

Electrochemistry of Layer-by-Layer Films: a review

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The use of nanostructured films to modify electrochemical electrodes has allowed a whole host of new systems/devices to be fabricated, with properties that may be tuned upon synergistic interactions between the film components. Films produced with the Layer-by-Layer (LbL) technique, in particular, have opened up the way for new approaches in electrochromism, electrocatalysis, bioelectrochemistry and electroanalysis, for organic and inorganic-organic hybrid nanoarchitectures may be achieved. In addition to the fabrication of novel, optimized materials, with the LbL method fundamental processes such as charge transfer mechanisms involving biomolecules and nanoparticles can be investigated at the molecular level. In this paper we highlight the recent trends in the electrochemistry of LbL films, with emphasis on their promising technological applications in sensing/biosensing and electrochromic devices.

Keywords: Layer-by-Layer, nanostructured films, modified electrodes, biological molecules, electrochemistry.

1. Introduction

The layer-by-layer (LbL) method [1] has become the prime choice for fabrication of nanostructured films in which synergy between distinct materials may be achieved in a straightforward, low-cost manner. With the LbL technique a wide diversity of materials may be employed [2], and film fabrication is performed under mild conditions, which is particularly important for preserving activity of biomolecules [3-83]. Among such materials are those with electroactive properties, which prompted researchers to employ LbL films for various applications, including electrochromism [84-108], catalysis [109-134], electrochemical sensing and biosensing [3-83], among others [135-234]. Significantly, the LbL method has also lent itself for investigation of fundamental

studies in electrochemistry, as in the use of the charge transport mechanisms and redox mediator immobilization [182-224].

In this paper, we provide an overview of recent advances in the electrochemistry of LbL films. After commenting upon the processes of film adsorption in the LbL approach in Section 2, we discuss new concepts of charge transport mechanisms in the LbL films in Section 3. Also provided is a table listing the types of electrochemical studies and associated references. We then chose – among the many possible applications suggested in the literature – a few topics in which the control of molecular architecture inherent in the LbL method is exploited. Accordingly, Section 4 discusses hybrid films with electrochromic properties, while the fabrication of electrodes for catalysis is addressed in Section 5. Because one of the main features of LbL films is the ability to have immobilized biomolecules with preserved activity, we emphasize the strategies employed in biosensing and electrochemical sensors in Section 6. Finally, before the Conclusions in Section 8, we discuss recent proposals to use the LbL approach in incorporating redox mediators that can not only improve sensing ability but also tune electrochemical properties of several systems.

2. The LbL adsorption process

The control of specific properties at the molecular level has been achieved for a number of supramolecular systems through self-organization concepts. The self-assembly of organic, layered heterostructures was pioneered by Sagiv and coworkers [236], who produced layered films via covalent adsorption of molecules with specific functional groups [236,237] onto a solid substrate. This strategy requires chemical affinity between the molecules to be adsorbed and the previously deposited layer. Although these self-assembled multilayers are remarkably stable and have been exploited in a number of applications [238,239], the choice of molecules is limited due to the need for chemical affinity. A more versatile approach is the LbL method introduced by Decher and collaborators [240,241], suitable for fabrication of layered heterostructures where a fine control over specific properties is required. The LbL technique was first applied to assemble oppositely charged polyelectrolytes, being rapidly extended to other systems such as polymeric nanocrystals [242,243], metal and semiconductor nanoparticles [244,245] and dendrimers [246]. Also noteworthy is the use of the LbL method for immobilizing biological components such as proteins, enzymes, DNA, cell membranes and viruses [247-250]. Applications of LbL films have been suggested for optics and optoelectronics [251], drug delivery [252] and electrochemistry.

The fundamental concepts and mechanisms involved in the LbL technique have been detailed in a series of papers (see for instance [1,253]). In most cases adsorption in LbL films is governed by electrostatic interactions between species bearing opposite charges, but secondary interactions have also been shown to be important [254-258]. The LbL technique is versatile with regard to the substrates that may be used, which include hydrophilic and hydrophobic glass, mica, silicon, metals, quartz, and polymers [258,257]. In addition, LbL films may be deposited directly onto colloidal suspensions [259-261]. A schematic diagram illustrating the LbL technique is shown in figure 1. The sequential multilayer deposition can be carried out by immersing the substrate into the cationic and anionic dipping solutions, alternately. After deposition of each layer the substrate is immersed into the

washing solution and dried under a nitrogen/air flow. The roughness, thickness and porosity of the film can be controlled at the molecular level upon adjusting experimental parameters such as pH, ionic strength and polyelectrolyte concentration.

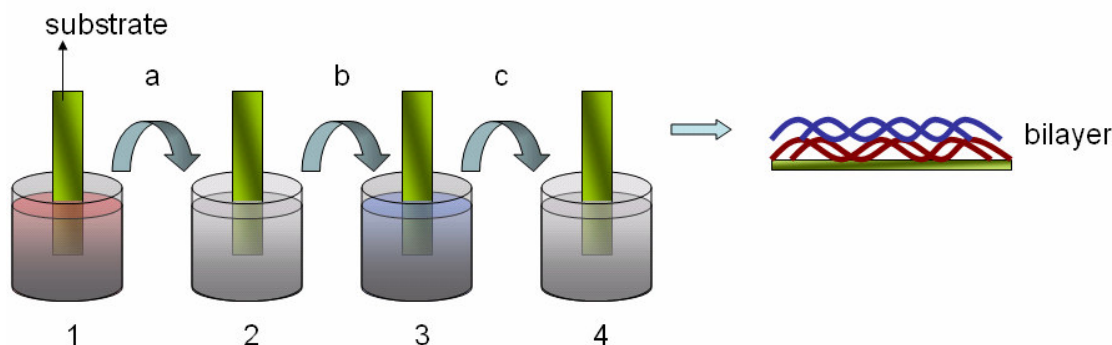


Figure 1. Schematic fabrication of a 1-bilayer LbL film. A solid substrate, bearing for example negative charges, is initially immersed in the polycationic solution (1). In the following step (a), the excess of molecules can be removed by immersing the substrate in the washing solution (2). The substrate containing the cationic layer is subsequently (b) immersed in the anionic polyelectrolyte solution (3). The molecules not effectively attached can be removed (c) in the washing solution (4).

3. Charge transport mechanisms

Among the non-conventional charge transport mechanisms recently described to explain phenomena occurring in LbL films, an important contribution came from Schlenoff's group, who studied LbL films with polyelectrolyte multilayers containing electrochemically active units [184,188,208]. Some important features were highlighted in their work: first, when the distance between a redox active layer and the electrode is varied by interposing non-electrochemically active layer pairs, the material within the redox active layer can be distributed over a distance of several layers, in this case 2.5 layer pairs. The electroactivity of the topmost layer can be determined through Cyclic Voltammetry (CV). According to Schlenoff's studies, the electron transport is facilitated because alternating polyelectrolyte layers are highly interpenetrating, and at least four layer pairs are required to fully insulate one redox active layer from another. In this case, no salt ions were detected in multilayers. Another point in Schlenoff's findings was that the redox active material is electrochemically addressable throughout the multilayer via electron hopping between neighboring sites, according to the scheme in Figure 2.

This concept opens up the way for manipulating new redox mediators and redox active molecules at the supramolecular scale, using the LbL approach. For example, synergy among different layers may be exploited to yield electrochromic and catalytic materials [84-131]. If hopping of electrons and non-salt ions occurs, the LbL films behave as an ion-exchange membrane. Control over membrane properties is interesting for innumerable applications in electrochemistry, such as those where transport of charge is limited by diffusion. The electroactive behavior between adjacent layers in

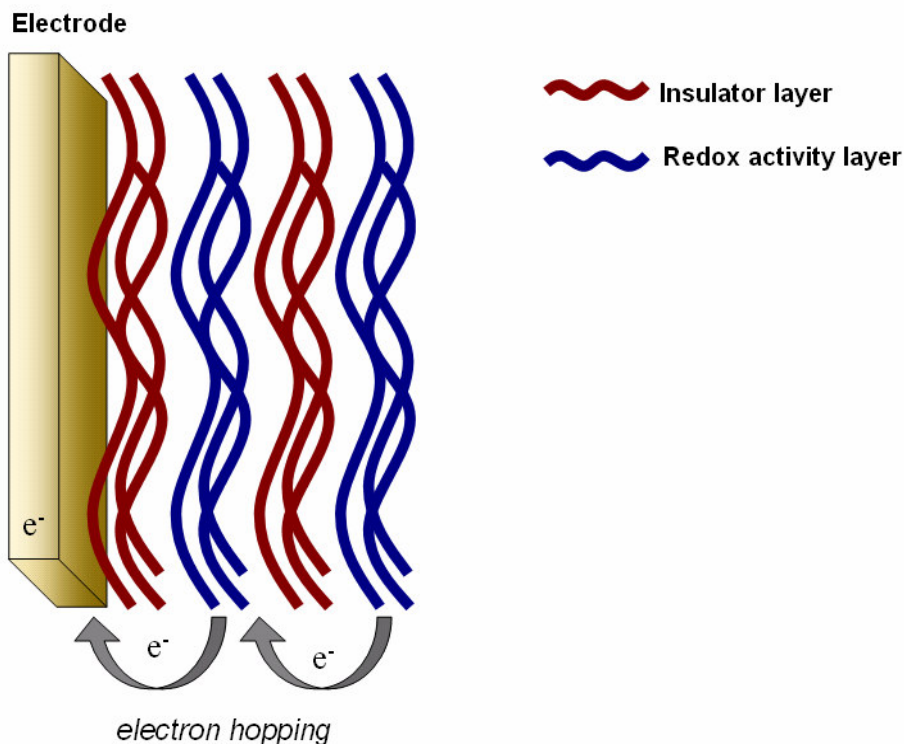


Figure 2. Diagram illustrating the insulator/redox activity in the multilayer structure: According to Schlenoff et al [184], the redox active material in the multilayer is electrochemically addressable via electron hopping between neighboring sites. Figure idealized from ref. 184.

LbL films is an important feature to understand the electrochemical properties [193,195,199]. Table 1 summarizes the most relevant topics regarding the electrochemistry of multilayered systems:

Table 1 - Important studies in electrochemistry of LbL films

Subject of Investigation	References
Electrochemistry of ultrathin organic film (1996)	185
Redox polyelectrolytes (1997)	184
Electroactive self-assembled multilayer / dyes molecules (1997)	186
Electrostatically bound redox couples – gold electrode (1997)	187
Electroactive ordered multilayer and redox-active polyelectrolyte (1997-1998)	187-191
Liquid/liquid electrochemical interfaces / polypeptides (1999)	190
Permeability and stability of layered polyelectrolytes (2000)	193
Electron-transfer between adjacent layers (2000)	195
Electron-transfer and selective redox reactions (2001)	199

<i>Continue</i>	Subject of Investigation	References
	Selectivity in layer-by-layer (2002)	202
	Redox driven swelling of layer-by-layer films / enzymes (2002)	203
	Phthalocyanine-containing multilayers for photovoltaic applications (2002)	204
	Redox polyelectrolytes and gold nanoparticles (2003)	206
	Ion transport through polyelectrolytes (2004)	213
	Polyelectrolyte hollow capsules functionalized for electron transfer (2004)	216
	Selective transport of ions and molecules through LbL membranes (2005)	221
	Ion exchange at the electrode/electrolyte interface (2005)	230

4. Electrochromic compounds in LbL modified electrodes

Optically active multilayers represent an important field in LbL films due to their potential applications in photonics and fabrication of organic light-emitting-diode displays. Electrochromic molecules have been used with different purposes, especially for studies of high-contrast electrochromism, electroluminescent diodes, waveguide spectroelectrochemical characterization, semitransparent thin films and photosensitive multilayers [94-107]. Using a creative concept of multilayer combination, DeLongchamp and co-workers [84] combined two electrochromic polymer composites, namely poly(hexyl viologen) (PXV) and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:SPS) colloid. The charge-trapping mechanism could be evaluated with the electrochemical processes involving multilayers, as shown in Figure 3. This new approach consisted of a “dual electrochromic” composite with the polycation and polyanion being both cathodically coloring electrochromic species, which led to a high-contrast electrochromic film.

