



Developing Langmuir–Blodgett strategies towards practical devices

G. Zhavnerko^{a,*}, G. Marletta^b

^a Institute of Chemistry of New Materials, National Academy of Sciences of Belarus, F.Skoriny 36, 220141 Minsk, Belarus

^b Laboratory for Molecular Surfaces and Nanotechnologies, Department of Chemical Sciences, University of Catania, Viale A.Doria 6, 95125 Catania, Italy

ARTICLE INFO

Article history:

Received 11 June 2009

Received in revised form

27 November 2009

Accepted 6 December 2009

Keywords:

Solid–fluid interfaces

Langmuir–Blodgett films

Roll-to-Roll technique

Drug encapsulation

Plastic electronics

ABSTRACT

Several industrially important aspects of functionalized surfaces are discussed including applications to artificial membranes, patterning materials, thin film optical devices, and displays. Special attention is focused on the design of nanostructured surfaces by update of Langmuir–Blodgett method. The potentialities of the method of horizontal precipitation of monolayer films for the formation of artificial membranes are demonstrated, and the formation of “raft” domains resulting in the self-organization of lipids in a monolayer is reported. Also, many approaches to flexible polymeric support modification using specially developed LB equipment are described, including examples dealing with the effective ways of capsulation of drugs, formation of hybrid structures, and surface patterning, from the standpoint of medical or plastic electronic applications.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

A huge spectrum of nanostructured surfaces of functional materials is currently developed in various application directions. The challenge consists primarily in using bottom-up methods of molecular and nanoscale architectures for their industrial production. Combination of molecular and supramolecular chemistry or more complex nanostructured building blocks (nanoparticles (NP), carbon nanotubes (CNT), etc.) with Langmuir–Blodgett (LB) method can result in new materials with new properties not otherwise accessible. Efforts in this direction are just beginning despite long history of LB method [1]. Indeed, there are numerous attempts to construct hybrid and patternable materials applying LB methodology [2–5], as in case of polymeric membranes [6,7], electronic and molecular electronic devices [8], organic light emitted diodes (OLED) [9], plastic solar cells [10], etc. there are numerous attempts to construct hybrid and patternable materials applying LB methodology [2–5], as in the case of polymeric membranes [6,7], electronic and molecular electronic devices [8], organic light emitted diodes (OLED) [9], plastic solar cells [10], etc.

LB technology is quite flexible because it allows to vary multiparameter conditions of film fabrication, such as subphase composition, nature of molecules and counter ions, and pressure of deposition. In particular, the formation of multicomponent films as well as self-organization of molecules at water interface is made possible. That is why it is highly desirable to extend the unique

properties of LB films to the outside world by improving existing fabrication methodologies. Automated LB methods could be the breaking factor to the fabrication of defect-free films on a large scale [11], this still being the most relevant problem limiting the practical development of LB materials. Thus, the fabrication of defect-free LB layers on square-meter scale is a major challenge.

Indeed, Langmuir–Schaefer (LS) method of deposition may be used [12,13] for robust and hydrated monolayer deposition instead of traditional vertical method (VM) [14] to solve the stress and deformation problems with film transfer onto solid substrate. However, in general, this approach is not able to solve the question of overcoming the critical limitation of the Langmuir–Blodgett assembly, deriving from its low throughput in terms of “worked” devices areas. This factor is indeed the one which appears incompatible with industrial-scale production.

The aim of the present paper is to discuss several examples of modified LB films to analyze the basic limitations of the current methodologies, suggesting possible ways to overcome the difficulties.

2. LB devices

Probably Langmuir–Schaefer method was the first attempt to improve the transfer of the Langmuir monolayer to obtain high-quality films [15]. The matter is that VM of monolayer transfer (Fig. 1) is complicated by compound aggregation at the three-phase “water–air–substrate” contact line, molecules overturning in meniscus, and blocking of deposition if impurities are present in subphase. LS method allows to detach a part of a monolayer

* Corresponding author. Tel.: +375 17 237 67 96; fax: +375 17 237 68 28.

E-mail address: zhavnerko@yahoo.co.uk (G. Zhavnerko).

