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Deposition of aminomalononitrile based films: kinetics, chemistry, and morphology

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Abstract:

In the last few years, the development of versatile coating chemistries has become a hot topic in surface science after the discovery that catecholamines can lead to conformal coatings upon oxidation from aqueous solutions. Recently, it was found that aminomalononitrile (AMN), a molecule implicated in the appearance of life on earth, is an excellent prototype of novel material-independent surface functionalizing agents leading to conformal and biocompatible coatings in a simple and direct chemical process from aqueous solutions. So far, very little insight has been gained regarding the mechanisms underlying coating deposition. In this paper we show that the chemical evolution of AMN film deposition under slightly basic conditions is different in solution and on silica. Thereon, the coating proceeds via a nucleation process followed by further deposition of islands which evolve to produce nitrogen-rich superhydrophilic fibrillar structures. Additionally, we show that AMN-based material can form films at the air-solution interface from unshaken solutions. These

results open new vistas into the chemistry of HCN-derived species of potential relevance in materials science.

Introduction

The seminal experiments by Stanley Miller and coworkers aimed at mimicking prebiotic chemical processes in the presence of electrical discharges¹ have disclosed a complex and fascinating chemical scenario relating to the ability of hydrogen cyanide (HCN) produced by an energy supply in a methane-ammonia-hydrogen and water-containing atmosphere to polymerize to form dimers (aminocyanocarbene), trimers (aminomalononitrile, AMN)², tetramers (diaminomalononitrile) and many other oligomers³. HCN-derived molecules can lead to diverse imidazole derivatives³, to purines at low temperature⁴ and to peptides⁵ under basic reaction conditions. In this latter case, the reaction leads to a complex mixture of soluble molecules and a polymer-like precipitate. Such molecules and materials are thought to be ubiquitous throughout the universe, and are found e.g. in the ice of comets and on Titan, the largest moon of Saturn⁶. These findings raised a plethora of issues regarding the mechanisms responsible for the appearance of life on early earth and their relevance to a “prebiotic soup” or to extra-terrestrial contexts. Very recently, attention shifted to the observation that the reddish-brown polymeric material derived from AMN salt containing solutions can adhere to almost all known classes of materials⁷. The kinetics of film deposition are accelerated when aldehydes, particularly phenolic aldehydes, are added to the AMN salt solution⁸. The autopolymerization process enabling these coatings has established trimers of HCN as members of a class of reactive molecules, along with catecholamines⁹⁻¹² and polyphenols^{13, 14}, that are able to coat a vast repertoire of surfaces. As with polydopamine⁹ based coatings, those made from AMN are amenable to secondary functionalization⁷. In addition, the biocompatible AMN based films are potentially useful for a broad range of biomedical and sensing applications⁸. However, their deposition mechanism is totally

unknown. In this paper we investigated the influence of AMN concentration at a constant pH of 8.6 ± 0.1 on the deposition kinetics and physical properties, namely the morphology and water wettability, of AMN based films. The main outcomes of the study include the identification of a lag phase preceding fast and concentration-dependent film deposition, the demonstration of spontaneous formation of self-assembled fibrils at the solid-liquid interface, verification of marked changes in the composition of AMN based films versus bulk material in the mixture, and the characterization of films produced at the liquid-air interface in comparison to their counterparts deposited from solution on solid substrate surfaces.

Materials and methods

Chemicals

Aminomalononitrile-*para*-toluenesulfonate (AMN, ref. 221147), sodium hydrogen phosphate (ref. S-9638) and potassium hexacyanoferrate (ref. P9387) were all purchased from Sigma-Aldrich and used without further purification. All solutions were made from double-distilled and deionized MilliQ water ($\rho = 18.2 \text{ M}\Omega\cdot\text{cm}$, Millipore). AMN was dissolved in 50 mM sodium phosphate buffer at pH = 7.5 at concentrations ranging from 5 to 40 $\text{mg}\cdot\text{mL}^{-1}$ corresponding to molar concentrations ranging from 19.7 mM to 158 mM. In all cases, the dissolution of AMN produced a significant concentration dependent reduction in pH which stabilized AMN. The reaction was triggered by adjusting the pH to 8.6 ± 0.1 with a concentrated sodium hydroxide solution. Immediately after pH adjustment, samples to be covered with a coating were immersed in the AMN solution. The pH of all solutions was measured with a three point calibrated Hi221 pH meter (Hanna Instruments).

Substrate materials

AMN films were deposited on quartz, glass and silicon wafer samples, for characterization by means of UV-Vis spectroscopy, Langmuir-Blodgett transfer and ellipsometry, respectively.

All of these substrates were cleaned in the same manner, just before deposition of the AMN based films. They were rinsed with ethanol, dried with a filtrated air flow and subjected to 15 min of O₂ plasma cleaning (PDC-32G-2, Harrick Scientific, USA).