Using the LbL method to combine inorganic and organic compounds, Huguenin et al. [124,137] studied the electrochemical and electrochromic properties of nanoarchitectures of V_2O_5 /chitosan and V_2O_5 alternated with a mixture of poly(ethylene oxide) (PEO) and chitosan. From results on multilayers of PEO/ V_2O_5 , the number of electrochemically active V_2O_5 sites was estimated, with a pronounced effect from PEO being observed in the migration/diffusion process, according to cyclic voltammetry and impedance spectroscopy data. V_2O_5 alternated with a blend of PEO and chitosan showed high electrochemical performance due to a large number of electrochemically-active sites. The charge transport was enhanced in this type of film when lithium was used as electrolyte, which makes the films candidates for charge storage and electrochromic nanodevices.

LbL films of porphyrins and phthalocyanines have also been investigated with regard to their electrochemical properties. Due to specific properties such as semiconductivity, well-defined redox activity and high thermal stability, metallic phthalocyanines are used in electrochemistry, nonlinear optics, optical memories, toxic vapour sensors, organic solar cells, secondary batteries,

microelectronics, gas sensing, and modified electrodes for catalysis [262-265]. Highly-stable modified electrodes containing metallic phthalocyanines, viz. iron tetrasulfonated phthalocyanine (FeTsPc), can be assembled using chitosan as cationic polyelectrolyte (Fig. 4a). Chitosan has been proven suitable for electrochemical studies of LbL films for not affecting the Faradaic current appreciably. For example, chitosan/FeTsPc modified ITO electrodes exhibited high electrochemical stability [262], preserving the voltammetric signal after several cycles (Fig. 4b). The anodic peak current varied linearly with the scan rate, which indicates that the peak current was due to charge transport in the chitosan/FeTsPc film.

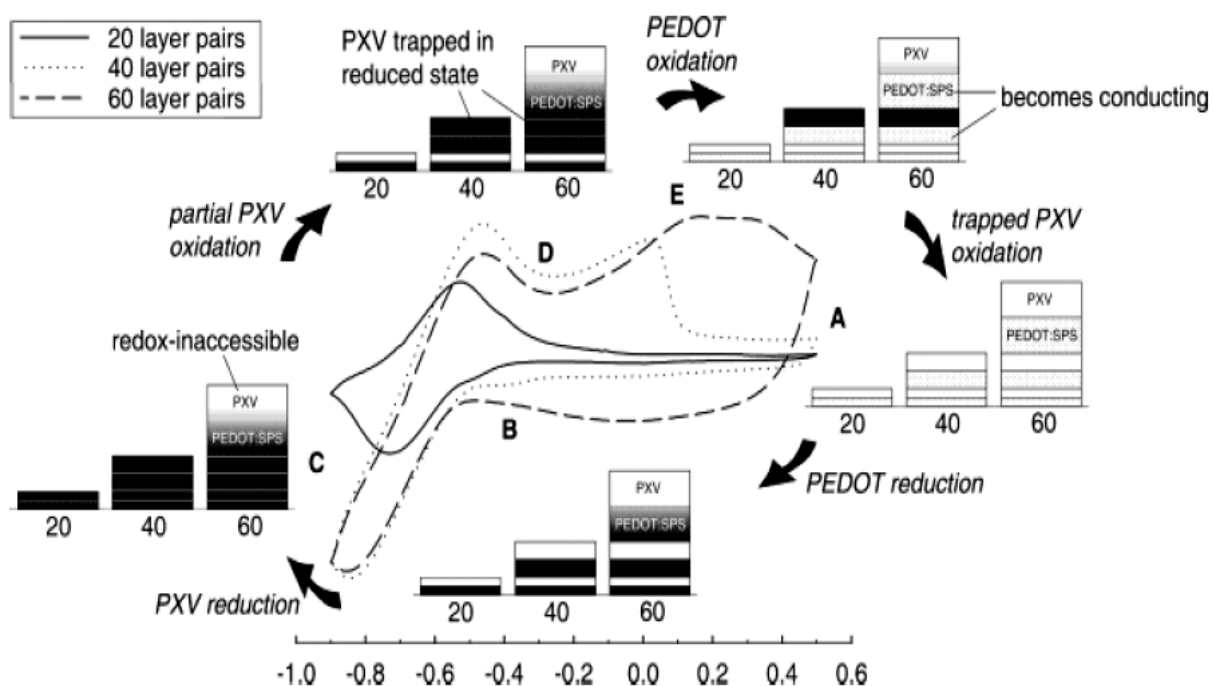


Figure 3. Charge-trapping mechanism proposed by DeLongchamp et al. (from ref. 84, with kind permission of ACS Publications). Depicted are cyclic voltammograms of PXV/PEDOT:SPS films. Illustrations of predicted states of the films at different points on the CV curves accompany the voltammograms. In these drawings, white color indicates oxidized film and black color indicates reduced film. More details can be found in reference 84.

Because electrodes prepared with LbL films may exhibit high electrochemical stability, use could be made of absorption spectroscopy in the visible range and electrochemistry to estimate the energy level diagram for dye molecules. For example, the gap energy (E_g), ionization potential (IP) and electronic affinity (EA) for phthalocyanines could be determined using the electrode shown in Fig. 4 [262]. The onset potentials (E') of the LbL films were estimated from the intersection between the two slopes drawn at the rising oxidation (or reduction) current and background current in the cyclic voltammograms. The oxidative potential was directly related to IP of the electrochemically active

phthalocyanine, while E_g and EA were obtained from the UV-vis spectra and cyclic voltammograms, respectively. Also interesting was to learn through the energy diagrams that LbL films from chitosan/FeTsPc and chitosan/NiTsPc were similar [262].

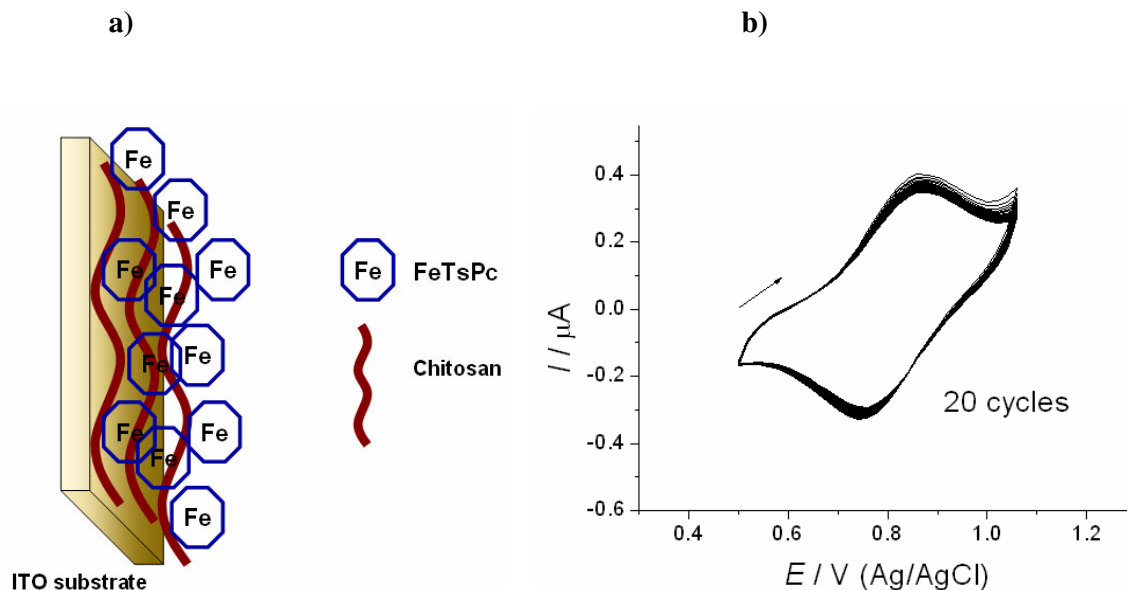


Figure 4. a) Idealized structure of ITO modified electrodes containing tetrasulfonated phthalocyanine (FeTsPc) using chitosan as cationic polyelectrolyte. b) Voltammograms with 20 cycles for 15-bilayer chitosan/FeTsPc films onto ITO. Electrolyte: HCl (pH=3.0). Scan rate: 50 mV s^{-1} . Figure from ref. 262 with kind permission of Electrochemical Science Group (ESG).

5. Dendrimer-based LbL films for catalysis

LbL films have been increasingly used in catalytic studies owing to the control over important parameters such as film thickness and roughness. For example, Abdelrahman et al. [149] demonstrated that three-dimensional multilayers of Au nanoparticles (AuNP) self-assembled onto a gold electrode are more effective for oxygen reduction than bare gold electrodes. The AuNP modified electrode displayed a well-defined wave for oxygen reduction at -0.12 V , i.e. 100 mV less negative than for the polycrystalline Au electrode. Furthermore, a number of studies regarding the catalytic activity in LbL films have been carried out using dendrimer-encapsulated nanoparticles [122, 266-268].

Dendrimers are polymers with special features, namely monodispersity and hyperbranched topology with terminal groups that may be modified through surface chemistry. With such characteristics, they serve as templates for nanoparticle growth and a number of other applications. Polyamidoamine (PAMAM) dendrimers, for example, have been used in catalysts, sensors, drug delivery and surface immobilization [122]. Crook and collaborators employed new synthetic routes to produce metallic nanoparticles embedded in PAMAM molecules, which behaved as nanoreactors [269-272]. Gold nanoparticles with 1-2-nm diameter could be obtained [269], while the PAMAM-Pt system was used as catalyst for electroreduction of oxygen [271]. A further advantage in using

dendrimers is in identifying materials with distinct electrocatalytic behavior toward methanol oxidation. Indeed, Crespilho et al. [122] produced LbL films of PAMAM dendrimers incorporating platinum nanoparticles alternated with poly(vinylsulfonic acid) (PVS), which displayed unusual electrochemical properties. These are illustrated in the voltammograms of Figure 6, from which one infers that the LbL films are fully tolerant to methanol oxidation for potentials below 1.0 V. These methanol-tolerant electrodes hold great promise for methanol fuel cells, since methanol crossover through the membrane is one of the most important drawbacks of direct-methanol fuel cells.

