to the bulk [52]. Shortening of the surface interatomic distance results in a positive surface stress (tensile stress, i.e. a positive displacement to bring the atoms back to an equilibrium distance with respect to the bulk [53, 54]). Subsequently, a positive charge injection at the surface will neutralize the existing excess negative surface charge, thereby lowering the tensile

surface stress. This results in the relaxation of the surface atom positions via an increase in the interatomic spacing. In order to preserve the mechanical equilibrium, bulk atoms experience less compressive stress, resulting in a positive outward (tensile) displacement [55]. Obviously, these surface stress-induced deformations are not detectable in macroscopic dense metals, but they are thought to become significant in nanostructured metals where the fraction of surface atoms versus bulk becomes substantial. For actuator applications, the electronic charge distribution at a nanoporous metal interface can effectively be tuned in an aqueous electrolyte during cycling voltammetry experiments, where relatively small electrical voltages, of the order of 1V, are needed to bring positive or negative charge carriers (ions) from the electrolyte to the nanoporous metal interface [56, 57].

CHALLENGES AND OPPORTUNITIES

Although nanoporous metal actuators offer a unique combination of low operating voltages, relatively large strain amplitudes, high stiffness and strength, the emergence of nanoporous metal actuators in practicable applications is still delayed. The challenge to their further development in viable applications can be considered threefold, but principally concerns the aqueous electrolyte that is needed to inject electronic charge in the space-charge region at the metal/electrolyte interface [58]. Firstly, an aqueous electrolyte limits the usage of metallic muscles to wet environments, whereas most of the practical applications require artificial muscles that can operate in dry environments. A second major concern is that the relatively low ionic conductivity of aqueous electrolytes limits the actuation rate of the actuator. Simply replacing the aqueous electrolyte by a solid one is not a better alternative because the actuation rate of all-solid-state electrochemical actuators is more severely hampered by the low room-temperature ionic conductivity of solid-state electrolytes. The third and final concern is the severe coarsening (undesired growth) of the ligaments in nanoporous metals during electrochemical processes [59] including actuation via redox reactions. Specifically, the undesired ligaments growth (coarsening) will cause the metallic muscle to lose in performance as a function of time, since the strain amplitude in nanoporous metal actuators is ligament-size dependent as shown in Fig. 6, where strain amplitudes are plotted as a function of the average ligament size. Consequently, ligaments growth in nanoporous metals during electrochemical actuation is undesirable.

In view of these various restrictions caused by the electrolyte, an electrolyte-free approach is desirable for actuation in nanoporous metals. In fact, the following features are a prerequisite for a breakthrough in the field of artificial muscles: (i) no usage of aqueous or solid electrolyte, (ii) a fast actuation rate and (iii) a single actuating component as in piezoelectric materials. In order to tackle those problems, in our Applied Physics-Materials Science group of the Zernike Institute for Advanced Materials in Groningen, we have been developing advanced nano-

porous metals composites for a new electrolyte-free actuation concept in metallic muscles, including nanoporous gold/SnO₂ (Fig. 7) and nanoporous gold/polymer composites (Fig. 8). In the latter case, we have specifically been exploiting nanoporous gold/polyaniline composites to put metallic muscles to work [12, 60, 61].

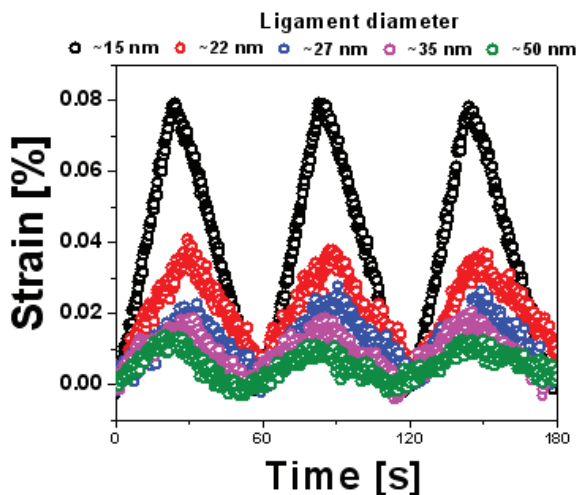


Figure 6. Ligament size-dependence of the charge-induced strain in nanoporous metals. The strain amplitude recorded on five NPG (nanoporous gold) samples with different ligament sizes decreases with increasing ligament size. This shows that ligaments growth during electrochemical actuation is undesirable.

