

Doctoral (Ph.D.) theses

Magnetic composites of electrically conducting polymers

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1. Introduction and objectives

If someone first hears the expression conducting polymer, may get confused, since most of the polymers are well known about their insulating property. In the last decades a new family of polymers – having extended Π -conjugated structure – has been discovered, in which polymers conductance can be changed by several orders of magnitude. The good mechanical properties and the electrical conductivity (comparable to the widely used conductors) brought these materials into the focus of research & development. The importance of this class of new materials was acknowledged by the Nobel Prize in Chemistry 2000, for the three pioneers of the field.

Conducting polymer-based composites are more and more intensively studied since the end of the 1990s. These inorganic–organic hybrids form a promising class of new materials, owing to the advantageous properties of the polymer matrix and the embedded inorganic particles. The combinations often lead to synergistic effects, resulting enhanced properties, making these materials applicable in various fields. Conjugated polymers such as polypyrrole (PPy), polyaniline (PAni), polyethylene-dioxythiophene (PEDOT) and different polythiophenes (PTh) have been successfully combined with different inorganic materials including metal nanoparticles (Ag, Au, Cu, and Pd), leading to nanocomposites with high conductivity, catalytic activity, thermoelectric property. Nanocomposites of conducting polymers and nanosized metallic oxides are in the focus due to the large variety of their potential applications, such as in electrocatalysis, corrosion protection, or as electrode materials for batteries. Incorporation of magnetic iron-oxides into conjugated polymer matrixes is intensively studied, because materials having both high conductivity and a high magnetic susceptibility can be used in nonlinear optics, for electrical and magnetic shielding, and as microwave absorbers. In the last few years, Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were incorporated into polypyrrole, polyaniline and PEDOT through different chemical and electrochemical synthetic procedures. The prepared nanocomposites were either bulk materials, separate micro/nanoparticles or thin layers, depending on the method of preparation.

Our research group is active in the field of conjugated polymer based hybrid materials since 2004. The first studies focused on tuning the electrical and thermoelectrical properties of different polymers by incorporating silver nanoparticles in their matrices. I started my scientific work in 2006, and our objective was to incorporate superparamagnetic and/or ferromagnetic iron-oxide nanoparticles into conducting polymers. In the scientific literature one can find almost only

chemical synthetic procedure, carried out in aqueous solutions, although this is a strong limitation from the side of the applicable polymer. As a starting point of my doctoral work, we aimed to study the feasibility of the composite preparation in organic media, and in case of success, to study the properties of the hybrids. Our further interest was to synthesize such hybrids electrochemically, and to study their possible applications in electrocatalytic reactions. We aimed also to investigate the photo-electro-catalytic O₂ reduction reaction, and the H₂O₂-decomposition on the prepared modified electrodes. We studied the enrichment of vitamin B12 in polypyrrole, – as it has been proved to be a potential mediator in bio-electrocatalytic processes– through the inclusion of B12 - covered magnetite particles.

2. Experimental methods

All chemicals were of analytical grade. Aqueous solutions were prepared by using deionized water made in a MilliQ RG Millipore instrument. The water content of nitrobenzene was determined by coulometric Karl-Fischer titration, and it was kept below 30 ppm. All solid chemicals have been dried in Büchi Glass Oven B-580 vacuum system before use.

The electrochemical measurements were performed on a potentiostat / galvanostat instrument, in a classical three electrode electrochemical cell. The working electrode was platinum or gold electrode (depending on the system). Ag/AgCl reference electrode was used, having a potential 0.200 V vs. SHE. All the potential values are given with respect of the silver/silver chloride electrode. The EQCM measurements were performed applying a quartz crystal resonator and analyzer, and using platinum- or gold-covered quartz crystal electrode ($f_0=10$ MHz).

Electrochemical impedance spectra were recorded on an SR830 lock-in amplifier. Each recorded impedance spectrum consisted of 45 points at frequency values ranging from 160 Hz to 10 kHz on a logarithmic scale.

UV-Vis spectroscopic measurements were carried out in solutions using a diode array spectrophotometer. The molecular structure of the composites has been investigated by FT-IR measurements. Studies on the surface change of the nanoparticles (adsorption) have been carried out in diffuse reflectance mode. In case of the composites possessing large absorptions photoacoustic (PAS) detection was used.

