Electrically Conductive Low Dimensional Nanostructures: Synthesis, Characterisation and Application

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List of Abbreviations

Latin letters
AAs  Aliphatic amines
AFM  Atomic Force Microscopy
APS  Ammonium persulfate
ATRP  Atom Transfer Radical Polymerization
CAFM  Conductive Atomic Force Microscopy
CB  Carbon black
CNT-g-  Multi-walled carbon nanotubes modified by covalent grafting of poly(2-
P2VP  vinylpyridine)
CNT, CNTs  Carbon nanotube(s)
CP  Conductive polymer
CP NWs  Conductive polymer nanowires
CSA  Camphor sulfonic acid
CVD  Chemical vapor deposition
DC, dc  Direct current
DCM  Dichloromethane
DMSO  Dimethyl sulfoxide
DNA  Deoxyribonucleic acid
DOS  Density of state
DP  Degree of polymerization
EMI  Electro-Magnetic Interference
GMM  Granular metal model
HDA  Hexadecyl amine
HOPG  Highly oriented pyrolytic graphite
HRTEM  High resolution transmission electron microscopy
IC  Intermittent contact mode of AFM
Mn  Number average molecular mass
Mw  Weight average molecular mass
MIT  Metal-insulator transition
MWNT  Multi-walled carbon nanotube
NCs  Nanoclusters
NPs  Nanoparticles
NW  Nanowire
OA  Octylamine
PAs  Poly anions
PACs  PAs amphiphile complexes
PANI  Polyanilin
PB  Prussian blue
PC  Poly cation
PDADMAC  Polydiallyldimethyl ammonium chloride
PDI  Polydispersity index
PE  Polyelectrolyte
PEDOT  Poly(3,4-ethylenedioxythiophene)
PEO  Polyethylene oxide
PMB, PMADAME  Poly(methacryloyloxyethyl dimethylbenzylammonium chloride)
PPy, PPy  Polypyrrole
PSA  Polystyrenesulfonic acid
PT  Percolation theory
P2VP  Poly(2-vinylpyridine)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>RA</td>
<td>Rotating – analyzer</td>
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<tr>
<td>RMS</td>
<td>Root-mean-square amplitude of cantilever oscillation, Root-mean-square roughness of the surface</td>
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<tr>
<td>SBS</td>
<td>Sodium bisulfite</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SPM</td>
<td>Scanning probe microscopy</td>
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<td>SWNTs</td>
<td>Single-walled nanotubes</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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<td>TEMPO</td>
<td>2,2,6,6-Tetramethyl-piperidin-1-oxyl</td>
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<tr>
<td>TGA</td>
<td>Thermo-gravimetrical analysis</td>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<tr>
<td>TM</td>
<td>Tapping Mode</td>
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<tr>
<td>UV</td>
<td>Ultraviolet spectroscopy</td>
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<td>VRH</td>
<td>Variable range hopping</td>
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Introduction

Motivation. The field of nanoscience and nanotechnology is a broad and interdisciplinary area of worldwide research which develops activity that has been growing explosively in the past few years. Nanosized objects such as nanoclusters, nanotubes, nanowires, etc., open a new era for fundamental science in understanding of the main relations at the nanoscale. Beside this, some features of the nanosized objects like small size and a feasibility for modulation of their properties via self-organization into superstructures make them perhaps the most promising and attractive candidates for commercial application in future.

Carbon nanotubes (CNTs) constitute one of the most attractive materials which hold on much promise to revolutionize fundamental science in an investigation of phenomena, like Coulomb blockade, ballistic conductance, metal-insulation transition, etc. High chemical stability, and extremely high mechanical strength, stiffness and availability peculiar for CNTs make such materials indispensable in a field of fabrication of conductive coatings and nano-composite materials. However, poor solubility of CNTs is a major obstacle. In principle, this problem can be solved via modification of CNTs surface with some solubilizing compounds, for instance, by attaching polymers. Simultaneously, developed polymeric shell on the CNTs surface would provide possibility to achieve necessary surface properties by the absorption of specific materials (conductive clusters, magnetic particles, etc.). CNTs modified with water-soluble polymeric shell is the first objective of this work.

Conducting polymer (CP) nanowires (NWs) are another kinds of nanomaterials promising for electronics and sensors. In addition to useful properties of CNTs and inorganic nanowires (e.g., variable conductivity and high surface-to-volume ratio), conducting polymer NWs possess the following important advantages: easy and cheap production (synthetic procedures exclude high temperatures and vacuum equipment); easy variability of chemical structure, size and shape of conductive polymer nanowires that allow a precise tuning of other properties (optical, electrical, surface functionality, charge, etc.). Several “template-less” approaches to 1D superstructures of conductive polymers based on self-assembly of conjugated polymers, oligomers or monomers were recently reported. Other methods to make conductive polymer nanowires involve chemical or electrochemical oxidative polycondensation in “hard templates” (such as zeolites, track-etched polymeric membranes, and porous alumina), or “soft templates” (surfactant micelles, or liquid crystalline phases). However, for various applications conductive polymer nanowires must be properly integrated into circuits, therefore additional steps, such as a release of the nanowire from the templates, their positioning in the device or/and enhancement of electrical contacts are always required.
It is, therefore, strongly desired to develop a method for growing conductive polymer nanowires in predefined places on the devices, for example between microelectrodes.

The approach developed in my thesis utilizes single molecules of polyelectrolytes as positive templates and provides a possibility to grow conductive polymer nanowires in predefined places. Utilization of polymer molecules as templates is a promising strategy to generate nanoparticles of desired size, shape, and location with specific properties since a variety of functional polymers with different architecture are now readily available. On the other hand, single molecules of polyelectrolyte allow relatively simple manipulation. Like conventional ropes, they could be stretched and aligned under external forces (e.g., centrifugal or capillary forces, electric or shear fields) and can be immobilized onto surfaces by simple procedures like casting or printing. According to the strategy developing in my thesis, conductive polymers are selectively grown from the polyelectrolyte molecules immobilized in the desired place. Thus, the second focus of the thesis is the fabrication of continuous and conductive polymer nanowires and investigation of their charge transport properties.

**Aims & objectives.** The general objective of the work aims at the development and understanding of nanoscopic electrically conductive entities.

*The first aim* of the thesis is the investigation of multi-walled CNTs chemically modified with PE, poly(2-vinylpyridine) (P2VP). I am interested in characterization of CNT-g-P2VP and their further modification with nanoclusters (NCs) which possess interesting conductive (for Pd NCs), semiconductive, magnetic and redox (for Prussian Blue NCs) properties. CNT-g-P2VP are also applied for fabrication of ultra-thin transparent conductive coatings.

*The second aim* of the work is the developing of the method to produce conductive polypyrrole (PPy) NWs using individual adsorbed molecules of polystyrenesulfonic acid (PSA) as soft positive templates. To achieve this goal, the method to immobilize single-molecule templates in ultimately stretched conformation is developed. I am also aimed at electrical characterization of the nanowires at the level of individual entities.

**Main results & achievements.**

- It was found that the polymer chains of P2VP grafted to CNTs form a shell. This shell makes the CNT-g-P2VP dispersible in organic solvents and in acidic water and it is responsible for the selective deposition of CNTs onto oppositely charged surfaces.
- It was established that the deposition of CNT-g-P2VP from aqueous dispersions at low pH is an effective method to prepare homogeneous ultrathin films with a tunable CNTs density. These films are characterised by a low percolation
threshold of 0.25 µg/cm² and a critical exponent $\alpha = 1.24$ that allows to describe them as a 2D random network. Although the multi-walled CNT films prepared in this work are less conductive and less transparent than the SWNTs films, they could find applications, e.g., in touch screens, reflective displays, EMI shielding and static charge dissipation.

- It was shown that P2VP grafted to CNTs is a universal support for the immobilization of Prussian Blue nanoclusters at the CNTs surface. A simple method for the preparation of charge-stabilized Prussian Blue nanoparticles of readily adjustable size is reported. Thus-formed Prussian Blue nanoparticles are crystalline and display a long-range ferromagnetic ordering at 5.1 K. Prussian Blue nanoparticles were selectively attached to the surface of carbon nanotubes (CNTs) functionalized with poly2-vinylpyridine (P2VP). These nanoparticle-based nanostructures might be useful materials for the manufacture of electrooptical devices, or mechanically robust ion-sieving membranes.

- A simple method to control the conformation and orientation of single adsorbed PE molecules by co-deposition with octylamine (OA) was developed. This method was used for stretching and positioning polystyrenesulfonic acid between gold electrodes necessary for the preparation of conductive polymer nanowires.

- A simple chemical route to fabricate conductive PPy NWs by the grafting of PPy from molecules of PSA PE was developed. The location and the length of the synthesized PPy NWs are defined by the location and the length of adsorbed single-molecule templates. The diameter of the NWs can be varied from a few nanometers to hundreds of nanometers by adjusting the polycondensation time and concentration of the reagents. In this work electrical characterization was done on the level of individual NWs and their conductance was unambiguously proved by “breaking experiments”. The $dc$ conductivity of individual PPy NWs approaches to the conductivity of PPy in bulk. The conductivity decreases with temperature decrease, as it is typical for semiconductors.

- The charge transport in PPy NWs was described in term of variable-range hopping model. It was found that at low temperature a change of the conductivity corresponds to a transition from 3D to quasi-1D conductor.

- I believe that results achieved in my thesis open new perspectives for the construction of molecule-based devices, such as sensors or transistors.
Outline of the thesis. The first chapter gives the theoretical background for the interpretation of experimental data. In this chapter the main aspect of the percolation model have been described. The second chapter describes basics, scope and limitation of the main research techniques: Atomic Force Microscopy, Ellipsometry, Conductive measurements. The third chapter discusses properties and applications of CNTs chemically modified with P2VP. The fourth chapter is dedicated to the fabrication and characterization of PPy NWs including immobilization of polyelectrolyte molecules in the stretched conformation; synthesis of PPy NWs and, finally, a comprehensive study of conductive properties of the PPy NWs in order to rationalize the electron transport mechanism.

Publications. The main results of the work were published in the following papers:

Chapter 3


Chapter 4

Proceedings. The results were presented at ACS Fall Meetings (2004 and 2006).


**Contribution to the conference.** Results were represented on following conferences:


Chapter 1

The main aspects of the percolation theory

Percolation Theory (PT) is a powerful tool for studying a behavior of great variety of materials and to model many of their properties. This theory has a great application in naturally occurring as well as man-made complex systems for which the process are particularly statistical and in which the role of connectivity of different elements or constituents is prominent. Examples include self-assembly of tobacco mosaic,\(^1\) lymphocyte patch and cap formation,\(^2\) describing the conductive behavior in CNTs network,\(^3\) and composites.\(^4\) The ideas of PT have been used to study and model of these objects and predict the quantitative description of morphological properties, electrical and Hall conductivities, elastic modulus and dielectric constants.\(^4\)

Percolation processes were first developed by Flory\(^5\) (1941) and Stockmayer\(^6\) (1943) to describe how small branching molecules react and form very large macromolecules. This polymerization process may lead to gelation, i.e. to the formation of a very large network of molecules connected by chemical bonds, the key concept of percolation theory. However, Flory and Stockmayer developed their theory of gelation for a special kind of network, namely, the Bethe lattice, an endlessly branching structure without any closed loops.\(^4\)\(^5\)

In the mathematical literature, percolation was introduced by Broadbent and Hammersley\(^7\) (1957). They originally dealt with the concept of the spread of hypothetical fluid particles through a random medium. The terms fluid and medium were viewed as totally general: a fluid can be liquid, vapor, heat flux, electric current, infection, a solar system, and so on. The medium - where the fluid is carried - can be the pore space of rock, an array of trees, or the universe. Generally speaking, the spread of a fluid through a disordered medium involves some random elements, but the underlying mechanisms for this might be one of two very different types. In one type, the randomness is ascribed to the fluid: the fluid particles decide where to go in the medium. This is the familiar diffusion process.

\(^5\) Flory, P. J. J. Am. Chem. Soc. 1941, 63, 3091.
In the other type, the randomness is ascribed to the medium: the medium dictates the paths of the particles. This was the new situation that was considered by Broadbent and Hammersley \(^8\) (1957). It also demanded its own terminology. It was decided to name it a percolation process, since it was thought that the spread of the fluid through the random medium resembled the flow of coffee in a percolator. \(^9\)

**Bond percolation and site percolation models.** The classical percolation theory centers around two main models: bond percolation and site percolation model. In the bond percolation model, the bonds of the network are either occupied (i.e. they are open to flow, diffusion and reaction, they are microscopic conducting elements of a composite, etc.) randomly and independently of each other with probability \(p\) or are vacant (i.e. they are closed to flow or current or have been plugged they are insulating elements of a composite) with probability \(1-p\). For a large network, this assignment is equivalent to removing a fraction \(1-p\) of all bonds at random. Two sites are called connected if there exists at least one path between them consisting solely of occupied bonds. A set of connected sites bounded by vacant bonds is called a cluster. If the network is of very large extent and if \(p\) is sufficiently small, the size of any connected cluster is small. But if \(p\) is close to 1, the network should be entirely connected, apart from occasional small holes. At some well-defined value of \(p\), there is a transition in the topological structure of the random network from a macroscopically disconnected structure to a connected one: this value is called the bond percolation threshold, \(p_{ch}\). This is the largest fraction of occupied bonds below which there is no sample-spanning cluster of occupied bonds.

Similarly, in the site percolation model sites of the network are occupied with probability \(p\) and vacant with probability \(1-p\). Two nearest neighbor sites are called connected if they are both occupied. Connected clusters on the network are again defined in the obvious way. There is a site percolation threshold \(p_{cs}\) above which an infinite (sample-spanning) cluster of occupied sites spans the network. Depending on a specific application, many variants of bond percolation or site percolation have been developed. \(^7\)

**Percolation quantities.** In addition to the percolation thresholds, the topological properties of percolation networks are characterized by several important quantities which are the same either for bond percolation theory or site percolation theory.

(i) **Percolation probability** \(P(p)\) is the probability that a given site belongs to the infinite (sample-spanning) cluster of occupied bonds when the fraction of occupied bonds is \(p\).

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(ii) Accessible fraction \( X^A(p) \) is the fraction of occupied bonds belonging to the infinite cluster.

(iii) Backbone fraction \( X^B(p) \) is the fraction of occupied bonds in the infinite cluster that actually carry flow or current (since some of the bonds in the cluster are dead-end and do not carry any flow). The backbone of a percolating system plays a fundamental role in its transport properties, because the tortuosity of the transport paths is controlled by the structure of the backbone.

(iv) Correlation length \( \xi(p) \) is the typical radius of the connected clusters for \( p < p_c \), where \( p_c \) is bond or site percolation threshold, and the length scale over which the random network is macroscopically homogeneous (i.e. the length scale over which the properties of the system are independent of its linear size \( L \)) for \( p > p_c \).

(v) Average number of clusters of size \( S \) (per lattice site) \( n_s(p) \). Since \( S_n(p) \) is the probability that a given site is part of an \( S \)-cluster, a mean cluster size \( S_p(p) \) can be defined by

\[
S_p(p) = \frac{\sum S^2 n_s}{\sum S n_s}
\]

(vi) Effective electrical conductivity \( g_e \) is the electrical conductivity of a random resistor network in which a fraction \( p \) of bonds are conducting and the rest are insulating.

(vii) Effective elastic modulus \( G \) are the elastic modulus of the network in which a fraction \( p \) of the bonds are elastic elements, while the rest have no rigidity or stiffness.

**Universal scaling laws for percolation quantities.** The numerical value of every percolation quantity for any \( p \) depends on the microscopic details of the system, such as its coordination number. But near the bond or site percolation threshold \( p_c \) most percolation quantities obey scaling laws that are largely insensitive to the network structure and its microscopic details. The quantitative statement of this insensitivity is that, near \( p_c \), the following scaling laws are true:

\[
P(p) \sim (p-p_c)^{\beta_p}, \quad \xi(p) \sim |p-p_c|^{\nu_p}, \quad X^A(p) \sim (p-p_c)^{\beta_p}, \quad S_p \sim |p-p_c|^\gamma_p,
\]

\[
X^B(p) \sim (p-p_c)^{\beta_B}, \quad g_e(p) \sim (p-p_c)^a, \quad G(p) \sim (p-p_c)^f.
\]

The topological exponents \( \beta_p, \nu_p, \gamma_p, \beta_B \) are completely universal, i.e. they are independent of the microscopic details of the system and depend only on the dimensionality of the system.
The transport exponents $\alpha$ and $\beta$ are also largely universal. In Table 1.1 the values of the critical exponents in two and three dimensions are compiled.

**Electrical conductivity.** Here I focus more detailed on the representation of conductive transport in the percolation theory. Conductivity can be imagine in the following way. In a percolation network a fraction $p$ of bonds are perfect conductors (their resistance is zero), while the rest are normal conductors (their resistance is finite). Then, below $p_c$ only finite clusters of perfect conductors are formed and $g_e$ is finite. As $p_c$ is approached from below, clusters of perfect conductors become larger and $g_e$ increases. Finally, $g_e$ diverges at $p_c$ such that near $p_c$ the following equation is valid

$$g_e(p) \sim (p-p_c)^\alpha,$$

where $\alpha$ depends only on the dimensionality of the system and $p_c$ varies from the macroscopic details of the system and as a consequence from describing model.

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<tr>
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<th>$d=2$</th>
<th>$d=3$</th>
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<tbody>
<tr>
<td>$\beta_p$</td>
<td>5/26</td>
<td>0.41</td>
</tr>
<tr>
<td>$\nu_p$</td>
<td>4/3</td>
<td>0.88</td>
</tr>
<tr>
<td>$\gamma_p$</td>
<td>43/18</td>
<td>1.82</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1.3</td>
<td>2.0</td>
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**Percolation in continua.** Regular networks is very often used as a mathematic model for investigating various phenomena in disordered systems. But many practical situations deal with random networks, where the coordination number varies from site to site. And its arised a question about possibility to use percolation theory for random networks. Jerauld *et al.* 10 (1984) showed that as long as the average coordination number of a random network and the coordination number of a regular network (e.g. the two-dimensional Voronoi and triangular networks) are about the same, many transport properties of the two systems are, for all practical purposes, identical, provided that the same bond conductance distribution is used for both networks. Since the topological exponents are totally universal, its possible to use a random or even a regular network to study percolation in a continuum.

Percolation theory is universal tool for describing of macroscopically connectivity in disordered media, determination dimensionality of the system and its properties.

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Chapter 2

Experimental Technique

2.1. Atomic Force Microscopy (AFM)

AFM belong to a family of Scanning Probe Microscopy (SPM) instruments that are used to measure properties of surfaces. AFM is being used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace and energy industries. Investigated materials include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers and semiconductors. The AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing. By using AFM one can not only image the surface in atomic resolution but, in addition, AFM offers a variety of new contrast mechanisms which provide information on differences in friction, adhesion, elasticity, hardness, electric fields, magnetic fields, carrier concentration, temperature distribution, spreading resistance and conductivity.

The main feature of AFM is a sharp tip on the end of a flexible cantilever, which moves across a sample surface. The tip-sample interaction is monitored by reflecting a laser off the back of the cantilever into a split photodiode detector. In general, physical nature and character of tip-sample interaction are quite complicated, since they are defined by tip characteristics, surface properties and surrounding medium. The main forces which contribute to exert the tip are: force, coming from mechanical contact of tip end atoms with sample (Figure 2.1), van der Waals force and capillary force, arising from condensation of water vapour in the contact area.

![Intermolecular force curve.](image)
AFM can be operated in many ways measuring different interactions between the probe tip and sample and using different types of detection schemes.

