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Processing of nanomaterials in Layer-by-Layer films: Potential applications in (bio)sensing and energy storage

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Abstract: The study and preparation of new nanostructures involving the integration of distinct nanomaterials have been important for the development of new electrochemical devices for (bio)sensing and energy storage. Such devices envisage miniaturized or flexible electronic equipment for emerging technologies, including adaptive displays, artificial skin and wearable devices. In this way, the processing of specific nanomaterials may lead to nanostructures with properties that permit the fabrication of multifunctional devices for different applications, including sensors and supercapacitors. Therefore, the use of a suitable method to manipulate nanomaterials in a same nanostructure is important for this purpose. Thus, we expect that this review provides the readers with a brief overview of the potential usage of the Layer-by-Layer technique to fabricate nanostructured films and their advantages for sensing and energy storage.

Key words: nanomaterials, Layer-by-Layer technique, nanostructures, electrochemical devices, sensors, supercapacitors.

INTRODUCTION

The ability of fabricating new specific functional structures nanometrically is the key to the development of composites with improved properties. In this sense, the areas of sensors and supercapacitors may benefit from the knowledge accumulated hitherto as to conceive new materials with specific properties that aim at potential applications in nanotechnology (Willner and Willner 2010, Li and Wei 2013, Yu et al. 2013). The success in developing sensors and supercapacitors requires infrastructure and knowledge to manipulate nanomaterials in the form of nanostructured films. The fundamental characteristic to be taken into account is the capacity to manipulate molecularly the materials being integrated in the device (sensor or supercapacitor). In this sense, ultrathin film preparation techniques are suitable for the formation of nanostructures containing materials of different nature in an organized manner and with nanoscale architecture control (Hammond 2004, Ariga et al. 2007, Lutkenhaus and Hammond 2007, Siqueira Jr.

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et al. 2010a, Oliveira Jr. et al. 2014). In addition, the proper combination between architecture and film thickness can propel synergy between materials, leading to the formation of nanostructures with unique characteristics unlikely to surface in the bulk regime. In this context, the Layer-by-Layer (LbL) technique is quite an interesting method to produce ultrathin films with enhanced properties. LbL is based on the physical and chemical interactions of layers of both organic and inorganic substances, such as carbon nanotubes, nanoparticles and biomolecules (Siqueira Jr. et al. 2010b, Oliveira Jr. et al. 2014). However, achieving success in the manufacture and application of such films requires careful study of the physico-chemical properties of the materials during preparation and post-formation stage of the films.

This review provides an overview on the use of nanostructure-based LbL films for application as electrochemical sensors and biosensors, and electrochemical capacitors (supercapacitors) for energy storage. The advantages of using nanomaterials in such devices are discussed throughout the text, focusing on the LbL technique potentiality of being applied in these two research fields. Emphasis will be placed on recent reports based on the use of different nanomaterials in LbL films. Perspectives and trends of both (bio)sensing and energy storage fields are also highlighted.

NANOMATERIALS

The study of materials at the nanoscale has permited the investigation of new nanostructures with unique and improved properties when compared to their bulk counterpart. The term "nanoparticles" has begun to be used in the early 1990s along with related concepts such as "nanoscaled'' or ''nanosized'' (Kruis et al. 1998). In 2011, the European Union defined nanomaterials as natural materials, incidental or manufactured, containing particles, in the unbound state or as aggregate or agglomerate, having 50% or more of the particles with dimensions between 1 and 100 nm (Shi et al. 2013, Ahmed et al. 2016). In most applications, the best performances occur when the particle size is around 10 nm. Under these conditions it is now known that this size reduction can modify the physical and chemical properties of the materials (Nel et al. 2006, Yang et al. 2008). In a bulk size, properties are generally dependent only on the chemical composition. On the other hand, at the nanometer scale, size may alter properties. The electronic structure is altered from the continuous electronic bands to discrete or quantized electronic levels. As a result, the continuous optical transitions between the electronic bands become discrete and the properties of the nanomaterial become size-dependent (Burda et al. 2005).

Several studies have been carried out on the production of nanoparticles (Ray et al. 2009, Song and Kim 2009). Their features brought new cientific and technological perspectives, becoming the application of nanoparticles attractive to many research areas (Lu et al. 2007). Currently, nanoparticles have been already found in many parts of our daily lives, where it is possible to find several nanomaterials in sports articles, tires, stain resistant clothing, sunscreens, cosmetics and electronics (Nel et al. 2006). The particle size of the nanomaterials lies between the size of atoms or molecules and the materials in the bulk scale. Due to the wide application field of these nanomaterials more knowledge regarding production processes was essential to study new synthesis methods (Anton et al. 2008).

Nanoparticles can be synthesized via two main ways: physical and chemical methods. Physical methods are generally based on the principle of subdividing precursor materials into smaller particles, reaching the nanometer scale. These methods are generally based on the vapor deposition technique (Kango et al. 2013). The chemical method usually used for metallic nanoparticles, for instance, is based on the reduction of metallic salts, also called precursors. In the reduction, parameters such as low precursor concentration, more viscous solvent, slow acting reducing agent and stabilizing agent are important. These precautions are necessary to avoid particle agglomeration (Pradeep et al. 2009). More techniques and improvements exist, making possible synthesize noble metallic nanoparticles and metal oxide nanoparticles with a wide range of sizes, shapes, and dielectric environments (Kelly et al. 2003), which is important to optical, electrical, and catalytic properties (Sun and Xia 2002).

Concerning the importance to the development of nanoscience and nanotechnology, carbon nanotubes and (CNTs) and graphene are the most studied nanomaterials over recent decades (Yu et al. 2013). These carbon nanostructures are promising in nanotechnological applications as they may provide new functionalities that can be employed in different fields. For instance, the excellent mechanical properties, as well as the electrical and thermal conductivities exhibited by these nanostructures may permit to develop useful nanocomposites with desirable features (Willner and Willner 2010, Li et al. 2013, Yu et al. 2013). Also, due to their unique optical and electrical properties, innovative electronic devices can be manufactured (Hammond 2004, Willner and Willner 2010, Li et al. 2013, Yu et al. 2013). Regarding the latter, both CNTs and graphene have been investigated in (bio)sensing and energy storage research fields for the development of electrochemical sensors and supercapacitors devices (Hammond 2004, Willner and Willner 2010, Li et al. 2013, Yu et al. 2013). Particularly, emphasis will be placed on the use of carbon nanostructures in both applications when they are assembled by the LbL method.

