REVIEW

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Cite this: *Mater. Horiz.*, 2021,
8, 1409

Liquid–liquid interfaces: a unique and advantageous environment to prepare and process thin films of complex materials

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Thin film technology is pervasive for many fields with high impact in our daily lives, which makes processing materials such as thin films a very important subject in materials science and technology. However, several paramount materials cannot be prepared as thin films through the well-known and consolidated deposition routes, which strongly limits their applicability. This is particularly noticeable for multi-component and complex nanocomposites, which present unique properties due to the synergic effect between the components, but have several limitations to be obtained as thin films, mainly if homogeneity and transparency are required. This review highlights the main advances of a novel approach to both process and synthesize different classes of materials as thin films, based on liquid/liquid interfaces. The so-called liquid/liquid interfacial route (LLIR) allows the deposition of thin films of single- or multi-component materials, easily transferable over any kind of substrate (plastics and flexible substrates included) with precise control of the thickness, homogeneity and transparency. More interesting, it allows the *in situ* synthesis of multi-component materials directly as thin films stabilized at the liquid/liquid interface, in which problems related to both the synthesis and processing are solved together in a single step. This review presents the basis of the LLIR and several examples of thin films obtained from different classes of materials, such as carbon nanostructures, metal and oxide nanoparticles, two-dimensional materials, organic and organometallic frameworks, and polymer-based nanocomposites, among others. Moreover, specific applications of those films in different technological fields are shown, taking advantage of the specific properties emerging from the unique preparation route.

Received 19th October 2020,
Accepted 4th January 2021

DOI: 10.1039/d0mh01676d

rsc.li/materials-horizons

1. Introduction

Concerns about the application of a specific material correspond to the main focus of the majority of scientific papers published in the field of materials science. Even papers related to pure and fundamental issues (for example the ones describing a novel synthetic pathway or fundamental understanding of some property) justify their subjects emphasizing the importance of the fundamental knowledge of materials to their real or potential applicability. This is a known and expected behavior due to the inseparable relationship between materials, their structures, their properties and their function (which orients the possibility of application).

The demonstration of a fantastic property of a material, however, is not enough to guarantee that it is ready to be used in a real device or system. For a lot of technological applications, materials should be processed to make the specific property useful in systems and devices. Materials processing

is an important link between science and technology, and it is often forgotten or underestimated by part of the scientific community.

Among different ways to process a material, deposition as a thin film corresponds to one of the most effective and efficient methods. A thin film is a very thin (from one atom to several microns thickness) and continuous layer of a material deposited over a support (usually referred to as a substrate).¹ Among several advantages, processing materials as thin films allows direct incorporation in a multi-component or multi-layer device, their use as a coating on practically any kind of substrate, and significant economy in the amount of material and economy in cost. It is not by coincidence that thin film technology is strongly present in a myriad of daily technologies, such as batteries, transistors, solar cells, supercapacitors, fuel cells, optics, sensors, microelectronics, transparent electrodes, magnetic devices, coatings, corrosion protection, micro-mechanics, actuators, biological implants, magnetic shielding, catalysis, data storage media, flat panel displays, food packing, electrochromism, and many more.¹ Nowadays thin film science and technology is a well-consolidated area, and some successful

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routes to deposit different materials as thin films have been developed, either starting from the raw target material or from suitable precursors to synthesize the desirable material directly as a film.^{1,2} Techniques such as spin- or dip-coating, spray pyrolysis, Langmuir–Blodgett, chemical or physical vapor deposition (CVD or PVD, respectively), doctor blade, casting, and electrochemical deposition, among others, are largely spread through the materials community. However, there are plenty of novel and complex materials that cannot be deposited using any of those well-known deposition techniques, either due to the characteristics of the material itself (insolubility, infusibility, and dispersability) or the limitation of the deposition technique (for example, methods requiring high temperature are not allowed for deposition of polymers or of any material over plastic substrates), or both. Usually those limitations become more evident if we consider the deposition of multi-component nanocomposite materials. So, novel, complex, multi-component and multi-functional materials have been obtained, demonstrating fascinating properties arising from synergistic effects, but their potentiality cannot be fully explored in several real applications due to the impossibility of their deposition as thin films over suitable substrates.

During the past years our research group has been working on a simple and very efficient route to deposit different kinds of materials as thin films which overcomes those limitations, based on the interface between two immiscible liquids. This so-called liquid/liquid interfacial route (LLIR) allows the deposition of high-quality films of different kinds of materials (one-, two- or multi-component; organic, inorganic, organic/organic, inorganic/inorganic or organic/inorganic), over any kind of substrate (different composition and shapes, plastics included), using a very simple procedure, cheap equipment and ambient conditions (temperature, pressure and atmosphere). Also and more interesting, the method allows the *in situ*

synthesis of complex materials that are directly obtained as thin films, in a process in which both the preparation and processing problems are solved together, in one single-pot and single-step procedure. In this review, the basic principles of the LLIR to obtain thin films are introduced; some variables and parameters that control the characteristics of the films are discussed; and several examples of the preparation of thin films of different classes of materials are demonstrated. Deposition on different substrates and application in different fields such as transparent and flexible electrodes, organic and flexible solar cells, electrochemistry, optical and electrical sensors, catalysis, batteries, photoconductors, non-linear optics, supercapacitors, transistors, substrates for surface-enhanced Raman spectroscopy (SERS), membranes for gas separation and water desalinization, and electrochromic devices, among others, will also be discussed.

The fundamental of the LLIR is based on self-organization of solid particles at the interface between two immiscible liquids, normally (but not necessarily) a water/oil interface. The adsorption of solid nanoparticles of different size and shape at liquid/liquid (L/L) interfaces has been the subject of several reports and reviews,^{3–12} starting from the work of Ramsden¹³ and Pickering¹⁴ at the beginning of the last century, that have received a lot of attention in the last few years.^{3–12} Some recent papers and reviews have been published on the nature and properties of L/L interfaces,^{4,15–17} as well as on the dynamics of solid particles stabilized at those interfaces.^{5,6,8,9,11,18,19} Deeper discussions on these subjects are beyond the scope of this review, and can be found on the cited literature.^{3–19} Also, there is recent growing interest in the preparation, stabilization, characterization and application of solids at L/L interfaces, but without any concern for removal to be applied out of the L/L interface: Rao and Kalyanikutty for example reported the stabilization of inorganic nanoparticles (metals, semiconductors and metal oxides) at L/L interfaces and proposed a model for the film growth;³ Thomas *et al.* also reported the preparation of thin films of similar materials at water/oil interfaces;⁴ the application of gold nano-films at L/L interfaces as platforms for redox electrocatalysis, nanoplasmonic sensors and electrovariable optics has been recently reviewed by Scanlon *et al.*;⁸ the self-assembly of Janus nanoparticles with different geometries at L/L interfaces was reported by Ruhland *et al.*;²⁰ the catalytic performance of metal and oxide nanoparticles at L/L interfaces has been demonstrated;^{21,22} and Dryfe's group has been publishing very elegant results in recent years on chemical functionalization and electrochemistry involving solids at different L/L interfaces, mainly immiscible electrolyte solutions.^{23–27} However, it is important to clarify that this review is focused on the thin film itself and its application in thin film technology, *i.e.* using the L/L interface to prepare films, seeking their removal and deposition over target substrates.

This review starts with a description of the main fundamentals of the LLIR (Section 2), followed by examples of thin films of several different materials prepared through this technique, primarily classified according to the genesis of the solid to be deposited: films deposited from pre-existent

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scientific interests are the synthesis, characterization, and study of properties and applications of different nanomaterials, such as carbon nanotubes, graphene, 2D-materials, metal nanoparticles and conducting polymer-based nanocomposites; their processing as thin films and their application in energy (batteries, supercapacitors, photovoltaics, and electrochromics), sensors and catalysis.

materials (Section 3); films deposited from *in situ* synthesized materials (Section 4) or films obtained by chemical functionalization at liquid interfaces (Section 5). Each section is subdivided into different classes of the materials. Finally, perspectives on the future of the field are presented and discussed. Hopefully, this review will spread the LLIR technique among the different actors directly related to the synthesis and processing of complex materials, and it can inspire novel developments in this modern and fascinating area.

2. The liquid/liquid interfacial route to thin films

The general basis of the LLIR is summarized in Fig. 1, and depends on the genesis of the solid to be deposited. Basically, two immiscible liquids are put in contact, and, in the first possibility, the solid to be deposited as a thin film is previously dispersed in one of them (Fig. 1). The L/L system is further stirred at a controlled speed (or put into an ultrasound bath) in order to create droplets of one liquid phase spread over the other phase, like a macro-emulsion. After a specific time, the stirring is interrupted and spontaneous self-organization of the dispersed solid at the interface between the two liquids is observed, leading to a connected film that looks like a malleable skin. Once stabilized as a film at the interface, the material can be easily removed and deposited over suitable substrates, by putting the substrate below the film (immersed in the bottom-phase liquid) and lifting the substrate in the film direction in a controlled matter, as schematically represented in Fig. 1. This process is similar to the deposition of a towel over a table. Bi- or multi-component films can be obtained through either the previous dispersion of the components in the same solvent or each component in each one of the solvents.

The second possibility in the LLIR is based on an *in situ* interfacial chemical reaction, resulting in a solid product that will be deposited at the L/L interface. For a general reaction represented by (1):

the reactants A and B are dissolved in solvent 1 and 2, respectively, so they will only meet together exactly at the interfaces of each droplet in the macro-emulsion resulting from the stirring, leading to a solid product that once formed will behave as described before, that is, it will migrate to the interface and self-organize as a thin film, transferable to substrates in the same way. Different from the films described earlier, obtained from a preexistent solid, some chemical reactions at the L/L interface can produce films in the absence of stirring, although the macro-emulsion obtained by stirring, shaking or ultrasound is mandatory for the majority of the cases, as will be further discussed.

The most sophisticated possibility in the LLIR is a combination between the two previous procedures: a chemical reaction in the presence of one (or two) dispersed material(s). The resulting solid, which will be obtained also as a thin film at the L/L interface, will be a (nano)composite between the previously dispersed solid and the solid resulting from the chemical reaction.

As will be seen further, the three possibilities presented before and schematically represented in Fig. 1 allow the preparation of a large number of different materials as thin films. But, before the demonstration of real examples, it is important to discuss some fundamentals of the process. The first question that emerges is why the solid migrates to the interface. The primary response is based on the interfacial energies and area. The solid particles tend to minimize the high L/L interfacial energy and decrease the interfacial area so the solid migration

Fig. 1 Schematic of the deposition of thin films through the LLIR.

to the interface is thermodynamically favorable and occurs spontaneously.^{10,28,29} Parameters like the particle size, shape, chemical composition, surface composition, and roughness, among others, play important roles in this process, which means that the optimized experimental conditions for a good quality film should be found for each class of material. However, other parameters are important here: (1) the quality of the dispersion. The dispersion of the solid in one of the solvents used at the beginning of the process should be minimally stable to guarantee solid migration to the interface, otherwise it will flocculate or aggregate. The degree of dispersion stability depends on the nature of the solvent, the solid and the L/L interface. So, the preparation of a minimally stable dispersion is a key step for the success of the LLIR. The use of ultrasound is a very common approach to get those dispersions; (2) stirring under a controlled rate (or some other controlled external mechanical work, such as manual shaking or sonication). Rarely a film is obtained at the L/L interface in a static environment. The mechanical stirring allows the occurrence of small droplets of one phase over the other one, like a macro-emulsion, increasing the L/L contact area and allowing the self-organization of the particles to give the film after interruption of the stirring and the coalescence of the two liquid phases. Stirring rate control is a very important issue to be considered for good-quality films at the L/L interface.

