Conductive multilayer film based on composite materials made of conjugated polyelectrolytes and inorganic particles

F.E. Jurin, Cédric C Buron, S. Clément, A. Mehdi, B. Lakard, N. Martin, C. Filiâtre

Conductive multilayer film based on composite materials made of conjugated polyelectrolytes and inorganic particles.

F. E. Jurin[1], C.C. Buron[1,*], S. Clément[2], A. Mehdi[2], B. Lakard[1]. N. Martin[3], C. Filiâtre[1]

[1] Institut UTINAM – UMR 6213 – CNRS – Univ. Bourgogne Franche-Comté

16, Route de Gray, 25030 Besançon Cedex, France

[2] Institut Charles Gerhardt Montpellier (ICGM), UMR 5253, CNRS-UM-ENSCM, Université de Montpellier,

34095 Montpellier Cedex 5, France

[3] Institut FEMTO-ST, UMR 6174 – CNRS – Univ. Bourgogne Franche-Comté

15B, Avenue des Montboucons, 25030 Besançon Cedex, France

* Corresponding author. Tel.: +33 3 81 59 25 ; E-mail address: cedric.buron@univ-fcomte.fr

ABSTRACT

Poly(3,4-ethylenedioxythiophene)–polystyrene sulfonate (PEDOT:PSS) conjugated polymer blend and a cationic poly(3-hexylthiophene) (P3HT)-based conjugated polyelectrolyte incorporating imidazolium ionic side groups were first adsorbed as monolayer on inorganic colloidal particles. At the plateau of adsorption isotherm, adsorbed amount of PEDOT:PSS on alumina particles appears lower than the adsorbed amount of P3HT on silica particles. Both polyelectrolytes strongly modify the surface charge of particles as reveals by zeta potential variation. Functionalized particles were then assembled using Layer-by-Layer method in order to prepare $(PDDA/Al_2O_3-PEDOT:PSS)_n$ and $(SiO_2-P3HT/PEDOT:PSS)_n$ conductive multilayer film. Thicker $PDDA/Al_2O_3-PEDOT:PSS$ films were elaborated when a drying step was added during the build-up. The same effect was observed when composite particle concentration was increased from 1 to 10 g.L^{-1}. Electrical behavior was completely modified in comparison with PDDA/PEDOT:PSS assembly. After heating at 150°C, no conductivity was detected due to visible cracks on SEM images. For $SiO_2-P3HT/PEDOT:PSS$ assembly, thickness is higher than for $PDDA/Al_2O_3-PEDOT:PSS$ assembly using the same experimental

procedure. However, even if two conductive polyelectrolytes were embedded into the film, conductivity was too low at 30°C to be measured by van der Pauw technique probably due to the cracking of the film induced by silica particles incorporation.

KEYWORDS: PEDOT:PSS, Multilayer, Conjugated polyelectrolyte, Polythiophene, Inorganic colloidal particle, Conductivity, Composite film.

INTRODUCTION

Conjugated polymers are nowadays an attractive class of materials to prepare thin conductive films for a wide range of applications such as organic light emitting diodes, electrochromic devices, sensors, capacitors or solar cells [1]. Aqueous dispersion of conjugated polymers have notably attracted considerable attention leading to the printing of flexible, transparent, and biocompatible conducting films, which can be useful for a wide range of applications including energy [2-4] or biomedical devices[5-8]. Because of its high conductivity, environmental and electrochemical stability, water solubility, biocompatibility and transparency in the visible range [9], the current material of choice for many applications is poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS).[10,11] More recently, π-conjugated polyelectrolytes (CPEs), have emerged as a promising alternative for elaborating aqueous dispersion of conjugated polymers since due to the presence of ionic side chains, they can be dissolved in aqueous media. Their intrinsic structure allow them to combine the physicochemical behavior of the polyelectrolytes with the optical and electronic properties of conjugated polymers [12,13]. Poly(3-hexylthiophene) (P3HT)-based conjugated polyelectrolytes have been in particular developed to elaborate organic conductive films finding applications in organic transistors [14,15] or organic solar cells [16-18].

To prepare thin conductive films based on PEDOT:PSS conjugated polymer blend or CPEs, several conventional techniques are available: dip coating, spin coating or drop casting. To elaborate complex film architectures, the layer-by-layer (LbL) technique is particularly appropriate due to its simplicity, robustness, low cost and versatility [19-21]. Using this technique, PEDOT:PSS can be associated with traditional polyelectrolytes such as poly(allylamine hydrochloride) (PAH), polydiallyldimethylammonium chloride (PDDA) or Polyethylenimine (PEI). The electrical conductivity of the resulting films can be tailored to the targeted applications but generally remains lower than pure PEDOT:PSS film due to the use of insulating polyelectrolyte. Considering multilayer films, conductivity mainly depends on the chemical parameters used during the build-up process if no post treatment is applied. To improve conductivity, which is an essential parameter for the performance of the organic devices, insulating polyelectrolytes can be replaced by CPEs or metal nanoparticles.

McCullough *et al.* have notably described the LbL assembly of anionic and cationic regioregular polythiophene-based CPEs leading to conductivity around 0.04 S.cm^{-1} [22]. More Recently, Buriak *et al.* reported the use of pyridinium-based polythiophene/PEDOT:PSS bilayers film as hole transporting layer in organic solar cells showing significant long-term stability and good photovoltaic performance [23,24]. Metallic silver nanoparticles were also combined with PEDOT:PSS leading to a conductive hybrid polyelectrolyte multilayer with an ordered architecture [25].

Exploiting metallic nanoparticles for LbL assembly represents a promising approach since in the colloidal dimensions, the total surface developed by one gram of particles, named specific area, is generally more than 100 m^2. Consequently, particles can be used to adsorb a large amount of CPEs prior to their self-assembly by LbL technique with another polyelectrolyte leading to produce conductive hybrid multilayer film.

Based on this approach, we decided to investigate the assemblies of functionalized silica or alumina colloidal particles with PEDOT:PSS and an imidazolium-based polythiophene CPE (named here P3HT). Adsorption isotherms of PEDOT:PSS on alumina particles and P3HT on silica particles were first determined in order to maximize the adsorbed amount of conjugated polymers on particles. Composite Al_2O_3-PEDOT:PSS was then assembled with P3HT and SiO_2-P3HT with PEDOT:PSS to prepare multilayer film. Effect of several parameters (composite particle and polymer concentrations, number of deposited bilayers, rinsing and drying steps) on film thickness and conductivity was investigated. Finally, scanning electron microscopy (SEM) was carried out to characterize the film morphology and to understand their electrical conductivity behavior.

EXPERIMENTAL

Chemicals, solutions and substrates

Powder of alumina particles with an average particle size of 50 nm (TEM analysis provided by the supplier) were purchased from Sigma-Aldrich. Silica nanoparticles Bindzil 30/220 (30 wt.% SiO_2 suspension in water, 20 nm average particle size) were purchased from Eka Chemicals AB. Particles were functionalized by adsorption of conjugated polyelectrolytes. The anionic conducting polyelectrolyte poly(3,4-ethylenedioxythiophene) – poly(styrene sulfonate), PEDOT:PSS (Clevios PH) was purchased from Heraeus. Poly(3-[N-(1-methylimidazolium-3-yl)hexyl]-thiophene-2,5-diyl bromide)), P3HT (M_n ~ 13 500 g.mol^{-1}, Đ = 1.27) was used as cationic polyelectrolyte and was synthesized as previously described [26]. Poly(diallyldimethylammonium chloride), PDDA (Sigma-Aldrich, M_w 100 000-200 000 g.mol^{-1}) was also used to build-up multilayer films. Other chemicals were obtained from Sigma-Aldrich and were used without further purification.