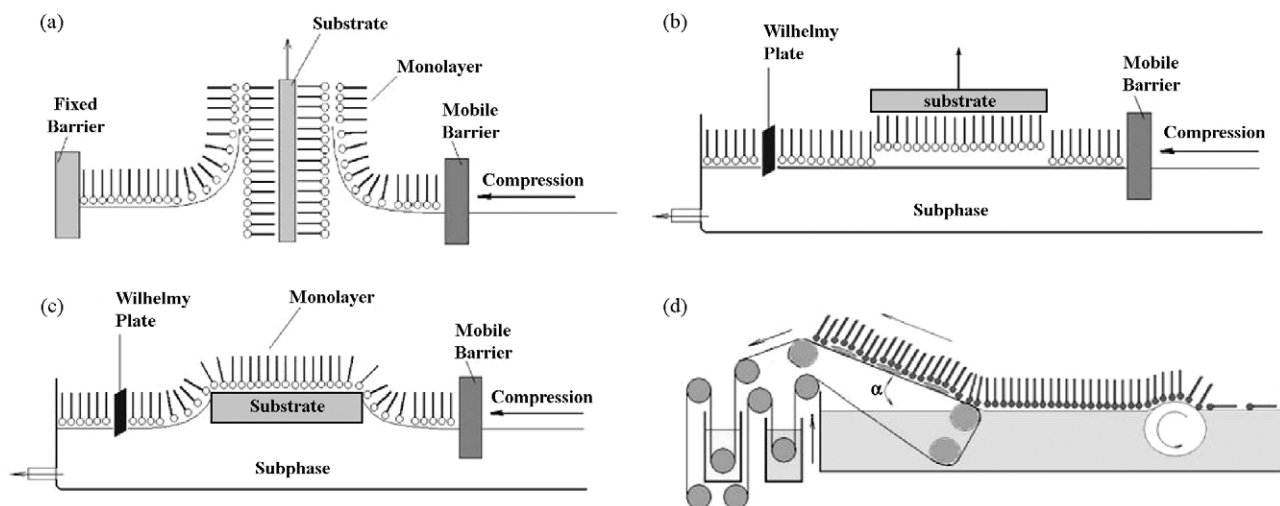


Fig. 1. Schematic illustration of different modes of Langmuir film deposition: (a) Langmuir–Blodgett vertical method, (b) Langmuir–Shaefer, (c) Horizontal Precipitation; (d) Roll-To-Roll deposition.

from water interface by bringing a horizontally oriented substrate in contact with the monolayer from the air side (Fig. 1b). In specific cases, uniform films can be obtained using LS technique, at variance of what is found with conventional Langmuir–Blodgett vertical method deposition [15].

An alternative way of overcoming the drawbacks of VM deposition consists in the transfer of the monolayer to solid support by just decreasing the level of water surface below the one of the substrate, initially located under water (Fig. 1c). Such approach, indicated as horizontal precipitation (HP) method, has also been recently realized in commercial LT-103 and LT-201 troughs [16] (Figs. 1 and 2).

There are several examples of advantages of HP method. In particular, using that method matching of the crystallographic lattice parameters of the film and substrate was found [17] on an example of behenic acid monolayer on mica. That finding demonstrated quasi-epitaxial deposition of floating fatty acid monolayer onto crystalline mica surface during the process of horizontal precipitation of a monolayer. In that case it was possible to visualize, by AFM, the phase transitions that occurred in a monolayer during its compression [17]. The method of horizontal precipitation can also be quite prominent for the preparation of multicomponent membrane structures to avoid the formation of multilayer lipid domains in the overall mesomorphic organization, which often occurs when

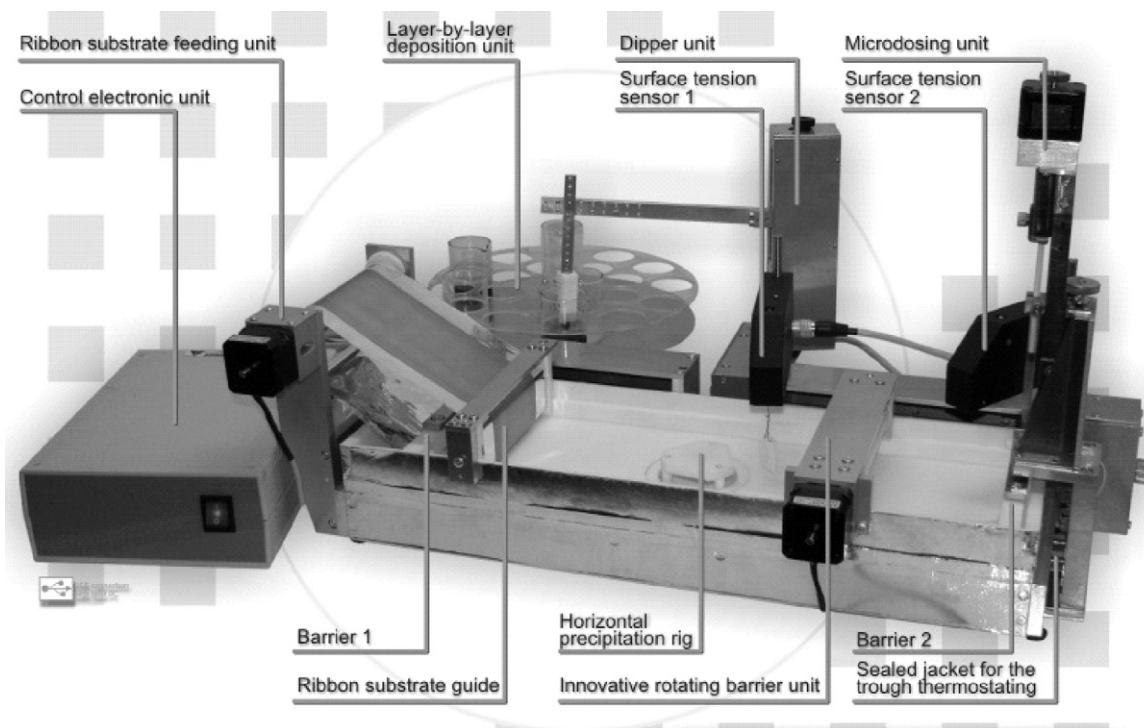


Fig. 2. LT-201 equipment for mono- and multilayer film formation by Langmuir–Blodgett, Roll-to-Roll and Layer-by-Layer (LbL) deposition. Langmuir–Blodgett trough is equipped with two surface tension sensors, rotating barrier and dispenser. Dipper unit allows to move a substrate between LB trough and LbL deposition unit to form both LB and LbL films in the same process.

