Soft Matter



PAPER

Check for updates

Cite this: Soft Matter, 2023, 19, 6018

Unexpected enhancement of pH-stability in Au³⁺/ Ag⁺ loaded H-bonded layer-by-layer thin films⁺

Nicolás Pomeraniec Altieri, ¹^b^a Lucy L. Coria-Oriundo, ¹^b^a Paula C. Angelomé, ¹^b Fernando Battaglini, ¹^b^a María Luz Martínez Ricci ¹^b*^a and Lucila P. Méndez De Leo ¹^b*^a

In this work, a polymeric film was synthesized through a layer-by-layer (LBL) self-assembly technique using polyacrylic acid (PAA) and polyethylene oxide (PEO), resulting in the formation of a hydrogenbonded LBL film. The formation of these films was evaluated by PMIRRAS and QCM-D. The synergy of these techniques allowed the understanding of the mechanism of formation of the film by showing the H-bonding formation and film growth. Au and Ag metal ions were successfully incorporated into the films, as corroborated by the combination of the information obtained by XRR and PMIRRAS. The films were exposed to increasing pH, showing a pronounced improvement in stability in films loaded with Au ions, extending the stability from pH 4 to 10. This behavior allows the use of this system in a wider range of applications, including the possibility of working in biological conditions. On the other hand, films loaded with Ag disintegrated at pH above 4. At acidic pH (below 3), these films released the Ag ions, which may be useful for the preparation of antibacterial stimuli-responsive nanomaterials. In both cases, the films were adequate to produce metal nanoparticles by metal loading and *in situ* reduction.

Received 7th July 2023, Accepted 22nd July 2023 DOI: 10.1039/d3sm00893b

rsc.li/soft-matter-journal

Introduction

Layer-by-layer (LbL) assembly has been widely used as a versatile method for fabricating multilayer thin films with controlled structure and composition.^{1,2} It is typically based on sequential adsorption of materials with complementary functional groups employing electrostatic interactions, hydrogen bonding, or covalent interactions. Due to their facile, inexpensive, and environmentally friendly nature, LbL-assembled multilayer thin films find broad applications ranging from energy and electrochemical devices to biological materials.^{3–6}

Initially, most of the work in this area was concentrated on the use of synthetic, charged polymers (polyelectrolytes) for the assembly of LbL films. Later, the need to prepare multilayer films from a wider array of components, and particularly natural non-toxic polymers that have uses in biomedical applications, has led to the development of multilayer films constructed based on non-electrostatic interactions. Such versatility in the driving force means that the LbL method is not restricted to charged materials. This observation is of critical importance as many functional polymers are uncharged. For instance, polyethylene oxide (PEO) presents numerous advantageous properties, including good dimensional stability, high ionic conductivity in amorphous form, satisfactory corrosion resistance, cost-effectiveness, as well as satisfactory complexing ability.⁷ Furthermore PEO is commonly used for biological applications: the PEO surface is highly resistant to protein and lipid deposition and PEO itself is non-toxic.⁸

Other type of interactions that do not depend on polymer charge and that have been explored in the last years correspond to hydrogen bonding, hydrophobic bonding, π - π stacking or host-guest interactions.4,9,10 One of the most studied, nonelectrostatic interactions used in LbL assembly to date is hydrogen bonding. This possibility arises because many polymers incorporate moieties that can act as hydrogen bonding donors and acceptors. H-bonded LBL films can be formed on solid substrates by sequential assembly of a layer of a proton acceptor followed by a layer of a proton donor. This kind of films are stabilized by interlayer hydrogen bonding. When these films are exposed to high pH the deprotonation of the acid moiety interferes with the H bonding and the films tend to disintegrate.¹¹ The requirement of suppressed ionization for the formation of hydrogen-bonded multilayer films presents the possibility of pH-tuneable film disassembly. While

^a Instituto de Química Física de los Materiales, Medio Ambiente y Energía (INQUIMAE – CONICET) Facultad de Ciencias Exactas y Naturales Universidad de Buenos Aires Intendente Guiraldes S/N – 1er piso, Buenos Aires, Argentina. E-mail: mricci@qi.fcen.uba.ar, lucilamdl@qi.fcen.uba.ar

^b Gerencia Química & Instituto de Nanociencia y Nanotecnología, Centro Atómico Constituyentes, CNEA, CONICET, Av. Gral. Paz 1499, 1650 San Martín, Buenos Aires, Argentina

[†] Electronic supplementary information (ESI) available. See DOI: https://doi.org/ 10.1039/d3sm00893b

Paper

the disassembly of hydrogen-bonded multilayers provides interesting possibilities for release applications, there is also a need to stabilize the films under certain conditions. In fact, stabilization of hydrogen-bonded multilayers at elevated pH has been explored by many research groups, particularly at moderate pH values that are useful in biomedical applications (*e.g.*, pH 5–8).^{12–14}

Poly(carboxylic acids) and proton-accepting nonionic polymers in solutions interact to form interpolymer complexes (IPC). According to Bailey and coworkers,¹⁵ the complexation between poly(carboxylic acids) and PEO is governed by hydrogen bonding and the IPC stoichiometry approaches 1:1. While at low pH (pH < 3.8), the interaction results in phase separation; at higher pH, the polycomplex exists in solution. In the neutral pH region, they also observed some interaction between the two polymers.¹⁶

LBL films have been used as nano-reactors for in situ synthesis of nanoparticles (NPs). In particular, the combination of metal NP with LBL films results of interest due to the synergy of both systems. Noble metal NPs are widely known because of their unique optical properties that arise from the excitation of the localized surface plasmon resonance (LSPR) at optical frequencies for metals such as gold or silver. At the resonance, the strong localization of electromagnetic energy is confined near the surface of the NP, that decays rapidly in distance. Due to the interesting properties metal NPs have, as the generation of hot carriers and strong heat localization, they have been incorporated in different platforms with applications in diverse areas as drug delivery,17 photovoltaics,18 sensors19,20 or as nanocatalyzers.^{21,22} When metallic NPs are desired, first the incorporation of metallic ions in multilayer systems is required.²³⁻²⁷ Once the polymeric LBL films are assembled, they are incubated in solutions containing the metal ions of interest (Cu²⁺, Ag⁺, AuCl₄⁻, PtCl₄²⁻, RuCl₅²⁻, etc.). These ions are incorporated into the film by electrostatic coordination or by forming complexes exchanging their original ligands with others present on the surface. This process results in the entrapment of the precursor ions^{23,24,28-30} and limits their free diffusion near the substrate surface. Therefore, the prerequisites for an LBL film to be used as a nanoreactor include (1) the presence of coordinating groups for the binding of metal ions, and (2) stability upon metal ion binding.³¹ Then, the metal ions can be reduced chemically, photochemically, or through electrochemical reduction. In this way, the polymeric films can act as nano-reactors that allow the formation of NPs in situ with electrical connectivity between them and with the underlying substrate. This exchange-reduction cycle can be repeated to increase the metal charge, that is, the size of the NPs, the density of the NPs in the polymeric matrix, or both.^{24,27} Through such control it is possible to exploit the sizedependent electrical and optical properties of NPs and their photophysical interactions. The net result is a nanocomposite composed of inorganic NPs dispersed in a molecularly assembled polymeric matrix.31 When electrostatic LBL films are used, the synthesis conditions have to be adjusted so that the multilayer thin films enclose a substantial amount of

nonionized carboxylic acid. Protons of these carboxylic acid groups are then substituted by metal ions by a simple aqueous exchange process.³² This task is somehow difficult, giving rise to coagulation and aggregation problems within the film.³³ A way to overcome this trouble is using H-bonded films. In this case, all carboxylic acid groups are protonated and available, in principle, to coordinate metal ions. Protons of these carboxylic acid groups are then displaced by metal ions. Nevertheless, the coordination of a metal ion by a carboxylic acid implies a disruption of a H-bond than can modify the stability of the film as has been previously reported by Zhang *et al.*³¹

In this work, poly acrylic acid (PAA) and poly (ethylene oxide) (PEO), forming a hydrogen bonded laver by laver (H-bonded LBL) film, were self-assembled to produce a polymeric film. The formation of the films was evaluated by polarized modulated infrared reflection absorption spectroscopy (PMIRRAS) and Quartz crystal microbalance measurements (QCM-D). Crosslinking strategically the information from PMIRRAS and QCM-D we could follow and understand the film growth and the H-bonding formation. XRR and PMIRRAS were also combined to corroborate the successful incorporation of Au and Ag metal ions into the film. On one hand, for films loaded with Au ions, when exposed to increasing pH, a clear stability improvement from pH 4 to 10 was detected, expanding the possible applications of this type of systems including the ones involving biological conditions. On the other hand, results showed that Ag ions loaded films disintegrated at pH above 5. Furthermore, in acidic conditions (pH below 3) the film remained stable, but the Ag ions were released. Ag ions play a significant role in killing bacteria³⁴ so that these results may be useful for the preparation of antibacterial stimuli-responsive nanomaterials. Silver and gold nanoparticles were synthetized in situ by chemical reduction of metal ions.