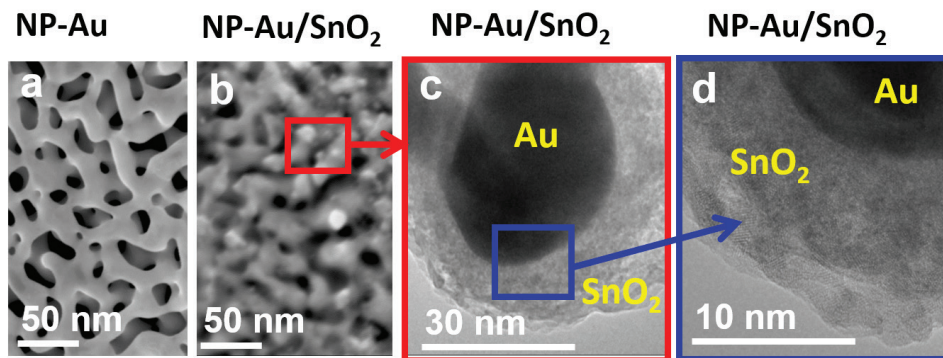


Figure 7. Nanoporous-Au/SnO₂ composite. (a) Scanning electron micrograph showing the bicontinuous morphology of NP-Au and (b) NP-Au/SnO₂ composite. SnO₂ was grown into pores of nanoporous Au by electrochemical deposition. (c,d) High resolution transmission electron micrographs showing a ~10 nm-thick coating of SnO₂ covering the ligaments of NP-Au.

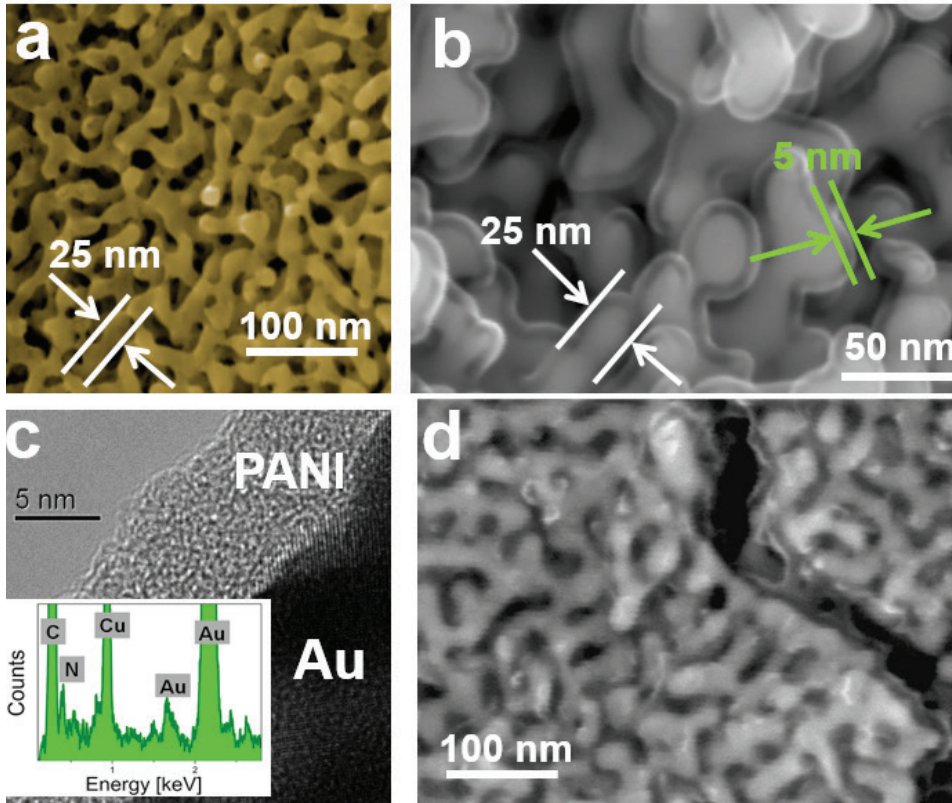


Figure 8. Microstructural characterization of NPG/PANI. (a) Scanning electron micrograph showing the bicontinuous morphology of NPG. (b, c) Scanning and transmission electron micrographs showing a ~ 5 nm-thick PANI skin covering the ligaments of NPG. The inset of c displays the EDX spectrum of PANI. C and N come from aniline (C_6H_7N), Cu and Au come respectively from the Cu grid used as sample holder and the NPG. (d) Fracture cross-section of NPG/PANI; it can be seen that the polymer envelope covering the ligaments is present into the bulk of the composite material.

The development of a nanoporous gold/polyaniline composite starts with the synthesis of nanoporous gold (NPG) using the standard dealloying method [62–68]. The typical bicontinuous morphology of the synthesized NPG is shown on Fig. 7a and Fig. 8a. Next, we use the electropolymerization procedure to grow a uniform nanocoating of polyaniline (PANI) onto the internal surface area of NPG [10, 11]. Dopant sulfate anions co-adsorbed in the polymer coating matrix are then exploited to tune the electronic charge density at the NPG/PANI interface and subsequently generate macroscopic dimensional changes in our NPG, as it will be shown in the next sections.

A schematic illustration of our NPG/PANI bulk heterojunction actuator is shown in Fig. 9a–d.

