International Journal of Research and Review Techniques (IJRRT), ISSN: 3006-1075
Volume 3, Issue 4, October - December, 2024, Available online at: https://ijrrt.com

To Study Pani-CNT Composites and Various Pani Nano-Structures using a Range of Chemical Techniques

Mukesh Kumar[1], **Dr. Richa Yadav**[2]

[1]Research Scholar, Monad University, Hapur
[2]Professor, Monad University, Hapur

ABSTRACT

By applying a DC electric field, charged powder particles that are suspended or distributed in a liquid media are drawn to and deposited onto a conductive substrate that has the opposite charge. This process is known as electrophoretic deposition, or EPD. The use of EPD derived from a colloidal suspension of a preferred conducting polymer (CP) offers a novel approach for customising nano-structured films with unique shape and packing density. It is well known that this novel and intriguing deposition method produces homogeneous, porous, pinhole-free CP films. Because of their small size, nano-structured conducting polymers, also known as nanotubes, nanorods, or nanospheres, have intriguing optical, electrical, and mechanical properties that present excellent opportunities for fusing biological recognition events with electronic signal transduction in the design of next-generation bioelectronic devices. Because of its special qualities, including (i) increased surface area for effective protein/enzyme immobilization, (ii) unique electron transfer capabilities, (iii) shorter penetration depth for target molecules, (iv) broad range of tuneable properties, (v) biocompatibility, (vi) long-term environmental stability, etc., nano-structured polyaniline (NS-PANI) is predicted to be an effective platform for designing diverse biosensing systems.

Keyword: Nano-Structured, Biocompatibility, Biosensing, Electron, Nanospheres

INTRODUCTION

It is the goal of nanoscience and nanotechnology to precisely and intentionally manipulate matter at the atomic level. It is the small-scale science with a wide range of possible uses. The prefix "nano" originates from the Greek word "νάνος," meaning midget. Nano in science refers to a equivalent to 10-9 units. Materials with at least one nanoscale dimension are referred to as nanomaterials. Thin films and surface coatings are examples of materials that are nanoscale in one dimension; nanowires and nanotubes are nanoscale in two dimensions; and particles, such as colloids or quantum dots (small particles of semiconductor materials), are nanoscale in three dimensions. This group also includes nanocrystalline materials, which are composed of granules the size of nanometers. These substances serve as a link between bulk systems and individual molecules.

The atomic molecules and bulk materials of the same composition differ dramatically from the chemical and physical characteristics of materials with nanometric dimensions. The study of this innovative class of materials is greatly motivated by the unique chemistry, structure, reactivity, and dynamics of nanostructures. Nanomaterials have a larger surface-to-volume ratio, better mechanical strength with a higher specific heat, and higher electrical resistivity than their traditional coarse-grained equivalents. The "miniaturization" that lies at the core of nanotechnology was highlighted by Feynman in his widely referenced 1959 speech, "There is plenty of room at the bottom." To surpass Moore's law and fit 1000 CDs onto a wristwatch is the task. Since energy level bands gradually convert into quantized discrete energy levels as the size approaches atomic dimensions and affects material characteristics, the idea of creating materials at the nanoscale is fundamentally intriguing.

REVIEW OF LITERATURE

N. Gospodinova et. al. (1) The polymer polyaniline (PANI) has been the subject of much research during the past 10 years. Determining the possible application areas (alternative energy sources and transformers, media for erasable optical information storage, non-linear optics, membranes, etc.) and establishing the scientific principles enabling management of its characteristics are significant scientific challenges. For the first time, we have demonstrated that the behaviour of this polymer is governed by the same fundamental ideas as the polymerization process. Aniline polymerization and the ensuing polyaniline transformations must both be viewed as typical redox processes, in which the concentrations and oxidation potentials of the reactants (as well as the medium's pH, which influences the reactants' oxidation potential values) determine the process's direction and point of equilibrium. By using this method, we can recognise the oxidative polymerization of aniline (and possibly thiophene and pyrrole) as a novel application of cationic polymerization, in which the electrochemical potential of the system can be used to express the conditions of chain initiation, propagation, and termination. Moreover, this facilitates the clarification of the principal issues pertaining to the primary categories of polymer transformations (referred to as oxidative and non-oxidative.

