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Mechanism of formation of templateless electrogenerated polypyrrole nanostructures.

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Abstract

In the presence of a high concentration of weak-acid anions, such as monohydrogenophosphate which confer to a pyrrole aqueous solution a pH around 9, an ultra thin non-conductive overoxidized polypyrrole film is deposited on the electrode under an anodic polarization. In the same experimental conditions, after addition of perchlorate anions ($C > 0.5$ mM) in the pyrrole solution the electrooxidation of the monomers leads to the synthesis of a superhydrophilic nanostructured conductive polypyrrole film (network of nanofibers or oriented nanowires, 50-120 nm in diameter).

The aim of the present paper is to confirm the mechanism that we have previously proposed and so to explain the spontaneous nanostructuration of the electrogenerated polypyrrole films. We have assumed that this templateless formation of nanostructures is notably due to the oxidation of water with production of hydroxyl radicals and nanobubbles of dioxygen. Due to the fact that pyrrole polymerization is associated to the release of protons, we have first verified that the electrode/solution interfacial pH is compatible with the water oxidation potential. For this purpose, during the monomer oxidation the interfacial pH variation has been monitored using a pH electrode having a flat glass membrane which was covered with a Pt grid used as the working electrode. Secondly, the presence of dioxygen nanobubbles has been indirectly confirmed by rotating the working electrode. Indeed rotation of the electrode allows eliminating the nanobubbles present inside the polypyrrole film. For the highest rotation speed tested (94 rad s^{-1}), a very thin overoxidized film was electrogenerated. Our results are in good agreement with the fact that the nanobubbles protect the PPy film against the action of the hydroxyl radicals which react with the polypyrrole film leading to its overoxidation.

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Keywords

Polypyrrole, nanowires, nanostructures, templateless electrochemical synthesis, interfacial pH, O₂ nanobubbles.

1. Introduction

Among all the conducting organic polymers, polypyrrole (PPy) is one of the most widely used due notably to its biocompatibility, environmental stability and ease of preparation even under nanostructured form. Indeed, polypyrrole nanostructures can be easily synthesized[1],[2],[3] by a chemical or an electrochemical way using templates such as soft-templates[4],[5],[6], hard-templates[7],[8],[9] or wire-templates[1],[2], or without the use of templates[10],[11],[12]. In the last case, polypyrrole nanostructures can be electrogenerated in the presence of a high concentration of weak-acid anions which confer to the pyrrole solution a pH between 6 and 10 and of non-acidic anions such as perchlorate ions.[13],[14],[15],[16],[17],[18] We have shown that for a pyrrole (Py) solution of pH 9, in the presence of low perchlorate concentration, oriented polypyrrole nanowires are obtained whereas for the highest perchlorate concentration, polypyrrole interconnected nanowire networks are electrogenerated (see Fig. 1).[19]

Whatever the route of preparation (chemical or electrochemical), the oxidation of pyrrole leads to the formation of polypyrrole under its oxidized form, the polymer is doped with anions (A^-), according to the following reaction:

where γ stands for the doping level of the polymer, this value ranging between 0.25 and 0.33. It should be noticed that the presence of anions is essential for Py polymerization. Actually it has been shown that the reaction rate of Py polymerization is directly proportional to the anion concentration in the Py solution.[20]

It has been reported that when only anions of weak acids (named weak-acid anions), such as monohydrogenophosphate, acetate, carbonate, monohydrogenocarbonate or tartrate ions, which confer a relatively high pH to the Py solution, are present in a pyrrole aqueous solution the

Figure 1: SEM micrographs (tilt 60°) of PPy nanostructures obtained after polarization at 0.78V for (A) 900 s, (B) 600 s in 0.15 M Py + 0.2 M K₂HPO₄ + (A) 10⁻³ M, (B) 10⁻² M LiClO₄ aqueous solution. Substrates: ITO.

electrooxidation of the monomers leads to a pinhole-free and very thin (about 10-20 nm) non-conductive overoxidized polypyrrole (OPPy) film, under potentiostatic or potentiodynamic conditions.[21, 22],[23] Actually, this overoxidation is indirectly related to the release of protons at the electrode/solution interface during Py oxidation (Reaction 1). Indeed, the protons which are released during Py polymerization are captured by the weak-acid anions. Thus if the current is high, *i.e.* if a lot of protons are released, at a moment a very few or no anions are available at the electrode/solution interface so that the Py oxidation cannot take place anymore. As a high potential is applied, water oxidation occurs leading to the generation of hydroxyl radicals that react with the already deposited PPy film resulting in its overoxidation:

However, when non-acidic anions such as perchlorate are added to a pyrrole solution containing a high concentration of K₂HPO₄ salt, polypyrrole nanowires (NWs) which are surrounded by OPpy are obtained.[10] Under potentiostatic conditions, the length of the NWs is a function of the electrode polarization duration. [10] Actually, this length can be tuned from several nanometers

to a few microns simply by changing the electrode polarization duration. The nanowire length depends linearly on the electrode polarization time. Besides it has been evidenced that the growth of the nanowires does not begin immediately after imposition of the potential but only after about 30 seconds of polarization. Therefore, it has been assumed that at least two main processes take place, one at the beginning of the electrode polarization (until about 30 s) following by the Py polymerization at the nanostructure extremity *i.e.* the growth of the nanowires. SEM observations (Fig. 2) have shown that a very thin homogeneous PPy film is formed before that the nanostructures begin to grow, therefore the nanostructure bases are not directly on the substrate.

Figure 2: Left: Schematic model showing the process of PPy nanowire electrogeneration under potentiostatic conditions. Step A: Electrodeposition of an ultra thin PPy film. Step B: Generation of $\text{OH}^\bullet$ which overoxidize PPy (OPPy) and of O_2 nanobubbles which protect PPy against the action of $\text{OH}^\bullet$. Step C: Growth of the PPy nanowires. Reaction ①: Py oxidation ; Reaction ②: water oxidation. Right: SEM micrograph of PPy deposited at 0.75 V/SCE in 0.15 M Py + 0.2 M K_2HPO_4 + 10^{-3} M LiClO_4 on Au/mica substrate. The Au substrate is visible due to the fact that the polymer film has been removed before SEM observation.

These nanostructured PPy films are conductive and superhydrophilic. XPS analyses have shown that they contain nearly only perchlorate ions as dopant anions. [19] Recently, we have demonstrated the influence of the perchlorate concentration of a pyrrole aqueous solution, which contains a high concentration of monohydrogenophosphate ions (0.2 M), on the electropolymerization process and its effects on the morphology of the films. The influence of the pH of the pyrrole solution was highlighted too.[19] Finally, we have proposed a reaction mechanism which allows to explain the one-step synthesis of such nanostructures without the use of template or of chemical additives. This mechanism is summarized in Fig. 2.[10] It also allows us to explain the shape of the chronoamperometric curves. Briefly, it is composed of three steps (named A, B, C in Fig. 2). The first one is the classical electrodeposition of a thin PPy film associated with a proton release and therefore to a decrease of weak-acidic anion concentration at the electrode/electrolyte interface. The second step, in very short time, concerns the oxidation of water leading in some places to the overoxidation of the polymer formed during the first step, this overoxidation being due to the action of the hydroxyl radicals (reactions 2 and 3), and in other places to the formation of O₂ nanobubbles (reaction 4) that protect the polymer against the action of hydroxyl radicals *i.e.* against overoxidation which leads to a non-conductive polymer. Finally, at the film/solution interface, when the anion concentration begins to increase, due to the anion diffusion from the electrolyte bulk and polymer dedoping (anions are expelled from the polymer when it is overoxidized), PPy nanowires start to grow at the places where O₂ has been formed during step 2.

Since the synthesis mechanism implies water oxidation, it has been verify that the electrode/solution interfacial pH is compatible with this pH dependent reaction. Obviously during Py polymerization (Eq. 1) the interfacial pH should be different from the pH in the bulk of the

solution since protons are released. In order to measure the interfacial pH, the technique initially proposed by Romankiw [24] was used. It consists on the use of a pH electrode having a flat glass membrane. Actually, a thin mesh metallic grid which is used as the working electrode is maintained in contact with the planar membrane of the pH electrode. Therefore, the pH of the small liquid volume contained inside the holes of the grid is measured by the glass electrode.