The quality of the solid assembling at the L/L interface should also be considered. If the final objective is the production of a thin film to be removed and deposited over substrates, particles should be assembled at the L/L interface in some organized way, resulting in a uniform and connected film. The successful connection between the solid entities depends on the nature of the interface and on the size, shape and chemical characteristics of the solid. Under favorable conditions, the aggregation and connection of the particles are energetically more stable than disordered or individual dissociated objects.¹⁰ Under unfavorable conditions, the solid migrates to the L/L interface behaving like a precipitated and/or disorderly agglomerated material, in which the lack of uniformity (and consequently absence of a useful film) is evident. Due to the different attractive/repulsive forces inherent to each material, to find these optimal conditions is expected to be empirical and, as said before, dependent on characteristics such as the surface and chemical composition, size and shape of the materials.

The deposition step, *i.e.*, the removal of the film from the L/L interface to an adequate substrate, is a very critical step in the LLIR. Among several possibilities, we optimized a process in which the substrate is fixed to an L-shaped stem, immersed into the downside liquid and carefully pulled in the film direction.^{30,31} This process can be done manually or by a step-motor controlled arm, to avoid shaking, such as the ones used in deep-coating commercial equipment. Experimentally, it is done in a two-step process. The substrate in the L-shaped stem is put inside of an empty flask, and the entire system (liquid 1/solid film stabilized at the interface/liquid 2) is transferred to this flask (Fig. 1). In a few minutes, the system

self-organizes again and the film is located above the substrate, ready to be deposited. This is a very interesting property of the films stabilized at L/L interfaces: once formed, if some external force acts to destroy the film, it spontaneously self-organizes by simply waiting for the entire system to rest. The quality of the deposited film is directly dependent on the transfer process from the L/L interface to the solid substrate. Substrates of different sizes and shapes can be used. Also, the deposition process can be done at both sides of the substrate (pulling it perpendicularly towards the L/L film). Several consecutive depositions over the same substrate can also be carried out, in a layer-by-layer-like process. Examples of all these deposition possibilities and their effect on the properties and applications of films of several materials will be demonstrated in the following.

3. Thin film deposition and applications: films deposited from pre-existent materials

3.1. Carbon nanostructures

As presented in Fig. 1, films can be prepared by the LLIR starting from materials previously dispersed in one of the liquid phases. Films based on carbon nanomaterials (such as different samples of multi-, double- or single-walled carbon nanotubes, fullerenes and graphene) have been prepared and deposited over several substrates (glass, polymers such as polyethylene terephthalate – PET and silicones, silicon, silicon oxide, and quartz, among others). Biswas and Drzal have demonstrated a close-packed self-assembled monolayer of graphene sheets at a water/chloroform interface. The films deposited over glass slides presented a 4 nm thickness, 70% transmittance at 500 nm and average sheet resistance of $10^2 \Omega \text{ sq}^{-1}$.²⁸ Tang *et al.* produced thin films of graphene deposited over silica based on a cyclohexane/*N*-methyl-pyrrolidone (NMP) interface.³² The graphene was obtained through a top down approach to solvothermally exfoliate graphite in NMP. Our group has developed systematic work on LLIR thin films based on different carbon nanostructures.^{30,31} Fig. 2a shows photographic images of some carbon nanotubes or graphene films prepared at a water/toluene L/L interface and deposited over both glass (upper line, Fig. 2a) and PET (bottom line, Fig. 2a) substrates.³⁰ The films have been positioned over text to demonstrate their evident homogeneity and transparency. Those films have been applied as flexible and transparent electrodes, as can be seen in Fig. 2b, in which a bent single-walled carbon nanotube (SWCNT) film deposited over PET is employed to close an electric circuit and light a LED.³⁰ The conductivity of the films deposited over plastic substrates remains unchanged after several cycles of bending (Fig. 2c), as presented in Fig. 2d for the same SWCNT film demonstrated before.³⁰ Similar results have been obtained for different types of multi-walled carbon nanotubes (MWCNTs),³⁰ double-walled carbon nanotubes³¹ and graphene,³⁰ indicating the excellent adherence of the films over the plastic substrates and their facility to accommodate themselves under different degrees of strain.

Fig. 2 (a) Photographs of the different carbon-based films deposited over PET (up) and glass (down); (b) photograph showing a film of SWCNTs deposited over a PET substrate, in which it is possible to see the flexibility, transparency and conductivity by lighting an LED even when bent; (c) photograph of a SWCNT deposited over a PET film under applied strain; (d) sheet resistance as a function of bending cycles of a SWCNT deposited over a PET film; and (e–h) SEM images of films deposited over glass, rGO (e), SWCNTs (f), MWCNT-1 (g) and MWCNT-2 (h).³⁰ Acronyms: reduced graphene oxide, rGO; single-walled carbon nanotubes, SW; and two different samples of multi-walled carbon nanotubes, MW1 and MW2. Copyright 2016, Elsevier.

These results open several possibilities for application as transparent electrodes in flexible devices, since the most popular material for transparent electrodes (tin-doped indium oxide, ITO) is brittle and cracks under bending when deposited over plastics. The performance of those materials as electrodes in electrochemical cells has also been demonstrated, showing similar results in electrochemical processes when compared to ITO/glass electrodes, such as in the ferro/ferricyanide redox pair in solution, or in an electrochemical polymerization of aniline.³⁰ Fig. 2e–h show some scanning electron microscopy (SEM) images of graphene films (reduced graphene oxide, rGO), and single- (SW) and two samples of multi-walled carbon nanotubes (MW1 and MW2). The images are elucidative with respect to the way in which the entities organize themselves to give the films. All of them have a homogeneous distribution of the material over the entire substrate, and the nanostructures are connected between themselves. SEM images show a sheet-like morphology for graphene (Fig. 2e), connected bundles for the SWCNTs (Fig. 2f) and a spaghetti-like morphology for both MWCNT samples (Fig. 2g and h).³⁰

Besides CNTs and graphene, C₆₀-based films have also been prepared through the LLIR. Shresta *et al.* have prepared fullerene thin films with different architectures by a modified LLIR approach they called L/L interfacial precipitation.^{33–35} They start from a fullerene dispersion in one of the liquid phases and, instead of waiting for the spontaneous migration of the

dispersed material to the L/L interface, they add another solvent in which the dispersed fullerene is insoluble, accelerating the coalescence of the particles at the L/L interface.^{33–35} The morphology of the C₆₀ 2D-crystal films, including porous films, was demonstrated to be controlled by selecting the temperature, and the nature and the relative amounts of the solvents and antisolvents.^{33–35} Using a similar methodology, Banya *et al.* prepared a L/L interfacial system starting from an aqueous dispersion of microparticles of C₆₀-(1,2-diaminoethane) adducts and hexane.³⁶ After methanol injection, the dispersed particles in the aqueous phase migrate to the water-methanol/hexane interface and self-organize as a thin film that was deposited over pre-treated ITO/glass substrates. The obtained film was modified with tetraphenylporphyrin and the photo-current generation was demonstrated.³⁶

Films based on carbon nanostructures have been prepared starting from either the carbon nanomaterials initially dispersed in an organic solvent^{31,32} or in water,³⁷ evidencing the amplitude of the technique. The effect of previous chemical treatment on the samples, aiming at (i) purification (through the chemical dissolution/etching of side-products); (ii) chemical modification of the surface, or (iii) adding functionalities to stabilize the solid in dispersions, has also been demonstrated.³² For double-walled carbon nanotubes, for example, the homogeneity of the resulting films and subsequently their main properties for application as flexible transparent electrodes (conductivity, transparency

Fig. 3 Thickness (a), sheet resistance (b) and transmittance at 550 nm of a MWCNT film prepared through the LLIR at a water/toluene L/L interface, deposited over glass substrates, as a function of the amount of CNTs initially dispersed in toluene. Film photography with increasing amounts of CNTs from left to right in the (b) inset.³⁰ Copyright 2016 Elsevier.

and integrity after different cycles of bending) have been shown to be strongly dependent on the chemical treatment previously carried out on the sample.³²

One of the most important properties of thin films of different materials, as well as an important challenge for any thin film deposition route, corresponds to the control of the film thickness and the homogeneity control through the entire film area. Another fascinating characteristic of the LLIR is the facility with which this parameter can be controlled, simply managing the amount of material initially dispersed before the beginning of the deposition process. Fig. 3a shows the relationship between the thickness and transmittance of several films of MWCNTs obtained from different amounts of initially dispersed samples, at a toluene/water L/L interface.³⁰ The increase in the thickness and the decrease in the transmittance according to the increasing amount of MWCNTs available in the initial dispersion are evident. The photograph of five different samples prepared in this way is presented in the inset of Fig. 3b, in which one important property of the films – conductivity – is related to their transmittance. This is a simple and didactic demonstration of the capacity of the LLIR to prepare versatile films, adjusting their properties for specific applications: the film thickness

influences both the transparency and conductivity, which can be easily tuned by the simple control of the “concentration” of the dispersion at the beginning of the LLIR processing.

There is also another way to control the thickness of the films: adjusting the size of the flask in which the LLIR will be carried out. Specifically for round-bottom flasks, a direct relationship between the film thickness and the flask diameter was demonstrated.³⁸ Keeping all the deposition process parameters constant (volumes of both phases, temperature, stirring velocity and amount of solid dispersed in one of the phases), increasing the diameter of the round-bottom flask increases the planar interfacial area between the two immiscible liquids. In this scenario the dispersed solid is more spread out over at the L/L interface, resulting in a thinnest film.³⁸

Besides the application as transparent and flexible electrodes, films of carbon nanotubes or graphene deposited through the LLIR have been applied also as gas sensors, for which a sensitivity 3.4 times higher for oxygen detection has been demonstrated when compared to films of the same sample deposited through regular casting methods, due to the film homogeneity guaranteed by the LLIR technique.³⁹ Another very interesting application is the utilization of thin films of carbon nanostructures deposited through the LLIR as precursors for more complex materials, aiming at specific properties. For example, we developed a very interesting strategy to prepare thin films of nanocomposites between carbon nanotubes and Prussian blue (and its analogues), through a heterogeneous electrochemical reaction between iron species intrinsically present inside of the carbon nanotube cavities and ferricyanide ions available in aqueous solution.⁴⁰ Prussian blue (PB), or iron hexacyanoferrate, is the most known member of the large family of the so-called hexacyanometallate (HCM) compounds, represented by the general formula $A_xM_y[M'(CN)_6]_z \cdot nH_2O$, where A is an intercalation cation (K^+ , Na^+ , Li^+) and M and M' are transition metals in octahedral coordination with N and C, respectively, giving a zeolite-like structure.⁴¹ If the M and M' sites are occupied both by Fe, the compound is the so-called PB, and any other combination of M and M' gives the so-called Prussian blue analogue (PBA) structures.⁴¹ Some problems related to PB and PBAs, such as low electrochemical stability and low resistance to neutral or basic pH, can be avoided by preparing nanocomposites with carbon nanotubes or graphene. A myriad of novel possibilities for application emerges from thin films of these nanocomposites. We deposited Fe-filled^{42–44} or Co-filled^{42,45} carbon nanotube films using the LLIR over transparent electrodes such as ITO/glass, and afterwards performed the electrochemical reaction to synthesize PB or a PBA, yielding transparent and thin films of CNT/PBA. These films differ from conventional CNT/PB(A) ones because the chemical reaction is governed by the slow release of the iron (or cobalt) species from the CNT cavities, which is the step responsible for the reaction kinetics.⁴⁴ This controlled deposition process results in a very well-controlled morphology of the films, characterized by PB(A) nanocube growth directly over the CNT walls, improving the contact and consequently the properties of the material. The CNT/PB(A) films are multifunctional materials, which have been

applied as electrochemical sensors for H_2O_2 ,⁴⁵ electrochromic materials,⁴³ and cathodes for Li-, K- or Na-ion transparent batteries operating in water.⁴² An ITO-free, flexible and transparent electrode for K-ion secondary batteries based on the initial deposition of a CNT film over PET through the LLIR has been also demonstrated.⁴⁶