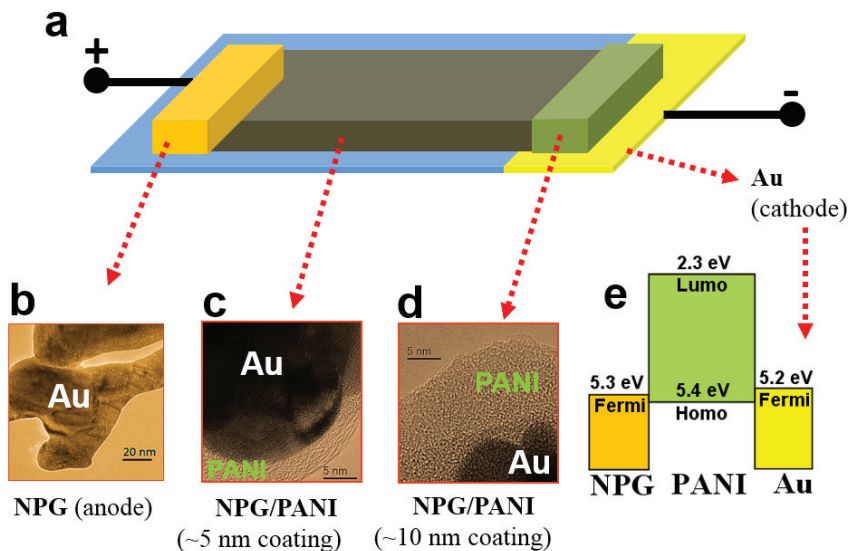


Figure 9. The NPG/PANI bulk heterojunction actuator. (a, c) The main part of the actuator consists of NPG whose ligaments are coated with a ~5 nm-layer of PANI. (b) One edge connected to the positive terminal of the voltage supplier consists of NPG. (d) The other edge connected to the negative terminal consists of NPG having its ligaments covered with ~10 nm thick layer of PANI. (e) Energy-level diagram of the NPG/PANI/Au system in the absence of external electrical potential.

The actuator is connected to the voltage supplier in one of the following two configurations: NPG/PANI/Au with NPG as anode and solid Au as cathode, or Au/PANI/NPG with solid Au as anode and NPG as cathode. Both configurations can be used because the two contact electrodes consisting of NPG and dense Au are made of the same material. Since the work functions of NPG and solid Au are comparable with the highest occupied molecular orbital (HOMO) of PANI on the one hand [69], and since PANI is a p-type semiconductor on the other hand [70], electronic charge transport in the NPG/PANI hybrid actuator is only controlled by conduction of holes (i.e. “hole-only” device), because the high offset between the Fermi level of the metal and the lowest unoccupied molecular orbital (LUMO) of PANI restricts electron injection from the metal into the LUMO of the polymer [71]. We used an external electric potential to inject holes from the metal anode (either NPG or solid Au) into the HOMO of the PANI nanocoating [72]. A particularity of NPG/PANI/Au and Au/PANI/NPG configurations is that electronic charges injected from the anode flow through the PANI coating before reaching

the cathode. We have found that the electronic charge transport through the polymer coating follows an Ohmic behavior at ambient temperatures [73].

We have measured reversible dimensional changes in the NPG/PANI bulk heterojunction material during successive forward-reverse voltage cycles between 0 and 2 V, and at various sweep rates ranging from 1 to 2000 mV/s. Note that when metallic muscles are put to work via aqueous electrolytes, the corresponding dimensional changes vanish at sweep rates beyond few tens of mV/s. In contrast, reversible dimensional changes were still observed in our NPG/PANI electrolyte-free actuator at sweep rates far beyond 1 mV/s as illustrated in Fig. 10a and 10b, where the strain amplitudes are plotted as a function of time and sweep rate, respectively.

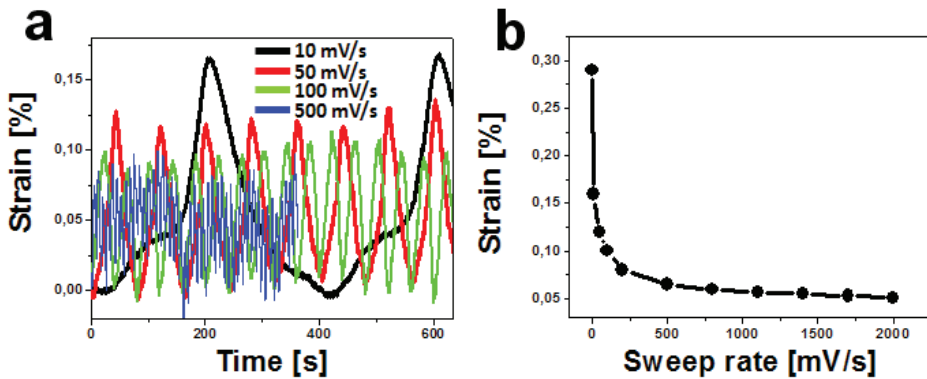


Figure 10. Fast actuation responses. Reversible dimensional changes are recorded at various sweep rates far beyond 1 mV/s (a) as a function of the time and (b) as a function of the sweep rate.

