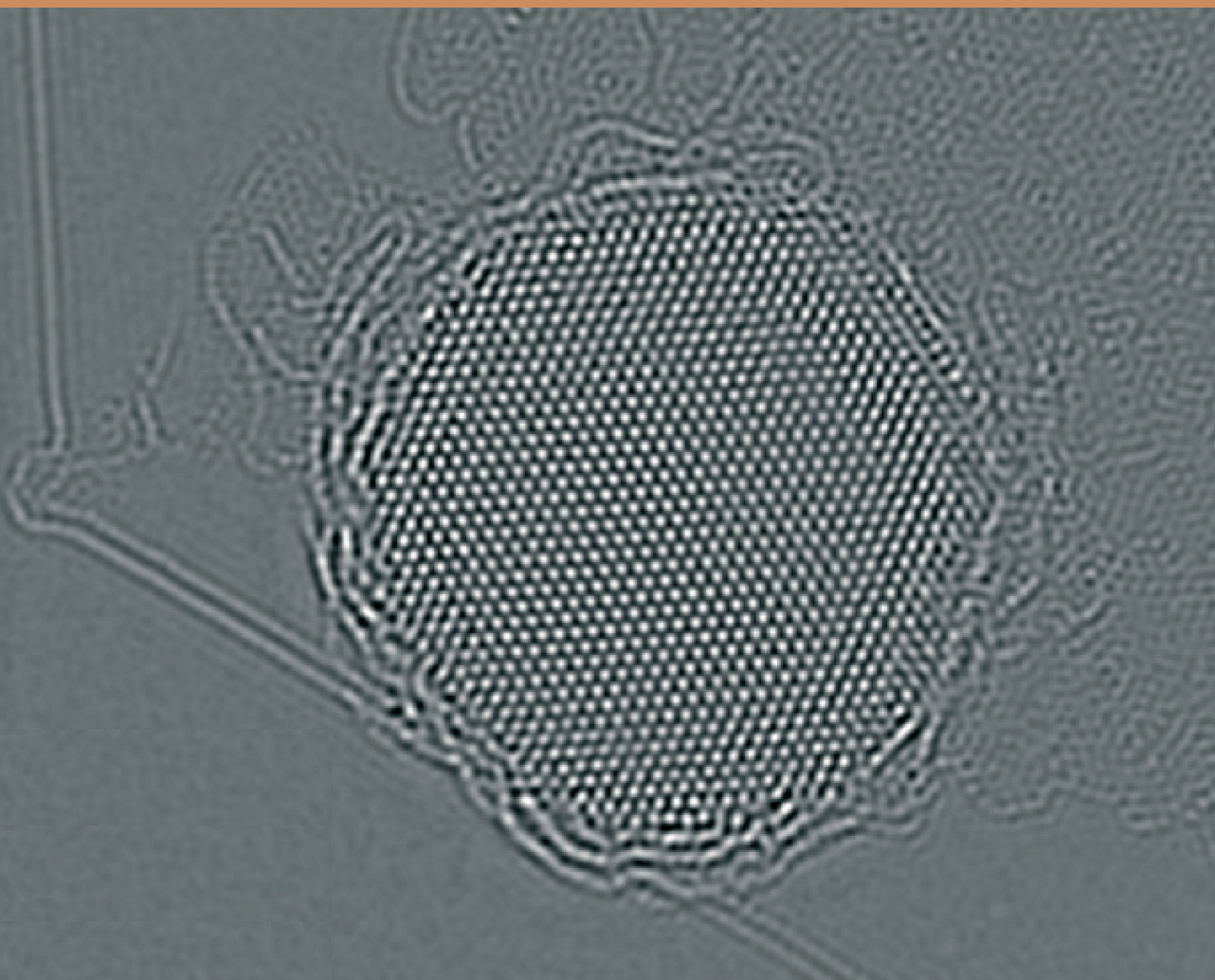


SERBIAN ACADEMY OF SCIENCES AND ARTS
СРПСКА АКАДЕМИЈА НАУКА И УМЕТНОСТИ



FASCINATING WORLD OF NANOSCIENCES
AND NANOTECHNOLOGIES
ФАСЦИНАНТНИ СВЕТ НАНОНАУКА
И НАНОТЕХНОЛОГИЈА

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FASCINATING WORLD OF NANOSCIENCE
AND NANOTECHNOLOGY

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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, Јагранка 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 BaTaO ₃ -NaFe ₂ O 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.

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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 нанонауци 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. Срдиха 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 нанонаука 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
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Џеф Т. М. ДеХосон
Краљевска холандска академија наука и уметности

NANOSTRUCTURES OF ELECTROCONDUCTING POLYMERS AND CARBON NANOMATERIALS PRODUCED BY THEIR CARBONIZATION

GORDANA ĆIRIĆ-MARJANOVIĆ*

A b s t r a c t. – Conjugated polymers that are able to conduct electricity – *electroconducting polymers* constitute a separate class of synthetic polymers. Typical examples are polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), and their derivatives. These polymers belong to the so-called ‘intelligent materials’ since they possess complex and dynamic structures owing to whose design their properties can be tuned and controlled, and their response to various stimuli can be manipulated. Over the past decade there has been rapidly increasing interest in the *nanostructures of electroconducting polymers*. They have elicited much interest because of fundamental aspects and their increased applicability, owing to their enhanced properties. This paper focuses specifically on the most important findings of our research related to the synthesis, mechanism of formation, and physicochemical properties of PANI and PPy nanostructures. *Carbon nanomaterials* constitute another large group of advanced materials that have been the subject of extensive research because of their interesting properties and versatile applicability. Particular attention is drawn on *carbon nanostructures doped by covalently bonded heteroatoms* (N, B, P, etc.), the introduction of which have led to their improved properties. We have been developing novel *N-doped electroconducting carbon nanomaterials* by applying the simple method of *carbonization of nanostructured PANIs*. The morphology and properties of produced carbon nanomaterials can be tuned by making an appropriate choice of polymer precursor’s morphology and properties and by setting appropriate carbonization conditions. This class of nanomaterials exhibits excellent performance in terms of their versatile applicability (supercapacitors, electrocatalysis, photocatalysis, etc.). The selected results of our research on carbon nanomaterials produced from nanostructured PANIs and PPys are presented.

Keywords: electroconducting polymers, nanostructures, carbon nanomaterials, carbonization, polyaniline, polypyrrole

INTRODUCTION TO ELECTROCONDUCTING POLYMERS

Electroconducting polymers (frequently referred to as *conducting polymers*, CPs) constitute a separate class of *conjugated synthetic polymers* that are able to conduct electricity, and are also called *synthetic metals*. Typical examples are polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT), and their derivatives (Fig. 1).

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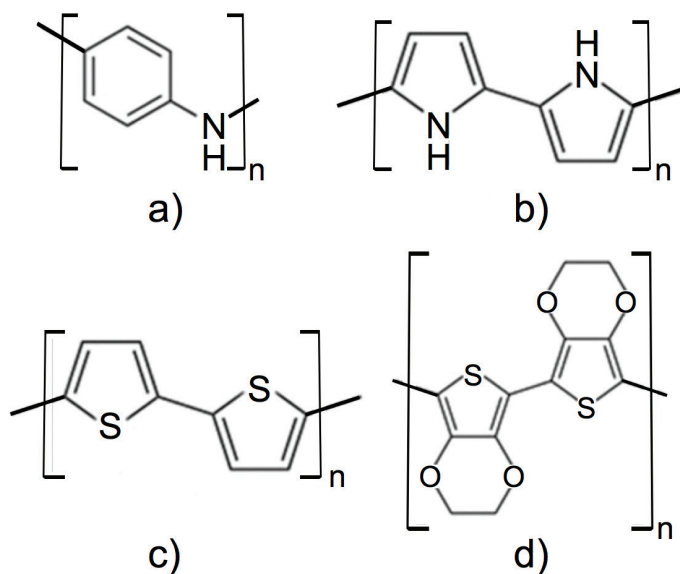


Figure 1. Typical electroconducting polymers (in their undoped forms): a) polyaniline, b) polypyrrole, c) polythiophene, and d) poly(3,4-ethylenedioxythiophene)

Their particular structural forms (i.e. 'doped state', with the specific oxidation/protonation level) are inherently conducting and can achieve the range of conductivity of metals (up to $\sim 10^3 \text{ S cm}^{-1}$). However, besides electrical conductivity, they possess many other unique and interesting properties that are used for multiple applications. The most important properties are: i) the ability to change oxidation state and the extent of protonation, i.e. to exist in different acid–base and redox forms and show redox-activity, ii) the ability to change colour once the change in potential takes place (electrochromism), iii) the ability to switch from conducting (doped) to a non-conducting (undoped) state upon alkali treatment, and vice versa upon acid treatment (property especially usable for sensors), iv) the ability to exchange dopant counterions that are attached to the polymer chains and to simultaneously change the volume (property usable for actuators), v) some of their structural forms may contain unpaired electrons and show paramagnetism. The structure of CPs is versatile, dynamic, controllable and can be tuned by choosing different synthesis conditions and/or post-synthetic treatment that also dictates their properties (chemical, optical, electrical, electrochemical, magnetic, mechanical, etc.). Simultaneously, it is possible to manipulate their response to different stimuli (e.g. electrical). Given that they are capable of recognizing specific environmental stimuli, as well as of processing the information arising from the stimuli, and of exhibiting the appropriate response to stimuli, CPs belong to the class of the so-called *intelligent materials* [1]. The importance of research in the field of CPs was recognized in 2000, when the Nobel Prize in Chemistry was awarded to three scientists: Alan MacDiarmid, Alan Heeger and Hideki Shirakawa

“for the discovery and development of conductive polymers”. The *extended π -electron conjugation* is the fundamental requirement for the *electrical conductivity* of CPs (being predominantly electronic conductivity) as well as for the appearance of other phenomena (optical, electrical, magnetic, etc.).

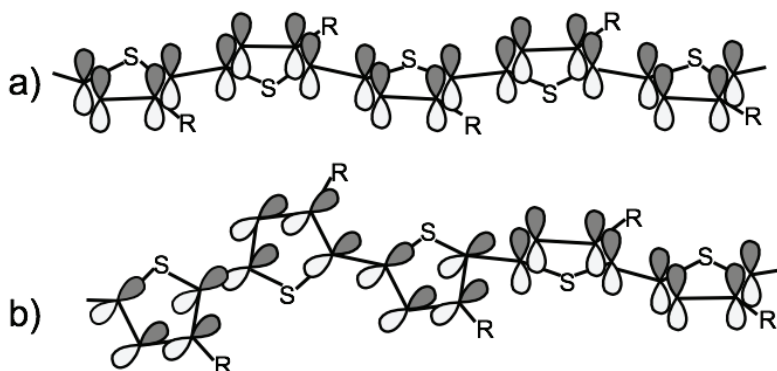


Figure 2. Schematic presentation of conjugated π orbitals in substituted polythiophene (R is the substituent): a) polymer chain form with full coplanarity of aromatic rings, b) polymer chain with a deviation from coplanarity (twisted form)

Conjugation is realized by the overlap of the π orbitals, which is conditioned by the coplanarity of aromatic rings in the polymer skeleton (Fig. 2). The coplanarity of rings is also one of the requirements necessary for the extended conformation of polymer chains and a good conductivity of CPs (Fig. 2). In addition to electronic conductivity, CPs also possess certain ionic conductivity due to an electrolyte and a solvent incorporated during the synthesis. The experimental conditions during the synthesis (e.g. type of counterions, temperature, pH, electrode potential, etc.) affect the conductivity of the resulting polymer.