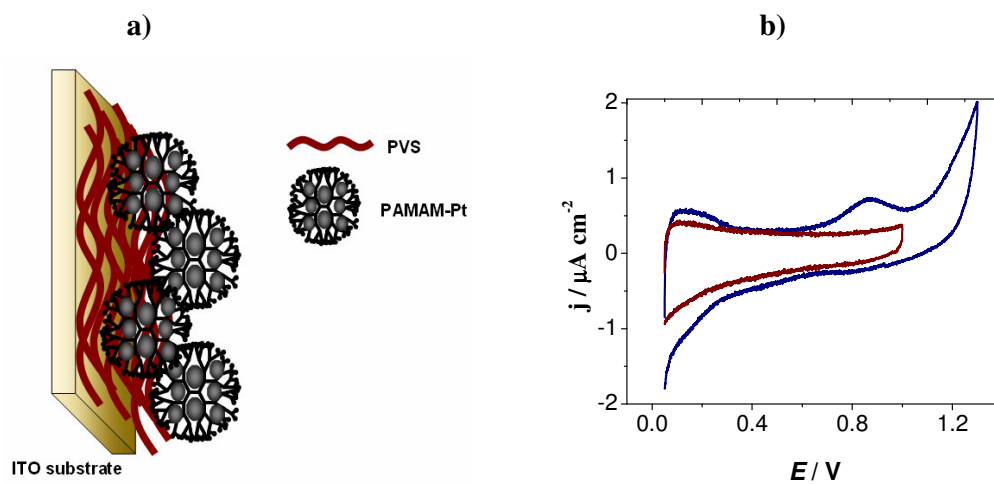


Figure 5. a) Idealized structure of PVS/PAMAM-Pt LbL films. b) Cyclic voltammograms (after several cycles) for a 10-bilayer Pt-PAMAM/PVS LbL film adsorbed on ITO, in a sulfuric acid solution (pH 1) with 1 mol L^{-1} methanol in the solution. The voltammogram in red was recorded up to 1.0 V and shows no methanol current peak. Methanol oxidation occurs when the same electrode was cycled at potentials of 1.3 V (blue-color line). *Figure from ref. 122 with kind permission of Elsevier.*

6. Immobilization of biomolecules and electrochemical sensors

One of the main challenges in the use of biological films or nanostructured films containing biomolecules is the preservation of the bioactivity, particularly because these films are used in their dry state. In this context, the LbL method has been proven excellent for immobilization of biomolecules with preserved activity for long periods because film fabrication is performed under mild conditions and one can choose various materials as templates or scaffolds [3-83]. Just to illustrate the suitability of the LbL method, one may mention that tens of proteins and enzymes have been successfully immobilized by different research groups (see a review in ref. 273). An obvious application of immobilized biomolecules is in biosensing, for their capability of molecular recognition may lead to highly-sensitive, selective biosensors [273]. In the following paragraphs we shall describe several sensors and biosensors made with LbL films.

Naturally-occurring humic acids (HAs) have been incorporated into LbL films, with HA layers alternated with layers of a cationic polyelectrolyte. Galeska et al. [34] immobilized HA in LbL films

used as semipermeable membranes for electrochemical sensing of glucose. The growth of these films depended strongly on pH and ionic strength of HA solutions, which correlated with the degree of ionization of the carboxyl groups and neutralization-induced surface spreading. LbL films of HA and poly(allylamine hydrochloride) (PAH) were deposited onto ITO electrodes and used as modified electrodes for detecting pentachlorophenol (PCP) [274]. One important characteristic of these films was its smoothness, with average roughness varying from 0.8 to 2 nm. The HA/PAH films displayed electroactivity and could be used to detect pesticides, as illustrated in Figure 6 for PCP. The sensitivity was very high, with a detection limit of 1.6×10^{-9} mol L⁻¹. It is worth noting that in this concentration the PCP oxidation peak was not observed with a bare ITO electrode. Indeed, the presence of HA molecules improved adsorption of PCP at the electrode surface, and enhanced the electron transfer between PCP and the electrode [274].

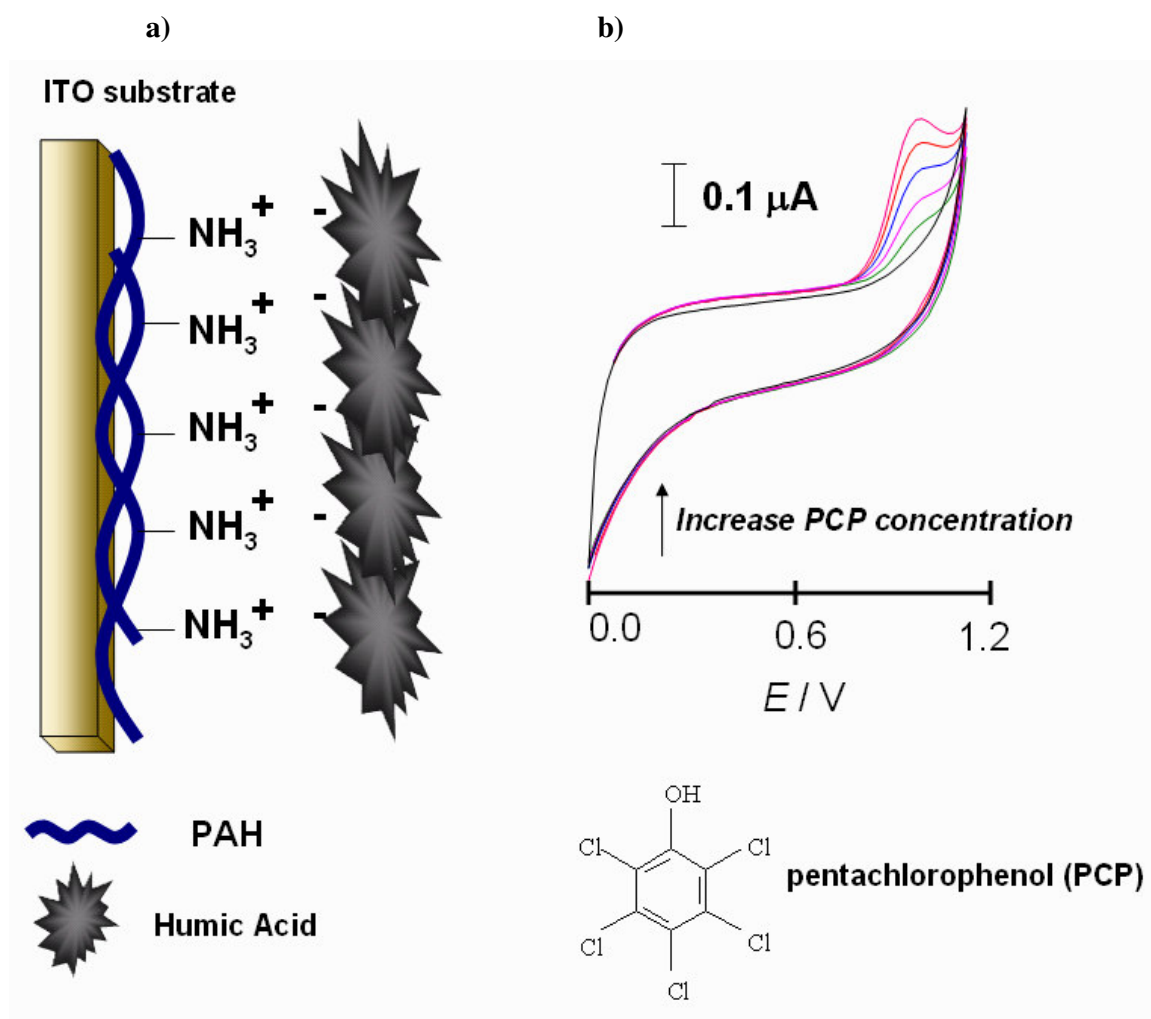


Figure 6. a) Schematic fabrication of LbL films comprising humic acid (HA) and poly(allylamine hydrochloride) (PAH). b) Electrochemical response of an ITO-(PAH/HA)₆ film obtained in aqueous solution containing different concentrations of PCP (from ref. 273, with kind permission of ACS Publications). The oxidation peak shows a linear dependence with the amount of PCP in the electrolytic solution. Electrolyte: NaCl 0.5 mol.L⁻¹ (pH=4.0); scan rate: 50 mV s⁻¹.

Amperometric biosensors made of LbL films of horseradish peroxidase (HRP) on a thiol-modified gold surface have been used by Yang et al. to detect phenolic compounds in the micromolar range [5]. The HRP sensor had sensitivity of $48.91 \mu\text{mol L}^{-1} \text{ nA}$, comparable to other electrodes and a very fast response time, with 95% of the maximum response being attained in only 2 s, which is attributed to the nanostructured nature of the LbL film. Hybrid materials with novel electrochemical properties have been prepared using biological structures immobilized onto electrodes surface. For example, the size effect of polystyrene (PS) latex beads on the electrochemical and electrocatalytic activity of LbL PS-protein/PSS films was investigated by Sun and Hu [81,110,120]. Using PS beads of different diameters as the cores, and adsorbed hemoglobin (Hb) or myoglobin (Mb) as the shells, core-shell PS-protein particles were fabricated. The electrochemical and electrocatalytic activity of the proteins at these electrodes were influenced by the size of PS beads.

The multilayer growth in LbL films has been studied for negatively charged Au nanoparticles and positively charged Mb on electrode surfaces [4]. One important point in electrochemistry of Mb at (Au/Mb) $_n$ film is that electrodes can be used to electrocatalyze the reduction of oxygen and hydrogen peroxide. In addition, the LbL films can exhibit high biocompatibility between Au nanoparticles and adsorbed Mb. The electrochemical and electrocatalytic properties may be strongly affected by the size of the Au nanoparticles. Using a different approach, negatively charged Hb or Mb and positively charged poly(diallyldimethylammonium) (PDDA) could be adsorbed on nanoparticles surface such as CaCO_3 nanoparticles, to form core-shell CaCO_3 -[PDDA/(protein/PDDA)] ([protein-m]) nanoclusters (Figure 7). According to Liu and Hu [3], protein/PSS and protein/ CaCO_3 films on electrodes exhibited well-defined cyclic voltammograms and good electrocatalytic activity toward H_2O_2 . Protein nanocluster films were advantageous over the ordinary LbL films, including the larger fraction of electroactive proteins, better electrocatalytic activity, higher porosity, and better stability.

