

Nanoscale Precipitation Coating: The Deposition of Inorganic Films through Step-by-Step Spray-Assembly

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Thin films and functional surfaces constitute an important field in materials science^{1–10} with applications in areas such as device engineering, corrosion protection, antistatic coatings, photovoltaics, or biosensing, to name a few. The last decades have brought the evolution of film deposition methods involving transfer through the gas phase such as physical vapor deposition (PVD), chemical vapor deposition (CVD), sputtering, and some variants. However, vacuum-based techniques are somewhat hampered because conformal coatings are often limited to small surface areas on smooth objects, because they are more difficult to integrate in production processes than solution based techniques, because they are often time-consuming and costly, or because it is highly desirable to improve the sustainability benchmarks of the corresponding products. Consequently, solvent based methods such as surface^{11,12} or more recently nanometric¹³ or spray pyrolysis¹⁴ have increasingly been investigated for the fabrication of inorganic coatings. A particularly interesting technique for producing a large variety of different inorganic films is the step-by-step dipping method or SILAR (successive ionic layer adsorption and reaction) first reported by Nicolau in 1984.^{15–17} A major advantage of the SILAR method over surface sol–gel technology is that inorganic films composed of a much wider range of inorganic components can be prepared using a single process.

One aspect of the SILAR method, the consecutive immersion of surfaces in differ-

ABSTRACT Thin films and surface coatings play an important role in basic and applied research. Here we report on a new, versatile, and simple method (“precipitation coating”) for the preparation of inorganic films, based on the alternate spraying of complementary inorganic salt solutions against a receiving surface on which the inorganic deposit forms. The method applies whenever the solubility of the deposited material is smaller than that of the salts in the solutions of the reactants. The film thickness is controlled from nanometers to hundreds of micrometers simply by varying the number of spraying steps; 200 spray cycles, corresponding to less than 15 min deposition time, yield films with thicknesses exceeding one micrometer and reaching tens of micrometers in some cases. The new solution-based process is also compatible with conventional layer-by-layer assembly and permits the fabrication of multimaterial sandwich-like coatings.

KEYWORDS: inorganic coatings · spray assembly · aqueous solutions · nucleation and growth · thin films

ent liquids, is somewhat similar to the well-known layer-by-layer (LbL)^{4,18,19} deposition of organic, polymeric, or hybrid thin films that has become attractive because of a wealth of different functionalities available for incorporation in such nanometric coatings.^{20–27} Both SILAR and LbL methods allow the construction of nanometer-sized coatings with precise thickness, but they both suffer from the same drawback, namely that the immersion of an object in a liquid and its subsequent withdrawal, especially if carried out hundreds of times in different solutions, is a time-consuming process and therefore limited to the coating of small and simply shaped objects from which the adhering liquid easily drains. Not surprisingly, multistep dipping-based methods are difficult to implement in industrial production with the possible exception of roll-to-roll processes. Inevitably, the LbL-assembly of thin multimaterial films has

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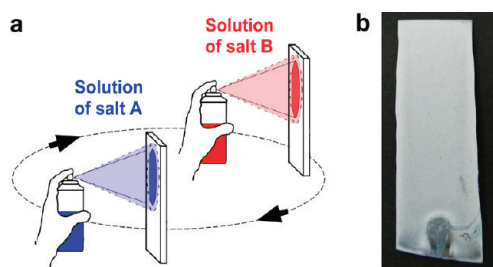


Figure 1. (a) Schematic depiction of the deposition of purely inorganic films AB from aqueous solutions by consecutively spraying solutions of the complementary salts A and B onto a receiving solid surface. (b) Optical micrograph of a film of calcium phosphate after 75 spray cycles deposited on a silicon wafer of a size of 1.5×5.0 cm. Due to its polycrystallinity and nanoporous morphology the film appears white in reflected light. Besides a mark at the bottom that originates from mounting the wafer, the film is macroscopically very homogeneous.

gained enormously from the introduction of spray-assisted deposition as reported by, for example, Schlenoff,²⁸ Winterton,²⁹ Izquierdo,³⁰ Kotov,³¹ or Hammond.³² LbL-films assembled by spray deposition can often be prepared in a fraction of the time as compared to deposition by dipping and often possess a superior homogeneity sometimes in combination with improved materials properties.