Polyelectrolyte and particles solutions were prepared in ultrapure water (Milli-Q Plus, Millipore, resistivity > 18 MΩ.cm). Polyelectrolyte concentrations were ranged from 0.25 g.L^{-1} to 1 g.L^{-1} and ionic strength was fixed at 3.10^{-3} M using NaCl. Particles were dispersed in 3.10^{-3} M NaCl solutions up to desired concentrations. pH of solutions was adjusted by addition of HCl or NaOH solution.

Substrates were oxidized silicon wafers (105 ± 0.5 nm of SiO_2) purchased from ACM (France) and cleaned, before experiments, by using Piranha solution (3:1 volume ratio of concentrated H_2SO_4 (98 %) and H_2O_2 (30 %)) for 15 min, followed by rinsing with ultrapure water and dried under a nitrogen flow.

Polyelectrolyte adsorption on particles

To determine adsorption isotherm, series of PEDOT:PSS solutions in 3.10^{-3} M NaCl at pH 3 and pH 5.5 with an initial concentration range between 50 and 1150 mg.L^{-1} were prepared. Alumina particles were then added in each solution to reach a particle concentration equal to 10 g.L^{-1}. Adsorption of PEDOT:PSS was carried out during 4h or 22h.

For adsorption of P3HT on silica particles, polyelectrolyte solutions were prepared with an initial concentration range between 25 and 500 mg.L^{-1} in 3.10^{-3} M NaCl at pH 9. Silica particle concentration was then adjusted at 1 g.L^{-1} and solutions were stirred during 4h.

Composite particles

Alumina particles coated by PEDOT:PSS, denoted Al_2O_3-PEDOT:PSS, were obtained from an alumina suspension at 10 g.L^{-1} (20 min in the ultrasonic bath) and a PEDOT:PSS concentration equal to 750 mg.L^{-1} in NaCl 3.10^{-3} M. The pH of the solution was adjusted to 3 and the suspension was stirred during 4h followed by a centrifugation step (20000 rpm – 10 min) to remove the excess of unadsorbed polyelectrolyte. The composite particles were dispersed in NaCl 3.10^{-3} M using sonication and the pH of the suspension was adjusted to 7.

Silica particles coated by P3HT, denoted SiO_2-P3HT, were prepared using a silica suspension at 1 g.L^{-1} and a P3HT concentration equal to 100 mg.L^{-1} in NaCl 3.10^{-3} M. The pH of the solution was adjusted to 9 and the suspension was stirred during 4h. Afterward, the pH of SiO_2-P3HT particles solution was adjusted to 3.

Fabrication of LbL films

Multilayer films were built-up by dip-coating and started by dipping substrates for 5 min into the solution containing cationic polyelectrolyte (PDDA) (or positive composite particles, SiO_2-P3HT). Adsorption of the first polyelectrolyte layer was followed by a rinsing step of 30 s. Substrates were then dipped in a Al_2O_3-PEDOT:PSS (or PEDOT:PSS) solution for 5 min and rinsed during 30 s. This procedure was repeated n times to obtain a film of n bilayers referred to as (PDDA/Al_2O_3-PEDOT:PSS)$_n$ or (SiO_2-P3HT/PEDOT:PSS)$_n$ LbL assembly. The influence of a drying step before each new adsorption step was also analyzed by using a flow of warm air (around 60°C) during 10 s.

Characterization of particles and LbL films

Film thickness was measured with a Dektak 150 surface profiler (VEECO) equipped with a diamond stylus having a 12.5 µm tip radius. Zeta potential and average particle size were measured using a Zetasizer NanoZS from Malvern Instruments. A Shimadzu TOC-L analyzer was used to determine adsorption isotherm of polymer onto particles. Conductivity of composite multilayer films was measured using the van der Pauw four point probe technique [27-29]. The conductivity values of LbL films were obtained using an upward temperature ramp from 30 to 150°C followed by a downward temperature ramp from 150 to 30°C (2°C.min^{-1}). The temperature at 30, 50, 100 and 150°C was maintained during 10 min. The uncertainty about conductivity measurement is around 10%. Finally, surface morphology was investigated using scanning electron microscope, Quanta 450 W from FEI equipped with EDS EDAX APEX 2i for elemental analysis.

RESULTS AND DISCUSSION

Formation of Al$_2$O$_3$-PEDOT:PSS and SiO$_2$-P3HT composite particles

The hydrodynamic diameter of alumina particles was first measured as a function of pH in 3.10^{-3} M aqueous NaCl solution by dynamic light-scattering (DLS) measurements using the Zetasizer Nano ZS. As shown in Figure 1, the alumina particles reach their smaller size below pH = 5 with an average particle size around 250 nm at pH = 3 or pH = 11.
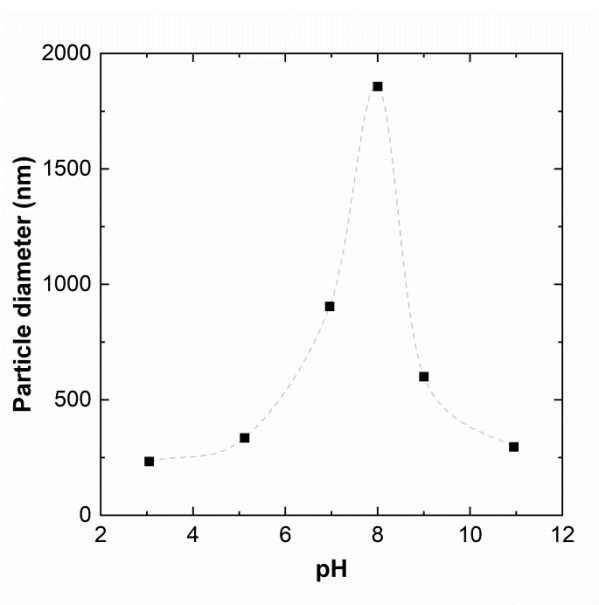

Figure 1: Size distribution of alumina particles *vs.* pH of suspension (NaCl 3.10^{-3} M).

Amphoteric Al-OH groups are present on the surface of Al$_2$O$_3$ particles dispersed in aqueous solution. As such, the surface of Al$_2$O$_3$ particles is positively charged in aqueous solutions at a pH below the point of zero charge (pzc), which was found to be around pH = 9 (Figure 2a). At pH = 5, zeta potential is very high and the electrostatic repulsion forces between particles is close to its maximum. When the pH increases, the size of the particles increases until reaching a maximum size (around 2 µm) at pH 8, which is close to pzc. By moving away from the pzc to more basic pH's, the amphoteric groups become negatively charged leading to an increase of electrostatic repulsion forces, and consequently, a decrease of particles size.

7

Finally, it can be noticed that, in suspension, the size is higher than in the powder (50 nm) meaning that Al_2O_3 particles are aggregated. Indeed, during the dispersion process, van der Waals forces are too strong in the powder to overcome repulsive electrostatic forces if even these repulsive forces reach their maximum values for pH far from pzc.