MOLECULAR STRUCTURE OF POLYANILINE AND POLYPYRROLE

PANI can exist in a variety of acid-base and redox forms [2]. The general structural formula of PANI base forms, in which all nitrogen atoms are not protonated, is presented in Fig. 3. Depending on the content of benzenoid (B) and quinonoid (Q) rings, different forms are possible. The most typical forms are fully reduced form – leucoemeraldine ($y=1$), half-oxidized form – emeraldine ($y=0.5$), and fully oxidized form – pernigraniline ($y=0$), but intermediate states are also possible.

The only electroconductive form of PANI is the protonated, half-oxidized emeraldine salt form (PANI-ES), presented in Fig. 4 [2]. Experimental evidence suggests that PANI-ES represents a mixture of polaronic and bipolaronic structures in various proportions, depending on a synthetic procedure, in which aniline monomer units are exclusively connected by para N–C coupling.

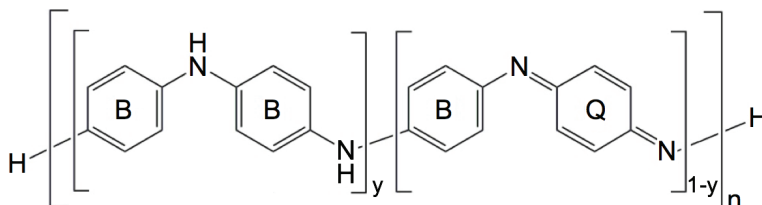


Figure 3. General structural formula of PANI base forms. For leucoemeraldine, emeraldine and pernigraniline form y takes values 1, 0.5 and 0, respectively. Benzenoid and quinonoid ring are marked with B and Q, respectively.

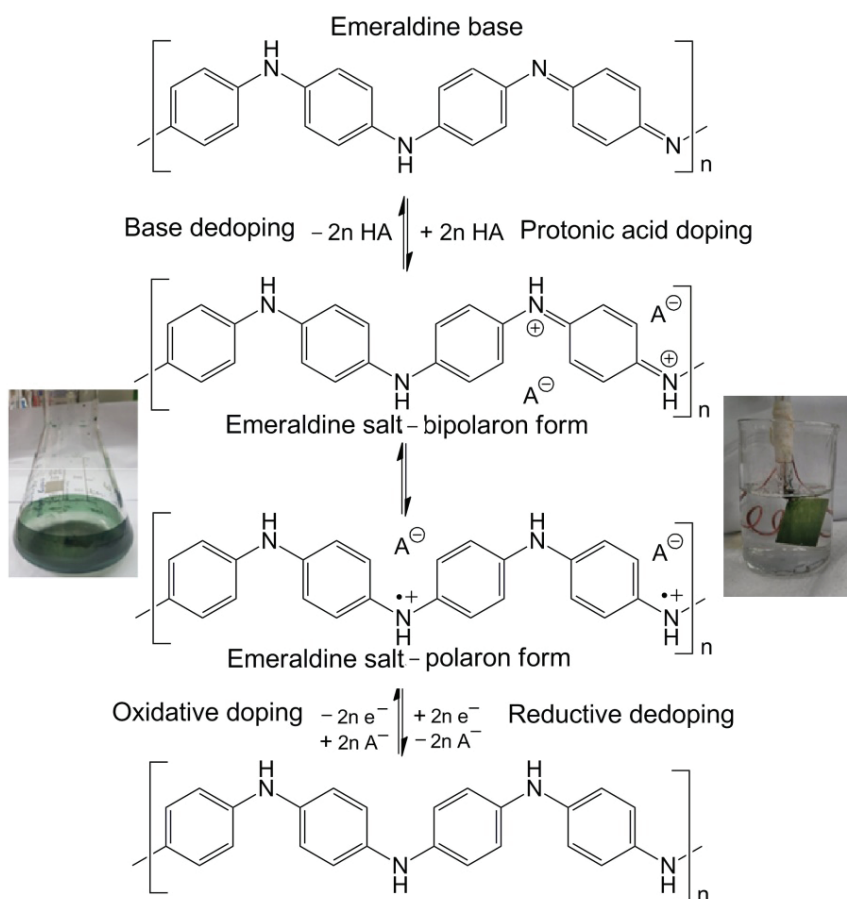
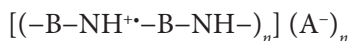


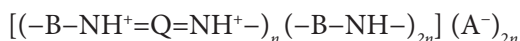
Figure 4. Typical structural forms of PANI: doping of nonconducting emeraldine base by protonic acid (HA) to conducting PANI-ES and oxidative doping of nonconducting leucoemeraldine to conducting PANI-ES form (A⁻ denotes an anion, counterion). PANI-ES may exist in two forms: polaron and bipolaron form. Green films of PANI-ES formed on the wall of reaction flask (left) and on the platinum electrode (right) by the chemical and electrochemical oxidative polymerization reactions, respectively, are also shown.

An ideal polaronic form of PANI-ES ('polaronic lattice') can be presented by the formula:



where A^- is a counterion. Paramagnetism of this form originates from unpaired electrons in $-NH^{+\bullet}$ cation radicals (polarons).

The bipolaronic form of PANI-ES can be described by the formula:



This form is dicationic, and it does not contain unpaired electrons. It is widely accepted that the polaronic form with delocalized polarons is responsible for the electrical conductivity of PANI [2, 3].

Besides ordinary PANI units, the presence of atypical structural units (such as N-N and C-C coupled aniline units, phenazine-, N-phenylphenazine-, and phenoxazine-type units, branched 1,2,4-trisubstituted and 1,2,4,5-tetrasubstituted benzenoid units, substituted monoimino-1,4-benzoquinone units etc.) is also detected in the PANI and oligoaniline samples, depending on the synthesis conditions [2, 3].

Typical molecular structures of protonated (salt form) and deprotonated (base form) PPy are shown in Fig. 5 [4]. The distribution of positive charges on PPy chains and the structures with unpaired electrons (polarons), similar to those in PANI, is still open to discussion.

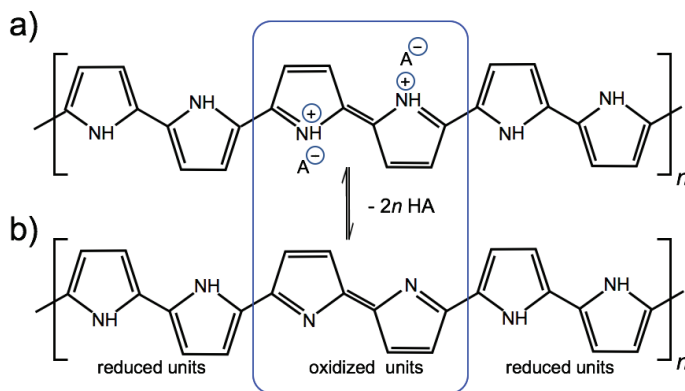


Figure 5. Structural forms of PPy: a) protonated (salt) form, and b) deprotonated (base) form; A^- denotes a counter-ion originating from the acid HA

SYNTHESES OF POLYANIINE AND POLYPYRROLE

The most frequently used methods for the syntheses of CPs are the chemical and electrochemical oxidative polymerizations of monomer (aniline, pyrrole, thiophene etc.) [1-3]. Other unconventional methods have been rarely used, e.g. plasma polymerization [1,2].

For the chemical polymerization, various chemical oxidants have been used to initiate polymerization: ammonium peroxydisulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8, \text{APS}]$, iron (III)chloride, potassium dichromate, hydrogen peroxide, ceric sulfate, etc. [1-3]. Special cases represent chemical polymerizations catalyzed by the enzymes [5], e.g. polymerization using the H_2O_2 /horseradish peroxidase [6] or O_2 /lacasse [7] as oxidant/catalyst systems.

The oxidation of aniline with APS is a frequently used reaction. It has been typically performed at low pH (lower than c.a. 2.5) in the presence of strong dopant acids, leading to PANI (Fig. 6) with granular morphology, good conductivity ($\sim 1 \text{ S cm}^{-1}$) and high molar mass [1–3, 8]. In these cases anilinium cation is predominant over neutral aniline in the system, as the pKa value of anilinium cation is 4.6.

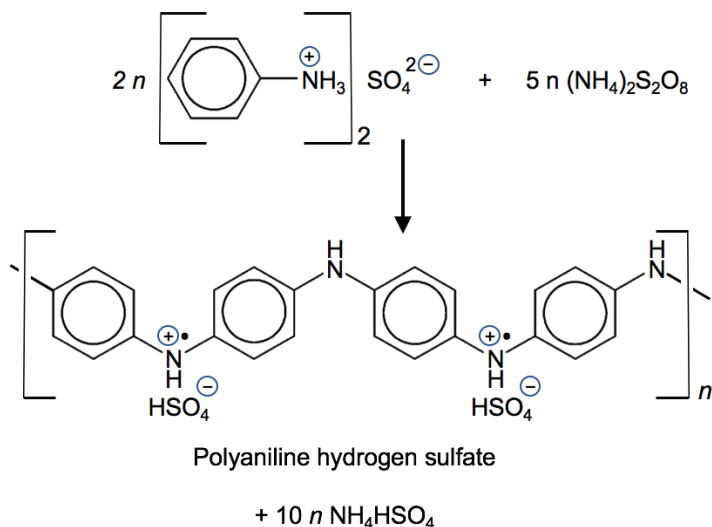


Figure 6. The reaction of anilinium cation oxidation with APS leading to PANI in its conductive ES form. This reaction is predominant at low pH values when anilinium cation is present in higher concentration related to neutral aniline.

In the cases with higher initial pH (higher than about 4.6), the neutral aniline is predominant over the anilinium cation, and its oxidation with APS can be presented by the equation in Fig. 7 [9]. The mechanism of this reaction is different from that in the case with high initial acidity [10-15].