THE LAYER-BY-LAYER TECHNIQUE

In recent years, areas related to nanoscience and nanotechnology aimed at the development of new nanocomposites have benefited greatly from the advent of the Layer-by-Layer (LbL) technique (Hammond 2004, Ariga et al. 2007, Lutkenhaus and Hammond 2007, Siqueira Jr. et al. 2010a, Oliveira Jr. et al. 2014). This technique makes use of oppositely charged materials that build up a multilayered architecture via electrostatic interactions to form highly stable nanostructured films on a solid substrate (Hammond 2004, Ariga et al. 2007, Lutkenhaus and Hammond 2007, Siqueira Jr. et al. 2010a, Oliveira Jr. et al. 2014).

The simplicity of the experimental apparatus used to fabricate LbL films represents one of the main advantages of the LbL technique. In principle, this method can be used for the coating of surfaces of any shape or size. Initially, the technique was applied by Sagiv et al. (1980) in the preparation of so-called multilayer systems based on chemical interactions (usually covalent bonds) between deposited layers (Sagiv 1980, Hammond 2004, Ariga et al. 2007, Lutkenhaus and Hammond 2007, Siqueira Jr. et al. 2010a, Oliveira Jr. et al. 2014). This process, although still used, has disadvantages, such as the need for synthesis of molecules with specific functionalities for the construction of the layers, which is an important limitation of the method. To overcome these limitations, Decher et al. (1992) (Hammond 2004, Ariga et al. 2007, Lutkenhaus and Hammond 2007, Siqueira Jr. et al. 2010a, Oliveira Jr. et al. 2014) proposed a new method of obtaining thin films by self-assembly. Instead of chemical adsorption between layers, Decher proposed a technique based on physical (electrostatic) interactions of layers with opposite charge. In this way, anionic and cationic polyelectrolytes can be alternately adsorbed onto solid substrates. Unlike the technique used by Sagiv, no covalent bond needs to be formed to build up the bilayers. In summary, for instance, when a negatively charged solid substrate is immersed in a cationic solution, a layer of polycation adsorbs on the surface of the substrate. Afterwards, the substrate is immersed in the anionic solution, promoting the adsorption of the polyanion on the previously adsorbed polycation layer. Then a bilayer is formed, and the repetition of the process allows the production of thin films composed of as many layers as desired (Hammond 2004, Ariga et al. 2007, Lutkenhaus and Hammond 2007, Siqueira Jr. et al. 2010a, Oliveira Jr. et al. 2014, Oliveira et al. 2017). Figure 1 illustrates the adsorption process of bilayers by using the LbL method.

Another great advantage of the LbL technique is that it allows for the use of a myriad of materials, ranging from polyelectrolytes and dye polymers to ceramic, metallic and semiconductor materials, as well as biological materials (Hammond 2004). This variety of materials provides several characteristics that can imply in different forms for the layers' adsorption, including ionic interactions in highly charged polyelectrolytes, ionic interactions in partially charged polyelectrolytes, secondary bonds such as hydrogen bonds or hydrophobic interactions, or in conjunction with electrostatic interactions.

Besides these features, the LbL method may also allow for the emergence of synergism between the materials used, promoting the enhancement or even the appearance of new specific properties that could not be possible by combining the materials in their bulk form (Hammond 2004, Ariga et al. 2007). Other important advantages that the technique offers are: i) the possibility of combining distinct materials into specific nanostructures without loss of their properties; ii) control of the molecular architecture that allows to explore the intimate contact between the components of the film; iii) small amount of material is required for the film fabrication. Therefore, the versatility of the LbL technique to use materials of different nature has catapulted the manufacture of nanostructured films with unique properties, benefiting several areas of nanoscience and nanotechnology such as optoelectronic devices, fuel cells and photovoltaic cells, biological markers, sensors and biosensors, and energy storage (Lutkenhaus and Hammond 2007, Lee et al. 2010, Siqueira Jr. et al. 2010b, Niu et al. 2012, Oliveira Jr. et al. 2014).

Among many nanomaterials employed in LbL films, carbon nanotubes and graphene have been demonstrated to be important materials in the development of nanocomposites due to their physicochemical characteristics that differ significantly from their microscopic phases (bulk) and also due to their potential applications (Katz and Willner 2004, Novoselov et al. 2012). Recently, LbL films have been used in the formation of nanostructured films containing these carbon-based nanomaterials combined with other different types of nanoparticles for application in sensors and supercapacitors (Katz and Willner 2004, Lee et al. 2010, Willner and Willner 2010, Novoselov et al. 2012, Li and Wei 2013, Yu et al. 2013, Madhu et al. 2016), especially the combination of a molecular-sized diameter (at the order of 1 nm) with a length at the microscopic-scale.

SENSORS AND BIOSSENSORS BASED ON LAYER-BY-LAYER FILMS

The interest of integrating nanomaterials and biological materials in devices for biosensors comes especially from the compatibility of the size, since the components of the electronic circuits have dimensions comparable to biomolecules. The electrostatic interactions and the typical charge transfer of biological processes can be detected by electronic nanocircuits, being advantageous to detect biological species. In addition, the high reactivity and effective area of these nanomaterials provide a natural combination for biological molecules (Willner and Willner 2010). In this sense, in recent years, the number of studies aiming at the incorporation of nanomaterials complexed with biomolecules in devices for (bio)sensing has increased toward the detection of different