The two most commonly used modes of operation are contact mode AFM and TappingMode™ or intermittent contact mode (IC-mode). AFM measurements in this work were performed in intermittent contact mode (IC-mode) or tapping mode™. In IC-mode, a probe cantilever is driven to vibrate with high amplitude (10–100nm) near its resonant frequency by a piezoelectric element. Since the contact time between the tip and the sample is two orders shorter as compared to contact mode, the IC-mode is less damaging and typically used for imaging topography of soft materials. Because of the high amplitude of oscillation, the tip propagates through regions of attractive (Van der Waals, electrostatic) and repulsive forces in a single oscillation cycle (Figure 2.1). The amplitude and the frequency of the cantilever decrease while approaching the sample surface. Upon scanning, these parameters (and, hence, the force gradient) are maintained constant at a set-point level, by adjusting the tip-sample distance. This is controlled by feedback loop. The feedback signal and the phase lag of the cantilever oscillation relative to the driving oscillation are displayed yielding height and phase images, respectively.

**AFM Experimental Setup.** Multimode AFM instrument or NanoScope IV-D3100 (Digital Instruments, Santa Barbara) was used for sample characterization, operating in the tapping mode. Silicon tips with radius of 10-20nm, spring constant of 30N/m and resonance frequency of 250-300 KHz were used. The amplitude set-point ratio ($A_{sp}/A_0$) was in the range of 0.99-0.85 for the “light” tapping mode. All measurements were done at ambient conditions (temperature 21±2°C; relative humidity 50-70%). Special experiments, which were done for Chapter 4, demonstrated that decrease of the amplitude setpoint by 15% leads to decrease of the molecular height of PE by about 15-20% (i.e., from 1.0 to 0.9-0.8nm).

### 2.2. Electrical force microscopy and AFM conductive measurement

Conductive AFM is a powerful current sensing technique for electrical characterization of conductivity variations in resistive samples. It allows current measurements in the range of a femto- to nearly a microamperes. Conductive AFM can simultaneously map the topography and current distribution of a sample. It is a measurement useful in a wide variety of material characterization and application, including dielectric films, ferro-electric films, nanotubes, conductive polymers, etc.
**Conductive AFM Experimental Setup.** In our work I use ORCA, the conductive AFM module option for the MFP-3D (Asylum Research)\(^{11}\), that provides a wide range of current measurement options with near Johnson Noise-limited performance. The ORCA module consists of a specially-designed cantilever holder that includes a transimpedance amplifier. The gain of the amplifier can be chosen by the user. Standard values range from \(5 \times 10^7\) to \(5 \times 10^9\) volts/amperes. The cantilever holder is used with conductive AFM probes to make the measurement. Our sample represents the Si-wafer substrate with the gold electrodes on it. Our conductive structure is attached with one end to the gold contact and a second contact is the tip. I firstly localized conductive structure in tapping mode AFM imaging then switch to the contact mode. I applied voltage on tip (normally I use range from -4V till 4V) and with help of IGOR Pro software (WaveMetrics, Inc., USA)\(^{12}\) moved the tip to the place of interest (the NPS™ Nanopositioning closed loop sensors on the MFP-3D make possible reproducibly position the cantilever at a point of interest) on the conductive structure and fell tip down until contact occurred and the response current measured. Data in this application note were made using a gain of \(5.15 \times 10^8\) volts/amperes on the initial stage. On the MFP-3D, the output of the ORCA was digitised with one of the auxiliary 100kHz analog-to-digital converters and then digitally filtered at 1kHz. The measured RMS noise for these settings was 0.5pA, consistent with the Johnson Noise performance predicted.

As a tip I used Pt/Ir coated tip for Electrical measurement (Olympus), with a nominal spring constant of 1-2N/m and good wear characteristics. Note, however, that contact mode imaging causes tip wear. Coated cantilevers are especially vulnerable to imaging artefacts associated with irreversible changes in the tip shape or coating. This is an important consideration when interpreting ORCA measurements. All data for such measurements are represented in Supplementary materials.

### 2.3. Ellipsometry

Ellipsometry is a versatile and powerful optical technique for the investigation of the dielectrical properties (complex refractive index or dielectrical function of thin films). It has applications in many different fields, from semiconductor physics to microelectronics and biology, from basic research to industrial applications. Ellipsometry is a very sensitive

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\(^{11}\) Orca Conductive AFM Applic Note 02  
\(^{12}\) http://www.wavemetrics.com/index.html
measurement technique and provides unequalled capabilities for thin film metrology. As an optical technique, spectroscopic ellipsometry is non-destructive and contactless.

Ellipsometry measures two of the four Stokes parameters, which are conventionally denoted by \( \Psi \) and \( \Delta \). Ellipsometry measures change in polarization of monochromatic reflected upon a flat surface with single or multiple layers on it. The polarization state of the light incident upon the sample may be decomposed into an \( s \) and a \( p \) component (the \( s \) component is oscillating perpendicular to the plane of incidence and parallel to the sample surface, and the \( p \) component is oscillating parallel to the plane of incidence). The amplitudes of the \( s \) and \( p \) components, after reflection and normalized to their initial value, are denoted by \( r_s \) and \( r_p \), respectively. Ellipsometry measures the ratio of \( r_s \) and \( r_p \), which is described by the fundamental equation of ellipsometry:

\[
\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}
\]

Thus, \( \tan\Psi \) is the amplitude ratio upon reflection, and \( \Delta \) is the phase shift (difference). The measurement of \( \Delta \) and \( \Psi \) at one wavelength and one angle of incidence allows to determine two real parameters such as refractive index and thickness. For a given multilayer interface it is appropriate ellipsometry measurement after each stage of film preparation. Since ellipsometry is measuring the ratio (or difference) of two values (rather than the absolute value of either), it is very robust, accurate, and reproducible. For instance, it is relatively insensitive to scattering and fluctuations, and requires no standard sample or reference beam.

**Ellipsometry. Experimental Setup.** Ellipsometric measurements were carried out on a rotating-analyzer (RA) ellipsometer SE400 (SENTECH Instruments GmbH, Germany). The instrument uses a He-Ne laser as a light source (\( \lambda = 632.8 \text{ nm} \)) and is equipped with focusing optics collimating a laser beam in a 30 \( \mu \text{m} \) size spot on sample surface and a XY-stage for mapping measurements. The incident angle was fixed at 70\(^\circ\). The measurements were done for Chapter 3. The thickness of the graphite constituted the given MWNTs film was calculated using a three-layer model: Si-SiO\(_2\)/graphite/air. The ellipsometric parameters were fitted using the Elli program developed by Optrel GBRmBH (thickness of SiO\(_2\) = 149\( \pm \)1.5 nm; \( n_{\text{SiO}_2} = 1.4598; \) \( n_{\text{Si}} = (3.858-i0.018); \) \( n_{\text{air}} = 1; \) \( n_{\text{graphite}} = 2.10-i(0.6-0.8) \), where \( n \) is a refractive index of corresponding materials) (was fixed).
2.4. Equipment for electrical measurements

Electrical measurements were made in special equipped room (Figure 2.2).

Electrical measurements for Chapter 3 were followed using two electrodes (1 cm in width) covered by an aluminium foil and fixed on the sample surface with an interdistance of 0.5 cm. DC-electrical measurements were performed with a Keithley 2400 Source-Measure Unit. At least 10 electrical measurements were undertaken for each sample.

Electrical measurements for Chapter 4 were followed using 18-finger gold micro-electrodes (step height ~50 nm, width ~500 nm, separation ~1 µm) were fabricated by photolithography on Si-wafer with an insulating SiO$_2$ layer (~300 nm) and probehead with tungsten needles for contact realization (Figure 2.3).

The Model 2400 SourceMeter solution is a 20 W instrument that allows sourcing and measuring voltage from ±5 µV (sourcing) and ±1 µV (measuring) to ±200 V DC and current from ±10 pA to ±1 A. All data were automatically transferred to computer and treated by LabVIEW™ program.

Figure 2.2 Room for electrical measurement

Figure 2.3 Probehead with needles for contact realization
Chapter 3

Nanotubes modified by covalent grafting of poly(2-vinylpyridine)

Abstract

Multi-walled carbon nanotubes modified by covalent grafting of poly(2-vinylpyridine) (CNT-g-P2VP) form stable dispersions in good solvents for P2VP, including water at low pH. The positively charged P2VP shell allows the immobilization of the CNTs onto oppositely charged surface. Deposition of CNT-g-P2VP from aqueous dispersions at low pH is an effective method to prepare homogeneous ultra-thin films with a tunable CNTs density. A percolation threshold of 0.2 µg/cm² and critical exponent α=1.24 are found from dc conductivity measurements. The sheet resistance value agrees with the percolation theory for 2D-films. According to AFM and electrical measurements, even when only 5% of the surface is covered by CNT-g-P2VPs, the sheet resistance is of the order of 1MΩ/sq, which indicates that conductivity is imparted by a network of an ultra-low density. When the film transmittance decreases down to ~70% at 550nm, the occupied surface area is ~15% and sheet resistance falls down to ~90kΩ/sq. These data show that undesired in-plane clustering does not occur upon the dispersion casting of the films and that high quality networks of CNT-g-P2VPs are built up. The electrosteric stabilization of the CNT-g-P2VP dispersions in water at low pH is at the origin of this desired behavior. Although the MWNT films prepared in this work are less conductive and less transparent than the SWNTs films, they could find applications, e.g., in touch screens, reflective displays, EMI shielding and static charge dissipation. Moreover, the polymer shell of CNT-g-P2VP serves as a scaffold for immobilization of various materials that have an affinity to P2VP, including nanoclusters of Prussian Blue. These nanoparticle-based nanostructures might be useful materials for manufacture of electrooptical devices, biosensors or mechanically robust ion-sieving membranes.

3.1. Synthesis and solubilization of carbon nanotubes: state of the art

Carbon nanotubes are molecular-scale tubes of graphitic carbon with outstanding properties. They are well-known by the stiffest and strongest fibres and have remarkable electronic properties and many other unique characteristics.
For these reasons, they have attracted huge academic and industrial interest. The current interest in nanotubes is a direct consequence of the series of experiments on the vaporisation of graphite making by Harry Kroto and Richard Smalley who obtained fullerene, C_{60}, in 1985. The discovery that carbon could form stable, ordered structures other than graphite and diamond stimulated researchers worldwide to search for other new forms of carbon. The search was given new impetus when it was shown in 1990 that C_{60} could be produced in a simple arc-evaporation apparatus readily available in all laboratories and as an additional products carbon nanotubes were discovered by the electron microscopist Summio Iijima, of the Nec laboratories in Japan, in 1991.\textsuperscript{13} Carbon nanotubes are recognized as the ultimate carbon fiber with the highest strength of any material\textsuperscript{14} and the highest thermal conductivity\textsuperscript{15}, and, as been shown, to possess outstanding field emission properties.\textsuperscript{16} Transport in metallic carbon nanotubes has had ballistic nature, than means, that electron moves in a medium with negligible electrical resistance.\textsuperscript{17} They often have been used as the active semiconductors in nanoscale devices\textsuperscript{18}, due to their unique topologically controlled electronic properties.\textsuperscript{19} The tubes containing one-two layers of graphite are called single-walled nanotubes (SWNTs). The tubes which consist of many layers are designated as multi-walled nanonotubes (MWNTs). Nanotube diameters range from 0.4nm to more than 3nm for SWNTs and from 1.4nm to at least 100nm for MWNTs.\textsuperscript{20} Useful composite research requires a bulk supply of nanotubes of high purity and in an usable (i.e., easily dispersible) form. Existing technologies for the production of single-wall nanotubes (SWNTs) do not yield sufficient quantities and lack the required purity. Purification of these materials is often tedious, low in yield, and damaging to the tube’s structure through oxidative shortening.\textsuperscript{21,22} For some applications such as conductive fillers or as reinforcing fibers, MWNTs are likely to be preferred over SWNTs on a cost basis. In the next paragraph, devoted to nanotubes I focus on the synthesis of carbon nanotubes in general with preferential attention to MWNT.

**Synthesis.** The hybridisation of carbon’s orbital in nanotubes is sp², with each atom joined to three neighbours, as in graphite. The tubes can therefore be considered as rolled-up graphene sheets (graphene is an individual graphite layer). There are three distinct ways in which a

\begin{thebibliography}{99}
\end{thebibliography}
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graphene sheet can be rolled into a tube. The first two, known as “armchair” and “zig-zag” have a high degree of symmetry. The terms "armchair" and "zig-zag" refer to the arrangement of hexagons around the circumference. The third class of tubes, which in practice is the most common, is known as chiral, meaning that it can exist in two mirror-related forms.

Carbon nanotubes can be produced using two techniques: non-catalytic and catalytic. The “classical” method of non-catalytic technique is arc-evaporation synthesis. The original method was represented by Iijima\textsuperscript{23} that was slightly modified by Kraetschmer-Huffman. The electrodes are two graphite rods, usually of high purity, although there is no evidence that exceptionally pure graphite is necessary. Typically, the anode is a long rod approximately 6mm in diameter and cathode is a much shorter rod 9mm in diameter. Efficient water-cooling of the cathode has been shown to be essential in producing good quality nanotubes. The position of the anode should be adjustable from outside the chamber, so that a constant gap can be maintained during arc-evaporation. A voltage-stabilized DC power supply is normally used, and discharge is typically carried out at a voltage of 20V. The current depends on the diameter of the rods, their separation, the gas pressure, etc. But it is usually in the range of 50-100A.\textsuperscript{24} When the pressure is stabilized, the voltage should be turned on. At the start of the experiment the electrodes should not be touching, so no current will initially flow. The moveable anode is not gradually moved closer to the cathode until arcing occurs. When a stable arc achieved, the gap between the rods should be maintained at approximately 1mm or less; the rod is normally consumed at a rate a few millimeters per minute. When the rod is consumed, the power should be turned off and the chamber left to cool before opening. A number of factors have been shown to be important in producing a good yield of high quality nanotubes. The pressure of the helium in the evaporation chamber (500Torr appears to be the optimum) and the current are the most important parameters.

Non-catalytic methods are characterized with high quality tubes possess different structure. These methods are simple and useful for SWNTs and MWNTs, but the yield of the pure tubes is not so high. In the best sample, the ratio of the nanotubes to nanoparticles is of the order of 2:1 and, as a result, an additional purification of seed is necessary. This leads to high prices, especially for SWNT. Catalytic methods of syntheses were proposed to produce high-quality aligned nanotubes in bulk at low cost.

It was well known for over the century that filamentous carbon can be formed by catalytic decomposition of a carbon containing gas on a hot surface. The phenomenon was

\textsuperscript{24}Ebbesen, T.W.; Ajayan, P.M. Nature 1992, 358, 220.
firstly observed by Kroto and C. Schultzenberger in 1890.\textsuperscript{25,26} Work, established in the 1950s, was shown that filaments could be produced by the interaction of wide range of hydrocarbons and other gases with metals, the most effective of which were iron, cobalt and nickel.

The system for synthesis of CNTs is relatively simple and consisting of a quartz tube reactor within a multizone furnace (Figure 3.1). The system configuration involves entraining a mixture of xylene and ferrocene (as suggested by Rao et al.\textsuperscript{27,28}) into an inert gas stream. During the decomposition of the ferrocene-xylene mixtures at temperatures in the range 625-775°C and at atmospheric pressure, iron nanoparticles are nucleated and begin to deposit carbon (from xylene and ferrocene) as well-aligned pure nanotubes arrays on the quartz surfaces (reactor walls and substrates). From short-duration experiments (2-10min), it appears that once growth initiates, the MWNTs rapidly grow to a maximum length (typically 50µm). The most effective catalyst have been shown to be iron, nickel, and cobalt.\textsuperscript{29}

**Figure 3.1** Schematic of floating catalytic CVD reactor system to produce MWNTs.

Nanotube synthesis by chemical vapour deposition (CVD) has many advantages over other production routes, including the high purity of the product, which requires no further processing to yield a usable product. However, the significantly lower temperatures used in the synthesis, compared to those of arc or laser production methods, tend to produce nanotubes with less well-defined graphene structure.\textsuperscript{30} This can be rectified by a post-treatment in which the nanotubes are heated in an inert atmosphere to a high temperature in the range 1800-2600°C. This graphitisation process removes many of the structural defects,

\textsuperscript{25} Schultzenberger, C. R. Acad. Sci., 1890, 111, 774-778.
but it has been also shown to be a successful method for removing all of the residual iron catalyst.\textsuperscript{31}

**Solubilization.** It is very difficult to explore the full application potential for pure carbon nanotubes. The major barrier is their poor solubility and low dispersibility in aqueous and organic liquids, leading to difficulties in their manipulation. CNTs typically exist as ropes or bundles. They are a few micrometers long; the CNTs ropes are entangled together in the solid state to form a highly dense, complex network structure. The low dispersibility stems from the strong tendency to aggregation due to the van der Waals attraction rather than to disperse in common solvent. A recent calculation for SWNTs suggests that the typical intertube attraction is $36\times k_B T$ (where $k_B$ is Boltzmann constant, $T$ is absolute temperature) for every nanometer of overlap between adjacent tubes, leading to cohesive energy of a few thousands of $k_B T$ per micrometer-long tubes.\textsuperscript{32} Unlike the case of classical colloids, the attraction is short-ranged and decay to a negligible value over a distance of a few nanometers. Most of the methods for dispersion and modification are designed to reduce the short-range attraction between the nanotubes via the introduction of a repulsive interaction of similar strength. A number of groups have reported successful modification and solubilisation of carbon nanotubes. These reactions may be roughly divided into covalent and non-covalent attachment of functional groups or polymers direct to the graphite surfaces.

It is possible to wet the SWNT raw soot in refluxing nitric acid, whereby the end caps of the tubes are oxidized to carboxylic acid and other weakly acidic functionalities. These “acid-purified” SWNTs can be dispersed in various amide-type organic solvents under the influence of an ultrasonic force field.\textsuperscript{33} The nitric acid purifies the carbon nanotubes by removal of some of the metal catalysts used in the synthesis of the tubes and some of the amorphous carbon that is a by-product of most synthetic methods. However, the nitric acid treatment introduces defects on the nanotube surface,\textsuperscript{34} oxidizes (hole dopes) the carbon nanotubes and produces impurity states at the Fermi level of the nanotubes.\textsuperscript{33} This latter effect may be viewed as an intercalation of the nanotube lattice by oxidizing agents, with concomitant effects on the electronic properties of the nanotubes,\textsuperscript{35} a process which is quite familiar from the intercalation of graphite and fullerene lattices by various redox reagents. The defect sites


that are introduced into the carbon nanotubes can lead to shorten and eventually destroy the carbon nanotubes under similar oxidizing conditions.

Direct reaction of the acid-purified SWNTs with long-chain amines led to soluble materials by the formation of zwitterions (Scheme 3.1). A variety of oligomeric and polymeric compounds have been also used in the functionalization of carbon nanotubes.

Scheme 3.1

Rather than small molecules, polymer chains were chemically attached to the tubes, with the purpose to make them dispersible in organic solvents and within polymer matrices. In this respect, ”grafting from” and ”grafting to” methods were proposed. The ”grafting from” approach relies on the immobilization of initiators for the living/controlled polymerization of various monomers followed by chain growth from the surface and formation of polymer brushes of possibly high grafting density. The anionic grafting of polystyrene is one example, whereas initiators for the controlled radical polymerization of n-butyl methacrylate, methyl methacrylate and polystyrene by ATRP have also been attached


to the CNTs surface and used in a “grafting from” process. However, final contamination by metal residues may be a concern. The “grafting to” method is based on reaction of pre-formed polymer chains with the substrate to be modified, as illustrated recently by Qin et al. for the covalently grafting of polystyrene to CNTs according to a multi-step process and the cycloaddition reaction of azide end-capped polystyrene.