Materials

Poly(acrylic acid) (PAA) (35% wt in water M_w 100000); poly(ethylene imine) (PEI) (M_w 750000); poly(ethylene oxide) (PEO) (M_w 100000) were obtained from Sigma-Aldrich. AgNO₃ (pro analysis grade) was obtained from Merck and HAuCl₄ was Aldrich 99.999% trace metals basis. Sodium borohydride ReagentPlus[®], 99% was purchased from Aldrich. Other reagents were of analytical grade and were used without further purification. Polyelectrolyte solutions were prepared with 18 MOhm cm Milli-Q (Millipore) deionized water and their pH was adjusted using 1 M or 10 M HCl. The glass electrode used to measure the pH in all solutions was calibrated with a pH 4.01, pH 7.01 and pH 10.0 buffer.

Preparation of substrates

Silicon substrates were cut from Silicon wafers. Glass substrates were cut from glass slides. Gold substrates were prepared by coating silicon (111) substrates with a 20 nm titanium and 20 nm palladium adhesion layer and a 200 nm gold layer, thermally evaporated with an Edwards Auto 306 vacuum

coating system at $P < 10^{-8}$ bar. Prior to use, the substrates were cleaned by UV/ozone (Digital UV Ozone System, Novascan) for 15 min.

Methods

Layer-by-layer self-assembly

Multilayer films were prepared on silicon (111) substrates, glass substrates or gold on silicon substrates depending on the employed characterization technique. First, a single PEI adhesion layer was deposited on the substrate by immersion in a 10 mM PEI solution for 15 min and thoroughly rinsed with Milli-Q water with adjusted pH to the desired value by addition of HCl if necessary. Afterwards, the substrate was immersed in 10 mM PAA solution and thoroughly rinsed with Milli-Q water. The procedure was repeated using a 10 mM PEO solution for the immersion step. The alternate assembly of the PAA and PEO was repeated until the deposition of the desired number of layers was achieved. The solutions of PAA and PEO were all adjusted to pH 2.00 using 1 M HCl (see Scheme 1).

Loading of metal ions into the films

The PEO/PAA films were brought into contact with aqueous solutions of silver nitrate or gold chloride. The solution concentrations were 5 mM. The system was allowed to equilibrate for approximately 30 minutes. Samples were carefully rinsed with deionized water and dried with a flow of nitrogen gas before acquisition of infrared, UV-Vis and XRR spectra.

Metal nanoparticle reduction

The films loaded with metal ions were immersed in sodium borohydride 10 mM aqueous solution for 5 minutes. The process of loading and reduction of metal ions was defined as a cycle which was repeated several times to increase the concentration and size of nanoparticles formed.

IR spectroscopy

PMIRRAS – polarized modulated infrared reflection absorption spectroscopy experiments were performed on a Thermo Nicolet 8700 spectrometer equipped with a custom-made external tabletop optical mount, a MCT-A detector (Nicolet), a photoelastic modulator, PEM (PM-90 with II/Zs50 ZnSe 50 kHz optical head, Hinds Instrument), and syncronous sampling demodulator, SSD, (GWC Instruments). Gold substrates were used. The IR spectra were acquired with the PEM set for a half wave retardation at 1500 cm⁻¹. The angle of incidence was set at 80°, which gives the maximum of mean square electric field strength for the air/gold interface. The signal was corrected by the PEM response using a method described by Frey *et al.*³⁵ Typically 200 scans were performed and the resolution was set for 4 cm⁻¹.

FTIR – transmission spectra for solid polymers were measured using KBr pellets. Resolution was set to 4 $\rm cm^{-1}$ and 200 scans were performed.

UV-visible spectroscopy

Extinction spectra were obtained using a Shimadzu UV-1603 UV-vis spectrophotometer. Spectra were recorded in the range 300–700 nm. The spectra of the glass substrate modified with the LBL were used as 100% transmittance blanks.

Quartz crystal microbalance measurements (QCM-D)

The QCM-D experiments were performed using a Q-Sense Instrument (QCM-D, QSense E1) equipped with Q-Sense Flow Module (QFM 401). For all measurements, QSX 301 gold sensors were used. Samples were perfused using a peristatic microflow system (ISMATEC, ISM 596). Gold sensors were activated with O3 and UV for 15 minutes immediately before use. All experiments were performed at a flow rate of 50 μ L min⁻¹ at 25 °C. The gold sensor was modified following the same procedure as described for silicon substrate. The polyelectrolyte solutions were passed for 4 minutes, then the flow was stopped and each solution was left in contact with the gold sensor for 15 minutes. Then, the solution was removed by fluxing washing solution until stabilization was achieved. Frequency and dissipation changes were recorded from the 1st up to 13th overtone. The mass adsorbed was calculated using 3rd overtone and Sauerbrey model. Dissipation changes were analyzed for the 3rd overtone. A decrease in frequency is related to mass adsorbed over the sensor while an increase in dissipation is related to an increase of the film stiffness.36



Scheme 1 Layer by layer procedure: a first adhesion layer of PEI is deposited followed by n cycles of PEO and PAA deposition steps.

Paper

X-ray reflectometry (XRR)

The measurements were performed with a Panalytical Empyrean X-ray diffractometer with an incident beam of Cu K α radiation (1.54 Å) and a reflectometry configuration. Metal loading was estimated analyzing the critical angle change due to the electron density change following previously published procedures.^{37,38} All measurements were done on LBL films self-assembled on silicon substrates at relative humidity (RH) of 10%.

Scanning electron microscopy

The measurements were performed with an SUPRATM 40 field emission SEM (Carl Zeiss SMT AG) working at an electron beam energy of 5 keV (CMA, FCEyN, UBA). All measurements were done on LBL films self-assembled on silicon substrates.

Ellipsometry

The ellipsometric thickness of LbL films was determined using a Sentech SE400 ellipsometer equipped with a 632.8 nm laser as a polarized-light source. All measurements were performed at an incidence angle of 70° and avoiding any variations of the substrate position in order to keep the system alignment. The ellipsometric parameters, Ψ and Δ , were collected on the dried sample after each adsorption step. These parameters were analyzed with a model that considers a homogeneous film of varying thickness and constant refractive index (n = 1.5) and extinction coefficient (k = 0.03) on a semiinfinite gold substrate.³⁹

Results and discussions

Layer by layer formation of the PEO-PAA films

H-bonding among functional groups of polymers. The interaction between PEO and PAA was evaluated by IR spectroscopy. Fig. 1 shows the PMIRRA spectrum of a LBL film formed by 5 bilayers of PEO-PAA grown at pH 2.0, and compared to the transmission spectra of PAA and PEO KBr pellets. The IR spectrum of PAA is characterized by relatively broad and conformationally sensitive backbone modes and hydrogen-bonded COOH modes. The broad peak at $\sim 1700 \text{ cm}^{-1}$ corresponds to the stretching of C=O in COOH. The position of the peak maximum (1711 cm^{-1}) can be attributed to the stretching of dimers while the shoulder at 1734 cm⁻¹ can be assigned to free (non-hydrogen-bonded) COOH. A small shoulder appears at $\sim 1660 \text{ cm}^{-1}$ that can be ascribed to polymeric hydrogen bonding among carboxylic moieties.⁴⁰ The peak at 1452 cm⁻¹ can be attributed to CH₂ deformation while the peaks at 1412, 1242 and 1173 cm⁻¹ correspond the C–OH in plane vibrations. The peak at 1115 cm⁻¹ can be assigned to C-CH₂ stretching or CH₂ rock.^{40,41} The spectrum of PEO shows O–CH₂ deformation absorption peaks at 1470 and 1454 $\rm cm^{-1},$ and the O-CH_2 wagging absorption peaks at 1362 and 1342 cm⁻¹. The peaks at 1149, 1099 and 1061 cm⁻¹ correspond to C-O-C stretching vibrations.42,43



Fig. 1 IR spectra of PAA, PEO and a 5 bilayers film. PAA and PEO are transmission spectra of KBr pellet. (PEO-PAA)₅ is a PMIRRA spectrum of 5 bilayers of PEO-PAA after a PEI adhesion layer.

