Electrochemical atomic force microscopy: In situ monitoring of electrochemical processes

Melania Reggente, Daniele Passeri, Marco Rossi, Emanuela Tamburri, and Maria Letizia Terranova

View Online   Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Electrochemical Atomic Force Microscopy: In Situ Monitoring of Electrochemical Processes

Melania Reggente[1,a)], Daniele Passeri[1], Marco Rossi[1,2], Emanuela Tamburri[3] and Maria Letizia Terranova[3]

[1]*Department of Basic and Applied Sciences for Engineering, SAPIENZA University of Rome, Via A. Scarpa 16, 00161, Rome, Italy*
[2]*Research Center for Nanotechnology applied to Engineering of SAPIENZA University of Rome (CNIS), Piazzale A. Moro 5, 00185, Rome, Italy*
[3]*Department of Chemical Science and Technology - Minimalab, University of Rome "Tor Vergata", Via della Ricerca Scientifica, 00133, Rome, Italy*

[a)]Corresponding author: melania.reggente@uniroma1.it

Abstract. The in-situ electrodeposition of polyaniline (PANI), one of the most attractive conducting polymers (CP), has been monitored performing electrochemical atomic force microscopy (EC-AFM) experiments. The electropolymerization of PANI on a Pt working electrode has been observed performing cyclic voltammetry experiments and controlling the evolution of current flowing through the electrode surface, together with a standard AFM image. The working principle and the potentialities of this emerging technique are briefly reviewed and factors limiting the studying of the in-situ electrosynthesis of organic compounds discussed.

INTRODUCTION

Many technological processes (such as, electrorefining, electroplanting and all those involved in the energy storage systems) result from electrochemical oxidation and reduction reactions occurring at an electrified solid surface immersed in a suitable electrolyte solution, generally known as solid-liquid interface [1–3]. These electrochemical (EC) reactions strongly depend on: (*i*) the reactants mass transport from the bulk solution to the charged surface and (*ii*) the rate of the electron transfer between the electrolytes and the metallic surface [4]. If the former is the slower phenomenon involved in the reaction the system is diffusion limited, otherwise the system is called charged limited [4, 5]. Since these two phenomena are strictly interdependent, knowing the relationships existing between the surface reactivity and the morphology of the solid-liquid interface is of crucial importance in order to obtain an efficient control of the electrochemical process. Electrochemical atomic force microscopy (EC-AFM) is an AFM based technique, which allows the in situ analysis of the electrochemical reactions occurring at the solid-liquid interfaces at the first early stages of the process [6]. Thus, it allows probing, in real-time and in-situ, the evolution of a conductive surface immersed in an electrolytic solution under a specific applied potential. In EC-AFM, a standard AFM apparatus is equipped with a three-electrode electrochemical cell, whose working electrode is the sample surface where the process takes place, and a potentiostat. Thus, both the AFM tip and the sample are immersed in an electrolytic solution allowing the in-situ imaging of the electrochemical reactions [6, 7]. Depending on the tip polarization, two different configurations are possible: (*i*) a passive or (*ii*) an active probe configuration. In the former, using an unbiased AFM probe, the in-situ surface morphology evolution is monitored [6]. Instead, the latter allows the detection of the surface electroactivity by applying at the tip a specific potential [8, 9].