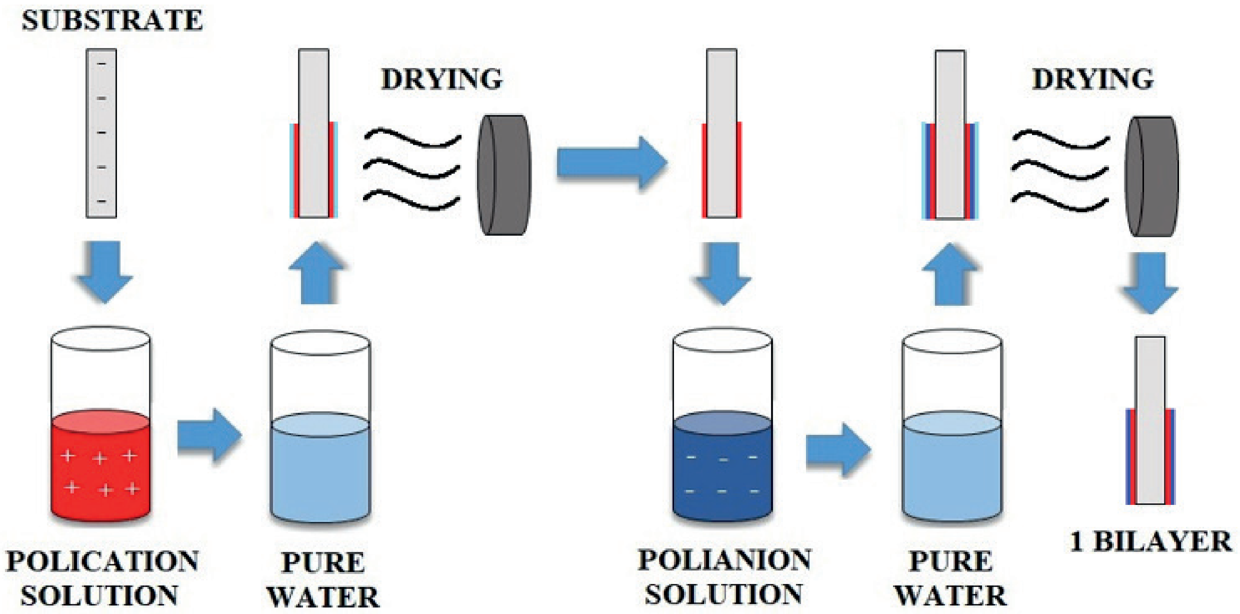

Figure 1 - Schematic representation of LbL method for fabrication of nanostructured multilayer films.

compounds of biological interest. In particular, specific systems are focused on diagnosis of different diseases such as cancer, for example. The increasing number of systems investigating the use of nanomaterials as sensor units or biomarkers for the diagnosis of tumor cells has allowed the development of more specific and selective molecular recognition devices, demonstrating the relevance of this research area for biomedical application (Siqueira Jr. et al. 2010b). The same principle can be applied to sensing systems focusing on detection of pollutants substances for environmental porposes (Siqueira Jr. et al. 2010b).

Based on the multitude of combination and complexation among different substances and materials of distinct nature, the LbL method has proved to be attractive to study new sensors and biosensors systems (Crespilho et al. 2006, Zhao et al. 2006, Siqueira Jr. et al. 2010b, Oliveira Jr. et al. 2014). In general, the LbL film acts as a (bio)compatible layer (sensing unit) onto the sensor suface and it is responsabile for the molecular recognition between the device and the substance to be detected (analyte) (Crespilho et al. 2006, Zhao et al. 2006, Siqueira Jr. et al. 2010b, Oliveira Jr. et al. 2014). The incorporation of carbon nanotubes, graphene and several nanoparticles with diverse biomolecules, such as DNA, proteins, antigen-antibody and enzymes in different LbL nanostructures have permitted to develop diverse proof-of-concept sensors and biosensors (Crespilho et al. 2006, Zhao et al. 2006, Ariga et al. 2007, Lutkenhaus and Hammond 2007, Oliveira Jr. et al. 2014). Generally, most of the reports involve the fabrication of sensors based on modified electrodes, chips, and probes, in which an electroactive compound (e.g. redox substances, enzymes, antibody) is immobilized as recognition element on their surface (Crespilho et al. 2006, Zhao et al. 2006). The interest in such LbL sensors lies in their intrinsic synergistic properties with other substances. In particular, the electrical properties allow carbon nanotubes, reduced graphene oxide and metallic nanoparticles to be able to enhance the mediation of charge transfer of reactions with electroactive species in solution, while the optical and magnetic properties enable semiconductor and magnetic nanoparticles to act as markers of biological species (Crespilho et al. 2006, Oliveira Jr. et al. 2014). Other advantages come from the increase of the electrode surface area, the ability to catalyze redox reactions of analytes, functionalization with several functional groups, in addition to the immobilization of biomolecules without loss of biological activity and improvement of the properties of the sensors, including high sensitivity and rapid response time (Zhao et al. 2006, Crespilho et al. 2006, Gui et al. 2018). More advantages in using LbL films are related to the high sensitivity and faster response time that can be exhibited than thick-film sensors. In addition, the technique allows for the combination of materials in the preparation of specific sensing units, assuring intimate contact between the sensor components by controlling the film architecture. Other advantages are the use of small amounts of film material and the preservation of the activity of biomolecules for a higher period (Hammond 2004, Crespilho et al. 2006, Zhao et al. 2006, Ariga et al. 2007, Lutkenhaus and Hammond 2007, Siqueira Jr. et al. 2010b, Oliveira Jr. et al. 2014).

Electrochemical methods for (bio)sensing are the most used platform to investigate and develop new sensor concepts for biomedical and environmental purposes. The signal transducer is based on charge-transfer or charge-transport mechanisms, in which the signal for detection lies from changes in faradaic or capacitive currents, according to the recognition element features. LbL films have been widely studied for such model of (bio)sensors applications (Oliveira Jr. et al. 2014). For instance, a sensor of dopamine (DA) and uric acid (UA) was reported (Wang et al. 2007). The determination of DA is a subject of great importance for investigating its physiological functions and diagnosing nervous diseases resulting from DA abnormal metabolism, such as epilepsy, senile dementia, Parkinsonism, schizophrenia and HIV infection and extreme abnormalities of UA levels are symptoms of several diseases (e.g. gout, hyperuricaemia and Lesch–Nyhan syndrome). The sensor was assembled on glassy carbon electrode (GCE) coated with a gold nanoparticle/choline (GNP/Ch). The modified electrode exhibited strong electrochemical catalytic activity toward the oxidation of DA and UA, with detections limit of 0.12 and 0.6 μM, respectively. The electrochemical sensor showed excellent selectivity, good sensitivity and high stability.

A hydrogen peroxide sensor was studied by Xi et al. (2012). The great importance of this study is that hydrogen peroxide is cytotoxic and may be a signaling molecule for several biological processes. The device was made with Au nanoparticles and graphene nanosheets functionalized with bovine serum albumin in a fluorine-doped SnO_2 (FTO) electrode, to oxidation of H_2O_2. Porous structures, high surface area and effective electron transfer lead to sensor with a 0.1 μM detection limit. The lower value in the sensitivity showed the efficiency of the LbL in production of sensors.

LbL films have also been attractive for resistive gas sensors systems. Liu et al. (2018) reported that LbL nanostructured films were advantageous in terms of surface-to-volume ratio and high specific surface area, demonstrading great potential in improving the glycol gas sensing property. The structural and morphology features of the film improved its sensing activity due to their porous structure and high surface permeability. Du and coworkers (2007) also observed advantages of the LbL technique when studying NH_3 detection. A LbL film combining polyelectrolytes (PSS and PDDA) and metallic oxides (In_2O_3, NiO, SnO_2, Fe_2O_3, and CuO) were prepared as sensing units to reduce NH_3 gas. The detection of this substance is important for many fields as food processing, fertilizers, chemical technology, medical diagnosis, fire power plants, and environmental protection. The sensors exhibited good reproducibility and low response times due to the presence of large surface area and porous structure in the films. The best performance was observed for the filmo of In_2O_3, being possible to detect ammonia at concentration at levels of 20 ppm.