The spectrum of the film shows absorption peaks of both polymers, indicating that the film is built and both polymers are present. Furthermore, it can be noticed a shift of the maximum of the C==O stretching peak to higher wavenumbers, revealing that the intermolecular dimers of PAA have been replaced by interactions with the PEO. It is known that when an ether group interacts with a COOH group, alternate forms of hydrogen bonding are possible. When the carboxyl C==O is hydrogen-bonded but not dimerized, as in alcohol-carbonyl bonding, the –COOH stretching band shifts to ~1730 cm^{-1.44–46} The peak assignment is presented in Table 1.

Film growth. The growth of the LbL assembly was followed by ellipsometry, quartz crystal microbalance with dissipation (QCM-D) and PMIRRAS (Fig. 2 and Fig. S1-S4, ESI[†]). Fig. S1 (ESI[†]) shows that the thickness of the PEO/PAA LbL film (measured by ellipsometry) monotonically increases as a function of the number of deposited layers. QCM-D was used to evaluate the adsorbed mass in each step and the changes in the stiffness of the films. The dissipation change depends on the stiffness of the film and the mass adsorbed, 47,48 therefore the nature of each layer can be analyzed from the relative dissipation change $(-\Delta D/\Delta F)$, reported on Table 2. Additionally, Fig. S2 (ESI[†]) shows the frequency changes (ΔF) vs. time for each layer of the PEO/PAA assembly washing with water at pH 2. As it can be noticed, 15 minutes is enough to ensure layer deposition and consequent film formation. In order to evaluate the film growth by PMIRRAS, the area of the stretching peak of COOH (~1700 cm⁻¹) was considered. The area of the peak

Soft Matter

Table 1 Spectral mode assignment of transmission FTIR spectra of PEO and PAA in KBr pellet and PMIRRA spectrum of LBL of (PEO-PAA)₅ on Au surface

Assignment	PAA (cm^{-1})	PEO (cm^{-1})	$(PEO-PAA)_5 (cm^{-1})$
C=O stretching (COOH)	1711 (broad)		1734
CH ₂ deformation	1452		1454
O-CH ₂ deformation		1470	
C-OH in-plane bending	1412	1416	1417
O-CH ₂ wagging		1362, 1342	1350
C-OH in-plane bending/C-O stretching of COOH groups + O-H bending	1242	1242	
C-OH in-plane bending C-O stretching of COOH groups/O-H bending	1173		1171
Stretching vibrations of C–O–C		1149, 1099, 1061	
C-CH ₂ stretching/CH ₂ rock	1115		1115



Fig. 2 Fig. 2 (A) PMIRRAS spectra of films with increasing number of layers. Inset: area of C=O stretching peak of -COOH (B) Top: frequency change (ΔF), adsorbed mass change (Δm) and Bottom: dissipation change (ΔD) for each layer of the PEO/PAA assembly.

corresponding to the CH₂ deformation of the PAA (~1450 cm⁻¹) can also account for the amount of PAA adsorbed on the surface, and its area changes in accordance to the changes in area of the COOH band. The observed non-linear growth is similar to that previously observed for some poly(carboxylicacid)/PEO LbL films.^{11,49–51}

The influence of the pH of the water used for rinsing the film between each polymer deposition step during LbL assembly was evaluated. pH = 2, similar to the pH of the polymer solution, and pH = 6 (non-adjusted, pH of water) were used. The PEO does not have an ionization equilibrium while the PAA does, changing from highly protonated at pH = 2 to mostly ionized at pH = 6. According to the relative dissipation values obtained for QCM measurements, the films do not present a viscoelastic behavior $(-\Delta D/\Delta F \le 0.47 \times 10^{-6} \text{ Hz}^{-1})$. The films

are sufficiently rigid to assess the mass adsorbed using the Sauerbrey equation.³⁶ Considering that PEO and PAA films generally present a hydration percentage of 50% and 30% respectively,^{52,53} it is possible to estimate the thicknesses associated with each of the deposited layers (Table S1, ESI†). The results show that PEO films are thinner, due to a lower adsorbed mass and a high rigidity, while PAA films are thicker due to a much higher amount of adsorbed material. A thickness of 100 nm was estimated for a 5 bilayers film rinsed at pH = 2, while a thickness of 25 nm was estimated for LBL prepared washing with water at pH = 6, in complete accordance to ellipsometric measurements (Fig. S1, ESI†). Furthermore, it was observed that the stiffness of PEO $(-\Delta D/\Delta F)$ layers was higher when washing at pH = 2 than when washing at pH = 6, while stiffness of PAA layers seemed not to have been affected

Table 2 Adsorbed mass change (Δm), dissipation change (ΔD) and relative dissipation change ($-\Delta D/\Delta F$) for each layer, and mass adsorbed ratio (Δm PAA/ Δm PEO) for bilayer in the PEO/PAA assembly

Layer	$\Delta m \ (\mu g \ cm^{-2})$	$\Delta D (10^{-6})$	$-\Delta D/\Delta F (10^{-6} \text{ Hz}^{-1})$	$\frac{\Delta m_{\rm PAA}}{\Delta m_{\rm PEA}}$
-	,	. ,	. ,	Ampeo
PEO-1	0.016	0.59	0.65	73
PAA-1	1.176	0.97	0.02	
PEO-2	nd	0.35	nd	nd
PAA-2	0.619	0.37	0.01	
PEO-3	0.197	0.21	0.02	5.9
PAA-3	1.156	0.05	nd	
PEO-4	0.317	0.80	0.05	6.7
PAA-4	2.130	1.20	0.01	
PEO-5	2.063	6.78	0.06	2.4
PAA-5	5.014	9.89	0.04	
Total PEO	2.579			
Total PAA	10.10			
Total assembly	12.68			
*nd: not detect	able.			

by this rinsing step (Table 2 and Table S2, ESI[†]). These facts can be explained taking into account that at pH = 2 the amount of H-bonding interactions between COOH of PAA and -O- of PEO increases due to high availability of COOH. This fact causes both, that a higher amount of PEO adsorbs on the film, and that a higher number of -O- of PEO interact through Hbonding to COOH, increasing the stiffness of the layer.⁵⁴ At pH = 6, due to lower availability of COOH from PAA to form H-bonds, less polymer is adsorbed. Nonetheless, many -Ogroups of PEO are free to coordinate water, which might be included in the layer, making it less stiff (see Table S2, ESI[†]). In conclusion, the results show that the pH of the washing step modifies both the amount of deposited material and the stiffness of the resulting layer (see Fig. 2 and Fig. S1, S3 and S4, ESI[†]).

Since the resulting film was thicker assembling the same number of layers, and no significant changes in stability were observed, the washing step pH was set to 2 for the next experiments, except specifically noted. The number of bilayers chosen to be deposited was 5 since it ensures that there is enough mass to have an independent behavior of the underlying surface and also allows an adequate analysis of the interaction among the polymers in the film.

Fig. 2(A) shows the evolution of the PMIRRA spectra as the number of bilayers of the film increase. In particular, it is possible to observe the growth of a characteristic peaks at $\sim 1750 \text{ cm}^{-1}$ that correspond to C=O stretching from COOH of PAA and the peak at 1420 cm⁻¹ corresponding to the bending of CH₂ of PAA (see Table 2), respectively. Fig. 2(A) inset shows the area of the COOH stretching peaks as a function of number of bilayers. It can be observed that the area of the peaks increases exponentially as the number of layers increases.

The QCM-D analysis results are presented in Fig. 2(B) and show that in the first bilayer, the mass of PEO adsorbed was minor, less than 20 nanograms. In the following steps, the mass adsorbed increased after deposition of the each PAA layer. In fact, during the deposition process, the adsorbed mass and the dissipation of the film, ΔD , increased exponentially as the number of layers increased. The results show that, in each bilayer, the mass of PAA adsorbed was higher than the corresponding mass of PEO adsorbed. Furthermore, it was observed that both PEO and PAA masses increased as the number of bilayers increased, while the mass ratio PAA/PEO decreased (see Table 2). After five layers, the mass of PEO adsorbed was around 4 times higher than the mass of PEO adsorbed.