For silica particles, silanol (Si-OH) surface groups in aqueous media have a pzc around pH = 2 (Figure 2b). Therefore, above this pH, surface of SiO_2 nanoparticles is negatively charged. A negative zeta potential was obtained for all investigated pH values with the magnitude increasing from a value of -7 mV at pH = 2.3 to a value of about -30 mV above pH = 7. In the range of investigated pH, silica particle size distribution is almost the same and the hydrodynamic diameter is around 24 ± 5 nm.
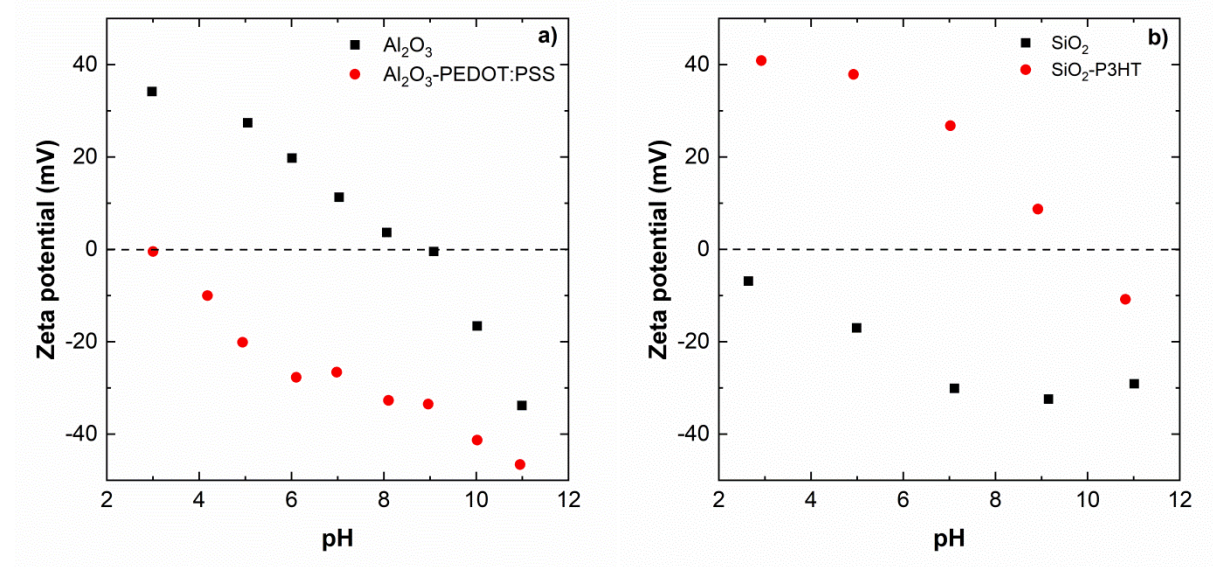

Figure 2 : Zeta potential *vs*. pH of Al_2O_3 and Al_2O_3-PEDOT:PSS particles (a) and SiO_2 and SiO_2-P3HT particles (b).

Adsorption isotherms of PEDOT:PSS on alumina and P3HT on silica were carried out in order to determine the maximum adsorbed amount of each polyelectrolyte. Adsorption isotherm of PEDOT:PSS was performed with adsorption times equal to 4h or 22h. By comparing isotherms, the amount of adsorbed polymer was found to be similar which means that the equilibrium state is reached after 4h (See supplementary material). Equilibrium

isotherms were then carried out at pH = 3 and pH = 5.5 where alumina particles are positively

charged and PEDOT:PSS is negatively charged. The results (Inset of Figure 3a) show that the

amount of adsorbed polyelectrolyte on the surface of particles depends on pH of suspension

as it was shown in other studies [30]. At pH = 3, the maximum amount of adsorbed polymer

at the plateau is equal to 75 mg.g^{-1} while this amount is reduced to 40 mg.g^{-1} at pH 5.5.

Similar decrease in the amount of adsorbed polymer as a function of pH was observed during

the adsorption of poly(acrylic acid sodium salt) (PAA) on alumina particles [31]. As shown

previously, there are differences in terms of size and zeta potential of alumina particles at pH

= 3 and pH = 5.5. The differences in diameter and zeta potential (250 nm and +34 mV at pH =

3 *vs*. 400 nm and +24 mV at pH 5.5) indicates that alumina particles in suspension at pH = 3

possess a higher specific surface area and that stronger attractive electrostatic interactions take

place between polyelectrolyte and particles, which increase the amount of adsorbed polymer.

The maximum amount of PEDOT:PSS (75 mg.g^{-1}) is reached for an initial polyelectrolyte

concentration of about 750 mg.g^{-1}, which corresponds to an equilibrium PEDOT:PSS

concentration equal to 40 mg.g^{-1} (Figure 3a). The adsorption isotherm of PEDOT:PSS doesn't

correspond to the criteria to be fitted by the Langmuir model. However, the adsorption

isotherm shape seems to be a high affinity adsorption isotherm [32]. The amount of adsorbed

PEDOT:PSS *vs*. PEDOT:PSS concentration initially introduced is depicted in Figure 4a and

the red curve represents 100 % of adsorbed polymer. At pH = 3, experimental points follow

this straight line up to an initial PEDOT:PSS concentration of 750 mg.L^{-1}, which corresponds

to the beginning of the adsorption plateau. The affinity between the polyelectrolyte and the

particle is so strong that the concentration of free polyelectrolyte is close to 0 until the

adsorption plateau is reached. At pH = 5.5, the total amount of polyelectrolyte initially

introduced is adsorbed for polyelectrolyte concentration below 400 mg.L^{-1}. Adsorption

isotherms of anionic polyelectrolytes such as PAA, poly(styrene sulfonate) (PSS) or

poly(methacrylic acid) (PMAA) on alumina particles were proved to be also isotherms of high affinity [31,33,34].

Adsorption isotherm of P3HT on silica particles at pH = 9 is shown in Figure 3b. The maximum amount of adsorbed P3HT is about 200 mg.L^{-1}. This amount is reached at an initial polyelectrolyte concentration of about 500 mg.L^{-1} which corresponds to an equilibrium P3HT concentration equal to 200 mg.L^{-1}. Adsorption data were fitted to the Langmuir monolayer adsorption isotherm (Figure 4b). From the linear fit of the Langmuir model, Γ_{max}, K and b were calculated and were equal to 212 mg.g^{-1}, 7.36 mg.L^{-1} and 0.136 L.mg^{-1}, respectively. According to Hall *et al*. [35], the main parameters of the Langmuir isotherm can be expressed by a dimensionless equilibrium parameter R_L, which is defined by the following relation:

$$R_L = \frac{1}{1 + (b \cdot C_0)}$$

with R_L the equilibrium parameter, b the Langmuir constant (L.mg^{-1}) and C_0 the initial concentration (mg.L^{-1}). The R_L parameter indicates whether adsorption is rather unfavorable (R_L> 1), linear (R_L = 1), favorable (0> R_L> 1) or irreversible (R_L = 0). For P3HT adsorption, the initial concentrations are between 25 and 500 mg.L^{-1} and Langmuir constant b is 0.136 µg.mL^{-1}. Under these conditions, R_L ranges between 0.015 and 0.227, which means that the adsorption of P3HT on silica particles is favorable.
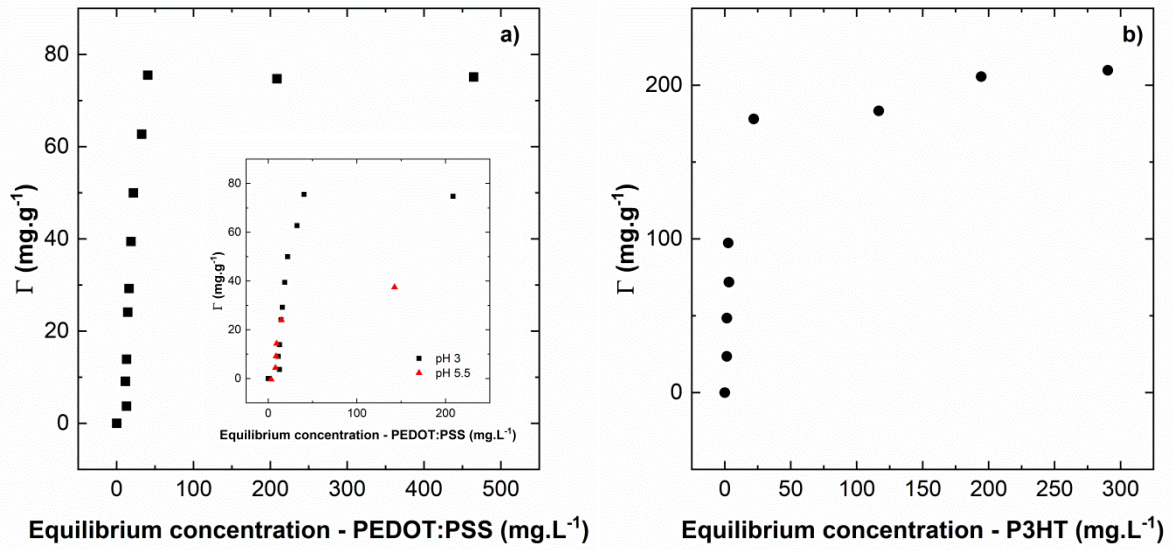
Figure 3 : Adsorption isotherms of PEDOT:PSS on Al_2O_3 at pH = 3 and pH = 5.5 (a) and P3HT on SiO_2 at pH = 9 (b). Contact time: 4 hours at RT.
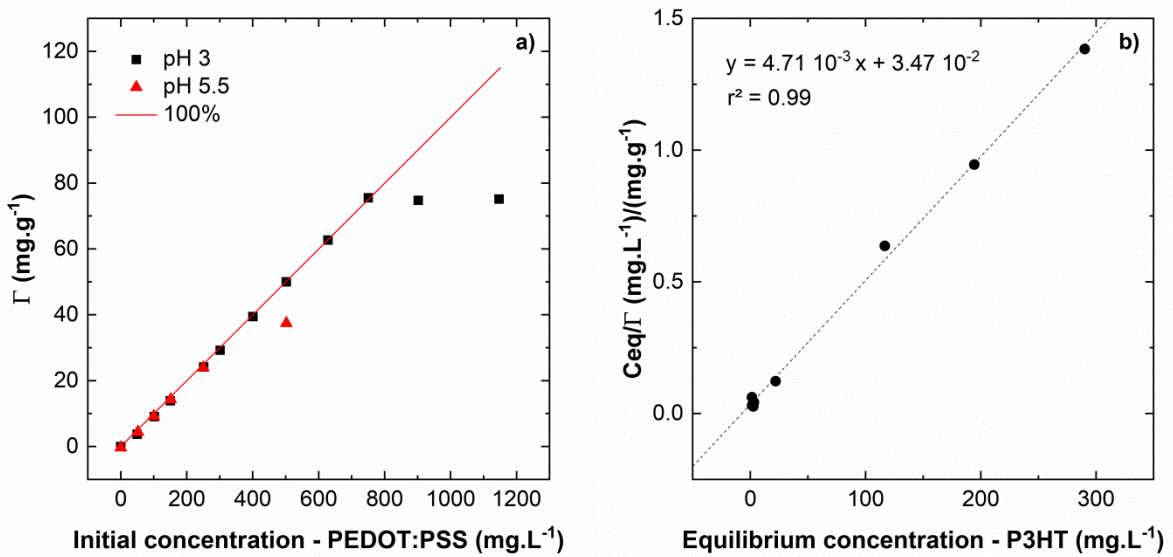

Figure 4 : Adsorbed amount of PEDOT:PSS on Al_2O_3 as a function of initial concentration at pH = 3 and pH = 5.5 (a). Plots of Langmuir adsorption isotherm for P3HT-SiO_2 system (b).

In order to investigate the effect of polyelectrolyte adsorption on the electrophoretic properties of Al_2O_3 or SiO_2, functionalized particles were prepared. Initial polymer concentration was fixed at a value corresponding to the beginning of the isotherm plateau (750 mg.L^{-1} for PEDOT:PSS and 100 mg.L^{-1} for P3HT). However, sedimentation of composite Al_2O_3-PEDOT:PSS particles was clearly visible at pH = 3 while Al_2O_3 suspension was stable at the same pH. This was also observed for SiO_2-P3HT suspension at pH = 9.

11

These basic observations indicate a modification of the surface charge of particles. Therefore, zeta potentials of composite polyelectrolyte-inorganic particles were measured as a function of pH. For Al_2O_3-PEDOT:PSS (Figure 2a), variation of zeta potential is completely different. An isoelectric point (iep) appears at pH = 3 which also attests the adsorption of PEDOT:PSS on alumina particles. Starting from this pH, composite particles are negatively charged. In case of SiO_2-P3HT composite particles, an iep is noticed as well. Due to adsorption of a cationic polyelectrolyte, iep is shifted towards a basic pH equal to 9 (Figure 2b). For Al_2O_3-PEDOT:PSS suspension, in order to avoid a partial desorption of PEDOT: PSS from alumina surface and to keep composite particles with enough negative charges for layer-by-layer adsorption, pH was fixed at pH 7. For SiO_2-P3HT suspension, pH of suspensions was adjusted to maximize zeta potential, i.e. to increase electrostatic repulsive interactions between particles to avoid particle aggregation. Consequently, LbL assemblies were carried out with SiO_2-P3HT suspension at pH = 3.

Polyelectrolyte/composite particle film: influence of build-up parameters.

(PDDA/Al_2O_3-PEDOT:PSS)$_n$ and (SiO_2-P3HT/PEDOT:PSS)$_n$ multilayer films were built-up at polyelectrolyte and composite particle concentrations equal to 1 g.L^{-1} with or without a rinsing/drying step between each polymer adsorption. Thickness variations of (PDDA/Al_2O_3-PEDOT:PSS)$_{10}$ film measured by profilometry are summarized in Table 1.

Assemblies	n	Build-up parameters (Rinsing: R; Drying: D)		Thickness (nm)
(PDDA/ Al_2O_3-PEDOT:PSS)$_n$	10	-	-	95
		R	-	71
		-	D	589
		R	D	440
(SiO_2-P3HT/ PEDOT:PSS)$_n$	10	-	D	1634
		R	D	1428
	20	-	D	4402

Table 1 : Thickness of (PDDA/Al$_2$O$_3$-PEDOT:PSS)n and (SiO$_2$-P3HT/PEDOT:PSS)$_n$ multilayer film *versus* build-up parameters. C$_{PDDA}$ 1 g.L^{-1} , C$_{Particles}$ 1 g.L^{-1} , C$_{PEDOT:PSS}$ 1 g.L^{-1} C$_{NaCl}$ 3.10^{-3} M.

When a rinsing step is performed after polyelectrolyte adsorption, the average thickness of the film decreases for both types of LbL assemblies. This result is entirely consistent since the main objective of the rinsing step is to remove weakly adsorbed species (polymer chains or particles) adsorbed on the surface. The drying step seems to be essential for obtaining thicker films. Without this step, the thickness of the film does not exceed one hundred nanometers, which suggests that the particles are not incorporated in the films. Drying improves the adhesion of particles on the surface. Since composite particles remain on the surface, the chains of PDDA can be adsorbed thanks to the excess of negative charges brought by PEDOT:PSS. Construction of (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_{10}$ multilayer films requires then a drying step after each adsorption to exceed more than one hundred nanometers.