In contrast to the reaction in Fig.6, which occurs via one exothermic step with the preceding induction period, the reaction at higher initial pH, presented in Fig.7, occurs via two exothermic phases separated with a plateau (Fig. 8), leading to nanostructured PANIs that exhibit the morphology of nanotubes and/or nanorods. This reaction proceeds with a continual and pronounced decrease in the pH of the reaction medium (Fig. 8) [9, 13, 14, 16], and therefore it is called the 'falling-pH method' for producing 1-D PANI nanostructures, without added template.

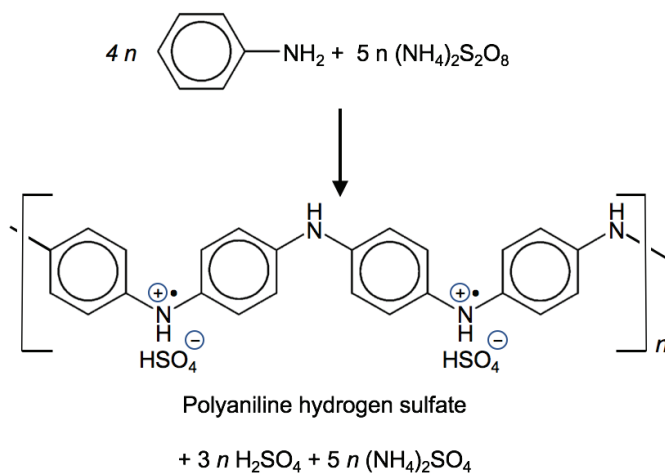


Figure 7. The reaction of aniline oxidation with APS leading to PANI in its electroconductive ES form. This reaction is predominant at pH values higher than 4.6 when neutral aniline is present in higher concentration related to anilinium cation.

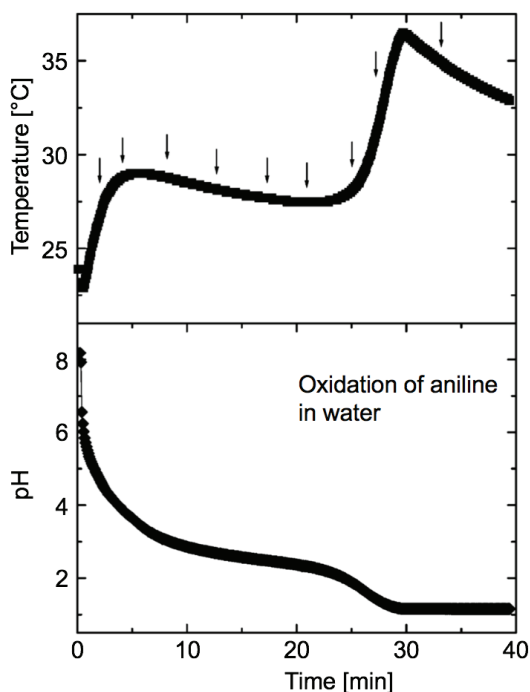


Figure 8. Changes in temperature (top) and acidity (bottom) during the oxidation of 0.2 M aniline with 0.25 M ammonium peroxydisulfate in water, without added acid. There are two exothermic reaction phases. (Reprinted and adapted with permission from *Journal of Physical Chemistry B*, Evolution of polyaniline nanotubes: The oxidation of aniline in water, by M. Trchová et al. 110, 9461–9468, Copyright (2006) American Chemical Society).

SUPRAMOLECULAR STRUCTURE OF ELECTROCONDUCTING POLYMERS

The *Supramolecular structure* of polymers can be defined as an assembly of macromolecules into the well-defined objects that have a specific shape. CPs appear in a variety of supramolecular structures, such as rods, tubes, fibers, spheres (hole or solid), sheets, belts, etc. The dimensions of supramolecular assemblies can range from nanometers to micrometers. Nanosized supramolecular structures are considered in the next subsection. Desired supramolecular structures of CPs can be produced by applying the concept of *self-organization* of polymer/oligomer chains using suitable conditions of syntheses, or by using different *templates* that are added in the polymerization system with the aim of dictating polymer growth i.e. the structure and organization of polymer chains [1]. The self-organization of polymer/oligomer chains refers to their ability to assemble into thermodynamically stable structures in which macromolecules are held together by different noncovalent interactions: van der Waals forces, electrostatic interactions, hydrogen bonds, π - π interactions, hydrophobic or hydrophilic interactions. Due to these specific and directed interactions, a higher level of chain ordering occurs leading to the formation of the stable, well defined structures. Self-organization is the spontaneous appearance of ordering, governed by thermodynamically favoured processes.

NANOSTRUCTURES OF ELECTROCONDUCTING POLYMERS

Nanostructures are objects (or structural arrangements) at the nanoscale, with at least one dimension less than 100 nm. They are classified based on the number of dimensions that are *outside* the nanoscale range as zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D). CPs exhibit all these types of nanostructures (Fig. 9) [17-19].

According to this classification, in *zero-dimensional* (0-D) nanostructures all three dimensions are measured within the nanoscale, i.e. ≤ 100 nm (Fig. 9a). Most commonly, 0-D nanostructures are solid nanospheres (nanoparticles) [17, 20]. In *one-dimensional* nanostructures (1-D), one dimension is outside the nanoscale, while other two dimensions are within the nanoscale (Fig. 9b). This class includes nanotubes, nanorods, nanofibers, and nanowires [17-19, 21]. In *two-dimensional* nanostructures (2-D), two dimensions are outside the nanoscale, while third dimension is at the nanoscale, ≤ 100 nm (Fig. 9c). This class includes plate-like shapes (nanosheets, nanoleaves, nanobelts...) [17, 22]. *Three-dimensional* nanostructures (3-D) are complex hierarchical structures built of 0-D, 1-D and 2-D nanostructures (Fig. 9d). Typical examples are bundles of nanotubes or nanofibers, dendritic structures, structures with the shape of star, urchin or flower of CPs [17, 23].

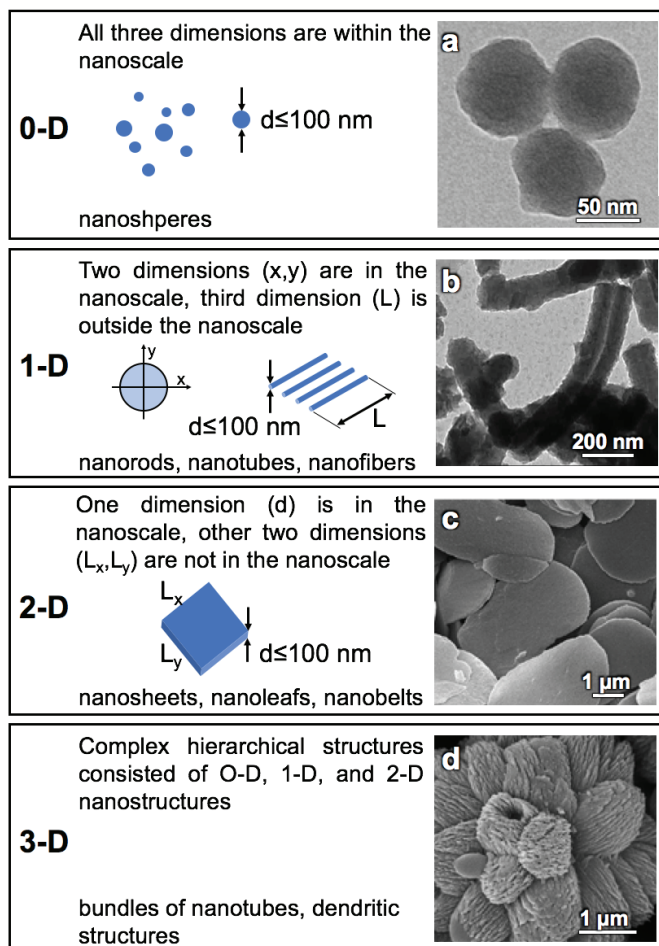


Figure 9. Classification of nanostructures as 0-D, 1-D, 2-D and 3-D (left), and the scanning/transmission electron micrographs of typical examples of CPs for each type of nanostructures (right): a) nanospheres (Reprinted and adapted with permission from *Journal of Physical Chemistry C*, Pt Nanoparticles Supported on Polypyrrole Nanospheres as a Catalytic Counter Electrode for Dye-Sensitized Solar Cells, by S. S. Jeon et al. 115, 22035–22039, Copyright (2011) American Chemical Society), b) nanotubes/nanorods (Reprinted and adapted with permission from *Journal of Physical Chemistry B*, Synthesis and Characterization of Self-Assembled Polyaniline Nanotubes/Silica Nanocomposites, by G. Ćirić-Marjanović et al. 113, 7116–7127, Copyright (2009) American Chemical Society), c) nanoplates (Reprinted and adapted with permission from *Macromolecules*, Controllable Synthesis of Polyaniline Multidimensional Architectures: From Plate-like Structures to Flower-like Superstructures, by C. Zhou et al. 41, 6473–6479, Copyright (2008) American Chemical Society), d) hierarchical flower-like structure (Reprinted and adapted with permission from *Macromolecules*, Controllable Synthesis of Polyaniline Multidimensional Architectures: From Plate-like Structures to Flower-like Superstructures, by C. Zhou et al. 41, 6473–6479, Copyright (2008) American Chemical Society).

The interest in CPs nanostructures has grown dramatically over the past two decades. They have elicited much interest because of fundamental aspects (study of the mechanism of their formation, specificities in molecular, supramolecular or crystalline structure, etc.), as well as because of their possible applications, since their performance is usually improved when compared to analogous materials that are not nanostructured [1, 2, 17]. For example, they have exhibited improved dispersibility and processability, higher capacitance in supercapacitors, shorter response in sensors, etc. [1, 2, 17].

There is a large number of methods available for producing CPs nanostructures. They can be generally classified into chemical, electrochemical and physical types of methods, Fig. 10. The present work is focused mainly on the chemical methods, which can be divided into those with template and without template (template-free), Fig. 10.