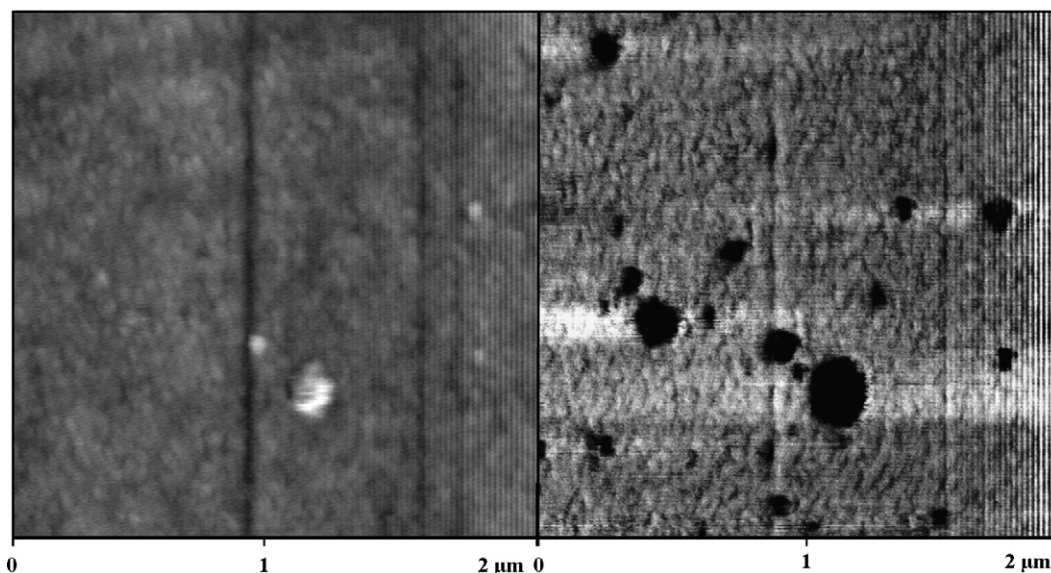


Fig. 3. The film morphology and corresponding friction properties for the DPPC:Sphingomyelin:Cholesterol = 1:1:0.1 composition. The film was transferred on mica surface from water interface by HP method of deposition at 20 mN/m of surface pressure. AFM-image was taken in a contact mode at a speed 5 Hz. Lateral force mode was realized due to scanning at 90° relatively to the fast scan direction, which gives an opportunity to recognize the domains with different rigidity. Black spots on right image correspond to “raft” domains that formed in Langmuir monolayer in a result of association of the molecules.

bilayer is formed by vesicle fusion or by original Langmuir–Blodgett vertical dipping technique. An opportunity of aggregated structure formation is also excluded using the method of horizontal precipitation. As an example, Fig. 3 reports the formation of “raft” domains in monolayer film formed through self-organization of cholesterol (CHL), sphingomyelin (SM), and dipalmitoylphosphatidylcholine (DPPC) [18]. The domains that are essentially different in friction have been found by lateral force microscopy (Fig. 3). They are practically indiscernible in topography image. Someone can correlate the dark color of the domains in friction image with close-packed molecules in determined regions, we believe in “raft domains”. On the contrary, extremely homogeneous film was formed for DPPC:SM:CHL mixture at significant (~30%) content of cholesterol [18].

Another approach was realized in LT-201 device [16], which is oriented on monolayer film transfer by automatic Roll-to-Roll (RTR) processing. In this case, a trough separated in two parts by rotating barrier has been developed, as shown in Fig. 2. Feedback control between dispenser and tensiometer (Wilhelmy method) allows to maintain automatically surface pressure rather low. Then, the transfer of surface-active molecules by rotating barrier to a compartment for deposition and film formation on a flexible tape takes place. The tape is withdrawn through a monolayer under a small angle relative to water interface (see Fig. 1d). Such kind of deposition is similar to RTR process to the film manufacture in different areas such as newspapers and labels [19]. Similar RTR-LB processing can offer a significant advantage compared with the conventional LB process, as it can be mixed with advanced technologies and the integration of nanoscale materials into devices can take place that have practical significance such as membranes, sensors, flexible displays and solar cells. The fields of LB applications that can arise from RTR-LB technique are characterized below.

3. LB films for membrane surfaces and capsulation technologies

Supported lipid mono- and bilayers can be used as platforms for membrane-associated ligands and receptors. Protein incorporation in membrane structures is aimed at understanding the functions

of natural membranes or sensor fabrication based on molecular recognition processes. For example, LB technique can improve antibody orientation on surfaces for immunosensor designs [20]. Modelling the functions of lipid membranes will allow understanding the mechanisms of lipid interactions with peptides, enzymes, proteins, nanocarriers, etc. [21] that can be used to develop both artificial membrane systems and efficient drug delivery systems [22].