The nanoscale “precipitation coating” technique that we introduce here is based on the step-by-step spraying of solutions of complementary salts (Figure 1a) that possess a non-negligible difference of the solubility products compared to that of the solid inorganic product that forms a film on the receiving surface by precipitation due to a local supersaturation.

It is as versatile for the preparation of inorganic coatings as the SILAR method, but it is very fast and has the additional advantage that spray technology is widely accepted in industrial production. In contrast to spray-LbL which is mostly used for the assembly of polyelectrolyte and related multilayer films, it is more difficult to prevent small salt ions (such as Ca^{2+} , F^- , Cl^- , $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$) adsorbed on a surface in the previous deposition step or even nanocrystals from being washed off under the shear of the sprayed solution in the next adsorption step. It actually turns out that the subsequent removal or dissolution of previously adsorbed material is a critical factor that must, in some cases, be controlled for growing high quality films. The very short contact times of the complementary liquids attainable only by spraying against a receiving surface can clearly be shown, for example, in the case of CaHPO_4 , to be essential for precisely controlling the film growth over hundreds of spray cycles.

The consecutive spray application of solution A and solution B can be repeated hundreds of times in a few minutes to increase the thickness of the inorganic coating until a film with the desired thickness (from a few nanometers up to several micrometers or more) is obtained. It should be clear that these inorganic coatings

do not possess a multilayer structure as in the case of classic polyelectrolyte multilayer films; however, they are fabricated in the same way by employing the step-by-step assembly method as adapted to spray deposition. The following complementary salt pairs (for solubility data see Table S1 in Supporting Information) were chosen as model cases for demonstrating the fabrication of inorganic films by step-by-step spraying: (i) CaCl_2 and NaF which yields calcium fluoride (CaF_2) possessing a high UV transparency which makes it interesting for applications in optical components such as lenses, prisms or windows and because it forms very dense and rather smooth inorganic films. (ii) CaCl_2 and $(\text{NH}_4)_2\text{HPO}_4$ which yields calcium phosphate (CaHPO_4), a material that has wide ranging applications in the biomedical field, for example for bone reconstruction. (iii) $\text{Ca}(\text{NO}_3)_2$ and $\text{Na}_2\text{C}_2\text{O}_4$ which yields calcium oxalate (CaC_2O_4) serving as an example for the use of a carbon-based anion.

RESULTS AND DISCUSSION

Preparation of Inorganic Films by Spray Deposition. The spray-assembly of inorganic films—a typical sample is shown in Figure 1b—was carried out by using conventional air pump spray cans equipped with single-component nozzles. We refer to a spraying cycle (A/B)₁ as a process consisting of the spraying of a component A for about 2 s followed by spraying of a component B for about 2 s. The desired spray cycles can be repeated *n* times to form (A/B)_{*n*} films. Prior to the deposition of the inorganic films the receiving surface was coated with at least one polyelectrolyte layer to promote its adhesion, in some cases the receiving surface was coated with a LbL-film of collagen and poly(styrene sulfonate) (COL/PSS)₈ with a thickness of about 10 nm because the combination of calcium phosphate with collagen has a certain interest for the reconstruction of bone or cartilage. However, the deposition of inorganic films does not require the presence of collagen in the layer underneath, and similar films can be prepared on many other types of surfaces.

While the first spraying step only leads to the formation of a thin liquid film of solution A, the subsequent spraying step of solution B “into” the draining film of solution A leads to a reaction between both complementary salt solutions. If the solutions of the two complementary starting materials (*e.g.*, CaCl_2 and NaF) are chosen such that the resulting reaction product (in this case CaF_2) becomes supersaturated in the liquid film close to the surface of the solid, nucleation will start and germs close to the surface will, depending on the chemical nature of the surface, attach to it. However, since solution B was sprayed last it will, depending on the sprayed volume, now be in excess and the subsequent spray application of solution A will again produce a supersaturated solution of the reaction product (in this case CaF_2). Starting with the third spray application, nucleation is either starting as before or induced