7. Redox mediators in LbL films

Metal hexacyanoferrate films are interesting redox mediators since they are mixed-valence clusters, exhibiting semiconductor characteristics, and may transfer electrons during reduction and oxidation processes [275-277]. These films were investigated for different purposes as catalytic oxidation of NADH [278], oxidation of dopamine [279], amperometric determination of morphine [280], hydrazine [281] and thiosulphate [282]. Glucose biosensors were developed on cobalt hexacyanoferrates-coated glassy-carbon electrodes [283] and also on carbon film electrodes modified with cobalt hexacyanoferrate [275]. With the LbL approach, hybrid compounds containing Prussian Blue (PB) redox mediator were widely used in biosensing, especially for oxidase-based biosensors that exploit the catalytic properties of PB. For instance, Zhao et al. [70] used PB nanoparticles protected by PDDA in alternating layers with the negatively charged glucose oxidase (GOx). These multilayers were adsorbed on already-formed LbL films of PDDA and poly(sodium 4-styrenesulfonate) (PSS) on 3-mercaptopropylsulfonic acid modified Au electrode. The modified electrodes were able to catalyze the electroreduction of hydrogen peroxide formed from the enzymatic reaction at a lower potential than for the bare electrode and inhibited interference from ascorbic and uric acid. The

schematic preparation of GOx electrochemical sensor is shown in Figure 8. The performance of the multilayer films could be tailored by controlling the number of bilayers. The glucose biosensor exhibited good stability and reproducibility [70].

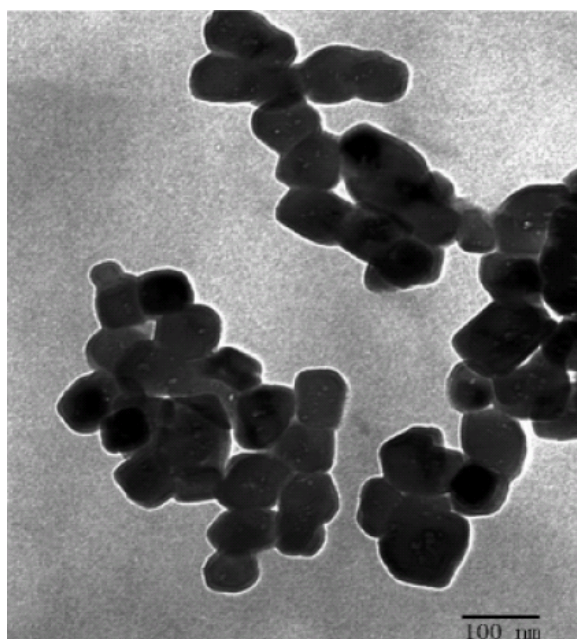
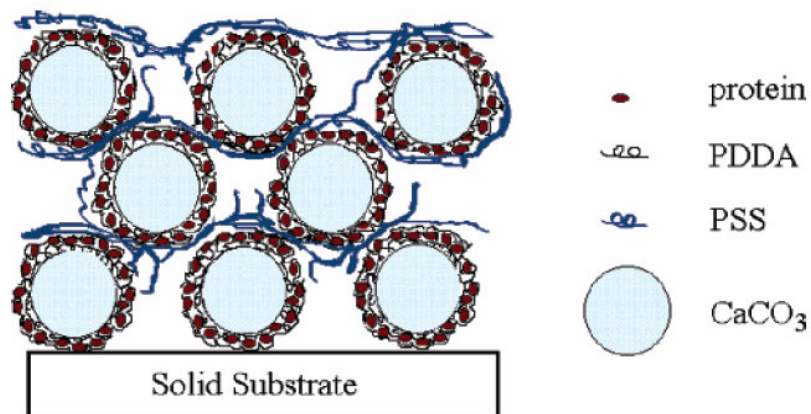


Figure 7. Schematic diagram of $\{[\text{CaCO}_3\text{-PDDA}/(\text{Protein}/\text{PDDA})_1]/\text{PSS}\}_3$ or $\{[\text{Protein-1}]/\text{PSS}\}_3$ nanocluster and TEM images of $\text{CaCO}_3\text{-PDDA}/(\text{Mb}/\text{PDDA})_3$ nanocluster. *Figure from ref. 274, with kind permission of ACS Publications.*

Jaiswal and co-workers [284] prepared hybrid materials using an aqueous colloidal solution of PB. The cyclic voltammograms and the TEM images from these hybrid lamellar materials are shown in figure 9. The films exhibited good electroactivity, with sets of peaks corresponding to two reversible

redox reactions of PB. The peak current increased linearly with the number of deposited layers, confirming that the same amount of PB was adsorbed in each immersion step.

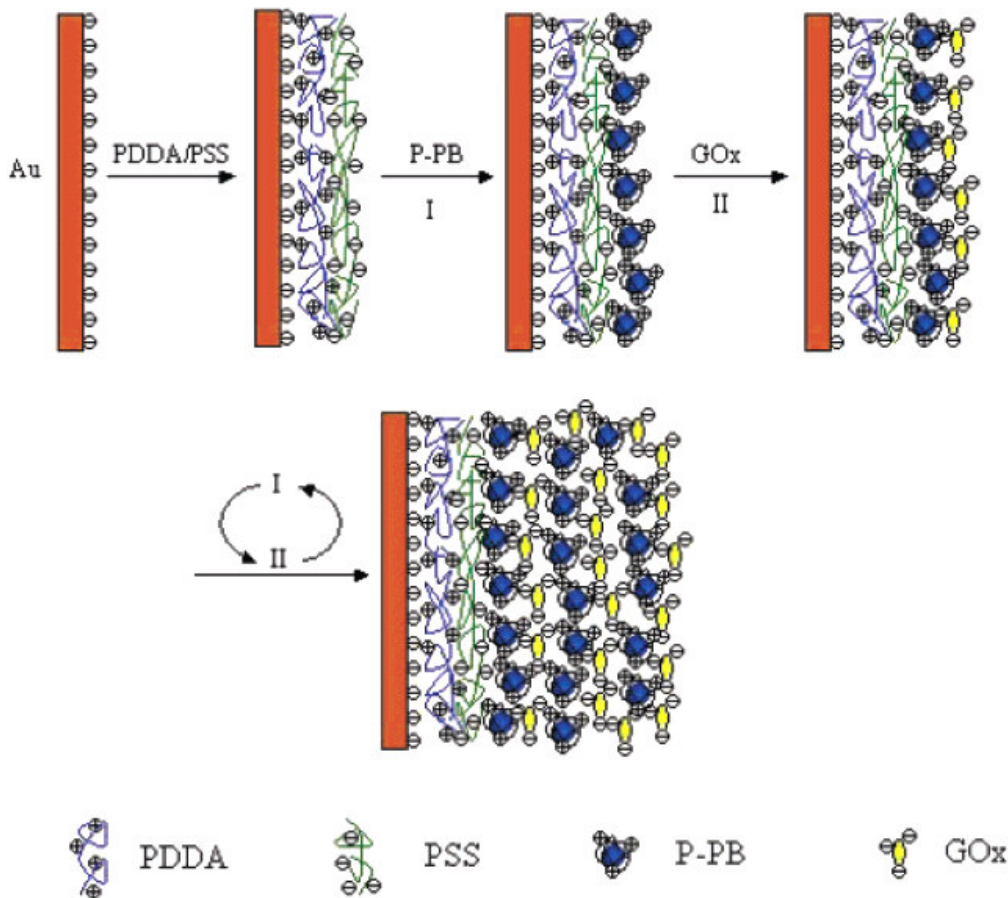


Figure 8. Scheme of sequential multilayer film assembly on the gold surface (from ref. 70, with kind permission of ACS Publications), where a bilayer of PDDA/PSS is consecutively adsorbed on 3-mercaptopropyl-1-propanesulfonic acid modified Au electrode surfaces.

A hexacyanoferrate solution was used to adsorb PB onto AuNp [267], forming the heterostructure depicted in Figure 10, which also includes the voltammograms corresponding to the formation of a new core-shell system (Au@PB). In the first potential cycle, a redox pair appeared due to hexacyanoferrate (II)/(III), in addition to the oxidation and reduction peaks of the gold nanoparticles. After 2h of reaction, the gold oxidation peaks were no longer observed and the cyclic voltammogram of the PVS/PAMAM-Au modified electrode (figure 10) revealed the reversible reduction and oxidation of PB. This indicates that the PB film completely covered the Au nanoparticle surface, with formation of an ITO-PVS/ PAMAM-Au@PB electrode. This system can be applied in biosensors and nanoelectronics where a reversible redox mediator is required.

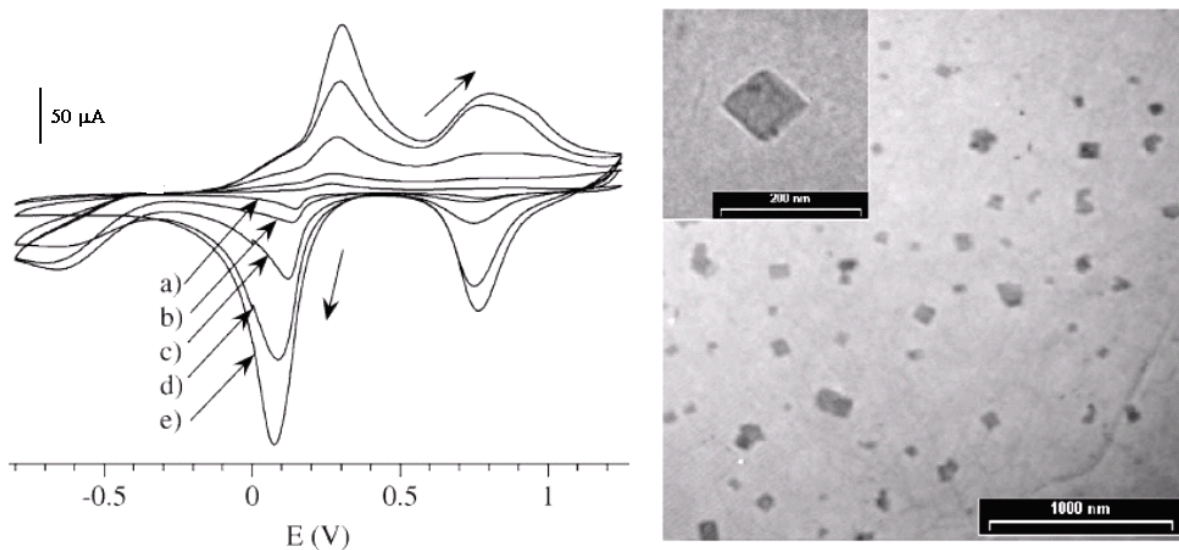


Figure 9. Cyclic voltammograms in aqueous 0.5 M KCl of a PEI/PSS/PEI/PB film formed by (a) 1, (b) 3, (c) 12, (d) 24, (e) 35 times of immersion of 10 min in a 10^{-3} mol L $^{-1}$ PB solution/rinsing with water. In the right-hand side, TEM images of PB colloids present in the solution. *Figures from ref. 283, with kind permission of Elsevier.*