The XRD pattern of freshly prepared samples was determined in the reflection mode with Cu-K α radiation ($\lambda=0.1542$ nm). The scanning range was between $2\theta=20 - 80$ degrees. Identification of the synthesized iron oxide was based on the position of characteristic peaks in the diffractograms using the JCPDS (Joint Committee on Powder Diffraction Standards) database.

The incorporation of magnetic nanoparticles was proved by transmission electron microscopy (TEM) operating at an acceleration voltage of 100 kV. The morphology of the hybrids was studied by scanning electron microscopy (SEM).

Mössbauer spectra were recorded at room temperature using a conventional constant-acceleration type Mössbauer spectrometer (Ranger). A $^{57}\text{Co}(\text{Rh})$ source of 109 Bq activity was used.

Magnetization measurements were performed using a physical properties measurement system (PPMS) of Quantum Design. Temperature dependence of magnetization was measured between 2 K and 300 K.

The iron-oxide content of the composites was determined by ICP-AAS technique after dissolution of the samples in concentrated sulfuric acid – H₂O₂ mixture (“piranha solution”). For some selected samples, thermogravimetric measurements were performed at a heating rate of 10 °C / min in both oxygen and nitrogen, from room temperature up to 650 °C. EDX spectroscopy (Röntec QX2) was used to obtain direct data for the elementary composition.

2. Summary of new scientific results

T1. Preparation of Poly(3-octyl-thiophene) / γ -Fe₂O₃ nanocomposites

1.1. As a preliminary study, we demonstrated that electrically conducting poly(3-octyl-thiophene) – maghemite nanocomposite can be synthesized not only in aqueous solutions, where magnetic nanoparticles are generally prepared. Oppositely, we transferred maghemite nanoparticles to non-aqueous chloroform solution, where chemical polymerization of thiophene-type monomers can be performed, thus maghemite can be incorporated up to a concentration of 5 mass% (detected by both ICP-AAS and EDX). We proved by PAS-FTIR and UV-Vis measurements that the presence of the nanoparticles does not change the molecular structure (conjugation length, doping state) of the polymer.

1.2. Modification of both short and longer range interactions, related to the supramolecular structure could be detected by XRD and SEM measurements. The built-in nanoparticles form seeds for the deposition of the polymer, leading to a globular, assumingly core-shell structure and a more compact polymer.

1.3. The structural changes can be correlated with both increased π -stack and supramolecular side chain interactions, resulting in advanced electric properties such as an increased conductance and capacity of the composite (20 times larger, compared to the neat polymer).

T2. Chemisorption of thiophene-3-acetic-acid on magnetite nanoparticles

2.1. We prepared magnetite nanoparticles through co-precipitation method, with an average diameter of 12 nm. In order to redisperse the particles in nonaqueous (NB) solution, we covered their surface by TAA, this way, monomers themselves acted as a stabilizer. Based on the modifications in the FT-IR spectrum, we proved that the adsorption is a chemisorption, realized through a chemical interaction between the surface –OH groups of the magnetite nanoparticles and the –COOH groups of the monomers.

T3. Synthesis of Poly(thiophene-3-acetic-acid) / magnetite composites through chemical polymerization

3.1. In order to prepare magnetic iron-oxide / conducting polymer composites, we exploited the above mentioned chemical interaction in an easy and large scale production of the composite by chemical polymerization. XRD and PAS-IR measurements gave evidences on the composite formation.

3.2 The magnetite content was determined by ICP-AES, TGA and Mössbauer spectroscopic methods. This latter gave the opportunity to divide the total iron content between the magnetic component and the residual oxidant (FeCl_3). This way we could estimate the iron-oxide content more accurately. We found that it could be varied by the composition of the polymerization mixture, and can be increased up to more than 20 m/m%.

3.3. Magnetic data obtained from SQUID measurements proved that our composites show superparamagnetic behaviour. It is also demonstrated that magnetic moments depend on the magnetite content of the composites, this way we could tune the magnetic behaviour of our hybrids by the initial synthetic parameters. It is important to point out that according to cyclic voltammetric studies – performed with the casted composites on Pt –, we obtained electrochemically active materials, which fact opens opportunity to use them as a component of magnetically modified electrodes.