(SiO$_2$-P3HT/PEDOT:PSS)$_n$ multilayer films are much thicker than (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_n$ multilayer films obtained in the same conditions (Table 1). Indeed, for 10 adsorbed bilayers, thickness of multilayer films composed of composite alumina particles is approximately 600 nm whereas it exceeds 1.6 μm for multilayer films composed of composite silica particles. Use of silica nanoparticles (60 nm) seems to favor the growth of the multilayer films of (SiO$_2$-P3HT/PEDOT:PSS)$_n$. However, the particle size is not the only parameter that affects the thickness. Indeed, for multilayer films build up without particles, optical reflectometry analyses have demonstrated that the adsorbed amount of (P3HT/PEDOT:PSS)$_n$ is higher than the adsorbed amount of (PDDA/PEDOT:PSS)$_n$.[36].

Polyelectrolyte/composite particle film: influence of polymer and particle concentrations

Concentration of composite particles is a major parameter that can affect the growth of a multilayer film. Indeed, when concentration of composite alumina particles increases, film thickness also increases even if a rinsing step is added during build-up (Figure 5).
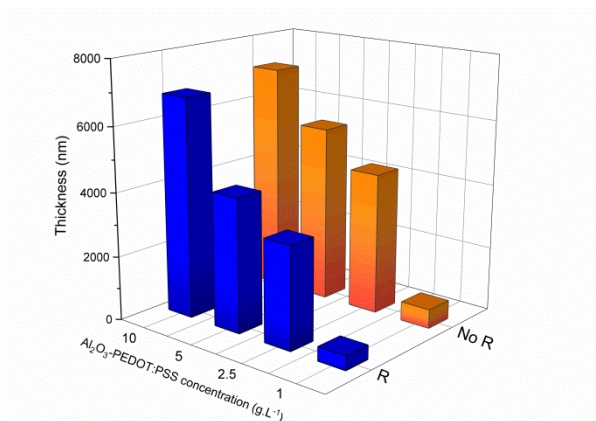

Figure 5 : Effect of composite particle concentration on (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_{10}$ film thickness with (R) or without a rinsing step (No R).

With an assembly of only 10 bilayers, the thickness of (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_n$ films can reach 7 μm for a particle concentration of 10 g.L^{-1} while it is of about 500 nm at a concentration of 1 g.L^{-1}. Film prepared with the same experimental conditions and made of 10 bilayers, but without particles, has a thickness of about 500 nm. These results clearly indicate that using particles as conductive polymer carriers promotes the growth of multilayer films. By introducing particles or not, multilayer film thickness can be tuned from a few tens of nanometers (polymers assembly) to a few tens of micrometers (polymer/particle assembly).

Finally, influence of the PDDA concentration was studied. Indeed, in a previous study[37], we showed that thickness of polyelectrolyte multilayer film decreases when concentration of PDDA is reduced. Therefore, the construction of multilayer films (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_n$ was made with solutions containing different concentrations of PDDA: 0.25, 0.5 and 1 g.L^{-1}. Film thicknesses are summarized in Table 2. As for (PDDA/PEDOT:PSS)$_n$ multilayer films, the smaller the concentration of PDDA, the smaller the film thickness. Indeed, thickness is equal to about 7 μm at a PDDA concentration of 1 g.L^{-1} whereas it is reduced to about 5 μm at a PDDA concentration of 0.25 g.L^{-1}. This decrease in thickness can

be explained by a decrease in the amount of adsorbed cationic PDDA which in turn limits the adsorption of the anionic composite particles.

Film electrical conductivity and structural characterization

Electrical conductivity of (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_n$ composite multilayer films was then determined by the van der Pauw method. Electrical conductivity was measured only for films prepared from particle suspensions concentration at 10 g.L^{-1}. It can then be assumed that below this value, the distribution of the composite particles is not compact and enough homogeneous to ensure an electrical percolation between PEDOT oligomers. Conductivity of the films was characterized at different temperatures according to the protocol described in the experimental section. Results reveal a slight increase of conductivity as a function of temperature up to values between 100 and 150°C (Figure 6). After this step, conductivity of (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_{10}$ films decreases and when the temperature is returned to 30°C, no conductivity is detected.

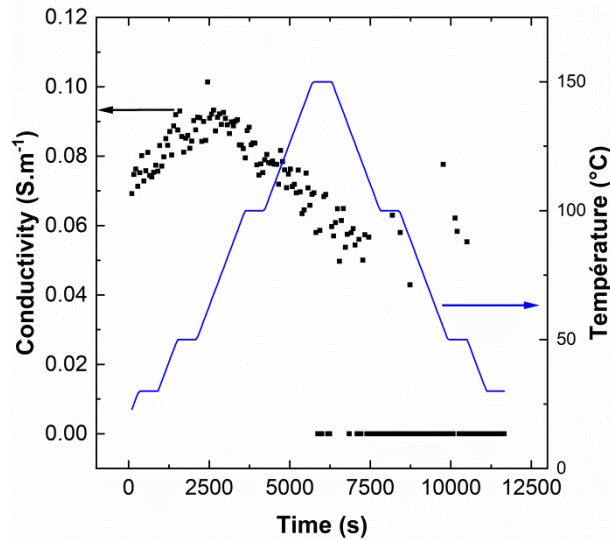
Figure 6 : Electrical conductivity of (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_{10}$ at different temperatures.

The conductivity of multilayer (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_n$ films appears to be temperature sensitive while the conductivity of multilayer (PDDA/PEDOT:PSS)$_n$ films remains at about the same value after identical temperature variations. Therefore, conductivity of the multilayer

15

films was only characterized at a fixed temperature of 30°C. Influence of rinsing step, PDDA concentration and number N of bilayers on the film thickness and conductivity was then investigated (Table 2). Rinsing step after each adsorption induces a slight decrease of conductivity compared to those obtained without rinsing. Weakly adsorbed polyelectrolytes which are removed during rinsing seem to not participate in conductivity phenomenon.

PDDA concentration (g.L^{-1})	Number of bilayers N	Rinsing step	Thickness (nm)	Conductivity (S.m^{-1})
1	10	-	7095	0.094
		R	6826	0.069
0.5	10	-	6428	0.106
		R	5278	0.105
0.25	10	-	5169	0.192
		R	4329	0.123
0.25	5	-	3122	0.481
		R	2868	0.441

Table 2 : Thickness and conductivity of (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_n$ multilayer. $C_{composite\ particles}$ 10 g.L^{-1}.

Concentration of PDDA appears to modify conductivity: the smaller the PDDA concentration, the greater the conductivity. For example, conductivity is 0.094 S.m^{-1} for a film built up without a rinsing step at a PDDA concentration of 1 g.L^{-1} while it is doubled when PDDA concentration is 0.25 g.L^{-1} (0.192 S.m^{-1}). Similar observations have already been done for multilayer films without colloidal particles [37]. Indeed, when PDDA concentration is decreased from 1 g.L^{-1} to 0.25 g.L^{-1} during the preparation of a multilayer film made of 50 bilayers of PDDA/PEDOT:PSS, conductivity increases from 0.072 S.m^{-1} to 0.163 S.m^{-1} at 30°C. Decreasing the amount of insulating polymers embedded into the film leads to an increase in electrical conductivity of both the multilayer (polymer/polymer) and (polymer/composite particles) films.