In this work, first we review some interesting applications of this emerging and fascinating technique and then we show our preliminary results regarding the in situ electrodeposition of polyaniline (PANI), one of the most attractive conducting polymers (CP) [10–15].
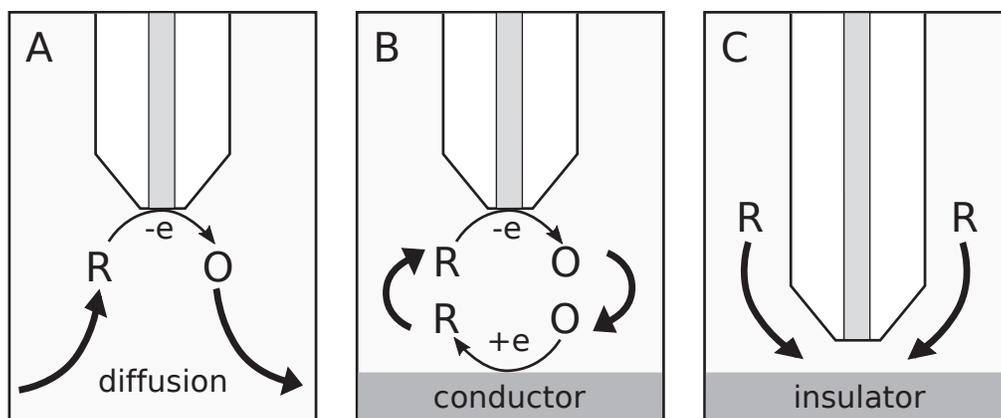
FIGURE 1. Sketch of the EC-AFM set-up using an active probe configuration (A) and of the reaction occurring at the tip-electrode if it is scanned over a conductor surface (B) or an insulator substrate (C).

TECHNIQUES

Active probe configuration

In the active probe configuration, the tip apex is substituted with a submicrometer electrode, which enables the simultaneous measurement of the surface morphology (i.e., height image) and its electrochemical reactivity (i.e., current image) [9]. Both topographic and current images are achieved. Topographical maps are obtained as in a standard tapping mode AFM experiment. Instead, surface reactivity maps are acquired by applying a specific voltage on the tip, keeping a constant tip-substrate distance during the scanning. In this way, the electrolyte species diffuse toward the surface of the electrode where they can be either reduced or oxidized (Figure 1a). Firstly, a specific voltage is applied to the tip and, secondly, the current flowing through it is measured. Since this current is sensitive to the fate of reactant at the substrate surface, the current images are influenced by the substrate nature [9]. Referring to Figure 1b, in conductive substrates, the oxidized species (O), electrochemically generated at the tip surface by an oxidation reaction, diffuse towards the substrate where they can be transformed into reduced species (R). Whereas, in insulator substrates, the R species, oxidized into O species at the begging of the reaction, cannot react with the surface and the current, detected by the tip at a small distance from the surface, decays exponentially (Figure 1c).

The application of this configuration concerns: (*i*) the transport mechanism through membranes and (*ii*) dissolution process and (*iii*) surface reactivity. In particular, EC-AFM in active probe configuration has been employed to characterize the performance of proton-based polymer membranes, used as solid electrolytes in fuel cells [16, 17]. These membranes must permit the migration of hydrogen ions (protons), simultaneously preventing the electrons flow. Indeed, the efficiency of the fuel cell heavily depends on the protonic conductivity of the membranes and on its degree of hydration. In this context, Nafion, a special perfluorosulfonate polymer, is the most studied and employed material, thanks to its good ionic conductivity and chemical stability. The ionic conductivity of Nafion is strictly related to the density of active ion channels. EC-AFM allowed studying the characteristics of protonic polymer membranes by simulating the operating conditions of a fuel cell: the membrane has been deposited on a platinum layer that acted as an anode and a coated platinum tip, used as cathode, was held in contact with the surface of the membrane during scanning. In this way, a current image of the proton current flowing between the tip and the anode, has been obtained together with the surface topography. These studies have shown that EC-AFM is a valid technique for the in situ characterization of polymeric membranes with proton exchange highlighting the presence of a non-uniform distribution of active proton channels on the membranes [16, 17].