Nohria et al. (2006) produced an LbL film consisting of PAH and PSS for sensing humidity. The precise control of humidity levels is particularly important in many areas such food processing, textile technology, storage areas, computer rooms, hospitals, museums, libraries, high voltage engineering and accelerator systems. The detection was based on the resistance of polymer sensors, that was reduced with increase of relative humidity. LbL sensors presented better detection performance in terms of response time, sensitivity and repeatability with detections at levels of 11%. Another humidity sensor was reported by Zhang et al. (2014). The authors developed a flexible sensor based on LbL film contaning rGO/PDDA on polyimide substrate with interdigital microelectrodes structure. The detection mechanism was based on the increasement of the resistance in the presence of humidity. It was possible to manufacture a flexible film through the technique without loss of sensing activities, with sensitivity linear relationship toward the humidity range from 11% to 97%.

Another sensor platform that has benefited from the incorporation of LbL films is the (bio) sensors based on field-effect devices (FEDs) (Oliveira Jr. et al. 2014). Such devices are silicon-based sensors deriving from field-effect transistors and are sensitive to any electrical interaction at or nearby the between sensistive layer (gate) and the substance to be detected (electrolyte) (Schöning and Poghossian 2006, 2014, Siqueira Jr. et al. 2010b). For instance, Siqueira Jr. et al. realized a set of studies incorporating carbon nanotubes (CNTs) in a LbL fashion nanostructure with PAMAM dendrimers and the enzyme penicillinase to detect penicillin G using two types of FEDs, the electrolyte-insulator-semiconductor (EIS) (Siqueira Jr. et al. 2009b, 2010b) and the light-addressable-potentiometric-sensor (LAPS) (Siqueira Jr. et al. 2009a, 2010b). The detection principle of a penicillin biosensor by means of FEDs is the changes in the concentration of H^+ ions that are released from the hydrolysis of penicillin into penicilloic acid by the enzyme penicillinase. A penicillin biosensor has an important application in food control, as undesirable residues of this substance can interfere on food quality (e.g. milk, meat). These studies concluded that the morphology of the PAMAM/CNTs LbL films had a direct effect on the sensing performance of EIS and LAPS sensors. Both systems exhibited enhanced sensing properties and performance toward penicillin G with the presence of the LbL film, achieving stable output signals with low drifts and hysteresis and higher sensitivity (of ca. 100 mV/decade) compared with their respective bare devices and with other similar EIS and LAPS systems for penicillin G detection.

Abouzar et al. also reported an EIS system for penicillin G detection. For this system the LbL films were made by using PAH, PAMAM dendrimer and the enzyme penicillinase onto an Al-Si–SiO_2 EIS structure. The LbL films provided a larger amount of enzymes immobilized per sensor area, reducing enzyme leaching effects and thus enhancing the stability and lifetime of the biosensor even after two months. A sensitivity of ca. 80-100 mV/decade toward penicillin was revealed with a low detection limit of about 20 mM (Abouzar et al. 2010).

In another case which proved the suitability of employing the LbL films in FEDs for sensing, Morais et al. (2017) studied nanofilms combining ZnO nanocrystals, PAH and CNTs in an EIS structure for detecting glucose and urea in the same clinical diagnosis range. The enzymes glucose oxidase and urease were immobilized on film's surface for detection of glucose and urea, respectively. The study was aimed at optimizing the ideal number of bilayers onto the EIS chip in order to achieve the best performance toward the detection tests. In terms of exhibiting high sensitivity and output signal, the glucose biosensor showed better performance for a LbL film with 10 bilayers. On the other hand, the urea biosensor presented enhanced properties for only 1 bilayer. Figure 2 shows the schematic representation of this EIS system.

SUPERCAPACITORS BASED ON LAYER-BY-LAYER FILMS

Supercapacitors, also called electrochemical capacitors or ultracapacitors, are energy storage devices with capacitance values much higher than those of regular capacitors. Unlike ordinary capacitors, which rely on the conventional solid dieletric, supercapacitors use the electrostatic double-layer capacitance (Lee et al. 2010, Niu et al. 2012, Novoselov et al. 2012, Li and Wei 2013, Yu et al. 2013, Madhu et al. 2016) and the pseudocapacitance that comes from the faradaic reactions of an electrochemical redox system (Lee et al. 2010, Madhu et al. 2016, Novoselov et al. 2012). Since 1957, when the practical use of electrochemical capacitors was demonstrated and patented by General Electric, supercapacitors have generated great interest for several potential applications in energy storage, including portable electronic devices and hybrid vehicles (Wang et al. 2009, Li and Wei 2013, Yu et al. 2013). For the latter, the supercapacitors can provide the necessary energy during acceleration and promote energy recovery during braking (Li and Wei 2013, Yu et al. 2013).

In terms of properties, supercapacitors have attracted a lot of attention because of their higher power density and longer life cycle than batteries, followed by their high storage capacity in relation to their size, high energy density, long periods of loading and unloading cycles and high energy efficiency (Luo et al. 2012, Zhang et al. 2017). An ideal supercapacitor device preferably contains high surface area, porosity and high conductivity (Fu et al. 2018, Kumar et al. 2018). In this sense, carbon materials, metal oxides and conducting polymers have been employed as electrode materials (Kandasamy and Kandasamy 2018). However, current materials still lack efficiency, as the application in hybrid cars and energy cells demand an increase in energy capacity and power density to improve project costs and performance (Lee et al. 2010, Niu et al. 2012, Li and Wei 2013, Yu et al. 2013).

For this reason, the research for the development of new materials to increase the performance of the supercapacitors has being carried out and some materials have become promising in the use as electrodes, such as carbon nanotubes and graphene (Lee et al. 2010, Niu et al. 2012, Li and Wei 2013, Yu et al. 2013), metallic and metallic oxide nanoparticles (Liu et al. 2013, Zhi et al. 2013), as well as conductive polymers (Jeon et al. 2013, 2014, Mike and Lutkenhaus 2013, Shao et al. 2014). Although supercapacitors produced with carbon nanotubes and graphene have excellent electrical conductivity and large surface area, the contact resistance between the electrode and the current collector prevents them from reaching the expected performance. Thus, to increase the capacitance of the electrode, metallic oxides (in the form of bulk or nanoparticle) (Li and Wei 2013, Liu et al. 2013, Yu et al. 2013, Zhi et al. 2013) or conductive polymers (electroactives) (Jeon et al. 2013, 2014, Mike and Lutkenhaus 2013, Shao et al. 2014) have been complexed together with these carbon materials to decrease contact resistance and increase the energy density of supercapacitors.