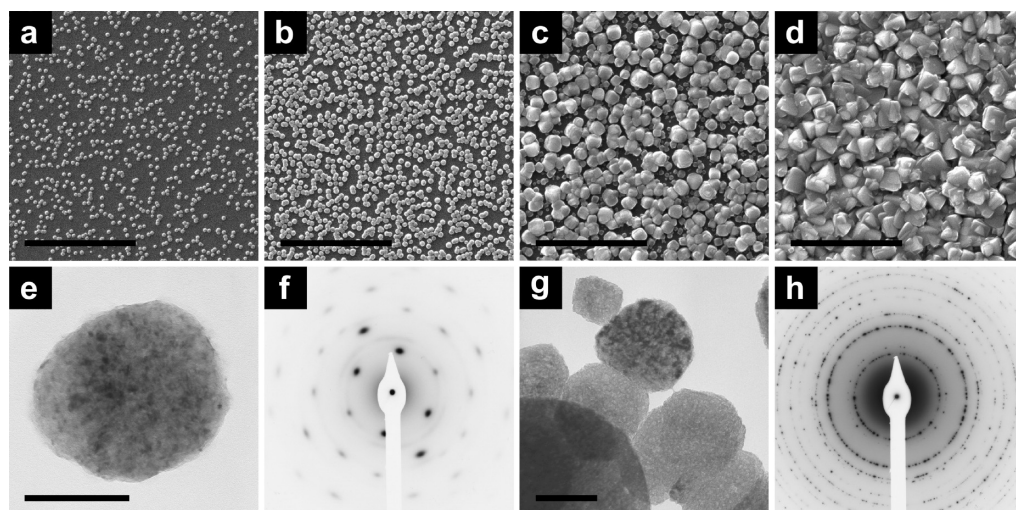


Figure 2. Top view scanning electron micrographs of films composed of CaF_2 (a–d) at various stages of film growth. The numbers of spray cycles for each sample are as follows: 3 (a), 10 (b), 50 (c) and 200 (d). The scale bar represents 10 μm . Electron micrographs and diffraction patterns were obtained by transmission electron microscopy from CaF_2 crystals after one cycle (e, f) and three cycles (g, h). Scale bars represent 100 nm for image e and 200 nm for image g.

by crystals already attached to the surface thus accelerating the growth of the inorganic film.

Films of all different materials were spray-assembled up to a given thickness by adjusting the number of deposition cycles, dried in a stream of air or nitrogen, and then characterized. The chemical composition and crystalline phase of the components were determined by electron and X-ray diffraction by comparison with known data (see Tables S2–S4 and Figure S1 in Supporting Information). The alternate spraying of CaCl_2 and NaF yields fluorine films (CaF_2), the spraying of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ yields calcium phosphate films (brushite, CaHPO_4), and the spraying of CaCl_2 and $\text{Na}_2\text{C}_2\text{O}_4$ yields calcium oxalate films (CaC_2O_4).

Dense Polycrystalline Films: Spray Deposition of Calcium Fluoride Films. For CaF_2 , scanning electron microscopy (SEM) revealed that the film growth starts by the forma-

tion of nanocrystals with a very small lateral density (Figure 2a). By increasing the number of spray cycles, the size and density of crystals increases until most voids are filled and layer growth proceeds predominantly along the layer normal (Figure 2a–d). Transmission electron microscopy (TEM) and electron diffraction show that in the case of CaF_2 the smallest observable crystals (about 70 nm) are monocrystalline (Figure 2e,f) which further increase in size (Figure 2b–d) and become polycrystalline (Figure 2g,h).

Porous Polycrystalline Films: Spray Deposition of Calcium Phosphate and Oxalate Films. In the case of CaHPO_4 , the film growth proceeds by nucleation of additional small crystals rather than by crystal growth (Figure 3a–d) which also leads to more porous film morphology. In contrast to CaF_2 , even the smallest crystals are polycrystalline (Figure 3e,f) as evidenced by the circular diffrac-