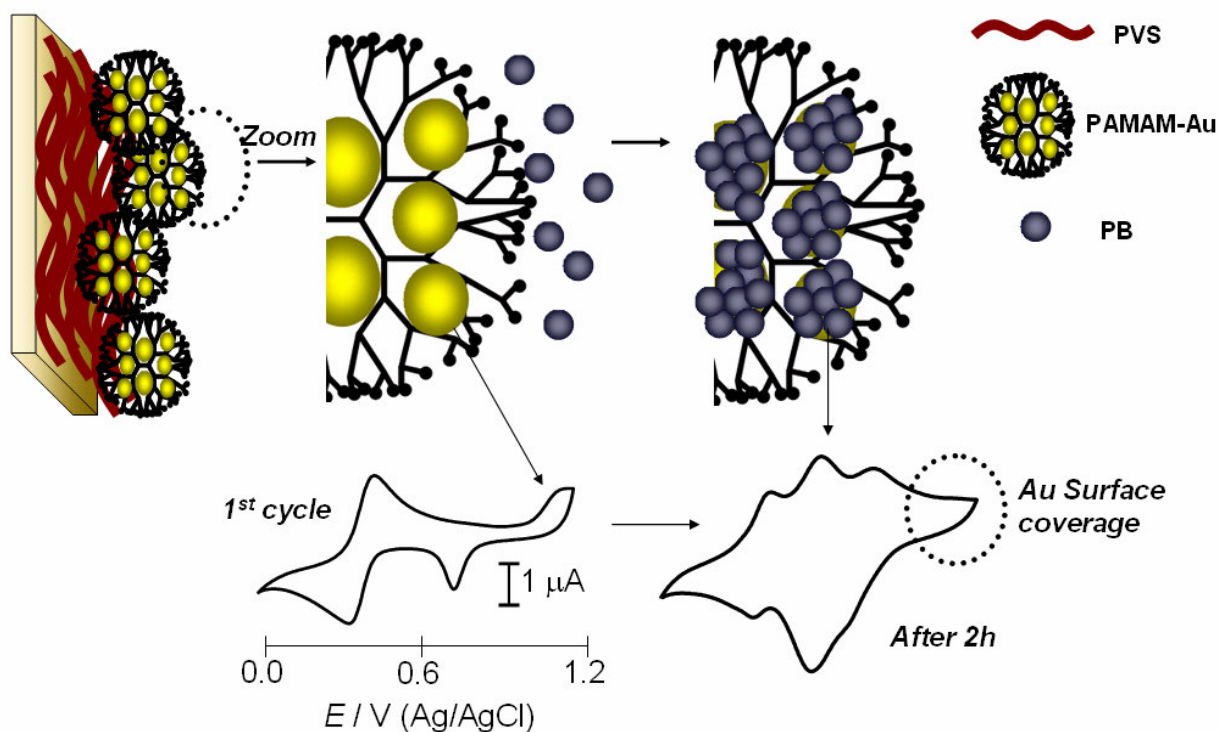


Figure 10. Cyclic voltammograms of Au@PB formation on a 6-bilayer ITO-PVS/PAMAM-Au electrode in a solution of 5.0 mmol L $^{-1}$ hexacyanoferrate (III) in 0.5 mol L $^{-1}$ H $_2$ SO $_4$, scan rate 50 mV s $^{-1}$. After 2 h the surface of gold nanoparticles was completely covered by PB. *Figure adapted from ref. 267.*

8. CONCLUSIONS

The LbL strategy has become an important tool in the fabrication of layered, nanostructured devices for electrochemical applications, especially in those cases where control at the molecular level is required. In this paper we presented an overview of the recent advances in the manipulation of electroactive architectures employing inorganic and organic/biological molecules. As well as to the fundamental aspects concerning transport mechanisms inside the LbL electroactive layers, we mentioned various technological applications in which such materials are desired, including electrochemical and biological sensing, in addition to electrochromic and charge-storage devices.

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References

1. Decher, G., *Science*, 277 (1997)1232.
2. O. N. Oliveira Jr., J-A. He, V. Zucolotto, S. Balasubramanian, L. Li, H. S. Nalwa, J. Kumar and S. K. Tripathy, in Handbook of Polyelectrolytes and Their Applications, edited Jayant Kumar e. H. S. Nalwa, American Scientific Publishers, Los Angeles, CA (2002), Vol 1, p. 1.
3. H. Liu and N. Hu, *J. Phys. Chem. B* 109 (2005) 10464.
4. H. Zhang, H. Lu, and N. Hu, *J. Phys. Chem. B* 109 (2005) 10464.
5. S. Yang, Y. Li, X. Jiang, Z. Chen and X. Lin, *Sens. Actuators*, B114 (2006) 774.
6. J. Hodak, R. Etchenique, E.J. Calvo, K. Singhal and P.N. Bartlett, *Langmuir* 13 (1997) 2708.
7. C. Q. Sun, J. H. Zhao, H.D. Xu, Y.P. Sun, X. Zhang and J. C. Shen, *J. Electroanal. Chem.* 435 (1997) 63.
8. M. M. Montrel, G. B. Sukhorukov, A.I. Petrov, L.I. Shabarchina and B. I. Sukhorukov, *Sens. Actuators*, B. 42 (1997) 225.
9. S. F. Hou, H.Q. Fang and H.Y. Chen, *Anal. Lett.* 30 (1997) 1631.
10. Y. M. Lvov, Zh. Lu, J.B. Schenkman, X. Zu and J. M. Rusling, *J. Am. Chem. Soc.* 120 (1998) 4073.
11. S.F. Hou, K.S. Yang, H.Q. Fang and H.Y.Chen, *Talanta* 47 (1998) 561.
12. Y. Kobayashi, S. Kuwazawa, H. Saiki, T. Hoshi, Y. Kashiwagi and J. Anzai, *Electrochem.* 67 (1999) 1147.
13. M. Onda, K. Ariga and T. Kunitake, *J. Biosci. Bioeng.* 87 (1999) 69.
14. Ch. Sun, W. Li, Y. Sun, X. Zhang and J. Shen, *Electrochim. Acta*, 44 (1999) 3401.
15. F. Caruso, H. Fiedler and K. Haage, *Colloids Surf. A*, 169 (2000) 287.
16. A. Narvaez, G. Suarez, I. C. Popescu, I. Katakis, E. Dominguez, *Biosens. Bioelectron.* 15 (2000) 43.
17. T. Hoshi, H. Saiki, S. Kuwazawa, Y. Kobayashi and J. Anzai, *Anal. Sci.* 16 (2000) 1009.
18. W.J. Li, Z. Wang, C.Q. Sun, M. Xian and M.Y. Zhao, *Anal. Chim. Acta* 418 (2000) 225.
19. L. Kumpumbu-Kalemab and M. Leclerc, *J. Chem. Soc., Chem. Commun.* (2000) 1847.
20. E.J. Calvo, F. Battaglini, C. Danilowicz, A. Wolosiuk and M. Otero, *Faraday Discuss.* 116 (2000) 47.
21. E. S. Forzani, V. M. Solis and E. J. Calvo, *Anal. Chem.* 72 (2000) 5300.
22. T. Chen, K. A. Friedman, I. Lei and A. Heller, *Anal. Chem.* 72 (2000) 3757.
23. K. Sirkar, A. Revzin and M. V. Pishko, *Anal. Chem.* 72 (2000) 2930.

24. L. Zhou and J.F. Rusling, *Anal. Chem.* 73 (2001) 4780.
25. Calvo, C. Danilowicz, C. M. Lagier, J. Manrique, and M. Otero, *Biosens. Bioelectron.* 19 (2004) 1219.
26. E. J. Calvo, and A. Wolosiuk, *ChemPhysChem* 5 (2004) 235.
27. S. V. P. Barreira, V. Garcia-Morales, C. M. Pereira, J. A. Manzanares, and F. Silva, *J. Phys. Chem. B* 108 (2004) 17973.
28. M. K. Beissenhirtz, F. W. Scheller, and F. Lisdat, *Anal. Chem.* 76 (2004) 4665.
29. M. K. Beissenhirtz, F. W. Scheller, W. F. M. Stocklein, D. G. Kurth, H. Mohwald, and F. Lisdat, *Angew. Chem., Int. Ed.* 43 (2004) 4357.
30. K. Beissenhirtz Moritz, W. Scheller Frieder, F. M. Stocklein Walter, G. Kurth Dirk, H. Mohwald, and F. Lisdat, *Angew. Chem., Int. Ed.* 43 (2004) 4357.
31. Y.D. Jin, Y. Shao and S.J. Dong, *Langmuir* 19 (2003) 4771.
32. Z. Li, N. Hu, *J. Colloid Interface Sci.* 254 (2002) 257.
33. T. Hoshi, H. Saiki, S. Kuwazawa, C. Tsuchiya, Q. Chen and J.I. Anzai, *Anal. Chem.* 73 (2001) 5310.
34. I. Galeska, T. Hickey, F. Moussy, D. Kreutzer and F. Papadimitrakopoulos, *Biomacromolecules* 2 (2001) 1249.
35. E.J. Calvo, R. Etchenique, L. Pietrasanta and A. Wolosiuk, *Anal. Chem.* 73 (2001) 1161.
36. -C. Chen, S.-H. Xu, H.-F. Lin, S.-M. Yang, and X.-F. Lin, *Wuli Huaxue Xuebao* 20 (2004) 1267.
37. M. Ferreira, P. A. Fiorito, O. N. Oliveira Jr., and S. I. Córdoba de Torresi, *Biosens. Bioelectron.* 19 (2004) 1611.
38. N. Ferreyra, L. Coche-Guerente, and P. Labbe, *Electrochim. Acta* 49 (2004) 477.
39. T. Hoshi, T. Noguchi, and J. Anzai, *ITE Letters on Batteries, New Technologies & Medicine* 5 (2004) 345.
40. T. Hoshi, T. Noguchi, and J. Anzai, *Chemical Sensors* 20 (2004) 520.
41. J. Ji, Q. Tan, and J. Shen, *Polym. Adv. Technol.* 15 (2004) 490.
42. N. Loew, F. W. Scheller, and U. Wollenberger, *Electroanalysis* 16 (2004) 1149.
43. E. Lojou, and P. Bianco, *Langmuir* 20 (2004) 748.
44. E. Lojou, and P. Bianco, *J. Electroanal. Chem.* 573 (2004) 159.
45. L.-P. Lu, S.-Q. Wang, and X.-Q. Lin, *Anal. Chim. Acta* 519 (2004) 161.
46. A. Mugweru, B. Wang, and J. Rusling, *Anal. Chem.* 76 (2004) 5557.
47. P. Rijiravanich, K. Aoki, J. Chen, W. Surareungchai, and M. Somasundrum, *Electroanalysis* 16 (2004) 605.
48. M. Wang, L. Wang, H. Yuan, X. Ji, C. Sun, L. Ma, Y. Bai, T. Li, and J. Li, *Electroanalysis* 16 (2004) 757.
49. X. Wang, Y.-G. Kim, C. Drew, B.-C. Ku, J. Kumar, and L. A. Samuelson, *Nano Lett.* 4 (2004) 331.
50. W. Zhang, Y. Huang, H. Dai, X. Wang, C. Fan, and G. Li, *Anal. Biochem.* 329 (2004) 85.
51. S. Zhang, Y. Niu, and C. Sun, *Electrochim. Acta* 49 (2004) 4777.
52. G.D. Liu and Y.H. Lin, *J. Nanosci. Nanotechnol.* 6 (2006) 948.
53. A. K. M. Kafi, F. Yin, H.K. Shin, Y.S. Kwon, *Thin Solid Films* 499 (2006) 420.
54. H. T. Zhao and H. X. Ju, *Anal. Biochem.* 350 (2006) 138.
55. A. J. Wang, J. J. Xu and H. Y. Chen, *J. Chromatogr., A* 1107 (2006) 257.
56. H. Y. Lu, J. Yang, J. F. Rusling, N. F. Hu, *Electroanalysis* 18 (2006) 379.
57. S. X. Zhang, W. W. Yang, Y. M. Niu, Y. C. Li, M. Zhang and C. Q. Sun, *Anal. Bioanal. Chem.* 384 (2006) 736.
58. A. H Liu, D. L. Li, I. Honma and H.S. Zhou, *Electrochem. Commun.* 8 (2006) 206.
59. H. T. Zhao and H. X. Ju, *Anal. Biochem.* 350 (2006) 138.
60. A. J. Wang, J. J. Xu and H. Y. Chen, *J. Chromatogr., A* 1107 (2006) 257.