The use of carbon nanotubes and graphene in supercapacitors is interesting due to their flexibility and relative transparency, which can also lead to the development of flexible electronic products that can be incorporated into clothing or applied in the production of malleable cell phone and computers, for instance (Li and Wei 2013, Yu et al. 2013, Zhi et al. 2013). In particular, graphene has been shown to be a strong candidate for supercapacitors devices because

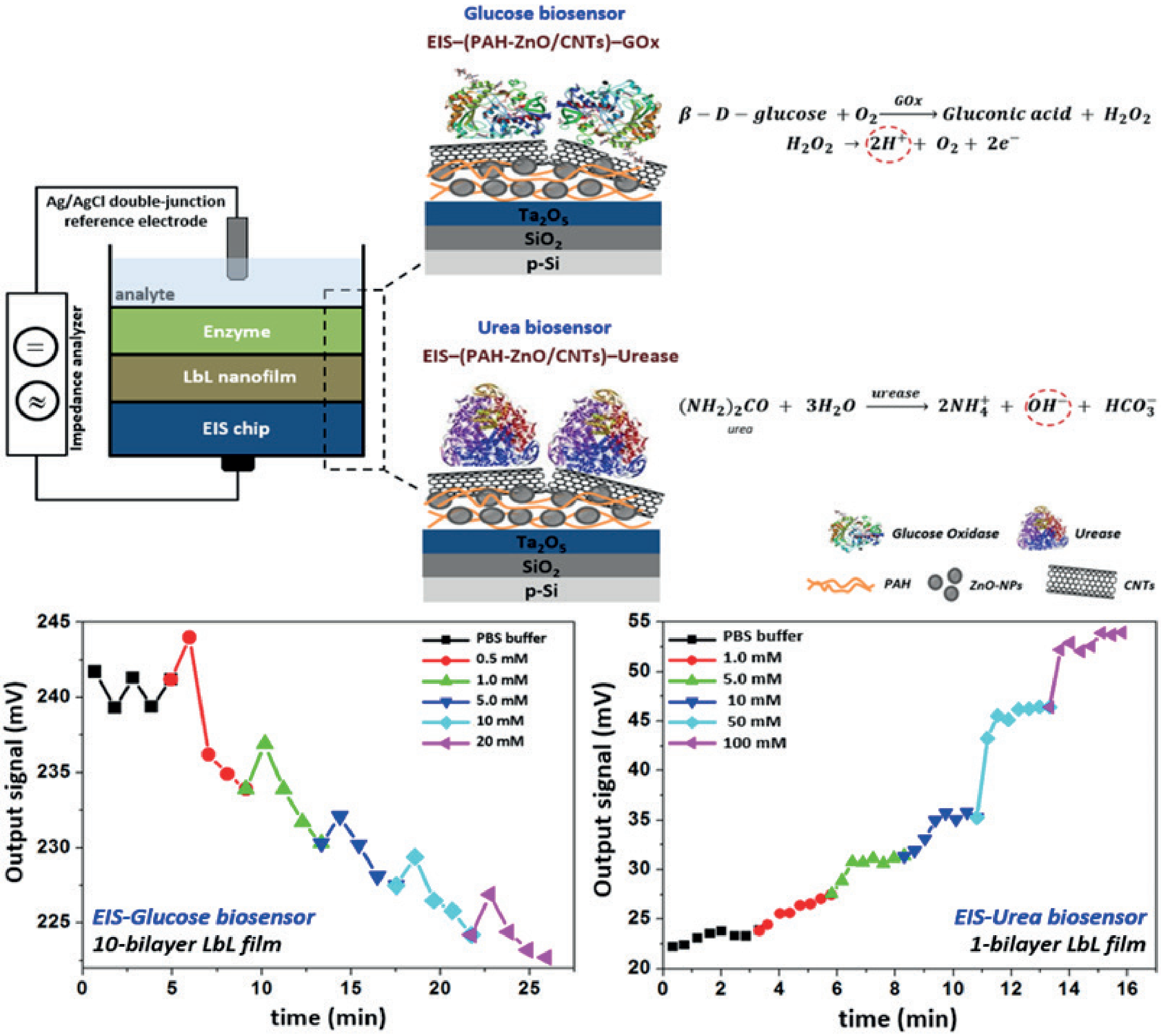

Figure 2 - Schematic representation of an EIS (p-Si–SiO$_2$–Ta$_2$O$_5$) sensor modified with PAH-ZnO/CNTs LbL film, including the mechanism of operation principle and enzymatic reactions for glucose and urea detections (top). Respective ConCap curves for both EIS biosensors toward different concentrations of glucose and urea (bottom). Modified with permission from Morais et al. (2017). Copyright 2017 Springer Nature.

of properties such as high electrical conductivity, surface area, flexibility, mechanical strength, low weight, and easy chemical manipulation that allows it to be combined with various nanomaterials (Li and Wei 2013, Yu et al. 2013, Zhi et al. 2013). However, there is a challenge in the manufacturing of graphene electrodes in transferring these exceptional properties from nanoplatforms to macroscale structures. The effective surface area of graphene materials depends on their deposition layers, i.e., the lower the thickness of the layers, the larger the surface area will be. To overcome the agglomeration of graphene layers in the macrostructures, nanoparticles are used to separate the graphene sheets, leading to decorated nanostructures that exhibit enhanced electrochemical properties and, therefore, improved performance to store energy (Li and Wei 2013, Yu et al. 2013, Zhi et al. 2013). Based on this, the LbL technique also appears as an ideal method to investigate the formation of new nanostructures for studies in supercapacitors. The advantage of using this technique lies on the formation of ordered multilayer films with fine control of the architecture and the thickness in nanoscale by using the wide range of specific materials commonly used for this application, including carbon materials (Li and Wei 2013), nanoparticles (Niu et al. 2012) and conductive polymers (Mike and Lutkenhaus 2013, Shao et al. 2014).

Not only should ideal oxides for supercapacitors have the desired electrochemical properties, but they should also be of low cost and toxicity (Zhi et al. 2013). For instance, ruthenium oxide has high capacitance in acid solutions due to its high electrical conductivity, however, its high cost and toxicity hampers its scalability. On the other hand, magnesium oxide has low cost and toxicity, which makes it a promising oxide for improving the energy density of supercapacitors (Zhi et al. 2013). Some cobalt oxides and hydroxides also have high reduction capacity and high reversibility, demonstrating that there is a large area of study on the choice of the best oxide for the production of more efficient supercapacitors (Zhi et al. 2013).