3.2. Metal nanoparticles

Starting from previously synthesized samples, films of different metal nanoparticles have also been prepared by the LLIR. For example, polyvinylpyrrolidone (PVP)-stabilized nickel nanoparticles with either an fcc or hcp structure have been prepared by our group through the polyol route, and transferred to a water/toluene biphasic system to get interfacial films, which were deposited over ITO/glass substrates and applied as an amperometric sensor for glycerol.⁴⁷ Du *et al.* prepared gold and silver nanoparticles stabilized by an amphiphilic multiblock copolymer, [poly(4-vinylpyridine)-*b*-polystyrene-*b*-poly(4-vinylpyridine)]_{*n*} (P4VP-PS-P4VP)_{*n*}.⁴⁸ Diethyl ether was added to a DMF- H_2O solution of those (P4VP-PS-P4VP)_{*n*}-capped nanoparticles creating a biphasic system (Fig. 4a). The L/L system was stirred and the nanoparticles were assembled as a thin film at the L/L interface (Fig. 4b), which was transferred onto solid substrates by casting the mixture into a Petri dish.⁴⁸ Images collected by transmission electron microscopy (TEM) demonstrate that the film is composed of polydisperse-size nanoparticles with sizes of 8.8 ± 2.4 nm (Fig. 4c) and that the thin films did not exhibit long-range order.⁴⁸ Le Ouay *et al.* prepared a dichloromethane

solution of mercaptopropyltrimethoxysilane (MPTMS)-capped Au NPs (diameter of 5.2 ± 0.9 nm), which mixed with an acidic water solution results in an unstable oil-in-water emulsion that coalesces after a few seconds, resulting in a free-standing membrane at the dichloromethane/water interface, characterized by close-packing of AuNPs cross-linked *via* the MPTMS ligands, as schematically represented in Fig. 4d and e.⁴⁹ The chemical interaction between the individual nanoparticles results in the formation of a continuous 2D membrane spanning over several square centimeters. Films have been deposited by immersing different substrates (copper grids, and cellulose-ester) into the solution and bringing them in contact with the self-assembled membrane (Fig. 4f).

3.3. Two-dimensional materials

The exciting class of two-dimensional (2D) materials beyond graphene also benefited from the LLIR. Films from dispersions of exfoliated 2D materials in aqueous or organic solvents have been reported recently. For example, the emerging family of 2D transition metal carbides and nitrides (the so-called MXenes) presents intriguing properties and functional groups that allow their chemical functionalization.^{50,51} MXenes are represented by the general formula $\text{M}_{n+1}\text{X}_n\text{T}_x$ (M is a transition metal, X is carbon and/or nitrogen, T_x is functional groups -O, OH, and F- on the MXene surface, and *n* can be between 1 and 3).^{50,51} Dong *et al.* demonstrated the non-linear optical properties of the MXene $\text{Ti}_3\text{C}_2\text{T}_x$, showing for the first time its excellent performance as a saturable absorption material aiming photonic

Fig. 4 (a) The biphasic mixture with the diethyl ether phase on top (colorless) and DMF- H_2O phase containing the (P4VP-PS-P4VP)_{*n*}-capped Au nanoparticles below (wine-red color) before stirring;⁴⁸ (b) the same system after stirring showing the wine-red nanoparticles assembled at the L/L interface;⁴⁸ and (c) TEM image of the thin film of (P4VP-PS-P4VP)_{*n*}-capped Au nanoparticles.⁴⁸ Copyright Royal Society of Chemistry, 2010. (d) Scheme of the mechanism for the formation of (MPTMS)-capped Au NP membranes, in which the mechanical stability of the membrane is due to the condensation of the MPTMS ligands around the nanoparticles at the interface;⁴⁹ (e) TEM images of an (MPTMS)-capped Au NP membrane supported on a carbon film, the scale bars represent 50 nm;⁴⁹ and (f) photograph of a cellulose ester substrate coated with an (MPTMS)-capped Au NP membrane.⁴⁹ Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 2016.

applications.⁵² According to the authors, although some films of this material have been prepared before using conventional thin film deposition techniques such as spin/drop-casting, spray coating and rolling, the variability in the uniformity of the films obtained through those techniques was prohibitive to guarantee a systematic study of the saturable absorption behavior. The preparation of thin films using the LLIR, at a water/toluene interface and starting from the exfoliated MXene dispersed in water, was the way to overcome this problem, producing very thin and uniform films.⁵² As a result, novel attributes of the nonlinear optical properties of MXenes have been revealed, leading to the possibility of fabricating novel and ultracompact passive photonic diodes.⁵²

MXene-based 2D nanopore membranes have been prepared by Mojtavavi *et al.* through the LLIR.⁵³ An MXene dispersion in a water/methanol mixture was dropped over a chloroform bath in a Petri dish, leading to interfacial MXene film formation. The film was deposited over a hole on a SiNx/Si chip, behaving like a freestanding membrane. Nanopores ranging from 3 to 10 nm were fabricated in the freestanding MXene membranes using a focused electron beam, and their application as solid-state porous membranes for DNA translocation and single-molecule sensing applications has been demonstrated.⁵³

The 2D materials known as transition metal dicalchogenides (TMDs), such as MoS₂, MoSe₂ and WS₂, have also been deposited over solid surfaces through the LLIR. We demonstrated that acetonitrile can exfoliate, disperse and stabilize MoS₂.⁵³ Upon mixing this acetonitrile dispersion in a water/toluene biphasic system, spontaneous migration of the dispersed solid to the L/L interface occurs, giving a continuous thin film as can be seen in Fig. 5a.⁵³ Films starting from different samples and varying ratios of the acetonitrile dispersion have been prepared and deposited over planar quartz substrates, showing transparency,

high optical quality and transmittance spectra in the UV-vis region characteristic of the exfoliated MoS₂, as observed in Fig. 5b and c.⁵⁴

MoS₂, WS₂ and ReS₂ films were also prepared at an octadecene/dimethyl formamide (DMF) interface starting from the exfoliated TMDs dispersed in DMF.⁵⁵ The films were deposited dipping the solid substrates across the films at the L/L interface. It was demonstrated that the TMD nanoflakes are in an edge-to-edge arrangement in the thin film over the substrate. Similarly, Yu *et al.* prepared a hexylamine dispersion of exfoliated WS₂ and carefully injected this dispersion into the hexane phase near the L/L interface in a previously prepared ethyleneglycol/hexane biphasic system.⁵⁶ The hexylamine rapidly dilutes into the hexane layer, and the exfoliated WS₂ becomes confined by the two non-solvents and self-organizes as a connected film at the L/L interface. The deposition over different substrates is carried out by first removing the hexane and further removing the ethyleneglycol from the bottom, through fritted glass (Fig. 5d). The resulting WSe₂ films with a thickness of 25 nm (Fig. 5e) exhibit sustained p-type photocurrent under simulated solar illumination without added catalyst, and the functionalization of these films with Pt allows their application as electrodes for solar-to-hydrogen energy conversion.⁵⁶ The same group reported recently a continuous mode system to deposit TMD films from the L/L interface on flexible ITO-coated PET substrates, based on a roll-to-roll process (Fig. 5f and g).⁵⁷ The exfoliated TMDs were dispersed in butanol and continuously injected in the aqueous phase in an *n*-heptane/water biphasic system. Butanol, less dense than water, carries the TMD nanoflakes to the *n*-heptane/water interface, resulting in the self-assembled film. A set of computer-controlled paddles pushes the interfacial film to the substrate, which is continuously moving on a roll system (Fig. 5f and g).⁵⁷ This deposition apparatus represents an important step towards industrial application of the LLIR technique.

Fig. 5 (a) Photography of the thin film obtained at an acetonitrile–water/toluene interface of an exfoliated MoS₂ sample;⁵⁴ and (b and c) photography of films prepared starting from different MoS₂ samples deposited over planar glass substrates.⁵⁴ Copyright Elsevier, 2019. (d) Schematic of the deposition method of WSe₂ at an ethylene glycol/hexane interface: (1) injection of the WSe₂ dispersion; (2) self-assembly at the L/L interface; (3) hexane removal; (4) ethylene glycol removal and film deposition; and (5) drying;⁵⁶ and (e) photograph of a single-flake-layer WSe₂ thin film deposited on flexible ITO-coated PET plastic.⁵⁶ Copyright Springer Nature, 2015. (f) Schematic side view of the roll-to-roll deposition apparatus;⁵⁷ and (g) photograph of the roll-to-roll deposition apparatus, where the inset gives a close-up overhead view.⁵⁷ Copyright American Chemical Society.

3.4. Organic crystals

The simplicity and excellence of the LLIR have been also explored for obtaining thin films of different organic crystals. Matsui *et al.* prepared nanocrystals of polydiacetylene (pDCHD) with a square-shape (~ 30 nm in width and length) or wire-shape (~ 30 nm in width and $0.5\text{--}1$ μm in length). The films were obtained in a vessel containing an aqueous dispersion of the nanocrystal and hexane.⁵⁸ The pDCHD nanocrystal was assembled at the L/L interface by adding ethanol. The films were transferred onto a solid substrate by immersing a substrate into the interface at a controlled rate. Different films from varying concentrations of the nanocrystal dispersions were obtained and characterized. The pDCHD nanocrystals interact by π - π interactions due to the close packed structure in which the film was assembled.⁵⁸ Sasmal *et al.* described thin films of crystalline and porous covalent organic framework (COF) nanospheres with different chemical structures.⁵⁹ Imine linked (TpOMeAzo and TpOMeDPP) or β -ketoenamine linked (TpAzo and TpDPP) COF nanospheres with high crystallinity and porosity have been synthesized using an innovative methodology based on an *in situ* polymerization process of the monomers. In order to prepare the COF thin film, a dispersion of COF nanospheres in dichloromethane (DCM) was mixed in water to create a L/L biphasic system. A self-assembled film at the water/DCM interface is observable on adding small amounts of trifluoroacetic acid, after 20 h at rest. The process can be accelerated by shaking the biphasic system vigorously to give an emulsion, followed by letting the system rest to separate into two phases, resulting in a thin film at the L/L interface after 5 min.⁵⁹ The COF thin films presented thicknesses varying from $\sim 160 \pm 10$ nm to $\sim 630 \pm 10$ nm, tunable by varying the amount of initially dispersed COF nanospheres in DCM. The mechanism of the film self-assembly based on the chemical interaction between the nanospheres has been proposed. The films deposited over alumina hollow fiber membranes have shown potential for application as membranes for selective molecular separation of He and O₂, He and CO₂, and He and N₂.⁵⁹

3.5. Multi-component (nanocomposite) films

Starting from available materials, different methodologies may be possible for the deposition of thin films of more than one component through the LLIR, basically summarized in three approaches: (i) a multi-component material was previously synthesized as a powder, and after the synthesis it is dispersed in one of the immiscible solvents; (ii) all the individual components are initially dispersed in one single solvent; or (iii) different components are initially dispersed in each one of the solvents.