61. S. X. Zhang, W. W. Yang, Y. M. Niu, Y. C. Li, M. Zhang and C. Q. Sun, *Anal. Bioanal. Chem.* 384 (2006) 736.
62. H. Zhang, H. Y. Lu and N. F. Hu, *J. Phys. Chem. B* 110 (2006) 2171.
63. G. D. Liu and Y. H. Lin, *Anal. Chem.* 78 (2006) 835.
64. G. D. Liu and Y. H. Lin, *Electrochem. Commun* 8 (2006) 251.
65. G. Zhao, J. J. Xu and H. Y. Chen, *Electrochem. Commun* 8 (2006) 148.
66. P. L. He, M. Li and N. F. Hu, *Biopolymer* 79 (2005) 310.
67. Z. A. Xu, N. Gao, H. J. Chen and S. J. Dong, *Langmuir* 21 (2005) 10808.
68. J. Hartung, J. Kowalik, C. Kranz, J. Janata, M. Josowicz, A. Sinha and K. McCoy, *J. Electrochem. Soc.* 152 (2005) 345.
69. D. P. Tang, R. Yuan, Y. Q. Chai, Y. Z. Fu, J. Y. Dai, Y. Liu and X. Zhong, *Biosens. Bioelectron.* 21 (2005) 809.
70. W. Zhao, J. J. Xu, C. G. Shi and H. Y. Chen, *Langmuir* 21 (2005) 9630.
71. M. H. Yang, Y. Yang, H. F. Yang, G. L. Shen and R. Q. Yu, *Biomaterials* 27 (2006) 246.
72. S. Suye, T. Matsuura, T. Kimura, H. Zheng, T. Hori, Y. Amano and H. Katayama, *Microelectron. Eng.* 81 (2005) 441.
73. F. L. Qu, M. H. Yang, J. H. Jiang, G. L. Shen and R. Q. Yu, *Anal. Biochem.* 344 (2005) 108.
74. B. Munge, G. D. Liu, G. Collins and J. Wang, *Anal. Chem.* 77 (2005) 4662.
75. P. G. He and M. Bayachou, *Langmuir* 21 (2005) 6086.
76. H. Y. Liu and N. F. Hu, *J. Phys. Chem. B* 109 (2005) 10464.
77. L. Shen and N. F. Hu, *Biomacromolecules* 6 (2005) 1475.
78. M. Li, P. L. He, Y. Zhang and N. F. Hu, *Biochim. Biophys. Acta, Proteins Proteomics* 1749 (2005) 43.
79. G. E. Pacey, S. D. Puckett, L. Cheng, S. Khatib-Shahidi and J. A. Cox, *Anal. Chim. Acta* 533 (2005) 135.
80. M. N. Zhang, K. P. Gong, H. W. Zhang and L. Q. Mao, *Biosens. Bioelectron.* , 20 (2005) 270.
81. H. Sun and N. F. Hu, *Analyst (Cambridge, U. K.)* 130 (2005) 76.
82. J. Y. Liu, Y. D. Jin, A. G. Wu, Z. Li and S. J. Dong, *Electroanalysis* 16 (2004) 1931.
83. M. L. Guo, J. H. Chen, J. Li, L. H. Nie and S. Z. Yao, *Electroanalysis* 16 (2004) 1992.
84. D. M. DeLongchamp, M. Kastantin and P. T. Hammond, *Chem. Mater.* 15 (2003) 1575.
85. H. H. Rmaile and J. B. Schlenoff, *J. Am. Chem. Soc.* 125 (2003) 6602.
86. M. Onoda and K. Yoshino, *Jpn. J. Appl. Phys.* 34, (1995) 260.
87. H. Hong, D. Davidov, M. Tarabia, H. Chayet, I. Benjamin, E.Z. Faraggi, Y. Avny and R. Neumann, *Synt. Met.* 85, (1997) 1265.
88. K. Yang, X. Wang, S. Balasubramanian, J. Kumar, S.K. Tripathy, *Polym. Prepr. Am. Chem. Soc. Polym. Chem. Div.* 39 (1998) 1129.
89. P.K.H. Ho, M. Granström, R.H. Friend and N.C. Greenham, *Adv. Mater.* 10 (1998) 769.
90. J. Stepp and J.B. Schlenoff, *J. Electrochem. Soc.* 144 (1997) 155.
91. M. Lahav-M, V. Heleg-Shabtai, J. Wasserman, E. Katz, I. Willner, H. Durr-H, Y.Z. Hu and S.H. Bossmann, *J. Am. Chem. Soc.* 122 (2000) 11480.
92. C.R. Cutler, M. Bouguettaya and J.R. Reynolds, *Adv. Mater.* 14 (2002) 684.
93. J.J. Kakkassery, D.J. Fermín and H.H. Girault, *Chem. Commun.* 1240 (2002)
94. D. M. DeLongchamp, and P. T. Hammond, *Chem. Mater.* 16 (2004) 4799.
95. D. M. DeLongchamp, and P. T. Hammond, *Adv. Funct. Mater.* 14 (2004) 224.
96. G. Gao, L. Xu, W. Wang, W. An, and Y. Qiu, *J. Mater. Chem.* 14 (2004) 2024.
97. Z. Guo, Y. Shen, F. Zhao, M. Wang, and S. Dong, *Analyst (Cambridge, U. K.)* 129 (2004) 657.
98. Z. Guo, Y. Shen, M. Wang, F. Zhao, and S. Dong, *Anal. Chem.* 76 (2004) 184.
99. S. Jung, H. Kim, M. Han, Y. Kang, and E. Kim, *Mater. Sci. Eng., C* 24 (2004) 57.
100. K. Y. K. Man, H. L. Wong, W. K. Chan, C. Y. Kwong, and A. B. Djuricic, *Chem. Mater.* 16 (2004) 365.

101. G.X Li, X.W. Zheng and Z.J.Zhang, *Microchim. Acta* 154 (2006) 153.
102. K. Abe, A. Ishii, M. Hirano and J.F. Rusling, *Electroanalysis* 24 (2005) 2266.
103. E. Kim and S. Jung, *Chem. Mater.* 17 (2005) 6381.
104. G.G. Gao, L. Xu, W.J. Wang, Z.O. Wang, Y.F. Qiu and E.B. Wang, *J. Electrochem. Soc.* 152 (2005) 102.
105. Y.H. Feng, J. Peng, Z.G. Han and H.Y. Ma, *J. Colloid Interface Sci.* 286 (2005) 589.
106. G.G. Gao, L. Xu, W.J. Wang, W.J. An, Y.F. Qiu, Z.Q. Wang and E.B. Wang, *J. Phys. Chem. B*, 109 (2005) 8948.
107. N.S. Gaikwad, G. Waldner, A. Bruger, A. Belaidi, S.M. Chaqour and M. Neumann-Spallart, *J. Electrochem. Soc.* 152 (2005) 411.
108. C.H. Ge, W.J. Doherty, S.B. Mendes, N.R. Armstrong and S.S. Saavedra, *Talanta* 65 (2005) 1126.
109. W. Jomaa and J.B. Schlenoff, *Langmuir* 21 (2005) 8081.
110. H. Sun and N. Hu, *J. Electroanal. Chem* 588 (2006) 207.
111. X. Zu, Zh. Lu, J.B. Schenkman and J.R. Rusling, *Langmuir* 15 (1999) 7372.
112. G.M. Kloster and F.C. Anson, *J. Electrochim Acta* 44 (1999) 2271.
113. L. Cheng, J.Y. Liu and S.J. Dong, *Anal. Chim. Acta* 417 (2000) 133.
114. L. Cheng and S. Dong *J. Electroanal. Chem* 481 (2000) 168.
115. W. J. Li, M. Xian, Z. C. Wang, C. Q. Sun and M. Y. Zhao, *Thin Solid Films* 386 (2001) 121.
116. L. Dennany, R.J. Forster, J.F. Rusling, *J. Am. Chem. Soc.* 125 (2003) 5213.
117. Y. Shen, J.Y. Liu, A.G. Wu, J.G. Jiang, L.H. Bi, B.F. Liu, Z. Li and S.J. Dong, *Langmuir* 19 (2003) 5397.
118. J. Qu, Y. Shen, X. Qu, and S. Dong, *Electroanalysis* 16 (2004) 1444.
119. J. F. Rusling, *Biosens. Bioelectron.* 20 (2004) 1022.
120. H. Sun and N. Hu, *J. Electroanal. Chem.* 588 (2006) 207.
121. G.S. Nunes, H.E. Toma and K. Araki, *Eur. J. Inorg. Chem.* 4 (2006) 850.
122. F.N. Crespilho, F. Huguenin, V. Zucolotto, P. Olivi, F.C. Nart and O.N. Oliveira Jr., *Electrochem. Commun.* 8 (2006) 348.
123. L.Y. Zhao, H.Y. Liu and N.F. Hu, *Anal. Bioanal. Chem.* 384 (2006) 414.
124. F. Huguenin, V. Zucolotto, A.J.F. Carvalho, E.R. Gonzalez, and O.N. Oliveira Jr., *Chem. Mater.* 17 (2005) 6739.
125. Y. Liu, H.Y. Liu and N.F. Hu, *Biophys. Chem.* 117 (2005) 27.
126. I. Mayer, M.N. Eberlin, D.M. Tomazela, H.E. Toma and K. Araki, *J. Braz. Chem. Soc.* 16 (2005) 418.
127. F. Huguenin, E.R. Gonzalez and O.N. Oliveira Jr., *J. Phys. Chem. B* 109 (2005) 12837.
128. P.H. Yang, Z.J. Zhou and J.Y. Cai, *Colloids Surf., A* 257 (2005) 467.
129. T. Frey, K.A. Friedrich, L. Jorissen and J. Garche, *J. Electrochem. Soc.* 152 (2005) 545.
130. X. Ma, X.J. Liu, H. Xiao and G.X. Li, *Biosens. Bioelectron.* 20 (9) (2005) 1836..
131. L. Cheng, J.A. Cox, *Chem. Mater.* 14 (2002) 6.
132. M. Chojak, M. Mascetti, R. Wlodarczyk, R. Marassi, K. Karnicka, K. Miecznikowski, and P. Kulesza, *J. Solid State Electrochem.* 8 (2004) 854.
133. M. Zhang, Y. Yan, K. Gong, L. Mao, Z. Guo, and Y. Chen, *Langmuir* 20 (2004) 8781.
134. J. Travas-Sejdic, R. Soman and H. Peng, *Thin Solid Films* 497 (2006) 96.
135. L. C. Recksiedler, B. A. Deore and M. S. Freund, *Langmuir* 22 (2006) 2811.
136. A. Baba, M.K. Park, R. C. Advincula and W. Knoll, *Langmuir* 18 (2002) 4648.
137. F. Huguenin and R. M. Torresi, *Quim. Nova* 27 (2004) 393.
138. J.H. Cheung, A.F. Fou, M. Ferreira and M.F. Rubner, *Polym. Prepr. Am. Chem. Soc. Polym. Chem. Div.* 34 (1993) 757.
139. .F. Fou, D. Ellis, M. Ferreira and M.F. Rubner, *Polym. Prepr. Am. Chem. Soc. Polym. Chem. Div.* 35 (1994) 221.