Xiaofeng Lu et. al. (2) Since their discovery in the 1970s, intrinsically conducting polymers have been the subject of intense research due to their interesting electrical and redox characteristics and various potential uses in many sectors. The rise of nanotechnology has led to a great deal of interest in the manufacture of multi-functionalized conducting polymer nanocomposites to expand and improve their activities. An overview of the production, characteristics, and uses of one-dimensional (1D) conducting polymer nanocomposites is provided in this article. Conducting polymers and one or more constituents, such as metals, oxide nanoparticles, chalcogenides, insulating or conducting polymers, biological materials, metal phthalocyanines and porphyrins, etc., are the constituents of nanocomposites. There will be extensive discussion of the characteristics of 1D conducting polymer nanocomposites. The differences between bulk conducting polymers and 1D conducting polymer nanocomposites are given particular consideration. The applications of 1D conducting polymer nanocomposites that are discussed include biomedicine, microwave absorption and electromagnetic interference (EMI) shielding, chemical and biological sensors, energy, catalysis and electrocatalysis, and electrorheological (ER) fluids. Highlighted are the benefits of 1D conducting polymer nanocomposites above their parent conducting polymers. In several areas of nanotechnology, 1D conducting polymer nanocomposites are expected to be significant due to their inherent qualities and the synergistic influence of each component.

Jaroslav Stejskal et. al. (3) Aniline undergoes oxidative polymerization to produce polyaniline, which is available in a range of forms with varying electrical conductivity and colour. A system of connected structures is suggested, along with a collection of formulas that enumerate the chemical changes involved and explain all of the spectroscopic and conductometric data.

E.M. Geniès et. al. (4) In addition to well over 200 references covering chemical, electrochemical, and gas-phase preparations; polymerization mechanisms; physical, chemical, and electrochemical properties; redox mechanisms; theoretical investigations; and applications, this article summarises a few chosen studies conducted on polyaniline. The purpose of this paper is not to critically examine the conclusions that may be made from the numerous scientific studies that have been conducted on this material, but rather to present a survey of some of the literature that is currently accessible on this conducting organic polymer.

Ehsan Nazarzadeh Zare Et. al. (6) Conjugated chains with alternating single and double bonds are the basis of a particular class of synthetic polymers known as intrinsically conducting polymers (ICPs), which have unique electro-optic characteristics. One of the most well-known ICPs, polyaniline (PANI), has a wide range of potential uses in biomedicine due to its hydrophilic nature, low toxicity, strong environmental stability, and nanostructured shape, which all contribute to its high electrical conductivity and biocompatibility. PANI's limited processability and degradability are two of its drawbacks, although they may be addressed by creating blends and nanocomposites of it using other (bio)polymers and nanomaterials, respectively. The most recent biological activity and uses of conductive PANI-based nanocomposites in biomedical domains, including antibacterial treatment, drug transport, biosensors, nerve regeneration, and tissue engineering, are covered in this study. To set the stage for future study, the most recent developments in PANI-based nanocomposites' biological applications are discussed.

Mohammad Shahadat et. al. (7) Because of its special qualities and doping chemistry, polyaniline (PANI), one of the many electrically conducting polymers, has drawn interest. Several electrically conducting biodegradable polymers have been created by adding biodegradable materials to the PANI matrix, such as cellulose, chitin, chitosan, etc. Additionally, the hybrid materials are used in fuel cells, photocatalysts, antibacterial agents, sensors, and medicinal applications. These biodegradable and biocompatible conducting polymers are also used in targeted medicine delivery, dental implants, and tissue engineering. The most recent developments in PANI-based biodegradable polymers are reviewed here, along with their distinct uses and methods of synthesis across a range of industries. The production of PANI-grafted biodegradable nanocomposite material is anticipated to pave the door for novel uses of these remarkable materials in the future.