Film stability. Effect of pH. As stated before, when H-bonded LbL films are exposed to high pH, the deprotonation of the carboxylic acid interferes with the H bonding and the films tend to disintegrate.¹¹ In this section, the stability of the films prepared at pH = 2 was studied by QCM-D and PMIRRAS exposing a 5 bilayer (PEO-PAA)₅ film to increasing pH from 2 to 10.

QCM-D is sensitive to all mass adsorbed on the surface (including water molecules that coordinate with the polymers). These measurements are directly linked to the amount of lost mass due to pH exposure. Additionally, the stability of the film was evaluated by PMIRRAS. The addition of the areas of the stretching peak of COOH ($\sim 1700 \text{ cm}^{-1}$) and the stretching peak of COO- (1550 cm⁻¹) of PAA was considered. The area of the peak corresponding to the CH₂ deformation of the PAA $(\sim 1450 \text{ cm}^{-1})$ can also account for the amount of PAA adsorbed on the surface, and its area changes in accordance to the changes in area of the carboxy-peaks (COOH + COO⁻ stretching peaks). In any case, PMIRRAS only accounts for the amount of PAA adsorbed on the surface, being this an indirect measurement of the disintegration of the film. Furthermore, analysis of the dissipation of the system allows the discussion of the stiffness of the film, which is directly related to the absorption of water by coordination with the polymers (the more water is adsorbed, the less stiff is the film) and the formation/rupture of H-bonds among the polymer chains. The combination of these two techniques is very advantageous to study this kind of systems.

According to the results shown in Fig. 3, up to pH 6 the total mass of the film does not change appreciably or increases/ decreases slightly while the area of the carboxy-peaks decreases in a monotonous way. At the same time, the dissipation increased to some extent. This suggests that water molecules were being incorporated into the film, decreasing its stiffness (since dissipation increased slightly) while a fraction of PAA was desorbed, somehow keeping the total mass constant. A different behavior is clearly observed when the film was exposed to pH = 7. The mass decreased significantly while the dissipation increased markedly. It should be noted that, in all pH experiments, the frequency and dissipation measurements were taken until the system was stabilized, taking in some cases more than 30 minutes (exposure time used for the PMIRRAS measurements). Fig. S5 (ESI⁺) shows that on exposure to pH = 7, a decrease in mass (increase in frequency) occurs in the first few minutes, and afterwards the mass decreases significantly taking about 2 hours to stabilize. In Fig. 3 it can be noted that the tendency of the area of the carboxy-peaks does not change significantly at pH = 7, and keeps decreasing. These



Fig. 3 Area of $COOH-COO^-$ stretching peaks (blue circles) relative to pH = 2 initial area, percentage adsorbed mass (black squares) and relative dissipation change (red triangles) for the assembly with 5 bilayers exposed to a solution with different pHs.

phenomena can be explained if we contemplate that the exposure of the outmost PAA layer to this pH (in which the ionization percentage is about 50%, see Fig. 6) produces the deprotonation of a fraction of COOH groups, thus removing hydrated protons from the film and breaking H-bonds that were responsible of giving structure to the film, in this way reducing its stiffness and disintegrating the film. According to QCM-D results, a high percentage of the film (64% of the total mass) is lost while considering the area of the carboxy-peaks (by PMIRRAS), only a part of the outermost layer of PAA is lost (around 39%).

At pH = 8, the film continued to lose mass, the total area of the carboxy-peaks decreased, and the dissipation returned to a value similar to that reported before exposure to pH 7, indicating that the film was indeed disintegrating and the remaining bilayers on the surface recovered the initial stiffness. The change in carboxy-peaks area decreased to around 50%, indicative of an important desorption of PAA.

At pH = 9, the relative area of the carboxy-peaks and mass are practically unchanged, while the dissipation decreases by 50%. Taking into account that the relative area obtained by PMIRRAS is associated only with PAA, and that the change in mass in most cases involves simultaneous processes of adsorption and desorption of molecules, the observed changes could be associated with changes in the film due to desorption of PEO. Finally, at pH = 10 the relative area decreases to 30%. It is important to note that even at pH 10 a few bilayers appear to remain adsorbed on the surface. Despite the fact that the mass does not change, the dissipation increases by 90%, indicating that this desorption process occurs simultaneously with an increase in the hydration of the system, decreasing its rigidity.

Film stability. Effect of silver and gold aqueous ions

Complexation of the film with silver and gold ions. Films prepared with an adhesion layer of PEI and 5 bilayers of PEO–PAA were brought into contact with silver nitrate and gold chloride aqueous solutions for 30 minutes, following the procedure described in the Materials section. PMIRRA spectra of

the films were taken at increasing immersion time during the metal loading. The coordination of the carboxylic groups of PAA by the metal produces its deprotonation. Following the formation of carboxylate groups on the surface can give a measurement of the extent of metal loading of the surface with respect to the maximum possible loading. As observed in Fig. S6 and S7 (ESI†), the area of the carboxylate stretching peak increases sharply at first, to reach the maximum at 25–30 minutes of immersion. In conclusion, 30 minutes is enough time to saturate the film in the metal ion and this time was used for experiments.

XRR and PMIRRAS measurements were done to characterize the behavior of the LBL after metal ion loading.

Fig. 4 shows XRR measurements done over LBL assemblies to determine if ions were loaded in the structure. XRR signals depend on the electron density of the thin film as defined by $\rho_{\rm el} = \frac{\pi}{\lambda^2 r_{\rm c}} \theta_{\rm e}^2$, ⁵⁵ where λ corresponds to the X-ray wavelength, $r_{\rm c}$ is the electron radius and $\theta_{\rm c}^{\circ}$ is called the critical angle, which corresponds to the angle at which X-rays reflect totally. As it is possible to observe from last equation, θ_c depends on the electron density of the film, which can be usually distinguished as a steep in the intensity signal. θ_{c} is defined as the angle at which the decay corresponds to 0.5 times the maximum intensity. Fig. 4(A) and (B) show in grey line a mild decay for the polymeric thin film, the θ_c position is shown in grey dashed line (defined as the extension of the decay up to 0.5). Fig. 4(A) denotes, in red line, a clear shift of the θ_{c} due to the electron density increment when Ag ions have been loaded in the thin film. Red dashed line denotes the θ_c° position change for the $(PEO-PAA)_5 + Ag$ sample. A similar behavior is observed in Fig. 4(B) for the incorporation of Au ions, though the blue dashed line shows a smaller shift in comparison to Ag case. The metal ion volume fraction, F_{ion} can be calculated according to



Fig. 4 XRR measurements over LBL assemblies as prepared (grey) and loaded with (A) silver ions (red) and (B) gold ions (blue).

 $F_{\rm ion} = \frac{\rho_{\rm poly+ion} - \rho_{\rm poly}}{\rho_{\rm poly}}$ where $\rho_{\rm poly}$ corresponds to the electronic $\rho_{\rm ion}$ density of the (PEO–PAA)₅ thin film and $\rho_{\text{poly+ion}}$ to the (PEO– PAA)₅ + ion thin film. δ_{ion} corresponds to the electronic density of the ion that can be calculated as $\rho_{\text{ion}} = \frac{\delta_{\text{ion}} n_{\text{ion}} N_{\text{A}}}{A_{\text{ion}}}$, where δ_{ion} is the ion mass density, η_{ion} is the ion atomic number, A_{ion} the ion atomic mass, and N_A is Avogadro's number. In Ag case, F_{ion} $\approx 4\%$ where it has been considered that Ag ions are interacting with carboxylates moieties by displacement of its proton. For Au case, since the incorporated Au ions could be interacting with carboxylate functionalities by the substitution of one or more chloride ligands of the Au by the carboxylate, the F_{ion} ranges from [1-4]%, according to the degree of replacement of the chloride ions by the carboxylate moieties of the polymer film.⁵⁶ These results, where the calculated F_{ion} are in accordance to previous similar studies done over electrostatic bonding polymers,⁴⁵ show that, effectively, ions are being incorporated into the polymeric film.