140. J.H. Cheung, A. F. Fou and M. F. Rubner, *Thin Solid Films*, 244, (1994) 985.
141. A.C. Fou and M.F. Rubner, *Macromolecules* 28 (1995) 7115.
142. J.H. Cheung, W.B. Stockton and M.F. Rubner, *Macromolecules* 30 (1997) 2712.
143. C.L Recksiedler, B. A. Deore and M.S. Freund, *Langmuir* 22 (2006) 2811.
144. P.J. Kulesza, M. Skunik, B. Baranowska, K. Miecznikowski, M. Chojak, K. Karnicka, E. Frackowiak, F. Beguin, A. Kuhn, M.H. Delville, B. Starobrzynska and A. Ernst, *Electrochim. Acta* 51 (2006) 2373.
145. V. Zucolotto, M. Ferreira, M.R. Cordeiro, C.J.L. Constantino, W.C. Moreira and O.N. Oliveira Jr., *Sens. Actuators, B* 113 (2006) 809.
146. Y. Lan, E.B. Wang, Y.H. Song, Y.L. Song, Z.H. Kang, L. Xu and Z. Li, *Polymer* 47 (2006) 1480.
147. T.R. Farhat and P.T. Hammond, *Chem. Mater.* 18 (2006) 41.
148. A. Kepas and M. Grzeszczuk, *J. Electroanal. Chem.* 582 (2005) 209.
149. A. I. Abdelrahman, A. M. Mohammad, T. Okajima and Takeo Ohsaka, *J. Phys. Chem. B* 109 (2005) 10464.
150. M. Chirea, V. Garcí'a-Morales, J.A. Manzanares, C. Pereira, R. Gulaboski and F. Silva, *J. Phys. Chem. B* 109 (2005) 10464.
151. C. Lin and C. R. Kagan, *J. Am. Chem. Soc.* 125 (2003) 336.
152. J. Zhao, C. R. Bradbury, S. Huclova, I. Potapova, M. Carrara and D. J. Fermin, *J. Phys. Chem. B* 109 (2005) 22985.
153. Z. Liu, X. Wang, H. Wu and C. Li, *J. Colloid Interface Sci.* 287 (2005) 604.
154. Q. Sun, Y. P. Sun, X. Zhang, X. Y. Zhang, D. Jiang, Q. Gao, H. D. Xu and J. C. Shen, *Thin Solid Films* 288 (1996) 291.
155. T. Haraszti, L. Turi, I. Dékány and J. H. Fendler, *ACH Models Chem.* 134 (1997) 785.
156. F. Caruso, K. Niikura, D.N. Furlong and Y. Okahata, *Langmuir* 13 (1997) 3422.
157. Y. Liu, Y. Wang and R.O. Claus, *Chem. Phys. Lett.* 298 (1998) 315.
158. A.N. Shipway, M. Lahav, R. Blonder and I. Willner, *Adv. Mater.* 12 (2000) 993.
159. M.K. Ram, M. Adami, S. Paddeu and C. Nicolini, *Nanotechnology* 11 (2000) 112.
160. P. He and N. Hu, *Electroanalysis* 16 (2004) 1122.
161. M. Kijak, R. K. Perdue and J. A. Cox, *J. Solid State Electrochem.* 8 (2004) 376.
162. W. W. Yang, J. X. Wang, S. Zhao, Y. Y. Sun and C. Q. Sun, *Electrochem. Commun.* 8 (2006) 665.
163. D. R. Blasini, S. Flores-Torres, D. M. Smilgies and H. D. Abruna, *Langmuir* 22 (2006) 2082.
164. D. F. Acevedo, J. Balach, C. R. Rivarola, M. C. Miras and C. A. Barbero, *Faraday Discuss.* 131 (2006) 235.
165. A. I. Abdelrahman, A.M. Mohammad, T. Okajima and T. Ohsaka, *J. Phys. Chem. B* 110 (2006) 2798.
166. A. B. F. Martinson, A. M. Massari, S. J. Lee, R. W. Gurney, K. E. Splan, J. T. Hupp and S. T. Nguyen, *J. Electrochem. Soc.* 153 (2006) 527.
167. A. H. Liu, D. L. Li, I. Honma and H. S. Zhou, *Electrochem. Commun.* 8 (2006) 206.
168. J. D. Huang, Y. Yang, H. B. Shi, Z. Song, Z. X. Zhao, J. Anzai, T. Osa, Q. Chen, *Mater. Sci. Eng., C* 26 (2006) 113.
169. A. Baba, J. Locklin, R. S. Xu and R. Advincula, *J. Phys. Chem. B* 110 (2006) 42.
170. M. Chirea, V. Garcia-Morales, J. A. Manzanares, C. Pereira, R. Gulaboski, F. Silva, *J. Phys. Chem. B* 109 (2004) 21808.
171. M. N. Zhang, L. Su and L. Q. Mao, *Carbon* 44 (2006) 276.
172. H. M. Ding, X. Q. Zhang, M. K. Ram and C. Nicolini, *J. Colloid Interface Sci.* 209 (2005) 166.
173. J. H. Cho and F. Caruso, *Chem. Mater.* 17 (2005) 4547.
174. Y. M. Yan, M. N. Zhang, K. P. Gong, L. Su, Z. X. Guo and L. Q. Mao, *Chem. Mater.* 17 (2005) 3457.

175. M. A. Murphy, G. D. Wilcox, R. H. Dahm and F. Marken, *Indian J. Chem., Sect. A: Inorg., Bioinorg., Phys., Theor. Anal. Chem.* 44 (2005) 924.
176. L. Qian and X. R. Yang, *Electrochem. Commun.* 7 (2005) 547.
177. F. Shi, Z. Q. Wang and X. Zhang, *Adv. Mater.* 17 (2005) 1005.
178. M. H. Huang, Y. Shen, W. L. Cheng, Y. Shao, X. P. Sun, B. F. Liu and S. J. Dong, *Anal. Chim. Acta* 535 (2005) 15.
179. Y. Lan, E. B. Wang, Y. H. Song, Z. H. Kang, M. Jiang, L. Gao, S. Y. Lian, D. Wu, L. Xu and Z. Li, *J. Colloid Interface Sci.* 284 (2005) 216.
180. Y. G. Guo, J. S. Hu, H. P. Liang, L. J. Wan and C. L. Bai, *Adv. Funct. Mater.* 15 (2005) 196.
181. M. L. Guo, J. H. Chen, J. Li, L. H. Nie and S. Z. Yao, *Electroanalysis* 16 (2004) 1992.
182. S. V. P. Barreira, V. Garcí'a-Morales, C. M. Pereira, J. A. Manzanares and F. Silva, *J. Phys. Chem. B* 108 (2004) 17973.
183. V. Pardo-Yissar, E. Katz, O. Lioubashevski and I. Willner, *Langmuir* 17 (2001) 1110.
184. D. Laurent and J. B. Schlenoff, *Langmuir* 13 (1997) 1552.
185. B. Lindholm-Sethson, *Langmuir* 12 (1996) 3305.
186. D. Yoo, A. Wu, J. Lee and M.F. Rubner, *Synt. Mat.* 85 (1997) 1425.
187. D.A. Lowy and H.O. Finklea, *Electrochim. Acta* 42 (1997) 1325.
188. J.B. Schlenoff, D. Laurent, H. Ly and J. Stepp, *Adv. Mater.* 10 (1998) 347.
189. Yu.M. Lvov, G.N. Kamau, D.L. Zhou and J.F. Rusling, *J. Colloid Interface Sci.*, 212 (1999) 1570.
190. Y. Cheng and R.M. Corn, *J. Phys. Chem. B* 103 (1999) 8726.
191. Y. Shimazaki, M. Mitsuishi, S. Ito and M. Yamamoto, *Macromolecules* 32 (1999) 8153.
192. R. Georgieva, S. Moya, S. Leporatti, B. Neu, H. Bäumlér, C. Reichle, E. Donath and H. Möhwald, *Langmuir* 16 (2000) 7075.
193. J. J. Harris and M. L. Bruening, *Langmuir* 16 (2000) 2006.
194. H.Y. Ma, N.F. Hu and J.F. Rusling, *Langmuir* 16 (2000) 4969.
195. V. B. P. Leite, M. Ferreira, O. N. Oliveira Jr., *Chem. Phys. Lett.* 316 (2000) 343.
196. L.S. Li and A.D.Q. Li, *J. Phys. Chem., B* 105 (2001) 10022.
197. G. Zotti, S. Zecchin, A. Berlin, G. Schiavon and G. Giro, *Chem. Mater.* 13 (2001) 43.
198. G. Zotti, G. Schiavon, S. Zecchin, A. Berlin and G. Giro, *Synt. Met.* 121 (2001) 1381.
199. V. Pardo-Yissar, E. Katz, O. Lioubashevski and I. Willner, *Langmuir* 17 (2001) 1110.
200. A. Baba, M.K. Park, R. C. Advincula and W. Knoll, *Langmuir* 18 (2002) 4648.
201. Zhen Li and Naifei Hu, *J. Colloid Interface Sci.* 254 (2002) 257.
202. E.J. Calvo and Wolosiuk, *J. Am. Chem. Soc.* 124 (2002) 8490.
203. E.S. Forzani, M.A. Pérez, M. Lopez Teijelo and E.J. Calvo, *Macromolecules* 35 (2002) 9867.
204. L.S. Li, Q. X. Jia and A.D.Q. Li, *Chem. Mater.* 14 (2002) 1159.
205. C.J. Slevin, A. Malkia, P. Liljeroth, M. Toiminen and K. Kontturi, *Langmuir* 19 (2003) 1287.
206. N. Ferreyra, L. Coche-Guérente, J. Fatisson, M. Lopez Teijelo and P. Labbé, *Chem. Commun.* (2003) 2056.
207. A. Liu and J. Anzai, *Langmuir* 19 (2003) 4043.
208. C. B. Bucur, H. H. Rmaile and J. B. Schlenoff, *Polymeric Materials Science and Engineering* 90 (2004) 522.
209. C.J. Slevin, A. Malkia, P. Liljeroth, M. Toiminen and K. Kontturi, *Langmuir* 19 (2003) 1287.
210. N. Ferreyra, L. Coche-Guérente, J. Fatisson, M. Lopez Teijelo and P. Labbé, *Chem. Commun.* (2003) 2056.
211. A. Liu and J. Anzai, *Langmuir* 19 (2003) 4043.
212. D. M. DeLongchamp and P. T. Hammond, *Langmuir* 20 (2004) 5403.
213. V. Garcia-Morales, T. H. Silva, C. Moura, J. A. Manzanares and F. Silva, *Journal J. Electroanal. Chem.* 569 (2004) 111.
214. H. Hoffmannova, D. Fermin and P. Krtíl, *J. Electroanal. Chem.* 562 (2004) 261.