By setting the sweep rate at 2000 mV/s, a strain of $\sim 0.05\%$ was achieved in our electrolyte-free actuator in 1 s, rather than 1400 s as with the electrolyte [74]. This corresponds to a strain rate of 5×10^{-4} per second, which is thus about 1400 times higher than that achieved in metallic muscles via an electrolyte. These results demonstrate that by virtue of the novel electrolyte-free actuation approach, metallic muscles can operate in dry environments at high strain rates, much higher than those of common electrochemical artificial muscles. Besides electrolyte-free actuation, it is worth mentioning that we have also exploited the combination of a nanoporous metal and a polymer to add a new functionality to metallic muscles operating in aqueous electrolytes. Specifically, when our NPG/PANI composite is used as an electrochemical actuator, the NPG undergoes reversible dimensional changes while the PANI undergoes reversible changes in color during oxidation/reduction [11].

As mentioned above, dimensional changes could take place in nanoporous metals as a result of electronic charge accumulation in the space-charge region at

the nanoporous metal interface. This should be the case for our NPG/PANI composite, if an opposite space-charge builds up in the polymer coating during the voltage sweeps. However, we have found that hole-transport in the PANI coating is governed by an Ohmic current, rather than a space-charge limited-current [75]. This excludes the possibility of dimensional changes in our NPG/PANI composite as the result of the build-up of a space-charge in the polymer coating. As schematized in Fig.11a, in its non-conducting state, the blue emeraldine base form of PANI consists of electrically neutral molecular chains [76].

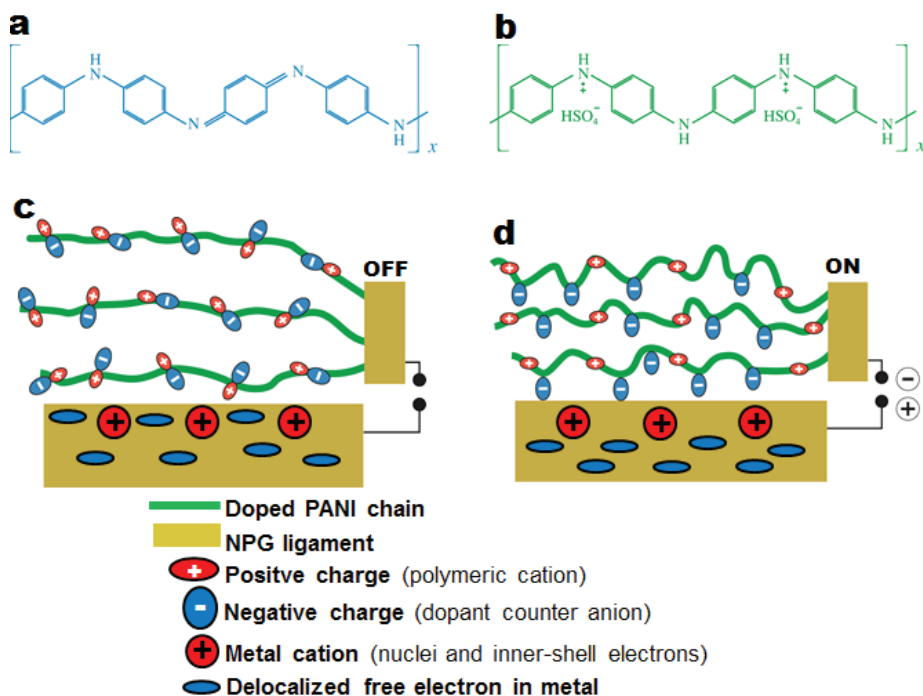


Figure 11. Potential-induced charge redistribution at the NPG surface. (a) Undoped PANI (blue insulating emeraldine base). (b) Doped PANI (green conducting emeraldine salt). (c) NPG/PANI interface in the absence of an electrical potential. Both positive and negative charge carriers along the polymer chains are held together by electrostatic interaction. An initial electronic charge distribution exists at the metal surface. (d) NPG/PANI interface in the presence of an electrical potential. Positive charge carriers along the polymer chains become involved in electrical conduction; localized negative charge carriers along the polymer chains electrostatically interact with the positive metal electrode, giving rise to electronic charge redistribution at the metal surface.

PANI becomes conductive (green emeraldine salt) by protonic acid doping or oxidative doping. During oxidative doping, an electron is removed from the pi-conjugated backbone, resulting in a free radical and a positive charge (poly-