PMIRRAS was used to characterize the interaction between the metal ions and the polymers in the film. Fig. 5, left panel, shows the PMIRRA spectra obtained before and after incubation in the Ag or Au solutions. The pH of the Ag containing solutions was around 5.5 while the pH of the Au containing solutions was around 2. As it can be observed, the main change in the spectra after incubation in the metal solution is the decrease in the area of the peak corresponding to -COOH stretching peak ($\sim 1700 \text{ cm}^{-1}$), the appearance of a peak at $\sim 1500 \text{ cm}^{-1}$ that can be assigned to COO⁻ asymmetric stretch, and a new band centered at 1402 cm⁻¹ for Ag ion and

1427 cm⁻¹ for Au ion, which can be assigned to the symmetric stretching vibrations of the carboxylate ion. These changes in the spectra correspond to the deprotonation of the PAA due to a complexation with the metal ions, that is, the protons are replaced by the metal ions in the carboxylic acid functionality. This happens despite the low pH of the metal containing solution. Note that, even for the case of films in contact with the very acidic gold solution (pH ~ 2), there is a high percentage of carboxylate moieties. Furthermore, according to previous studies by various authors,^{57–59} the shift of the position of the COO⁻ asymmetric stretch peak is due to different ways of coordination of the carboxylate moiety with the metal ions. In fact, peaks appearing at $1550-1580 \text{ cm}^{-1}$ have been attributed to the formation of a chelating bidentate coordination complex, while peaks at $\sim 1610 \text{ cm}^{-1}$ to a bridging bidentate coordination complex between metal ions and carboxylate groups, for different cations including silver, copper, calcium, aluminum and lanthanum with polycarboxylate polymers.^{57,59,60} When the carboxylate binds as a chelating bidentate ligand, mononuclear complexes are formed with one or two carboxylates bound to the metal cation. In the case of a bridging bidentate binding, two metal ions with two pairs of adjacent carboxylate groups associate forming a binuclear complex where the metal ions are bridged by four carboxylate groups. In our case, for samples incubated in Ag solutions, a broad peak at 1551 cm^{-1} appeared, indicating the predominance of the formation of chelating bidentate coordination complex. Differently, samples incubated in Au solutions show a band at 1597 cm⁻¹ with a shoulder at 1554 cm^{-1} . This suggests that these samples form mostly bridging bidentate coordination complexes, in



Fig. 5 PMIRRA spectra of 5 bilayers of the film as prepared (top) and incubated for 30 minutes in a 5 mM silver (middle) or gold (bottom) solution. Left panel: Spectra taken immediately after contact with solutions. Right panel: spectra taken after immersion in solution at pH = 5.

an analogous way to a luminum interacting with the PMAA, as reported by Erel-Unal $et\ al.^{57}$

The samples loaded with silver or gold ions, as well as the LBL film as prepared, were immersed for 30 minutes in a solution at pH = 5, to discard effects due to difference in the pH of the ion solutions. PMIRRA spectra were taken and are shown in the right panel of Fig. 5. As it can be seen, there are no significant changes in the spectra of Ag and Au loaded films before and after immersion, indicating that there is no change in the ionization degree of carboxylic acid moieties. On the other hand, the film without ions shows an incipient band at around 1555 cm⁻¹, corresponding to the beginning of ionization of the carboxylic acid moieties.⁵⁷

Response to pH. In order to characterize the behavior and stability of the films with pH, the films as prepared (pristine films) and those loaded with Ag and Au ions were immersed in solutions of increasing pH ranging from 2 to 10 and studied by PMIRRAS.

In the case of films loaded with Ag, it was observed that upon immersion in solution at pH = 2, the spectrum of the film changed and was similar to that of films without Ag at all (data not shown). This effect had already been observed by Zhang *et al.*,³¹ for hydrogen-bonded poly(vinyl pyrrolidone)/PAA system, and can be ascribed to the displacement of the complex equilibrium Ag-COO⁻ by the highly concentrated proton in acidic solutions. In consequence, the films loaded with silver were studied starting from pH = 5 and up to pH = 10. The effect of displacement of the cations by protons was not observed for Au loaded films. It is worth noticing that the native pH of the Au solutions is 2.

The PMIRRA spectra of the films exposed to solutions of increasing pH were acquired and are shown in Fig. S8–S10 (ESI[†]). The spectra (from 1300 to 2000 cm⁻¹) were fitted by 4 or 5 Gaussian functions, as needed. In most spectra, two Gaussian functions were necessary to appropriately fit COOH stretching peaks and COO⁻ stretching peaks, due to different coordination modes among carboxylic acid moieties and with metallic ions. The area of the COOH (A_{COOH}) and COO⁻ (A_{COO-}) stretching peaks were calculated and are shown in Fig. 6. Left panel of Fig. 6 shows the area of COO⁻ peak, COOH peak and the total area of the carboxy-peaks, while the right panel shows the ionization degree of carboxylate, calculated as:⁶¹

$$\alpha_{\rm COO^-} = \frac{A_{\rm COO^-}}{A_{\rm COOH} + A_{\rm COO^-}}$$

Accordingly, the portion of non-ionized carboxylic acid moieties was calculated:

$$\alpha_{\rm COOH} = \frac{A_{\rm COOH}}{A_{\rm COOH} + A_{\rm COO^-}}$$

In Fig. 6 it can be noticed that for films loaded with Au ions, the total area of the peaks does not vary appreciably (less than 15%) after exposure, even at pH = 10, while for pristine films or films loaded with Ag, a marked decrease (around 50–60%) in

the total area can be seen, attributable to dissolution of the film. As shown before, LBL films formed by H-bond interactions would not be stable at high pH, due to deprotonation of carboxylic moieties and consequent breakage of H-bonds with the proton acceptor, PEO. In the case of gold ion loaded films, the ions intercalated into the film might be forming strong complexes with functional groups of both polymers, causing an extra stability of the system. A stabilization of this kind has already been reported by Zhang et al.,³¹ for hydrogen-bonded poly(vinyl pyrrolidone)/PAA that increased its stability in water when it had been loaded with silver ions. In our case, the silver ions do not seem to be increasing the stability of the film. In fact, dissolution seems to be very pronounced from pH = 6 and higher, even more than dissolution of the pristine films. It is interesting to note that even after increasing the pH to 10, a few layers of the film still remain on the surface for the silver loaded and no metal loaded films.

The analysis of the tendency of the ionization degree with pH shows differences in the behavior of the three systems. It is worth mentioning that even when a few layers remain on the surface for films without ions and films loaded with Ag ions, the acid-base equilibrium of the PAA takes place and the ionization degree goes back to its original value when pH is lowered from 10 to 2 (empty and full circles). The pristine film shows a typical acid-base behavior with a $pK_a \sim 6$ (where $\alpha_{\rm COO^-} = \alpha_{\rm COOH} = 0.5$). For the films loaded with Ag, the shape of the curve is more irregular, probably due to the huge loss of polymer because of pH change. In the case of films loaded with Au, at a pH as acidic as 2, there is a high proportion of carboxylate moieties that are most likely coordinating Au ions. This proportion increases to $\alpha_{\rm COO^-} = 1.0$ as pH is increased to 10.

The p K_a of PAA is 4.5,⁶² which means that at pH >6.5 the concentration carboxylic acid vs. carboxylate in the film should be negligible (less than 1%). Yet, it is interesting to note, for pristine films, at pH = 10 (well above 6,5), the ionization degree $\alpha_{COO^{-}}$ is 0.9. This means that even at such a high pH, there is still a 10% of carboxylic acid present in the film. In contrast, films loaded with Ag or Au, at pH = 10, show α_{COO^-} = 1.0, that is, the amount of COOH present in the film is not detectable. This fact can be explained taking into account that for films without metal ions the interaction of PAA with PEO takes place through H bonds that seem to remain (even at pH = 10, well above the pK_a). These bonds would be responsible of the persistence of a fraction ($\sim 20\%$) of polymers on the surface, even at such unfavorable conditions of pH. In the case of metal ion loaded films, the H bonds were probably displaced by the coordination of silver and gold ions that crosslinked PAA and PEO polymer chains. The results show that this crosslink is more effective in the case of Au that increases the film stability to pH as high as 10, while for Ag, the stability of the film is similar to that of no ion-loaded films.