Concerning the effect of the number of bilayers, only 5 adsorbed bilayers are necessary to obtain a conductive (PDDA/Al$_2$O$_3$-PEDOT:PSS) film while no conductivity was detected for (PDDA/PEDOT:PSS) assemblies below 30 bilayers in the same experimental conditions. Moreover, when a few numbers of bilayers are deposited, electrical conductivity of the multilayer films is improved. Indeed, conductivity of (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_5$ is approximately 0.400 S.m^{-1} whereas conductivity is about 0.200 S.m^{-1} when the number of bilayers is doubled. In the same time, thickness is multiplied by two between a film of 5 and

10 bilayers (Table 2). For multilayer films without particles, when 30 bilayers of PDDA/PEDOT:PSS are adsorbed, conductivity at 30°C is equal to 0.119 $S.m^{-1}$ and decreases to 0.072 $S.m^{-1}$ for 50 bilayers for a PDDA concentration of $1g.L^{-1}$ [37]. However multilayer film conductivity usually increases for thin film until it reaches a plateau for thicker film depending on PEDOT:PSS weight ratio [38]. In the present work, two explanations can be proposed. First, using PDDA polyelectrolyte, a progressive increase of insulating polymer into the polymeric matrix leads to a decrease of conductivity. At the opposite, this may also suggest that when the conductivity is measured by the van der Pauw method, only the upper part of the film participates in the conductivity phenomenon. Indeed, in the equation proposed by van der Pauw, resistivity depends on film thickness and measured electrical resistances. Investigations are in progress to clearly identify the major factor involved in conductivity decrease.

Elemental analysis and morphology observations of the multilayer films were then carried out. First, EDX analysis confirms the presence of composite alumina particles within the multilayer films since it reveals the presence of oxygen, aluminum and sulfur elements which refers to the alumina particles and PEDOT:PSS chains (See supplementary material). Observations of (PDDA/Al_2O_3-PEDOT:PSS)$_{10}$ films by scanning electron microscopy (Figure 7) show slight cracks on the multilayer films prepared with a PDDA concentration of 0.5 and 1 $g.L^{-1}$. Moreover, after a thermal cycle with a maximum temperature of 150°C (Image d), the cracks appear more numerous and wider. No cracks were observed for a PDDA concentration of 0.25 $g.L^{-1}$ before and after heating. When concentration of PDDA is high, multilayer films are thicker. During drying step, internal stresses in the multilayer film are intensified, which cause a widening of the cracks already present and/or create new ones. Heating process accentuates crack formation that explains why films are no longer conductive.

Multilayer films made of SiO_2-P3HT composite particles were also characterized at 30 °C using the van der Pauw method. Although these films seem to be conductive (measurements with a multimeter), measurements by van der Pauw method have shown that the ohmic character of the sample contacts is not respected (no significant linear interpolation of I-V measurements). So, these measurements do not present the validity criteria. SEM investigations have revealed that composite particles modify the structure of the multilayer films. $(SiO_2$-P3HT/PEDOT:PSS$)_{10}$ films made with rinsing steps does not show visible cracks at this magnification but the surface is not homogeneous (Figure 8a). Therefore, films made of 20 bilayers of $(SiO_2$-P3HT/PEDOT:PSS) were built-up. Unfortunately, cracks were visible on these films due to the thickness increase. In addition, multilayer films made without a rinsing step (Figure 8b) exhibit large cracks. As for multilayer films composed of composite alumina particles, the presence of cracks causes a poor circulation of electrons which does not allow multilayer films $(SiO_2$-P3HT/PEDOT:PSS) to be conductive.
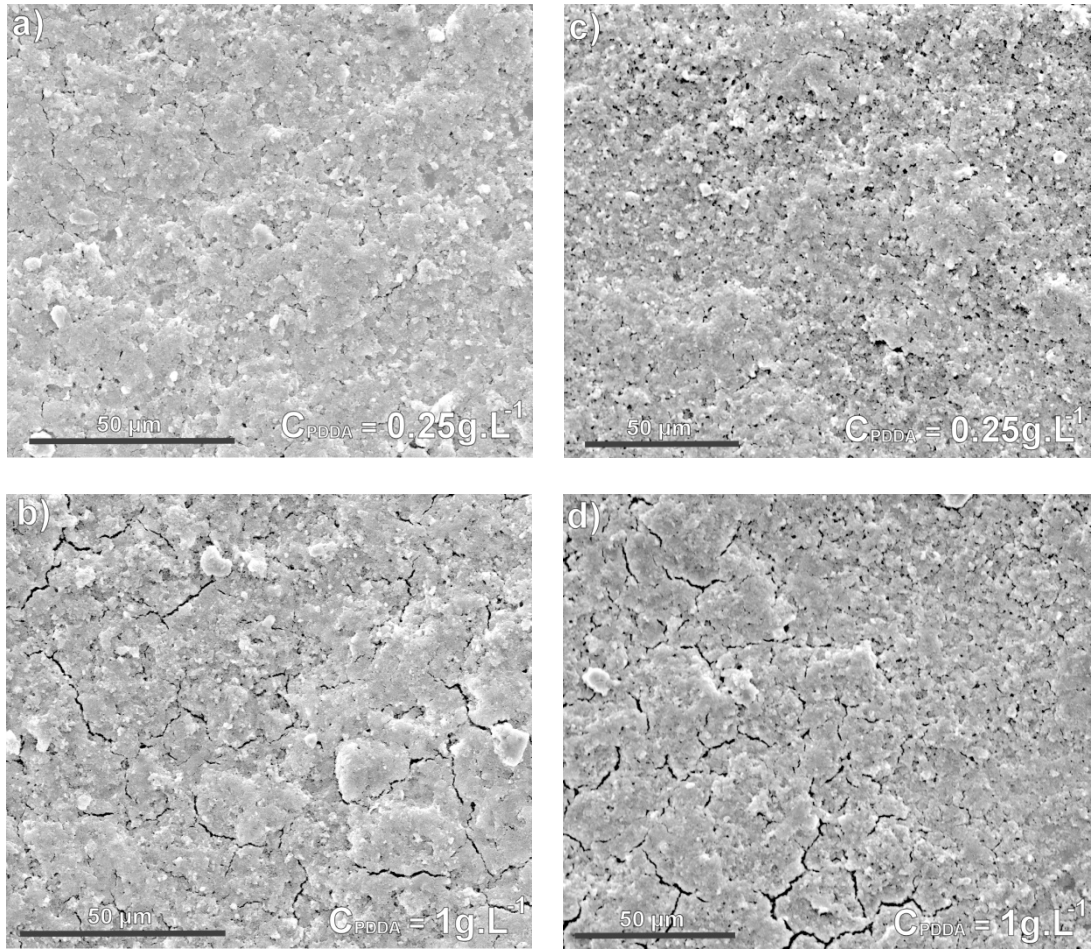
Figure 7 : SEM images of (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_{10}$ films built-up at two PDDA concentration: 0.25 g.L^{-1} and 1 g.L^{-1} before (a, b) and after heating at 150°C (c, d). C$_{particles}$ = 10 g.L^{-1}.
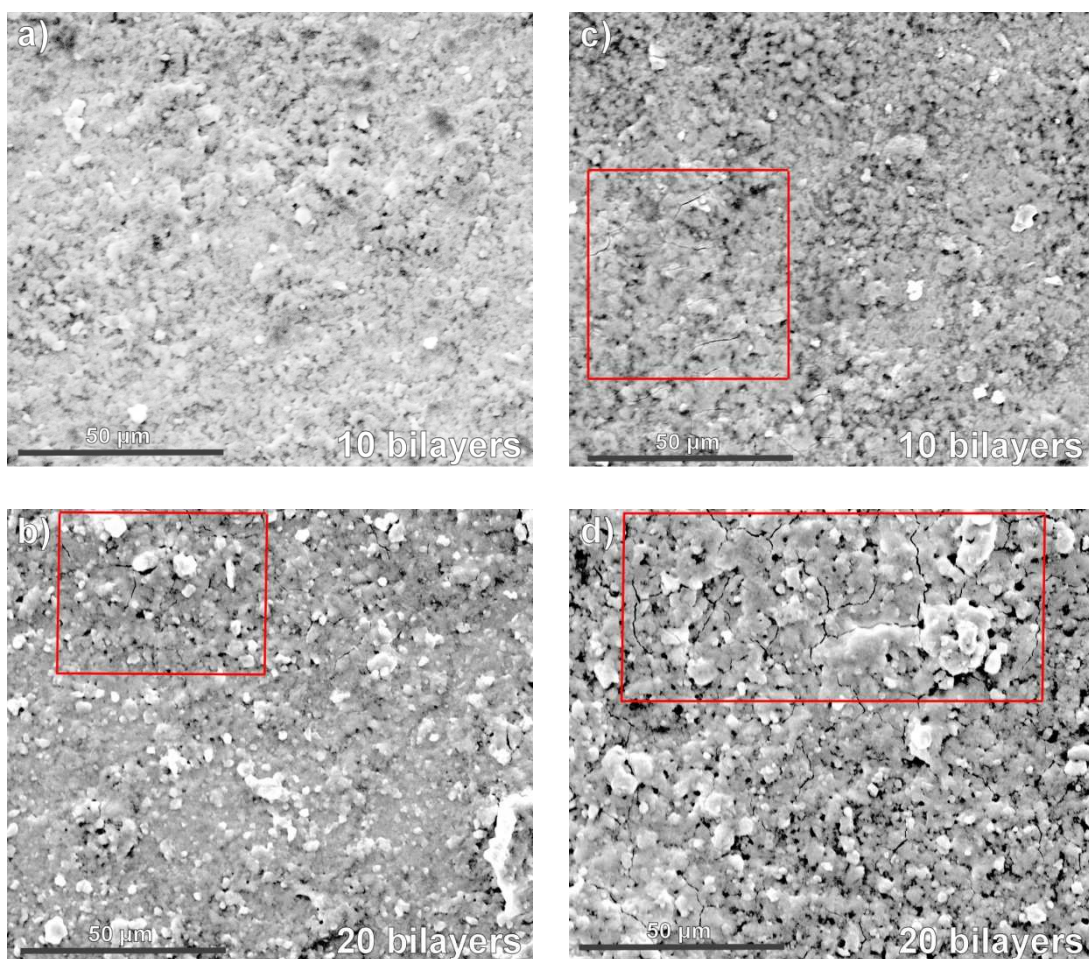
Figure 8 : SEM images of $(SiO_2\text{-}P3HT/PEDOT:PSS)_n$ films built-up with rinsing step (a, b) or without rinsing step (c, d). $C_{particles}$ 1 g.L^{-1}