Wu et al. (2014) used the LbL method to development of large-area, highly uniform, ultrathin, nitrogen and boron co-doped graphene (BNG) films for supercapacitor applications. The assembly of film is based in anionic graphene oxide (GO) nanosheets and cationic poly-L-Lysine (PLL) as a nitrogen-containing precursor, followed by intercalation of H_3BO_3 within the layers and annealing. The film was further subjected to treatment at 800°C in nitrogen atmosphere to convert the H_3BO_3-intercalated (PLL/GO) into a BNG film and the (PLL/GO) film into a nitrogen-doped graphene. Even with the thermal treatment, the film remained stable and a capacitance in order of 488 F/cm² at 10 mV/s was observed.

Multilayer films of Co-Al layered double hydroxide nanosheets (Co-Al LDH-NS) and graphene oxide (GO) were fabricated through LbL assembly by Dong et al. (2011) onto flexible PET substrate. The results indicated that is possible to obtain films well organized layered structure, as well as with finely controlled film thickness and uniformity. An improved specific capacitance (880 F/g under scan rate of 5 mV/s) was attributed to the face-to-face contact of the Co-Al LDH-NS and GO sheet, which contributes to the electron transport efficiently. The film exhibited good cycle stability over 2000 cycles.

Recently, Fávero et al. (2018) demonstrated that the use of zinc oxide nanoparticles dispersed into a polymeric matrix of polyalyllamine hydrochloride (PAH) and combined with carbon nanotubes (CNT) onto an indium tin oxide (ITO)/PET substrate have attractive properties in the formation of supercapacitor electrodes. This system presented LbL films with high surface area with a high areal capacitance of ca. 1000 $\mu F/cm^2$ for a 10-bilayer LbL film at a current density of 1.0×10^{-5} A/cm^2 and high cycling stability with a capacitive retention of 96% over 1000 cycles. Yang et al. (2014) used the LbL method for preparation of shelled NiO hollow nanospheres organized on the surface of carbon spheres. The highly active surface area, due to its porous structure, provided ion diffusion path for effective electrolyte diffusion, culminating in a capacitance of 612.5 F/g at current of 0.5 A/g with over 90% specific capacitance retention after 1000 charge and discharge cycles.

Another study involving LbL process was used to assembly a film of positive poly(ethyleneimine)-modified graphene sheets with negative acid-oxidized multi-walled to form a hybrid carbon films on a silicone or ITO glass (Yu and Dai 2009). An interconnected network of carbon structures with well-defined nanopores was observed. Such morphology acted as fast electronic and ionic conducting channels to show a rectangular cyclic voltammogram even at a high scan rate of 1 V/s, in which capacitance was about of 120 F/g that is considerably higher for supercapacitor-based CNT electrodes. A flexible supercapacitor electrode of aramida nanofibers (ANFs) and graphene oxide (GO) sheets, reported by Kwon et al. (2017), using a thermical (TRGO) and chemical method (CRGO) to reduce the GO. CRGO presented a better performance, exhibiting a high areal capacitance of 221 μF/cm^2, corresponding to 78 F/cm^3. The LbL permitted a suitable interaction between the materials in the electrodes that showed excellent durability toward repeated flexure tests, in which no cracks appeared after 1000 cycles.

Also important, electroactive polymers are also advantageous in electrochemical energy storage devices, not only as electrolyte (used in the case of batteries) but also as electrodes (Jeon et al. 2013, 2014, Mike and Lutkenhaus 2013, Shao et al. 2014), which permits the manufacture of flexible electrodes that can lead to the development of portable devices at a lower cost. Among some possible applications, one can envisage the use of supercapacitors as wearable devices in clothing for operation of portable devices (e.g. sensor arrays, cell phones) (Jeon et al. 2013, 2014, Mike and Lutkenhaus 2013, Shao et al. 2014). Shao et al. (2011) developed a film using the LbL technique, combining (3-aminopropyl)-triethoxysilane (APTES), polyaniline (PANI) and V_2O_5 materials for energy storage applications. The best performance exhibited a capacity in range of 264 mAh/cm^3 based on 1 μA/cm^2. After 500 cycles, the electrode maintained 80% of its original capacity at a discharge current of 20 μA/cm^2. In another study, Shao et al. (2013) investigated a LbL film of polyaniline nanofibers (PANI NF) and V_2O_5 to form hybrid electrodes for electrochemical energy storage. The resulting electrode was highly porous and significantly exceeded in performance compraing to analogous electrodes assembled with conventional PANI. A maximum capacity of 320 mA h g^{-1} was obtained for the electrode containing PANI NF, which indicated contributions from both PANI and V_2O_5. The PANI NF/V_2O_5 LbL electrodes retained 75% of its original capacity after 100 cycles and presented high capacity caused by simultaneous diffusion-limited and nondiffusion-limited redox processes.

In other polyanille-based LbL films, Jeon et al. (2013) reported the uses of a doped polyaniline:poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PANI:PAAMPSA) onto ITO-coated glass substrate for energy storage. This study comprised three different polyaniline-based LbL electrodes of PANI/PAAMPSA, PANI/PANI:PAAMPSA, and poly(ethylenimine)/PANI:PAAMPSA for comparison in terms of film growth, charge storage, and reversibility. The results showed that the PANI/PANI:PAAMPSA electrode presented the best performance in terms of capacity and cycle life, with capacities in the order of 97 mAh/g. Differently, Shao et al. (2014) developed a PANI/V_2O_5 LbL film cathodes for Li-ion batteries using spray-assisted LbL assembly. This LbL variant mode is suitable to coating over large areas faster then by diping mode. As a result, the films formed a water-processable hybrid cathode with high capacity of 232 mA h g^{-1} at a discharge current of 5 mA cm^{-2}, specific energy of 650 mW h g^{-1} at a discharge current of 0.5 mA cm^{-2}, specific power of 3395 mW g^{-1} at a discharge current of 25 mA cm^{-2}, and good cycle life 11-fold faster than dip-assisted LbL assembly.

Kwon et al. (2015) studied the LbL spray-assisted film of PANI NF with reduced graphene oxide (rGO). The film was highly porous (74% void), which facilitated ion transport. Compared with dip-assisted LbL electrodes, spray-assisted LbL electrodes exhibited an improved capacitance and a higher power, which were attributed to the enhanced porosity of the films. Moreover, this system showed that spray-assisted LbL assembly was over 70 times faster and yielded electrodes with better capacitance relative to dip-assisted LbL assembly.