Reduction of metal ions to form nanoparticles

Samples prepared on glass slides or silicon substrates and loaded with metal ions were immersed in freshly prepared



Fig. 6 Left panel: areas of COO⁻ and COOH PMIRRAS stretching peaks vs. pH. Right panel: ionization degree vs. pH. Top: film (5 bilayers of PAA, PEO on a PEI adhesion layer). Middle: film loaded with silver ions. Bottom: film loaded with gold ions. Full squares represent carboxilate, empty squares represent carboxilic acid. Full diamonds in left panel represent the total area of COOH-COO⁻ stretching peaks. Circles represent values at pH 2 after a full cicle increasing pH up to 10.

borohydride solution 10 mM for 5 minutes. UV-Vis spectra of the sample in transmission mode was registered for different cycles of re-loading and reduction as described in the Materials and methods section. Fig. 7(A) shows the evolution with cycles of the expected local surface plasmon resonance (LSPR) for Ag⁰ nanoparticles. It is possible to observe a broad band resonance with a maximum at $\lambda_{\text{LSPR}} = (406 \pm 10)$ nm. This resonance position is in good accordance with the expected position according to the Frölich⁶³ condition $n_{\text{re}}^{\text{Ag}}(\lambda_{\text{LSPR}})^2 = 2 \times (n^{\text{poly}})^2$ where $n_{\text{re}}^{\text{Ag}}(\lambda_{\text{LSPR}})$ corresponds to the real part of the Ag refractive index and n^{poly} corresponds to the refractive index of the polymer/s in the neighborhood of the Ag nanoparticle ($n^{\text{PEO}} \approx 1.454, n^{\text{PAA}} \approx 1.52$).⁶⁴ To fulfill this condition, nanoparticle's size in this configuration should be much smaller than incident wavelength (typically d < 20 nm). Fig. 7(B) shows a representative SEM image of (PEO–PAA)₅–Ag with 3 cycles of reduction of Ag, where it is possible to observe the formation of a polydisperse distribution of spherical Ag⁰ nanoparticles of mean NP diameter of (18 ± 6) nm, in accordance to the λ_{LSPR} position. The complete analysis of the particle distribution is detailed in Fig. 7(C) where it is possible to clearly observe the polydispersity distribution, which can be responsible for the broad FWHM of the plasmon resonance of Fig. 7(A).

A different behavior is observable for Au reduction in Fig. 7(D) where no LSPR was observable even for more than 5 cycles though the increase of the extinction at low wavelengths confirms the presence of the ions/nanoparticles in the LBL as already shown in Fig. 4(B). However, in Fig. 7(E) a representative SEM image shows the presence of Au nanoparticles in a (PEO-PAA)₅ self-assembled film loaded with 5 cycles of Au ions



Fig. 7 (PEO–PAA)₅ film loaded with Ag ions and subsequent reduction: (A) evolution of the extinction spectra for 1, 2 and 3 cycles of reduction. (B) SEM image with (C) its corresponding histogram. (PEO–PAA)₅ film loaded with Au ions and subsequent reduction where on (D) it is not possible to observe the plasmon response, (E) SEM of Au nanoparticles with (F) its corresponding size distribution.

treated with NaBH₄. Fig. 7(F) shows the corresponding histogram, showing a mean nanoparticle diameter of $(27 \pm 10 \text{ nm})$. SEM images with less magnification (Fig. S11, ESI†) show a comparison of samples loaded with AgNPs and AuNPs. Samples loaded with AgNPs show regions of higher density of nanoparticles, while for AuNPs loaded samples, nanoparticles appear disperse all over the polymer film, probably due to the lower Au ion loading in the film (observed by XRR, see before). This low concentration may explain the lack of sensibility of the UV-Vis technique to observe the LSPR extinction band.

Final remarks

Metal ions Ag and Au have been loaded in H-bonded PEO/PAA LBL films by immersing the film in metal ion solutions. The metal ions coordinate with the COOH moiety of the PAA (replacing the proton) and the -O- of the PEO. The films remain stable even though the H-bond between PAA and PEO are disturbed, because the metal ions bridge between the polymers. In the case of Ag, the ions can be unloaded from the film immersing it in acidic solutions. Au ions seem to form much stronger complexes. In fact, the kind of coordination between metal ions and COO⁻ moieties is different for Au and Ag, as seen by IR spectroscopy. The amount of Ag loaded is 4 times higher than the amount of Au loaded (4% and 1% respectively). The stability of the films at increasing pH was studied. Pristine films and films loaded with Ag dissolve progressively at pH above 4, while films loaded with Au are stable even at pH as high as 10. This seems to indicate that the coordination among PAA-Au-PEO is strong and prevents dissolution of the film. In both cases, the films were adequate to produce metal nanoparticles by metal loading and in situ reduction, though the low quantities of Au that can be loaded into the film encompasses a low quantity of AuNPs.

The resultant samples obtained for the films loaded with Au transform them in potentially useful platforms for sensors, because of their high stability at a wide range of pHs, the remaining non-coordinated carboxylic acid/carboxylate moieties, ready for post-functionalization, and their hydrophilicity. In the case of films loaded with Ag ions, since Ag ions play a significant role in killing bacteria because they can readily adsorb to most biomolecules (DNA, membrane protein, enzymes, or intracellular cofactors) in bacteria to inactivate their functions,³⁴ the fact that low pH causes the unloading of the ions, and high pH causes the disintegration of the film (and the consequent release of Ag ions) is interesting for the development of pH responsive antibacterial materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially supported by Universidad de Buenos Aires (20020190200245BA, 20020190200295BA), Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina (CON-ICET, PIP-11220200102008CO) and Agencia Nacional de Promoción de la Investigación, el Desarrollo Tecnológico y la Innovación, Argentina (PICT-2020 SERIEA-01758). N. P. A. gratefully acknowledges an undergraduate fellowship from Universidad de Buenos Aires, L. L. C. gratefully acknowledges a postdoctoral fellowship from CONICET, and P. C. A., F. B., M. L. M. R. and L. P. M. D. L. are research staff of CONICET.

References

- G. Decher, Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites, *Science*, 1997, 277(5330), 1232–1237, DOI: 10.1126/science.277.5330.1232.
- 2 P. T. Hammond, Form and Function in Multilayer Assembly: New Applications at the Nanoscale, *Adv. Mater.*, 2004, **16**(15), 1271–1293, DOI: **10.1002/adma.200400760**.
- 3 B. S. Kim, S. W. Park and P. T. Hammond, Hydrogen-Bonding Layer-by-Layer-Assembled Biodegradable Polymeric Micelles as Drug Delivery Vehicles from Surfaces, *ACS Nano*, 2008, 2(2), 386–392, DOI: 10.1021/nn700408z.
- 4 E. Guzmán, F. Ortega and R. G. Rubio, Layer-by-Layer Materials for the Fabrication of Devices with Electrochemical Applications, *Energies*, 2022, 15(9), 3399, DOI: 10.3390/ en15093399.
- 5 L. Wågberg and J. Erlandsson, The Use of Layer-by-Layer Self-Assembly and Nanocellulose to Prepare Advanced Functional Materials, *Adv. Mater.*, 2021, 33(28), 2001474, DOI: 10.1002/adma.202001474.
- 6 A. M. Díez-Pascual and A. Rahdar, LbL Nano-Assemblies: A Versatile Tool for Biomedical and Healthcare Applications, *Nanomaterials*, 2022, 12(6), 949, DOI: 10.3390/nano12060949.
- 7 S. B. Aziz, R. B. Marif, M. A. Brza, A. N. Hassan, H. A. Ahmad, Y. A. Faidhalla and M. F. Z. Kadir, Structural, Thermal, Morphological and Optical Properties of PEO Filled with Biosynthesized Ag Nanoparticles: New Insights to Band Gap Study, *Results Phys.*, 2019, 13, 102220, DOI: 10.1016/ j.rinp.2019.102220.
- 8 J. F. Quinn, A. P. R. Johnston, G. K. Such, A. N. Zelikin and F. Caruso, Next Generation, Sequentially Assembled Ultrathin Films: Beyond Electrostatics, *Chem. Soc. Rev.*, 2007, 36(5), 707–718, DOI: 10.1039/b610778h.
- 9 J. Zhang, X. Huang, L. Zhang, Y. Si, S. Guo, H. Su and J. Liu, Layer-by-Layer Assembly for Immobilizing Enzymes in Enzymatic Biofuel Cells, *Sustainable Energy Fuels*, 2020, 4(1), 68–79, DOI: 10.1039/C9SE00643E.
- 10 A. Rodriguez-Abetxuko, D. Sánchez-deAlcázar, A. L. Cortajarena and A. Beloqui, A Versatile Approach for the Assembly of Highly Tunable Biocatalytic Thin Films, *Adv. Mater. Interfaces*, 2019, 6(18), 1900598, DOI: 10.1002/admi.201900598.
- S. A. Sukhishvili and S. Granick, Layered, Erasable Polymer Multilayers Formed by Hydrogen-Bonded Sequential Self-Assembly, *Macromolecules*, 2002, 35(1), 301–310, DOI: 10.1021/ma011346c.
- J. F. Quinn and F. Caruso, Multivalent-Ion-Mediated Stabilization of Hydrogen-Bonded Multilayers, *Adv. Funct. Mater.*, 2006, 16(9), 1179–1186, DOI: 10.1002/adfm.200500530.
- 13 J. Chen and W. Cao, Fabrication of a Covalently Attached Self-Assembly Multilayer Film *via* H-Bonding Attraction and Subsequent UV-Irradiation, *Chem. Commun.*, 1999, (17), 1711–1712, DOI: 10.1039/A905629G.
- 14 S. Y. Yang and M. F. Rubner, Micropatterning of Polymer Thin Films with PH-Sensitive and Cross-Linkable Hydrogen-Bonded Polyelectrolyte Multilayers, *J. Am. Chem. Soc.*, 2002, 124(10), 2100–2101, DOI: 10.1021/ja017681y.