One of the serious problems for the application of LB-based materials is the low mechanical stability of multilayer films due to lateral mobility of molecules, especially in the presence of water. So, there is a problem of film stabilization onto solid substrate. The possibility of a combination of LB films with polyelectrolyte ones on dimethyldioctadecylammonium bromide/poly(vinyl sulfate)/poly(allylaminehydrochloride) by the alteration of Langmuir–Blodgett and Layer-by-Layer (LbL) methods [23] was proved. The ionic cross-linking (i.e., “gluing”) of a Langmuir–Blodgett bilayer derived from a cationic calix[6]-arene has been found to be useful for the formation of stable hydrophobic complexes due to the strong electrostatic interaction between the surfactant headgroups and polymer backbone [24]. It was also demonstrated that two monolayers of calix[6]arene that were glued to poly(styrene sulfonate) (PSS) exhibited a He/N₂ gas permeation selectivity [7,25]. Such finding gives an opportunity to improve the membranes properties and have led to the design of synthetic composite membranes, combining structural features and functional advantages of both the microporous and the homogeneous membranes.

LB films for gas separations at the industrial level may be on the horizon using RTR-LB technology. RTR-LB processing in combination with automatized LbL treatment in solution (see schematics in Fig. 1d) may bring an additional possibility of extra layer deposition through self-organization or chemical cross-linking reactions.

For RTR-LB processing it also seems new applications in the field of electronic paper production and liquid crystal capsulation. For example, E-ink Corporation uses a microencapsulated electrophoretic material that consists of millions of microcapsules containing charged pigment particles [26]. A pixel-encapsulated flexible LCD with a multifunctional elastomer substrate fabricated by a replica molding [27] was also reported. Technical

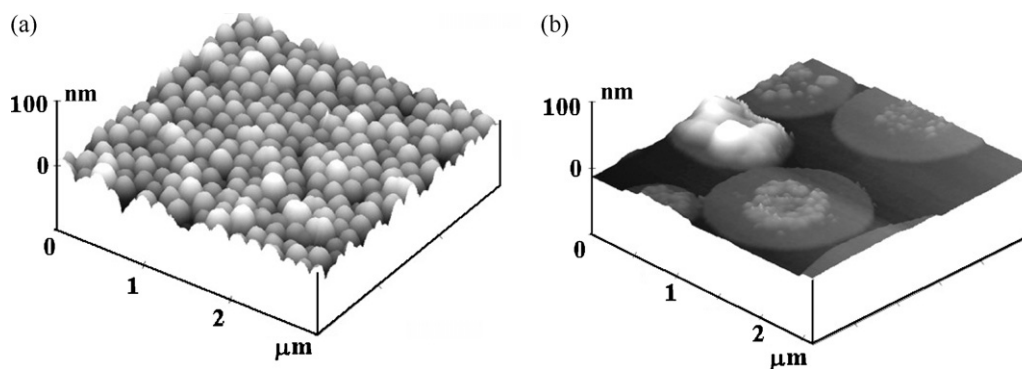


Fig. 4. (a) AFM images of LB monolayer of encapsulated dye in block copolymer shell that was covered with additional polysiloxane one. Polysiloxane shell was formed in the result of tetraethoxysilane hydrolysis in basic media. (b) LB film of the same composition without polysiloxane shell. It is possible to see both dye in the center part of a circles and block copolymer shell around dye. the images were taken in tapping mode with standard tips (RTESP) using nanoscope-3A microscope.

approaches include polymer-dispersed liquid crystals (PDLCs), pixel-encapsulated liquid crystals, photoenforced stratification, and encapsulating liquid crystals into polymer capsules. It is attractive to use LB technology for the production of thin film encapsulated materials. It can be done with block copolymer compositions. As an example of possibilities for preparing capsulated LB films, both a part of LB layer with capsulated dye and LB film of inner part of capsules are shown in Fig. 4.

Thus, RTR-LB deposition can be also used both for the separation and deposition of capsulated drugs.

4. Formation of hybrid structures and surface patterning

Advancement has been made in the chemical synthesis of nano-materials and building blocks of a wide range of materials can be now made with good control over their size, shape, and crystallinity. Compression of Langmuir monolayer is a very versatile approach to fabricate both closely packed nanoparticle superstructures and well-defined patterns with low density of particles. The Langmuir–Blodgett technique provides a suitable way to control the thickness of metalorganic film due to the variations in surface pressure of deposition. Additionally, the inorganic lattice and the pH of the subphase play an important role in organizing LB films [28], for example, in the case of octadecylphosphonic acid with various divalent, trivalent, and tetravalent metal ions [29,30]. Indeed, the use of LB films as precursors to metal-oxide films has been employed in the production of Zn and Ti oxide films and other films [31,32]. Typically, the metal ions are incorporated into the water subphase, prior to LB deposition, to allow binding of the ions to the polar heads of the constituent monolayer molecules or metallocomplexes, which are incorporated within the monolayer precursor. The metal-oxide films can be subsequently generated through plasma or UV treatment. Such metal-oxide films can be used as coatings to prevent corrosion, to promote thermal stability or, as ZrO₂ films, replace dielectric for SiO₂ or oxynitrides in complementary metal-oxide semiconductor (CMOS) technology [2].