Actually, two types of experiment were conducted in order to confirm the mechanism of PPy nanostructure formation that we have previously proposed. In the first one, the variation of electrode/electrolyte interfacial pH was studied in order to verify that this pH is compatible with the water oxidation potential ($E = 0.99 - 0.06 \text{ pH V vs. SCE}$, at 25°C). Since, according to our assumption, this reaction is essential for the formation of polypyrrole nanostructures. In the second one, PPy films have been electrogenerated by rotating the working electrode in order to expel the oxygen nanobubbles that protect the film against the action of the hydroxyl radicals *i.e.* against its overoxidation.

2. Experimental

Pyrrole solution was distilled before use. Py solution, K_2HPO_4 and LiClO_4 salts were purchased from Aldrich. All the solutions were prepared with bi-distilled water.

The electrochemical experiments were performed in a classical three-electrode electrochemical cell. A platinum grid was used as counter electrode and a saturated calomel electrode (SCE) as the reference one. The working electrode was either a Pt rotating disk electrode (RDE) ($S = 0.07 \text{ cm}^2$) or a Pt grid for interfacial pH measurement or an ITO substrate for SEM observations. The pyrrole polymerization was conducted under potentiostatic conditions. The potentiostat used was an Autolab PGSTAT30 (Ecochemie).

Figure 3: Optical image of the flat-bottom pH electrode embedded with the Pt grid used as the working electrode, set-up used for the interfacial pH measurements.

After the PPy film electrogeneration, the superhydrophilic character of the films was controlled by the drop test experiment. In this test, a small water droplet is deposited onto the polypyrrole film and the spreading behaviour of the drop is analysed. This test allows detecting the presence of polypyrrole nanostructures as confirmed by the observations done with a field emission gun scanning electron microscope (FEG-SEM), Ultra55 Zeiss, operating at 3 kV.

Interfacial pH measurements were performed following Romankiw's method. The working electrode made of a Pt grid was maintained in contact with the planar glass membrane of the pH electrode[25],[26] by a seal which also allows to delimit the electrode surface in contact with the electrolyte (see Fig. 3). Between two experiments, the Pt grid was flamed to remove the deposited polymer.

3. Results and discussion

3.1 Variation of the interfacial pH during PPy synthesis

Various experiments were conducted to monitor the interfacial pH as a function of the electrode polarization time, of the applied potential and of the anionic composition of the pyrrole solution. The first experiments were performed in a Py solution containing only perchlorate ions as anions. It is well known that in these conditions a compact PPy film having a classical cauliflower-like structure is formed. The initial pH of the Py solution was 6.9. Actually, two experiments were performed: one starting at this pH (Fig 4A) and the other by adjusting the pH to 9.2 (same pH as the 0.2 M K_2HPO_4 solution) before measurement by addition of KOH (Fig 4B). Fig. 4 shows that, as soon as the electrode is polarized at 0.7 or 0.78 V vs. SCE, an anodic current due to Py oxidation appears and the interfacial pH decreases hugely up to acidic values. It has to be noticed that at the same time no change of the bulk electrolyte pH was detected.

Therefore, when only perchlorate anions are present in the Py solution, the anodic current and the interfacial pH are function of the applied potential. The values of interfacial pH (2.7 and 3.35 according to Figs. 4A and 4B, respectively) are in good agreement with the anodic current; the higher the anodic current, the lower the interfacial pH. Taking into account the applied potential at the electrode, at these interfacial pH the water oxidation cannot occur and therefore polypyrrole nanostructures formation is impossible according to the proposed mechanism (Fig. 2). Indeed for pH 2.7 and 3.35, the water oxidation thermodynamic potential is 0.789 and 0.825 V vs. SCE (at 25°C), respectively.

Similar experiments were conducted in a Py solution containing 0.2 M K_2HPO_4 and small amounts of LiClO_4 *i.e.* under conditions for which nanostructured PPy films are electrogenerated.[10, 19] Figures 4C and 4D show the results obtained in the presence of 10^{-3} M and 10^{-2} M of perchlorate ions, respectively. Due to the presence of HPO_4^{2-} , the initial pH is

Figure 4: Electrode/solution interfacial pH (left) and anodic current (right) vs. time at a Pt grid electrode under open circuit potential (beginning and end) and under an applied potential (A), (C) and (D) 0.78 V/SCE, (B) 0.70 V/SCE, in 0.15 M pyrrole aqueous solution containing (A) and (B) 0.2 M LiClO₄, (C) 0.2 M K₂HPO₄ + 10⁻³ M LiClO₄, (D) 0.2 M K₂HPO₄ + 10⁻² M LiClO₄.