Moreover, it has been shown that an electrochemical process, localized in proximity of an AFM can be exploited to locally etch thin metallic films or deposited metallic and polymeric structures on different substrates, performing the so called EC nanolitography (ENL) [18–20]. The bias is directly applied on the AFM tip in order to initiate local EC reaction and perform nanolithography, which is a nanofabrication process aiming at the development of patterned surfaces [19]. To this aim, Pt stripes have been deposited on Si substrates, scanning a positively biased H_2PtCl_6-coated tip across a Si surface [20]. Furthermore, Maynor et al. demonstrated the electrochemical deposition
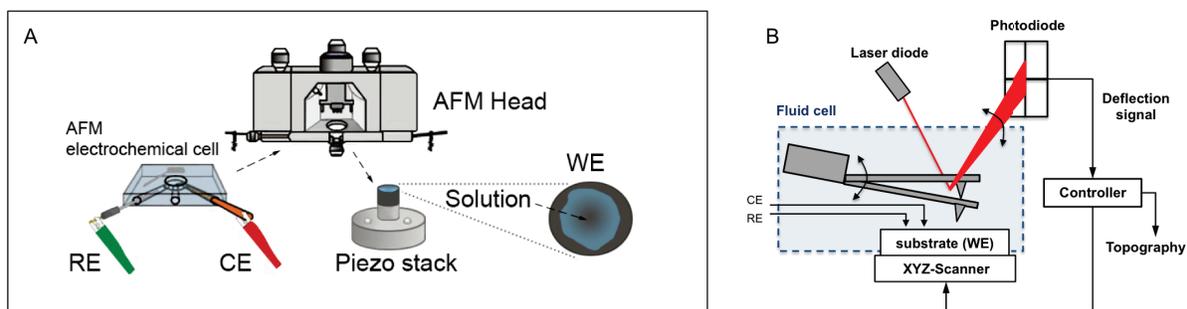
FIGURE 2. Sketch of a multimode AFM head (Bruker) equipped with its three electrodes electrochemical cell (A). Representation of the passive probe EC-AFM set-up (B).

of poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires on semiconducting and insulating substrates by applying a negative tip bias [21]. Instead, by applying intermittent voltage pulses on a tip immersed in a 1mM H_2SO_4 electrolytic solution, stripes and rings have been etched both on copper and cobalt films [19].

Passive probe configuration

The passive probe configuration uses an unbiased tip to elucidate structural and morphological changes of the sample surface as a function of time, applied potential and current flow through the sample itself. The latter acts as the working electrode (WE) of a three-electrodes cell with which the AFM head is equipped. The EC reactions occurring at the WE are monitored performing Cyclic Voltammetry (CV) experiments, measuring the current flowing through the WE surface. Simultaneously, standard AFM imaging is employed to follow the evolution of the WE morphology. In this way the topography changes are recorded by sweeping the potential applied at the WE.

This configuration has been employed to study different phenomena occurring at the solid-liquid interface such as: ions adsorption, electrodeposition, corrosion and volume changes in electroactive polymers [7]. In particular, by monitoring the surface morphology of diamond electrodes during the ferro-ferricianide redox reaction, it has been shown that diamonds electrodes do not undergo degradation during redox reactions [22]. When applied to conducting polymers, which are considered as "intelligent materials" able to react to external stimuli, most of the works related to the detection of their topographical evolution, caused by the transition from the doped to the undoped state [7, 23–25]. Indeed, they are generally synthesized by an electrochemical oxidation of the monomer, which induces a cationic character on the polymer backbone. For charge compensation, anions (i.e., dopants) from the electrolytic solution are entrapment in the polymer structure. Thus, by varying the oxidation state (i.e., the doping level), volume changes of the polymer are provoked. In particular, if the considered dopant is a small mobile anion, the volume decreases upon reduction causing a polymer contraction; whereas, if the dopant is a large and immobile anion, the volume of the polymer expands. This reversible volume change is attractive for actuator applications, such as the fabrication of artificial muscles (actuators) and the design of scaffolds for the nervous tissue regeneration. Indeed, they can provide both mechanical and electrical stimuli during nerve and muscle tissue regeneration [7]. In this context, EC-AFM has been proposed as a technique able to directly visualize and quantify the dynamic actuation (volume changes) of a conducting polymer at the nanometer scale as a function of the applied potential. In particular, the dynamic actuation of ultrathin polypyrrole (PPy) films doped with polystyrene sulfonate (PSS) [26] and dodecylbenzenesulfonate (DBS) [24] have been studied with EC-AFM performing cyclic voltammogram experiments while the surface morphologies were recorded disabling the slow scan direction (i.e., measuring the polymer thickness variation always on the same line).