OBJECTIVES OF THE STUDY

1. Creation of PANI-CNT composites and various PANI nano-structures using a range of chemical techniques.
2. Using their well-dispersed colloidal suspensions, these nanoscale PANI structures were electrophoretically deposited onto glass plates covered with indium tin oxide (ITO).

RESEARCH METHODOLOGY

This work includes research on two topics: 1) Preparing nano-patterned PANI, PANI nanotubes, PANI nanospheres, and PANI-CNT composite, then fabricating their films onto ITO-coated glass plates; and 2) Immobilizing biomolecules (ChOx, LIP, GDH, etc.) onto conducting PANI-based electrodes to investigate their potential uses for triglyceride and cholesterol detection. These bioelectrodes and electrodes that were fabricated have undergone different stages of preparation. These stages have included characterization through the use of X-ray diffraction (XRD), UV-Visible (UV-Vis) spectroscopy, Fourier Transform Infrared (FT-IR) spectroscopy, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Contact Angle (CA), and electrochemical techniques [Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), and Electrochemical Impedance Spectroscopy (EIS)].

Infrared Fourier Transform Spectroscopy (FT-IR)

One of the most significant analytical methods for differentiating between organic and inorganic materials that has gained widespread recognition is Fourier transform infrared spectroscopy.1-2 In FT-IR, the beam divides into two parts: one beam is used as a reference beam while the other passes through the sample (transmission) or is alternatively reflected. Once a route difference is added, this transmitted or reflected beam recombines with the reference beam. The spectrum of a desired substance being studied as a function of wavelength or wave number of incident radiation is obtained by Fourier transformation of the interference pattern so created. Using time domain measurements of electromagnetic radiation or another kind of radiation, spectra are gathered based on measurements of the temporal coherence of a radiative source in Fourier transform infrared spectroscopy, a characterisation technique. A molecule's atoms move around a mean location rather than maintaining a constant relative position. This type of vibration is known as infrared (IR) active when the dipole moment periodically alternates throughout the oscillation. Only the radiation that the vibrating molecule can interact with in a coherent way—that is, the radiation of its own oscillation frequency—is absorbed by the molecule.3–4. The presence or absence of specific vibrational frequencies in the FT-IR spectra provides important details on the structure of a given molecule. Because each functional group has a unique spectrum of vibrational frequencies and is highly sensitive to the chemical environment, knowing which functional groups are present in a given sample is important for further characterizing those groups.