Amorphous carbon working electrodes (CHI ref. 104 from CHI instruments, Austin, Texas) previously polished on a silicon carbide (SiC) disk were further polished using alumina (Al₂O₃) slurries (Escil, France) with a grain size of 1.0 μm and 0.1 μm, respectively. Then, the electrodes were successively sonicated in two separate water baths for 2 min each. The efficiency of this cleaning method was tested by measuring the faradaic current in the presence of 1.0 mM potassium hexacyanoferrate (K₄Fe(CN)₆) dissolved in 50 mM sodium phosphate buffer. The quality of the electrodes was checked upon measurement of the difference of the potentials corresponding to the oxidation and the reduction peak currents. Only electrodes in line with a potential difference lower than 80 mV were selected for further experiments, recalling that the expected theoretical value for a reversible one electron transfer process at 25 °C is 59 mV.

UV-Vis spectroscopy

UV-Vis spectra (wavelength ranging from 200 to 750 nm) of the AMN based films deposited on quartz slides were obtained against a pristine cleaned quartz slide as a reference using a double beam mc² spectrophotometer (Safas, Monaco, France). The same spectrophotometer was used to measure the spectra of AMN containing solutions after different reaction times and appropriate dilution with sodium phosphate buffer, using the same buffer as the reference. The solutions were contained in ethanol cleaned and dried quartz cuvettes with an 1 cm optical path (Thuét, Blodeslheim, France).

Ellipsometry

The AMN based films deposited for a reaction time t on freshly cleaned silicon substrates (featuring a naturally grown SiO₂ layer about 2 nm in thickness) were characterized

by constant wavelength (632.8 nm) ellipsometry at a constant angle of incidence (70°) using a PZ 2000 ellipsometer (Horiba, France). For the calculation of the film thickness from the measured ellipsometric angles, the real part of the refractive index was fixed to 1.6 whereas its imaginary part was fixed equal to 0 owing to the film transparency (Figure S1) at the used wavelength. The given thickness values are the average of 5 measurements ($\pm$ one standard deviation) on regularly spaced spots along the major axis of the silicon wafer.

Quartz crystal microbalance with dissipation monitoring (QCM-D)

The film deposition kinetics were monitored *in situ* under a constant flow of AMN solution (0.25 mL.min⁻¹) with a QCM-D E1 device (QSence AB, Göteborg, Sweden). The substrates were freshly cleaned silica coated quartz crystals (ref: QSX303, QSence AB). The silica coating was performed by the furnisher using a sol-gel deposition method.

The deposition of molecules on a piezoelectric crystal is accompanied by changes in its resonance frequency and energy dissipation in the surrounding medium¹⁵. The changes in resonance frequency during AMN deposition were monitored at the 3rd, the 5th and the 7th harmonic of the quartz crystal, but only the frequency changes recorded at the 3rd harmonic are represented for clarity.

X-ray photoelectron spectroscopy (XPS)

The analysis of the AMN coated glass slide was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical, Manchester, UK) with a monochromated Al K α source at a power of 168 W (14 kV $\times$ 12 mA), a hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture. The sample analysis area was 0.3 mm $\times$ 0.7 mm. Survey spectra were obtained at a pass energy of 160 eV. CasaXPS processing software version 2.3.15 (Casa Software Ltd., Teignmouth, UK) was used to perform data processing, with all elements present being identified from survey spectra. Calculation of the atomic

concentrations of the detected elements were derived from integral peak intensities and the sensitivity factors supplied by the manufacturer.

Scanning electron microscopy (SEM)

SEM images were acquired by a ZEISS Gemini SEM 450 (ZEISS, Germany) at an acceleration voltage of 5 kV. Energy-dispersive X-ray spectroscopy (EDS) was carried out with an X-Max EDS system (Oxford Instruments, Oxford, UK) at an acceleration voltage of 15 kV. The AMN coated glass slides were mounted on an aluminium stub with carbon tape and coated with iridium using a Polaron range SC5750 sputter coater. The iridium coating was performed for 45 s at 50 mA yielding a coating thickness of approximately 20 nm.

Atomic force microscopy (AFM)

AMN based films deposited on silicon wafers from $10 \text{ mg}\cdot\text{mL}^{-1}$ AMN solutions were rinsed with distilled water and dried under a stream of filtered air before imaging in the contact mode with a MLCT-C cantilever (nominal spring constant = $10 \text{ mN}\cdot\text{m}^{-1}$) using a Nanoscope III atomic force microscope (Bruker, Mannheim, Germany). Images were analysed with the Nanoscope Analysis software after flattening to determine the mean squared roughness of the AMN based films.