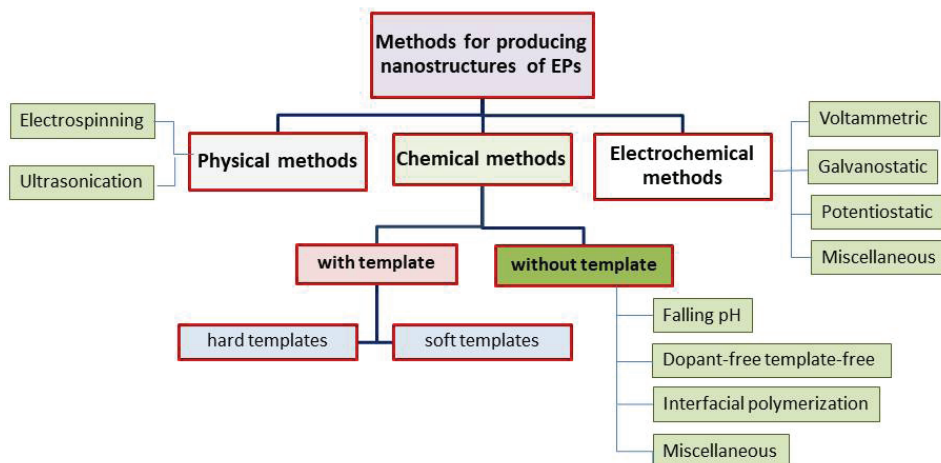


Figure 10. Main methods for producing nanostructures of CPs

Commonly used hard templates are porous materials, such as aluminosilicate MCM-41, anodic aluminum oxide (AAO), or polycarbonate (PC) track-etched membrane [24-26]. The porous hard template method enables the production of 1D nanostructures of conducting polymers, e.g. nanofibers, nanorods or nanotubes, whose diameter is determined by the diameter of the pores in the template [17, 27]. As hard templates for the preparation of nanostructured conducting polymers, small amounts of materials with desired nanostructured morphology were used, i.e. *nanostructured seed templates*, such as carbon nanotubes (CNTs) or V_2O_5 nanofibers [28]. The shape of seed nanoparticles dictates the morphology of the resulting conducting polymer [17].

The soft-template methods use various structure-directing molecules as templates. They can be soluble oligomers and polymers, e.g. DNA [29]. Surfactants

(e.g. sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB)) [30, 31], amphiphilic acids (e.g. β -naphthalenesulfonic acid (β -NSA), p-toluenesulfonic acid (p-TSA), dodecylbenzenesulfonic acid (DBSA)), or their mixture, have been frequently used as soft templates [32–35]. Such molecules are able to form, alone or with the monomer (e.g. aniline, pyrrole), supramolecular aggregates, e.g. cylindrical micelles that further guide supramolecular organization of resulting conducting polymer [17]. As an example, the chemical oxidative polymerization of the pyrrole monomer at the surface of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse cylindrical micelles resulted in the formation of tubular PPy nanostructures [36]. Dye molecules, such as methyl orange [37] or Acid Blue 25 [38], were used as soft templates for the production of PPy nanotubes [37] and nanowires [38].

There is a number of used methods without added template [17]: the *falling-pH method* [14, 39, 40] whose specific case is the *dopant-free template-free method* (without added template and without added dopant acid) [9, 13, 15, 39, 41, 42], *interfacial polymerization* (usage of at least two immiscible, aqueous/organic phases [43, 44]; the monomer is dissolved in one phase and the oxidant in the other phase and the formation of conducting polymer nanofibers occurs at their interface), the *rapid mixing* method [45, 46], etc. Electrochemical template-free methods have been also reported. For example, a PPy nanofiber network was electrochemically synthesized in an aqueous solution by using phosphate buffer solution (PBS) in the absence of any (hard or soft) template [47]. In the proposed mechanism for the nanofiber formation, the presence of the hydrogen bonding between phosphate dopant ions and Py oligomers was suggested to be essential, Fig. 11 [47].

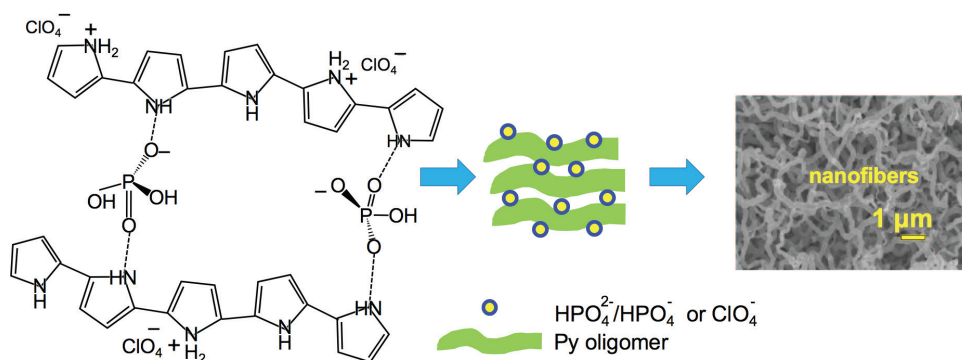


Figure 11. Electrochemical template-free preparation of PPy nanofibers (Reprinted and adapted with permission from *Macromolecules*, Template-Free Electrochemical Synthesis of Superhydrophilic Polypyrrole Nanofiber Network by J. Zang et al. 41, 7053–7057, Copyright (2008) American Chemical Society)

Structural characterization of polyaniline 1D nanostructures produced by the falling-pH method, without added template

FTIR spectra. – It was found that the FTIR spectra of PANI nano-tube/nanorods prepared by the falling-pH method in water without added acid (initial pH about 7), without any template, exhibited some specific features, compared to the spectra of 'ordinary', granular PANI-ES prepared from the highly acidic media [9, 14, 39, 40], Fig. 12. The most important characteristic features are: the appearance of the bands at about 1414 and 1445 cm^{-1} attributed to specific oligomers (these bands are especially pronounced during the early stage of the reaction; the band at 1414 cm^{-1} has been attributed to phenazine-type structural units), the bands which indicate mono-, 1,2- and 1,2,4- substitution patterns on benzene rings (observed at c.a. 695, 726, 740, 848, 860, 880, 906, and 974 cm^{-1} , indicating chain branching and the presence of phenazine-type units) besides the 1,4-substitution pattern typical for linear chains in standard PANI (observed through the band at c.a. 827 cm^{-1}), and the band at c.a. 1040 cm^{-1} due to vibrations of $-\text{OSO}_3^-$ and SO_3^- groups, indicative for benzene ring sulfonation and sulfation

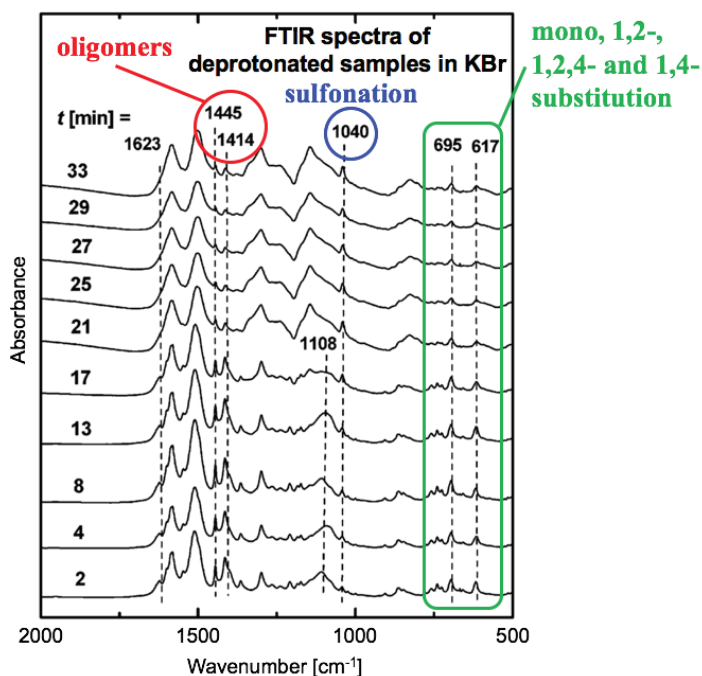


Figure 12. FTIR spectra of reaction intermediates/products collected at different times during the reaction of aniline with APS in water (without added acid), and then deprotonated. (Reprinted and adapted with permission from *Journal of Physical Chemistry B*, Evolution of polyaniline nanotubes: The oxidation of aniline in water, by M. Trchová et al. 110, 9461–9468, Copyright (2006) American Chemical Society).

(Fig. 12) [9, 14, 39–41]. The spectra of reaction intermediates/products recorded during the reaction show drastic change at the beginning of the second exothermic phase (Fig. 12, 21. min). The bands indicative for branching and phenazine-type units are relatively more intense in the spectra recorded before the second exothermic phase (i.e. for $t < 21$ min in Fig. 8); they are also seen later (for $t \geq 21$ min, Fig. 8), but dominating bands in the spectra are those characteristic of ordinary PANI with linear chains and N–C4 coupled units.

The FTIR spectroscopy clearly showed that the molecular structure of PANI nanotubes/nanorods produced by the falling-pH method, without added external template, differed from that of ordinary, granular PANI produced from the highly acidic media. The formation of phenazine-like units by the intramolecular oxidative cyclization at the branching site after the oxidation of 1,2,4-trisubstituted ring structure, and at the beginning of the chain after the oxidation of 1,2-disubstituted ring structure, is shown in Fig. 13.

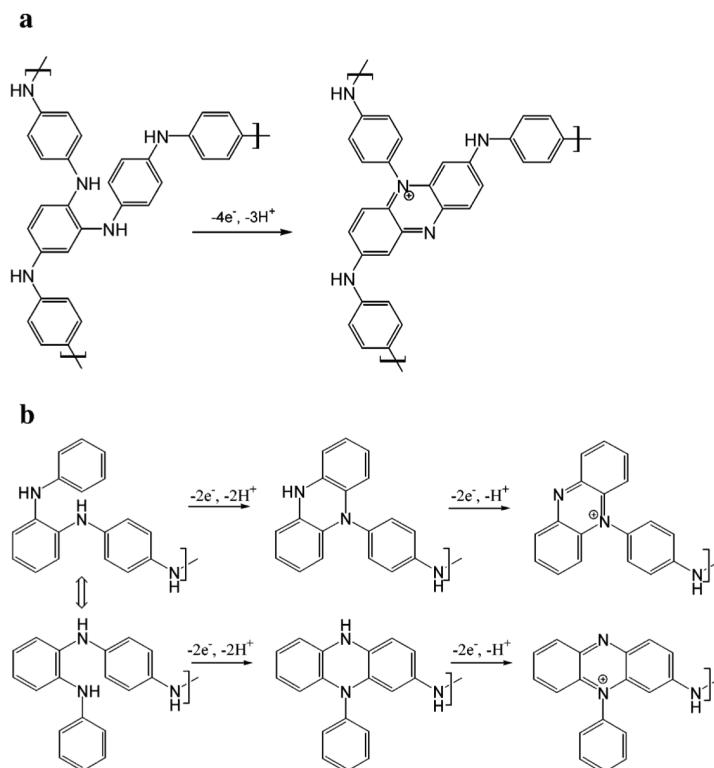


Figure 13. Phenazine-like units formed a) at the branching site after the oxidation of 1,2,4-trisubstituted ring structure, b) at the beginning of the chain after the oxidation of 1,2-disubstituted ring structure. (Reprinted with permission from *Journal of Physical Chemistry B*, Evolution of polyaniline nanotubes: The oxidation of aniline in water, by M. Trchová et al. 110, 9461–9468, Copyright (2006) American Chemical Society).