meric cation) as schematized in Fig.11b. In the case of sulfuric acid doping [27] the charge neutrality in the doped PANI is maintained by negative sulfate counter ions co-adsorbed into the polymer matrix during the doping process [77–79]. The schematic structure of a doped PANI chain is shown in Fig.11b; both polymer cations and sulfate counter anions are held together by electrostatic interactions [80]. In the absence of an external electrical potential (“off” stand in Fig. 11c), polymer chains adopt shapes that favor minimal intra- and inter electrostatic interactions in the molecular chains. These shapes can be linear as reported by Lee et al. for a monolayer coating of PANI on a single Au crystal [78]. When a suitable electrical potential is applied on the hybrid actuator, e.g. in the NPG/PANI/Au configuration (“on” stand in Fig.11d), holes are injected from the positive NPG electrode into the PANI coating. The transport of these holes across the polymer film involves the cations and free radicals on the pi-conjugate backbone, the positive charges on the pi-conjugated backbone become mobile during electrical conduction whereas the negative sulfate counter ions are localized along the chains. The total amount of negative charges in the polymer matrix, arising from co-adsorbed sulfate anions was estimated for a 5 nm-thick PANI coating and was found to be ~ 3.2 C per m^2 coating, assuming that each repeating unit of PANI contributes with two sulfate anions as illustrated in Fig.11b. This amount of charge is comparable to the quantity of electronic charge involved in dimensional changes in nanoporous metal/electrolyte hybrid actuators. During the potential sweeps, this relatively large amount of negative charge dispersed into the thin polymer matrix electrostatically interacts with the positive NPG electrode. PANI molecular chains undergo conformational changes in order to bring the sulfate anions (i.e. negative charge carriers) in the proximity of the positive metal electrode; sulfate anions present in the first monolayer of PANI are eventually electro-adsorbed onto the metal electrode as reported by Lee et al. and illustrated in Fig.11d [25]. The electrical potential-induced interactions between sulfate anions and the ligaments of NPG give rise to electronic charges redistribution at the ligaments interface. Typically, the delocalized free electrons in the metal move from the interface towards the bulk, leaving the metal interface with positively charged metal ions (see Fig.11d). These metal cations consist of nuclei and inner-shell electrons of metal atoms. As mentioned, the delocalization of negative charges from the metal surface towards the bulk weakens the interatomic bounds between metal surface atoms, resulting in relaxation of these metal surface atoms. This gives rise to an increase in tensile stress at the surface of the ligaments. Due to the high surface-area-to-volume ratio of NPG, the dimensional changes in the ligaments result in an overall macroscopic volume change in the NPG electrode, which is experimentally measured during forward voltage sweeps in the NPG/PANI/Au configuration.

During the reverse voltage sweep where the applied electrical potential is gradually removed, electrostatic interactions between the negative sulfate ions and the positive metal electrode gradually vanish, charge redistribution takes place again at the metal interface and the initial charge distribution is restored.

Although the dimensional changes in the NPG/PANI hybrid actuator do not come from actuation in PANI as emphasized above, in the present understanding of the process, it is believed that conformational changes in the polymer chains play an important role during actuation: (i) changes in molecular shapes of the polymer bring the sulfate anions in the proximity of the metal electrode, or take these counter anions away from the metal electrode depending on the sign of the potential applied at this electrode. (ii) The high rate of which conducting polymers undergo conformational changes as highlighted by Yip and co-workers [81] might justify the high actuation rate recorded on the NPG/PANI composite material: rapid shape changes in polymer chains favor a fast exposure of sulfate anions to the positive NPG electrode and consequently rapid charge redistribution at the NPG interface. In contrast, when ions are transported through an electrolyte, a high actuation rate is hampered because of the low ionic conductivity of electrolytes [82].

SUMMARY AND OUTLOOK

In conclusion, we have demonstrated a new electrolyte-free approach to generate work from metallic muscles made of nanoporous metals with high surface-area-to-volume ratios, by exploiting a nanoporous metal/polymer interface rather than the common nanoporous metal/electrolyte interface. In this actuation concept, a doped polymer coating is grown onto the ligaments of a nanoporous metal and dopant counter ions present in the polymer coating matrix are exploited to modulate the electronic charge distribution at the nanoporous metal surface, resulting in surface stress changes and dimensional changes in the nanoporous metal. With this actuation approach, the various drawbacks encountered in metallic muscles operating in aqueous electrolytes have been overcome. In particular, the electrolyte-free actuator consists of a single-component hybrid material, in contrast to the three-component configuration required in nanoporous metal/electrolyte composite actuators; the nanoporous metal/polymer hybrid actuator is an all-solid-state device like piezoceramic actuators, and its actuation rate is about three orders of magnitude higher than that of metallic muscles operating in aqueous electrolytes.

An interesting observation is that a thin polymer coating grown onto the metallic ligaments of nanoporous gold can be exploited to add a new functionality to nanoporous metals operating as electrochemical actuators. By doing so, a metallic muscle would become smarter because in addition to its reversible dimensional changes, it also undergoes reversible changes in color. This combination of electromechanical and optical properties could open the door to new applications in artificial muscles. A straightforward application includes a metallic muscle that can give feedback on the progress on its work simply by changing its color [61, 83].