Jeon et al. (2015a) also studied energy storage systems based on LbL films of positive polyaniline nanofibers (PANI NF) combined with negative charged graphene oxide (GO) sheets and their subsequent electrochemical reduction (ERGO) on ITO substrate (Figure 3). This system presented capacities that varied from 85 to 184 mAh/cm^3 (188 to 461 mAh/g) at 0.1 A/g (electrode mass basis), and achieved the highest specific energy measured of ca. 1395 mWh/g at a specific power of 1590 mW/g, and the highest specific power of ca. 60252 mW/g at a specific energy of 927 mWh/g.

RECENT TRENDS USING MULTIFUNCTIONAL NANOSTRUCTURES

Multifunctional devices may be produced by bringing together materials that confer specific tasks on the electrode. In this context, the investigation of films combining appropriate materials (e.g. carbon nanomaterials, conductive polymers, metallic oxide nanoparticles) can result on nanostructured films with improved mechanical and electrochemical properties, allowing for the formation of flexible electrodes that can be applied to develop wearable electronics devices (Du et al. 2014). For instance, Kwon et al. (2017) reported electrodes consisting of rGO sheets and aramine nanofibers (ANFs) prepared by vacum filtration. The mechanical properties of RGO, ANFs, and rGO/ANF nanocomposite paper electrodes were examined by tensile testing. The Young's modulus and maximum tensile strength increased substantially with the increasing amount of ANFs. As a result, the mechanical and electrochemical properties revealed high toughness (982 ± 109 kJ/m^3) and high specific capacitance ranging from 90 to 210 F/g, respectively, for and rGO/ANF nanocomposite supercapacitor electrodes containing from 1 to 25 wt % ANFs. Another report involving flexible vacuum-assisted LbL films was based on PANi nanofibers and multi-walled carbon nanotubes (MWNT) onto carbon paper substrate

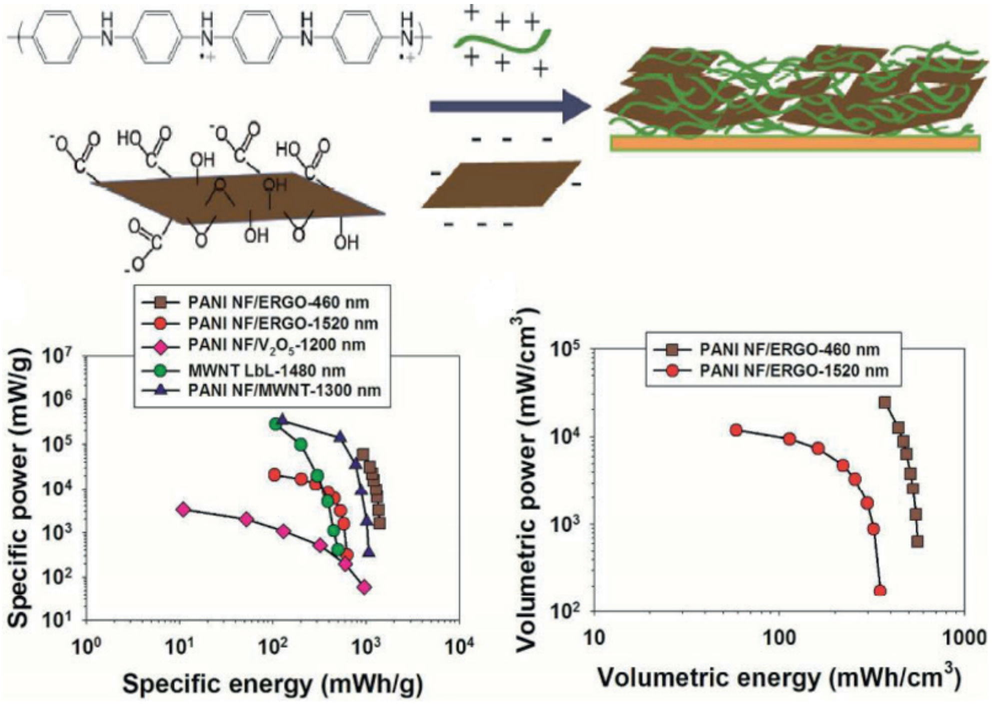

Figure 3 - Illustration of a LbL assembly of PANI-NFs and GO sheets (top). Ragone plots based on mass (left) and volume (right) of the different PANI NF-based LbL films (bottom). Modified with permission from Jeon and et al. (2015). Copyright 2015 Royal Society of Chemistry.

(Hyder et al. 2014). This study exhibited films with high specific capacity of 147 mAh/g at a rate of 0.05 A/g and excellent charge/discharge stability over 10,000 cycles. Such properties were originated from MWNTs and redox active PANI nanofibers that store charges through both electrical double-layer and faradaic mechanisms.

Concercing structures with more than one functionality, Madhu et al. (2016) reported a modified glassy carbon electrode (GCE) combining activated carbon and zinc oxide (ZAC) at different proportions for both applications in sensing and energy storage. The main results depicted a system with remarkable electrochemical properties for simultaneous detection of ascorbic acid (AA), dopamine (DA), and uric acid (UA), as well as hazardous pollutants such as hydrogen peroxide (H_2O_2) and hydrazine (N_2H_4) with desirable sensitivity, selectivity, and detection limits. Moreover, the ZAC-modified stainless-steel electrodes also showed superior performances for supercapacitor applications (see Figure 4).

The idea to obtain self-charging supercapacitor consists of using piezoelectric materials. In this way, Ramadoss et al. (2015) studied a piezoelectric self-charging supercapacitor power cell (SCSPC) using MnO_2 nanowires as positive and negative electrodes and a polyvinylidene difluoride (PVDF)-ZnO film as a separator (and also a piezoelectric layer). The enhancement in the self-charging process was trigged by the increase in piezopotential with the higher applied strain (compressive force). After the self-charging process, the device was discharged back to its original voltage under a constant discharge current of 1 μA. These results permit to envisage the development of self-powered flexible