Raman spectra. – Similarly to the FTIR spectra, the Raman spectra of PANI nanotube/ nanorods, prepared by the falling-pH method, show features that indicate the presence of specific, phenazine-type units-containing structures, in addition to ordinary benzenoid, quinonoid, and semiquinonoid structures [13, 14, 40, 41]. The bands attributable to phenazine-type units are observed at c.a. 1645–1630, 1420–1400, 1380–1365, ~575, and ~415 cm^{-1} , Fig. 14.

The Raman spectra of oligoanilines, produced in the earlier phase of the reaction (at $t < 21$ min), differ from those of PANI nanotubes and nanorods, formed later (at $t \geq 21$ min) [13]. Broadening of the bands observed for a later stage of reaction (for $t \geq 21$ min, Fig. 14) indicated the formation of the conductive, polaron form of PANI.

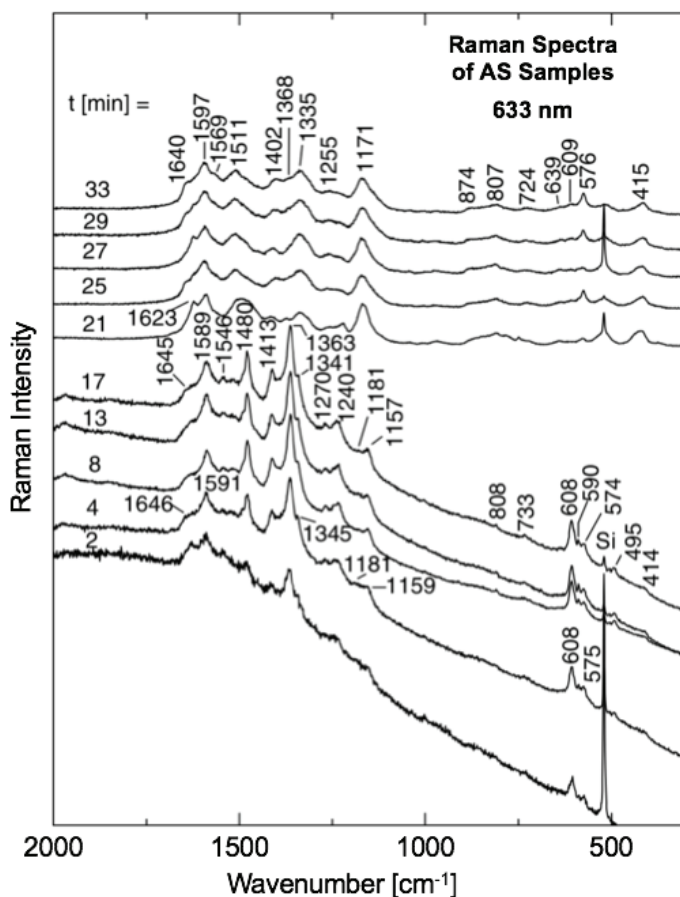


Figure 14. Raman spectra of reaction intermediates/products collected at different times during the reaction of aniline with APS in water (without added acid), deposited on Si windows. (Reprinted and adapted with permission from *Journal of Raman Spectroscopy*, The chemical oxidative polymerization of aniline in water: Raman Spectroscopy, by G. Ćirić-Marjanović et al. 39, 1375–1387, Copyright (2008) Wiley).

Formation mechanism of polyaniline nanotubes and nanorods by the template-free falling-pH method

Our results showed that the morphology of PANI strongly depends on the mole ratio of aniline and dopant acid (i.e. on the initial pH value, pH_0), aniline concentration, and the type of dopant acid [14, 16, 40, 41]. Thus, in the presence of 5-sulfosalicylic acid (SSA), by varying initial mole ratio $[\text{SSA}]/[\text{aniline}]$, PANI nanotubes/nanorods are obtained at $[\text{SSA}]/[\text{aniline}] = 0.25$ and $\text{pH}_0 = 4.6$, while at $[\text{SSA}]/[\text{aniline}] = 0.5$ ($\text{pH}_0 = 3.5$) and 1.0 ($\text{pH}_0 = 1.7$) only granular morphology is seen [14].

The nanotubes are well evidenced by TEM measurements that allow us to see the hole interior of a tube, and thus this method allows us to distinguish between nanotubes and nanorods. The examples of PANI nanotubes/nanorods, prepared from the solution of SSA at $\text{pH}_0 = 4.6$, and in water without added acid, are shown in Fig. 15. Nanotubes have outer diameters in the range of 100-200 nm, inner diameters of 10-60 nm, while their lengths are from 0.4 to 1.5 μm [14]. Nanorods, without hole interior, were also observed (Fig. 15 b).

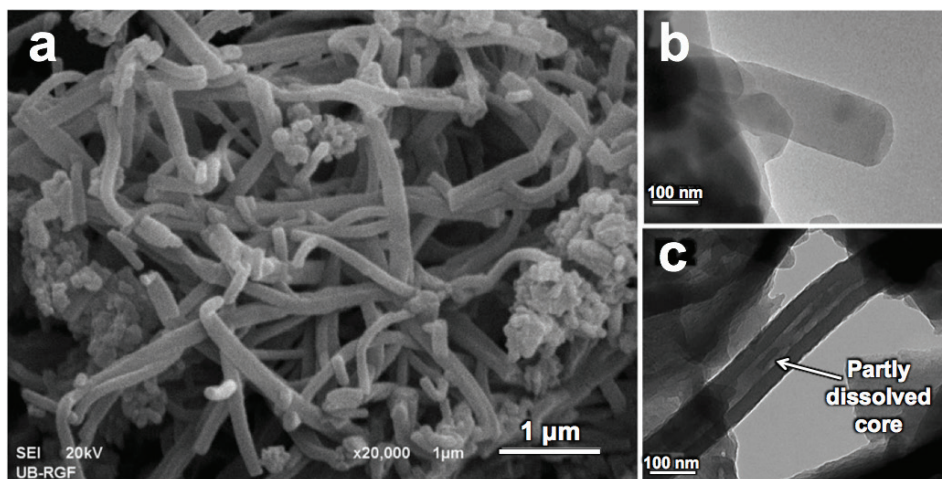


Figure 15. SEM (a) and TEM (b, c) images of PANI nanotubes/nanorods prepared by the chemical oxidative polymerization–falling pH method with APS as an oxidant: (a, b) from the solution with mole ratio $[\text{SSA}]/[\text{aniline}] = 0.25$ and $\text{pH}_0 = 4.6$, c) from the aqueous solution without added acid. A 1D-nanostructure with a partly dissolved core is shown in c). A nanorod is shown in figure b). (Reprinted and adapted with permission from *Carbon*, High-performance charge storage by N-containing nanostructured carbon derived from polyaniline, by N. Gavrilov et al. 50, 3915-3927, Copyright (2012) Elsevier).

According to the concept developed by the groups of Stejskal and Ćirić-Marjanović [10–15], the growth of PANI nanotubes during the synthesis by the falling-pH method is dictated by the *self-organization of aniline oligomers* formed

in the early stages of the reaction. The ordered oligomers serve as internal templates for the growth of PANI 1D-nanostructures. It is suggested that the major role in the self-organization of oligomers plays the thermodynamically favorable π - π stacking of substituted phenazines-containing oligomers (Fig.16.), based on MM2/MNDO-PM3/COSMO computations [14]. The protonation of nitrogen atoms in phenazine rings causes the destacking [14].

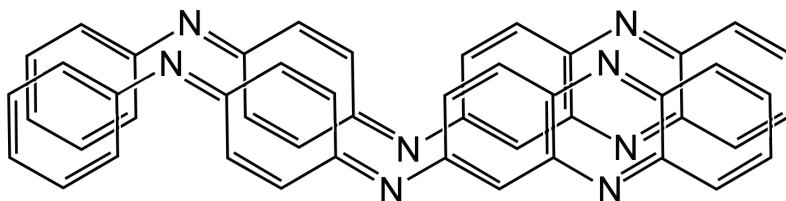


Figure 16. Thermodynamically favorable π - π stacking of substituted phenazine rings between two phenazine unit-containing aniline oligomers, as shown by MM2/MNDO-PM3/COSMO computations in ref. [14].

This ordering of oligoanilines leads to the formation of internal nanotemplates, such as needle-like nanocrystallites. They are nonconducting and contain a high amount of fully oxidized, substituted phenazine and pernigraniline-like oligomers. During the second exothermic reaction phase (polymerization phase), these templates become coated with the conducting PANI-ES film, which leads to the formation of nanorods with nonconducting oligomeric core and conducting PANI wall. It was proposed that the dissolution of the core appeared when pH fell below c.a. 2.5, initiated by the protonation of oligomers. This mechanism is supported by TEM images, which show a 'partly dissolved core', see Fig. 15c). The TEM measurements also support this concept by the observation that the wall thickness of nanotubes is always about the same, while their diameter varies.

However, we have observed that in the case of different fenolic acid, i.e. 3,5-dinitrosalicylic acid (DNSA), despite similar initial reaction conditions ($\text{pH}_0 = 4.6$, APS as an oxidant), the formation of nanotubes by the falling-pH method was completely suppressed, and only nanorods as 1D-nanostructures were formed [40], see Fig. 17.

The explanation can be found in the light of the above described mechanism of nanotube formation by the oligomer core dissolution. In the presence of DNSA the core shows the resistance to the dissolution, most probably due to the strong π - π stacking and hydrogen bonding interactions between DNSA and oligoanilines. This is supported by a known fact that the DNSA molecule is completely flat due to intramolecular hydrogen bonds and thereby is suitable for the construction of hydrogen-bonded structural motifs. It was reported that DNSA and phenazine formed a 1:1 molecular complex via hydrogen bonds and that the formation of similar complexes was possible between DNSA and phenazine-con-

taining oligomers [40]. It was found that the highest amount of well-defined nanorods was produced at mole ratio $[\text{DNSA}]/[\text{aniline}] = 0.5$ and aniline concentration $C_{\text{Ani}} = 0.022 \text{ M}$.