Moving forward, we anticipate that nanoporous metallic actuators could play a key role in novel energy-efficient MEMS technologies, far beyond the low actuation voltage concept discussed in the present contribution. As a future direction, and building upon our previous work on light interaction with monolithic nanoporous metals [83], we have been exploring ways of taking advantage of light-matter interaction to develop a new class of autonomous metallic muscles that can operate under light irradiation. Light-induced actuation, the direct conversion of solar energy into mechanical work without the need for external electrical energy supply is highly desirable in several MEMS technologies, including scanning mirrors used in a wide range of applications involving deflection of light such as laser beam positioning, optical switching, LiDAR, laser displays, barcode reading and microscopy [84–97]. In LiDAR for instance, the profiles of objects such as landscapes and buildings are mapped using scanning mirrors, which collect laser pulses from the measuring object and deflect them to a photodetector [87, 88, 94, 95]. Key components in MEMS scanning mirrors are microactuators including piezoelectric, electrostatic, thermal, and magnetic actuators [84, 85, 96, 98–102]. Currently, there are several ongoing challenges involving these microactuators. Two of these changes include:

- (i) The necessity to use small voltages and small currents at small length scales and in mobile applications [103–108]. For instance, in the case of electrostatic microactuators, which consist of parallel capacitor plates [98], a relatively “high electric voltage” of the order of tens up to hundreds of volts is usually required to charge and induce actuation through the attractive electrostatic force between the two plates [94, 109]. In the case of thermal microactuators [98], where electric power is used to heat the actuating component through the Joule effect and induce actuation by thermal expansion, a relatively “high input electric current” of the order of tens up to hundreds of milliamps is required [110, 111]. A similar high input electric current is also needed in magnetic microactuators [95, 98] in order to induce a magnetic field around the actuating material and generate actuation through Lorentz forces. Microactuators operating with small voltages or small currents are more suitable for small length scale and mobile applications. In particular, while high-voltage microactuators, such as electrostatic and piezoelectric ones do not necessarily need a high input power for actuation, their high-voltage requirement restricts their use in mobile applications where they can only be powered by low-voltage batteries [103, 104]. On the other hand, high-current microactuators, such as thermal and magnetic ones, are associated with high-power consumption since the driving power for actuation is proportional to the current. Therefore, developing and integrating low-current actuators in microscale systems is desirable and compatible with the growing awareness for sustainability.

- (ii) The desire to remove wire connections at the microscale, as they commonly give rise to undesirable contact resistances and heat issues at small length scales [112–116].

Light-induced actuation represents a promising approach to overcome these drawbacks [117–125], and we have been exploring a new sustainable actuation mechanism in monolithic nanoporous metal/semiconductor composites during which light is used to remotely induce mechanical work without the need for any wired connections at the microscale. This new actuation concept uses 3D high-surface-to-volume ratio nanoporous metals, in which the pore walls are conformally coated with a semiconducting nanolayer as in our previous work from Fig. 7, in the case of NP-Au/SnO₂, to form a 3D Schottky junction. Light-induced charge transfer across the Schottky junction (i.e. reversible transfer of electrons between the conduction band of the semiconductor and the metal Fermi level) is harnessed to optically manipulate the density of free electrons at the metal/semiconductor interface, and produce significant surface stress and strains in the 3D metal/semiconductor nanocomposite. An illustration of this new actuation mechanism is shown in Fig. 12, along with the conventional actuation mechanism in aqueous electrolytes. We anticipate that the resultant light-induced actuation in metallic muscles will enable sustainable MEMS scanning mirror applications as illustrated in Fig 13.

As far as nanoporous metallic systems are concerned, besides in the field of sensors and actuators, they might have a significant impact in the field of energy-related materials. New technologies for vehicles such as battery electric vehicles could contribute significantly to fixing our environmental issues, mainly caused by our high consumption of fossil fuels and air pollution by combustion vehicles. Lithium-ion batteries have long been seen as very promising power sources for electric vehicles. However, nowadays, there are strong indications that lithium-ion technology could not revolutionize the transportation sector. The specific energy of state-of-the-art lithium-ion batteries is still relatively low, compared to that of internal combustion vehicles. Besides, raw lithium resources are not available for large-scale electrochemical energy storage applications. Lithium-ion technology makes use of lithium-ion insertion in the bulk of a solid host anode material. The short lifetime and failure of high-capacity metal-ion batteries are caused by the large volume changes taking place in the anode during metal-ion insertions [126–128]. Although for lithium-ion batteries it is now well-recognized that porous architectures can be used to effectively accommodate these large volume changes [129, 130] and to allow rapid transport of lithium ions throughout the electrode material, so far, nanostructured porous anodes have not yet being exploited in great detail. Recently we have synthesized hierarchical nanoporous tin for high-performance lithium-ion batteries anodes, as illustrated in Fig. 14 [131, 132]. The following burning questions should be addressed in this research: does a nanoporous architecture improve the performance of battery anodes? If so, how?