CONCLUSIONS

LbL films were built-up by assembly of conjugated polymers and composite polymer-inorganic particles. Particles were used as carriers of conducting polymers in the aim to modulate the thickness and to increase the amount of conducting polymers into the films. Alumina and silica particles were functionalized with PEDOT:PSS conjugated polymer blend and an ionic-based 3HT, respectively. The best conditions for the adsorption of polyelectrolytes on particles were first determined to ensure a stable suspension. Thickness of $(PDDA/Al_2O_3\text{-}PEDOT:PSS)_n$ films varies from about 70 nm to 7 µm depending on

21

parameters used during the LbL assembly: composite particle and insulating polymer concentrations, number of deposited bilayers, rinsing and drying steps. Electrical conductivity was only measured for the highest concentration of composite alumina particles (10 g.L^{-1}). Hybrid films made of 5 bilayers reach a conductivity of 0.4 S.m^{-1} while 30 bilayers of (PDDA/PEDOT:PSS) are necessary to obtain the same value. So conducting polymer supported by particles allows to modulate the film thickness and to reduce the number of dipping steps and so the time to built-up LbL conductive films. However, cracks are observed after heating (PDDA/Al$_2$O$_3$-PEDOT:PSS)$_n$ films at 150°C and no conductivity is then detected. Films made of (SiO$_2$-P3HT/PEDOT:PSS)$_n$ are not conductive even though two conductive polyelectrolytes compose the film.

Consequently, the use of particle-supported polyelectrolyte during the growth of polyelectrolyte multilayer film is an interesting strategy to decrease the steps in film production process which is usually time and products consuming. Moreover the conductivity and the thickness of PEDOT:PSS-based thin films can be optimized. Nevertheless, mechanical properties of these composite films are strongly impacted that could be an interesting way to elaborate temperature sensor that provide an irreversible evidence of a high-temperature deviation.
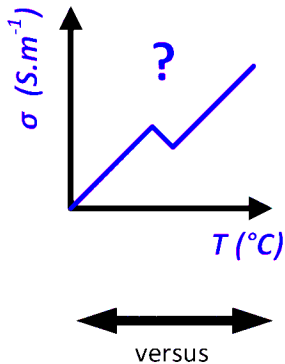
REFERENCES

[1]   J. R. Reynolds, B. C. Thompson, T. A. Skotheim, **Conjugated Polymers: Properties, Processing, and Applications**, CRC Press, 2019.

[2]   F. J. M. Colberts, M. M. Wienk, R. A. J. Janssen, **Aqueous Nanoparticle Polymer Solar Cells: Effects of Surfactant Concentration and Processing on Device Performance**, ACS Applied Materials & Interfaces, 9 (2017), 13380.

[3]   C. Xie, T. Heumüller, W. Gruber, X. Tang, A. Classen, I. Schuldes, M. Bidwell, A. Späth, R. H. Fink, T. Unruh, I. McCulloch, N. Li, C. J. Brabec, **Overcoming efficiency and stability limits in water-processing nanoparticular organic photovoltaics by minimizing microstructure defects**, Nature Communications, 9 (2018), 5335.

[4]   G. Prunet, L. Parrenin, E. Pavlopoulou, G. Pecastaings, C. Brochon, G. Hadziioannou, E. Cloutet, **Aqueous PCDTBT:PC71BM Photovoltaic Inks Made by Nanoprecipitation**, Macromolecular Rapid Communications, 39 (2018), 1700504.

[5]   S. Inal, J. Rivnay, A. I. Hofmann, I. Uguz, M. Mumtaz, D. Katsigiannopoulos, C. Brochon, E. Cloutet, G. Hadziioannou, G. G. Malliaras, **Organic electrochemical transistors based on PEDOT with different anionic polyelectrolyte dopants**, Journal of Polymer Science Part B: Polymer Physics, 54 (2016), 147.

[6]   S. Inal, J. Rivnay, A.-O. Suiu, G. G. Malliaras, I. McCulloch, **Conjugated Polymers in Bioelectronics**, Accounts of Chemical Research, 51 (2018), 1368.

[7]   D. Khodagholy, T. Doublet, P. Quilichini, M. Gurfinkel, P. Leleux, A. Ghestem, E. Ismailova, T. Hervé, S. Sanaur, C. Bernard, G. G. Malliaras, **In vivo recordings of brain activity using organic transistors**, Nature Communications, 4 (2013), 1575.

[8]   E. Zeglio, A. L. Rutz, T. E. Winkler, G. G. Malliaras, A. Herland, **Conjugated Polymers for Assessing and Controlling Biological Functions**, Advanced Materials, 31 (2019), 1806712.

[9]   G. Heywang, F. Jonas, **Poly(alkylenedioxythiophene)s—new, very stable conducting polymers**, Advanced Materials, 4 (1992), 116.

[10]   Y. Wen, J. Xu, **Scientific Importance of Water-Processable PEDOT–PSS and Preparation, Challenge and New Application in Sensors of Its Film Electrode: A Review**, Journal of Polymer Science Part A: Polymer Chemistry, 55 (2017), 1121.

[11]   F. Greco, A. Zucca, S. Taccola, A. Menciassi, T. Fujie, H. Haniuda, S. Takeoka, P. Dario, V. Mattoli, **Ultra-thin conductive free-standing PEDOT/PSS nanofilms**, Soft Matter, 7 (2011), 10642.