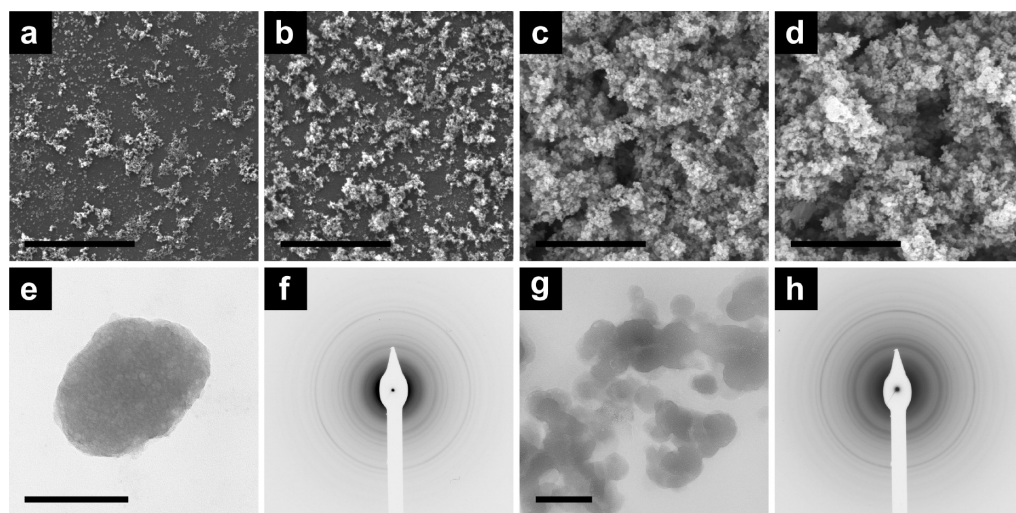


Figure 3. Top view scanning electron micrographs of films composed of CaHPO_4 (a–d) at various stages of film growth. The numbers of spray cycles for each sample are as follows: 3 (a), 10 (b), 50 (c) and 200 (d). The scale bar represents 10 μm . Electron micrographs and diffraction patterns were obtained by transmission electron microscopy from CaHPO_4 crystals after one cycle (e, f) and three cycles (g, h). Scale bars represent 100 nm for image e and 200 nm for images g.