Nanocomposites between graphene and Ni(OH)₂ nanoparticles were prepared by us through a modified polyol method from a chemical reaction between graphene oxide (GO) and nickel acetate in ethylene glycol.⁶⁰ The product is obtained as a powder and samples containing different graphene/Ni(OH)₂ ratios were obtained, characterized by very small Ni(OH)₂ particles (median diameter of 5 nm) homogeneously dispersed over the rGO sheets. Thin films of all these samples have been deposited in a water/

toluene system in which the nanocomposites have been previously dispersed into the toluene phase. Fig. 6A–F show the photography of these films and Fig. 6G the relationship between both the thickness and transmittance and the percentage of nickel hydroxide in each sample.⁶⁰ These films presented multiple functions and have been applied as electrochromic materials, electrochemical sensors for glycerol and electrodes for alkaline batteries, with performances significantly superior to those ones found from their individual components (rGO or Ni(OH)₂) as thin films prepared as control samples.⁶⁰ Both rigid and flexible alkaline battery devices using these films as cathodes and activated carbon as the anode have recently been demonstrated, as can be seen in Fig. 6H, in which four devices (1×1 cm) connected in series can be seen lighting a LED.⁶¹

Using the same methodology for rGO/Ni(OH)₂ nanocomposites but varying the temperature of the reaction, we demonstrated the preparation of rGO/Ni nanoparticle nanocomposites deposited over glass substrates using the same water/toluene system and applied as catalysts for hydrogen production from borohydride hydrolysis.⁶² The field of catalysis is a fascinating possibility of application for films prepared through the LLIR, because it allows the deposition, easy recuperation and reuse of the catalyst (simply removing the film/substrate from the reactor), solving one of the largest problems related to heterogeneous catalysis, *e.g.* the facile separation of powdered catalysts from the reaction. Also, the deposition as a thin film represents the maximum efficiency related to the amount of catalyst. For several applications in catalysis the superior performance of the same catalyst deposited as thin films through the LLIR when compared to the powdered material was demonstrated, as will be seen in this review. Lifting the substrate perpendicularly to the L/L interface, the rGO/Ni nanocomposite was deposited over both sides of a glass substrate, increasing the contact area and the amount of hydrogen generated, as can be seen in Fig. 6.⁶² Films containing a very low amount of catalyst (~ 0.12 mg) presented optimal production of H₂ of 3.0×10^4 mL min⁻¹ g⁻¹, which is among the highest catalytic activities towards H₂ production reported.⁶² Interestingly, the catalyst thin film can be easily removed at the end of the process, washed with water and reused, remaining structurally and morphologically integrate and presenting the same performance for at least 10 catalytic cycles.⁶²

CNT-based nanocomposite thin films with metals⁴⁹ or oxides⁶³ can be prepared from the components initially dispersed in each one of the liquid phases. For example, a CNT/AuNP thin film at the dichloromethane/water interface has been obtained starting from MPTMS-capped AuNPs dispersed in dichloromethane and SWCNTs dispersed in water with a surfactant (Triton X-100).⁴⁹ CNT/TiO₂ thin films were prepared starting from Fe-filled CNTs and commercial TiO₂ particles.⁶³ A toluene/water interface was prepared with the CNTs dispersed in toluene and the TiO₂ dispersed in water. The two liquids were mixed and stirred for 2 h. The self-assembled film formed at the L/L interface when the stirring was interrupted was transferred to glass/ITO substrates. The film was characterized by a homogeneous distribution of the two components along the substrate,

Fig. 6 (A) Photography of thin films of neat $\text{Ni}(\text{OH})_2$, (B–E) different $\text{rGO}/\text{Ni}(\text{OH})_2$ nanocomposites, containing different $\text{rGO}/\text{Ni}(\text{OH})_2$ ratios, and (F) neat rGO thin films deposited over glass substrates;⁶⁰ (G) thickness and transmittance at 550 nm of the $\text{rGO}/\text{Ni}(\text{OH})_2$ samples as a function of the $\text{Ni}(\text{OH})_2$ percentage in the samples.⁶⁰ Copyright Springer Nature, 2016. (H) Photography of four asymmetric battery devices using $\text{rGO}/\text{Ni}(\text{OH})_2$ as the cathode and activated carbon as the anode, both prepared as thin films using the LLIR, connected in series lighting a LED.⁶¹ Copyright Elsevier, 2020. (I) Schematic illustration of the LLIR deposition of rGO/Ni nanocomposite thin films over both sides of a glass substrate, and their application for hydrogen production. Photographs show the hydrogen production stage.⁶² Copyright Royal Society of Chemistry, 2018.

with CNTs well dispersed among TiO_2 particles, resulting in very effective contact.⁶³ This film was used as a precursor for a $\text{CNT}/\text{TiO}_2/\text{PB}$ nanocomposite, by the *in situ* electrosynthesis of PB by cyclic voltammetry between the iron species encapsulated into CNT cavities and the $\text{K}_3[\text{Fe}(\text{CN})_6]$ in aqueous solution present in the electrolyte. The tri-component nanocomposite was used as a photoanode in a dye-sensitized solar cell (DSSC), presenting some breakthroughs, such as the demonstration of the possibility of use of PB as an absorber in a DSSC, the mixture of the absorber and the semiconductor (TiO_2) in a single film and adding a good electronic conductor (CNTs) to facilitate the electron transfer processes (from absorber to semiconductor to electrode). The intimate contact between the components, which is due to the specific way in which the film was prepared, was demonstrated to be responsible for the improved photocurrent response observed.⁶³

Bi-component films based on PVP-capped silver nanowires (NWs) and oleylamine-capped gold nanostructures have been prepared by Zhang *et al.*⁶⁴ The Ag NWs were dispersed in water and the Au-NPs dispersed in chloroform. The two dispersions were mixed and vigorously shaken, resulting afterwards in a Ag-NW/Au-NP film around the water phase. The films were transferred onto substrates (a glass slide or Si) by placing them under the floating film and then quickly lifting up. Films with different Au-NP/Ag-NW ratios have been prepared, and their use as SERS substrates for the molecule 3,3'-diethylthiatricarbocyanine iodide (DTTCI) has been demonstrated. The SERS intensities showed high dependence on the Au-NP/Ag-NW ratio and on the layer number of the co-assembled thin films.⁶⁴

The octadecene/dimethyl formamide (DMF) interface containing exfoliated TMDs dispersed in DMF described before has also been used to prepare composite bi-component films of MoS_2 and WS_2 , simply by mixing two different TMD suspensions together, before the film assembly at the L/L interface.⁵⁵

Self-supported films of polymeric nanocomposites with different inorganic nanoparticles have been produced starting from an organic solution of the polymer and an aqueous dispersion of the nanoparticles.⁶⁵ Polymers such as paraffin wax, poly(styrene), poly(propylene), and poly(methyl methacrylate) dissolved in different solvents (ethyl acetate, hexane, toluene, and xylene) have been mixed with aqueous dispersions of inorganic nanoparticles such as oxides (Fe_3O_4 and IrO_x), semiconductor quantum dots (CdSe/ZnS) or carbonaceous materials (MWCNTs, Vulcan carbon or activated charcoal). The organic solvent was allowed to evaporate at a controlled rate, resulting in a nanoparticle-incorporated polymeric film self-supported at the aqueous–air interface that can easily be manipulated with tweezers. The authors demonstrated that the facility to combine different polymers and different inorganic nanoparticles allows obtaining tunable properties of the final material.⁶⁵ Similar methodologies have been employed for polymer/metal ion films with various morphologies, such as foam, nanoflowers and honeycomb-like, at L/L interfaces between organic solutions of polymers (especially amphiphilic block copolymers) and aqueous solutions of metal salts.^{66–68} The application and performance of those films deposited over glass substrates as heterogeneous catalysts have been demonstrated for several reactions, showing high catalytic activity and good recyclability.^{66–68}

4. Thin film deposition and applications: films deposited from *in situ* synthesized materials

The LLIR thin film deposition starting from materials previously available described in the early sections opens several possibilities for novel applications and compositions, some of them unique due to the specificity of the LLIR. However, the great breakthrough of the technique consists in taking advantage of the L/L interface to synthesize materials directly as thin films, combining the synthesis and processing in a single-pot and single-step. The possibility of novelties ingrained in this procedure is enormous, mainly for multi-component (composite) materials, allowing thin films of combined materials which are impossible to prepare starting from other experimental approaches.

4.1. Semiconductors quantum dots

Sathaye *et al.* have proposed a Langmuir–Blodgett (LB)-like L/L interface route to prepare different materials, obtained through interfacial reactions resulting in solid films at the L/L interface. The films were deposited over solid substrates in an LB tray after the evaporation of the organic solvent.^{69–71} For example, CdS nanoparticles have been synthesized in an LB tray filled with an aqueous solution of Cd^{2+} ions. A CS_2 solution in carbon tetrachloride was sprayed over the aqueous solution, and CdS was at the water/carbon tetrachloride interface.⁶⁹ After the CCl_4 evaporation, the film (now at the water/air interface) was transferred to solid substrates using the well-known LB-based transfer process. Films based on CdSe ⁷¹ or silver nanoparticles⁷⁰ have been also obtained in similar ways, choosing adequate precursors for the interfacial reaction.