equivalent for both experiments and close to 9.2. At this pH, the water oxidation potential is 0.44 V vs. SCE, at 25 °C. Therefore it is much lower than the applied potential (0.78 V vs. SCE). As already observed, when the electrode is polarized at 0.78 V/SCE, an anodic current appears. However, contrary to the case in the presence of solely perchlorate ions in the Py solution only a small change in the interfacial pH (see Fig 4) can be observed. This small variation is consistent

Figure 5 : Interfacial pH vs. anodic charge passed through a Pt grid electrode polarized at (a) 0.70 V/SCE, (b), (c) and (d) 0.78 V/SCE in 0.15 M pyrrole aqueous solution containing (a) and (b) 0.2 M LiClO₄, (c) 0.2 M K₂HPO₄ + 10⁻³ M LiClO₄, (d) 0.2 M K₂HPO₄ + 10⁻² M LiClO₄ (Data from Fig. 4).

with the presence in the Py solution of weak-acid anions (HPO₄²⁻) which capture the protons released during the oxidation of the pyrrole monomers (reaction 1).

Figure 5 shows clearly that, for a given anodic charge, the interfacial pH is function of the applied potential for a given Py solution and of the anionic composition of the Py solution for a given applied potential. For example, for an anodic charge of 0.25 C the interfacial pH could vary from 2.65 to 8.73.

In the presence of HPO₄²⁻, the interfacial pH variation which is function of the anodic current, remains low compared to the previous results even for relatively high perchlorate ions concentration in the Py solution (see Fig 4D). This low interfacial pH decrease is consistent with the water oxidation that will allow the formation of polypyrrole nanostructures according to the proposed mechanism schematized in Fig. 2.

Figure 6: SEM micrograph of PPy nanowires generated at 0.75 V/SCE for 240 s in 0.15 M Py + 0.2 M K_2HPO_4 + 10^{-3} M $LiClO_4$. The arrows indicated some nanowires (the largest ones) which are partly hollow.

Through these experiments, it has been shown that, using 0.2 M weak-acid anions solutions in the presence of less than 0.01 M perchlorate anions, templateless polypyrrole nanostructures are obtained. The interfacial pH, which range between 8-9, is compatible with water oxidation. The probable role of oxygen nanobubbles in the formation of PPy nanostructures is supported by the SEM micrograph shown in Fig. 6. Indeed, it can be seen that some nanowires, among the largest ones, are partly hollow, pointing out the effect of gas nanobubbles.

Besides, one can notice that the shape of the chronoamperometric curves shown in Figs. 4C and 4D (red lines) is in good agreement with the nanowire growth process proposed herein. Indeed, the initial current is high (leading to a high release of protons) and decreases very rapidly until a low value which is attributed to water oxidation. Then, after about 30 seconds, the anodic current slightly increases due to the growth of the PPy nanostructures (see also curve a, Fig. 7). In all cases, the final anodic current is very lower than the initial one. This is notably due to the fact that the conducting surface (top of the nanowires) is smaller than the initial one which is actually partially insulating due to the presence of OPPy around the nanowires.

Figure 7: Current vs. time at a Pt rotating disk electrode ($S = 0.07 \text{ cm}^2$) polarized at 0.78 V vs. SCE in 0.15 M Py + 0.2 M K_2HPO_4 + 5 mM LiClO_4 aqueous solution. Electrode rotation rate: (a) 0, (b) 10.5 rad s^{-1} , (c) 31.4 rad s^{-1} , (d) 62.8 rad s^{-1} , (e) 94.2 rad s^{-1} .

3.2 Influence of the electrode rotation speed

After verifying the thermodynamic conditions for a possible dioxygen evolution, the ability to O_2 nanobubbles after being generated by electrolysis to stay at the electrode surface was checked mechanically by rotating the electrode. It is implicitly assumed that these nanobubbles would have a sufficient life time during the polymer film synthesis (see Fig. 2, step B). Recent progresses in interfacial physics devoted to wetting of solid surfaces have evidenced the role played by nanoscopic gaseous domains that are formed at the solid/liquid interface.[6, 27-29] As clearly stated by the authors, a full understanding about these phenomena is not obtained yet. However the most surprising and well established conclusion was that these nanodomains, instead of dissolving in a very short time, persist for a sufficiently long time to be considered as stable to bulk dissolution.