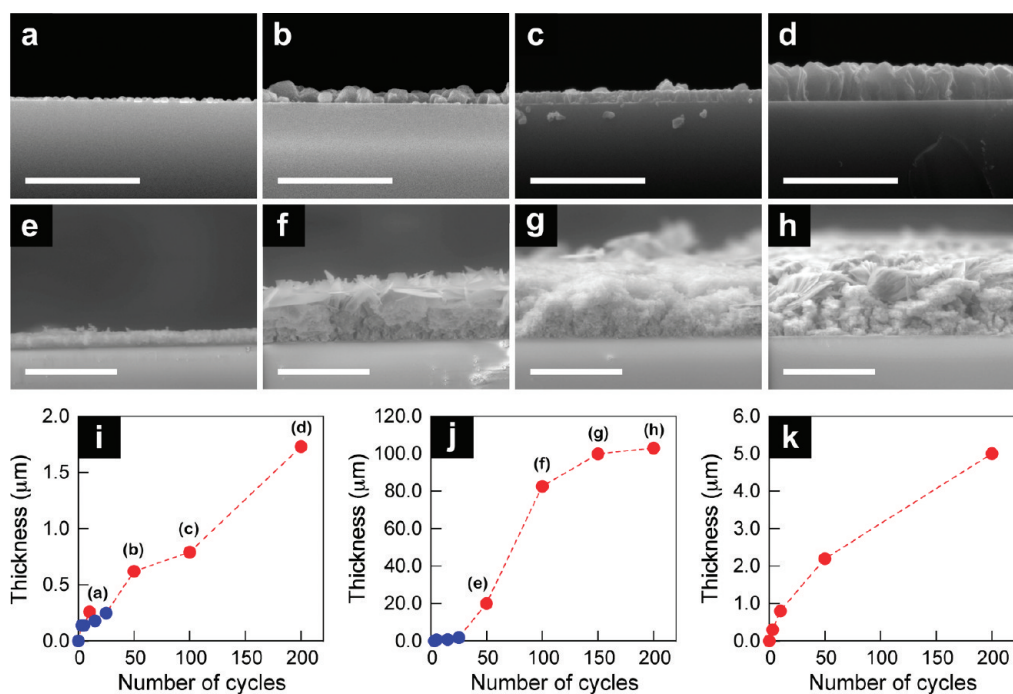


Figure 4. Side-view scanning electron micrographs of films composed of CaF₂ (a–d) and CaHPO₄ (e–h) at various stages of film growth. Evolution of the thickness of (i) CaF₂, (j) CaHPO₄, and (k) Ca₂O₄ films versus the number of spraying cycles. Thicknesses were determined either by AFM (scratch of the coating: blue circles) and SEM side-view (red circles). The numbers of spray cycles for each sample are as follows: 10 (a), 50 (b, e), 100 (c, f), 150 (g), and 200 (d, g). The scale bars represent 5 μm for (a–d) and 100 μm for (e–h). Dotted lines are guides.

tion pattern. Please note that the high magnification in Figure 3d leaves the impression of a rather irregular film morphology. However, Figure 1b and Figure S2 clearly underlines the good film homogeneity at a larger scale. The same porous morphology of Ca₂O₄ films was observed (see Figure S3 in Supporting Information).

Analysis of Film Growth. Because of the large range of attainable film thicknesses to the solution-based deposition and to the polycrystalline and porous nature of the films, it was impossible to characterize the film thickness by some of the usual methods such as ellipsometry or quartz crystal microbalance. Film thicknesses were therefore determined by AFM (below 200 nm) and SEM (up to the 100 μm range) (Figure 4) and also estimated by UV–vis spectrophotometry (Figure 5).

From left to right in the case of CaF₂ (Figure 4a–d) and CaHPO₄ (Figure 4e–h), one clearly observes the increasing film thickness with an increasing number of

spray cycles. In all cases presently investigated, films reached a thickness above 1 μm after 200 spray cycles (Figure 4i–k). In the case of CaHPO₄ a thickness of about 1 μm is reached after a few spray cycles and film growth leveled off at a thickness of about 100 μm. All three cases show that the thickness of the inorganic films is controlled by the number of spray cycles.

Factors Controlling Film Growth. Depending on the exact chemical composition of each pair of complementary salts, a second control mechanism becomes important: the control of contact times and thus the speed by which one solution can be replaced by the following complementary one. As we show in Figure 5 the spraying time has a strong influence on the buildup of inorganic films. While in the case of CaF₂ (Figure 5a) a spraying time of 2 s leads to films with twice the absorbance (corresponding approximately to twice the thickness) as compared to films sprayed for 1 s, the thickness of films of Ca₂O₄ are almost independent of spraying

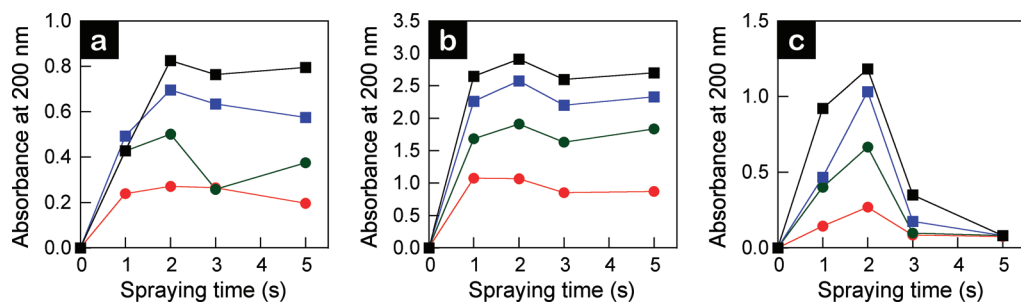


Figure 5. Evolution of the absorbance measured by UV at 200 nm versus spraying time of (a) CaF₂, (b) Ca₂O₄, and (c) CaHPO₄ coatings after 5 (red), 10 (green), 15 (blue), and 20 (black) cycles. Solid lines are guides.

times above 1 s (Figure 5b). CaHPO_4 films even start to redissolve at spraying times longer than 2 s (Figure 5c).