Large-area PbSe films were prepared by Jana *et al.* based on a L/L interfacial reaction between lead cupferronate ($\text{Pb}(\text{cup})_2$) in toluene/octylamine solution and selenourea in aqueous solution.⁷² The resulting gray films stabilized at the L/L interface are comprised of (111)-faceted PbSe crystallites and were transferred to planar glass substrates for characterization and application as photoconductor materials in the near-infrared region.⁷² Granular films comprising cube-like PbSe crystallites or cuboctahedron-like crystallites could be obtained by controlling the concentration of the precursors and the diameter of the beaker in which the interfacial reaction took place.⁷² Both CdS and CdSe thin films have been prepared by Albrasi *et al.* using a three layered water–oil–amphiphile/salt system.⁷³ The authors found the adequate volumes of water, decane, 2-butoxyethanol and NaCl, as well as the optimal NaCl concentration that yields three immiscible liquid layers. Under those conditions, keeping a thin middle liquid layer, dissolving cadmium diethyldithiocarbamate in decane and Na_2SeSO_3 (or Na_2S) in water, and heating the system at 50 °C, an orange (CdSe) or yellow (CdS) film adhering to the upper L/L interface was found.⁷³ The three layered system exhibits a tiny central liquid layer separating the reactants initially dispersed in the top and bottom liquid layers, allowing controlled diffusion for the organized deposition of CdSe or CdS.⁷³ Nanocrystalline metal sulfide (CdS, PbS, CuS

and ZnS) thin films were also obtained by Thomas *et al.* through a chemical reaction between toluene solutions of thiobiuret complexes $[\text{M}(\text{SON}(\text{CN}^i\text{Pr}_2)_2)_2]$ ($\text{M} = \text{Cd}, \text{Zn}, \text{Pb}$ or Cu) and an aqueous solution of Na_2S , and transferred from the L/L interface to solid substrates (glass, quartz, mica slides or ITO-coated glass slides) by dipping the substrate perpendicular to the interface into the aqueous layer and withdrawing it out of the vessel.⁷⁴

4.2. Metal nanoparticles

Metallic nanoparticles, single or bi-component, varying the composition, shape, size, stabilizer and precursors, aiming at applications in a broad range of fields, have been synthesized *in situ* and processed as thin films using a distinct combination of L/L phases. Platinum nanoparticle thin films have been obtained by Hoseini *et al.* at a toluene/water interface using organoplatinum(II) complexes as precursors.⁷⁵ The biphasic system was prepared with a toluene solution of the organometallic compound *cis*- $[\text{Pt}(p\text{-MeC}_6\text{H}_4)_2(\text{SMe}_2)_2]$ and water. Sequentially, the reducing agent NaBH_4 was added with a syringe into the aqueous phase, allowing Pt(II) to Pt(0) reduction and giving the thin film at the interface. The film was deposited over solid substrates by removing slowly the upper toluene phase, inserting the substrate into the aqueous phase and pulling it out towards the film direction.⁷⁵ The Pt film deposited over a glassy carbon electrode was demonstrated to have high electrocatalytic activity toward methanol oxidation.⁷⁵ Pt- and Pt-based alloy (PtPd, PtNi and PdAu) thin films have also been obtained using diverse organometallic precursors, and employed as catalysts for dye degradation or electrocatalysts for methanol oxidation.^{76,77}

An electrochemical immunosensor for alpha-fetoprotein (AFP) detection was developed based on an Au-NP-antibody thin film prepared through the LLIR in a toluene/water biphasic system.⁷⁸ The Au-NPs were synthesized *in situ* in the biphasic system and the antibody immobilization was carried out directly over the film stabilized at the L/L interface. The immunosensor was prepared by transferring the film over an ITO/glass substrate. Due to the unique way in which the film was prepared, the immunosensor exhibited improved properties such as a low detection limit, a wide linear range, high reproducibility and sensitivity and long-term stability.⁷⁸ The water/toluene interface was also the system used to produce thin films of Au-NPs, Ag-NPs and Ag–Au alloy-NPs with different Au/Ag ratios, extending to areas of several square centimeters, based on the reaction of chlorotris(triphenylphosphine)silver(I) and/or chlorotriphenylphosphine gold(I) in toluene with tetrakis(hydroxymethyl)phosphonium chloride in aqueous solution.⁷⁹ The transport properties of the films were studied and indicated the presence of continuous films arising from the connection between the individual nanoparticles. Interestingly, the film resistance scales up exponentially with the Ag/Au ratio, changing from metallic to non-metallic behavior when the amount of Ag-NPs falls below 70%.⁷⁹ Ultra-large films of single-crystal Ag-NPs were also described by Yao *et al.* via a chloroform/water interfacial reaction between an aqueous solution of AgNO_3 as a precursor and chloroform solution of *o*-ethoxyaniline (OEA) as a reductant.⁸⁰ The influence of the experimental parameters such as the reagent

concentrations, temperature and organic phase used to produce the L/L interface on the film morphology was demonstrated, as well as the SERS activity of the films deposited over silicon wafers.⁸⁰ The application as SERS substrates was also demonstrated for the silver chain-like nanobelt (NB) films prepared by Zhang *et al.*, at a redox-active ionic liquid/water interface.⁸¹ A silver nitrate aqueous solution was mixed with the ionic liquid ferrocenylmethyl)dodecyldimethylammoniumtetrakis[3,5bis(trifluoromethyl)phenyl] borate ([FcMDDA⁺][TFPB⁻]), which was used as both the reducing agent and the liquid phase in the interfacial system. The film obtained is characterized by a morphology of Ag chain-like NBs, due to the linkage of silver nanoparticles through oriented growth along the L/L interface.⁸¹

4.3. Oxide nanoparticles

In situ synthesis of metal oxide thin films has been chemically or electrochemically described using the LLIR. Iron oxide nanostructured films have been described by Srivastava and Kumara, obtained by a chemical reaction between iron cupferronate in toluene and NaOH in water,⁸² varying the reaction time. The freestanding film obtained at the L/L interface was transferred to Si substrates for characterization. Both the morphology and crystalline phase of the product depend on the reaction time: dendritic structures of α -Fe₂O₃ have been obtained at short reaction times and a mixture of α -Fe₂O₃ and γ -Fe₂O₃ at long times.⁸² Applying an electric field across an organic/water interface in which iridium metal nanoparticles have been previously stabilized, a thin film of iridium oxide nanoparticles has been obtained by Sebastian *et al.*⁸³ The electrochemical process to oxidize the Ir nanoparticles at the L/L interface yields films with the individual oxide nanoparticles interconnected *via* oxygen bonds. The authors demonstrated the amphipathic nature of the resulting film, with hydrophilic characteristics on the face originally facing the aqueous phase and hydrophobic ones at the face originally in contact with the organic phase.⁸³

4.4. 2D materials beyond graphene

The LLIR has proved to be extremely efficient to synthesize thin films of inorganic, organic or metallorganic bi-dimensional films, such as TMDs, COFs, metalloporphyrins or metal-organic frameworks (MOFs). The thermal decomposition of the molybdenum coordination complex tetrakis(*N,N*-diethyldithiocarbamate)molybdenum(IV) dissolved in 1,2-dichlorobenzene (DCB) in a DCB/water biphasic system was demonstrated to be an effective route to MoS₂ thin films at the L/L interface.⁸⁴ Some experimental cares have been done by the authors in order to efficiently remove the films from the water/DCB interface, including chemical treatment of the substrates or adding surfactants to the system prior to the film removal.⁸⁴ Similarly, using a toluene/water biphasic system containing molybdenylacetylacetonate (MoO₂(acac)₂) dissolved in the organic solvent and HNO₃ or Na₂S or Na₂Se in the aqueous phase, Prabhu *et al.* demonstrated a hydrothermal approach to MoO₃, MoS₂ or MoSe₂, respectively.⁸⁵ The hydrothermal conditions (sealed system and temperature, autoclave at 130 °C for 20 h) have the same role as stirring the reaction under ambient conditions, thus creating an

emulsion of toluene and water. The reaction between MoO₂(acac)₂ and the chalcogenide precursor takes place at the interfaces of toluene in water droplets, which coalesce when the reaction is quenched, restoring the bulk liquid phases with the film self-organized at the interface.⁸⁵ The film thickness can be controlled by varying the concentration of the molybdenum precursor. The application of the MoS₂ film deposited over glass/ITO substrates for electrocatalytic water splitting was also demonstrated.⁸⁵

A new type of 2D micro- and nanosheet structures based on a bis(dipyrrinato)zinc(II) complex (N2) was described by Sakamoto *et al.*, built *via* the interaction between a porphyrin-dipyrrin hybrid ligand (L2) with 4-fold symmetry and zinc ions (Fig. 7a).^{86,87} The film obtained at the L/L interface from a

Fig. 7 (a) Chemical structures of the expected lattice of the bis(dipyrrinato)zinc(II) complex (N2) based on a porphyrin-dipyrrin hybrid ligand molecule L2;⁸⁷ and (b) schematic representation of the liquid/liquid interfacial synthesis of micro- or nanosheet N2, and a photograph of microsheet N2 transferred to a quartz substrate (py = pyridine).⁸⁷ Copyright Wiley-VCH, 2017. (c) Schematic illustration of the fabrication process of CuBDC MOF thin films by a spray method;⁹¹ and (d–f) photographs of (d) a CuBDC free-standing film, and (e and f) CuBDC/deposited over a hydrophobic membrane.⁹¹ Copyright American Chemical Society, 2018.

reaction between an aqueous solution of zinc acetate and a dichloromethane/pyridine solution of the dipyrin-porphyrin ligand was deposited over transparent electrode substrates (Fig. 7b). Further, it was applied as an active material for a photoelectric conversion system, taking advantage of the coexistence of the porphyrin and bis(dipyrinato)zinc(II) complex units in the material, in which the absorption bands cover the whole visible-light spectrum.⁸⁷

Various MOF structures have been synthesized *in situ* at L/L interfaces since the pioneering work by Amellot *et al.*, who prepared thin films of the MOF HKUST-1 using a water/1-octanol biphasic system, each containing one of the two MOF precursors.⁸⁸ Films of the ZIF-8 and CuBTC MOFs were grown on either the outer or inner side of polymeric hollow fiber membranes in a similar approach, using a water/chloroform biphasic system, yielding membranes presenting efficient performance in gas separation processes.⁸⁹ Joshi *et al.* prepared a series of catechol-metal organometallic polymers through the *in situ* reaction between a catechol derivative in dichloromethane (DCM) or in toluene and an aqueous solution of Fe^{2+} or Cu^{2+} precursors.⁹⁰ The resulting interfacial films were transferred to commercial cotton and polyester cloth pieces, by placing the substrates at the bottom of the vessel before interface polymerization, and removing both liquids after film formation. The films showed superhydrophobic characteristics and high separation efficiencies for oil/water mixtures.⁹⁰ Bai *et al.* reported a very innovative preparation route for fabrication of large area free-standing MOF thin films at room temperature based on miscible L/L interfaces.⁹¹ To prepare the copper 1,4-benzenedicarboxylate (CuBDC) MOF, an *N,N*-

dimethylformamide/acetonitrile (DMF/ACN) solution of metal ions (Cu^{2+}) was sprayed onto the surface of a DMF/ACN solution containing the ligand (BDC), resulting in a free-standing MOF blue film floating on the liquid interface (Fig. 7c–f). The thin films were deposited onto a hydrophobic filter membrane and applied as a high performance flowing membrane reactor for the catalytic reduction of 4-nitrophenol.⁹¹

4.5. Graphene

Neat graphene and different graphene-based nanocomposite thin films have been obtained *in situ* at the L/L interface starting from different precursors. Concerning neat graphene, it can be prepared in both a top down or bottom up fashion. An unusual mechanochemical process has been proposed by us to achieve tri-layer graphene enriched thin films starting from raw graphite.⁹² The electronic band structure differs from mono-, bi- and tri-layer graphene, and obtaining graphene-like samples with controlled stacked layers is a great challenge in the field. The mechanochemical approach to get this sample is summarized in Fig. 8(a), based on initial mechanical exfoliation of graphite over a piece of magnesium foil, followed by a strong exothermal reaction between magnesium-containing graphite and an acidic water solution in a water/toluene biphasic system.⁹² The heat generated during the reaction between the magnesium and the acid solution is absorbed by the previously mechanically exfoliated graphite over the magnesium, resulting in its exfoliation. Carrying out the process in the water/toluene biphasic system leads the resulting graphene toward the L/L interface, allowing deposition as thin films over glass or plastic substrates (with high flexibility), as illustrated in Fig. 8b and c.⁹² Different characterization