- 15 F. E. Bailey Jr., R. D. Lundberg and R. W. Callard, Some Factors Affecting the Molecular Association of Poly(Ethylene Oxide) and Poly(Acrylic Acid) in Aqueous Solution, *J. Polym. Sci., Part A: Gen. Pap.*, 1964, 2(2), 845–851, DOI: 10.1002/ pol.1964.100020221.
- 16 V. V. Khutoryanskiy, A. V. Dubolazov, Z. S. Nurkeeva and G. A. Mun, PH Effects in the Complex Formation and Blending of Poly(Acrylic Acid) with Poly(Ethylene Oxide), *Langmuir*, 2004, **20**(9), 3785–3790, DOI: **10.1021/la0498071**.
- 17 A. P. Stavropoulou, M. Theodosiou, E. Sakellis, N. Boukos, G. Papanastasiou, C. Wang, A. Tavares, C. A. Corral, D. Gournis, N. Chalmpes, O. L. Gobbo and E. K. Efthimiadou, Bimetallic Gold-Platinum Nanoparticles as a Drug Delivery System Coated with a New Drug to Target Glioblastoma, *Colloids Surf.*, B, 2022, 214, 112463, DOI: 10.1016/ j.colsurfb.2022.112463.
- L. T. M. Huynh, S. Kim and S. Yoon, Effect of Material and Shape of Nanoparticles on Hot Carrier Generation, *ACS Photonics*, 2022, 9(10), 3260–3267, DOI: 10.1021/acsphotonics.2c00530.
- 19 R. M. Gazoni, M. G. Bellino, M. Cecilia Fuertes, G. Giménez, G. J. A. A. Soler-Illia and M. L. M. Ricci, Designed Nanoparticle–Mesoporous Multilayer Nanocomposites as Tunable Plasmonic–Photonic Architectures for Electromagnetic Field Enhancement, *J. Mater. Chem. C*, 2017, 5(14), 3445–3455, DOI: 10.1039/C6TC05195B.
- 20 K. Behrouzi and L. Lin, Gold Nanoparticle Based Plasmonic Sensing for the Detection of SARS-CoV-2 Nucleocapsid Proteins, *Biosens. Bioelectron.*, 2022, 195, 113669, DOI: 10.1016/j.bios.2021.113669.
- 21 V. Jain, R. K. Kashyap and P. P. Pillai, Plasmonic Photocatalysis: Activating Chemical Bonds through Light and Plasmon, *Adv. Opt. Mater.*, 2022, 10(15), 2200463, DOI: 10.1002/adom.202200463.
- 22 M. Herran, A. Sousa-Castillo, C. Fan, S. Lee, W. Xie, M. Döblinger, B. Auguié and E. Cortés, Tailoring Plasmonic Bimetallic Nanocatalysts Toward Sunlight-Driven H2 Production, *Adv. Funct. Mater.*, 2022, 32(38), 2203418, DOI: 10.1002/adfm.202203418.
- 23 S. Joly, R. Kane, L. Radzilowski, T. Wang, A. Wu, R. E. Cohen, E. L. Thomas and M. F. Rubner, Multilayer Nanoreactors for Metallic and Semiconducting Particles, *Lang-muir*, 2000, **16**(3), 1354–1359, DOI: **10.1021/la991089t**.
- 24 T. C. Wang, M. F. Rubner and R. E. Cohen, Polyelectrolyte Multilayer Nanoreactors for Preparing Silver Nanoparticle Composites: Controlling Metal Concentration and Nanoparticle Size, *Langmuir*, 2002, **18**(8), 3370–3375, DOI: **10.1021**/ **1a015725a**.
- 25 X. Zhang, G. Zhang, B. Zhang and Z. Su, Synthesis of Hollow Ag–Au Bimetallic Nanoparticles in Polyelectrolyte Multilayers, *Langmuir*, 2013, **29**(22), 6722–6727, DOI: **10.1021**/ **la400728k**.
- 26 D. M. Dotzauer, J. Dai, L. Sun and M. L. Bruening, Catalytic Membranes Prepared Using Layer-by-Layer Adsorption of Polyelectrolyte/Metal Nanoparticle Films in Porous Supports, *Nano Lett.*, 2006, 6(10), 2268–2272, DOI: 10.1021/ nl061700q.

- 27 Z. Wang, G. Zhang, Z. Zhong, Y. Lin and Z. Su, *In Situ* Synthesis of Platinum Nanoclusters in Polyelectrolyte Multilayer Films, *Thin Solid Films*, 2018, 660, 59–64, DOI: 10.1016/ j.tsf.2018.05.051.
- 28 X. Zhang, F. Shi, X. Yu, H. Liu, Y. Fu, Z. Wang, L. Jiang and X. Li, Polyelectrolyte Multilayer as Matrix for Electrochemical Deposition of Gold Clusters: Toward Super-Hydrophobic Surface, *J. Am. Chem. Soc.*, 2004, **126**(10), 3064–3065, DOI: **10.1021/ja0398722.**
- 29 A. I. Abdelrahman, A. M. Mohammad, T. Okajima and T. Ohsaka, Fabrication and Electrochemical Application of Three-Dimensional Gold Nanoparticles: Self-Assembly, *J. Phys. Chem. B*, 2006, **110**(6), 2798–2803, DOI: **10.1021**/ **jp056238x**.
- 30 M. Vago, M. Tagliazucchi, F. J. Williams and E. J. Calvo, Electrodeposition of a Palladium Nanocatalyst by Ion Confinement in Polyelectrolyte Multilayers, *Chem. Commun.*, 2008, 5746–5748.
- 31 W. Zhang, A. Zhang, Y. Guan, Y. Zhang and X. X. Zhu, Silver-Loading in Uncrosslinked Hydrogen-Bonded LBL Films: Structure Change and Improved Stability, *J. Mater. Chem.*, 2011, 21(2), 548–555, DOI: 10.1039/c0jm02369h.
- 32 D. Lee, M. F. Rubner and R. E. Cohen, Formation of Nanoparticle-Loaded Microcapsules Based on Hydrogen-Bonded Multilayers, *Chem. Mater.*, 2005, 17(5), 1099–1105, DOI: 10.1021/cm048441v.
- 33 N. Kato, P. Schuetz, A. Fery and F. Caruso, Thin Multilayer Films of Weak Polyelectrolytes on Colloid Particles, *Macromolecules*, 2002, 35(26), 9780–9787, DOI: 10.1021/ ma0209388.
- 34 Z. Xu, C. Zhang, X. Wang and D. Liu, Release Strategies of Silver Ions from Materials for Bacterial Killing, ACS Appl. Bio Mater., 2021, 4(5), 3985–3999, DOI: 10.1021/acsabm.0c01485.
- 35 B. L. Frey; R. M. Corn and S. C. Weibel, Polarization-Modulation Approaches to Reflection-Absorption Spectroscopy, in *Handbook of Vibrational Spectroscopy*, ed. J. M. Chalmers and P. R. Griffiths, John Wiley & Sons, 2001, vol. 2.
- 36 G. Sauerbrey, Verwendung von Schwingquarzen Zur Wägung Dünner Schichten Und Zur Mikrowägung, Z. Phys., 1959, 155(2), 206–222, DOI: 10.1007/BF01337937.
- 37 M. C. Fuertes, M. Marchena, M. C. Marchi, A. Wolosiuk and G. J. A. A. Soler-Illia, Controlled Deposition of Silver Nanoparticles in Mesoporous Single- or Multilayer Thin Films: From Tuned Pore Filling to Selective Spatial Location of Nanometric Objects, *Small*, 2009, 5(2), 272–280, DOI: 10.1002/smll.200800894.
- 38 A. Fischereder, M. L. Martinez-Ricci, A. Wolosiuk, W. Haas, F. Hofer, G. Trimmel and G. J. A. A. Soler-Illia, Mesoporous ZnS Thin Films Prepared by a Nanocasting Route, *Chem. Mater.*, 2012, 24(10), 1837–1845, DOI: 10.1021/cm300395m.
- 39 E. S. Forzani, M. Otero, M. A. Pe, M. Lo and E. J. Calvo, The Structure of Layer-by-Layer Self-Assembled Glucose Oxidase and Os (Bpy)₂ ClPyCH₂ NH - Poly(Allylamine) Multilayers: Ellipsometric and Quartz Crystal Microbalance Studies, *Langmuir*, 2002, **18**(10), 4020–4029, DOI: **10.1021/la025507x**.