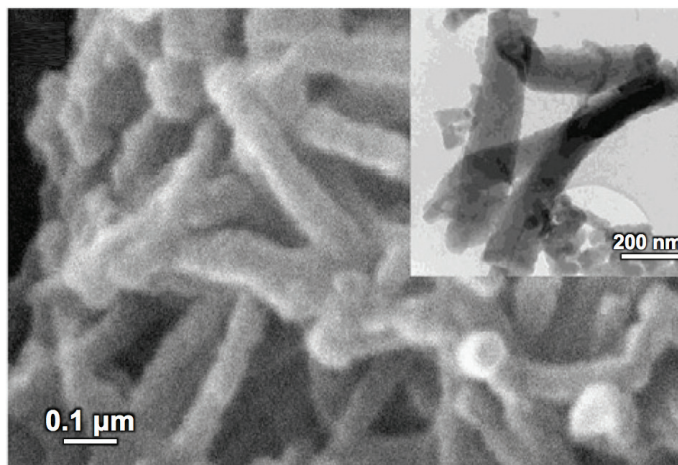


Figure 17. PANI-DNSA nanorods produced at mole ratio $[\text{DNSA}]/[\text{aniline}] = 0.5$ and aniline concentration $C_{\text{Ani}} = 0.022 \text{ M}$. (Reprinted and adapted with permission from *Materials Letters*, 3,5-Dinitrosalicylic acid-assisted synthesis of self-assembled polyaniline nanorods, by A. Janošević et al. 64, 2337–2340, Copyright (2010) Elsevier).

CARBON NANOMATERIALS PRODUCED BY THE CARBONIZATION OF NANOSTRUCTURED PANI AND PPy

The carbonization of nanostructured PANI and PPy in an inert atmosphere (e.g. N_2 , Ar, He) has been shown to be a simple, efficient and scalable method for producing interesting and widely applicable carbon nanomaterials with covalently incorporated nitrogen atoms. Langer and Golczak found for the first time that the nanotubular/microtubular morphology of PANI was preserved after its carbonization [48]. They performed the carbonization of PANI nanotubes that were synthesized by the oxidation of aniline with APS in an aqueous solution of NaCl in the presence of surfactant CTAB at $800 \text{ }^\circ\text{C}$ during 120 min in He atmosphere. The produced nanotubular carbon material had low conductivity, $\sim 10^{-6} \text{ S cm}^{-1}$. Later, we have reported successful preparation of *electroconducting* carbonized PANI nanotubes ($\sim 10^0 \text{ S cm}^{-1}$) by the carbonization of conducting nanotubular PANI prepared by the dopant-free template-free method [49]. Instead of heating at constant temperature, we have used gradual heating from the room temperature to $800 \text{ }^\circ\text{C}$, in N_2 gas atmosphere. In ref. [48], unfavorable conditions for successful graphitization and high conductivity were the presence of organic impurities (surfactant), and the usage of overoxidized PANI precursor (prepared at mole

ratio APS/aniline c.a. 9, which is much higher than the optimal value of 1.25 for producing conducting emeraldine salt). It was shown by our and other groups, on many examples of PANIs or PPys used as precursors, that their 1D-nanostructured morphology (nanotube, nanorods, nanofibers...) was preserved upon carbonization (Fig. 18) and that *electroconducting N-containing carbon 1D-nanomaterials* were produced by their carbonization [21, 49–56]. In addition to the fact that the desired morphology of N-containing carbon nanomaterials can be adjusted by the proper choice of precursor morphology, it was also shown that the properties (e.g. electrical conductivity, textural properties, surface content of N- and O-containing groups) of the produced carbon nanomaterial can be finely adjusted by tuning the molecular structure (via synthesis conditions, e.g. by the choice of dopant ion) and electrical conductivity of conducting polymer precursor, as well as by setting the conditions of carbonization.

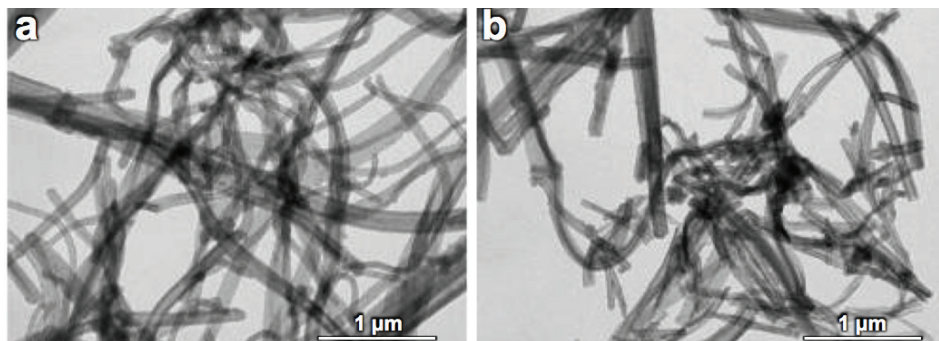


Figure 18. TEM images of salt form of PPy nanotubes (a) and product of their carbonization (b). (Reprinted and adapted with permission from *Journal of Physical Chemistry C*, Synthesis, Characterization and Electrochemistry of Nanotubular Polypyrrole and Polypyrrole-Derived Carbon Nanotubes, by G. Ćirić-Marjanović et al. 118, 14770-14784, Copyright (2014) American Chemical Society).

There are only a few review articles that focus on carbon nanomaterials produced by the carbonization of nanostructured PANIs and PPys [2, 57, 58]. Regarding the improvements of performance in various applications, it is an important finding that the nanotube/nanorod morphology of PANI precursors is also preserved upon the carbonization of their composites with oxides, such as SiO₂ [59] and TiO₂ [60].

Structure and properties of carbonized nanostructured PANIs and PPys

Different structures of carbonized nanostructured PANIs were suggested in the literature. Three main types of nitrogen chemical states were reported to be pyridinic, pyrrolic and quaternary nitrogen (Fig. 19), as determined by XPS technique [2, 57, 58].

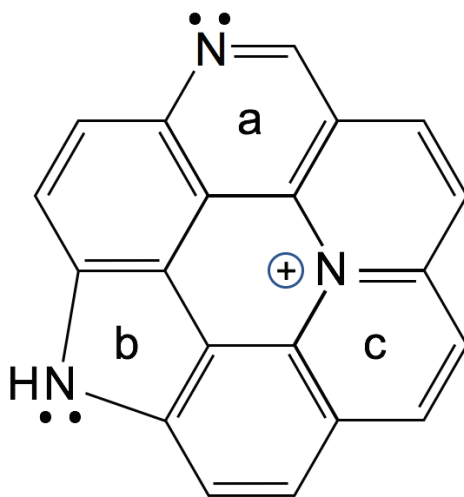


Figure 19. Main types of nitrogen chemical state in carbonized nanostructured PANIs: a- pyridinic, b- pyrrolic and c- quaternary nitrogen

A small amount of other species, such as N-oxide, was also found. The typical deconvolution of N1s peak of the XPS spectra of carbonized PANIs is shown in Fig. 20. The binding energy values of c.a. 398.3, 399.8, 400.8 eV and 402.6–404.4 eV correspond to pyridinic nitrogen (N-6), pyrrolic nitrogen (N-5), quaternary nitrogen (N-Q), and N-oxide species (N⁺-O), respectively, Fig. 20 [61, 62]. It is suggested that phenazine (Phz)-type of pyridinic nitrogen also contributes to a peak at c.a. 398.3 eV [61]. The presence of Phz-type rings in carbonized PANI is expected since Phz-like structural units are constitutional units in nanostructured PANI precursors prepared by the self-assembly method, and they can be formed via crosslinking reactions during the carbonization of PANI, see Fig. 21 [49, 61].

Bulk nitrogen content in the nanostructured carbon materials produced by the carbonization of nanostructured PANI salts was in the range 8.9–9.9 wt.%, as determined by the elemental microanalysis [49, 52]. It was found that the total surface content of nitrogen, determined by XPS, differed from the bulk content of nitrogen. Generally, the surface concentration of heteroatoms (both nitrogen and oxygen) was found to be lower than their bulk concentration, while the surface carbon content was significantly higher than the bulk carbon content. These results indicated that the carbonization of the surfaces of all the used nanostructured PANI precursors was much more efficient than their bulk carbonization [61]. The surface fraction of nitrogen in carbonized PANIs varied in the range of 5.5–7.0 at.%, depending on the type of counter ion in the PANI precursor. Based on the XPS analysis of the surface content and the elemental microanalysis of the bulk content of nitrogen and carbon, it was concluded that 5-sulfosalicylate anions in the structure of PANI precursor inhibited nitrogen release during the carbonization most effectively and catalyzed the carbonization process more efficiently

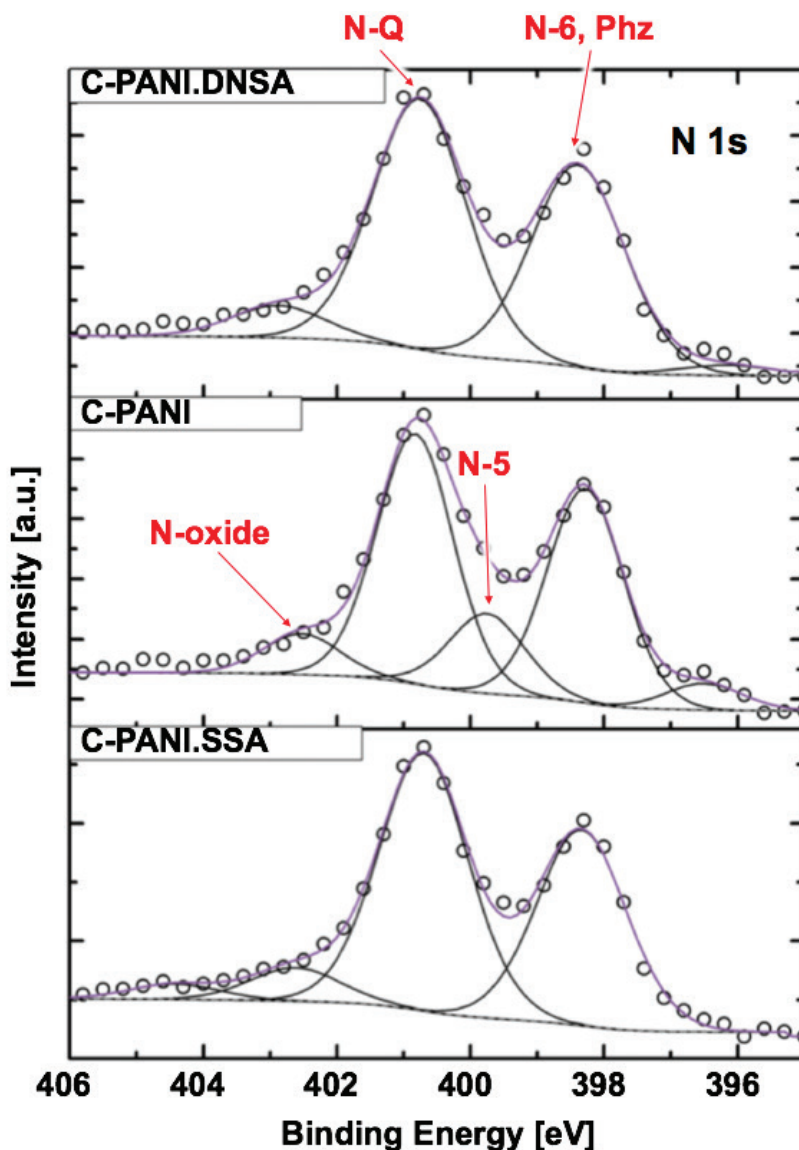


Figure 20. Fitted high-resolution XPS N1s spectra of three 1D-nanostructured carbonized nanostructured PANIs, C-PANI.DNSA, C-PANI and C-PANI.SSA, prepared by the carbonization of 1D-nanostructured PANI salt precursors: PANI 3,5-dinitrosalicylate (PANI.DNSA) nanorods, PANI 5-sulfosalicylate (PANI.SSA) nanorods/nanotubes, and PANI hydrogen sulfate nanorods/nanotubes/nanosheets produced without added acid (PANI), respectively. (Reprinted and adapted with permission from *Carbon*, High-performance charge storage by N-containing nanostructured carbon derived from polyaniline by N. Gavrilov et al. 50, 3915–3927, Copyright (2012) Elsevier).

than hydrogen sulfate and 3,5-dinitrosalicylate counter-anions [61]. This finding shows the importance of the counter anion type in PANI salt precursors on the carbonization mechanism, and consequently on the physico-chemical properties and behaviour of the produced carbon nanomaterial.