Fig. 8 (a) Schematic of the mechanochemical approach for graphene thin films: graphite is rubbed on wax paper; magnesium foil and the paper are rubbed together; graphite is transferred from the paper to the magnesium foil; the magnesium foil holding the graphite is added to an aqueous HCl solution/toluene biphasic system; magnesium is dissolved in an exothermic reaction; the mixture is subjected to an ultrasonic bath producing a water/toluene macro-emulsion; and the mixture is kept still and the dispersed graphene migrates to the interface, being further transferred to the substrate;⁹² (b) photographs of transparent graphene films deposited on quartz substrates (upper) and plastic (PET) substrates (bottom);⁹² and (c) a picture of the flexibility of the graphene film on the PET substrate.⁹² Copyright Elsevier, 2013. (d) SEM image of a large graphene sheet chemically synthesized;⁹⁴ (e) schematic of the bottom up preparation and film deposition of graphene in a benzene/water L/L system, on the right a digital picture (1 × 2 cm) of the graphene film deposited over a glass substrate;⁹⁴ and (f) proposed mechanism of benzene-to-graphene conversion according to the experimental procedure detailed in (e).⁹⁴ Copyright Royal Society of Chemistry, 2018.

techniques indicate that the films are composed in the majority (59%) of tri-layer graphene. The amount of graphite-containing magnesium foil added to the water/toluene mixture can be used to control the thickness and transmittance.⁹²

A bottom up approach to graphene has been also recently reported by our group, in which the L/L interface has a crucial role.^{93,94} Starting from a heterogeneous reaction between solid iron chloride and simple molecules such as benzene or *n*-hexane at a water/oil interface, the largest graphene sheets chemically synthesized (Fig. 8d) ever reported (micrometer lateral size) were obtained as a film deposited at the liquid/liquid (L/L) interface. The proposed mechanism (confirmed by different characterization techniques) demonstrates the importance of water, which acts not only as a liquid phase to give the L/L interface, but fundamentally as a key reactant. Starting from a water/benzene biphasic system (Fig. 8e), the process is based on an electrophilic aromatic substitution reaction between benzene and FeCl₃, giving a carbocation (Fig. 8f).⁹⁴ The carbocation reacts with another benzene molecule to give a more reactive biphenyl species (which through successive reactions will be converted into graphene), allowed by the presence of water acting as a base.⁹⁴ This is a very interesting contribution demonstrating the dual role of both water and benzene: they are the liquids that are mixed to give the L/L interface (and therefore to support the possibility to get the synthesized sample directly as a thin film), and they also act as reactants in a chemical reaction for a very sophisticated material. Dissolving pyridine into benzene, an N-doped graphene sample could be obtained, demonstrating the versatility of the technique.⁹⁴ We have shown that the resulting films are actually a mixture composed mainly of micrometer-size graphene and minor fractions of amorphous carbon and iron oxide, which are side-products of the reaction. Seeking applications, it was demonstrated that the iron oxide can be employed as a reactant for Prussian blue electrodeposition, yielding very thin films of graphene/Prussian blue nanocomposites with great potential to be applied as both electrochromic materials and as cathodes for aqueous-operating K-ion batteries.⁹⁵

4.6. Multi-component (nanocomposite) materials

The preparation of thin films of multi-component (nano)composite materials represents the maximum level of complexity for the LLIR, even in cases in which simple chemical processes are engaged. For example, we reported the synthesis of graphene/silver nanoparticle nanocomposite thin films in a toluene/water biphasic system through two different methods:³⁸ in the first one, both Ag⁺ cations and GO are mixed in the aqueous phase, and they are reduced simultaneously by NaBH₄, resulting in a rGO/Ag NP film at the interface at the end of the reaction; in the second one there is a physical separation of the rGO previously prepared and dispersed in the organic phase, and the Ag⁺ dissolved into the aqueous phase (so the only chemical reaction that happens is the reduction of the Ag⁺ cations).³⁸ The films are obtained with the silver nanoparticles sprayed over the connected graphene sheets, and this work demonstrates again the relationship between the experimental details and the characteristics of the final product: the thickness

and transparency of the films, as well as the shape, size, agglomeration degree and distribution of the Ag nanoparticles over the graphene sheets, are strongly dependent on the GO/rGO/Ag⁺ precursor ratio and on the methodology applied to prepare the samples. These films have been applied as SERS substrates and their performance was also dependent on the structure, as expected.³⁸ Similar methodologies have been used to prepare graphene/copper or graphene/copper oxide nanoparticle thin films (starting from an aqueous solution of copper nitrate as a precursor), resulting in 20 different samples in which the composition, size and shape of the nanoparticles distributed over the graphene sheets could be controlled through the tuning of the experimental parameters.⁹⁶ Analogous approaches have been also described for other graphene/metal nanoparticle thin films, as described by Bramhaiah and John for rGO/Au, rGO/Pd or rGO/Au, starting from the organometallic precursors Au(PPh₃)Cl, Pd(PPh₃)₂Cl₂ or Ag(PPh₃)₄NO₃ dissolved in toluene and GO dispersed in water.⁹⁷ Simultaneous reduction was carried out by tetrakis(hydroxymethyl)phosphonium chloride, and the films deposited over silicon substrates have been used as catalysts in the *p*-nitrophenol reduction reaction.⁹⁷ Graphene/Pd-NPs or graphene/Pd-Pt-NPs have been also obtained, adding NaBH₄ solution over a biphasic system previously prepared with a solution of [PdCl₂(cod)] (or a mixture of [PdCl₂(cod)] and [PtCl₂(cod)]) in toluene and an aqueous dispersion of GO.^{98,99} The resulting thin films were used as catalysts in the Suzuki-Miyaura coupling reaction⁹⁸ or in the methanol oxidation reaction.⁹⁹

The entire chemical synthesis of Prussian blue/CNT nanocomposites has also been recently developed by us, based on the acid decomposition of ferricyanide ions together with electron transfer through the liquid/liquid interface between 1,10-dimethylferrocene in the organic phase and ferricyanide ions in the aqueous phase (Fig. 9).¹⁰⁰ A thin film of PB is observed at the L/L interface after a few hours. By carrying out the same reaction in the presence of a pre-stabilized carbon nanotube film at the L/L interface, a CNT/PB nanocomposite is obtained, with the PB nanocubes decorating the CNT walls.¹⁰⁰ Free-standing nanocomposite films were deposited over different substrates and their application as cathode materials in aqueous rechargeable potassium-ion batteries was demonstrated, both in half-cells and full-cells in a coin cell setup.¹⁰⁰

Among the myriad of complex materials that can be synthesized *in situ* at the L/L interface, the class of conducting polymer-based nanocomposites is versatile and presents high technological relevance. Conducting polymers (CP) such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PT) can be prepared either by chemical or electrochemical oxidation of suitable monomers, and their nanocomposites are usually prepared to achieve synergetic or complementary behaviours between the components, resulting in novel and multiple functionalities. The type of interaction between the components is a key point for good nanocomposites, which is a characteristic directly dependent on the synthetic pathway. Carbon nanostructure/conducting polymer nanocomposites represent typical examples of this class of materials, but their deposition as thin films is a

Fig. 9 (a) Experimental steps to prepare CNT/PB thin films at the L/L interface;¹⁰⁰ (b and c) photograph of different CNT/PB nanocomposite thin films deposited over (b) PVDF membranes and (c) ITO/glass substrates;¹⁰⁰ and (d and e) photographs of four coin-cell batteries (built using the CNT/PB deposited over PDMF membranes as cathodes) in series at (d) open and (e) closed circuit to light a LED.¹⁰⁰ Copyright Elsevier, 2020.

great challenge: similar to carbon nanostructures, conducting polymers are insoluble in the large majority of solvents (with a few exceptions of some high-boiling point solvents such as NMP, which has the inconvenience of being hard to be further removed), and CP/carbon nanostructures are usually obtained as insoluble powders, hard to process. The electrochemical synthesis of a CP (over electrodes containing the carbon nanostructures) yields films with poor contact between the components, not to mention the fact that electrochemically synthesized CPs have defective structures compared to chemically synthesized ones (branches, cross-linking, and punctual defects), which decreases their conductivity and stability. The LLIR is a way to overcome all those problems.

The interfacial chemical polymerization of aniline (*i.e.* chemical polymerization at a L/L interface in which the monomer is dissolved in the organic phase and the oxidizing agent is dissolved in the aqueous one) was proposed by some researchers aiming at the production of polyaniline nanofibers which migrate to the aqueous phase resulting in very stable water dispersions.^{101,102} Michaelson and McEvoy were the first researchers to suggest an interfacial reaction of aniline in the presence of surfactants in a water/chloroform system, with the monomer dissolved in a surfactant-enriched chloroform solution and the oxidizing agent in the aqueous phase.¹⁰³ The surfactant-containing polyaniline was formed at the water/chloroform interface as a self-standing film, which was removed by putting a glass slide below the film and waiting for solvent evaporation.

Our first approach to neat polyaniline (without surfactants or any other additives) or polyaniline/carbon nanotube nanocomposite thin films was starting from a toluene/water biphasic system containing aniline dissolved in toluene and ammonium persulphate/sulfuric acid dissolved in water.¹⁰⁴ During continuous stirring, a green solid material became observable, and after 22 h when the stirring is interrupted the material self-assembles at the L/L interface as a thin film, characterized as the most conductive form of polyaniline, the green-coloured emeraldine salt. The reaction also occurs in the absence of stirring, but the product precipitates in the aqueous phase as a green powder. The same reaction conducted in the presence of carbon nanotubes, initially dispersed in the organic phase, yields CNT/PANI nanocomposites.¹⁰⁴ Varying the initial CNT/aniline ratios, CNT/PANI thin films containing different proportions of the components could be obtained, as presented in Fig. 10a. A picture showing a thick CNT/PANI film at the water/toluene interface (purposefully prepared thick to take a picture) deposited over a piece of glass substrate is shown in Fig. 10b.¹⁰⁵

The LLIR allows intimate contact between PANI and the CNTs, responsible for the observed modulation of several characteristics and properties of polyaniline due to the presence of the CNTs in the nanocomposites. Several sets of spectroscopic, microscopic and electrochemical data demonstrate that the presence of CNTs induces important changes in the electronic structure of PANI, and that the interaction between the components occurs through charge transfer from the polymer to the CNTs.^{104–109} This interaction changes the

Fig. 10 (a) Photograph of the CNT/PANI films deposited over round glass substrates. The amount of CNTs in the films increases from left to right.¹⁰⁴ Copyright American Chemical Society, 2010. (b) Glass substrate being lifted and removing an interfacial CNT/PANI film.¹⁰⁵ Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 2013. (c and d) TEM images of a CNT/PANI film.