215. H.-X. Huang, D.-J. Qian, N. Nakamura, C. Nakamura, T. Wakayama and J. Miyake, *Electrochim. Acta* 49 (2004) 1491.
216. L. Li, C. Tedeschi, D. G. Kurth and H. Moehwald, *Chem. Mater.* 16 (2004) 570.
217. C. Tedeschi, L. Li, H. Moehwald, C. Spitz, D. von Seggern, R. Menzel and S. Kirstein, *J. Am. Chem. Soc.* 126 (2004) 3218.
218. S. Y. Gao, R. Cao and X. Li, *Thin Solid Films* 500 (2006) 283.
219. H. Y. Lu, J. Yang, J. F. Rusling and N. F. Hu, *Electroanalysis* 18 (2006) 379.
220. Y. X. Hou, S. Helali, A. D. Zhang, N. Jaffrezic-Renault, C. Martelet, J. Minic, T. Gorojankina, M. A. Persuy, E. Pajot-Augy, R. Salesse, F. Bessueille, J. Samitier, A. Errachid, V. Akimov, L. Reggiani, C. Pennetta and E. Alfinito, *Biosens. Bioelectron.* 21 (2006) 1393.
221. B. Tieke, A. Toutianoush and W. Q. Jin, *Adv. Colloid Interface Sci.* 116 (2005) 121.
222. M. K. Beissenhirtz, B. Kafka, D. Schafer, M. Wolny and F. Lisdat, *Electroanalysis* 17 (2005) 1931.
223. M. Yuasa and K. Oyaizu, *Curr. Org. Chem.* 9 (2005) 1685.
224. K. H. Boubbou and T. H. Ghaddar, *Langmuir* 21 (2005) 8844.
225. G. Q. Lu, J. Y. Du and C. W. Hu, *Chem. Res. Chin. Univ.* 21 (2005) 401.
226. T. Fushimi, A. Oda, H. Ohkita and S. Ito, *Thin Solid Films* 484 (2005) 318.
227. L. Qian, Q. Gao, Y. H. Song, Z. A. Li and X. R. Yang, *Sens. Actuators, B* 107 (2005) 303.
228. S. H. Cha, H. C. Koo and J. J. Kim, *J. Electrochem. Soc.* 152 (2005) 388.
229. K. J. McKenzie, P. M. King, F. Marken, C. E. Gardner and J. V. Macpherson, *J. Electrochem. Soc.* 579 (2005) 267.
230. C. A. Barbero, *Phys. Chem. Chem. Phys.* 7 (2005) 1885.
231. J. P. Diard, N. Glandut, C. Montella and J. Y. Sanchez, *J. Electrochem. Soc.* 578 (2005) 247.
232. L. H. Bi, Y. Shen, J. G. Jiang, E. K. Wang and S. J. Dong, *Anal. Chim. Acta* 534 (2005) 343.
233. H. Sun and N. F. Hu, *Analyst* 130 (2005) 76.
234. J. Y. Liu, Y. D. Jin, A. G. Wu, Z. Li and S. J. Dong, *Electroanalysis* 16 (2004) 1931.
235. L. Netzer and J. Sagiv, *J. Am. Chem. Soc.* 105 (1983) 674.
236. N. Tillman, A. Ulman and T. L. Penner, *Langmuir* 5 (1989) 101.
237. J. Richer, L. Stolberg and J. Lipkowski, *Langmuir* 2 (1986) 630.
238. X.M. Zhao, J.L. Wilbur and G.M. Whitesides, *Langmuir* 12 (1996) 3257.
239. Y. Xia, J.A. Rogers, K.E. Paul and G.M. Whitesides, *Chem. Rev.* 99 (1999) 1823.
240. G. Decher, J.D. Hong and J. Schmitt, *Thin Solid Films* 210/211 (1992) 831.
241. Y. Lvov, H. Haas, G. Decher and H. Möhwald, *J. Phys. Chem.* 97 (1993) 12835.
242. S. K. Tripathy, H. Katagi, H. Kasai, S. Balasubramanian, H. Oshikiri, J. Kumar, H. Oikawa, S. Okada and H. Nakanishi, *Jpn. J. Appl. Phys.* 37(1998), L343.
243. V. Zucolotto, K.M. Gattás-Asfura, T. Tumolo, A.C. Perinotto, P.A. Antunes, C.J.L. Constantino, M.S. Baptista, R.M. Leblanc and O.N. Oliveira Jr., *Applied Surface Science*, 246 (2005) 397.
244. J. H. Fendler, *Chem. Mater.* 8 (1996) 1616.
245. T. Cassagneau and J. H. Fendler, *J. Phys. Chem. B* 103 (1999) 1789.
246. J.-A. He, R. Valluzzi, K. Yang, T. Dolukhanyan, C. M. Sung, J. Kumar, S. K. Tripathy, L. Samuelson, L. Balogh and D. A. Tomalia, *Chem. Mater.*, 11 (1999) 3268.
247. Y. Lvov, K. Ariga, I. Ichinose and T. Kunitake, *J. Am. Chem. Soc.* 117, 6117 (1995).
248. Y. Lvov, K. Ariga and T. Kunitake, *Chem Lett* 12 (1994) 2323.
249. F. Caruso and H. Mohwald, *J. Am. Chem. Soc.* 121 (1999) 6039.
250. J.-A. He, L. A. Samuelson, L. Li, J. Kumar and S. K. Tripathy, *Langmuir* 14 (1998) 1674.
251. J.-A. He., S.P. Bian., L. Li, J. Kumar, Tripathy S.K. and Samuelson L.A., *Appl. Phys. Lett.*, 76 (2000) 3233.
252. A.J. Khopade and F. Caruso, *Biomacromolecules* 3 (2002) 1154.
253. O. N. Oliveira Jr., M. Raposo, A. Dhanabalan, in *Handbook of Surfaces and Interfaces of Materials*, edited H.S. Nalwa, Academic Press, San Diego, CA (2001) Vol. 4, p. 1.

254. N.G. Hoogeveen, M. A. Cohen-Stuart, G. F. Fleer and M.R. Böhmer, *Langmuir* 12, 3675 (1996).
255. V. Zucolotto, P. J. Strack, F. R. Santos, D. T. Balogh, C. J. L. Constantino, C. R. Mendonça, O. N. Oliveira Jr., *Thin Solid Films*, vol 453-454C, pp 110-113, 2004.
256. P.T. Hammond, *Current Opinion in Coll. and Interface Sci.* 4, 430 (2000).
257. W.B. Stockton and M.F. Rubner, *Macromolecules* 30, 2717 (1997).
258. J. Anzai, Y. Kobayashi, N. Nakamura, M. Nishimura and T. Hoshi, *Langmuir* 15, 221 (1999).
259. I. Ichinose, H. Tagawa, S. Mizuki, Y. Lvov and T. Kunitake, *Langmuir* 14, 187 (1998).
260. S.L. Clark, M.F. Montague and P. T. Hammond, *Macromolecules* 30, 7237 (1997).
261. E. Donath, D. Walther, V.N. Shilov, E. Knippel, A. Budde, K. Lowack, C.A. Helm and H. Möhwald, *Langmuir* 13, 5294 (1997).
262. F. N. Crespilho, V. Zucolotto, J. R. Siqueira Jr., A. J. F. Carvalho, F. C. Nart and O. N. Oliveira Jr., *Int. J. Electrochem. Sci.* 1 (2006) 151.
263. W. T Gao, S. F. Zhang, J. Z. Yang, L. Huang, *Dyes Pigm.* 44 (2000) 155.
264. V. R. Albertini, A. Generosi, B. Paci, P. Perfetti, G. Rossi, A. Capobianchi, A. M. Paoletti, R. Caminiti, *Appl. Phys Lett.* 82 (2003) 3868.
265. C. C. Leznoff, A. B. P. Lever (Eds), *Phthalocyanines: Properties and Applications*, vols.1-4, Wiley-VCH, Cambridge, 1989-1996.
266. F. N. Crespilho, T. F. C. C. Borges, V. Zucolotto, E. R. Leite, F. C. Nart, O. N. Oliveira Jr., *J. Nanosci. Nanotechnol.* 6 (2006) 2588.
267. F. N. Crespilho, V. Zucolotto, C.M.A. Brett, O. N. Oliveira Jr., F. C. Nart, *J. Phys. Chem. B.* (2006) in press.
268. M. Q. Zhao and R. M. Crooks, *Adv. Mater.* 11 (1999) 217.
269. M. Q. Zhao and R. M. Crooks, *Chem. Mater.* 11 (1999) 3379.
270. H. Ye and R. M. Crooks, *J. Am. Chem. Soc.* 127 (2005) 4930.
271. Y-G. Kim, S-K Oh, R. M Crooks, *Chem. Mater.* 16 (2004) 167.
272. M. Campas, C. O'Sullivan *Analy. Letters* 36 (2003) 2569.
273. F. N. Crespilho, V Zucolotto, J. R. Siqueira Jr., C. J. L Constantino, F. C Nart and O. N. Oliveira Jr. *Environ. Sci. Technol.* 39 (2005) 5385.
274. M. Florescu, C.M.A. Brett. *Analytical Letters* 37(5) (2004) 871-886.
275. S. M. Chen. *Electrochimica Acta* 43 (1998) 3359-3369.
276. R.O. Lezna, R. Romagnoli, N.R. de Tacconi, K. Rajeshwar *J. Phys. Chem. B* 106 (2002) 3612-3621.
277. C.-X. Cai, H.-X. Ju, H.-Y. Chen. *J. Electroanal. Chem.* 397 (1995) 185-190.
278. Z. Xun, C. Cai, W. Xing, T. Lu. *J. Electroanal. Chem.* 545 (2003) 19-27.
279. F. Xu, M. Gao, L. Wang, T. Zhou, L. Jin, J. Jin. *Talanta* 58 (2002) 427-432.
280. D.R. Shankaran, S.S. Narayanan, ? Russ. *J. Electrochem.* 38 (2002) 987-991.
281. D.R. Shankaran, S.S. Narayanan, *Sensors & Actuators B* 86 (2002) 180-184.
282. M.S. Lin, Y.C. Wu, B.I. Jan, *Biotechnol. Bioeng.* 62 (1999) 56-61.
283. A. Jaiswal, J. Colins, B. Agricole, P. Delhaes, and S. Ravaine, *J. Colloid Interface Sci.* 261 (2003) 330.