It was shown [33] that absorption and luminescence bands of the monolayers on hydrophilic glass retain the general properties of isolated crystallites. LB technique has also proved to be ideal for forming highly dense assemblies of nanocrystals and nanowires over unprecedented surface areas [34]. Collective properties of the NP try to explore in the potential applications, such as ultrahigh-density magnetic storage media and magneto-optical devices [35,36].

The cooperative behavior of metal particles and supports under density control on the Pt nanoparticles NP layer can be used in catalyst production [37]. Metallic or semiconducting SWNTs in close-packed state should also be applicable for interconnection

or high-speed transistor applications at large scale [38]. Special progress can be done through the integration of QD/polymer hybrid structures in devices by LB technique, for example, in QD-LED structures [39]. The approach and its functional use by inserting patterned and unpatterned QD monolayers into active QD-LED structures have been recently demonstrated [5]. RTR-LB deposition may give additional possibilities for fine control of the thickness and homogeneity of the monolayer, the domain structure and packing density for multilayer deposition.

Nafion (E.I. DuPont de Nemours Inc.) seems also to be a very perspective material for roller-coatings due to its cation-exchange properties and high thermal stability [40]. LS films of Nafion with incorporated TiO₂ nanoparticles have been recently produced [12], this seems perspective for photocatalytic applications and membrane technologies.

Patterned surfaces, for example lines in the sub-50 nm range, the thickness of which is controlled at the single particle level [41], can be prepared by LB technique in combination with electron-beam lithography (EBL). As an alternative, monolayer self-organization in the LB transfer process itself can be used to form patterns onto solid substrate [42]. Different monolayer systems, e.g. fatty acid esters, DPPC, or NP can be used for patterning by LB method, see [43]. However, large-scale patterning of nanostructures is difficult to achieve by convenient LB method due to the limitation of geometrical parameters of standard LB trough. On the contrary, RTR-LB processing seems to be an alternative way to produce large-scale LB patterns on flexible supports.

5. Electronic and optical applications

So-called E-tongue, an example of electronic applications of LB films, represents multi-sensor system for liquid analysis to simulate the human tongue's taste ability. Such system consists of an array of non-specific sensors with wide sensitivity toward different components of analyte sensor elements comprise LB films from conductive polymers, fatty acids, phthalocyanines, and based on impedance measurements largely employed in the analysis of ions, medicine and pollutants at the parts-per-billion level [44]. At present, "electronic tongue" system has the capability of measuring up to eight different sensor sets, each comprising an array of eight sensor units [45]. The advantage of E-tongue based on LB films over other ones, for example, the carbon paste electrodes, is high resolving electrochemical response and very good repeatability [46]. RTR-LB mode of deposition has potential in surface patterning with lipids by Fuchs method [42] and subsequent treatment of an array in solution for film stabilization on interdigital electrodes, resulting in an increasing of sensitivity and selectivity of "electronic tongue" system.

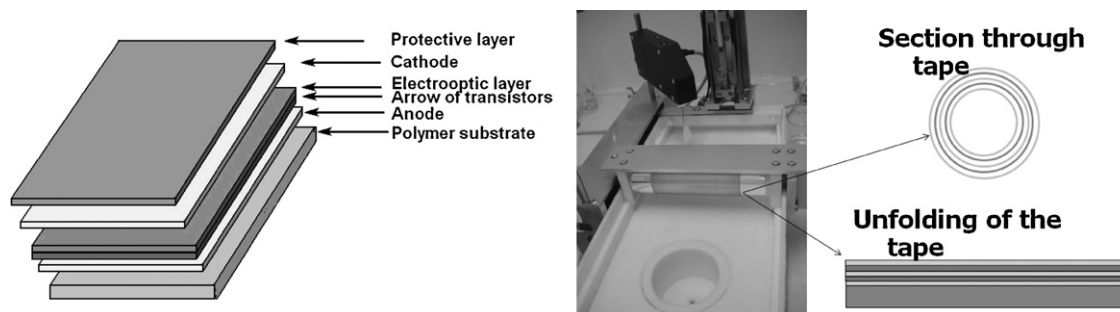


Fig. 5. Cartoon of cross-sectional structure of flexible displays (left) and schematics of multilayer film, which can be formed by RTR-LB processing (right).

Plastic electronics aimed on high-throughput and inexpensive production, mechanical flexibility, and light-weight devices. Conductive polymers are attractive for the development of organic light emitting diodes, and organic field effect transistors (OFETs), photovoltaic devices, rechargeable batteries, lasers, etc. [9,10,47,48]. Polymers such as polyphenylene and poly(p-phenylene vinylene) have been investigated as emitting materials of OLEDs, while polythiophene derivatives have been investigated as active materials for OTFTs or solar cells [49]. One of the main problems with polymer LEDs is that charge carriers (holes in particular) may go through the device without recombining and creating a photon. For solar cells the charges generated in the donor–acceptor interface have to be separated from each other to prevent the charge recombination and to deliver to the electric circuit [9,50].