Another interesting process is the electrodeposition that allows coating conducive substrates by giving desired properties, such as: (*i*) wear resistance; (*ii*) corrosion protection or (*iii*) decorative purposes [27]. In this technique, an electrical current is used to reduce cations of a desired material onto a conductive substrate. EC-AFM allows probing in-situ the variations of the substrate's surface as a function of time, applied potential and reagents concentrations. Several materials, such as copper [27], nickel [28] and hydroxyapatite [29] have been electrodeposited and in-situ studied with EC-AFM. However, there is still a lack of studies concerning the in-situ deposition of organic materials because of their compliant nature which makes challenging the real-time monitoring of their electrosynthesis [23].
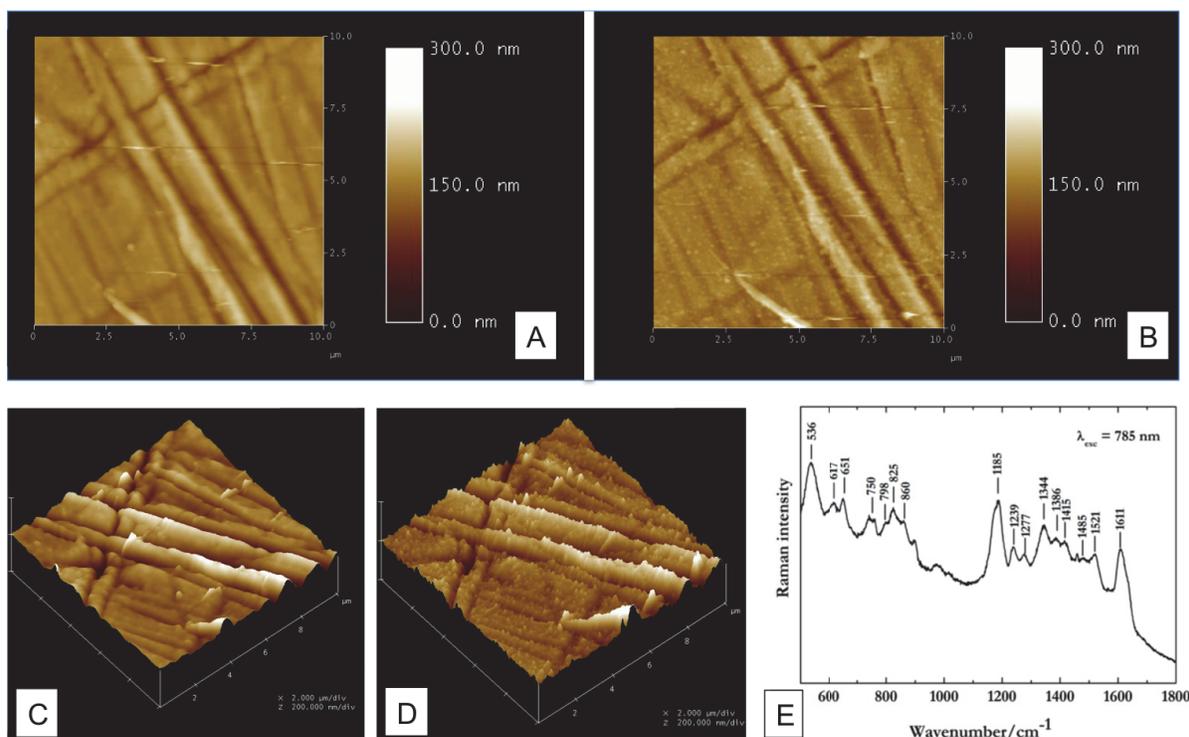
FIGURE 3. Pt surface topography at the beginning of the PANI electrodeposition reaction (A). AFM topography of PANI deposits on Pt after 20 min of electrosyntesis performed in H_2SO_4 (B). 3D images reconstruction of the Pt surface at the beginning of the electrosyntesis (C) and after 20 min (D). Raman spectrum of the deposited PANI.