T4. Electrochemical synthesis of Poly(thiophene-3-acetic-acid) / magnetite composites

4.1. After redispersing the TAA coated magnetite nanoparticles in nitrobenzene, we carried out the successful electrosynthesis of PTAA- Fe_3O_4 nanocomposite layers. EQCM data acquired during the polymerization clearly showed that the incorporated amount of magnetite nanoparticles increases with the concentration of Fe_3O_4 in the polymerization sol, leading later to a saturation pattern. This limiting value is equal to about 80 m/m % magnetite.

4.2. Cyclic voltammetric results evidenced that the polymer formation depends only on the polymerization charge, and the electrochemical behaviour of the film is not disturbed by the presence of the different amount of iron-oxide.

4.3. The presence of the built-in nanoparticles led to a novel morphology, where an aligned, band-like microstructure showed up, consisting of about 1 μm wide stripes.

T5. The mechanism of magnetite inclusion into Polypyrrole / magnetite thin layers

5.1. We investigated the mechanism of the incorporation of magnetite nanoparticles into polypyrrole, based on the procedure available in the literature. We evidenced the iron-oxalate formation on the nanoparticles surface – as a consequence of the interaction between the nanoparticles and the potassium-tetraoxalate electrolyte – by making diffuse reflectance FT-IR measurements. This surface reaction results in a negative surface charge, enabling the nanoparticles to be incorporated into the polymeric film as part of the charge compensation

during the polymerization. Electrochemical quartz crystal microbalance data indicated the incorporation of 27 m/m% magnetite.

T6. Properties of Polypyrrole / magnetite thin layers, and its catalytic activity towards O₂-reduction

6.1. The electrochemical studies proved that the voltammograms of the polypyrrole / magnetite layers became asymmetric in the presence of oxygen. We proved that the cathodic charge surplus is larger at lower sweep rates, and it is related to O₂-reduction.

6.2. We have shown that under illumination, significantly higher currents can be measured, and that under chrono-amperometric circumstances the photocurrent is the double of the dark current. The more thorough investigations showed that the mechanism of the O₂-reduction is also different under illumination.

6.3. The electrocatalytic decomposition of H₂O₂ (as the intermediate of the O₂-reduction reaction) was also studied, and the composite layers showed 7,5 times larger catalytic activity compared to the neat polypyrrole. Moreover, we proved that the chrono-amperometric currents are linearly proportional with the H₂O₂ concentration, even at very small concentrations, which can be exploited in sensor application.

T7. Adsorption of vitamin B12 on magnetite surface, and its immobilization in Polypyrrole / magnetite / B12 hybrid layers.

7.1. The adsorption of B12 on the magnetite surface was demonstrated by the decrease in absorbance of the vitamin in the supernatant liquid, after B12 has been in contact with magnetite sol overnight. B12 covered magnetite nanoparticles have been incorporated into a conducting polypyrrole through the electropolymerization of pyrrole in the presence of the B12-coated magnetite. EQCM data indicated the incorporation of 15 m/m% B12.

7.2. The electrochemical behaviour of the films unambiguously showed the complex redox activity of the composites, and the current surplus was quantified by the redox capacity of the layers. These data show the doubling of the redox capacity in case of the hybrid material compared to the neat polymer. During the redox transformations the film showed anion-exchanging behaviour, and we also presented the different hydrophobic / hydrophilic character of the composite compared to neat polypyrrole.

4. Scientific publications

Publications related to the scientific topic of the dissertation

1. **C. Janáky, C. Visy:**
Synthesis and characterization of poly(3-octylthiophene)/ γ -Fe₂O₃ nanocomposite -A promising combination of superparamagnetic-thermoelectric-conducting properties
Synthetic Metals, 158 (2008), 1009-1014
IF=1.962
2. **C. Janáky, C. Visy, O. Berkesi, E. Tombácz:**
Conducting polymer based electrode with magnetic behavior: electrochemical synthesis of poly(3-thiophene-acetic-acid) / magnetite nanocomposite thin layers
Journal of Physical Chemistry C, 113 (2009) 1352-1358
IF₂₀₀₈=3.396
3. **C. Janáky, B. Endrődi, A. Hajdú, C. Visy:**
Synthesis and characterization of polypyrrole–magnetite–vitamin B12 hybrid composite electrodes
Journal of Solid State Electrochemistry, 14 (2010) 339-346
IF₂₀₀₈=1.597
4. **C. Janáky, B. Endrődi, K. Kovács, M. Timko, A. Sápi, C. Visy:**
Chemical synthesis of poly(3-thiophene-acetic-acid) / magnetite nanocomposites with tunable magnetic behaviour
Synthetic Metals, 160 (2010) 65-71
IF₂₀₀₈=1.962
5. **C. Janáky, B. Endrődi, O. Berkesi, C. Visy:**
Electrochemical synthesis of polypyrrole / magnetite hybrid modified electrodes for photo-electrocatalytic O₂-reduction
In preparation