Non-covalent dispersing methods mainly based on the physical adsorption of polymers (surfactants). Attempts to dissolve and characterize SWNT in solution with charged surfactants such as Triton–X 100, sodium or lithium dodecyl sulphate or cetyl trimethylammonium bromide have been reported. Also non-covalent dispersion was made using block copolymer (poly(ethylene oxide) 100-b-poly(propylene oxide)65-b-poly(ethylene oxide)100) or non-covalent attachment of the pyrene containing polymer to the MWNT. The main advantages of this method is low expenditure, negligible modification of the nanotube surfaces and as a result, keeping intrinsic conductive and initial mechanical characteristics. This treatment is very often applicable to the formation of transparent conductive coating, which are widely used in plastic electronics.

**CNTs films.** Selective localization of all the CNTs at an interface instead of a homogeneous dispersion within the whole composite volume is an alternative approach to conductive materials with a low CNTs content, provided however that the surface (2D) conductivity is high enough. This general concept was illustrated several years ago by the selective localization of carbon black particles (CB) at the interface of a co-continuous two-phase polymer blend. Conductivity was observed at loadings as low as 0.4 wt% CB content. An intermediate situation between the 3D dispersion of CNTs and the 2D localization at an interface may be found in the preparation of ultrathin films of CNTs containing polymers. The CNTs dispersion is then borderline between a 2D and a 3D space. Moreover, much attention is paid nowadays to highly conductive ultrathin films and coatings for their

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performances in electromagnetic interference (EMI) shielding, heat and static charge dissipation and field-emission sources.

The key issue for the manufacture of high quality films with optimised transparency and conductivity is the capability to disperse properly CNTs in an appropriate solvent and to prevent the unfavourable in-plane clustering of CNTs upon drying. Kumar, Smalley, et al. dispersed single-wall carbon nanotubes (SWNTs) in oleum. The strong electrostatic repulsion of the protonated CNTs could prevent the CNTs from aggregating, and highly conductive films were prepared by casting. The use of an extremely aggressive solvent is however a major drawback. Wu et al. and Grüner et al. proposed a technique based on the fast filtration of suspensions of SWNTs through a membrane intended to be dissolved afterwards. The in-plane aggregation of the collected CNTs did not occur because of the fast release of the solvent. Rogers et al. reported on the controlled flocculation of SWNTs from surfactant-stabilized suspensions by addition of proper solvents. Recently, Manohar et al. prepared 1500 nm films by the direct casting of SWNT dispersion in an aqueous solution of Triton-X 100. Sheet resistance (~80Ω/sq), dc conductivity (~50Scm⁻¹) and transmittance (~80%) were measured. At the time being, all the methods proposed to prepare CNTs-based transparent conductive coatings have been tested with SWNTs. However, the use of multi-wall carbon nanotubes (MWNTs) is much more attractive because of a larger availability.

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Chapter 3 Nanotubes modified by covalent grafting of poly(2-vinylpyridine)

Despite of obvious advantages, all above-mentioned methods of preparation of CNTs films, including drop-drying, airbrushing, Langmuir-Blodgett,\textsuperscript{56} spin coating and fast-filtration-deposition methods, have some disadvantages that limit their potential application. For example, utilization of extremely aggressive solvents as solubilizing agents is not compatible with many plastics and further applications. Deposition of nanotubes from aqueous solutions using non-covalent interaction sometimes result in low surface, that makes hardly possible further modifications of such films (for example, modifications with metal or magnetic particles).

3.2. Own results

3.2.1. Modification and immobilisation of CNTs

Commercially available MWNTs (Nanocyl S.A., Belgium, 50 µm long, average inner diameter 6 nm, outer diameter 25 nm, and purity higher than 95 wt%) were used in this work. They were modified by the reaction of sp\textsuperscript{2} hybridized carbons of CNTs with 2,2,6,6-tetramethyl-piperidin-1oxyl (TEMPO) end-capped poly(2-vinylpyridine) (P2VP) chains. This preparation was performed by our collaborator from Belgium.\textsuperscript{57} Upon heating, polymeric radicals are released, which are reactive towards the surface, as shown in Scheme 3.2. In contrast to other methods of CNTs modification, the macroradical addition does not require any hard oxidative pre-treatment of the CNTs, which preserves their original size.

Scheme 3.2


Chapter 3 Nanotubes modified by covalent grafting of poly(2-vinylpyridine)

There are several reasons for choosing P2VP. First of all, its solution behavior can be extremely changed from being a hydrophobic polymer in apolar solvents to a cationic polyelectrolyte in water at low pH. Moreover, P2VP has complexing properties towards inorganic ions, used as precursors for nanometer scale semiconductive particles. Finally, the positively charged polymer interacts spontaneously with oppositely charged solid surfaces.

P2VP of controlled molecular weight (3–5kg/mol), narrow molecular weight distribution (PDI=1.25) and end-capped by TEMPO (P2VP-TEMPO) was prepared by controlled radical polymerization of 2-vinylpyridine in the presence of benzoyl peroxide and TEMPO. A 0.3 wt% dispersion of such modified CNTs (CNT-g-P2VP) in dry toluene was stirred with a 100-fold wt excess of P2VP-TEMPO at 120 °C for 7-48h (Table 3.1).

Table 3.1 Molecular characteristics of TEMPO end-capped poly(2-vinylpyridine) and grafting ratio of the CNTs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ [kg mol$^{-1}$]</th>
<th>$M_w/M_n$</th>
<th>Reaction Time [h]</th>
<th>Grafting Ratio$^c$ [%]</th>
</tr>
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<td>A</td>
<td>3.0</td>
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<td>10</td>
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<tr>
<td>D</td>
<td>5.0</td>
<td>1.30</td>
<td>48</td>
<td>11.5</td>
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</tbody>
</table>

$^{a)}$ Grafting conditions: 2.0 g of (co)polymer, 20 mg of CNTs in 6 ml of toluene, 120 °C. $^{b)}$ $M_n$, SEC based on polystyrene standards. $^{c)}$ GR: grafting ratio (mass fraction P2VP in CNT-g-P2VP) determined by TGA.

After reaction, the modified CNTs (CNT-g-P2VP) were recovered by filtration through a 0.2 μm Teflon membrane. They were redispersed in THF and filtered again. This procedure was repeated at least four times until no polymer was extracted anymore. In order to remove completely possible traces of nongrafted P2VP chains, CNT-g-P2VP was "dissolved" in acidic water (HCl, pH 2) and recovered by centrifugation (4000g, 1 hour, where g is standard gravity).

In contrast to neat CNTs, the CNT-g-P2VP tubes are easily dispersed in organic solvents and acidic water. Figure 3.2a compares the stability of 0.05wt% dispersions of CNT-g-P2VP and pristine CNTs in water, at different pH, 3 hours after ultrasonication. The visual aspect of the dispersions is drastically different, depending on pH and whether the CNTs were surface modified or not. In order to confirm that the dispersion stability does not merely result

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from physiosorption of P2VP to the nanotube surface, CNTs were treated with a P2VP
\( M_n = 5\text{kg/mol} \) under the aforementioned experimental conditions, except that chains did not
contain TEMPO end-group (anionic synthesis). In sharp contrast to CNT-g-P2VP, the carbon
nanotubes did not form any stable dispersion in THF.

The absorbance of CNT-g-P2VP dispersion in 0.5 M HCl decreases gradually from UV
to near-IR, similarly to previously reported spectra of other surface-modified CNTs.\(^{61}\) The
P2VP chains grafted to CNTs were selectively degraded by heating (TGA) at 10°C/min under
nitrogen. Figure 3.2b compares the TGA curves for pristine CNTs, P2VP, and CNT-g-P2VP.
Curve B shows that the P2VP chains grafted onto CNTs are degraded at the same temperature
as P2VP, whereas neat CNTs are stable in the same temperature range. Therefore, the grafting
ratio, defined as the mass ratio of the grafted polymer to the nanotubes can be determined by
TGA. It is found to be of the 6-12% range as listed in Table 3.1

\[ \text{Figure 3.2 (a) CNTs dispersions in different aqueous solutions, 3 h after ultrasonication, for pristine}
\]

\[ \text{CNTs: i) acidic water (HCl, pH 2.0); ii) neutral water; iii) basic water (NaOH, pH 12); and for CNT-g-}
\]

\[ \text{P2VP: iv) acidic water (HCl, pH 2.0); v) neutral water; vi) basic water (NaOH, pH 12). (b) Thermogravimetric}
\]

\[ \text{analysis under nitrogen at 10°C/min: (A) pristine CNTs; (B) CNT-g-P2VP; (C) P2VP-TEMPO (} M_n = 5000)\].

The direct observation of CNTs confirms the strong influence of P2VP grafting shell to the disentanglement of the tubes after dispersion in water at low pH. Upon casting of the dispersion onto a carbon-coated copper grid, transmission electron microscopy (TEM) shows (locally) densely entangled network of pristine CNTs (Figure 3.3a). In contrast, a very loose network of CNTs is observed after surface modification, in line with a homogeneous dispersion in water and a homogeneous deposition on the grid which accounts for a lower number of tubes per surface area (Figure 3.3b).

Because of the extensive disentanglement of the CNT bundles, after grafting of P2VP, individual nanotubes indeed can be deposited onto a solid support and directly observed. Figure 3.3c shows representative AFM images of an isolated CNT-g-P2VP tube of 10-20nm in diameter with smooth side walls.
Deposition of an amorphous shell at the surface of CNTs was confirmed by TEM observations. Figure 3a shows modified nanotubes with closed ends and a relatively smooth surface (see the insets of Figure 3.4a). High-resolution images (Figure 3.4b) reveal the multi-wall crystal lattice of the carbon nanotubes (3.43 Å) that have an average inner diameter of 6 nm, outer diameter of 22 nm and a polymer shell of about 2 nm. On the assumption that density of the graphite and P2VP is 2.2 g/cm³ and 1 g/cm³, respectively, the 2 nm thick polymer shell amounts is corresponded to approximately 13.6 wt% that nicely fits the TGA data (12 wt%).

**Figure 3.4.** a) TEM images of CNT-g-P2VP; high-magnification images (insets) show the closed ends of the CNT-g-P2VP. b) The HR TEM image shows the multi-wall crystal lattice of the carbon nanotube (3.43 Å); the arrow indicates a 2 nm thick amorphous layer, presumably of P2VP.

**Adsorption of CNT-g-P2VP to the oppositely charged surfaces.** For various applications CNTs must be deposited as individual objects on a surface, but more importantly, one should be able to deposit them very selectively on a particular spot of a multicomponent surface. In order to illustrate that such achievement is feasible, positively charged CNT-g-P2VP dispersed in acidic water have been deposited onto a (macroscopically) patterned surface,
consisting of oppositely charged surface areas. For this purpose, a freshly cleaned Si-wafer has been completely immersed in an aqueous solution of poly(diallyldimethyl ammonium chloride) (PDADMAC) for 10 minutes, so charging the whole surface positively. After thorough washing with water, half of the wafer was vertically dipped into an aqueous solution of polystyrene sulfonic acid (PSA) (0.1g/l) for few seconds followed by repeated washing. Half the Si-wafer surface area is thus positively charged due to the adsorbed PDADMAC layer, and the second half is negatively charged being covered by PSA. This two-component surface then is completely immersed in a dispersion of CNT-g-P2VP in acidic water (HCl, pH2) for 30 sec, and washed with water again. Figure 3.5 is the AFM image of the boundary area of the substrate after deposition of the carbon nanotubes. A sharp boundary between the positive PDADMAC layer and PDADMAC-PSA bilayer is observed as a 1nm high step.

![AFM image of a macroscopically patterned Si-wafer](image)

**Figure 3.5** AFM image of a macroscopically patterned Si-wafer, after dipping into a dispersion of CNT-g-P2VP in acidic water, the upper part was covered by a positively charged PDADMAC layer, and the lower part by a positively charged PDADMAC-PSA bilayer. The high selectivity of the CNT-g-P2VP is highlighted.

The upper part of the image is coated by PDADMAC and only one nanotube can be observed. In sharp contrast, a rather homogeneous deposition of CNTs is observed on PSA layer, which is strong evidence that the tube deposition can be highly selective on a chemically heterogeneous surface.
3.2.2. Polymer-modified multi-walled CNTs for ultrathin transparent conductive coatings

Most of the methods of CNTs modification reported so far require the oxidative pretreatment of the surface which leads to the nanotubes shortening and thus to the increase of the percolation threshold. In contrast, no oxidative pretreatments of CNTs were used in this work and the P2VP chains have been covalently grafted to the nanotubes by the addition of TEMPO end-capped P2VP.\(^\text{62}\) Using a P2VP with a molecular weight (Mn) of 7606g/mol, the modified MWNTs contain 13% of grafted P2VP and the thickness of this polymer shell of about 3 nm has proved to be sufficient to solubilize CNT-g-P2VP in “good” solvents for P2VP (~3mg/ml), including acidified water and THF. These dispersions were used for the preparation of CNT-g-P2VP thin films on Si-wafers and glass slides.

Si-wafers with an insulating SiO\(_2\) layer of about 300nm (from Wacker-Chemitronics) and glass slides (Menzel-Glaser) were repeatedly cleaned (at least 3 times) in a ultrasonic bath with dichloromethane (DCM) for 5min, and then treated with a cleaning solution of NH\(_4\)OH and H\(_2\)O\(_2\) at 60ºC for one hour. Si-wafers (or glass slides) were placed onto a heating stage at 150ºC. One drop of the CNT-g-P2VP dispersion of well-defined volume and concentration (Table 3.2) was deposited on the surface.

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</tbody>
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Almost no deposition of carbon nanotubes is observed when aqueous dispersion of CNT-g-P2VP (pH = 2; ~3mg modified MWNT/ml) is spin-coated onto freshly cleaned Si-

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wafers or glass slides. However, smooth and transparent grey films are formed upon drop casting of the same dispersions of CNT-g-P2VP, followed by solvent elimination at high temperature (150°C) and normal pressure. The samples deposited on both cleaned Si and glass slides have been analyzed by dc electrical measurements, AFM, ellipsometry and UV-vis spectroscopy (Figure 3.6 and Table 3.2).

Samples with different nanotube’s surface density, \( M \), i.e., weight of CNT-g-P2VPs per cm\(^2\), have been prepared on Si-wafers and glass slides. Assuming that the nanotubes homogeneously cover the whole surface area, the surface density of the nanotubes has been calculated as \( M = \frac{V \times C}{S} \), where \( C \) is the weight concentration of the CNT in the dispersion of CNT-g-P2VP, \( V \) is the volume of the dispersion used for the film preparation and \( S \) is the coated surface. Different spots of the surface have been probed by ellipsometry in order to estimate the homogeneity of the CNT-g-P2VP deposition. Ellipsometry was used in this work to measure the surface density of the nanotubes rather than to determine the real film thickness (the thickness was measured by atomic force microscopy (\( d_{AFM} \), AFM). An accurate measurement of the thickness of the CNT-g-P2VP films by ellipsometry was impossible, since the film porosity is unknown and changes from sample to sample. Using ellipsometry I measured psi and delta angles for each film and, from the known refractive index of graphite (\( n=2.1 \)), I calculated the thickness of graphite that constitutes the nanotubes.
in the given film \((d_\ell)\).\(^{63}\) The surface density of the nanotubes \((M_\ell)\) in each sample has been calculated from the ellipsometrically derived thickness of graphite, density of graphite \(\rho=2.25\ \text{g/cm}^3\) and CNTs content in the CNT-g-P2VP composite.\(^{64}\) As a rule, the agreement is rather good between the surface densities estimated by ellipsometry \((M_\ell)\) and calculated from the amount of deposited nanotubes \((M)\), especially for thinner and more homogeneous films (Table 3.2).\(^{65}\)

The resistance of CNT-g-P2VP films measured by a standard two-probe method, depends on the deposited amount of CNT-g-P2VP. The reproducibility of the \(I-V\) characteristics (Figure 3.7) together with the predictable dependence of the resistance on the film thickness and the interelectrodes distance support that the experimental obtained resistance is due to nanotube films and not the resistance of the nanotube/electrode junction. Moreover, the sheet resistance (here and next \(R_\square\) or \(R_{sq}\) are symbols for sheet resistance which can be determined as \(R_\square=R*(W/L)\), where \(W\) and \(L\) are the size of the nanotube channel between electrodes, \(R\) is DC resistance between electrodes, measured by two-probe method. For this Chapter \(W\) is equal 1cm and \(L\)-2mm) \((R_\square)\) is ~1k\(\Omega\)/sq.

![Figure 3.7 I-V characteristics of the CNT-g-P2VP films of different transparency \((T)\) deposited on glass slides](image)

The CNT-g-P2VP films have been observed by AFM, as illustrated by Figure 3.8 in relation to the surface density. At low \(M\), the nanotubes are loosely packed and bare Si-surface is extensively exposed (Figure 3.8a). At higher \(M\), entangled networks of nanotubes are formed (Figures 3.8b-c). The film thickness has been approximated by the standard AFM


\(^{65}\) Stauffer, G. "Introduction to percolation theory"; Taylor & Francis: London, 1985

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Chapter 3 Nanotubes modified by covalent grafting of poly(2-vinylpyridine)

scratch-test ($d_{AFM}$ in Table 3.2). The images for the film of the lower density (Figure 3.9a) have been analyzed to measure the contour length of the individual nanotubes with a dedicated software. A weight average contour length of the nanotubes ($l_{AFM}=2.4 \, \mu m$, Figure 3.9b) has been calculated by a statistical treatment of these data. In our cases, I use the percolation theory for model of randomly distributed “conductive stick” (CS) and this value corresponds to the length of a CS. The apparent width of individual CNTs ($D_{AFM}$) and their occupied surface area ($S_{AFM}$) have also been determined with a standard software, $l_{AFM}$ being the $S_{AFM}/D_{AFM}$ ratio.

The width of the nanotubes measured by AFM is overestimated by the tip-broadening effect. For instance, a nanotube with a height (and diameter) of 25 nm is observed by AFM as a 98 nm thick object. However, this overestimation is systematic and basically constant for

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67 Stauffer, G. Introduction to percolation theory; Taylor & Francis: London, 1985
69 WSxM v4.0 Develop 8.1: [http://www.nanotec.es/](http://www.nanotec.es/)
images recorded at the same length scale. Therefore, the statistical treatment of the data allows the overall length of nanotubes ($\Sigma L$) and the number density of the “conducting sticks” ($N$) on the image of area $s$ to be calculated even for samples with highly entangled nanotubes:

$$\Sigma L = \Sigma S / D_{AFM}; N = \Sigma L / (s \times l_{AFM})$$

The critical number density of “conductive sticks” ($N_C$)\textsuperscript{70} at the percolation threshold has been calculated from $l_{AFM}$:

$$l \sqrt{\pi N_C} = 4.236; \quad N_C = \frac{4.236^2}{\pi \times l_{AFM}^2} = \frac{17.94}{2.4^2} \times 3.14 = 0.99 \ (1/\mu m^2).$$

The sheet resistance is the higher ($R\square \sim 5\text{M}\Omega$) for sample #1 ($s=24.6\mu m^2$), for which the overall contour length of the nanotubes and the number density of “conducting sticks” (with the length equal to $2.4\mu m$) have been calculated from the AFM data. $\Sigma S$ and $D_{AFM}$ are $6.15\mu m^2$ and $0.098\mu m$, respectively, as determined by the image processing:

$$\Sigma L = \Sigma S / D_{AFM} = 6.15 / 0.098 = 62.8; N_{#1} = \Sigma L / (s \times l_{AFM}) = 62.8 / (24.6 \times 2.4) = 1.06 \ (1/\mu m^2)$$

Figure 3.10 shows that the dependence of the sheet conductance ($1/R\square$) on the surface density ($M$) of the CNT-g-P2VPs is typical for a percolative behavior. According to the percolation theory, the sheet conductance depends on the density of the conductive filler and universal for every model:

$$1/R\square \propto 1/R\square^0 (M-M_C)^\alpha,$$

where $1/R\square^0$ is the sheet conductance of the bulk material, $M_C$ is the critical density at the percolation threshold, which dependent on lengths of the CS,\textsuperscript{71} and $\alpha$ is a critical exponent.\textsuperscript{72} The fit of the experimental data was done using module for nonlinear fitting available in Origin7.5. Belehradek model\textsuperscript{73} have been used for fitting. The goodness of the fitting was determined by coefficient of determination ($R^2$) and for our fitting it was equal 0.94. The following parameters were available after fitting $1/R\square^0=53.31963\pm12.3 \ (1/k\text{Ohms per Sq}); M_C=0.00025\pm0.00045(\text{mg/cm}^2); \alpha=1.24\pm0.03$.