EXPERIMENTAL

In situ EC-AFM observations were performed using an AFM system (Multimode, Bruker Inc.) equipped with a three electrode electrochemical cell (see Figure 2b). The WE was a Pt foil placed on the bottom of the cell; the reference electrode (RE) was an Ag/AgCl microelectrode and the counter electrode (CE) was a coiled Pt wire with a diameter of 0.25 mm. The PANI electropolymerization was carried out performing cyclic voltammetry experiments (by sweeping the potential between -0.2 V and +1.0 V with a scan rate of 50 mV/s), in a 1 mM aniline dissolved in 5 mM H_2SO_4 aqueous solution. Simultaneously, topographic images were carried out in tapping mode using an unbiased tip (SCANASYST-FLUID, Bruker Inc.) with a nominal spring constant of 0.7 N/m. The scanning rate was set to 0.6 Hz. Moreover, we performed ex situ measurements of the deposited material at different distances from the region where the tip was located. An AFM system (Dimension Icon, Bruker Inc.) equipped with standard silicon tip (RTESP, Bruker Inc.) were employed and all the images were recorded in air at3 room conditions.

RESULTS

The AFM tip scanned the Pt surface while the electrodeposition of the monomer occured. At the beginning of the electrosyntesis, the AFM image displays the typical features of Pt surface characterized by deep scratches and smooth areas (Figure 3a). Figure 3b reveals deposits of PANI on Pt substrate after 20 min of electrosyntesis. Whereas, Figure 3c and Figure 3d, display the corresponding 3D topographies reconstruction. In particular, after 20 min of deposition the sample topography show the presence of PANI nuclei (Figure 3d). Raman spectroscopy was used to characterize the oxidation state of the deposited polymer. The spectrum, reported in Figure 3e, reveals the signals of the semioxidation state of the deposited polyaniline confirming its successful deposition. Despite several scanning probe microscopies have been used to study ex situ the initial growth mechanism of elecrtrodeposited materials, a lack of information concerns their in situ monitoring. Indeed, as far as we know, even if the copper and nickel electrodeposi-
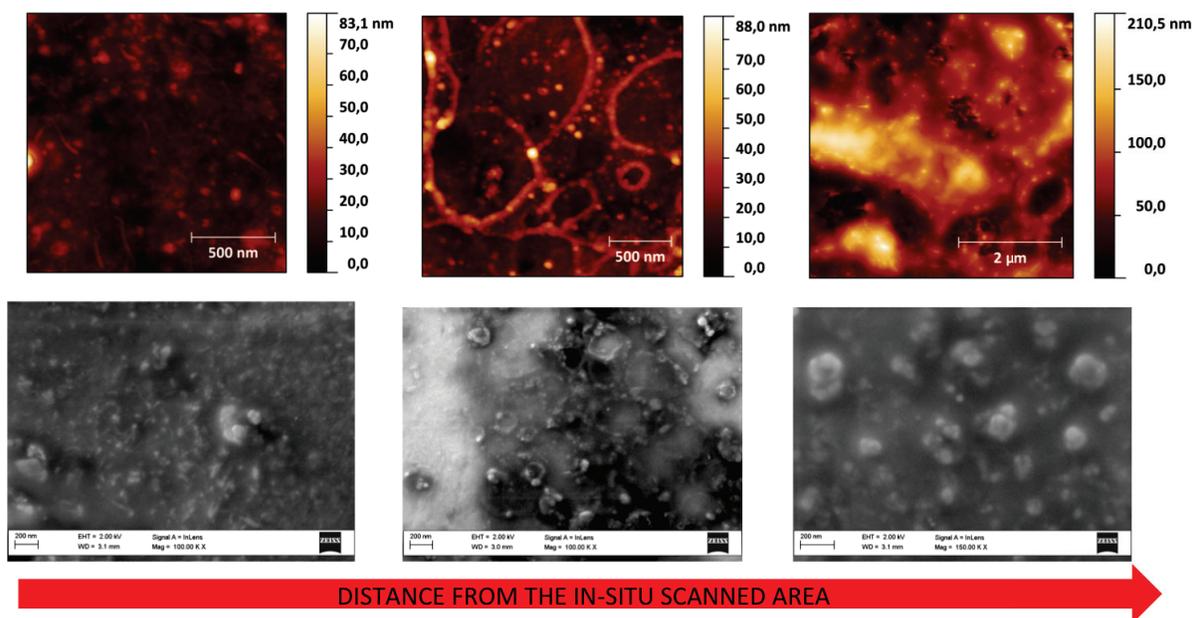
FIGURE 4. Top: SEM micrographs of the PANI deposits; Bottom: ex-situ AFM topographies. All of them have been registered increasing the distance from the area where scanned by the AFM during the EC-AFM experiments.