Other publications

6. C. Visy, **C. Janáky**, E. Kriván:
Solvation/desolvation during the redox transformation of poly(3-methylthiophene)
Journal of Solid State Electrochemistry, 9 (2005) 330-336
IF=1.158
7. G. Bencsik, **C. Janáky**, E. Krivan, Zs. Lukács, B. Endrodi, C. Visy:
Conducting polymer based multifunctional electrodes
Reaction Kinetics and Catalysis Letters, 96 (2009) 421-428
IF₂₀₀₈=0.610

8. E. Krivan, G. Bencsik, **C. Janáky**, P.S. Tóth, B. Roósz, G. Sós, C. Visy:
Study on the electrodeposition of organic and inorganic thermoelectric materials for composite preparation
 Reaction Kinetics and Catalysis Letters, 96 (2009) 429-436
IF₂₀₀₈=0.610
9. **C. Janáky**, G. Cseh, P.S. Tóth, C. Visy:
Application of classical and new, direct analytical methods for the elucidation of ion movements during the redox transformation of polypyrrole
 Journal of Solid State Electrochemistry, DOI 10.1007/s10008-009-1000-5
IF₂₀₀₈=1.597
10. **C. Janáky**, G. Bencsik, Á. Rácz, C. Visy, NR. de Tacconi, W. Chanmanee, K. Rajeshwar:
Electrochemical Grafting of Poly(3,4-ethylenedioxythiophene) Into a Titanium Dioxide Nanotube Host Network
 Langmuir, submitted for publication

$\Sigma_{IF}=12.892$

Conference lectures and posters

1. **C. Janáky**, C. Visy: Oral
 Studies on solvation/desolvation of poly(3-methyl-thiophene) film by EQCM technique
 2th European Student Conference on Physical, Organic, and Polymer Chemistry, Vienna 2004
2. **C. Janáky**, C. Visy: Oral
 Studies on solvation/desolvation of poly(3-methyl-thiophene) film by EQCM technique
 The 9th International Symposium for Students in Chemistry, Timisoara 2004
3. **C. Janáky**, C. Visy: Oral
 The role of solvent during the preparation of conducting polymers and its participation in the redox transformations
 Frühjahrssymposium, 7th Young Scientists Conference on Chemistry, Berlin 2005
4. **C. Janáky**, C. Visy: Oral
 The role of solvent during the preparation and redox transformation of conducting polymers
 IV. Hungarian Scientific Conference of Vojvodinian Students, Subotica 2005
5. **C. Janáky**, C. Visy: Poster
 Preparation of a poly(3-octylthiophene) / γ -Fe₂O₃ nanocomposite
 Frühjahrssymposium, 8th Young Scientists Conference on Chemistry, Konstanz 2006
6. **C. Visy**, E. Pintér, P. Makra, Z.A. Fekete, **C. Janáky**, G. Bencsik, Á. Patzkó:
 Conducting Polymer Based Transition Metal Containing Composites
 International Workshop on the Electrochemistry of Electroactive Materials, Saint-Petersburg 2006
7. **C. Visy**, I. Csízi, **C. Janáky**, Z. Fekete, G. Bencsik, Á. Patzkó, E. Pintér:
 Nanoscale composites of conducting polymers: characterization and possible applications
 ICSM Meeting, Dublin 2006