RESULT AND DATA INTERPRETATION

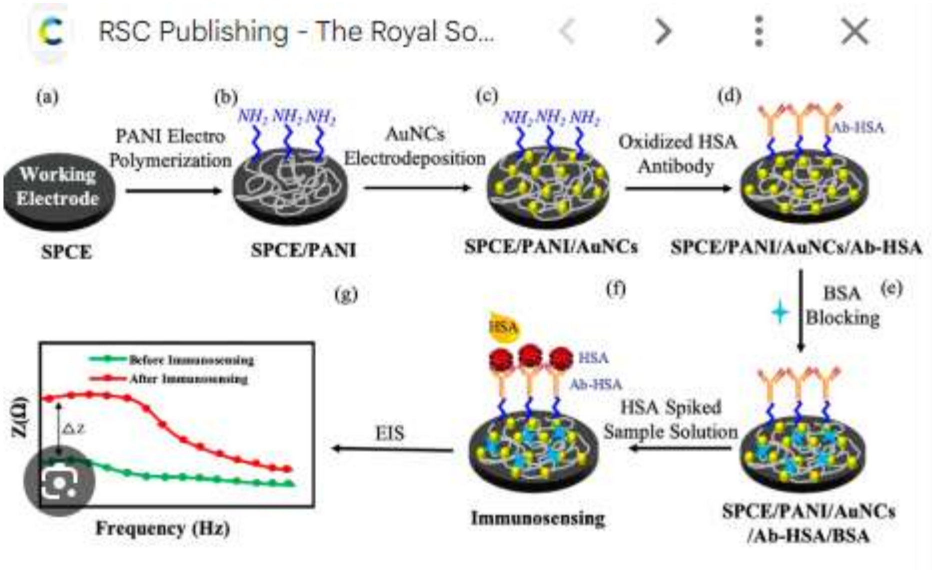
Conducting polymers have become attractive materials for the creation of biosensors due to their electrical conductivity, environmental stability, ease of controlled processing, and biocompatibility.PANI is regarded as special within the conjugated polymer family of conducting polymers because of its straightforward and reversible acid/base doping/dedoping chemistry, which permits control over attributes including free volume,solubility, electrical conductivity, and optical activity. Since they combine the qualities of high surface area materials and low-dimensional organic conductors, NS-PANI (nanotubes, nanorods, and nanospheres) have attracted a lot of scientific attention recently. This could lead to improved performance anywhere a sizable interfacial area between PANI and its surroundings is required. For instance, NS-PANI has been shown to have higher sensitivity and a quicker reaction time than its traditional bulk equivalent in biosensor applications. The extremely sensitive modulation of electrical conductance/resistance of nano-structures caused by variations in the electrostatic charges from surface adsorption of different molecules, which results in the depletion or accumulation of the carriers in the "bulk" of nanoscale dimension structures, is responsible for the observed high sensitivity.

Using hard templates like zeolite channels, track-etched polycarbonate, anodized alumina, and so on, or soft templates like surfactants, liquid crystals, thiolated cyclodextrins, polyacids, and so on, are some of the conventional chemical oxidative polymerization techniques used to create NS-PANI. It has been reported that 1-D PANI nano-structures with diameters less than 100 nm may be grown under the guidance of these templates. Nevertheless, in order to extract NS–PANI from the products, a post-synthetic procedure is needed to eliminate these templates. A “non-template” method for synthesizing PANI-NT with CSA acting as a dopant. Since CSA/anilinium ion micelles serve as pseudo-templates in the creation of PANI-NT, this process may be classified as a self-assembly approach. Recent research by Huang et al. describes an efficient interfacial polymerization technique that suppresses secondary development by performing the polymerization process at an immiscible organic/aqueous interface.Under ambient circumstances, it has been observed that this simple chemical method produces PANI-NF with relatively uniform diameters between 30 and 50 nm and lengths ranging from 500 nm to several micrometers. Zhang and colleagues have reported the creation of unique nanofibers by the seeding technique. It has been suggested that the chemical environment around PANI nanostructures might have an impact on their shape. In this particular situation, Baker et al. have shown the fast and reversible activation of flash-welding PANI-NF mats when certain aqueous acids and bases are present. The actuation process involves the introduction of anionic dopants into the positively charged nanofibers, which leads to the p-doping of the EB form of PANI to form ES upon acid exposure. This mechanism is reversible at basic pH levels. The process of polymerizing PANI nano-structures involves both intra- and inter-chain interactions, including hydrogen bonding and π-π interactions, which are influenced by the kind of solvent used. By managing these interactions, PANI with different morphologies may be produced. Wu et al. have shown that the introduction of phenol additives in the reaction mixture reduces the rate of polymerization of PANI nanostructures by rupturing intra- and inter-chain hydrogen bonding. Poly(acrylic acid) (PAA) was used as a template and CSA as a dopant to create PANI. It has been noted that aniline-CSA (acid-base interaction) interaction is crucial for the creation of chiral PANI complexes. The inclusion of an organic solvent is predicted to cause this acid-base interaction to be weaker, which lowers the reaction medium's dielectric constant. The PAA/Aniline/CSA complex may become unstable due to these diminished acid-base interactions, which would lower the chirality of the nanocomposite. Numerous techniques are available for the production of different PANI nanostructures. Nanofibrillar shape appears to be essential to PANI, hence creating nanospheres remains a difficult process. Because of its enormous surface area, PANI-NS are especially useful for optoelectronics and sensors.