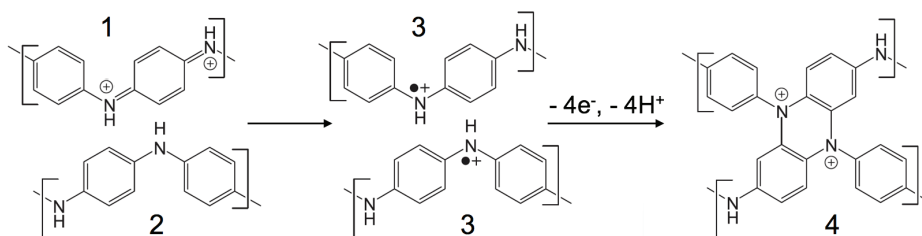


Figure 21. The scheme of crosslinking of PANI chains during heating, as a consequence of the thermally induced solid-state redox reaction of protonated iminoquinonoid units (1, oxidant) with phenylenediamine segments (2, reductant) and the recombination reaction of semi-quinonoid cation radicals (3), leading to formation of phenazine unit (4), according to ref. [49].

Besides nitrogen, oxygen heteroatom is also present in the structure of nanostructured carbonized PANIs. Surface oxygen groups are identified by the deconvolution of the corresponding O1s XPS signals. Characteristic peaks are found at binding energies of 530.7, 531.7 and 533.0 eV and attributed to C=O quinone type groups (O-I), C-OH phenol groups (O-II)/ ether C-O-C groups, and -COOH carboxyl groups (O-III), respectively [61, 62]. Both N and O heteroatoms were found to be important for the properties of carbonized PANIs in their applications, such as electrocatalysis and charge-storage.

For all investigated cases of carbonization (gradual heating, in N_2 , up to 800 °C) of nanostructured PANI salts precursors, prepared by the pH falling method without template and containing different counter ions, we have found that the electrical conductivity of produced nanostructured carbonized PANIs was higher than that of the precursors, for at least one level of magnitude. For example, the electrical conductivity increased from 0.04 S cm^{-1} for PANI.SSA to 0.8 S cm^{-1} for its carbonized counterpart, C-PANI.SSA [52].

Some drastic changes of the textural properties also occurred upon carbonization. By the nitrogen sorption measurements, it was found that the specific surface area (S_{BET}) and micropore volume (V_{mic}) increased by one order of magnitude upon the carbonization of nanostructured PANIs [52, 53]. For example, S_{BET} increases from 34.0 to $317 \text{ m}^2\text{g}^{-1}$ and V_{mic} increases from 0.013 to $0.128 \text{ cm}^3\text{g}^{-1}$ as a consequence of the carbonization of PANI.SSA nanotubes/nanorods [52]. However, again, the type of counter ion and fine differences in the molecular structure of PANI precursor reflect the differences in textural properties of produced N-containing carbon materials. Thus, the carbonization of PANI.DNSA led to the completely microporous carbon material with small mesopore volume

(V_{meso}), Fig. 22 [53], while the carbonization of PANI.SSA led to the increase of both V_{mic} and V_{meso} , and gave micro/mesoporous material [52].

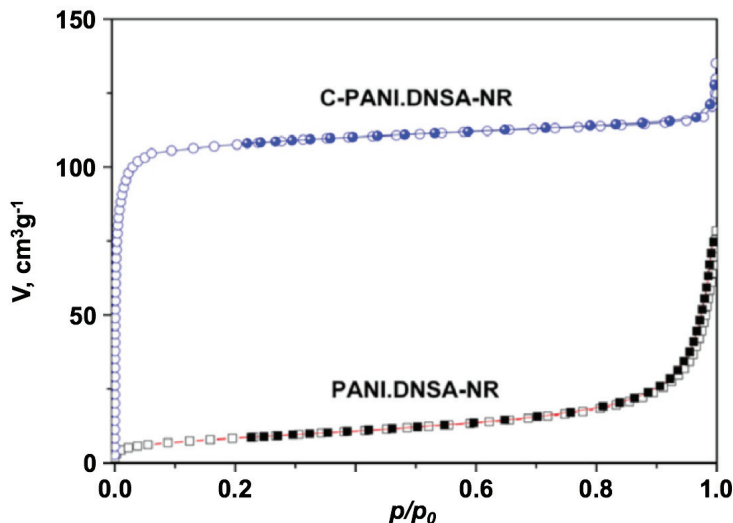


Figure 22. Nitrogen adsorption-desorption isotherms of PANI.DNSA nanorods (lower curve) and carbonized PANI.DNSA nanorods (upper curve) (Reprinted with permission from *Microporous & Mesoporous Materials*, Microporous conducting carbonized polyaniline nanorods: Synthesis, characterization and electrocatalytic properties, by A. Janošević et al, 152, 50–57, Copyright (2012) Elsevier). The empty symbols are used for adsorption, whereas the filled symbols are used for desorption.

Applications of carbon nanomaterials produced by the carbonization of nanostructured PANIs and PPys

It was shown that N-containing carbon nanostructured materials produced by the carbonization of nanostructured PANIs and PPys are promising materials for various applications: electrocatalysis [52, 53, 62–68], supercapacitors [54, 61, 66, 69, 70], electroanalysis [71–73], sensors [74], photocatalysis [75], batteries [76–78], hydrogen adsorption [80], etc. They can be used as-prepared, post synthetically activated, or within the composites with metals (Pt, Pd, Fe), metal oxides (TiO_2 , MnO_2 , MnFe_2O_4), carbon (nano)materials, etc. Here, some selected examples of applications of carbonized PANIs and PPys are presented.

Application in electrocatalysis of oxygen reduction reaction. – Different carbon-based materials have been intensively studied in recent years with the aim of replacing expensive and scarce platinum as electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells as promising power sources. It was shown that nitrogen doping of CNTs led to the significantly improved ORR activity of the resulting NCNT material [81].

We have synthesized N-containing carbon nanomaterials, abbreviated as C-PANI.DNSA, C-PANI.SSA and C-PANI, by the carbonization of three 1D-nanostructured polyaniline (PANI) salt precursors: PANI 3,5-dinitrosalicylate (PANI.DNSA) nanorods, PANI 5-sulfosalicylate (PANI.SSA) nanorods/nanotubes, and PANI hydrogen sulfate nanorods/nanotubes/nanosheets produced without added acid (PANI), respectively, and have compared their electrocatalytic activity for ORR, Fig. 23 [62]. The measurements were performed in alkaline solution using rotating disk electrode voltammetry. It was shown that the electrocatalytic activity changed in the order C-PANI.DNSA < C-PANI < C-PANI.SSA. The differences in electrocatalytic activity of these N-containing carbon materials were explained by the differences in their textural properties (determined by N₂ sorption analysis), the surface content of nitrogen and the surface content of pyridinic nitrogen group (measured by XPS). C-PANI.SSA has the highest content of mesopores, highest surface content of nitrogen (7.04 at.%) and the highest surface content of pyridinic nitrogen (51%). This material shows excellent electrocatalytic activity with the most positive onset potential amounting to -0.15 V vs. SCE at the catalyst loading of 250 μg cm⁻² and -0.05 V vs. SCE at the catalyst loading of 500 μg cm⁻² [52, 62]. An apparent number of electrons exchanged per O₂ molecule amounted from c.a. 2 for C-PANI.DNSA to c.a. 3.7 for C-PANI.SSA, Fig.23. By comparing the results with other carbon nanomaterials it was concluded that C-PANI.SSA and C-PANI represented excellent ORR electrocatalysts for application in low temperature fuel cells. For example, they exhibit properties comparable to that of vertically aligned N-containing carbon nanotubes (NCNTs) [81]. Also, both C-PANI.SSA and C-PANI display onset potentials up to even 100 mV more positive, with the increased number of electrons consumed per O₂ molecule in the investigated potential window, compared to different nanostructured carbon materials studied in the work of Kruusenberg et al. [82]. It was found that a low temperature hydrothermal treatment of C-PANI in alkaline medium at 200 °C significantly improved electrocatalytic behaviour toward ORR [66].

Carbonized nanotubular PPys (C-PPy-NTs) have been also probed as the electrocatalyst for ORR [54, 83]. High ORR activity has been observed with the onset potential at -0.1 V vs. SCE and apparent number of electrons consumed per O₂ molecule above 3 [54]. This high electrocatalytic activity has been linked with a high fraction of mesopores and the presence of pyridinic and pyrrolic nitrogen surface groups, as well as with a high degree of structural disorder.

A p p l i c a t i o n f o r s u p e r c a p a c i t o r s . – Supercapacitors are devices that can store energy at a high rate by forming electrochemical double layers of charges (electrochemical double layer capacitors) or through fast pseudo-capacitive surface redox reactions (pseudo-capacitors). They exhibit a high power density and long cyclic stability, and use high surface area electrodes. The application of various nanostructured materials for supercapacitors has been the subject of intensive research aiming at providing enhanced energy density of these devices [84].