The problem of non-recombining charge carriers can be addressed using multilayer films. Schematics of multilayer film construction is shown in Fig. 5a. Proper film morphology and film consequences must be achieved to optimize the performance of the device. In general, different approaches for multilayer structure fabrication by RTR method can be realized using LT-201 device. Multilayers can be prepared at water interface as one-step-process using plastic foil as a substrate on rotating barrier and two different monolayers in different compartments. Synchronous movement of a rotating barrier with compressing barriers can produce multilayer structure (Fig. 5b).

Unique properties of block copolymers can also be used for the formation of monolayer film or multilayer ones with encapsulated material (QDs, dyes, electronactive components). For example, block copolymers can produce extremely thin two-dimensional

“envelopes” in a form of LB film for capsulation of necessary compounds (Fig. 6a).

There has been much research dedicated to find a way to obtain high-quality films at low temperatures by developing new deposition technologies and improving the deposition processes, including sputter deposition [51] or electrobeam deposition [52]. Due to the ease of film preparation by RTR-LB technique there can be a lot of combinations of the typical block copolymer architectures and the unique electronic functions of conjugated polymers [10], which may result in the development of new organic photovoltaic materials with high solar energy conversion efficiency.

A multilayer thin film encapsulation is possible, where multilayer thin films are directly deposited on the OLED structures, providing a thinner device structure compared to the polymer film encapsulation. Besides polyaniline (PANI), conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT), mainly due to its excellent electrical conductivity and optoelectronic properties, has been introduced into OLEDs as hole injection layer in a composition with polyelectrolyte (polystyrene sulfonate, PSS) counterions. Due to the small α angle in RTR processing (Fig. 2), it may be possible to avoid the use of PSS for deposition of film from functional material with poor amphiphilic properties and to prepare well layer-ordered film on the analogy with poly(vinylcarbazole) layer presented in Fig. 6b.

RTR-LB deposition seemed to be a perspective for the separation of charge carriers. The use of polymer multilayers is also important for polymer solar cells. Here the object is to separate the charges of an exciton formed by light absorption, into two different polymers. Electrons are then transported to one electrode, holes to the other,

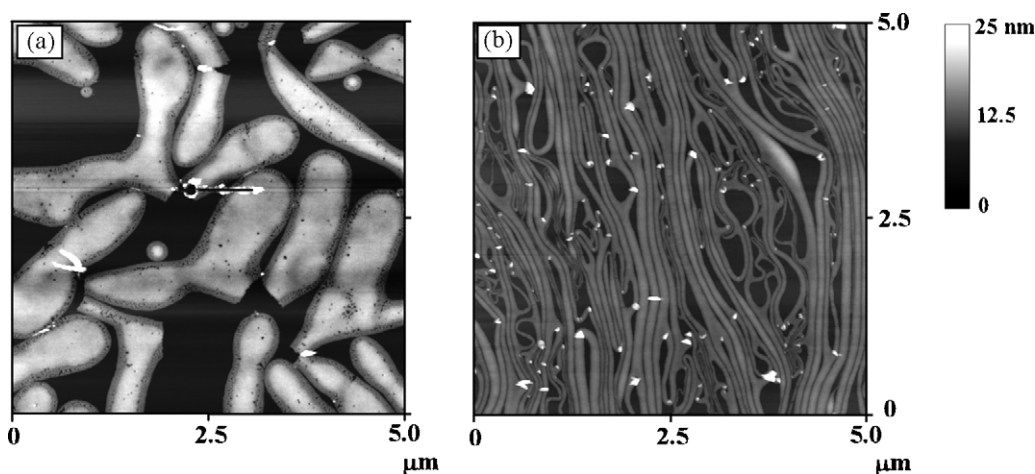


Fig. 6. Morphology of Langmuir film from (a) encapsulated dye in block copolymer “envelope”, (b) monolayer of poly(vinylcarbazole) transferred by HP method of deposition on silicon substrate. β -Diketonate Europium complex (dye) was spread at a water interface from chloroform solution with block copolymer additive and the monolayer was compressed to 7 mN/m of surface pressure before deposition by HP method. In the case of (b) image 2000 kDa polyvinylcarbazole with a concentration of 1 mg/ml in chloroform solution was used for nanostructured film formation and deposition at 10 mN/m of surface pressure.

thus creating a current. PEDOT can be used as transparent anode, as it exhibits very high conductivity of about 300 S/cm and is almost transparent in thin, oxidized films and shows a very high stability in the oxidized state [53].

LS method was already used for the evaluation of the possibility of fabrication of a solid-state switching device based on so-called catenane molecules [8]. The challenge of improvement by HP and RTR processing of both catenane and rotaxane monolayer film quality for the production of future molecular electronic devices also exists.