tion has been in real-time monitored [27, 28], conductive polymers have been deposited by moving the tip away from the sample surface (i.e., stopping the scanning) and the first polymer nuclei have been imaged after few seconds of reaction [23]. Thus, in order to verify if in our configuration the presence of the tip affected the deposition process, ex situ AFM measurements and scanning electron microscopy (SEM) analysis have been performed to investigate the sample surface in different areas of the working electrode. As highlighted in Figure 4, increasing the distance from the in situ scanned area, the deposited PANI results more compact. Indeed, in the region where the tip was located we detected isolated agglomerates of polymer; whereas, moving away from this area, a continuous film has been deposited, suggesting that the polymer preferentially grown far away the scanned area. This is probably induced by the presence of the scanning tip which can both limit the diffusion of the reactants and remove the organic compounds freshly deposited.

CONCLUSION

EC-AFM measurement has been used to monitor in-situ electrodeposition of PANI on Pt substrates. Ex-situ analysis of the deposits have shown that the polymer is preferentially deposited in areas not perturbed by the presence of the AFM tip. This result suggests that microscope parameters (such as the pressure exerted by the cantilever and its stiffness) must be optimized to not limiting the diffusion of the reactants in a way to allow the in-situ monitoring of the polymer electrosynthesis.

REFERENCES

[1]   G. G. Botte, The Electrochemical Society Interface **23**, 49–55 (2014).
[2]   N. Perez *et al.*, *Electrochemistry and corrosion science*, Vol. 412 (Springer, 2004).
[3]   M. Inaba, S.-K. Jeong, and Z. Ogumi, The Electrochemical Society Interface **20**, 55–59 (2011).
[4]   J. Wang, *Analytical electrochemistry* (John Wiley & Sons, 2006).
[5]   J. H. Bae, J.-H. Han, and T. D. Chung, Physical Chemistry Chemical Physics **14**, 448–463 (2012).
[6]   A. A. Gewirth and B. K. Niece, Chemical reviews **97**, 1129–1162 (1997).
[7]   A. Eftekhari, *Nanostructured conductive polymers* (John Wiley & Sons, 2011).

[8]   C. E. Gardner and J. V. Macpherson, Atomic force microscopy probes go electrochemical, 2002.

[9]   A. J. Wain, D. Cox, S. Zhou, and A. Turnbull, Electrochemistry Communications **13**, 78–81 (2011).