It is noteworthy that nanospheres may be solvated efficiently because of their globular shape, which improves their solubility in standard solvents for spectroscopic structural analysis.22 In this respect, it should be mentioned that there aren't many cases of PANI-NS synthesis that have been described, including the usage of templates such polystyrene spheres, hydroxy alkyl cellulose, and salicylic acid-assisted polymerization.24–25 Recently, Anilkumar et al. created 4-[4-hydroxy-2((Z)-pentadec-8-enyl)phenylazo], a novel amphiphilic dopant molecule.The chemical moiety benzenesulfonic acid was employed as a fluorescent probe and a structure-directing agent to create a range of PANI nano-structures, such as PANI-NS.26-27 The synthesis and method of nanosphere creation are yet unknown, and unlike its counterparts in nanofibres, it has been discovered that the production of nanospheres is very sensitive to dopant/aniline concentration and the polymerization pathway. In this chapter, we've gathered the findings from methodical investigations into the preparation of PANI-NS using micelle polymerized CSA doped PANI-NT morphological transformation while ethylene glycol (EG) was used as a solvent. PANI-NS thin films have been produced non-electrophoretically on an ITO surface using the solution casting technique. Further investigation into these nanostructured films' potential as a substrate for cholesterol oxidase immobilization has shown promise for the detection of free cholesterol.

Fixing ChOx on PANI-NS/ITO Electrode

Using NHS (0.1 M) as an activator and EDC (0.4 M) as the coupling agent, ChOx (15µL) is covalently immobilized onto PANI-NS/ITO electrode by the creation of an amide bond between the -NH or $-NH_2$ groups of PANI and the -COOH group of ChOx [Scheme 3.1]. 28 The resulting bioelectrode (ChOx/PANI-NS/ITO) is kept at 4 oC when not in use and is properly cleaned with PBS (50 mM, pH 7.4) containing NaCl (0.9%) and Tween 20 (0.05%) to wash off any unbound enzyme.



Scheme 5.1: Illustrative Depiction Of The Biochemical Reaction Involved In Cholesterol Sensing, Immobilization Of Chox, And Morphological Transition Of The Pani-Nt To Pani-Ns.

Safety Measures

i) Caution should be exercised when dispersing PANI-NT with formic acid.

ii) Because EG has a high boiling point, it is necessary to maintain consistent vacuum conditions while fabricating PANI-NS films using the solution casting method.

Research on X-ray Diffraction (XRD)

The three distinct peaks (designated as 1, 2, and 3) centered at 2θ = 15o, 20.53o, and 25.28 o associated with PANI are seen in the X-ray diffraction (XRD) pattern of (i) CSA doped PANI-NT and (ii) PANI-NS/ITO film, as shown in Figure 3.1. The peaks seen at 20.53o and 25.28o, respectively, can be attributed to periodicity along and perpendicular to the polymer chains, as shown by Pauget et al.29 When PANI-NS is present, there is no extra peak at 2θ = 6.4o (labeled as 4), which shows how the PANI chains are organized into nanotubes or lamellae.