- 40 J. Dong, Y. Ozaki and K. Nakashima, Infrared, Raman, and Near-Infrared Spectroscopic Evidence for the Coexistence of Various Hydrogen-Bond Forms in Poly(Acrylic Acid), *Macromolecules*, 1997, **30**(4), 1111–1117, DOI: **10.1021/ma960693x**.
- 41 J. Dong, Y. Ozaki and K. Nakashima, FTIR Studies of Conformational Energies of Poly(Acrylic Acid) in Cast Films, *J. Polym. Sci., Part B: Polym. Phys.*, 1997, 35(3), 507–515, DOI: 10.1002/(SICI)1099-0488(199702)35:3 < 507::AID-POLB9 > 3.0.CO;2-O.
- 42 M. Kawaguchi, T. Hada and A. Takahashi, Displacement of Polymers by Displacers. 2. Poly(Ethylene Oxide) at the Silica Surface, *Macromolecules*, 1989, 22(10), 4045–4047, DOI: 10.1021/ma00200a038.
- 43 J. Dybal, J. Straka, B. Schneider and P. Schmidt, Structure and Interactions in Homopolymers and Blends as Studied by the Methods of Vibrational and Nmr Spectroscopy, *Macromol. Symp.*, 1995, 94(1), 19–31, DOI: 10.1002/ masy.19950940104.
- 44 L. Daniliuc, C. De Kesel and C. David, Intermolecular Interactions in Blends of Poly(Vinyl Alcohol) with Poly(Acrylic Acid)—1. FTIR and DSC Studies, *Eur. Polym. J.*, 1992, 28(11), 1365–1371, DOI: 10.1016/0014-3057(92)90277-9.
- 45 S. H. Jeon and T. Ree, Characterization of Poly(Carboxylic Acid)/Poly(Ethylene Oxide) Blends Formed through Hydrogen Bonding by Spectroscopic and Calorimetric Analyses, *J. Polym. Sci., Part A: Polym. Chem.*, 1988, 26(5), 1419–1428, DOI: 10.1002/pola.1988.080260514.
- 46 D. Lin-Vein; N. B. Colthup; W. B. Fateley and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press Inc., San Diego, CA, 1991.
- 47 I. Reviakine, D. Johannsmann and R. P. Richter, Hearing What You Cannot See and Visualizing What You Hear: Interpreting Quartz Crystal Microbalance Data from Solvated Interfaces, *Anal. Chem.*, 2011, 83(23), 8838–8848, DOI: 10.1021/ac201778h.
- 48 G. Liu and G. Zhang, Basic Principles of QCM-D. In QCM-D Studies on Polymer Behavior at Interfaces, *SpringerBriefs in Molecular Science*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2013, pp.1–8, DOI: 10.1007/978-3-642-39790-5_1.
- 49 L. Maldonado, G. Debais, F. Davia, L. P. Méndez De Leo and M. Tagliazucchi, Interpolymer Complexes of Poly(Sulfonic Acid)s and Poly(Ethylene Oxide): An Unexpected Association, *Soft Matter*, 2019, **15**(45), 9318–9324, DOI: **10.1039**/ **C9SM01768B**.
- 50 E. Kharlampieva and S. A. Sukhishvili, Hydrogen-Bonded Layer-by-Layer Polymer Films, *Polym. Rev.*, 2006, **46**(4), 377–395, DOI: **10.1080/15583720600945386**.
- 51 J. Seo, J. L. Lutkenhaus, J. Kim, P. T. Hammond and K. Char, Effect of the Layer-by-Layer (LbL) Deposition Method on the Surface Morphology and Wetting Behavior of Hydrophobically Modified PEO and PAA LbL Films, *Langmuir*, 2008, 24(15), 7995–8000, DOI: 10.1021/la800906x.
- 52 S. M. Notley, M. Eriksson and L. Wågberg, Visco-Elastic and Adhesive Properties of Adsorbed Polyelectrolyte Multilayers Determined *in Situ* with QCM-D and AFM Measurements,

J. Colloid Interface Sci., 2005, 292(1), 29–37, DOI: 10.1016/ j.jcis.2005.05.057.

- 53 U. R. Dahal, Z. Wang and E. E. Dormidontova, Hydration and Mobility of Poly(Ethylene Oxide) Brushes, *Macromolecules*, 2017, 50(17), 6722–6732, DOI: 10.1021/acs.macromol.7b01369.
- 54 S. Kawasaki and M. Kobayashi, Affirmation of the Effect of PH on Shake-Gel and Shear Thickening of a Mixed Suspension of Polyethylene Oxide and Silica Nanoparticles, *Colloids Surf., A*, 2018, 537, 236–242, DOI: 10.1016/j.colsurfa.2017.10.033.
- 55 A. van der Lee, Grazing Incidence Specular Reflectivity: Theory, Experiment, and Applications, *Solid State Sci.*, 2000, 2(2), 257–278, DOI: 10.1016/S1293-2558(00)00119-9.
- 56 N. S. Akhmadullina, A. V. Churakov, V. M. Retivov, R. A. Sandu and O. N. Shishilov, Gold(III) Chloride and Acetate Complexes with Bipyridine and Phenanthroline, *Russ. J. Coord. Chem.*, 2012, 38(9), 589–595, DOI: 10.1134/S1070328412080015.
- 57 S. K. Chatterjee, A. M. Khan, S. Ghosh and D. Yadav, Study of Multicomponent Complexes between Polycarboxylic Acid, Transition Metal Ions and Non-Ionic Polymers, *Angew. Makromol. Chem.*, 1990, **181**(1), 93–101, DOI: **10.1002**/ **apmc.1990.051810108**.
- 58 L. Q. Yang, Z. M. Xie and Z. M. Li, Studies on Coordination-Crosslinking of Soap-Free Polyacrylate Hydrosol and Metal Ion,

J. Appl. Polym. Sci., 1997, **66**(13), 2457–2463, DOI: 10.1002/ (SICI)1097-4628(19971226)66:13 < 2457::AID-APP8 > 3.0.CO;2-H.

- 59 R. Konradi and J. Rühe, Interaction of Poly(Methacrylic Acid) Brushes with Metal Ions: An Infrared Investigation, *Macromolecules*, 2004, 37(18), 6954–6961, DOI: 10.1021/ ma049126x.
- 60 P. H. McCluskey, R. L. Snyder and R. A. Condrate, Infrared Spectral Studies of Various Metal Polyacrylates, *J. Solid State Chem.*, 1989, 83(2), 332–339, DOI: 10.1016/ 0022-4596(89)90183-7.
- 61 M. Müller, L. Wirth and B. Urban, Determination of the Carboxyl Dissociation Degree and pK_a Value of Mono and Polyacid Solutions by FTIR Titration, *Macromol. Chem. Phys.*, 2021, 222(4), 2000334, DOI: 10.1002/macp.202000334.
- 62 A. S. Michaels and O. Morelos, Polyelectrolyte Adsorption by Kaolinite, *Ind. Eng. Chem.*, 1955, 47(9), 1801–1809, DOI: 10.1021/ie50549a029.
- 63 S. A. Maier, *Plasmonics: Fundamentals and Applications*, Springer, New York, 2007, vol. 1.
- 64 F. Jabeen, M. Chen, B. Rasulev, M. Ossowski and P. Boudjouk, Refractive Indices of Diverse Data Set of Polymers: A Computational QSPR Based Study, *Comput. Mater. Sci.*, 2017, 137, 215–224, DOI: 10.1016/j.commatsci.2017.05.022.

Paper