The value of the critical exponent, $\alpha$, is only slightly lower than the value predicted by the percolation theory for 2D-films ($\alpha \sim 1.3$). Similar deviations of the critical exponent from the theoretical value have been previously observed for CNT-containing composites and accounted for by the very high aspect ratio of the filler. Whenever it is so, the percolation

\textsuperscript{71} The value of the surface density for the sample #1 was used as the critical density ($M_{#1} = M_C$) since the calculated density of conductive sticks for this sample ($N_{#1}=1.06 \ 1/\mu m^2$) is very close to the calculated critical density ($N_c=0.99 \ 1/\mu m^2$).
\textsuperscript{72} Stauffer, G. Introduction to percolation theory; Taylor & Francis: London, 1985
\textsuperscript{73} More information is available in Origin module “Help”
process is not actually statistical, it deviates from the random distribution of these too long individual objects.\textsuperscript{74, 75, 76}

![Figure 3.10 Sheet conductance vs surface density of the CNT-g-P2VP. The data in the percolation region were fitted with the critical exponent $\alpha=1.24$.](image)

The transmittance, $T$, of the CNT-g-P2VP films with different surface densities has been measured for samples cast on glass slides. Figure 3.11 shows how $T$ at 550nm changes with the sheet resistance $R\Box$. $R\Box$ is in the range of 20-50k$\Omega$ whenever $T$ does not exceed 70%. Beyond this $T$ value, $R\Box$ increases sharply. The data for transmittance represented in Table 3.3. The CNT-g-P2VPs nanotubes have also been dispersed in THF, and series of films of various thicknesses have been prepared. As a rule, the films are less homogeneous as seen by naked eyes and the sheet resistance is approximately of two orders of magnitude higher compared to the counterparts prepared from acidic aqueous dispersions.

**Discussion and conclusions.** Deposition of CNT-g-P2VP from aqueous dispersions at low pH is an effective method to prepare ultra-thin films with a tunable CNTs density. A percolation threshold of 0.25$\mu$g/cm$^2$ and a critical exponent $\alpha=1.24$ have been found from dc conductivity measurements. The $\alpha$ value agrees with the percolation theory for 2D-films.


According to AFM and electrical measurements, even when only 5% of the surface is covered by CNT-g-P2VPs, the sheet resistance is in order of 1MΩ/sq, which indicates that conductivity is imparted by a network of an ultra-low density. When the film transmittance decreases down to ~70% at 550nm, the occupied surface area is ~15% and $R_\square$ falls down to ~90kΩ/sq. These data show that undesired in-plane clustering does not occur upon the dispersion casting of the films and that high quality networks of CNT-g-P2VP are built up. The electrosteric stabilization of the CNT-g-P2VP dispersions in water at low pH is at the origin of this desired behavior.

### Table 3.3 Transmittance at 550nm and sheet resistance for CNT-g-P2VP films deposited onto glass slides

<table>
<thead>
<tr>
<th>entry</th>
<th>1</th>
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<th>3</th>
<th>4</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$R_\square$, KΩ/sq</td>
<td>325</td>
<td>250</td>
<td>150</td>
<td>140</td>
<td>120</td>
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<td>2.5</td>
</tr>
<tr>
<td>$T$, %</td>
<td>77</td>
<td>80</td>
<td>76</td>
<td>75</td>
<td>73</td>
<td>55</td>
<td>53</td>
<td>59</td>
<td>50</td>
<td>25</td>
</tr>
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</table>

### 3.2.3. Surface decoration of the individual CNT-g-P2VP with Prussian blue clusters.

CNTs have unique electronic properties, high chemical stability, and extremely high mechanical strength and stiffness. Properties of CNTs can be further modified via immobilization of certain materials on their surface. With this regards, the P2VP shell developed around CNTs would be an ideal scaffold for deposition of various metal, semiconductive or magnetic nanoclusters or some other desired materials that have an affinity to P2VP.

Prussian Blue\textsuperscript{77} (PB), an old pigment, is a coordination polymer formed by reaction of either hexacyanoferrate(II) anions with ferric (Fe(III)) cations, or hexacyanoferrate(III) anions with ferrous (Fe(II)) cations.\textsuperscript{78} According to X-ray diffraction analysis, PB is a three-dimensional crystal of ferric and ferrous ions, which alternates at the sites of a cubic lattice.\textsuperscript{79} The ferric ion is coordinated to the nitrogen atoms, and the ferrous ion to the carbon atoms, of the bridging cyanide ligands. The remaining charge is balanced either by potassium ions in the so-called “soluble” PB, or by ferric ions in the “insoluble” PB. The term “soluble”,

\textsuperscript{77}miscellanea Berolinensia ad incrementum scientiarum (1710) Berlin, p. 377.
\textsuperscript{79}Keggin, J.F; Miles, F.D. \textit{Nature} (London) \textbf{1936}, \textit{137}, 577.
however, does not refer to the true solubility but only to the tendency of PB to form colloidal solutions.\textsuperscript{80}

PB possesses some interesting physical properties.\textsuperscript{78} Neff et al. reported that the oxidation state of the iron centers could be controlled electrochemically, making possible dramatic color changes\textsuperscript{81,82} that could be used in electrochromic devices (such as flat panel displays or switchable pictograms).\textsuperscript{83} PB shows a long-range ferromagnetic ordering at 5.6K, whereas few PBs undergo magnetization at room temperature and even higher.\textsuperscript{84} Hashimoto et al. showed that the magnetic properties of PBs could be modulated not only by the chemical composition but also by an optical or electrical stimulation (photomagnetism and electromagnetism, respectively).\textsuperscript{85,86} PBs exhibit remarkable ion-sieving properties as result of an open pore zeolite-like structure.\textsuperscript{87}

On the other hands, because of its high activity and selectivity toward the reduction of hydrogen peroxide and oxygen, Prussian blue is usually considered as an “artificial enzyme peroxidase” and has been extensively used in the construction of electrochemical biosensors. Therefore, reinforcement of PB by CNTs might be a strategy for manufacturing mechanically robust ion-sieving membranes, and for creating electro-conductive pathways in a poorly conductive PB matrix for fabrication of biosensors. Furthermore, adsorption of CNT-g-P2VP onto oppositely charged surface results in transparent and highly conductive thin films, which can be used as high-surface area electrodes for fabrication of PB-based solid-state electrochromic devices with improved switching time.\textsuperscript{83}

PBs can interact with the polycations (PC) and form stable complex either on surface or in solution. It was shown that the main mechanism of adsorption between PC (such as P2VP) and PB is electrostatic interaction negatively charged hexacyanoferrate anions with positively charged units of the P2VP molecules.

Dispersion of PB clusters was prepared by mixing vigorously a solution of K$_4$Fe(CN)$_6$·3H$_2$O (1.18 mmol/l, Aldrich) in acidified water (HCl, pH 2.0) and an equal volume of a solution of FeCl$_3$ (Aldrich) at the same pH. Concentration of the FeCl$_3$ solution was either 0.296 mmol/l for intermediate PB2 clusters, or 0.444 mmol/l for larger PB3 clusters. A small amount of tetrahydrofuran (Ardrich) was added to the freshly prepared dispersions of PB in

\textsuperscript{80} Miscellaneous Berlinensis ad incrementum scientiarum (1710) Berlin, p. 377.
\textsuperscript{82} Keggin, J.F.; Miles, F.D. \textit{Nature} (London) \textbf{1936}, \textit{137}, 577.
order to separate the PB clusters from the unreacted K$_4$Fe(CN)$_6$ and KCl. PB clusters were collected by filtration, washed with a water-tetrahydrofuran solution (2:1), and redispersed in acidified water (HCl, pH 2).

Si-wafers (Wacker-Chemitronics) were first cleaned with dichloromethane (Aldrich) in an ultrasonic bath for 5 min (3 times), followed by cleaning with a solution prepared by mixing of 4 volume parts of deionized water, 1 volume part of 25% NH$_4$OH (Aldrich), and 1 volume part of 30% H$_2$O$_2$ (Aldrich) at 60°C for one hour. This NH$_4$OH:H$_2$O$_2$ solution must be handled cautiously because of violent reaction with organic compounds. Samples were finally exposed to 50% sulfuric acid for 15 min and then rinsed repeatedly with water purified through a Millipore (18 MQxcm) filter. Clean Si-wafers onto which CNT-g-P2VP nanotubes were deposited (concentration of the CNT-g-P2VP dispersion was 0.1 g/l), were dipped in the freshly prepared dispersion of PB2 (PB3) clusters for 3 min at 25°C, followed by washing with water and drying under an argon flow. Samples for TEM investigations were prepared by depositing a drop of the PMB or CNT-g-P2VP solution onto a standard TEM grid (Plano, Wetzlar, Germany) covered with a holey carbon film. After drying, the PB2 dispersion in acidified water (0.5 g/l) was added on the spot and removed with a filter paper one minute later. Finally, the grid was washed by adding a drop of water and removing it with a filter paper. These samples were investigated with AFM and TEM measurements. Figure 3.12 shows an AFM image of CNT-g-P2VP before and after decoration by PB2. As expected, the roughness of the nanotube surface is significantly increased. Low-magnification TEM images (Figure 3.13a) confirm that the carbon nanotubes are covered by particles of approximately 10 nm. This size is larger than the size of the pure PB2 estimated from the AFM observations (i.e., the height of the particles because the width is systematically overestimated by the tip-broadening effect). This difference is consistent with the embedding of the PB2 in the P2VP layer. The core-shell morphology of these particles was confirmed by high resolution TEM (HR TEM). As seen from the Figure 3.13, Prussian Blue nanoparticles are in the close contact with the nanotube surface that would be helpful for efficient charge injection from CNTs-based electrodes into the PB layer in electrochromic devices. A dense crystalline core with 3-5 nm diameter is surrounded by a few nanometer-thick amorphous shell (Figure 3.13b-d). The lattice of the PB nanodots is resolved with spacings of 2.09 Å, 1.95 Å and 1.82 Å that correspond to (422), (333) and (404) reflections (Figures 3.13d-e). The first reflection can be assigned to the Fe-N interatomic distance, and the last one to the Fe-C distance.

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Figure 3.12 Representative AFM image (a) and cross-section (c) of CNT-g-P2VP; AFM image (b) and cross-section (d) of the CNT-g-P2VP after PB deposition. The cross-sections (c,d) are repeated along the tubes shown in images (a) and (b).

![AFM images](image)

Figure 3.13 a) TEM images of the CNT-g-P2VP after deposition of PB2 clusters. b,c) HR TEM images of the core-shell structure of the particles consisting of a dense crystalline core (diameter of 3-5 nm) surrounded by a few nanometer-thick amorphous shell. HR TEM image (d) and selected area diffraction pattern (e) confirm the crystalline structure of the PB clusters (lattice distances of 2.09 Å (Fe-N), 1.96 Å and 1.83 Å (Fe-C) that correspond to the (422), (333) and (404) reflections, respectively.

![TEM images](image)
In conclusion, water-dispersible, charge-stabilized, surfactant-free Prussian Blue nanocrystals were prepared by mixing solutions of ferric chloride and excess of potassium ferrocyanide. The average size was readily controlled by the molar ratio of the two reagents. Thus formed PB nanoparticles are crystalline and display long-range ferromagnetic ordering at 5.1K that is slightly lower than the magnetization temperature of the bulk PB. PB nanoparticles can be selectively attached to single polycation molecules, or to the surface of CNTs pregrafted with P2VP. These Prussian Blue based nanostructures might be useful materials for manufacture of electrooptical devices or mechanically robust ion-sieving membranes. Recently, it was reported about interesting application for MWNT/PVP/PB composite\(^8^9\) in construction of amperometric biosensors for detection hydrogen peroxide. It is well known that PB has high activity and selectivity toward the reduction of hydrogen peroxide and oxygen, PB is usually considered as an ‘artificial enzyme peroxidase’. It was confirmed by electrochemical characterization that increasing of amperometric response in these composite is not only due to PB clusters but also due to synergistic effect of nanotubes.\(^8^9\)

Chapter 4

Polypyrrole nanowires grown from single polyelectrolyte molecules

Abstract

In this chapter I represent results, concerning a full circle of nanodevice fabrication utilizing polyelectrolyte molecules, starting from alignment of single-molecule templates, fixation of them between electrodes followed by growing of conductive polymer polypyrrole (PPy) selectively from them. In the first step, it was shown that spin coating of polycations onto mica in the presence of octylamine (OA) is a simple and general method of stretching and alignment of the chains. The contour length and molar mass for the stretched macromolecules can be directly measured by AFM, which makes this method a very useful analytical tool. The reason for the key role of OA has to be found in the formation of an ultra-thin liquid-like alkylamine film that reduces the surface energy of mica and weakens the interactions between the surface and the charged macromolecules. Similar method was used for the stretching and positioning of polystyrenesulfonic acid (PSA) between gold electrodes necessary for the preparation of conductive polymer nanowires. For this, silanization of Si-wafers with alkyl-silanes prior the spin coating of PSA, was found to be efficient method. I have developed a simple chemical route to conductive PPy nanowires by the grafting of PPy from molecules of PSA. The location and length of the synthesized PPy nanowires are defined by the location and length of adsorbed single-molecule templates. The diameter of the nanowires can be varied from a few nanometers to hundreds of nanometers by polymerization conditions. Since the nanowires are growing directly “on place” and, due to the fact of PPy deposition onto gold electrodes too, the resulting PPy NWs have good electrical contacts with the electrodes, as have been shown by electrical measurements. Electrical characterizations were done on the level of individual nanowires and their conductance was proved by “breaking experiments”. The dc conductivity of individual PPy nanowires approaches the conductivity of PPy in bulk. I found that the conductivity decreases with decreasing of temperature, as typical for semiconductors. The conductivity can be described using variable-range hopping model. According to this model the transition from 3D network to quasi 1-D structure of spherical conductive PPy grains was found. Achieved results open new and broad perspectives for the construction of molecule-based devices-sensors and transistors.
4.1 Synthesis of conductive polymer nanowires: a brief literature overview

**Introduction.** One dimensional nanostructures such as nanowires and nanotubes are one of the most promising candidates for the future nano-electronic device. It is generally agreed now that nanowires will not only be used as inter-connector of nano-device but will also be used as active circuit elements. Among nanowires and nanotubes of various materials, polymer nanowires and nanotubes will have advantage in several nanotechnology applications: as polymers, can be used in printable and wearable electronic devices. Sensors for chemical and biological applications can be made from polymers by chemical attaching of different functional groups. Metal decorated conducting polymers can act as hydrogen storage materials and they find important application in fuel cell technology. Due to such versatility, easy processing and low cost made, this class of system very interesting to material physic. Apart from various other applications, conducting polymer has shown its potential for organic electronic memory device. Conventional conducting polymers are already being used and/or examined for many applications including in batteries, actuators, catalysts, electromagnetic shielding, antistatic coatings, corrosion protection, separation membranes, electro-optic and electrochromic devices.\(^90,91\)

Conducting polymer nanofibers present a “soft”, organic model for studying one-dimensional systems at the nanometer scale, and hold great promise as active components for nanoscale molecular electronic devices. It is therefore of great technological and scientific interest to investigate whether nanostructures of conducting polymers can lead to better performance in these already established areas, and if they can cause new opportunities. Therefore, reliable and scalable synthetic methods for conducting polymer nanostructures must be developed in order to provide the necessary materials base for research and applications.

In general, 1D nanostructures can be synthesized: 1) by anisotropic crystal growing; 2) by utilization of supersaturation control to modify the growth of seed; 3) using of appropriate capping reagents to kinetically control the growth rates of various facers of a seed; 4) via self–assembly of 0D nanostructures; 5) size reduction of the microstructures; 6) template-directed synthesis. The later approach can be subdivided onto negative and positive templating that are growth of the desired material that will constitute 1D nanoobjects inside the porous 1D template or outside the 1D template, respectively. Schematically these methods are illustrated on Figure 4.1\(^92\)

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Below I will briefly consider only those methods to 1D nanostructures that relevant to conductive polymers.

**“Template-less” approaches.** Several “template-less” approaches to 1D superstructures of CPs\(^{93}\) based on self-assembly of conjugated polymers, oligomers or monomers\(^ {94}\) were recently reported. It has been known from the early years of conducting polymer research that polyaniline fibrils of \(\sim 100\text{nm}\) in diameter can form “naturally” during electrochemical polymerization on the electrodes surface.\(^ {95}\) Some recent work indicates that uniform polyaniline nanofibers can be obtained without needs for any template, simply by controlling

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Chapter 4 Polypyrrole nanowires grown from single polyelectrolyte molecules

kinetics of the electrochemical polymerization.\textsuperscript{96} It was found that the basic morphological unit for chemically synthesized polyaniline also appears to be nanofibers with diameters of tens of nanometers,\textsuperscript{97} similar to those observed in polyacetylene.\textsuperscript{98}

Two basic approaches to separate nanofiber formation from overgrowth in conventional aniline polymerization reactions have been discovered. In the first approach, the reaction is placed in a heterogeneous biphasic system, where the polymerization occurs primarily at the water/organic solvent interface.\textsuperscript{99} Since the as-made polyaniline product is synthesized in its hydrophilic emeraldine salt form, it diffuses away from the reactive interface into the water layer. This makes more reaction sites available at the interface and avoids further overgrowth. In this way, the nanofibers formed at the interface are collected in the water layer without severe secondary overgrowth.

Another method to prevent overgrowth is to stop the polymerization as soon as the nanofibers form. This has now been achieved by rapidly mixing the monomer and initiator solutions.\textsuperscript{99} When the reaction starts, the initiator molecules are consumed rapidly during polymerization and depleted after nanofiber formation. Therefore, the overgrowth of polyaniline is suppressed due to lack of initiator molecules. The same synthetic approach has been successfully applied to polyaniline derivatives.

\textbf{Electrochemical polymerization} is another powerful way to CP nanowires. Ramanathan et al\textsuperscript{100} applied this method for the preparation of pyrrole and aniline nonofibers. The deposition and growth of the nanowire chains are based on well-known electrochemical oxidative polymerization, starting with monomers and dopants. Multiple channels were etched between gold electrode pairs in the form of arrays to provide formation of any number of individual nanowires. The procedure is a single-step deposition process for each nanowire, and multiple-nanowire arrays of different materials can be deposited on the same wafer sequentially. Polypyrrole (PPy) and polyaniline (PANI) are used as models for demonstration of the method.