[12]   W. Lee, J. H. Seo, H. Y. Woo, **Conjugated polyelectrolytes: A new class of semiconducting material for organic electronic devices**, Polymer, 54 (2013), 5104.

[13]   H. Jiang, P. Taranekar, J. R. Reynolds, K. S. Schanze, **Conjugated Polyelectrolytes: Synthesis, Photophysics, and Applications**, Angewandte Chemie International Edition, 48 (2009), 4300.

[14]   M. M. Schmidt, M. ElMahmoudy, G. G. Malliaras, S. Inal, M. Thelakkat, **Smaller Counter Cation for Higher Transconductance in Anionic Conjugated Polyelectrolytes**, Macromolecular Chemistry and Physics, 219 (2018), 1700374.

[15]   M. Shao, Y. He, K. Hong, C. M. Rouleau, D. B. Geohegan, K. Xiao, **A water-soluble polythiophene for organic field-effect transistors**, Polymer Chemistry, 4 (2013), 5270.

[16]   M. Chevrier, J. E. Houston, J. Kesters, N. Van den Brande, A. E. Terry, S. Richeter, A. Mehdi, O. Coulembier, P. Dubois, R. Lazzaroni, B. Van Mele, W. Maes, R. C. Evans, S. Clement, **Self-assembled conjugated polyelectrolyte-surfactant complexes as efficient cathode interlayer materials for bulk heterojunction organic solar cells**, Journal of Materials Chemistry A, 3 (2015), 23905.

[17] J. Kesters, S. Govaerts, G. Pirotte, J. Drijkoningen, M. Chevrier, N. Van den Brande, X. Liu, M. Fahlman, B. Van Mele, L. Lutsen, D. Vanderzande, J. Manca, S. Clément, E. Von Hauff, W. Maes, **High-Permittivity Conjugated Polyelectrolyte Interlayers for High-Performance Bulk Heterojunction Organic Solar Cells**, ACS Applied Materials & Interfaces, 8 (2016), 6309.

[18] J. H. Seo, A. Gutacker, Y. Sun, H. Wu, F. Huang, Y. Cao, U. Scherf, A. J. Heeger, G. C. Bazan, **Improved High-Efficiency Organic Solar Cells via Incorporation of a Conjugated Polyelectrolyte Interlayer**, Journal of the American Chemical Society, 133 (2011), 8416.

[19] M. Schönhoff, **Self-assembled polyelectrolyte multilayers**, Current Opinion in Colloid & Interface Science, 8 (2003), 86.

[20] F.-X. Xiao, M. Pagliaro, Y.-J. Xu, B. Liu, **Layer-by-layer assembly of versatile nanoarchitectures with diverse dimensionality: a new perspective for rational construction of multilayer assemblies**, Chemical Society Reviews, 45 (2016), 3088.

[21] G. Decher, J. B. Schlenoff, **Multilayers thin films**, Wiley-VCH, Weinheim, 2003.

[22] L. Zhai, R. D. McCullough, **Layer-by-Layer Assembly of Polythiophene**, Advanced Materials, 14 (2002), 901.

[23] D. A. Rider, B. J. Worfolk, K. D. Harris, A. Lalany, K. Shahbazi, M. D. Fleischauer, M. J. Brett, J. M. Buriak, **Stable Inverted Polymer/Fullerene Solar Cells Using a Cationic Polythiophene Modified PEDOT:PSS Cathodic Interface**, Advanced Functional Materials, 20 (2010), 2404.

[24] B. J. Worfolk, T. C. Hauger, K. D. Harris, D. A. Rider, J. A. M. Fordyce, S. Beaupré, M. Leclerc, J. M. Buriak, **Work Function Control of Interfacial Buffer Layers for Efficient and Air-Stable Inverted Low-Bandgap Organic Photovoltaics**, Advanced Energy Materials, 2 (2012), 361.

[25] K. R. Knowles, C. C. Hanson, A. L. Fogel, B. Warhol, D. A. Rider, **Layer-by-Layer Assembled Multilayers of Polyethylenimine-Stabilized Platinum Nanoparticles and PEDOT:PSS as Anodes for the Methanol Oxidation Reaction**, ACS Applied Materials & Interfaces, 4 (2012), 3575.

[26] S. Clement, A. Tizit, S. Desbief, A. Mehdi, J. De Winter, P. Gerbaux, R. Lazzaroni, B. Boury, **Synthesis and characterisation of [small pi]-conjugated polymer/silica hybrids containing regioregular ionic polythiophenes**, Journal of Materials Chemistry, 21 (2011), 2733.

[27] L. J. Van der Pauw, **A method of measuring the resistivity and Hall effect of discs of arbitrary shape**, Philips Research Reports, 13 (1958), 1.

[28] D. K. Schroder, **Semiconductor Material and Device Characterization (2nd ed.)**, John Wiley & sons, New York, 1998.

[29] J. W. O. P. Blood, **The Electrical Characterization of Semiconductors: Majority Carriers and Electron States**, Academic Press, London, 1992.

[30] Y.-J. Shin, C.-C. Su, Y.-H. Shen, **Dispersion of aqueous nano-sized alumina suspensions using cationic polyelectrolyte**, Materials Research Bulletin, 41 (2006), 1964.

[31] G. Bertrand, C. Filiatre, H. Mahdjoub, A. Foissy, C. Coddet, **Influence of slurry characteristics on the morphology of spray-dried alumina powders**, Journal of the European Ceramic Society, 23 (2003), 263.

[32] H.-J. Butt, K. Graf, M. Kappl In **Physics and Chemistry of Interfaces**, (Eds.), Wiley-VCH Verlag GmbH & Co. KGaA, 2004; p. 177.

[33] A. M. Blokhus, K. Djurhuus, **Adsorption of poly(styrene sulfonate) of different molecular weights on α-alumina: Effect of added sodium dodecyl sulfate**, Journal of Colloid and Interface Science, 296 (2006), 64.

[34] A. Pettersson, G. Marino, A. Pursiheimo, J. B. Rosenholm, **Electrosteric Stabilization of Al2O3, ZrO2, and 3Y–ZrO2 Suspensions: Effect of Dissociation and Type of Polyelectrolyte**, Journal of Colloid and Interface Science, 228 (2000), 73.

[35] K. R. Hall, L. C. Eagleton, A. Acrivos, T. Vermeulen, **Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions**, Industrial & Engineering Chemistry Fundamentals, 5 (1966), 212.

[36] F. E. Jurin, C. C. Buron, S. Clément, A. Mehdi, L. Viau, B. Lakard, N. Martin, C. Filiâtre, **Flexible and conductive multilayer films based on the assembly of PEDOT:PSS and water soluble polythiophenes**, Organic Electronics, 46 (2017), 263.

[37] F. E. Jurin, C. C. Buron, N. Martin, S. Monney, C. Filiâtre, **Electrical conductivity enhancement and wettability modification of (PDDA/PEDOT:PSS)n multilayer film**, Thin Solid Films, 664 (2018), 33.

[38] R. R. Smith, A. P. Smith, J. T. Stricker, B. E. Taylor, M. F. Durstock, **Layer-by-Layer Assembly of Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate)**, Macromolecules, 39 (2006), 6071.

σ (S.m⁻¹)

?

T (°C)

versus
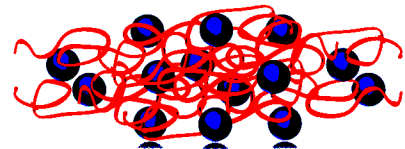
PEDOT:PSS or P3HT⁺ functionalized
Al₂O₃ or SiO₂ particles

PEDOT:PSS or P3HT⁺