6. Summary

The problems of the high technological industries cannot be separated from solid-state engineering. More work is needed to improve the quality of the deposited films. Langmuir–Blodgett technology produces perfect defect-free coverings and gives possibilities of the combination of molecular and supramolecular chemistry or more complex nanostructured building blocks that result in new materials with new properties.

Roll-to-Roll LB processing seemed to be as an alternative way to produce large-scale LB films on flexible supports that allow to overcome the critical limitation of the Langmuir–Blodgett vertical dipping technique, deriving from its low throughput in terms of “worked” device areas.

RTR-LB processing can offer a significant advantage compared with the conventional LB process, as it can be mixed with advanced technologies and the integration of nanoscale materials into devices can take place that have practical significance such as fabrication of membranes, sensors, flexible displays, and solar cells. Control of film morphology may be of higher importance for plastic electronics, since the electron/hole mobility is significantly higher for ordered than for amorphous films. Control over layer-by-layer deposition and molecular orientation has led researchers to use the LB films to combine properties in a single assembly, to form hybrid materials.

A way to put into practical applications and reduce production costs using mono- and multilayer films for membrane technologies, polymer-based and molecular electronics would be Roll-to-Roll processing.

Acknowledgement

The Authors thank the financial support of Project “WATERFALL: Sviluppo di biomateriali innovativi e metodologie ottiche avanzate per dispositivi oftalmici di nuova generazione” (RBIP06KEWY from MUR-Rome, Italy).