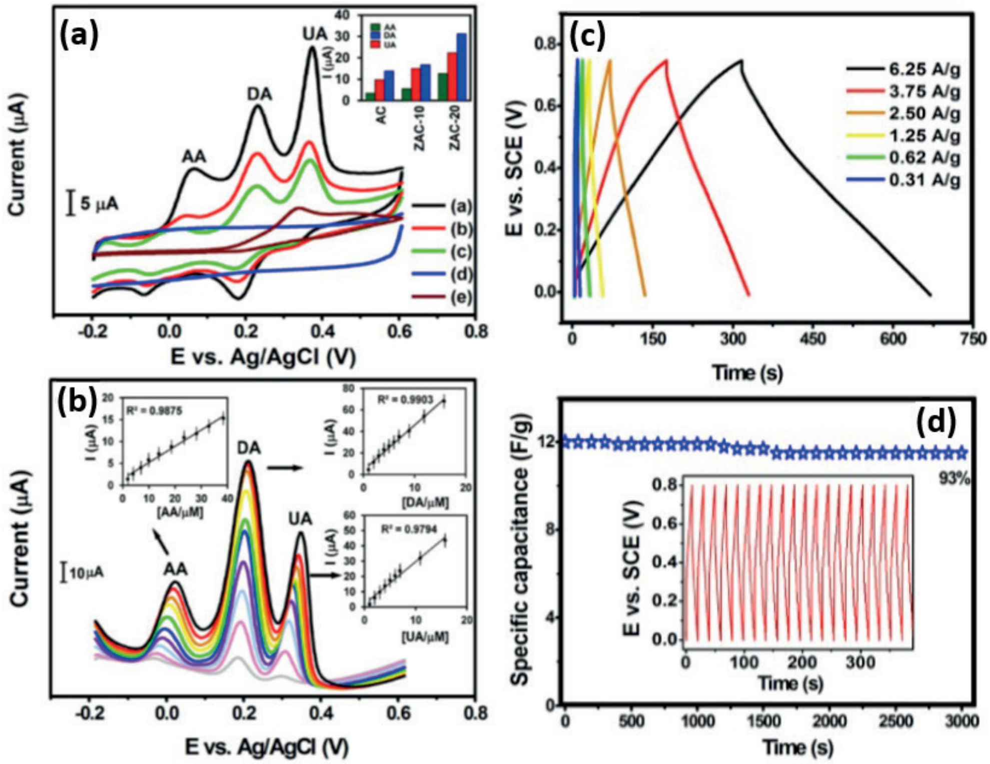

Figure 4 - Modified glassy carbon electrode (GCE) combining activated carbon and zinc oxide (ZAC) at different proportions for applications in sensing toward AA, DA and UA detection (**a** and **b**), and for energy storage as supercapacitor (**c** and **d**). Modified with permission from Madhu et al. (2016). Copyright 2016 Royal Society of Chemistry.

hybrid devices. Figure 5 display the schematic conception of the piezoelectric nanocomposite and the fabricated prototypes using an aluminium foil and a conductive fabric piece as the positive and negative electrodes.

Song et al. (2015) also developed a flexible piezoeletric supercapacitor by means of PVDF (polarized polyvinylidene fluoride) film coated with H_2SO_4/poly(vinyl alcohol) (PVA) gel electrolyte and functionalized carbon cloth (FCC) or pure carbon cloth (PCC) as both anode and cathode. The supercapacitor with PVDF separator presented areal capacitances varying about of 210-360 F/m^2 and a relatively good charge/discharge rate capability, retaining ca. 60% of the capacitance when the current density increased from 8 to 200 A/m^2. Another piezo-electrochemical study was developed by Jacques et al. (2015) using polyacrylonitrile-based carbon fibers that acted both as electrodes for Li-ion batteries and structural reinforcement for composites materials. By applying a tensile force to the carbon fiber bundles (used as Li-intercalating electrodes) resulted in a response of the electrode potential of a few millivolts which allowed, at low current densities, lithiation at higher electrode potential than delithiation. The measured harvested specific electrical power was in the order of 1 μW/g for current densities in the order of 1 mA/g.

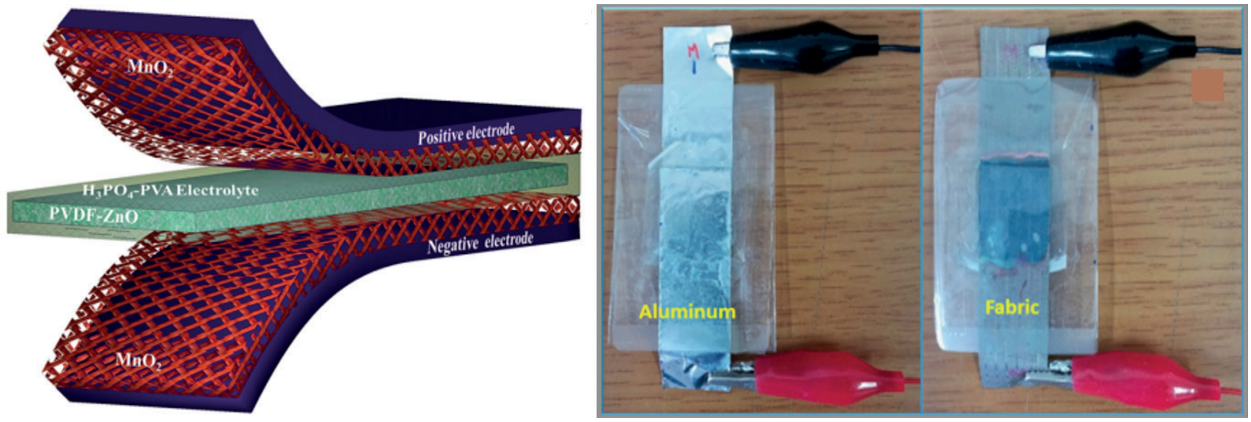

Figure 5 - Piezoelectric self-charging supercapacitor power cell (SCSPC) using MnO_2 nanowires as positive and negative electrodes and a polyvinylidene difluoride (PVDF)-ZnO film as a separator and also a piezoelectric layer (left). Fabricated prototypes using an aluminium foil and a conductive fabric piece as the positive and negative electrodes (right). Modified with permission from Ramadoss et al. (2015). Copyright 2015 American Chemical Society.

CONCLUSIONS

In this review, we provided highlighting snapshot of the importance and advantages of LbL films in (bio)sensing and energy storage. For (bio) sensing, attention was mainly paid to LbL systems employed as recognition layer for biomedical and environmental purposes under different sensing platforms. Concerning energy storage systems, emphasis was placed on supercapacitors electrodes consisting of the carbon nanomaterials, metal oxides and conductive polymers. With that in mind, one can envisage the fabrication of nanostructures that can serve for multifunctional purposes and prospect the development of new emerging electrochemical devices. We hope that the readers may be attracted by content of the review. We have highlighted two important research fields that benifited from a special method of materials manipulation and that have great potential for nanotechnological applications.

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AUTHOR CONTRIBUTIONS

All authors were committed and have equally contributed on the manuscript's writing and revision.

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