The chronoamperograms recorded during polypyrrole films synthesized in a Py solution containing 0.2 M K_2HPO_4 and 5.10^{-3} M $LiClO_4$ are shown in Fig. 7 for different electrode rotation rates. For the lower rotation speed, as expected for an electrochemical process which is at least limited by diffusion, the anodic current increases in comparison with the one obtained with a motionless electrode. However for the highest speeds tested the anodic current decreases. This is confirmed by the variation of the anodic charge with the rotation speed of the working electrode for different polypyrrole films synthesized in the presence of monohydrogenophosphate ions and various concentrations of perchlorates in the Py solution as shown in Fig. 8.

From Figs. 7 and 8, for all the Py solutions containing 0.2 M monohydrogenophosphate ions, we can clearly observe the influence of the rotation speed of the working electrode. Under these conditions, the anodic current and the anodic charge change. For the highest rotation speeds, overoxidized polypyrrole films are finally synthesized. Figure 8 confirms that when the rotation speed of the working electrode increases, the anodic charge of the synthesized polypyrrole films

Figure 8: Anodic charge vs. electrode rotation speed after 600 s of polarization at 0.78 V vs. SCE in 0.15 M Py + 0.2 M K_2HPO_4 + (●) 1 mM, (▲) 5 mM (data from Fig. 7), (◆) 10 mM $LiClO_4$ aqueous solution. () in 0.15 M Py + 0.2 M $LiClO_4$ aqueous solution. The black open squares indicate the superhydrophilic PPy films i.e. the films nanostructured.*

decreases. Taking into account the proposed mechanism (Fig. 2), it is assumed that the rotation of the working electrode leads to the expulsion of the dioxygen nanobubbles that locally protect the polypyrrole film against its overoxidation by the hydroxyl radicals. Finally, because locally the polymer film is no more protected against the action of the radicals it is entirely overoxidized. The chronoamperograms recorded for the higher rotation rates used (Fig. 7, curves d and e) and the very low anodic charges (less than 1 mC ; see Fig. 8) confirm that a very thin non-conductive OPPy film is obtained.

For polypyrrole film synthesized in the presence of only pyrrole monomers and perchlorate ions (Fig. 8, star scatters), no influence of the electrode rotation speed have been observed. Indeed whatever the electrode rotation rate, the anodic charge of the synthesized polypyrrole film remains high (about 670 mC after 600 s of polarization at 0.78 V vs. SCE), a thick non-superhydrophilic PPy film is formed on the electrode surface. It can be concluded that, in these conditions, there is a kinetic limitation of the growth of the film and not a diffusional limitation (pyrrole molecules and anions are in excess). Therefore this finding emphasizes that the Py polymerization process is not modified by the rotation of the electrode.

Figure 9 shows the dependence of the anodic charge after 600 s of polarization at 0.78 V/SCE with the perchlorate ion concentration of the Py solution containing 0.2 M K_2HPO_4 for polypyrrole films synthesized without and with rotation (62.8 rad s^{-1}) of the working electrode.

One can notice that the rotation of the working electrode leads to a shift of the kinetics of formation of superhydrophilic polypyrrole nanostructures since overoxidized polypyrrole films are formed for perchlorate ion concentrations less than 5.10^{-3} M whereas without rotation this threshold is in the range of 8.10^{-4} M of perchlorate ions. For example, an anodic charge about 20

Figure 9: Anodic charge vs. perchlorate concentration of the Py solution. Charge passed through a Pt RDE polarized at 0.78 V vs. SCE for 600 s. Electrolyte: 0.15 M Py + 0.2 M K₂HPO₄ + LiClO₄. Electrode rotation speed: (●) 0, (■) 62.8 rad s⁻¹. The black rectangles indicate the PPy films which are superhydrophilic i.e. which are nanostructured

mC is obtained using a perchlorate concentration of 2 mM without electrode rotation whereas this concentration is 5 times higher for an electrode rotation rate of 62.8 rad s⁻¹.