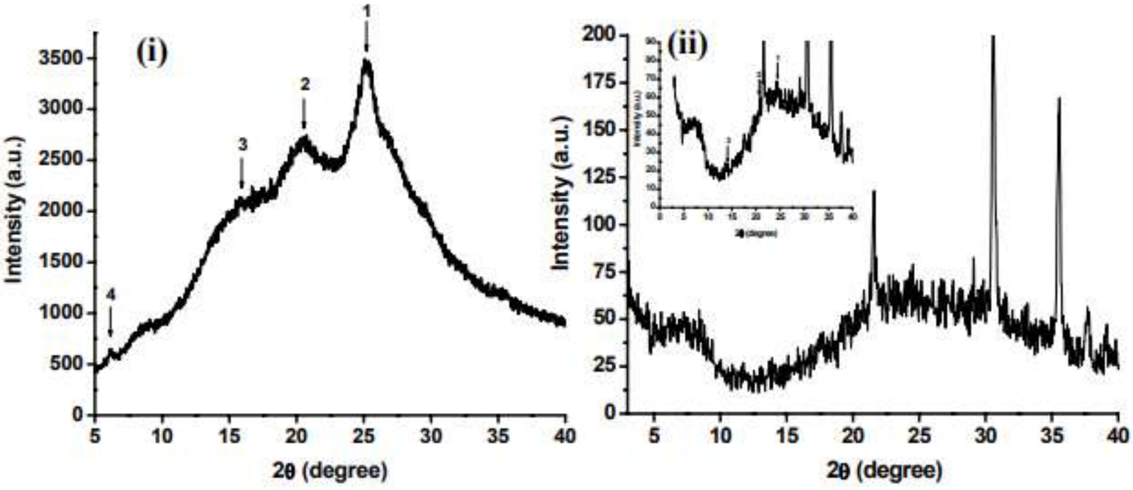


Figure 5.2: Pani-Nt And Pani-Ns/Ito Film's X-Ray Diffraction Patterns The Enlarged Image Of The Xrd (Intensity Ranging From 0 To 90 A.U.) Is Displayed In The Inset Of This Figure.

The CSA/anilinium micelles function as pseudo-templates during polymerization, allowing PANI to grow under control and take the shape of nanotubes, which explains the tubular morphology. The Debye-Scherrer formula ($D = 0.9\lambda/\beta\cos\theta$) is used to determine the crystallite size of PANI nanospheres, and the result is 71.8 nm. When doing XRD studies on PANI-NS/ITO films, the films are too thin (180 nm) to produce distinct diffraction patterns, and the substrate effect also predominates.

CONCLUSION

The unique properties of nano-structured conducting PANI matrices, such as their (i) larger surface area for effective protein/enzyme immobilization, (ii) distinct electron transfer capabilities, (iii) shallower penetration depth for target molecules, (iv) wide range of tuneable properties, (v) biocompatibility, (vi) long-term environmental stability, etc., make them useful platforms for designing and developing a variety of biosensing systems. Furthermore, the PANI matrix's increased charge transfer behavior and better biosensing properties are the outcome of the integration of carbon nanotubes. Several experiments have been methodically conducted to investigate the applications of electrophoretically fabricated nanostructured PANI based films for cholesterol and triglyceride detection. This is because the estimation of cholesterol and triglycerides is crucial in mitigating the risk associated with abnormal levels of these analytes in blood, and because EPD has the potential to generate nano-structured CP films.

The structure and morphological analysis of NS-PANI films, fabricated electrophoretically or non-electrophoretically onto ITO coated glass substrates, has been done using a variety of techniques, including Fourier Transform Infra-red Spectroscopy, UVVisible Spectrophotometry, X-ray Diffraction, Scanning Electron Microscopy, Transmission Electron Microscopy, Atomic Force Microscopy, and Contact Angle measurements that are described in this chapter. Additionally, to disclose their structure and morphology in solution, the UV-Vis, FT-IR, and TEM have been utilized. To investigate the biosensing response and uncover the electrochemical behavior of NS-PANI based bioelectrodes, methodologies such as linear sweep voltage monitoring, cyclic voltage measurement, and electrochemical impedance spectroscopy have been applied. This chapter also covers the different approaches used to immobilize the target biomolecules and the procedures followed to estimate different parameters related to the effectiveness of the conducting polymer-based cholesterol and triglyceride biosensor that is electrophoretically fabricated. The subsequent chapter discusses the many research projects on films based on non-electrophoretically formed polyaniline nanospheres for screening cholesterol.