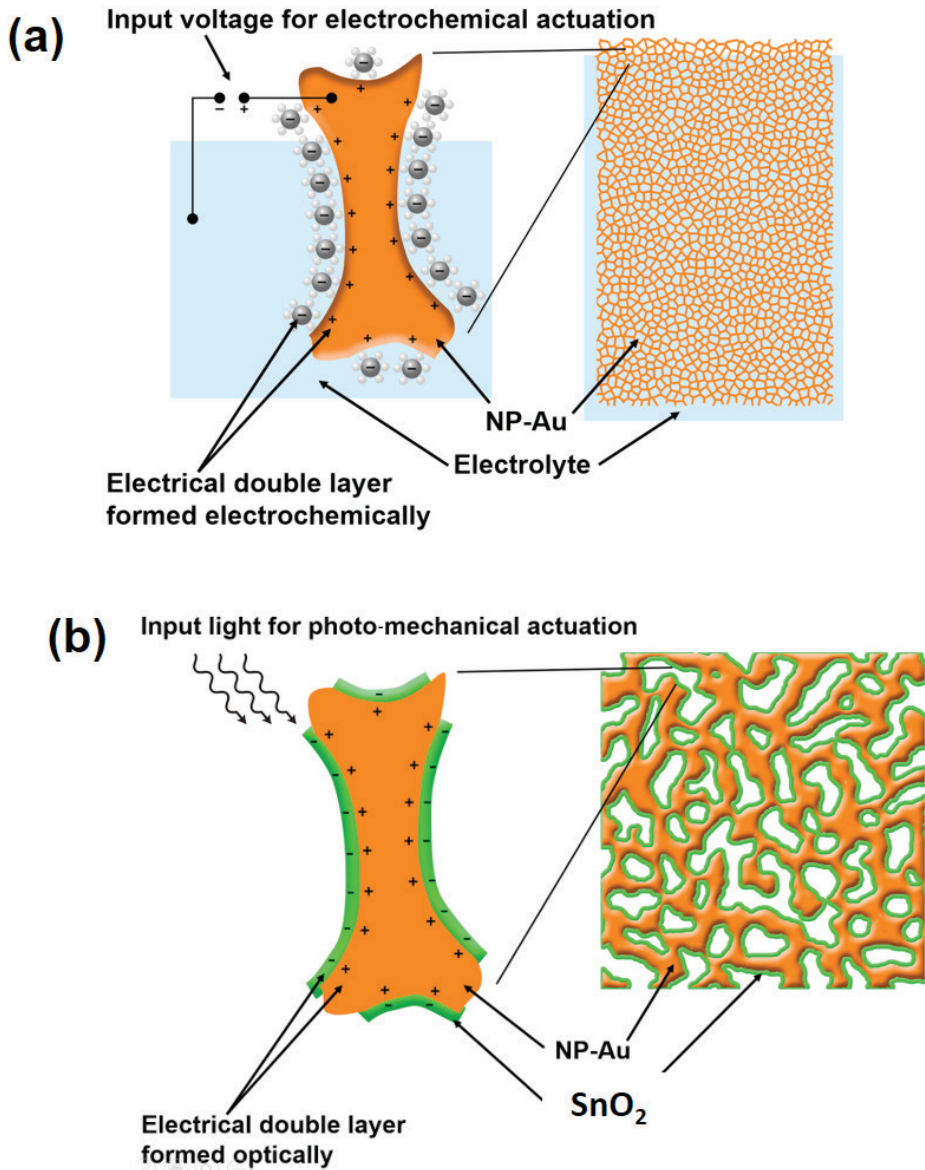


Figure 12. (a) Conventional actuation concept in nanoporous metals. Electrochemically formed electrical double layer at the interface of a high-surface-to-volume ratio nanoporous metal is responsible for surface-stress induced strains. (b) Our suggestion for a new actuation concept in nanoporous metals. Optically formed electrical double layer at the interface of a high-surface-to-volume ratio nanoporous metal is responsible for surface-stress induced dimensional changes.

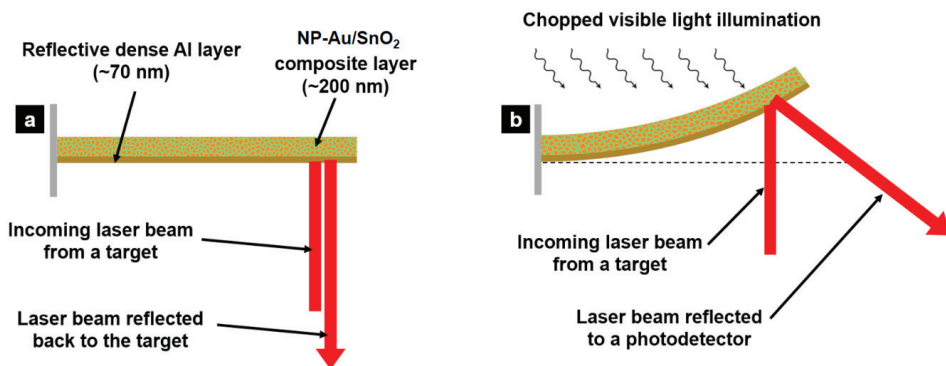


Figure 13. Wireless and sustainable (driven by visible light) microcantilever based on nanoporous metal composite, capable of deflecting a laser beam during actuation. Such a microactuator could be attractive for large-aperture LiDAR systems.