8. **C. Janáky**, C. Visy, P. Makra: Oral
Poly(3-octylthiophene)/ Fe₂O₃ nanocomposite: synthesis and characterization
1st European Chemistry Congress, Budapest 2006
9. **C. Visy**, **C. Janáky**, G. Bencsik: Poster
Conducting polymer based nanocomposites: characterization and possible applications
Nanotech Northern Europe, Helsinki, 2007
12. **C. Janáky**, C. Visy: Poster
Preparation of conducting polymer / magnetic iron-oxide nanocomposite materials
Frühjahrssymposium, 9th Young Scientists Conference on Chemistry, Chemnitz 2007
13. E. Kriván, **C. Janáky**, G. Bencsik, **C. Visy**:
Characterization and application possibilities of conducting polymer composites
211th ECS Meeting - Chicago, Illinois, 2007
14. **C. Visy**, E. Kriván, **C. Janáky**, G. Bencsik:
Synthesis and characterization of iron group element compound containing conducting polymer composites
58th ISE Meeting, Banff, 2007
15. **C. Janáky**, G. Bencsik, E. Peintler-Kriván, C. Visy: Poster
Elektromosan vezető összetett anyagok, kombinált tulajdonságok, új lehetőségek
Ipari Kapcsolatok Napja, Szeged, 2007
16. **C. Visy**, E. Kriván, **C. Janáky**, G. Bencsik:
Conducting polymer composites as new electrodes for clean energy technologies
6th Spring Meeting of ISE, Foz do Iguacu, 2008
17. **C. Janáky**, C. Visy: Poster
Preparation of a polythiophene / magnetic iron-oxide nanocomposite
1st International Conference on Functional Nanocoatings, Budapest, 2008
18. **C. Visy**, E. Kriván, **C. Janáky**, G. Bencsik:
Conducting polymer based multifunctional composites
CONPOEX EU6 Meeting, Borovets, 2008
19. **C. Janáky**, C. Visy: Oral
Chemical and electrochemical synthesis of poly(thiophene-3-acetic-acid) – magnetite nanocomposite
59th ISE Meeting, Seville, 2008
20. **C. Janáky**, C. Visy: Poster
Conducting polymer based magnetic nanocomposites – synthesis and characterization -
2nd European Chemistry Congress, Torino, 2008
21. **C. Janáky**, C. Visy: Oral
Magnetic nanocomposites based on conducting polymers – synthesis and characterization
Szeged International Workshop on Advances in Nanoscience (SIWAN), Szeged, 2008

22. G. Bencsik, **C. Janáky**, C. Visy:
Electrochemically synthesized conducting polymer based composite thin layer electrodes with photocatalytic and magnetic behaviour
VI. International Workshop on Electrodeposited Nanostructures, Berndorf, 2008
23. **C. Janáky**, G. Bencsik, E. Kriván, A. Patzkó, E. Pinter, C. Visy:
Conducting polymer based multifunctional nanocomposites
Zing Nanomaterials, Playa del Carmen, 2008
24. G. Cseh, **C. Janáky**, G. Galbács, C. Visy, M. Rodriguez:
Single shot thickness determination of thin layers by LIBS
5th International Conference on LIBS (LIBS 2008), Berlin, 2008
25. **C. Janáky**, B. Endrődi, C. Visy: Poster
Chemical and electrochemical synthesis of conducting polymer based magnetic nanocomposites
Frühjahrssymposium, 11th Young Scientists Conference on Chemistry, Essen, 2009
26. **C. Janáky**, O. Berkesi, E. Tombácz, C. Visy: Poster
Conducting polymer based electrode with magnetic behaviour: electrochemical synthesis of poly(3-thiophene-acetic-acid) / magnetite nanocomposite thin layers
7th ISE Spring Meeting, Szczyrk, 2009
27. **C. Janáky**, G. Bencsik, E. Kriván, Á. Patzkó, E. Pintér, C. Visy:
Multifunctional nanocomposites of conducting polymers
First International Conference on Multifunctional, Hybrid and Nanomaterials, Tours, 2009
28. **C. Janáky**, B. Endrődi, E. Kriván, C. Visy:
Properties of a polypyrrole/magnetite/vitamin B12 hybrid: a conducting polymer based electrode for bioelectrocatalysis
216th ECS Meeting - Vienna, 2009
29. **C. Janáky**, B. Endrődi, C. Visy: Oral
Synthesis, characterization and application of conducting polymer based magnetic electrodes
216th ECS Meeting - Vienna, 2009