\textsuperscript{99} Huang, J. X.; Kaner, R. B. \textit{Angew. Chem., Int. Ed.} \textbf{2004}, 43, 5817
Recently fibers of PANi–CSA (camphor sulfonic acid) blended with poly(ethylene oxide) (PANI–CSA/PEO) were fabricated by an electrostatic spinning technique.\textsuperscript{101} It was shown that fiber diameters below 30nm (near 5nm) could be obtained with optimized electrospinning process parameters.\textsuperscript{102}

CP nanowires can be also obtained using self-assembly methods. In that case the organization is usually driven by a combination of solvophobic, van der-Waals, $\pi$-stacking interactions and hydrogen bonding.\textsuperscript{103}

**Template-directed synthesis.** Template-directed synthesis represents a straightforward route to 1D nanostructures. In this approach, the template simply serves as a scaffold within (or around) which a different material is generated in situ and shaped into a nanostructure with its morphology complementary to that of the template. A wealth of templates have been successfully demonstrated by various research groups, with notable examples including step edges present on the surfaces of a solid substrate; channels within a porous material; mesoscale structures self-assembled from organic surfactants or block copolymers; biological macromolecules such as proteins\textsuperscript{104} and DNA strains or rod-shaped viruses; and existing nanostructures synthesized using other approaches. When the template is only involved physically, it is often necessary to selectively remove template using post-synthesis treatment (such as chemical etching and calcination) in order to harvest the resultant nanostructures. In a chemical process, the template is usually consumed as the reaction proceeds and it is possible to directly obtain the nanostructures as a pure product. It is generally accepted that template-directed synthesis provides a simple, high-through-put, and cost-effective procedure that also allows the complex topology present on the surface of a template to be duplicated in a single step. As a major drawback, nanostructures synthesized using template-directed methods are often polycrystalline, and the quantity of structures that can be produced in each run of synthesis is relatively limited. Here, I only briefly discuss four templating methods, with a focus on their capability, feasibility, and potential extension.


Inside porous materials. The method of electrochemical oxidative polycondensation in “hard templates”\textsuperscript{105} (such as zeolites, track-etched polymeric membranes, and porous alumina) leading to CP nanowires was introduced by Martin.\textsuperscript{106} Afterwards, variety of templates were utilized. Among them templates manganese oxide nanowires\textsuperscript{107} were used for fabrication of CP 1D nanostructures.

The advantage of the template-synthesis method is that the length and diameter of the polymer fibers and tubes can be controlled by the selected porous membrane, which results in more regular nanostructures. The template method has been used to synthesize nanofibers and tubes of PPy, poly(3,4-ethylenedioxythiophene) (PEDOT), PANi, and some other polymers. For example, PPy nanotubes have been synthesized using the pores of track-etched polycarbonate membranes as a template; the pore diameter of the template ranged from 50 to 200 nm.\textsuperscript{108} PANI and PEDOT nanofibers with diameters of 75–150 nm were synthesized electrochemically by the same method.\textsuperscript{109} A general feature of the conventional template method is that the membrane should be soluble so that it can be removed after synthesis in order to obtain single fibers or tubes. This restricts practical applications of this method and gives rise to a need for other techniques.

“Soft templates” (surfactant micelles, or liquid crystalline phases)\textsuperscript{110} were shown to be also useful 1D structure to direct growth of CPs. Hexadecyltrimethylammonium bromide and oxalic acid,\textsuperscript{111} heparin\textsuperscript{112} and other surfactants were utilized.

Templating by single molecules of polyelectrolyte. Single molecules of polyelectrolytes is another kind of useful soft templates applicable for fabrication of nanoscale wires. In contrast to above-described approaches, assumed the deposition of desired materials inside pores, in the method utilizing PE molecules the deposition is going on around the molecules and thus, the approach is, in fact, a “positive templating”. Historically, DNA was the first PE used as a

template for fabrication of metallic, semiconducting and conducting polymer nanowires.

113,114, 115, 116, 117

Coffer and co-workers were the first to utilize DNA as a stabilizer/template to form both CdS nanoparticles and mesoscopic aggregates from them. Their original efforts were based on the use of linear duplexes of DNA in solution as a stabilizer for forming CdS nanoparticles. The nanoparticles in their first study were formed by first mixing an aqueous solution of calf thymus DNA with Cd\(^{2+}\) ions in a sub-stoichiometric quantity.\(^ {118}\) Then, Na\(_2\)S was added, resulting in the formation of CdS. High-resolution transmission electron microscopy (HRTEM) confirmed the formation of polydisperse CdS nanoparticles with an average particle size of 5.6nm. The particles exhibited optical properties characteristic of the formation of quantum-confined particles with an absorption edge of 480 nm, which is blue-shifted from bulk CdS (510nm).

Scheme 4.1 DNA used as a template for binding and organization of fullerene C\(_{60}\) (Ref 120)

These results were suggestive of a DNA templating effect during the formation of the nanoparticles, although no direct evidence was obtained. To overcome the problems of forming well-defined mesoscale structures in solution, Coffer and coworkers developed a new strategy for binding a template DNA strand to a solid substrate.\(^ {119}\) Tour and co-workers recently have taken an approach similar to that of Coffer in using DNA to assemble DNA/fullerene hybrid organic materials.\(^ {120}\) In their strategy, the negative phosphate backbone

of DNA was used as a template to bind and organize $C_{60}$ fullerene molecules modified with a N,N-dimethylpyrroolidinium iodide moiety into defined mesoscopic architectures, Scheme 4.1.

Fullerenes were chosen as a complexing molecule since previous studies have demonstrated that carbon nanotubes can easily be imaged by TEM,$^{121}$ eliminating the need for other contrasting agents and stains. As depicted in Scheme 4.1, The modified fullerene is electrostatically complexed to the DNA backbone through cation exchange with sodium in DMSO. These experiments carried out using a circular plasmid DNA molecule ($\phi$X74 RFII, 5386 bp) have demonstrated that fullerenes could be organized into mesoscopic structures via templating and the structures could be imaged by TEM. They have also suggested that the electrostatic binders significantly influenced the structure of the plasmid templated. This work addresses some very important fundamental issues and limitations pertaining to the use of DNA as a scaffolding material.

**Schema 4.2** Preparation of nanometer-scale conductive silver wires, using DNA as a template (Ref 122)

Braun et al. have utilized DNA as a template to grow nanometer-scale conducting silver wires.$^{122}$ The basic assembly scheme for constructing of Ag nanowire attached to two gold electrodes is outlined in Scheme 4.2. Two gold electrodes separated by a defined distance (12-16 $\mu$m) were deposited onto a glass slide using photolithography. The gold electrodes

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subsequently were modified with noncomplementary hexane disulfide modified oligonucleotides through well-established thiol adsorption chemistry on Au.123 Subsequently, a fluorescently labeled strand of λ DNA (16 µm in length) containing “sticky ends” that are complementary to the oligonucleotides, attached to the electrodes, is introduced. Hybridization of the fluorescently tagged λ DNA molecule to the surface-confined alkylthiololigonucleotides was confirmed by fluorescence microscopy, which showed a fluorescent bridge connecting the two electrodes. After a single DNA bridge was observed, the excess hybridization reagents were removed. Silver ions then were deposited onto the DNA through cation exchange with sodium and complexation with the DNA bases. This process can be followed by monitoring the quenching of the fluorescent tag on the DNA by Ag ions. After almost complete quenching of the fluorescence, the silver ion bound to the template DNA is reduced, using standard hydroquinone reduction procedures,124 until formation of the small silver aggregates along the backbone of the DNA occurred. A contiguous silver wire is then formed by further Ag ion deposition onto the previously constructed silver aggregates followed by reduction. The characteristic size for silver wires formed by this process was found of 100 nm diameter, 12 µm long. The wires are comprised of 30-50 nm Ag grains that are contiguous along the DNA backbone. The fabrication of narrower Ag wires (less than 25 nm) resulted in discontinuous Ag structures.

Two terminal electrical measurements subsequently were performed on the Ag wire. When the current-voltage characteristics of the Ag wire were monitored, no current was observed at near zero bias (10V in either scan direction), indicating an extremely high resistance 10^{13} Ohms, the internal resistance of the instrument). At a higher bias, the wire becomes conductive. Surprisingly, the current-voltage characteristics were dependent on the direction of the scan rate, yielding different I-V curves. To explain such behaviors, it was suggested that the individual Ag grains that comprise the Ag nanowires may require simultaneous charging, or Ag corrosion may have occurred, resulting in the high resistance observed at low bias. By depositing more silver and thereby growing a thicker Ag nanowire, the no-current region was reduced from 10V to 0.5V, demonstrating crude control over the electrical properties of these systems. In addition, control experiments, where one of the components (DNA or Ag) was removed from the assembly, produced no current, establishing that all of the components are necessary to form the conducting Ag nanowires. This work is pioneer in row of attempts for creation conductive nanowires using PE as a template.

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Further, the deposition of gold, platinum, copper and palladium metal on DNA have been investigated as a potential approach for creating conductive nanowires. Besides DNA, other biological polyelectrolytes–polypeptides, polysugars and viruses–were used for fabrication of various nanowires.

Single DNA molecules were recently used for fabrication of conductive polyaniline nanowires. DNA molecules were covalently attached to a Si surface and activated with aniline, which was then polymerized enzymatically by adding peroxidase and H\textsubscript{2}O\textsubscript{2}. However, PANI nanowire networks produced in this way display have shown rather low conductivity even in doped states. The observed low conductivity is caused by the fact that a very limited amount of conductive material (PANI) is formed along the template. This amount is restricted by the quantity of aniline that can be attracted by the DNA, during the activation step due to electrostatic and hydrophobic interactions. In contrast to above-described approach, when conductive polymer was in-situ grown on the DNA template, Inganas et al. used positively charged conjugated polythiophene polyelectrolyte and complexed it with oppositely charged DNA.

Single-molecule studies of synthetic polymers are a still significantly less explored area of research. To some extend, this originates from technical difficulties, which one faces during investigations, since synthetic polymers usually are less defined and significantly less in size than DNA, proteins or viruses. That is why examples of utilization of synthetic polyelectrolytes as templates are rather limited. Studies of single molecules of synthetic polymers historically have started from investigations of “exotic” 3-dimensional structures like dendrimers, dendronized polymers and molecular brushes (graft copolymers). Investigations of such objects were essentially facilitated because of their large molecular thickness and shape-persistence.

Investigations of individual “normal-sized” macromolecules (with the molecular thickness from just a few angstroms) were started in 2002, when it was found out that even usual synthetic polymers, like protonated poly-2-vinylpyridine (P2VP), can be imaged with

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molecular resolution, if they adsorbed onto atomically flat mica surface.\textsuperscript{133} It was shown that P2VP molecules adsorbed onto atomically flat mica appear on SPM images as worm-like structures just few nanometer in the height. Furthermore, it was possible to manipulate their molecular conformations in a large diapason by simply varying pH, ionic strength of the solution.\textsuperscript{134}

Recently \textit{synthetic polyelectrolytes} of various architecture have been used for fabrication of nanoparticles. Particularly, an approach to produce wire-shaped Pd nanoparticles via metalization of flexible synthetic PE of linear architecture deposited onto the Si-wafer have been described.\textsuperscript{135} Metalization is based on ion exchange reaction between positively charged polymers and bivalent PdCl\textsubscript{4}\textsuperscript{2-} anions.

In another example, semiconducting negatively charged Prussian Blue NPs were selectively arranged along single polycation molecules.\textsuperscript{136} In another example, single molecules of amphiphilic brushes containing carboxylate groups were used by Müller et al. as templates for fabrication of elongated magnetic nanoparticles. It was confirmed by Mössbauer spectroscopy and magnetization measurements that these structures display superparamagnetic behavior.\textsuperscript{137}

In conclusion, single molecules of synthetic polyelectrolytes are very useful and versatile templates for fabrication of various nanowires, however, preparation of conductive polymer wires is still a challenge. In this chapter I represent results, concerning a full circle of nanodevice fabrication utilizing polyelectrolyte molecules, starting from alignment of single molecules of PSA, fixation of them between electrodes followed by growing of conductive polymer polypyrrole selectively from them.

\section*{4.2 Own results}

\subsection*{4.2.1. Alignment of polyelectrolyte molecules}

\textbf{Introduction.} PE macromolecules are potentially important and versatile building blocks for future molecular electronics. However, they are not shape-persistent and even in water solutions in salt-free conditions, where the molecules are highly charged and therefore locally


stretched, they adopt quite coiled conformation on a microscopic scale. At the same time, it is essential to have them deposited in a (fully) stretched conformation, in order to bridge microelectrodes and construct nanodevices on their basis. The second motivation for development of methods to stretch PE molecules comes from analytic needs. It is well-known that determination of molecular weight for charged macromolecules is a great challenge; on the other hand, the contour length and, the molecular weight distribution, can be directly determined by AFM if the molecules are adsorbed in ultimately stretched conformation.

Tapping mode (TM) AFM has recently been used to investigate single synthetic macromolecules, basically thick and stiff molecular brushes, dendronized and peptized polymers. The large thickness and high stiffness of these macromolecules made them well-suited to TM-AFM observation. It is, however, highly desirable to perform single molecule experiments with the very large range of non-exotic “thin” polymers. Recently, several “thin” PEs adsorbed onto atomically flat mica have been studied by us and others. In contrast to dendronized polymers and molecular brushes, whose the molecular height measured by AFM usually exceeds one nanometer, individual poly(2-vinylpyridine) (P2VP) chains adsorbed on mica show 0.2±0.1 nm thick AFM images. The thinner polymers, including industrially important ones, cannot be detected in their extended conformation at all. With the purpose of increasing the thickness of ultra-thin molecules, we have reported recently on the selective deposition of negatively charged bulky ions or clusters on single positively charged polymer chains. The alteration of the physico-chemical properties of these macromolecules is however a problem. There is thus a need for a general strategy of enhancing the AFM-contrast of single macromolecules while preserving their intrinsic properties (except for changing their conformation).

The substrate used for the immobilization and imaging of single molecules plays a pivotal role in single-molecule experiments. For individual molecules to be resolved, the substrate must be atomically flat and manifest optimal interactions with them. Most of the

145 In some cases single polymer molecules can be detected as bumps in collapsed form due to sufficiently large thickness of the molecular globules: Gallyamov, M.; Khokhlov, A. R.; Möller, M. Macromol. Rapid Commun. 2005, 26, 456.
experiments with single macromolecules have been carried out with either negatively charged, hydrophilic and high-surface energy mica, or hydrophobic, highly oriented graphite (HOPG) of low-surface energy. Linear macromolecules have been stretched and aligned with the assistance of a hydrodynamic flow, just like conventional ropes, which requires that the macromolecule/substrate interactions are accurately balanced. If they are too strong, and molecules are trapped in their solution conformations. In the reverse case, the adsorption is not feasible. In the ideal situation, the molecules are adsorbed onto the substrate enough for sliding along the flowing direction. Intrinsically stiff negatively charged ds-DNA molecules have been stretched and aligned on amino-functionalized mica and on substrates coated by hydrophobic polymers. Rabe et al. have reported on the stretching of moderately hydrophilic uncharged polyisocyanate on HOPG surface. PSA and some other polyanions (PAs) have been immobilized onto HOPG in stretched conformations by co-deposition with long-chain aliphatic amines (AAs). There is then complexation of the negatively charged PAs with the oppositely charged (in water) AAs with formation of relatively thick hydrophobic fibrillar structures. The PAs chains align themselves along the AAs lamellaes adsorbed on the basal plane of the crystalline graphite. Similarly, complexes of PSA and AAs can be fixed in a stretched conformation at the surface of mica, although neat PSA cannot be immobilized, because of their negative charge (as same as mica) in water. In contrast to PAs, polycations (PC) strongly adhere to oppositely charged mica, which results in the projection (trapping) of their in-solution (coiled) conformation, even though they are deposited with a spin-coater at very high rotation speed.

In the next paragraph I will report on simple method to control the conformation and orientation of single mica-adsorbed positively charged macromolecules by co-deposition with octylamine (OA).

Experimental Section. High molecular weight P2VP (Mn=385000g/mol; Mw/Mn=1.08) and poly(2-(dimethylamino)ethyl-methacrylate) (PMADAME) (Mn=328000g/mol; Mw/Mn=1.27) quaternized by N-(3-bromopropyl)pyrrole (PMADAME-Py) were used as

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153 Molecular weight of the samples was determined by SEC of the corresponding parent uncharged precursors in THF for P2VP and in THF/triethylamine (95/5) for PMADAME, using polystyrene standards
154 Detailed synthesis and characterization of the PMADAME-Py will be published elsewhere.
model polycations in this study. P2VP is water-soluble only at low pH as result of the protonation of the nitrogen atoms, whereas PMADAME-Py is positively charged in water at any pH. I found that the solution co-deposition of PCs and OA has a very beneficial effect on the resolution of single macromolecules. P2VP and PMADAME-Py immobilized onto mica by spin coating at 2000 rpm and 10000 rpm from the acidified aqueous (pH 2, HCl) with addition of 0.1 % of OA in THF in 1:1 per volume ratio.

**AFM measurements.** Multimode AFM instrument or NanoScope IV-D3100 (Digital Instruments, Santa Barbara) was operating in the tapping mode. Silicon tips with radius of 10-20nm, spring constant of 30N/m and resonance frequency of 250-300KHz were used. Although most of the measurements were performed at a relative humidity of about 40%, virtually the same results were obtained when the measurements were repeated in a dry nitrogen atmosphere. The highest possible value of amplitude setpoint was used in the all experiments. Special experiments demonstrated that decrease of the amplitude setpoint by 15% leads to a decrease of the molecular height by about 15-20% (i.e., from 1.0 to 0.9-0.8nm). The observed variations in molecular heights, induced by altering of the operation conditions, are negligible compared to the variations in the molecular heights caused by differences of the deposition conditions (e.g., 1.0±0.2nm vs 2.3±0.5nm for PMADAME-Py deposited without and with OA, respectively). Although the measured values of the molecular thickness might be not absolute, the errors in measurements are both systematic and reproducible and therefore, the operation conditions do not affect the conclusions made here.155

**Results and discussions.** Figure 4.2 shows representative TM-AFM images PCs macromolecules deposited by spin coating of low pH aqueous solutions (pH2, HCl) onto freshly cleaved mica at 10000r/min. TM-AFM images show random-coiled conformation, which prevents the molecular contour length from being determined.

In contrast, PCs molecules deposited with OA appear in considerable extended conformation. (Figure 4.3) They are also may have ultimately stretched conformations whenever the OA containing solution is spin-coated onto mica at a high rotation speed (10000rpm) (Figure 4.4).

155 Recently Kasumov et al. demonstrated that the observed variations of the molecular thickness of ds-DNA determined by TM-AFM are due to differences in the “molecule-substrate” interactions resulting in different compressing deformations of the molecule rather than because of the tip-induced deformations. Thus, TM-AFM reflects “real” conformations of the ds-DNA if the highest possible value of the amplitude setpoint is applied: A. Yu. Kasumov, D. V. Klinov, P.-E. Roche, S. Gueron, H. Bouchiat. *Appl. Phys. Lett.* 2004, 84, 1007.
It was found that the thickness of PE molecules, adsorbed on mica with OA, bigger than that, adsorbed without OA. Similar trends (significant distortion of an ideal spherical geometry) were previously reported for dendrimers,\textsuperscript{156} proteins, polystyrene nanoparticles\textsuperscript{157} and ds-DNA (ds mean double-stranded)\textsuperscript{158} adsorbed onto polar surfaces. Deformations are substantially lower in case of adsorption onto nonpolar surfaces. Several standard methods of hydrophobization of mica have been explored in this work with the purpose of stretching PCs and making them detectable on surfaces, however without success. For instance, silanization of mica (using alkoxi- and chloro-alkylsilanes)\textsuperscript{159} has resulted in the undesired contamination of the surface by large particles of polymerized silanes. Self-assembled monolayers of AAs (e.g., hexadecyl amine, HDA) on HOPG were previously reported for imaging single macromolecules.\textsuperscript{160} However, small islands of HDA are formed on mica rather than at

homogeneous monolayer,\textsuperscript{161} which is inappropriate to the detection relatively long macromolecules.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.3.png}
\caption{TM-AFM topography and phase images of P2VP (a) and PMADAME-Py (b-i) molecules co-deposited with OA by spin coating (2000 r/min). The samples corresponding to images (a-e) were investigated after equilibration at ambient conditions during 48 hours, whereas images (f-i) correspond to the sample investigated one hour later the preparation; (d,e) are cross-sections taken along the upper (d) and bottom (e) molecules shown in (c); (i) cross-section is taken along the chain in (g).}
\end{figure}

\textsuperscript{161} Benitez, J. J.; Ogletree, D. F.; Salmeron, M. \textit{Langmuir} 2003, \textbf{19}, 3276
The molecular thicknesses were measured by cross-section analysis of the *individual chains* in Figures 4.2, are 0.2±0.1nm and 0.6±0.2nm for P2VP and PMADAME-Py, respectively. These values are substantially smaller than the diameters calculated for chains in which the side-groups protrude symmetrically (Figure 4.5a,b,e).