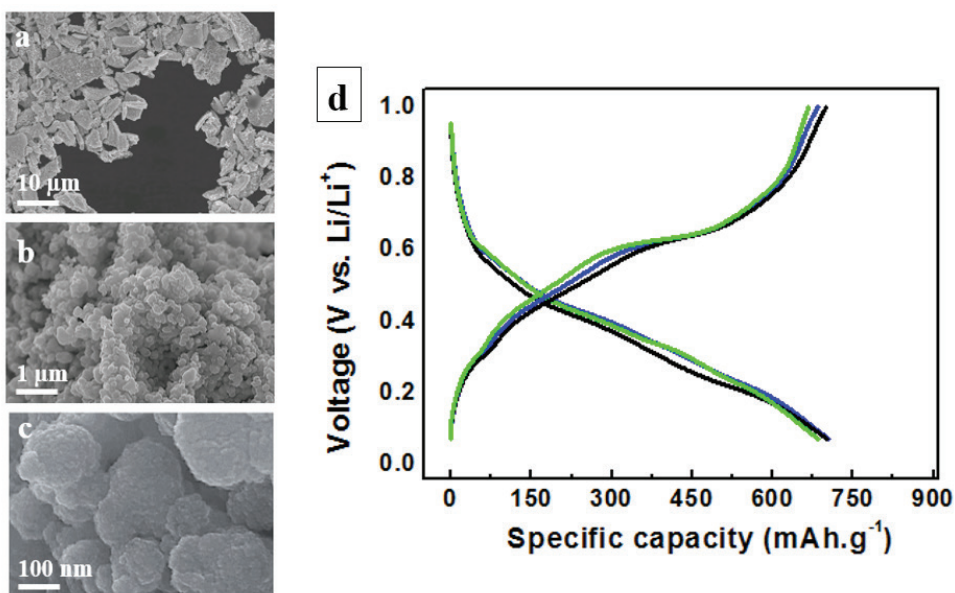


Figure 14. Nanoporous Tin (NP-Sn) as anode material for the next generation Li-ion battery (a) As-synthesized fine NP-Sn powder dispersed on a carbon substrate. The powder particles have random shapes and random size in the sub-10 μm ranges. (b) High magnification SEM showing that the powder particles are porous. (c) The ligaments exhibit granular-like morphology. TEM analysis reveals that these granular ligaments are in turn porous (not shown). (d) Examples of galvanostatic curves obtained using Li^+ . Good stability over a few hundred cycles can be achieved [12].

To provide answers to these important questions we propose *operando* experiments that should provide the very first experimental insights into the reaction mechanisms and phase performance during insertion/extraction of ions in/out the anode material in the case of dealloyed nanoporous systems.

In this contribution we did not touch in detail on recent advances in nanoporous materials for renewable energy resources conversion into fuels. In [133] we have presented an overview of common selective leaching strategies for the fabrication of 3D nanoporous materials, the applicability of these materials as heterogeneous (electro)catalysts for the conversion of renewable energy resources into fuels. The high internal surface area, high density of active catalytic sites, and remarkable intrinsic properties of these 3D nanoporous materials make them very attractive for large-scale applications. In fact, several recent reports have demonstrated the high performance dealloyed bulk nanoporous NiFe-based systems as water oxidation electrocatalysts [134, 135]. The performance of dealloyed 3D nanoporous catalyst materials can further be improved through structural design. Here, we believe that the ultimate architecture for this type of applications should involve hierarchical porous structures, where the big porous structures will account for mass transfer in/out the bulk of the material, while the small pore structures provide a large internal surface area for the catalytic reaction. Therefore, since roughly any type nanoporous material can be made utilizing the various new dealloying strategies, it should be possible to make nanoporous architecture of any material identified as high-performance (electro)catalyst.

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Џеф ДеХосон и Ерик Дејси

МЕТАЛНИ МИШИЋИ: НАНОСТРУКТУРЕ У АКЦИЈИ

Резиме

Метални системи који опонашају особине мишића условљене спољашњим стимулацијама, назване „вештачким мишићима” по аналогији са скелетним мишићима, идеални су покретачи са високим степеном енергетске ефикасности, брзим деформационим одговором и великом издржљивошћу. Уобичајено коришћење постојећих материјала за покретаче, као што су пиезокерамика и електроактивни полимери, ограничено је са више фактора, укључујући малу енергетску ефикасност, мале амплитуде деформације, ограничења замором и високим напонем потребним за покретање. У овом прилогу показаћемо да нанопорозни орвано-метални материјали могу да раде као покретачи, са јединственом комбинацијом особина: ниским радним напонем, релативно великим амплитудама деформације, великом крутошћу и чврстоћом. Посебно ће бити размотрено како, кроз интелигентно пројектовање материјала, постићи велику макроскопску амплитуду деформације, до 10%, и велику брзину деформације, до 10^{-2} s⁻¹, што је приближно до два, тј. до пет редова величина веће, респективно, него у било ком материјалу до сада. У закључку и будућим изгледима увешћемо концепт светлосно-активирајућих покретача у системима на бази металних мишића, односно директне конверзије соларне енергије у механички рад, без додатне спољне електричне енергије. На крају, као наставак ове теме везане за енергију, дискутоваћемо области у којим нанопорозни материјали могу имати велики допринос.