REFERENCES

[1]. N. Gospodinova, L. Terlemezyan, Conducting polymers prepared by oxidative polymerization: polyaniline, Prog. Polym. Sci. 23 (1998) 1443e1484.

[2]. X. Lu, W. Zhang, C. Wang, T.-C. Wen, Y. Wei, One-dimensional conducting polymer nanocomposites: synthesis, properties and applications, Prog. Polym. Sci. 36 (2011) 671e712.

[3]. J. Stejskal, P. Kratochvil, A.D. Jenkins, The formation of polyaniline and the nature of its structures, Polymer 37 (1996) 367e369.

[4]. C.O. Baker, X. Huang, W. Nelson, R.B. Kaner, Polyaniline nanofibers: broadening applications for conducting polymers, Chem. Soc. Rev. 46 (2017) 1510e1525.

[5]. E.M. Genies, A. Boyle, M. Lapkowski, C. Tsintavis, Polyaniline: a historical survey, Synth. Met. 36 (1990) 139e182.

[6]. E.N. Zare, P. Makvandi, B. Ashtari, F. Rossi, A. Motahari, G. Perale, Progress in conductive polyaniline-based nanocomposites for biomedical applications: a review, J. Med. Chem. 63 (2020) 1e22.

[7]. M. Shahadat, M.Z. Khan, P.F. Rupani, A. Embrandiri, S. Sultana, S.Z. Ahammad, S. Wazed Ali, T.R. Sreekrishnan, A critical review on the prospect of polyaniline-grafted biodegradable nanocomposite, Adv. Colloid Interface Sci. 249 (2017) 2e16.

[8]. P. Zarrintaj, H. Vahabi, M.R. Saeb, M. Mozafari, Chapter 14 - application of polyaniline and its derivatives, in: M. Mozafari, N.P.S. Chauhan (Eds.), Fundamentals and Emerging Applications of Polyaniline, Elsevier, 2019, pp. 259e272.

[9]. M. Omastov a, P. Bober, Z. Mor avkova, N. Pe ————————————rinka, M. Kaplanova, T. Syrový, J. Hromadkov a, M. Trchova, J. Stejskal, Towards conducting inks: polypyrroleesilver colloids, Electrochim. Acta 122 (2014) 296e302.

[10]. M. Omastova, M. Trchov a, J. Kova————————————rova, J. Stejskal, Synthesis and structural study of polypyrroles prepared in the presence of surfactants, Synth. Met. 138 (2003) 447e455.

[11]. J. Stejskal, M. Trchova, P. Bober, Z. Mor avkov a, D. Kopecký, M. Vrnata, ———————————— J. Proke————————————s, M. Varga, E. Watzlova, Polypyrrole salts and bases: superior conductivity of nanotubes and their stability towards the loss of conductivity by deprotonation, RSC Adv. 6 (2016) 88382e88391.

[12]. J. ———————————— Skodova, D. Kopecký, M. Vr nata, M. Varga, J. Proke ———————————— ————————————s, M. Cieslar, P. Bober, J. Stejskal, Polypyrroleesilver composites prepared by the reduction of silver ions with polypyrrole nanotubes, Polym. Chem. 4 (2013) 3610e3616.

[13]. I. Sapurina, J. Stejskal, I. ———————————— Sedenkov ———————————— a, M. Trchov a, J. Kov a————————————rova, J. Hrom adkov a, J. Kopecka, M. Cieslar, A.A. El-Nasr, M.M. Ayad, Catalytic activity of poly- pyrrole nanotubes decorated with noble-metal nanoparticles and their conversion to carbonized analogues, Synth. Met. 214 (2016) 14e22.