Nevertheless, according to semi-empirical calculations for tetramers of P2VP and PMADAME-Py, there are other energetically near-equivalent conformations. It must be noted that conformations with flattened side-groups (Figures 4.5c,d,f) have a molecular thickness of about 0.4nm and 0.6nm for P2VP and PMADAME-Py, respectively, i.e., close to the experimentally observed values. Flattened conformations with charged and polar atoms oriented toward the polar surface of mica are favorable to the adsorption of PCs and decrease of the surface energy.

In comparison, the molecular thicknesses of PCs co-deposited with OA are reproducibly increased up to 0.6±0.2nm for P2VP and 2.3±0.5nm for PMADAME-Py (Figure 4.3a-e). Significant increase of the molecular thicknesses, however, was only observed when PCs were equilibrated at ambient conditions (at 23°C and relative humidity of about 40%) for

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The Austin Model (AM1) is implemented in the HYPRCHEM package (Vs. 6.03)
more than 10 hours before the AFM-measurement (Figure 4.3 a-e). In contrast to the height of the *equilibrated* structures, the height of the PMADAME-Py molecules imaged immediately after the co-deposition with OA is only 1.0±0.3 nm, whereas the width is significantly larger compared to the *equilibrated* structures (Figures 4.3 f-i).

Remarkably enough, a kind of a "shell", 0.3 nm-thick and approximately 10nm-wide (marked by arrows in Figures 4.3 g,h) is observed along the chain contours (for a possible explanation of these structures see below). As a consequence, the chains are clearly visible on topography and phase images.

**Figure 4.5** Cross-sections (a,c,e,f) and top-views (b,d) of the 2VP (a-d) and MADAME-Py (e,f) tetramer molecules in two conformations derived by semi-empirical calculations (AM1-level, HyperChem Pro 6): (a,b,e) - *helical* conformations in which side groups emanate symmetrically from the backbones (a torsion angle between two adjacent groups is about 90°); (c,d,f) - flattened (*all-trans*) conformations (the torsion angle between two adjacent groups is about 180°).

The stretching of P2VP and PMADAME-Py co-deposited with OA onto mica is reminiscent of the behavior of PAs-amphiphile complexes (PACs) formed upon aggregation of negatively charged macromolecules and positively charged AAs.\(^{163}\)\(^\text{,}^{164}\) Despite of these visual similarities, the fundamentals of the observed phenomena are obviously different, since PCs and OA are charged in acidic water. At first glance, the thickening of the PCs molecules


on the surface might be due to adsorption of OA along the chains by hydrophobic interactions. This hypothesis must however be disregarded, because when a 10 nm-thin PMADAME-Py is prepared by spin coating of the acidic solution of PMADAME-Py and OA, the OA is essentially eliminated during the process. Moreover, although dry PMADAME-Py films are swollen by OA vapors by a factor of ~3, OA is released from the films at room temperature within 10 minutes. Therefore, the thickening of the PCs molecules (Figure 4.2 vs Figure 4.3) has nothing to do with OA uptake.

![Semi-stretched and Stretched PMADAME-Py molecules](image)

**Figure 4.6** Histograms of the contour length distributions for the PMADAME-Py molecules co-deposited with OA by spin coating at 2000 r/min (a) and 10000 r/min (b). The histograms summarize data for more than 100 molecules from 18 images

It is known that films of AAs strongly adhere to mica with the AAs molecules, oriented with the polar amino groups, facing the surface and the alkyl chains pointing towards air. This self-assembly of AAs might occur upon the co-deposition of PCs and OA, such that the adsorbed OA molecules would form a *liquid-like* monolayer on mica, making this surface more hydrophobic. In this respect, the contact angle of water is increased from 0-30 to ~80° when mica is pretreated with OA. This higher hydrophobicity reduces strongly the attractive forces between PCs and mica. PCs are then immobilized onto modified mica through weak hydrophobic interactions, which has several consequences. Indeed, the weekly-attached macromolecules can be stretched and aligned within a hydrodynamic flow. Moreover, the

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166 Here “local” conformations are conformations of macromolecular repeat units in usual for organic chemistry meaning...
“surface-molecule” interactions\textsuperscript{167} must also influence the local conformation of the macromolecules and orientation of the side-chains. Although PCs molecules are flattened by adsorption upon oppositely charged untreated mica (Figure 4.5c,d,f)\textsuperscript{168,169,170} these PCs molecules tend to minimize the contact area with the OA-modified surface, which is favorable to an helical\textsuperscript{171} conformation with the side-chains oriented upright to the surface (Figure 4.5a,b,e). It must be noted that the calculated molecular thickness for the 2-vinylpyridine (2VP) tetramer is \( \sim 0.4\text{nm} \) for the flattened all-trans conformation (Figure 4.5c) and \( \sim 0.88\text{nm} \) for the helical conformation (Figure 4.5a). These calculated values qualitatively agree with the trend observed by AFM for PCs adsorbed on hydrophilic and hydrophobic surfaces, respectively. Furthermore, the increased molecular thicknesses of PCs co-deposited with OA may not be explained by the collapse of the chains because their contour length evaluated from the AFM images is close to the value calculated for extended chains (Figure 4.6).

As a rule, the thicknesses of the PC molecules co-deposited with OA decreases upon increasing stretching, i.e., \( 0.6\pm0.2\text{ nm} \) for moderately stretched P2VP molecules (Figure 4.3a) and \( \sim 0.3\text{ nm} \) for the ultimately stretched chains (Figure 4.4a,b). Although the stretching of out-of-plane molecular loops is also a possible explanation, "local" reorganization from helical conformation to a more stretched and thus more flat all-trans conformation is thought to be more probable explanation here. This assumption is supported by semi-empirical calculations for the 2VP-tetramer. Indeed, compared to the all-trans conformation, for the helical conformation, the molecular thickness is higher (\( 0.88\text{nm} \) vs \( 0.4\text{nm} \), Figure 4.5a vs 4.5c) and the length of the monomer unit is smaller (\( \sim 0.20\text{ vs} \sim 0.25\text{nm} \), Figure 4.5b vs 4.5d).

As aforementioned, the images of the freshly prepared samples of PMADAME-Py co-deposited with OA are changing with time from thinner structures having “shell” (Figure 4.3f-i) to thicker “shell-free” one (Figure 4.3b-d). A possible explanation of the “shell” marked by arrows in the Figure 4.3 might be found in the mutual repulsion of the positively charged protonated OA molecules and the polyelectrolyte chains of the same charge during the deposition process. Then, the PCs molecules would lie on the surface of mica and would display a molecular thickness consistent with the flattened conformation (Figure 4.5f). The “shell” observed at this stage all along the chains contour (arrows in Figures 4.3g,h) might

\textsuperscript{167} In some cases single polymer molecules can be detected as bumps in collapsed form due to sufficiently large thickness of the molecular globules: Gallyamov, M.; Khokhlov, A. R.; Möller, M. Macromol. Rapid Commun. 2005, 26, 456.


\textsuperscript{171} The term "helical" conformation does not reflect a perfect helical order, like in peptides or in ds-DNA, but only emphasizes that a considerable fraction of the macromolecules repeat units are organized in such a way that emanating adjacent side-groups form a dihedral angle of about 90°.
however be an artifact of more attractive interactions of the tip with the surface where OA is not located (along the molecular contour) compared to the background hydrophobized with OA.\textsuperscript{172} Upon drying of the samples, the ionization of both the amine and the chains decreases and their mutual repulsion, as well. The OA then diffuses towards the originally unoccupied area that makes the surface beneath the PMADAME-Py chains more hydrophobic, results in a chain conformation with the side groups oriented upright to the surface with increased molecular thickness (Figure 4.5e) as well as in disappearance of the “shell” along the chains.

Our method can be directly apply for the calculation of contour length and, ultimately, the molecular weight distribution.

Figure 4.4 shows representative images of P2VP and PMADAME-Py with overstretched conformations, which allow the contour length to be determined easily. Figure 4.6 compares histograms for the contour length of PMADAME-Py molecules deposited in semi-stretched (Figure 4.3b) and extensively stretched (Figure 4.4c) conformations, respectively.

In general, the degree of polymerization, DP, can be determined by dividing the contour length, $L_N$, onto a length of a monomer unit for certain local conformation, $l_{mon}$ (for vinyl polymers $l_{mon}$ can vary from about 0.15 to 0.25nm, depending on the conformation). It is clear, that for semi-stretched chains a proper resolution of the molecular details is not guarantied (some of molecular fragments can be hidden in unresolved loops) and a complete uniformity of the local conformations for all repeat units can not be achieved. In contrast, in the case of the ultimately stretched chain the molecular contour can be easily resolved and the maximal possible value of the $l_{mon}$ equal to 0.25nm for “the longest” all-trans local conformation can be applied for DP determination. That is why the average contour length ($L_N$) extracted from Figure 4.6b for stretched PMADAME-Py deserves a special attention, because it gives access to the actual degree of polymerization and molecular weight. Indeed, DP of PMADAME-Py corresponds to the $L_N/l_{mon}$ ratio, where $l_{mon}$ is the length of a monomer unit for the all-trans fully stretched conformation (0.25nm, Figure 4.5d). DP of PMADAME is accordingly 2004, and the real molecular weight before and after quaternization with N-(3-bromopropyl)pyrrole is 315000 and 683400 g/mol, respectively. The molecular weight before quaternization fits very well the value determined by SEC in triethylamine containing THF ($M_{N,SEC} = 328000$ g/mol)\textsuperscript{173}, which indicates that the molecular weight determined by SEC in this solvent is the actual molecular weight of PMADAME. On the other hand, for the semi-

\textsuperscript{172} It was demonstrated that a hydrophilic tip is attracted to hydrophilic surfaces more strongly than to hydrophobic ones: S. J. T. Van Noort, K. O. Van der Werf, B. G. De Grooth, N. F. Van Hulst, J. Greve, Ultramicroscopy 1997, 69, 117.

\textsuperscript{173} Molecular weight of the samples was determined by SEC of the corresponding parent uncharged precursors in THF for P2VP and in THF/triethylamine (95/5) for PMADAME, using polystyrene standards.
stretched chains (Figure 4.6a) the $l_{mon}$ equal to 0.188nm was derived from the AFM data (assuming the same DP=2004), that is close to the theoretical $l_{mon}= 0.20$nm for the helical conformation found by the semi-empirical calculations (Figure 4.5b).

**In conclusion,** positively charged macromolecules co-deposited with octylamine onto mica appear in a considerably more stretched conformation compared to adsorption onto untreated mica. Furthermore, the molecular thickness is considerably larger whenever the macromolecules are co-deposited with OA, which indicates a change in the local conformations of the chains and the orientation of their side-groups with respect to the substrate. These observations have been explained by the formation of the ultra-thin liquid-like film of octylamine onto mica that decreases the surface energy, weakens the interactions of the individual macromolecules with the surface and allows them to be stretched. This finding is especially important for the conductive polymer precursor PMADAME-Py and similar compounds, whose individual molecules being stretched between microelectrodes and converted into a conductive state,$^{174}$ can serve as ultimately thin nanowires and exploited in fabrication of ultra-small devices. Since the contour length and molar mass for the stretched macromolecules can be directly measured, the herein reported method is also a very useful analytical tool. The increase in the molecular height in case of co-deposition with OA drastically improves the molecular resolution, makes even ultra-thin polycations detectable and thus extends significantly the range of objects, which can be involved in single-molecule experiments.

### 4.2.2. Synthesis of polypyrrole nanowires using polyelectrolyte molecules

In the present work I utilize single molecules of negatively charged synthetic polyelectrolyte (polystyrene sulfonic acid, PSA) to grow continuous and conductive polypyrrole (PPy) nanowires via “electroless” selectively deposition of PPy along PSA molecules.

Spin-coating of the PSA solution onto mica or thermally oxidized Si wafer at high rotation speed results in stretching and alignment of PSA chains (Figure 4.7a and 4.8). In first experiments mica-deposited PSA templates were incubated in pyrrole (Py) monomer solution, rinsed with deionized water to remove unattached Py, and placed in solution of ammonium persulfate (APS) to polymerize the Py attached to the templates. The resulting product appears on AFM images as a 1D sequence of apparently separated clusters of 2-4nm in height.

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Polypyrrole nanowires grown from single polyelectrolyte molecules

(Figure 4.7b). These structures are considerably higher than bare PSA molecules (~0.5nm)\(^{175}\) that, obviously, reflect the formation of PPy clusters.

![Figure 4.7](image)

**Figure 4.7** Topography AFM image of short (\(M_w=403\)kg/mol) PSA molecules (a). Representative AFM image Ppy nanoparticles formed when: mica-immobilized long (\(M_w=6940\) kg/mol) PSA molecules were incubated in the Py monomer solution, rinsed with water and oxidized with ammonium persulfate (b); Py and APS water solutions were placed onto mica-immobilized PSA templates for 20 seconds (nanoparticles in the images (c) and (d) were produced using PSA of \(M_w=403\) and 6940 kg/mol, respectively); (g) the same procedure as in (d), but a lack of ammonium persulfate was used; (e) and (f) cross-sections along the lines in (b) and (d), respectively.

To produce more continuous and thick PPy nanowires, I performed electroless deposition of PPy.\(^{176}\) PSA chains were deposited onto substrates in the stretched conformation and afterwards Py and APS water solutions were employed for up to 60 seconds (for details see Experimental Section). AFM and SEM investigations revealed the successful formation of PSA-PPy nanowires (Figure 4.7,4.9).

Diameter varies from few nm to hundreds of nm depending on polymerization time (Figure 4.7c,d). As expected for the template method, an aspect ratio of the nanowires (equal to \(~7\) and \(100\) for the nanowires in Figures 4.7c and d, respectively) is dependent on the


contour length of the PSA molecules. The resulting nanowires, however, are somewhat shorter than corresponding templates (usually by the factor of 1.5-3, depending on the polymerization time). The observed partial shrinkage of the nanowires is due to the attractive interactions between hydrophobic segments of PPy, that can be avoided, if PSA templates are properly fixed to the substrate.

Visual inspection of the AFM images shows that thin nanowires (diameter less than 5 nm) are still sequences of isolated PPy clusters, however nanowires become (quasi)continuous (the clusters are closely packed), if their diameter exceeds 10 nm. Clusters are localized predominantly along PSA chains that indicates rather high selectivity of the deposition.

In general, growth of PPy nanowires can be realized according to two schemes: a) precipitation of hydrophobic PPy nanoparticles preformed in solution onto the hydrophobic PSA-Py complex; and b) growing of PPy from the PSA-Py complex. I performed a set of experiments in order to decide which scheme is realized in our case. For this, I prepared colloidal dispersions of PPy by mixing of Py and APS solutions followed by quenching with excess of sodium bisulfite (SBS) as a reducing agent. So prepared colloids were placed on a substrate with pre-adsorbed PSA template molecules. However, the formation of PPy nanowires was never observed in these experiments irrespective of the activation time, size and concentration of PPy colloids which has been used. Thus, the prerequisite of nanowires growth is the presence of both Py-monomer and oxidative agent in solutions. This result, obviously, excludes the “grafting-to”, and supports the “grafting-from” scheme of PPy nanowires formation.

Variation of reaction conditions influences the morphology of PPy nanowires. When the oxidant was taken in excess, formed nanowires displayed relatively smooth morphology (Figure 4.7c,d). In contrast, a lack of oxidizer leads to the formation of “hairy nanowires” that resemble “molecular brushes” (Figure 4.7g). These observations are consistent with the “grafting-from” scheme of PPy growth.

Figure 4.8 AFM topography images of the mica-deposited PSA molecules (M₆=6940 kg/mol).

4.2.3. Electron transport in polypyrrole nanowires

A detailed characterization of electrical properties and stability of PPy NWs was performed with the use of samples prepared under different experimental conditions, which are summarized in Table 4.1 and Table 4.2. For samples 14, 15, 16, 17 and 19, I varied the polymerization time at constant concentration of the pyrrole monomer. For these samples, a continuous growth in diameter of the PPy nanowires from 20 nm till 90 nm was observed upon increase of the polymerization time from 40 till 60 seconds (Figure 4.10 and Figure 4.11). Further increase of the polymerization time (i.e., 75 sec, sample 17) results in the formation of continuous films, in which individual nanowires are no more resolvable by AFM. This is because the polymerization proceeds not only from the PE templates but also takes place in the bulk solution. After a while, PPy particles formed in solution aggregates and precipitate forming granular films on the surface. This process is time-dependent and leads to non-controllable film formation.

Before the electrical measurements, the samples were inspected by AFM. Let us consider sample 15, as an example. Figure 4.11 represents consequent zooms from the large-scale AFM images.

**Figure 4.9** SEM conformation of the formation of Ppy nanowire
From AFM images, the number of nanowires between the contacts, their heights, widths and lengths were calculated (Table 4.1). In this work the NWs were characterized by “two-contact” method. Although the “four-contact” measurements allow to eliminate contribution from well-known “contact” problems originating from possible defects on the electrode-nanowire interface, in our case the “four-contact” method was impossible to implement. The reason for this is that positioning of single nanowires on four electrodes is very difficult. Generally our attempts led to devices with nanowires that were mostly too short to bridge four electrodes. “Contact problems” associated with morphological defects in contact areas and improper charge-injection between NWs and gold electrodes cannot be recognized from the “two-contact” method of the conductivity measurements but it can be indirectly proved that existence of such problems are not likely in our case.

This conclusion comes, first of all, from the AFM inspection of the electrode-NWs interface. As seen from Figure 4.12 b-e, not only the interface is looking quite smooth on topography images, but also phase images reveal no contrast between the NWs and gold electrodes-suggesting rather good mechanical contact.
Indeed, PPy appears as a number of closely packed grains both on gold electrodes and on the nanowire (Figure 4.12 e). This observation proves that the deposition of PPy occurs not only onto PSA-molecules, but also onto gold electrodes with approximately the same rate, as can be concluded from measured thicknesses of the pristine gold electrode (thickness 50nm) and its thickness after the polymerization of PPy (100nm). It is clear, that such polymerization mode would lead to rather good contacts. The second proof of the absence of the contact and charge-injection problems comes from near linear Ohmic current-voltage (IV) characteristics for all samples (Figure 4.13).

The conductivities of single NWs were estimated using the following equation:

\[ \sigma = \frac{l}{R \cdot n \cdot h \cdot d}; \]

where \( l \) is the length of the nanowire taken as the length between the contacts and having a fixed value of either 2\( \mu \)m (for samples 13, 15, 19) or 1\( \mu \)m (for samples 12, 14, 16, 17, 18), \( R \) is the measured resistance between the contacts, \( n \) is the number of the nanowires between contacts, \( h \) is their average height, \( d \) is their average width. Electrical measurements were performed at room temperature and the results of the conductivity measurements are represented in Table 4.1 and show a change of the conductivity from 0.24 for the thinnest NW to 3S/cm for the thickest one.