Obviously, this finding does not appear consistent with the fact that the contribution of the anion at the electrode increases with the electrode rotation speed. It can be explained assuming that the dioxygen nanobubbles which locally protect the polypyrrole film against the action of the hydroxyl radicals are expelled mechanically when the electrode rotation rate is high enough. The removal of the dioxygen nanobubbles leads to the total overoxidation of the polypyrrole film formed at the very beginning of the electrode polarization (step A, Fig. 2). It has been shown by Hui *et al.* that a two-step process implying nanobubbles allowed to electrogenerate nanoporous PPy films.[6] First a cathodic polarization was applied to generate H₂ nanobubbles followed by an anodic polarization to oxidize Py monomers leading to the deposit the polymer around the nanobubbles stayed at the electrode surface. In our conditions, the polymer synthesis is

performed by applying only one anodic potential and the O₂ nanobubbles are located inside the PPy film formed during the first step of the synthesis (step A, Fig. 2). These nanobubbles do not mask the substrate avoiding the polymer growth as in Ref. 6, but protect the polymer against the action of the hydroxyl radicals and therefore allow it to retain its electrical conductivity since it is not overoxidized.

4. Conclusions

The experiments reported herein confirm that water oxidation with production of hydroxyl radical and dioxygen nanobubbles should take place for the templateless electrogeneration of polypyrrole nanostructures. Actually, this electrosynthesis route is based on two points: (i) the low interfacial concentration of anions in order to limit the Py oxidation in favour of water oxidation; (ii) an interfacial pH sufficiently high to allow water oxidation at the PPy polymerization potential.

The influence of the working electrode rotation speed has been studied and allowed to emphasize the presence of dioxygen nanobubbles which prevent the fully overoxidation of the polypyrrole synthesized film by preserving some circular conductive zones on which the polypyrrole nanostructures will be able to grow.

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REFERENCES

- [1] Z. Yin, Q. Zheng, Controlled Synthesis and Energy Applications of One-Dimensional Conducting Polymer Nanostructures: An Overview, *Advanced Energy Materials*, 2 (2012) 179-218.
- [2] X. Lu, W. Zhang, C. Wang, T.-C. Wen, Y. Wei, One-dimensional conducting polymer nanocomposites: Synthesis, properties and applications, *Progress in Polymer Science*, 36 (2011) 671-712.
- [3] Y.Z. Long, M.M. Li, C.Z. Gu, M.X. Wan, J.L. Duvail, Z.W. Liu, Z.Y. Fan, Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers, *Progress in Polymer Science*, 36 (2011) 1415-1442.
- [4] C.J. Brinker, Y.F. Lu, A. Sellinger, H.Y. Fan, Evaporation-induced self-assembly: Nanostructures made easy, *Advanced Materials*, 11 (1999) 579-585.
- [5] P. Anilkumar, M. Jayakannan, A Novel Supramolecular Organogel Nanotubular Template Approach for Conducting Nanomaterials, *Journal of Physical Chemistry B*, 114 (2010) 728-736.
- [6] F. Hui, B. Li, P. He, J. Hu, Y. Fang, Electrochemical fabrication of nanoporous polypyrrole film on HOPG using nanobubbles as templates, *Electrochemistry Communications*, 11 (2009) 639-642.
- [7] C.R. Martin, Membrane-based synthesis of nanomaterials, *Chemistry of Materials*, 8 (1996) 1739-1746.
- [8] J.I. Lee, S.H. Cho, S.-M. Park, J.K. Kim, J.K. Kim, J.-W. Yu, Y.C. Kim, T.P. Russell, Highly aligned ultrahigh density arrays of conducting polymer nanorods using block copolymer templates, *Nano Letters*, 8 (2008) 2315-2320.
- [9] L. Pan, H. Qiu, C. Dou, Y. Li, L. Pu, J. Xu, Y. Shi, Conducting Polymer Nanostructures: Template Synthesis and Applications in Energy Storage, *International Journal of Molecular Sciences*, 11 (2010) 2636-2657.
- [10] C. Debieuvre-Chouvy, Template-free one-step electrochemical formation of polypyrrole nanowire array, *Electrochemistry Communications*, 11 (2009) 298-301.
- [11] M. Wan, A template-free method towards conducting polymer nanostructures, *Advanced Materials*, 20 (2008) 2926-2932.
- [12] I.S. Chronakis, S. Grapenson, A. Jakob, Conductive polypyrrole nanofibers via electrospinning: Electrical and morphological properties, *Polymer*, 47 (2006) 1597-1603.
- [13] K. Ghanbari, S.Z. Bathaie, M.F. Mousavi, Electrochemically fabricated polypyrrole nanofiber-modified electrode as a new electrochemical DNA biosensor, *Biosensors & Bioelectronics*, 23 (2008) 1825-1831.