[10] E. Tamburri, S. Orlanducci, V. Guglielmotti, G. Reina, M. Rossi, and M. L. Terranova, Polymer **52**, 5001–5008 (2011).

[11] E. Tamburri, V. Guglielmotti, S. Orlanducci, M. L. Terranova, D. Sordi, D. Passeri, R. Matassa, and M. Rossi, Polymer **53**, 4045–4053 (2012).

[12] E. Tamburri, V. Guglielmotti, R. Matassa, S. Orlanducci, S. Gay, G. Reina, M. L. Terranova, D. Passeri, and M. Rossi, Journal of Materials Chemistry C **2**, 3703–3716 (2014).

[13] J. Stejskal, M. Trchová, P. Bober, P. Humpolíček, V. Kašpárková, I. Sapurina, M. A. Shishov, and M. Varga, Encyclopedia of Polymer Science and Technology (2015).

[14] D. Passeri, A. Biagioni, M. Rossi, E. Tamburri, and M. Terranova, European Polymer Journal **49**, 991–998 (2013).

[15] D. Passeri, E. Tamburri, M. L. Terranova, and M. Rossi, Nanoscale **7**, 14358–14367 (2015).

[16] E. Aleksandrova, R. Hiesgen, D. Eberhard, K. A. Friedrich, T. Kaz, and E. Roduner, ChemPhysChem **8**, 519–522 (2007).

[17] E. Aleksandrova, R. Hiesgen, K. A. Friedrich, and E. Roduner, Physical Chemistry Chemical Physics **9**, 2735–2743 (2007).

[18] X. N. Xie, H. Chung, C. Sow, and A. Wee, Materials Science and Engineering: R: Reports **54**, 1–48 (2006).

[19] O. De Abril, A. Gündel, F. Maroun, P. Allongue, and R. Schuster, Nanotechnology **19**, p. 325301 (2008).

[20] Y. Li, B. W. Maynor, and J. Liu, Journal of the American Chemical Society **123**, 2105–2106 (2001).

[21] B. W. Maynor, S. F. Filocamo, M. W. Grinstaff, and J. Liu, Journal of the American Chemical Society **124**, 522–523 (2002).

[22] E. Tamburri, M. Anjellari, A. Valguarnera, S. Orlanducci, M. L. Terranova, M. Reggente, D. Passeri, and M. Rossi, "Strategies for fabrication of innovative and highly biocompatible diamond electrodes," in *Nanotechnology (IEEE-NANO), 2015 IEEE 15th International Conference on* (IEEE, 2015), pp. 979–982.

[23] M. F. Suárez and R. G. Compton, Journal of Electroanalytical Chemistry **462**, 211–221 (1999).

[24] E. Smela and N. Gadegaard, The Journal of Physical Chemistry B **105**, 9395–9405 (2001).

[25] P. R. Singh, S. Mahajan, S. Rajwade, and A. Contractor, "Morphological changes with electrode potential in microtubules and nanowires of polyaniline: An in-situ ec-afm study," in *Physics of Semiconductor Devices, 2007. IWPSD 2007. International Workshop on* (IEEE, 2007), pp. 548–551.

[26] M. J. Higgins, S. T. McGovern, and G. G. Wallace, Langmuir **25**, 3627–3633 (2009).

[27] D. Grujicic and B. Pesic, Electrochimica Acta **47**, 2901–2912 (2002).

[28] D. Grujicic and B. Pesic, Electrochimica Acta **51**, 2678–2690 (2006).

[29] N. Eliaz and M. Eliyahu, Journal of Biomedical Materials Research Part A **80**, 621–634 (2007).

[30] T. A. Skotheim, *Handbook of conducting polymers* (CRC press, 1997).

[31] D. E. Tallman, G. Spinks, A. Dominis, and G. G. Wallace, Journal of Solid State Electrochemistry **6**, 73–84 (2002).