molecular conformation of the polyaniline, resulting in a more planar and conductive molecular structure. For a higher CNT proportion in the nanocomposite, these polymeric structural changes are more evident, which directly implies different properties, such as light absorption, conductivity, charge mobility and electrochemical properties, Fig. 10c. Transmission electron microscopy (TEM) images show a tiny shell of polymer totally surrounding the CNTs, resulting in a core-shell-like structure (Fig. 10c and d). A wide image of the entire film is presented in Fig. 10d and it is very elucidative regarding its morphology. In order to get this image, the film at the L/L interface was directly deposited over a TEM Cu grid without the usual supporting carbon film, which means that the image presented in Fig. 10d corresponds to the CNT/PANI film supported by itself. A random network of polyaniline-capped carbon nanotubes showing a spaghetti-like morphology is evident, in which the highly-resistive CNT-CNT boundary contact (characteristic of neat CNT films) is substituted by the contact of the polymeric shell, which acts as a conductive glue between the tubes, decreasing the contact resistance, hence leading to more conductive films.¹⁰⁵

The paper describing the carbon nanotube/polyaniline nanocomposites was the first report on the utilization of the LLIR to prepare thin nanocomposite-based films starting from

a chemical reaction in the presence of one component dispersed in one of the liquid phases.¹⁰⁴ From those experiments, several synthetic parameters could be modulated and correlated with some characteristics. It was demonstrated, for example, that the chemical reaction of aniline polymerization at the L/L interface is strongly affected by the presence of CNTs: the polymerization yield increases according to the increase in the amount of CNTs initially dispersed in toluene; also, the presence of CNTs affects dramatically the polymerization kinetics – for a higher CNT amount, the polymer starts to be produced more quickly.¹⁰⁴ Actually, starting from a very low concentration of the monomer, the polymer cannot be synthesized in the absence of CNTs, even after several days of reaction.¹⁰⁵ Based on all the experimental evidence, a mechanism of the formation of the CNT/PANI nanocomposite free-standing films was proposed, summarized in Fig. 11. Small drops of toluene (containing both the CNTs and aniline) become dispersed into the aqueous solution due to the stirring, giving a macro-emulsion. The CNTs dispersed in these aniline-containing toluene pools migrate to the toluene/water interface, where the aniline meets the oxidizing reactant (ammonium persulphate, APS) initially dissolved in water, and the polymerization begins over the CNT walls. The CNTs act as seeds for a heterogeneous nucleation reaction, which explains the occurrence of the core-shell structure (the polymer grows over the CNT walls) and the change in both the kinetics and yield of the polymerization reaction. Interrupting the stirring regenerates both the aqueous and toluene phase, which means that the toluene drops (now containing the CNT/PANI nanocomposite at the droplet/water interface) agglomerate to give the continuum phase of toluene. Additionally, all the polyaniline-capped CNTs at the toluene drop/water interface interact among themselves, giving a continuous network homogeneously located at the toluene/water interface, resulting in self-standing films.

The CNT/PANI nanocomposites are typical examples of the potentiality of the LLIR to tune the properties of materials by judiciously varying the experimental parameters. The control of the proportion between the components described before is one possibility, but there are many other ones. For example, the effects of the CNT dimensions on the thickness and transparency of the films have been demonstrated: fixing all the synthetic parameters and starting from two different samples of multiwalled CNTs of approximately the same length (2 μm), the films produced using the larger diameter nanotubes (70 nm average) are thicker (~ 190 nm thickness) and less transparent than the ones produced with smaller diameter CNTs (10 nm average), typically on the order of 50 nm thickness.¹⁰⁵ Another possibility is to design the experiments aiming at secondary-doped polyaniline *i.e.*, to get an expanded conformation of polyaniline chains by a proper interaction between the acid structure acting as a dopant and an adequate solvent (the so-called secondary dopant).¹¹⁰ So, CNT/PANI nanocomposite thin films can be prepared using camphorsulfonic acid (CSA), followed by exposure to meta-cresol, which results in secondary-doped polyaniline/carbon nanotube composites presenting increased conductivity from 2 to 3 orders of magnitude

Fig. 11 Schematic representation of the occurrence of CNT/PANI films at the water/toluene interface.¹⁰⁴ Copyright American Chemical Society, 2010.

when compared to the same samples prepared without the secondary doping.¹⁰⁵ This procedure allows the preparation of films with 89% transmittance at 550 nm and a sheet resistance of $295 \Omega \square^{-1}$, which is much closer to that observed for the ITO transparent electrode. The conductivity of this film deposited over PET kept constant after several cycles of bending and stretching (Fig. 12a), indicating the possibility of real application as transparent and flexible electrodes.¹⁰⁵ A flexible organic photovoltaic cell was built using this carbon nanotube/polyaniline deposited over PET as a transparent electrode. The scheme of the device and a picture showing its flexibility are shown in Fig. 12b. Similar devices have been built from commercial transparent electrodes such as ITO and FTO, whereas the highest efficiency was achieved by the device prepared from the CNT/PANI electrode.¹⁰⁵

The effect of polyaniline doping in CNT/PANI thin films on the sensitivity of those materials used as active layers for ammonia gas sensor devices was also evaluated.¹¹¹ The sensor sensibility increases in the nanocomposite, when compared to the films of neat PANI. Also, the sample in which the doping was performed with CSA (compared to the HCl-doped or to the undoped ones) presented the best sensor response with a limit of detection of 4 ppm, attributed to the better polymer configuration.¹¹¹ The multi-functionality of CNT/PANI thin films was attested by employing those films as electrochemical sensors for L-ascorbic acid.¹¹² Among different CNT/PANI ratio samples, the sensor presenting the best sensibility and limit of detection was the one built from the sample containing nanotubes most homogeneously dispersed through the polymeric matrix, which was controlled during the LLIR synthetic pathway.¹¹²

Other applications of CNT/PANI nanocomposites can be found starting from single-walled carbon nanotubes, yielding thin films for active compounds in field effect transistor devices¹⁰⁹ or for active components in flexible solid supercapacitors.¹¹³ In this last example, a very thin, flexible, all-solid and symmetric supercapacitor device was manufactured using two electrodes of PET covered with the CNT/PANI thin film separated by a gel electrolyte (Fig. 12c) presenting a specific capacitance of 76.7 F cm^{-3} , which remains even after several cycles of mechanical deformation, as can be seen in the charge-discharge curves presented in Fig. 12d.¹¹³ The device maintains 88% of its stability after 1000 cycles of charge/discharge. Interestingly, all the supercapacitor properties and the stability were improved when compared to similar devices built using only one of the components; once again, the effect of the CNT aspect ratio on both the specific capacitance and the thickness of the resulting film was shown.¹¹³

Conducting polymer/carbon nanostructure thin films can also be electrochemically prepared by the LLIR. For example, Toth *et al.* described the electrochemical polymerization of pyrrole at an interface between two immiscible electrolyte solutions in which a thin film of single-walled carbon nanotubes has been previously assembled at the L/L interface.¹¹⁴ The resulting SWCNT/polypyrrole thin film was transferred to solid substrates and the morphology was characterized as the CNTs were embedded in the polymeric matrix, indicating that the pyrrole was polymerized around the CNTs, as observed by the chemical polymerization of aniline discussed before.¹¹⁴

Polythiophene-based nanocomposite thin films have also been synthesized *in situ* using the LLIR. Starting from thiophene dissolved in the organic phase (*n*-hexane) and tetrachloroauric

Fig. 12 (a) Normalized sheet resistance of a CNT/PANI thin film deposited over PET after 100 bending cycles (circles) and stretching (triangles).¹⁰⁵ (b) Schematic configuration of the solar cell built using a CNT/PANI film deposited over PET as a transparent electrode, and the corresponding chemical structures of the organic layers. The photographs show the CNT/PANI film deposited over PET (I) and the final flexible solar cell (II).¹⁰⁵ Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 2013. (c) Digital images of an all-solid supercapacitor device straightened, twisted and folded. The device was built using a SWCNT/polyaniline thin film deposited over PET.¹¹³ (d) Charge–discharge curves of the device shown in (c) under different mechanical deformations. Copyright Elsevier, 2014.

acid (HAuCl_4) in the aqueous phase, polythiophene (PT)/gold nanoparticle (Au-NP) nanocomposite thin films have been obtained.¹¹⁵ The nanocomposite synthesis is based on a direct redox reaction in which both the polymer and the Au-NPs are synthesized together. HAuCl_4 has a dual role as the oxidizing agent (to initiate the oxidative polymerization of thiophene) and the Au-NP precursor, as schematically represented in Fig. 13a. Since the contact between the reactants will be at the L/L interface, the redox reaction can be controlled. The size and shape of the resulting Au-NPs, their agglomeration degree, their distribution among the polymeric fraction, and the PT/Au-NP ratio have been tuned varying both the precursor ratio and the reaction time, yielding films with different thicknesses and composition, as illustrated in Fig. 13b. A systematic study on the influence of these experimental parameters also on the size and structural organization of the PT chains has also been demonstrated.¹¹⁵ A complete electrochemical characterization of the samples has been done, including the demonstration of the electrochromic properties, opening the possibility of utilization of these films as active layers in electrochromic devices (Fig. 13c).¹¹⁵ Tri-component films of PT/Au-NP/CNT have been further obtained by reproducing the synthetic approach in the presence of carbon nanotubes dispersed in the organic phase.¹¹⁶ As observed for the CNT/PANI nanocomposites, the presence of CNTs affects both

the yield and the kinetics of the reaction, inducing the beginning of the redox reaction around them, which results in a three-component material with intimate contact between the components.¹¹⁶ The presence of CNTs increases the electrochemical stability of the films, and their utilization as electrochemical sensors for dopamine sensing has been demonstrated.¹¹⁶

Similar interfacial redox reactions have been proposed for polythiophene/gold¹¹⁷ or polypyrrole/silver¹¹⁸ thin film nanocomposites. In the first case, the redox reaction involves 2,2':5',2''-terthiophene dissolved in the highly hydrophobic ionic liquid trioctylmethylammonium bis-(nonafluorobutanesulfonyl)amide ($[\text{TOMA}^+][\text{C}_4\text{F}_9\text{SO}_2\text{N}^-]$) and $[\text{AuCl}_4]^-$ in water, producing Janus-like Au/polythiophene thin films;¹¹⁷ in the latter, the polymerization of pyrrole was carried out at a water/chloroform interface, using AgNO_3 in water as an oxidant to polymerize pyrrole initially in chloroform, yielding polypyrrole/silver films, which have been applied as electrochemical sensors for H_2O_2 .¹¹⁸ Also, the antibacterial activity of the films against both *Escherichia coli* and *Staphylococcus aureus* has been demonstrated.¹¹⁸

The experimental approach to polyaniline/carbon nanotube nanocomposites was naturally extended to polyaniline/graphene, starting from reduced graphene oxide (rGO) dispersed into organic solvent.¹¹⁹ The obtained films were thinner and more

Fig. 13 (a) Schematic representation of the synthetic approach to PT/Au nanocomposite thin films through the LLIR;¹¹⁵ (b) photographs of the films deposited over glass substrates, in which the amount of polythiophene grows from left to right;¹¹⁵ and (c) photographs of a PT/Au film, from the reduced to the oxidized state (from left to right) respectively, showing the electrochromic behavior.¹¹⁵ Copyright Elsevier, 2018. (d) Scheme of a total chemical synthesis of PT/graphene starting from benzene and thiophene using the LLIR;¹²⁰ (e) photographs of PT/graphene (left) and two neat polythiophene (middle and right) thin films deposited over glass slides;¹²⁰ and (f) photograph of a freshly synthesized polythiophene/graphene thin film at the L/L interface before the deposition of substrates.¹²⁰ Copyright Royal Society of Chemistry, 2018.