In spite of the fact that most of the samples have more than one NW between the gold contacts, we also succeeded to make electrical measurements of single NWs. Figure 4.12 shows 90nm thick PPy NW grown between two electrodes separated by a distance of 1 \( \mu \)m.

### Table 4.1 The size and electrical characterization of the Ppy nanowires grown in different conditions

<table>
<thead>
<tr>
<th>Number of Samples</th>
<th>Polymerization time (sec)</th>
<th>Monomer Concent. (mg/ml)</th>
<th>Height (nm)</th>
<th>Width (nm)</th>
<th>Resistance (Ohm)</th>
<th>Number of conductors, n</th>
<th>( \sigma ) (S/cm)</th>
<th>R per 1 conductor (Ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>40</td>
<td>3.5</td>
<td>16</td>
<td>150</td>
<td>9.46E6</td>
<td>4(19/18)</td>
<td>0.24</td>
<td>3.6E7</td>
</tr>
<tr>
<td>15</td>
<td>40</td>
<td>3.5</td>
<td>20</td>
<td>116</td>
<td>2.99E6</td>
<td>11(20/18)</td>
<td>0.31</td>
<td>3.3E7</td>
</tr>
<tr>
<td>15</td>
<td>40</td>
<td>3.5</td>
<td>20</td>
<td>150</td>
<td>20.73E6</td>
<td>1(20/17)</td>
<td>0.30</td>
<td>2.1E7</td>
</tr>
<tr>
<td>15(avg)</td>
<td></td>
<td></td>
<td>18</td>
<td>139</td>
<td></td>
<td></td>
<td>0.28</td>
<td>3E7</td>
</tr>
<tr>
<td>14</td>
<td>50</td>
<td>3.5</td>
<td>35</td>
<td>94</td>
<td>0.27E6</td>
<td>21(6/7)</td>
<td>0.48</td>
<td>5.7E6</td>
</tr>
<tr>
<td>19</td>
<td>60</td>
<td>3.5</td>
<td>49</td>
<td>139</td>
<td>0.22E6</td>
<td>9 (20/18)</td>
<td>0.14</td>
<td>2E6</td>
</tr>
<tr>
<td>16</td>
<td>65</td>
<td>3.5</td>
<td>90</td>
<td>168</td>
<td>4.5E5</td>
<td>25(19/18)</td>
<td>3.44</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>75</td>
<td>3.5</td>
<td>film</td>
<td></td>
<td></td>
<td></td>
<td>1.89E3</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>20</td>
<td>15</td>
<td>20</td>
<td>121</td>
<td>0.6E6</td>
<td>7 (5/8)</td>
<td>0.24</td>
<td>4.2E6</td>
</tr>
<tr>
<td>13</td>
<td>20</td>
<td>15</td>
<td>20</td>
<td>197</td>
<td>0.33E6</td>
<td>8(8/4)</td>
<td>0.21</td>
<td>2.64E6</td>
</tr>
<tr>
<td>12</td>
<td>40</td>
<td>7.5</td>
<td>62</td>
<td>157</td>
<td>0.007E6</td>
<td>21(5/7)</td>
<td>0.62</td>
<td>0.15E6</td>
</tr>
<tr>
<td>12</td>
<td>40</td>
<td>7.5</td>
<td>67</td>
<td>198</td>
<td>0.007E6</td>
<td>20(6/7)</td>
<td>0.61</td>
<td>0.14E6</td>
</tr>
</tbody>
</table>
The amount of produced PSA-PPy nanowires was adjusted in such a way that only few electrodes were bridged by PPy nanowires, while others remained disconnected. This allowed us to define the electrode pairs connected by only single NWs and perform the \textit{dc}-conductivity measurements.

\textbf{Fig 4.11} AFM pictures corresponded to the consequence characterization of contacts 19/18, 20/18 and 20/17 for sample 15
The electrical measurements revealed the resistance of single nanowires in a range of 0.6-1.5 MΩ that corresponds to their conductivity of about 1-3 S/cm. This rather high value approaches the conductivity of PPy in the bulk.\textsuperscript{180} The nanowires displayed a linear current-voltage dependence (Figure 4.12h) that reflects a good connectedness of PPy clusters along the PSA molecule.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_12.png}
\caption{AFM topography images of the representative Ppy nanowire (a); high-magnification topography (b-c) and phase (d-e) AFM images of the pristine Ppy nanowire (b, d); the same nanowire was broken applying high voltage (25 V) (c, e); cross sections (f, g) are taken along the nanowires (in the images (b) and (c), respectively). (h) Room-temperature resistivity-current characteristics: of the pristine nanowire with the resistivity 1.1 MΩ; the same nanowire after the breaking with high voltage displays the resistance of about 21 MΩ; inset in (h) demonstrates the linear I-V dependence for the pristine nanowire at low voltage.}
\end{figure}

\textsuperscript{180} Ch.-G. Wu; Ch.-Y. Chen, \textit{J. Mater. Chem.} 1997, 7, 1409.
One valid question which needs additional attention remains. Its not clear if the resistance, obtained during \textit{dc} measurements comes only from the single NW or this value also includes a parasitic background part (which might be sufficient enough to overlap with single NW resistance). To clarify this issue we have performed a series of control experiments in which the wire was broken by applying excessive potential as well as mechanically. To break a certain nanowire, we slowly increased the potential between electrodes until an abrupt increase of resistance was detected. For the NW shown in Figure 4.12b the resistance was raised from 1.1 to 21\text{M\Omega}. On the other hand, AFM inspection of the broken nanowires reveals formation of gaps (usually one or two per each broken wire, Figure 4.12b-g). Measuring the size of the formed gap by AFM is not trivial because of comparable dimensions of the AFM probe and the gap. Rough edges make it impossible for the tip to penetrate inside the cave and prevent a full detailed investigation of the gap. Increase in resistance indicates that NW responds to the bias and some changes take place but we can not consider such experiments as sufficiently conclusive. In another series of control experiments, NWs were mechanically broken by movement of the AFM tip operated in contact mode (Figure 4.14). In these cases,
the resistance jumped from few MΩ to GΩ. This significant increase proves that the measured resistance is indeed caused by the particular NW.

Figure 4.14 AFM topography images of the pristine Ppy nanowire with the resistance of about 10 MΩ (left); the same nanowire was broken in the contact mode AFM and after this procedure its resistance was higher than 1GΩ (right).

It was reported in literature that PPy films are usually not stable under ambient conditions and their conductivity decreases with time. In general, the stability of the polypyrrole films depends on many factors. The most important are their structures, mobility of the doping counterion\(^\text{181}\) and possible side reactions occurring during polymerisation of polypyrrole. These reactions lead to various defects in polymer chains and, consequently, enhance the degradation upon interaction with oxygen or water.\(^\text{182}\) (Figure 4.15) It was found that films of polypyrrole with Cl\(^-\) counterion lose more than 70% of their initial conductivity after 25 days due to high mobility of the counterions\(^\text{182}\).

Figure 4.15 Possible products of polypyrrole degradation in the presence of water and oxygen. The formation of such structures in the polymer chains causes ageing and loss in the conductivity


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Figure 4.16 Change of the resistance of the PPy nanowire upon exposure to ambient conditions.

On the other hand, aromatic counterions have no such high mobility and films have higher conductivity and stability.\textsuperscript{183}

In order to determine the stability of the PPy NWs exposed to air at room temperature the evolution of resistance between two contacts was monitored for 40 days. We have found that degradation of the NW becomes quite pronounced only after 20 days of exposure to air (Figure 4.16). Table 4.2 summarises the monitoring of resistance for sample 13 which was stored under inert atmosphere for 1.5 months. Under such conditions, our samples are stable for a long time. Such results suggest that the formation of structural defects due to penetration of oxygen and water inside the NWs are likely to play an important role.

Table 4.2 Monitoring of the resistance for the sample 13 stored under inert atmosphere

<table>
<thead>
<tr>
<th>Sample 13</th>
<th>Resistance, $R$ (MOhm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Days</td>
<td>11.05.2007</td>
</tr>
<tr>
<td>Contacts</td>
<td></td>
</tr>
<tr>
<td>6/7</td>
<td>0.212</td>
</tr>
<tr>
<td>5/7</td>
<td>0.600</td>
</tr>
<tr>
<td>5/8</td>
<td>0.440</td>
</tr>
<tr>
<td>4/8</td>
<td>0.270</td>
</tr>
<tr>
<td>4/9</td>
<td>0.180</td>
</tr>
<tr>
<td>3/9</td>
<td>0.180</td>
</tr>
</tbody>
</table>

Experimental Section. Polystyrene sulfonic acid (PSA) (M_w=6940kg/mol, PDI=1.3 and M_w=403kg/mol, PDI=1.3) was purchased from Polymer Standards Service, Mainz. Ammonium persulfate (APS), pyrrole (Py) and other chemicals were purchased from Aldrich. Synthesis of PPy nanowires. Stretched PSA molecules were deposited from water solution (0.01g/l) onto clean Si-wafers or freshly cleaved mica by spin-coating at high rotation speed (10000 rpm). 50 µl of Py (3g/l) and 50 µl of APS (30g/l) solutions in deionized water were placed for limited time (10-60 seconds) onto the substrates with pre-deposited PSA molecules. Afterwards, the samples were rinsed with water, dried, and investigated with tapping mode AFM (NanoScope IV-D3100, Digital Instruments, Santa Barbara). The diameter of the PPy nanowires was dependent on the polymerization time and equal to: <10, 10-30, and 30-60 nm for polymerization time of 15, 30 and 60 seconds, respectively. “Hairy nanowires” were produced using similar procedure, the only difference being that lower concentration of APS (6g/l) was used.

Electrical measurements. For electrical measurements (Keithley 236 Source-Measure Unit) 18-finger gold micro-electrodes (step height – 50nm, width –500nm, separation –1-2µm) were fabricated by photo-lithography on Si-wafer with an insulating SiO_2 layer (300nm). The accuracy of measurements not exceeds 7% if it is not pointed out in text.

4.2.4. Temperature dependence of the conductivity; conduction mechanism

More detailed information about the charge transport mechanism can be obtained from the temperature dependency of resistance.

In general, conductive polymers (like polyaniline and polypyrrole) belong to the class of highly conductive polymers that sometimes exhibit even “metallic” properties. The term “metallic” conductivity means not only high conductivity level (which anyway even for the best conductive polymer samples is several orders of magnitude lower than that of metals) but rather a certain dependence of the conductivity on temperature. Metals do not require any activation energy for injection of electrons into the conduction band. Decrease of temperature for metals leads to decrease Brownian motion of the crystalline lattice that diminishes its collisions with electrons and results in higher conductivity. In contrast, structure of conjugated polymers, in general, is much less ordered and some fragments of higher order are separated by disordered materials. Thus, conductive polymers require some energy to overcome these disordered fragments. Nevertheless, it was reported recently, that a polyaniline sample prepared under special conditions leading to controlled structure, reaches the conductivity level of about 1000 S/cm and shows dependence of the conductivity on
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temperature similar to that of metallic type conductivity. However, such an example is rather exceptional and conductive polymers usually do not exhibit metallic properties as a result of their insufficient order.

The disorder in conductive polymers arises from a combination of molecular-scale disorder and structural inhomogeneities at mesoscopic length scales. Such materials have been described as disordered metals or insulators near the metal-insulation transition (MIT). In contrast to the characteristics for metals, they have a finite density of states at \( E_F \), the thermally activated (phonon-assisted) \( dc \)-conductivity that decreases as the temperature is lowering.

On the insulating side of the MIT, the \( dc \)-conductivity is described in all theoretical models by well-known hopping expression:

\[
\sigma = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^\gamma \quad \text{(Equation 4.1)}
\]

where \( \gamma \) and \( T_0 \) depend on the details of concrete model. In general, \( \gamma = (\alpha+1)/(\alpha+d+1) \), where \( \alpha \) is the power exponent in a power-law density of state, and \( d \) is the dimensionality of the system. The original Mott theory for 3D variable range hopping with a constant density of states (DOS) at the Fermi energy predicts \( \gamma = 1/4 \), while several modifications of the model have been proposed to describe the frequently observed value \( \gamma = 1/2 \). A conductivity of this form is indicative of either 1) Granular-Metal behavior (GMM) or 2) quasi-one-dimensional variable range hopping (quasi-1D VRH) or 3) 1D VRH.

The quasi-1D VRH model emphasizes nearest-neighbor interchain hopping. This theory assumes strong localization of the electron wave function and weak coupling between

---

polymers bundles. For this model, $T_0=16/(k_B N(E_F)L||L_\perp^2)$ where $N(E_F)$ is the density of states at the Fermi level, and $L||$, $L_\perp$ is the localization length in the parallel and perpendicular directions.\textsuperscript{198,199,200} Joo et al. give the physical interpretation for $T_0$ as an effective energy barrier between localized states, which characterizes the degree of randomness in disordered regions.\textsuperscript{201} It is implied that $T_0$ and energy barrier are related by the Boltzmann constant. The generalized formula for the electric-field-dependent conductivity for disordered systems in low electric fields for quasi-1D VRH model ($E$ is approximately less than or equal to $10^3Vcm^{-1}$)\textsuperscript{202} is

$$\sigma(E)\approx \exp(eDE/k_B T) \quad (\text{Equation 4.2})$$

where $D$ is the most probable hopping distance, $e$ is the electron charge, $E$ is electrical field, $k_B$ - Boltzmann’s constant. At high electric fields ($i.e., E\gg k_B T/(eD)$ (Equation 4.3) can distinguish quasi-1D VRH and tunneling. When the applied $E$ field exceeds significantly the threshold field $E_0$, $\sigma(E)$ is described by

$$\sigma = \sigma_0 \exp \left[ \left( \frac{E}{E_0} \right)^{1/(d+1)} \right] \quad (\text{Equation 4.4})$$

where $d=0, 1, and 3$ correspond to the GMM,\textsuperscript{204,205} the quasi-1D VRH model,\textsuperscript{206,207} and the 3D VRH model,\textsuperscript{202} respectively and $E_0$ is a constant.\textsuperscript{208}

The granular metallic model of Sheng,\textsuperscript{204} incorporating charging-energy-limited tunneling, predicts the same temperature dependence of dc conductivity ($\gamma=1/2$) for low electrical field, like in case of quasi-1D VRH.\textsuperscript{205,206} In the GMM, the phase segregation into conducting (metallic) and insulating domains takes place. Electrons execute a three dimensional random walk over metallic islands that means that the electron wave function is

\textsuperscript{203} The energy gained by an electron in the electric field, $eDE$, is larger than the average hopping energy, allowing the electron to move by hopping to lower electrical field (E) level while emitting a phonon (this is the case of electron backscattering, ref. 200).
\textsuperscript{205} Li, Q.; Cruz, L.; Phillips, P., Phys. Rev. B 1993, 47, 1840.
\textsuperscript{208} Nakhdemov, E.P.; Prigodin, V.N.; Samukhin, A.N. Fiz.Tverd.Tela 1989, 31, 64.
\textsuperscript{210} At the present state of knowledge $\sigma_0$, $E_0$, and $T_0$ are introduced in theoretical models in order to fit the experimental data.

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‘3D delocalized”. From the GMM model of Sheng the dimension of the small metal particles \(W\) including the insulating surface can be estimated as \(^{209}\)

\[
W = \frac{k_B T_0}{4|e|E_0} \quad (\text{Equation 4.5})
\]

where \(T_0\)–constant from Equation 4.1, \(E_0\)–constant from Equation 4.4, \(k_B\)–Boltzmann’s constant, \(e\)–the electron charge.

Finally, for the region where \(E\) substantially smaller than \(E_0\), the electric-field dependence is

\[
\sigma(E) = \sigma_0 \exp(-E_0/E) \quad (\text{Equation 4.6})
\]

![Figure 4.16 Temperature dependence of dc conductivity for the samples: 12, 19, 13, 14 and 15 that were fitted using Equation 4.1](image)

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**Experiment.** Samples 12 and 13 characterized by the highest conductivity at the room-temperature were chosen for detailed low-temperature investigations. Sample 12 with the room-temperature resistance of 7 KOhm was investigated from 200 to 4.2K. Samples 14, 15 and 19 with relatively low room-temperature conductivity were impossible to characterize at the lowest temperatures because of low signal-to-noise ratio, these samples were investigated from 200 to 30K. The maximal conductivity of 3.4S/cm was observed for sample 16 (maximal height), which corresponded to the bulk conductivity of the polypyrrole.\textsuperscript{210} The two-probe \textit{dc}-conductance G=1/R vs \( T^{-1/2} \) for samples 12, 13, 14, 15 and 19 (see Table 4.1) are plotted in Figure 4.16.

As it was mentioned earlier, the temperature dependence of the conductance \( \sigma (T) \), can be expressed as

\[
\sigma = \sigma_0 \exp \left( - \frac{T_0}{T} \right)^\gamma
\]

The best fit of the experimental data (Figure 4.16) was obtained with \( \gamma =1/2 \).\textsuperscript{211, 212} More precisely the value of \( \gamma \) can be determined by plotting \( W = d(\ln G)/d(\ln T) \) (activation energy) vs \( \log T \) and fitting it to a straight line. In this case the slope of this line gives the value of \( \gamma \).\textsuperscript{213} The analysis of G(T) for sample 12 was carried out on the basic of Figure S5.3 (Supplementary materials). As shown in Figure S5.3 curve W against log T can be divided into straight lines with \( \gamma=1/4 \) and \( \gamma=1/2 \). This situation might be interpreted in term of Efros and Shklovskii Coulomb-gap model,\textsuperscript{214} or GMM.\textsuperscript{215} Both models predict a crossover from \( 1/2 \) to \( 1/4 \) in the region close to MIT. Depending on the resistivity ration \( \rho_r = \rho(1.4K)/\rho(300K) \) the metal side, insulating side and critical regime of the charge transport properties can be defined. As it was earlier reported for polypyrrole-hexafluorophosphate films, the metallic side of MIT corresponds to the value of \( \rho_r<10 \); in the critical regime \( \rho_r \) should be equal to 10 and \( \rho_r>10 \) on the insulating side.\textsuperscript{214, 216} Calculation of the resistivity


\textsuperscript{212} The \( \gamma \) value was determined using conductance G instead of the conductivity \( \sigma \). Replacing \( \sigma \) to G in the Equation 4.1 and the equation for the activation energy (S5.3) does not affect \( \gamma \)-value, because of their relation as \( \sigma = \alpha G \), where \( \alpha \) is a constant for chosen sample. The constants \( \sigma_0 \), \( E_a \) and \( T_0 \) were estimated using conductivity.