It is evident that in cases in which a fast switching between complementary solutions is required to prevent the redissolution of the film, spraying is the sole method applicable to create such coatings, since the whole surface of a substrate can almost simultaneously be exposed to the spray cone from the third dimension. In contrast, the immersion of a substrate into a liquid always leads to a distribution of contact times along the dipping direction except for a roll-to-roll process, which can only be used with foils and similar soft substrates. The observed redissolution of some inorganic films at longer contact times (Figure 5c) may be due to two different phenomena, the effects of each of which can equally and effectively be reduced at short spraying times. For films of inorganic salts composed of weakly adhering crystals, the draining liquid exercises a sufficient drag for removing poorly sticking crystals mechanically. For films in which the final inorganic product is partially soluble in one of the two solutions of the complementary starting materials, previously formed crystals can also partly or completely be redissolved.

Toward Multimaterial and Sandwich Films. The “precipitation coating” technique described above is also compatible with the classic LbL-assembly of polyelectrolytes and can be used for the fabrication of multimaterial sandwich films. Figure 6 shows profiling information obtained by confocal Raman microspectroscopy along the layer normal of a film prepared by 100 spray cycles of calcium oxalate followed by 100 spray cycles of calcium fluoride.

Despite of the limited spatial resolution it is evident that the film is rich in calcium oxalate at the bottom

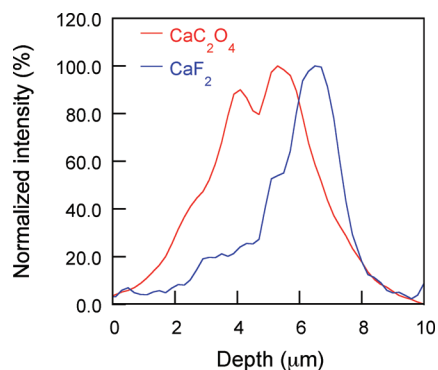


Figure 6. Depth profile for a $\text{PEI}-(\text{CaC}_2\text{O}_4)_{100}-(\text{PSS}/\text{PAH})_5-(\text{CaF}_2)_{100}$ hybrid film visualized as the intensities of the Raman bands of calcium oxalate (red line) at 1478 cm^{-1} and calcium fluoride (blue line) at 312 cm^{-1} as obtained by confocal Raman microspectroscopy. For each band, the intensity was normalized by attributing the value 100% to the maximum intensity.

and rich in calcium fluoride at the top. Because of its versatility and simplicity, we anticipate the “precipitation coating” technique to become a method of wide use for the preparation of inorganic nanoscale coatings. At the present time we have not yet optimized the materials properties of our new films with respect to evaluating their potential for application in devices. However, we do believe that our step-by-step spray process could become relevant for some applications because it does not seem to depend much on the shape and size of the receiving surface. Further, our method opens the possibility to fabricate films of hybrid precipitates by spraying more than one complementary component in each spraying step.

METHODS

Materials. Collagen (COL, batch: 07CBPE2040) was purchased from SYMATESE (Grenoble, France). Poly(ethylene imine) (PEI, $M_w = 700\,000\text{ g/mol}$), poly(styrene sulfonate) (PSS, $M_w = 70\,000\text{ g/mol}$), calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and Trizma hydrochloride (T32253) were purchased from Sigma Aldrich. Sodium acetate (CH_3COONa , aqueous 3 M solution), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), sodium fluoride (NaF), and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) were purchased from Fluka. Calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and acetic acid (CH_3COOH) were respectively purchased from Carlo Erba Reagents and VWR Prolabo. All the products were used without further purification. The salt solutions were prepared in ultrapure water (Milli-Q Gradient System, Millipore) with a resistivity of $18.2\text{ M}\Omega \cdot \text{cm}$. PEI solutions were prepared at a concentration of 2.5 mg/mL in Milli-Q water. One liter of acetate buffer (pH = 4) was prepared from acetic acid (8.1 mM), sodium acetate (1.8 mM), and NaCl (154 mM). COL solutions were prepared at a concentration of 0.2 mg/mL in acetate buffer at pH 4 where it is positively charged. PSS solutions were prepared at a concentration of 1 mg/mL in 0.15 M NaCl at pH 6.5. For calcium phosphate (CaHPO_4) synthesis, a calcium solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.32 M) and a phosphate solution of $(\text{NH}_4)_2\text{HPO}_4$ (0.19 M) were prepared in Tris buffer (10 mM Trizma, pH = 10). Calcium fluoride (CaF_2) was synthesized from a solution of CaCl_2 ($2 \times 10^{-2}\text{ M}$) and NaF ($2 \times 10^{-2}\text{ M}$) prepared in Milli-Q water. Calcium oxalate (CaC_2O_4) was prepared using

NaC_2O_4 (10^{-1} M) and CaCl_2 ($2 \times 10^{-1}\text{ M}$) prepared in Milli-Q water.