References

- [1] D.K. Schwartz, *Surf. Sci. Rep.* 27 (1997) 241–334.
- [2] S.M.D. Watson, K.S. Coleman, A.K. Chakraborty, *ACS Nano* 2 (2008) 643–650.
- [3] A.R. Tao, J. Huang, P. Yang, *Acc. Chem. Res.* 41 (2008) 1662–1673.
- [4] Q. Guo, X. Teng, S. Rahman, H. Yang, *J. Am. Chem. Soc.* 125 (2003) 630–631.
- [5] L.A. Kim, P.O. Anikeeva, S.A. Coe-Sullivan, J.S. Steckel, M.G. Bawendi, V. Bulovic, *Nano Lett.* 8 (2008) 4513–4517.
- [6] B. Tiek, *Adv. Mater.* 3 (1991) 532–541.
- [7] J. Li, V. Janout, S.L. Regen, *Chem. Mater.* 18 (2006) 5065–5069.
- [8] A.R. Pease, J.O. Jeppesen, J.F. Stoddart, Y. Luo, C.P. Collier, J.R. Heath, *Acc. Chem. Res.* 34 (2001) 433–444.
- [9] Y. Shao, Y. Yang, *Adv. Mater.* 17 (2005) 2841–2844.
- [10] U. Scherf, A. Gutacker, N. Koenen, *Acc. Chem. Res.* 41 (2008) 1086–1097.
- [11] O. Albrecht, K. Eguchi, H. Matsuda, T. Nakagiri, *Thin Solid Films* 284–285 (1996) 152–156.
- [12] P. Bertonecello, A. Notargiacomo, C. Nicolini, *Langmuir* 21 (2005) 172–177.
- [13] V. Ruiz, P.G. Nicholson, S. Jollands, P.A. Thomas, J.V. Macpherson, P.R. Unwin, *J. Phys. Chem. B* 109 (2005) 19335–19344.
- [14] I. Langmuir, V.J. Schaefer, *J. Am. Chem. Soc.* 60 (1938) 1351–1360.
- [15] K.B. Blodgett, I. Langmuir, *Phys. Rev.* 51 (1937) 964–982.
- [16] For LT-103 device see <http://microtm.com/lt103/lt103r.htm> website and <http://microtm.com/lt201/lt201e.htm> website for LT-201 device.
- [17] G.K. Zhavnerko, V.E. Agabekov, M.O. Gallyamov, I.V. Yaminsky, A.L. Rogach, *Colloids Surf. A: Physicochem. Eng. Aspects* 202 (2002) 233–241.
- [18] G.K. Zhavnerko, V.E. Agabekov, G. Marletta, in: S.V. Gaponenko, V.S. Gurin (Eds.), *Physics, Chemistry and Application of Nanostructures*, World Scientific Publ. Co., Singapore, 2009, pp. 349–352.
- [19] J.R. Sheats, *Proc. SPIE* 4688 (2002) 240–248.
- [20] F. Loscher, T. Ruckstuhl, T. Jaworek, G. Wegner, S. Seeger, *Langmuir* 14 (1998) 2786–2789.
- [21] N.C. de Souza, W. Caetano, R. Itri, C.A. Rodrigues, O.N. Oliveira, J.A. Giacometti, M. Ferreira, *J. Colloid Interf. Sci.* 297 (2006) 546–553.
- [22] Ch. Peetla, A. Stine, V. Labhasetwar, *Mol. Pharm.* 6 (2009) 1264–1276.
- [23] Yu. Lvov, F. Essler, C. Decher, *J. Phys. Chem.* 97 (1993) 13773–13777.
- [24] J. Li, V. Janout, S.L. Regen, *Langmuir* 20 (2004) 2048–2049.
- [25] X. Yan, V. Janout, J.T. Hsu, S.L. Regen, *J. Am. Chem. Soc.* 125 (2003) 8094–8095.
- [26] Y. Chen, J. Au, P. Kazlas, A. Ritenour, H. Gates, M. McCreary, *Nature* 423 (2003) 136–137.
- [27] Y.T. Kim, J.-H. Hong, T.Y. Yoon, S.D. Lee, *Appl. Phys. Lett.* 88 (2006) 263501–263503.
- [28] C.T. Seip, G.E. Granroth, M.W. Meisel, D.R. Talham, *J. Am. Chem. Soc.* 119 (1997) 7084–7094.
- [29] M.A. Petruska, D.R. Talham, *Langmuir* 16 (2000) 5123–5129.
- [30] A. Wu, D.R. Talham, *Langmuir* 16 (2000) 7449–7456.
- [31] D.M. Taylor, J.N. Lambi, *Thin Solid Films* 243 (1994) 384–388.
- [32] D.V. Paranjape, M. Sastry, P. Ganguly, *Appl. Phys. Lett.* 63 (1993) 18–20.
- [33] B.O. Dabbousi, C.B. Murray, M.F. Rubner, M.G. Bawendi, *Chem. Mater.* 6 (1994) 216–219.
- [34] T. Hyeon, S.S. Lee, J. Park, Y. Chung, H.B. Na, *J. Am. Chem. Soc.* 123 (2001) 12798–12801.
- [35] C.B. Murray, C.R. Kagan, M.G. Bawendi, *Annu. Rev. Mater. Sci.* 30 (2000) 545–610.
- [36] S.H. Sun, S. Anders, H.F. Hamann, J.U. Thiele, J.E.E. Baglin, T. Thomson, E.E. Fullerton, C.B. Murray, B.D. Terris, *J. Am. Chem. Soc.* 124 (2002) 2884–2885.
- [37] H. Song, F. Kim, S. Connor, G.A. Somorjai, P. Yang, *J. Phys. Chem. B* 109 (2005) 188–193.
- [38] X. Li, L. Zhang, X. Wang, I. Shimoyama, X. Sun, W.-S. Seo, H. Dai, *J. Am. Chem. Soc.* 129 (2007) 4890–4891.
- [39] N. Tomczak, D. Janczewski, M. Han, G.J. Vancso, *Prog. Polym. Sci.* 34 (2009) 393–430.
- [40] J. Wang, M. Musameh, Y. Lin, *J. Am. Chem. Soc.* 125 (2003) 2408–2409.
- [41] M.H.V. Werts, M. Lambert, J.-P. Bourgoin, M. Brust, *Nano Lett.* 2 (2002) 43–47.
- [42] X. Chen, S. Lenhart, M. Hirtz, N. Lu, H. Fuchs, L. Chi, *Acc. Chem. Res.* 40 (2007) 393–401.
- [43] X.D. Chen, A.L. Rogach, D.V. Talapin, H. Fuchs, L.F. Chi, *J. Am. Chem. Soc.* 128 (2006) 9592–9593.
- [44] A. Riul, A.M. Gallardo Soto, S.V. Mello, S. Bone, D.M. Taylor, L.H.C. Mattoso, *Synth. Met.* 132 (2003) 109–116.
- [45] B.A. da Silva, P.A. Antunes, D. Pasquini, A.A. Curvelo, R.F. Aroca, A.J. Riul, C.J. Constantino, *J. Nanosci. Nanotechnol.* 7 (2007) 510–514.
- [46] F.P.A. Cabral, B.B. Bergamo, C.A.R. Dantas, A. Riul, J.A. Giacometti, *Rev. Sci. Instrum.* 80 (2009) 026107.
- [47] T. Tatsuma, T. Sotomura, T. Sato, D.A. Buttry, N. Oyama, *J. Electrochem. Soc.* 142 (1995) 182–184.
- [48] F. Hide, M.A. Diaz-Garcia, B. Schwartz, M.R. Andersson, Q. Pei, A.J. Heeger, *Science* 273 (1996) 1833–1836.
- [49] M.-Ch. Choi, Y. Kim, Ch.-S. Ha, *Prog. Polym. Sci.* 33 (2008) 581–630.
- [50] F. Padinger, R.S. Rittberger, N.S. Sariciftci, *Adv. Funct. Mater.* 13 (2003) 85–88.
- [51] B.M. Henry, A.G. Erlat, A. McGuigan, C.R.M. Grovenor, G.A.D. Briggs, Y. Tsukahara, T. Miyamoto, N. Noguchi, T. Nijima, *Thin Solid Films* 382 (2001) 194–201.
- [52] C.-S. Deng, H.E. Assender, F. Dinelli, O.V. Kolosov, G.A.D. Briggs, T. Miyamoto, Y. Tsukahara, *J. Polym. Sci. B: Polym. Phys.* 38 (2000) 3151–3162.
- [53] B.L. Groenendaal, G. Zotti, P.-H. Aubert, S.M. Waybright, J.R. Reynolds, *Adv. Mater.* 15 (2003) 855–879.