\textsuperscript{213} The error bars are not represented due to the absence of the experimental data. The good reproducibility of the \( \gamma \)-value from the fitting G vs T data with Equation 4.1 for the same sample but different contacts indirect proves accuracy of the measurement.


ration for our PPy nanowires (sample 12) shows that this value exceeds 100 units. Since the conductivity of sample 12 (0.61 S/cm) is many orders of magnitude below than the minimum for the metallic conductivity (100S/cm) and because the conductance shows very strong temperature dependence, I conclude that sample 12 is far away from MIT. That means that neither Coulomb-gap model nor GMM can be applied for the interpretation of the crossover from 1/2 to 1/4 for sample 12. The clear crossover was found only for sample 12 within the temperature regime from 120 till 200K. Other samples show γ=1/2 before 120K and in the temperature regime from 120 till 200K γ value deviates from the 1/2 and reaches neither 1/2 nor 1/4. The reason for that might be in the contribution of a high-temperature transport part, such as carrier excitations across single particle gaps\textsuperscript{217}, bandlike electronic transport\textsuperscript{218} or small polaron transport.\textsuperscript{219} These charge transport modes in combination with the low – temperature contribution from phonon assistance hopping might cause deviation in γ value. Difficulties in the separation between different kinds of transport inside this temperature regime and absence of a theory for describing the crossover inside the insulation part of MIT forced us to disregard the experiments in this temperature regime and leave an explanation of such behaviours for further investigations. Values of T\textsubscript{0}, obtained from fitting ln (σ) vs T\textsuperscript{-1/2} for low-field regime are listed in Table 4.3. It is interesting that T\textsubscript{0} has approximately the same value for samples produced using the same concentration of pyrrole of 3.5 mg/ml but with different polymerization time (samples 15 and 19).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Sample & T\textsubscript{0}[K] & E\textsubscript{0}[V m\textsuperscript{-1}] & W [nm] \\
\hline
12 & 2561±116 & 3.08E+06±92 & 17.9±0.82 \\
13 & 4900±70 & 2.58E+06±248 & 31.3±0.45 \\
15 & 3744±112 & 4.78E+06±91 & 16.9±0.51 \\
19 & 3844±195 & 3.95E+06±191 & 21.0±1.05 \\
\hline
\end{tabular}
\caption{T\textsubscript{0} and E\textsubscript{0} were obtained from fitting of the experimental data by Equation 4.1 and 4.4, respectively. W is a dimension of small metallic grains in PPy NWs (Ref 209)}
\end{table}

**Dependence of the conductivity on the electrical field.** The typical electrical-field dependence characteristics for all samples are represented on Figure 4.17. The conductivity

decreases with the temperature decrease. This dependence has two characteristic regions. One of them is the low-field regime, in which the main mechanism of the charge transport is a thermally-activated phonon-assistance hopping. The second region is a high-field regime and the majority of charges here are created by the electrical field. The bend point on the plot is called $E_t$ (threshold tension). In this point contributions from the electrical field and from the energy of the thermal motion of carriers are equal.

At low temperatures, the low-field region decreases and disappears completely at $T=0K$. At the same time the high-field region increases (Figure 4.17). Determination of the $E_t$ is not a simple task, because it is not a point on the plot $1/\sigma$ vs $1/E$ but rather a region with a temperature-dependent size. An approximate value of $E_t$ for all samples till 50K is equal to 1.3E5V/m. For lower temperatures the low-field region collapses that significantly decreases accuracy for $E_t$ determination. At high electrical fields, the apparent resistance decreases rapidly (Figure 4.17, 4.18) and for high voltages there is a region of the saturation where the resistance does not change with changing of applying voltage. In this region the holes constitute the majority of charge carriers. The beginning of this region depends on the temperature and the voltage. For sample 12 this region can be clear resolved, for the temperature 4.2K it is marked as 'high-field region, saturation' on Figure 4.18. For higher temperatures this region also exists, but requires application of a big voltage, which can destroy samples.

\[\text{Figure 4.17 Dependence of } 1/\sigma \text{ on } 1/E \text{ for the sample 12 (at 60 K). The temperature dependence of this field-dependent } 1/\sigma \text{ is shown in the inset.}\]
In order to distinguish between different models, a fitting for the high electrical field region was performed by Equation 4.4, where the value of d determines one of the theoretical models. The best fit was found for d=1 (Figure S5.4 in supplementary materials). As a result, for fields significantly exceeding the threshold in the temperature regime from 30 till 120K Equation 4.4 turns into

\[ \sigma = \sigma_0 \exp \left( \frac{E}{E_0} \right) \]  

(Equation 4.7)

This situation corresponds to the GMM model and in this region the majority of charges are created by a field-induced tunneling between metallic grains. This model is valid for all samples. The size of the small “metallic” particles, W, (see Table 4.3), incorporated into the insulating matrix was estimated using Equation 4.5.

**Table 4.4** Dependence of the most probable hopping distance D on the temperature for quasi-1D VRH.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [nm]</td>
<td>7</td>
<td>2.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

\( E_0 \) was obtained from the fitting of \( \ln (\sigma) \) vs E for the lowest temperature where GMM model is still valid. Such a model was also found to be appropriate for polyaniline in the emeraldin form in the temperature range from 20 to 300K.\(^{220}\)

Below 30K GMM model can not be valid anymore as follows from the fitting of the temperature regime by the Equation 4.4 (Figure S5.5). For samples 12 and 13, a transition from the GMM model to the quasi-1D VRH was found. Too high values of the resistance at 30K close to the output device limit (Gohms) do not permit to make conclusions on the conductivity type for other samples since the signal/noise ratio is too low. At temperatures from 30 to 4.2K the field varies as

\[ \sigma = \sigma_0 \exp \left( \frac{E}{E_0} \right)^{1/2} \]  

(Equation 4.8)

that corresponded to the quasi-1D VRH model.

The most probable hopping distances for different T are given in the Table 4.4. In a disordered insulator, Mott\textsuperscript{221} first pointed out that at low temperature the most frequent electron hopping among localized sites would not be a hopping to the nearest neighbour. A hopping electron will always try to find the lowest activation energy and the shortest hopping distance. With the decreasing of the temperature the number of places in the neighbourhood with the low energy decreases and it’s forced electron to hop for bigger distances. In general, the hopping distance depends on the temperature, doping level of polymers and applied bias. In our case, the increase of the hoping distance with the decrease of the temperature for the low-field region is in a good agreement with the theoretical prediction\textsuperscript{221}. Our experimental values have the same order of magnitude as were reported in the literature for different conductive polymers. Maddison \textit{et al.}\textsuperscript{222} have investigated doped PPy films and found hopping distances ranging between 4-5 Å at 300K and 9.5-12.2 Å at 10K. The hopping distance for polyaniline at 25K was found to be 20 Å in the perpendicular direction and 110 Å in the parallel direction of the films stretching.\textsuperscript{223}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.18.png}
\caption{Dependence $1/\sigma$ vs $1/E$ for sample 12 at 4.2K.}
\end{figure}

\textbf{Discussion.} The temperature- and electrical field- dependences of the conductivity (Figures 4.16 and 4.17, see also Figures 5.3 and 5.4 of supplementary materials) obey the GMM model for the temperature region from 30 till 120K. According to this model, our polypyrrole wires can be represented as a sequence of more ordered PPy particles with the size from 20-30nm spread in regions of more disordered PPy. It is reasonable to suppose that these more ordered PPy particles have strong interchain coupling and “metallic” conductance. Decrease of the

\textsuperscript{221} Mott, N. F.; Davis, E. \textit{Electronic Processes in Non-Crystalline Materials} (Clarendon, Oxford) 1979
\textsuperscript{222} Maddison, D.; Unsworth J.; Roberts, R.B. \textit{Synth. Met.}, 1988, 26, 99
temperature leads to decrease of the thermal energy of electrons that decreases the probability of the inter-chain and inter-grain hopping.

To understand the charge transport mechanism, it is helpful to represent the PPy nanowire as an 3D-assembly of nanosized grains. Since the NWs are certainly elongated object that are stretched between the electrodes, most of the grains within the assembly are arranged along the main axis of PSA templates (lets denote it as x-axis). However, other grains (minor amounts) are aligned along two other axes (y- and z-), perpendicular to the x-axis. Since the x-axis coincides with the electric field direction, the movement of the charges along this axis is stimulated by the electric field. In contrast, the hopping of charges along y- and z-axis occurs only due to the thermal energy, since the electrons do not gain the potential energy by the movement in these directions. At sufficiently high temperature the carriers possess enough thermal energy to hope freely from the grain to grain in all directions, including the y- and z-axes thus searching an optimal pathway. However, from a certain low temperature value (in our case it is 30K) the charge carriers possess low thermal energy that is insufficient to jump along the y- and z-axes. Then, they can only move in the direction parallel to the electric field, e.g., along the nanowire. This temperature level corresponds to the transition from the 3D (GMM) to the quasi-1D model. (Figure S5.5) The hopping distance increases from 1.4 to 7nm with the decrease of the temperature.

**In conclusion,** I have developed a simple chemical route to create conductive PPy nanowires by the grafting of PPy from isolated synthetic polyelectrolyte molecules. The location and length of the synthesized PPy nanowires are defined by the location and length of adsorbed single-molecule templates. Diameter of the nanowires varies from a few nanometers to hundreds of nanometers and can be adjusted by polycondensation time and concentration of reagents. The dc conductivity of individual PPy nanowires approaches to the conductivity of PPy in the bulk. The conductive transport in PPy NWs was described using the variable-range hopping model. At low temperature the transition from 3D to quasi-1D conductor was found.

These results open broad opportunities for fabrication of electronic devices and sensors at the molecular level.
Chapter 5

Supplementary materials

5.1 Conductive measurement of individual MWNT

Diluted solution of the MWNT was deposited by spin coating on the device with a gold finger structures on the insulated SiO$_2$ surface. For conductive measurement I used AFM developed by Asylum research group with special equipment to obtain IV-characteristics of the single nanotube attached with one end to the gold electrode. Our work extends a previous experiment$^{224}$ performed with multiwalled carbon nanotubes (MWNTs) where AFM images, taken in a contact mode, showed a current map of MWNTs connected to a gold electrode on an insulating substrate.

Table 5.1 AFM characterization and resistance measurements for single MWNT

<table>
<thead>
<tr>
<th>Point</th>
<th>I (nm)</th>
<th>D (nm)</th>
<th>$\Delta I$ (nA)</th>
<th>$\Delta V$ (V)</th>
<th>R (MOhm)</th>
<th>$\sigma$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>point 1</td>
<td>74</td>
<td>25</td>
<td>2.93</td>
<td>0.01</td>
<td>3.4</td>
<td>0.44</td>
</tr>
<tr>
<td>point 2</td>
<td>200</td>
<td>25</td>
<td>4.6</td>
<td>0.012</td>
<td>2.6</td>
<td>1.57</td>
</tr>
<tr>
<td>point 3</td>
<td>298</td>
<td>25</td>
<td>7.94</td>
<td>0.067</td>
<td>8.4</td>
<td>0.72</td>
</tr>
<tr>
<td>point 4</td>
<td>400</td>
<td>25</td>
<td>2.54</td>
<td>0.01</td>
<td>4.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>

From those images, the resistance of the nanotubes could be obtained but not the IV-characteristics. Our device allows making electrical characterization of the SWNT along its length. Topography of the sample was made in a tapping mode. After taking an overview image, the scanning area is reduced while keeping the target nanotube in the center of the image. MWNT with a diameter of about 25 nm are selected to perform the experiments.

Afterward, AFM is switched to the contact mode using software for conductive measurements. By this program one can monitor and change a tip position inside the image. After the tip was localized on the nanotube, the voltage was applied and IV characteristics were obtained. A schema for our conductive measurements for one nanotube in different points is represented on Figure 5.1. I choose four different points along the tube and measurements were repeated three times per one point. Typical IV-characteristics for different points are represented on Figure 5.2. These data correspond to the measurement collected in Table 5.1

$^{224}$ H. Dai; E.W. Wong; C. M. Lieber Science 1996, 523, 272
Resistance measurements were previously reported for different MWNT types and results differ widely. The highest measured resistance for individual MWNT with a diameter of 10 nm was greater than 100 MOhm, while the lowest resistance, for an 18.2 nm tube, was about 200 Ohm. These values correspond to conductivities of 1S/cm and 1923S/cm, respectively, that is anyway significantly lower than the conductivity of pure graphite (2.5*10^8 S/cm).

In our experiments the conductivity varies in the range of 0.4-2 S/cm. Such small values could be explained by a superposition of at least 3 contributions: 1) from the contact resistances between nanotubes and the gold electrode; 2) from the contact resistances between nanotubes and the AFM tip; and 3) from the intrinsic resistance of the nanotube that depends on its length and the density of defects along the nanotube.

Results represented in Table 5.1 do not give us usual dependence of the conductivity on the conductor length (i.e., increase of the length leading to decrease of the conductivity). The

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225 Peter J.F. Harris Carbon nanotubes and related structures Cambridge University Press 2001
small value of conductivity gives us a reason to say that the contact resistance is very big that makes impossible to define the intrinsic conductivity of the nanotube. Unfortunately, the problems mentioned above were quite difficult to eliminate.

In principle, the contact resistances between nanotubes and gold electrode could be diminished, for example, by a deposition of gold on the top of the tubes by electron beam lithography. However, the problem coming out from the improper contact between the nanotube and the tip is much more difficult to eliminate since the nanotubes used in this work are significantly curved, as clearly seen from the AFM image (Figure 5.1). Furthermore, we suggest that they are curved not only in the surface plane, but also the axis perpendicular to the surface. Thus, it is very difficult to accomplish a proper contact simultaneously with the electrode and the tip.

**Fig 5.2** Dependence for points 4, 3 and 2 respectively
5.2. Conductive measurement of PPy NWs

Figure 5.3 An activation energy log[d(ln G)/d(ln T)] plots of measured G(T) against logT for the sample 12 at U=0.1V (low field regime) for three different contacts 5/8, 5/7, 6/7.
Figure 5.4 Electrical–field- dependent conductance of the sample 12 (temperature between 120 and 30K) measured using a two-probe method. The data are plotted as Ln (σ) vs E; Ln (σ) vs E^{1/4}; Ln (σ) vs E^{1/2} The best fit was obtained for Ln (σ) vs E. This corresponds to the GMM model.(Equation 4.4)
Figure 5.5 Electrical –field- dependent conductance of sample 12 (temperature between 30 and 4.2K) measured using a two-probe method. The data are plotted as Ln ($\sigma$) vs $E^1/2$, Ln ($\sigma$) vs $E^{1/4}$, Ln ($\sigma$) vs $E^{1/2}$. The best fit was obtained for Ln ($\sigma$) vs $E^{1/2}$. This corresponds to the quasi-1D VRH model. (Equation 4.4)
Summary and Outlook

**Summary.** Miniaturization has become a driving force in different areas of technology including microelectronics, sensoric- and bio-technologies and in fundamental science. Because of the well-known limitations of conventional lithographic methods, newly emerging bottom-up approach, utilizing self-assembly of various nanoobjects including single polymer molecules and carbon nanotubes constitutes a very promising alternative for fabrication of ultimately small devices.

Carbon nanotubes (CNTs) are attractive materials for nanotechnology and hold much promise to revolutionize fundamental science in a investigation of phenomena, associated with the nanometer–sized objects, like Coulomb blockade, ballistic conductance, metal-insulation transition and etc. Beside this, unique electronic properties, high chemical stability, and extremely high mechanical strength, stiffness and availability peculiar for CNTs, make such materials indispensable for a field of fabrication of conductive coatings and nano-composite materials. However, poor solubility of CNTs is a major problem. It can be solved via modification of CNTs surface with some solubilizing compounds, for instance, by attaching polymers. Simultaneously, developed polymeric shell on the CNTs surface would provide possibility to achieve necessary surface properties by the absorption of specific materials (conductive clusters, magnetic particles, etc.). It was found in this work that grafted chains of poly(2-vinylpyridine) form a shell covering the CNTs that makes the CNT-g-P2VP dispersible in organic solvents and in acidic water. The positively charged P2VP shell is responsible for the selective deposition of CNTs onto oppositely charged surfaces. It was established that the deposition of CNT-g-P2VP from aqueous dispersions at low pH is an effective method to prepare ultra-thin films with a tunable CNTs density. According to the percolation theory, modeled for conductive sticks, it was found that the thin film, near percolation threshold, behaves as 2D network. According to AFM and electrical measurements, even when only 5% of the surface is covered by CNT-g-P2VPs, the sheet resistance is of the order of 1 MΩ/sq, which indicates that conductivity is imparted by a network of an ultra-low density. When the film transmittance decreases down to ~70% at 550 nm, the occupied surface area is ~15% and the sheet resistance falls down to ~ 90 kΩ/sq. These data show that undesired in-plane clustering does not occur upon the dispersion casting of the films and that high quality networks of CNT-g-P2VPs are built up. The electrosteric stabilization of the CNT-g-P2VP dispersions in water at low pH is at the origin of this desired behavior.
It was shown that P2VP grafted to CNTs is a universal support for the immobilization of various nanoclusters at the CNTs surface. A simple method for the preparation of charge-stabilized Prussian Blue nanoparticles of readily adjustable size is reported. Thus-formed Prussian Blue nanoparticles are crystalline and display a long-range ferromagnetic ordering at 5.1 K. Prussian Blue nanoparticles were selectively attached to the surface of carbon nanotubes (CNTs) functionalized with poly2-vinylpyridine (P2VP). These nanoparticle-based nanostructures might be useful materials for manufacture of electrooptical devices, or mechanically robust ion-sieving membranes.

Conducting polymer (CP) nanowires (NWs) are another very promising kind of nanomaterials that could be also suitable for applications in nanodevices and nanosensors. In addition to the attractive properties of CNTs and inorganic NWs (e.g., variable conductivity and high surface-to-volume ratio), conducting polymer NWs possess the following important advantages: easy and cheap production (synthetic procedures exclude high temperatures and vacuum equipment); easy variability of chemical structure, size and shape of CP NWs allowing precise tuning of other properties (optical, electrical, surface functionality, charge, etc.). A number of template- and template-less methods to produce CP NWs were developed. However, for various applications CP NWs must be properly integrated into circuits, therefore at least one additional step, such as a release of the nanowires from the templates or/and their positioning in the device is always required. It is, therefore, strongly desired to develop a method for growing CP NWs in predefined places on the devices, for example between microelectrodes.

A simple method to control the conformation and orientation of single adsorbed polyelectrolyte molecules by co-deposition with octylamine (OA) was developed. This method was used for the stretching and positioning of polystyrenesulfonic acid between gold electrodes necessary for the preparation of conductive polymer nanowires.

A simple chemical route to conductive PPy nanowires by the grafting of PPy from molecules of polystyrenesulfonic acid was developed. The location and length of the synthesized PPy nanowires are defined by the location and length of adsorbed single-molecule templates. The diameter of the nanowires can be varied from a few nanometers to hundreds of nanometers by adjusting the polycondensation time and concentration of the reagents. In our work, electrical characterization was done on the level of individual nanowires and their conductance was unambiguously proved by “breaking experiments”. The dc conductivity of individual PPy nanowires approaches the conductivity of PPy in bulk. I found that the conductivity decreases with decreasing of temperature, as typical for semiconductors. The conductivity can be described using variable-range hopping model.
was found at low temperature change in conductivity, corresponded to the transition from quasi-1D to 3D conductor.

**Outlook.** The results achieved open new and broad perspectives for the construction of molecule-based devices - sensors and transistors. Chemical and biological sensors on the basis of (semi)conductive polymer nanowires grown from single polyelectrolyte molecules and operating as analyte-gated field effect transistors (FETs) are a promising way for the real-time detection of extremely low concentrations (up to single-molecule level) of multiple biological targets (proteins, viruses, DNA/RNA, etc.) in vitro, and possibly even in vivo, inside leaving cells and viable alternative to inorganic nanoscale materials. In addition to the attractive properties of the inorganic NWs (e.g., variable conductivity and high surface-to-volume ratio), conducting polymer NWs possess the following important advantages: easy and cheap production (synthetic procedures exclude high temperatures and vacuum equipment); easy variability of chemical structure, size and shape of CP NWs allowing precise tuning of other properties (optical, electrical, surface functionality, charge, etc.). The operation principle of such sensors is based on changing of the conductivity in the channel in response on changed environment. Since most biological species (proteins, DNA or viruses) are charged (in water solutions), their binding results in depletion or accumulation (depending on the charge of the analyte) of carriers within the transistor and, therefore, in altered conductance. In such a way CP NW FETs can serve as efficient transducers transforming the chemical signals (recognition and binding events) into a technologically relevant electrical signal.
PUBLICATIONS


**CONFERENCES**


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