Inorganic Spray Assembly. The spray deposition was carried out by using air pump spray cans (“Air Boy”) made of polypropylene and polyethylene purchased from Roth (reference number: 0110.1) with a height of 217 mm and a diameter of 55 mm; equipped with a nozzle of 0.40 mm). Each can was filled with the respective salt solution and then pressurized by pumping cycles in such a way that the spray rate remained approximately constant over the entire film deposition process. The spray rate was determined to be about 0.6 mL/s with pump flasks as they were received from the manufacturer. Spraying was carried out perpendicularly to the receiving surface which was fixed in a vertical orientation. Inorganic salt solutions were alternately sprayed for 2 s unless otherwise stated until the desired number of cycles. After a rest time of 60 s, a rinsing step with Milli-Q-water of $5 \times 1\text{ s}$ using the spraying bottles was applied to the inorganic film.

LBL-Multilayer Films. All the films were built on glass slides of 12 mm diameter (VWR, Fontenay sous Bois, France), silicon wafers (100) (Wafernet, Inc., San Jose, CA), or quartz plates (665.000-QS, HELMA, Paris, France) of the same size, previously cleaned for 1 h in a 1:1 mixture of CH_3OH and HCl, then cleaned with a H_2SO_4 solution (>1 h), and rinsed extensively with ultrapure water. The buildup of multilayer films by the spray technology consisted in the sequential spraying of the polycation (COL) and of the polyanion (PSS) solutions perpendicularly to the substrate in vertical position to allow the drainage of the solution, using com-

mercial paintbrushes (Airbrush 134) from SEDIP (Poncarrré, France) equipped with two-component nozzles with a diameter of 0.3 mm and operated at an air pressure of 1 bar. Each polyelectrolyte solution (COL or PSS) was sprayed onto the substrate surface for 5 s. After a rest time of 15 s, we rinsed with Milli-Q-water for 5 s. Finally, after a further rest time of 15 s, the deposition of the next polyelectrolyte layer followed the same sequence. Thereby, the deposition of a layer pair was achieved in 60 s. The obtained film is denoted (COL/PSS)_n after the deposition of *n* COL/PSS pairs of layers.

Transmission Electron Microscopy. The particle size of the inorganic crystals in films at various stages of growth was determined by transmission electron microscopy (TEM, Philips CM200) while their crystalline structure was studied by electron diffraction (ED) operating the instrument in the low-dose mode at 200 kV accelerating voltage. Images were taken with a numerical camera (Gatan, Orius 1000). The resolution of this setup is about of 0.2 nm.

Environmental Scanning Electron Microscopy. Side-views of the cross sections of the inorganic coatings were obtained by environmental scanning electron microscopy (ESEM, FEI Quanta 400) after appropriately cutting the corresponding coated glass substrate.

UV-Visible Spectroscopy. (UV-vis). UV-vis absorption spectra of inorganic layers were recorded on a Varian Cary 500 scan spectrometer on a quartz slides. The quartz slides were first cleaned with a 2% Hellmanex solution and then thoroughly rinsed with water. The polycrystallinity and sometimes the porosity of the films caused non-negligible light scattering and only allowed the monitoring of the absorbance up to a limited thickness of the coatings.

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Supporting Information Available: Table of solubility of investigated inorganic compounds, tables of observed and expected *d* spacings of CaF₂, α-C₂CaOα and Ca₅(PO₄)₃(OH) crystals, X-ray diffraction pattern of CaHPO₄ obtained by spraying, top view scanning electron micrographs of films composed of CaHPO₄ after 100 spray cycles and top view and side view scanning electron micrographs of films composed of CaC₂O₄ at various stages of film growth. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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