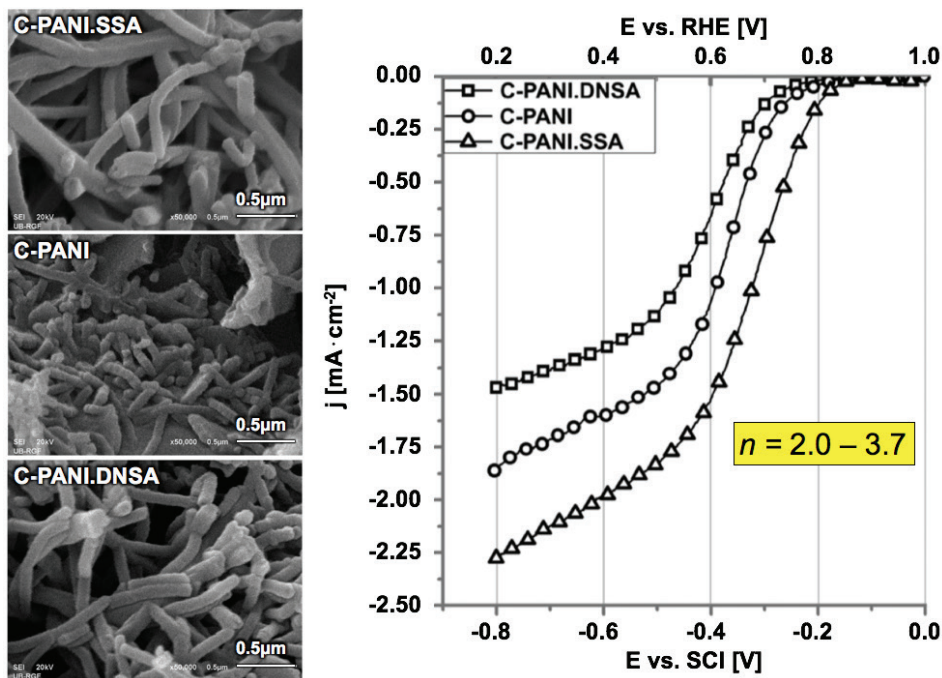


Figure 23. Left: SEM images of nanocarbons (C-PANIs) derived from different 1-D nanostructured PANI precursors that are prepared from the solution of SSA (PANI.SSA), DNSA (PANI.DNSA) and without added acid (PANI.H₂O). Right: Background-corrected RDE voltammograms of oxygen reduction (sweep in anodic direction) on PANI-derived-nanocarbon-modified GC electrodes in O₂-saturated 0.1 mol dm⁻³ KOH (loading 250 mg cm⁻²; rotation rate 600 rpm, sweep rate 20 mV s⁻¹). (Reprinted and adapted with permission from *Journal of Power Sources*, Electrocatalysis of oxygen reduction reaction on polyaniline-derived nitrogen-doped carbon nanoparticle surfaces in alkaline media, by Gavrilo et al. 220, 306–316, Copyright (2012) Elsevier).

1D-nanostructured N-containing carbon materials, which we have synthesized, C-PANI.DNSA, C-PANI.SSA and C-PANI, have been shown to be suitable materials for supercapacitors, Fig. 24 [61]. The specific capacitance has changed in the following order: C-PANI.DNSA < C-PANI < C-PANI.SSA, Fig. 24. The highest capacitance of 410 F g⁻¹, at scan rate 5 mV s⁻¹, has been exhibited by C-PANI.SSA. At 10 A g⁻¹, capacitance has showed stable value of 200 F g⁻¹ during 5000 cycles. The best charge storage performance of C-PANI.SSA has been attributed to its highest surface content of total N, the highest surface content of pyridinic N, the highest electrical conductivity and highest content of mesopores.

Hydrothermal alkali treatment (HAT) of C-PANI at 200 °C led to the significant improvement of charge storage performance [66]. Gravimetric capacitance increased up to 2 times related to untreated C-PANI and amounted to 363, 220

and 432 F g^{-1} , in 6 M KOH , 2 M KNO_3 and $1 \text{ M H}_2\text{SO}_4$, respectively, at 5 mV s^{-1} . The capacitance retention upon increasing sweep rate was also improved. The observed charge storage performance improvement was attributed to the redistribution of the N-containing surface groups, the increase of the surface nitrogen content and the increase of the surface oxygen content caused by HAT, providing an easier access of the electrolyte species responsible for double layer formation and pseudo-faradaic reactions.

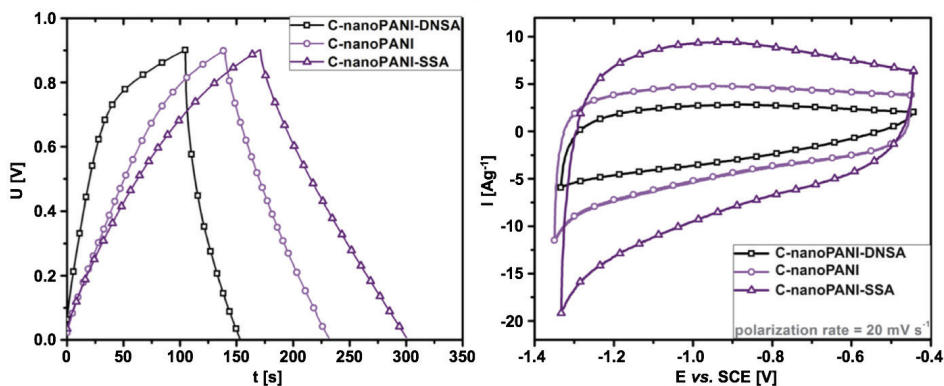


Figure 24. Left: galvanostatic charge/discharge curves of N-containing carbon materials: C-PANI.DNSA, C-PANI and C-PANI.DNSA, in 6 M KOH solution, at a current density of 1 A g^{-1} . Right: Cyclic voltammograms of these carbon materials in 6 M KOH , at the common scan rate of 20 mV s^{-1} . (Reprinted and adapted with permission from *Carbon*, High-performance charge storage by N-containing nanostructured carbon derived from polyaniline by Gavrilov, et al. 50, 3915–3927, Copyright (2012) Elsevier).

Application in electroanalytics. – Carbonized nanostructured PANIs, C-PANI.DNSA, C-PANI and C-PANI.DNSA were tested as electrode materials for the detection of nitrite ions and ascorbic acid using linear sweep voltammetry, based on the electrochemical oxidation of these analytes [72]. All three materials showed very good electrocatalytic activity for nitrate ions and ascorbic acid sensing. The lowest peak potential showed C-PANI for nitrite ion ($+0.87 \text{ V vs. SCE}$), and for ascorbic acid oxidation both C-PANI and C-PANI.SSA (c.a. $+0.13 \text{ V vs. SCE}$). This behaviour is explained by the differences in morphology, textural properties and differences in the surface content of oxygen- and nitrogen-containing groups. All three materials contain nanorods, while nanotubes are present only in C-PANI and C-PANI.SSA, therefore it is possible that nanoparticle surfaces in the last two materials possess a larger amount of edge-plane-like sites that enable faster electrode kinetics. The accessibility of the analyte, which depends on the pore structure of electrode materials, is better in C-PANI and C-PANI.SSA due to the larger fraction of mesopores in these materials compared with C-PANI.DNSA.

CONCLUSIONS AND OUTLOOK

Electroconducting polymer nanostructures have been intensively investigated in the last two decades. Their preparation and characterization have elicited much interest because of their significantly enhanced dispersibility and processability, and substantially improved performance in many applications, in comparison with granular and colloidal varieties. Various template and template-free methods have been developed for the preparation of conducting polymer nanostructures. Nevertheless, to devise simple and efficient preparation methods that would lead to highly controllable morphologies and particle sizes, especially on a large scale, is still challenging. Unique structural properties, atypical for the ordinary PANI with granular morphology, have been observed for nanostructured PANIs produced by self-assembly approach, and some new insights into the mechanism of aniline polymerization leading to PANI nanostructures have been provided. Several concepts on the mechanism of nanostructure formation have been offered, however it is still not fully understood.

The carbonization of PANI and PPy nanostructures is a simple and efficient way to fabricate N-containing carbon nanomaterials with the desired nanostructured morphology, textural characteristics, electrical conductivity, amount of incorporated nitrogen, and other properties. The properties of the resulting carbon nanomaterial are determined by the characteristics of the polymer precursor and the conditions of the carbonization process. Future research is directed towards the development of new advanced nanomaterials based on carbonized nanostructured PANI and PPy, with high performance for applications such as electrocatalysis, photocatalysis, supercapacitors, sensors, electroanalytics, adsorbents, membranes, etc. More systematic studies are needed in order to find relationships between the polymer precursor structure and properties and the structure and properties of resulting carbon nanostructures. Especially important is the possibility of tuning the types of N- and O-containing functional groups in the carbon nanomaterial by the structural modifications of polymer precursor. Further work on the preparation of composite materials of carbonized conducting polymer nanostructures with various metals, oxides, carbon nanomaterials (graphenes, carbon nanotubes/nanofibers, etc.), or organic/bioorganic compounds, opens up some new perspectives that can lead to further improvement in their performances for various applications. Another direction in research includes the introduction of other heteroatoms (P, B, etc.) in the structure of carbonized nanostructured conducting polymers with the aim of producing new advanced nanomaterials.

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Гордана Ћирић-Марјановић

НАНОСТРУКТУРЕ ЕЛЕКТРОПРОВОДНИХ ПОЛИМЕРА
И УГЉЕНИЧНИ МАТЕРИЈАЛИ ПРОИЗВЕДЕНИ
ЊИХОВОМ КАРБЕНИЗАЦИЈОМ

Резиме

Конјуговани полимери који имају способност да проводе електричну струју – *електропроводни полимери*, представљају посебну класу синтетичких полимера. Типични примери су полианилин (PANI), полипирол (PPy), политиофен (PTh) и њихови деривати. Ови полимери припадају такозваним ‘интелигентним материјалима’ зато што поседују комплексне и динамичке структуре чијим дизајнирањем се могу подешавати и контролисати њихова својства, односно подешавати њихов одговор на различите стимулусе. Током протекле деценије убрзано се повећало интересовање за наноструктуру електропроводних полимера. Оне су изазвале велико интересовање, како са фундаменталног аспекта тако и са аспекта примена, захваљујући побољшаним својствима. Овај рад је посебно фокусиран на најважније резултате наших истраживања у области синтезе, механизма формирања и физикохемијских својстава наноструктура PANI и PPy. *Угљенични наноматеријали* представљају другу велику групу напредних материјала који су били предмет опсежних истраживања због својих интересантних својстава и разноврсних примена. Поседна пажња је била посвећена угљеничним наноструктурама допираним ковалентно везаним хетероатомима (N, B, P, итд.), чије увођење води побољшању својстава. Ми смо развијали нове N-допиране електропроводне угљеничне наноматеријале применом једноставне методе карбенизације наноструктурних полианилина. Морфологија и својства ових угљеничних наноматеријала могу се подешавати погодним избором морфологије и својстава полимерног прекурсора и задавањем одговарајућих услова карбенизације. Ова класа наноматеријала показује одличне перформансе код различитих примена (суперкондензатори, електрокатализа, фотокатализа и др.). У раду су презентовани одабрани резултати наших истраживања на пољу угљеничних наноматеријала добијених из наноструктурних PANI и PPy.