conductive than the similar ones based on carbon nanotubes, with some presenting a transmittance at 550 nm of 89% and a sheet resistance of $60 \Omega \square^{-1}$. Regarding graphene-based nanocomposites, the LLIR allows a noticeable breakthrough in polymeric nanocomposite synthesis, in which for the first time we demonstrated the total chemical synthesis of a polymer/carbon nanostructure nanocomposite: both the polymer (polythiophene) and a carbon nanomaterial (graphene) were chemically synthesized in a one-step and one-pot reaction, starting from simple molecules such as thiophene and benzene.¹²⁰ We performed the chemical synthesis of graphene at a L/L interface between water and benzene using solid FeCl_3 as described earlier^{92,93} in the presence of thiophene molecules.¹²⁰ The FeCl_3 acts also as an oxidizing agent to begin the thiophene polymerization, yielding a polythiophene/graphene nanocomposite film at the L/L interface. The schematic of the nanocomposite synthesis and photographs of the films at both the L/L interface and deposited over glass substrates are presented in Fig. 13d–f, respectively.¹²⁰ Interestingly, films of neat PT could also be prepared starting from a water/non-aromatic solvent L/L interface (such as water/*n*-hexane or water/chloroform), allowing comparison between the neat PT and the PT/graphene films obtained through the same synthetic procedure. The improvement of the PT properties in the presence of graphene was evident: a redox reversibility not detectable for the neat polymer was observed, and the application as an electrochromic material was demonstrated; the charge mobility in the nanocomposites was 1 order of magnitude higher than for the neat polymer; and the efficiency of organic

photovoltaic devices using the nanocomposite as active layers was 4 times higher than that observed for the neat polymer.¹²⁰ The total chemical synthesis strategy employed to prepare polythiophene/graphene nanocomposite thin films starting from their simplest monomers was successfully applied to a polyaniline/graphene nanocomposite, evidencing the generality of the method.¹²¹ The nanocomposites prepared with different polymer/graphene ratios show excellent pseudocapacitive behaviors, with a specific capacitance of 267 F cm^{-3} . The construction of an ITO-free, all-solid, transparent, and flexible supercapacitor device from this kind of nanocomposite was demonstrated. The all-solid device retains its electrochemical response even when subjected to cycles of mechanical deformation.¹²¹

The interfacial polymerization of aniline at the L/L interface aiming at polyaniline-based nanocomposite thin films through the LLIR was also used as a strategy to increase the stability of black phosphorous (BP) against air.¹²² BP is a P-based physical analogue of graphite which can be exfoliated to generate graphene-like 2D entities (phosphorene) with intriguing potential applications.^{123,124} However, BP shows high instability against air,¹²⁵ which strongly limits its synthesis and processing and prevents the development of BP-based devices. BP/PANI nanocomposites have been obtained starting from aniline polymerization in an oxygen-free dispersion of exfoliated BP in acetonitrile.¹²² The polymer grows over the BP sheets, covering them and acting as a protecting barrier against air degradation. The resulting material is sequentially transferred to

a L/L biphasic system (aqueous HCl solution/toluene), leading to a BP/PANI nanocomposite thin film at the interface. The BP/PANI thin films show a stability increase against ambient conditions of more than 3000% when compared to bare BP, which allows their utilization in practical devices.¹²¹ Actually, we have used those BP/PANI nanocomposites to show the unprecedented application of a BP-based material fully operating in water and under ambient conditions,¹²⁶ as an electrode for aqueous Na-ion batteries demonstrating both high stability (despite the aggressive presence of both water and oxygen) and high performance: an impressive specific capacity of up to 200 mA h g⁻¹ was reached in NaCl aqueous solution electrolyte.¹²⁶

5. Thin film deposition and applications: chemical functionalization at liquid interfaces

Finally, novel and intriguing possibilities start to emerge using L/L interfaces to carry out surface modification (*i.e.* chemical functionalization) of different materials, resulting in thin films of chemically-functionalized materials.^{127–129} The chemical functionalization of materials' surfaces has been a very common approach to add new functionalities and modify materials' properties. The L/L interface can be considered a novel environment to perform some well-known functionalization reactions, or to create novel pathways to surface modification, in one single-process in which both the surface functionalization and the functionalized-material processing as thin films are solved together. For example, we reported the preparation of thiolated graphene oxide (GO) thin films rationally modified with cysteamine.¹²⁷ The reactants that perform the functionalization were mixed in a toluene/water L/L system containing a GO film previously stabilized at the interface. Samples with different degrees of functionalization were obtained by controlling the initial amount of those reactants in the L/L system. The functionalization mechanism was based on the so-called EDC/NHS process in which EDC (1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide) activates the carbonyl groups at the GO surface, leading to *O*-acylurea that is readily attacked by NHS (*N*-hydroxysuccinimide), leading to a stable succinimidyl ester. The ester subsequently reacts with cysteamine *via* a stable amide bond, leading to the functionalized film. The films were further used to prepare graphene/Ag nanoparticle nanocomposites, and both the functionalized films and the nanocomposites were applied as heterogeneous catalysts towards organophosphate and/or pesticide degradation, presenting one of the highest catalytic efficiencies reported for the degradation of the highly-toxic pesticide Paraoxon.¹²⁷ The functionalized graphene/Ag nanoparticle thin films were also applied as SERS substrates for sensing the probe molecule 4-ATP, allowing the detection of very diluted solution (around 10⁻¹⁰ mol L⁻¹) and an enhancement factor of 1.18 × 10⁻⁸, which is among the highest ever published for this kind of molecule. Most interesting is the combination of both functionalities of the nanocomposite thin film, acting as both a catalyst for the organophosphate

degradation and SERS sensor for the detection of the product of the same reaction, which means that one single film can both act as a detoxifying agent and sensor to determine if all the toxic compounds were already destroyed.¹²⁷

The EDC/NHS methodology has been also used by us to anchor different functional groups at the GO surface, such as imidazole¹²⁸ or hydroxamic acid,¹²⁹ yielding GO-functionalized thin films at the L/L interface, looking for efficient heterogeneous catalysts for organophosphate and pesticide degradation. Both the imidazole- and hydroxamic acid-functionalized GO materials were demonstrated to be very efficient materials for this purpose, figuring among the best catalysts for the degradation of the pesticide Paraxon or the organophosphate diethyl 2,4-dinitrophenyl phosphate (DEDNPP), showing better performance than similar homogeneous catalysis experiments. Interestingly, for GO-functionalized thin films, the chemical functionalization carried out at the L/L interface aiming at the direct and one-step production of the functionalized thin film is more efficient than the classical reaction in one liquid phase to get the functionalized powder (a functionalization degree of 46% for the thin film against 22% of the powder), which means that besides the facility to separate the catalyst from the reaction media, the catalytic efficiency of the thin film is higher.¹²⁸ Optimization of the thin film deposition targeting more efficient catalysts has been also demonstrated, through the deposition of successive thin film layers on both sides of a glass substrate. The effect of the number of layer-by-layer superimposed deposited films on the kinetic velocity constant for the reaction with DEDNPP was demonstrated, showing an abrupt velocity constant increase until 4 deposited layers, followed by a plateau, attributed to the inaccessibility of the more reactive groups on the most stacked layer films.¹²⁸

6. Conclusions and perspectives

The annual meeting of the American Physical Society in Pasadena, California, on December 29th, 1959, became famous due to a visionary talk by Richard Feynman, entitled "There's Plenty of Room at the Bottom", in which some principles of the nowadays well-known field of nanoscience and nanotechnology were pointed out for the first time. Paraphrasing Mr Feynman, there is plenty of room at immiscible interfaces. The highly energetic, dynamic and complex environment between immiscible liquids can be fully explored by scientists to process or prepare (or both process and prepare together) complex, multi-component and multi-functional materials as thin, homogeneous and transparent films with unique characteristics resultant from the preparative procedure.

The LLIR to thin films brings together several advantages when compared to traditional deposition pathways: (i) the film to be deposited could come from an already existing material, or it can be synthesized *in situ* directly in the biphasic system, in a one-pot process in which both the synthesis and the thin film processing are solved together in one single step; (ii) the entire process is easy to perform, simple and cheap; (iii) it

doesn't require sophisticated equipment, and it can be performed in a non-controlled environment (except for using a fume hood if one of the liquid phases presents some degree of toxicity); (iv) it is highly reproducible; (v) it doesn't require high temperatures, avoiding both substrate limitations (deposition over plastic substrates is not allowed for techniques requiring high temperatures) and composition limitations (polymers and soft matter can be easily managed, contrary to high temperature requiring methods); (vi) the films stabilized at the L/L interface can be transferrable to any kind of substrate (plastics included), of any shape (flat, curved, spheres, cylinders, *etc.*), and can cover different surfaces; (vii) it is excellent to get films of unprocessable and insoluble materials, and their different kinds of nanocomposites – many different materials with diverse compositions can be prepared by this route, which is unique for several ones; (viii) it allows thickness control; (ix) it allows roughness control; and (x) it allows transparency control.

The examples summarized in this review are representative of the broadness of the LLIR, covering films of organic, inorganic or hybrid materials; single-, bi- or multi-components; prepared in different combinations of immiscible liquids; starting from distinct precursors; using various experimental approaches to transfer the film from the L/L interface to substrates; and aiming at several technological applications. It is evident that the experimental conditions strongly affect the characteristics of the film: for example, using the same L/L interface, aiming at obtaining the same material, the use of different precursors produces films with different properties, and starting from the same precursors, the film will not be the same performing the process at different L/L interfaces. Considering the number of variables (the nature of the two liquids to give the interface; the origin and nature of the precursor; the kind of chemical reaction (if applicable); the presence of other species in the system (second or third phase, spectator ions or molecules, and surfactants), stirring, temperature, pH, procedures to transfer the film to substrates, the possibility of multi-layer deposition, *etc.*), the innovative potential of the technique is enormous. The potentiality of novel interfaces, such as the several organic/organic immiscible interfaces, the interfaces between concentrated aqueous solutions, miscible interfaces, and a whole combination of interfaces involving ionic liquids, is another experimental frontier to be explored. As an emergent field, there are several fundamental open questions on the relationship between all those variables and the expected characteristics of the final material. Many experimental and theoretical efforts are necessary to parametrize all these issues.

The LLIR has the potential to impact different fields, from the well-established to modern and emerging technologies, for example ones demanding flexibility, conductivity and transparency, such as flexible and transparent electrodes, stretchable sensors, flexible organic solar cells and OLEDs, flexible and transparent batteries and supercapacitors, and so on. Focusing on the real applicability of the technique, it becomes clear that the LLIR has huge potential to be used in large-scale production of thin films, aiming at industrially scaled

production. The roll-to-roll continuous deposition technique reported recently was the first real demonstration of this possibility,⁵⁷ but several other approaches can be developed by scientists and engineers willing to dedicate work to that.

Finally, it is expected that this review had demonstrated the fantastic and poorly-explored environment that exists at liquid interfaces and that it can stimulate materials scientists and engineers to explore this fascinating universe.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

I would like to acknowledge the students directly engaged in the research in the laboratory during the last 22 years; the scientific collaborators; Prof. Elisa S. Orth for the critical reading and suggestions; and the financial support of CNPq, CAPES, FINEP, Fundação Araucária, UFPR and INCT-Nanocarbon.

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