- [14] J. Huang, K. Wang, Z. Wei, Conducting polymer nanowire arrays with enhanced electrochemical performance, *Journal of Materials Chemistry*, 20 (2010) 1117-1121.
- [15] J. Liao, C. Ning, Z. Yin, G. Tan, S. Huang, Z. Zhou, J. Chen, H. Pan, Nanostructured Conducting Polymers as Intelligent Implant Surface: Fabricated on Biomedical Titanium with a Potential-Induced Reversible Switch in Wettability, *Chemphyschem*, 14 (2013) 3891-3894.
- [16] Z. Xia, S. Wang, L. Jiang, H. Sun, G. Sun, Controllable synthesis of vertically aligned polypyrrole nanowires as advanced electrode support for fuel cells, *Journal of Power Sources*, 256 (2014) 125-132.
- [17] J. Wang, Y.L. Xu, F. Yan, J.B. Zhu, J.P. Wang, Template-free prepared micro/nanostructured polypyrrole with ultrafast charging/discharging rate and long cycle life, *Journal of Power Sources*, 196 (2011) 2373-2379.
- [18] J. Zang, C.M. Li, S.-J. Bao, X. Cui, Q. Bao, C.Q. Sun, Template-free electrochemical synthesis of superhydrophilic polypyrrole nanofiber network, *Macromolecules*, 41 (2008) 7053-7057.
- [19] A. Fakhry, F. Pillier, C. Debiemme-Chouvy, Templateless electrogeneration of polypyrrole nanostructures: impact of the anionic composition and pH of the monomer solution, *Journal of Materials Chemistry A*, 2 (2014) 9859-9865.
- [20] Y.F. Li, Effect of anion concentration on the kinetics of electrochemical polymerization of pyrrole, *Journal of Electroanalytical Chemistry*, 433 (1997) 181-186.
- [21] C. Debiemme-Chouvy, T.T.M. Tran, An insight into the overoxidation of polypyrrole materials, *Electrochemistry Communications*, 10 (2008) 947-950.
- [22] C. Debiemme-Chouvy, One-step electrochemical synthesis of a very thin overoxidized polypyrrole film, *Electrochemical and Solid State Letters*, 10 (2007) E24-E26.
- [23] A. Fakhry, H. Cachet, C. Debiemme-Chouvy, Electrochemical characterisations of ultra thin overoxidized polypyrrole films obtained by one-step electrosynthesis, *Journal of the Electrochemical Society*, 160 (2013) D465-D470.
- [24] H. Deligianni, L.T. Romankiw, In situ surface pH measurement during electrolysis using a rotating pH electrode, *Ibm Journal of Research and Development*, 37 (1993) 85-95.
- [25] C. Deslouis, I. Frateur, G. Maurin, B. Tribollet, Interfacial pH measurement during the reduction of dissolved oxygen in a submerged impinging jet cell, *Journal of Applied Electrochemistry*, 27 (1997) 482-492.
- [26] M. Nobial, O. Devos, O.R. Mattos, B. Tribollet, The nitrate reduction process: A way for increasing interfacial pH, *Journal of Electroanalytical Chemistry*, 600 (2007) 87-94.

- [27] L. Zhang, Y. Zhang, X. Zhang, Z. Li, G. Shen, M. Ye, C. Fan, H. Fang, J. Hu, Electrochemically controlled formation and growth of hydrogen nanobubbles, *Langmuir*, 22 (2006) 8109-8113.
- [28] J.R.T. Seddon, D. Lohse, Nanobubbles and micropancakes: gaseous domains on immersed substrates, *Journal of Physics Condensed Matter*, 23 (2011) 133001.
- [29] H. Tarabkova, P. Janda, Nanobubble assisted nanopatterning utilized for ex situ identification of surface nanobubbles, *Journal of Physics Condensed Matter*, 25 (2013) 184001.