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was performed with a CHI 604B potentiostat (CHI Instruments, Austin, Texas) at a constant direct potential of +0.283 V vs. the Ag/AgCl reference electrode, corresponding to the oxidation potential peak of $\text{K}_4\text{Fe}(\text{CN})_6$ on the pristine carbon electrode. This potential was superimposed with a sinusoidal potential 5 mV in amplitude with a frequency varying between 10^5 and 10^{-2} Hz. 12 measurements were made in each frequency decade. The obtained Nyquist plots, the opposite of the imaginary part of the impedance ($-Z''$) plotted as a function of the real part of the impedance (Z'), were analyzed using the “eisanalyzer” software, freely available on the internet. These plots could

be fitted with a Randles equivalent circuit to yield the films' electrical resistance and their Warburg impedance, characterizing the diffusion of the redox probe through the AMN based coating¹⁶.

Contact angle measurements

For static water contact angle measurements, 5 μL of distilled water was put on the surface of AMN based films deposited on plasma cleaned quartz slides. The contact angle was measured after 10 s using an Attension Theta goniometer (Biolin Scientific, Sweden). At least ten measurements were averaged to get a reliable value.

Langmuir-Schaeffer transfer of AMN based films from the liquid-air interface

AMN films were grown for 16 h or 23 h at the liquid-air interface from a $10 \text{ mg}\cdot\text{mL}^{-1}$ AMN solution. Part of the film was aspirated by a pipette and a cleaned glass slide mounted horizontally on a sample holder was immersed below the freshly created uncovered liquid-air interface, starting from the freed interface. The slide was put below the apparent AMN film and the sample holder was removed in the upwards direction with a speed of $0.002 \text{ cm}\cdot\text{s}^{-1}$. The films were then rinsed thoroughly with pure water and dried under a flow of filtered air.

Results and discussion

AMN based film deposition was first investigated on quartz slides as a function of AMN salt (see the structure in the inset of Figure 1B) concentration from 5 to $40 \text{ mg}\cdot\text{mL}^{-1}$ (Figure 1A) in phosphate buffer at an initial pH equal to 8.6 ± 0.1 . Following absorbance changes with time at a wavelength of 423 nm, where a broad peak is apparent in the spectra of the coatings (Figure SI 1), two major observations were made:

- (i) A lag phase lasting over a few hours during which almost no film deposition can be detected spectroscopically (Figure 1A). The duration of this lag phase decreases as the initial concentration of AMN increases. At an initial concentration of 5

$\text{mg}\cdot\text{mL}^{-1}$ AMN, the lag phase duration was longer than 5 h, whereas it was less than 1 h at $40 \text{ mg}\cdot\text{mL}^{-1}$ AMN. The occurrence of such a lag phase was also apparent from film thickness measurements by ellipsometry on silicon wafers at different deposition times. (Figure S2). This behavior strongly suggested that a heterogeneous nucleation phase is required to initiate the deposition of AMN based films.

(ii) Following the lag phase, an almost linear increase in film absorbance with time did occur. The slope of this increase rose with initial AMN concentration (Figure 1B) in a rather complex manner, suggesting a film growth process in the steady state not compatible with first order kinetics with respect to the monomer.

It should be noted that the coating obtained after short reaction times looked homogeneous on the length scale of the quartz slide, as shown by optical pictures of the films (inset in Figure 1B), whereas for longer reaction times and particularly at the higher AMN concentrations, the films deposited on the quartz slides appeared darker close to the liquid-air interface (see Figure 6D). For this reason, the absorbance data reported in Figure 1 were taken at 1 cm above the lowest part of the immersed quartz slide. This observation suggests that the reaction rate is faster at the liquid-air interface than in the deeper parts of the medium. It cannot be excluded that dissolved O_2 plays a role in the chemical pathway leading to the AMN coating. It should be noted that the same observation is made when polydopamine is deposited on quartz slides from oxygenated dopamine solutions at pH 8.5¹⁷.

Figure 1:

A: Time evolution of the absorbance at $\lambda=423$ nm (See Figure SI1) of AMN based films deposited on quartz slides at different concentrations of AMN: 5 (●), 10 (●), 20 (●) and 40 (▲) $\text{mg}\cdot\text{mL}^{-1}$. The dashed lines are aimed to guide the eye and their extrapolation to the time axis yields the induction period preceding the deposition of the AMN based films.

B: Time evolution of the absorbance at $\lambda=423$ nm of AMN based films deposited on quartz slides at different concentrations of AMN: 10 (●), 20 (●), 30 (■) and 40 (▲) $\text{mg}\cdot\text{mL}^{-1}$. The full lines correspond to linear fits to the data allowing to estimate the growth rate of the AMN based films after the initial lag phase. The inset represents a picture of a coated quartz slide after 5 h of deposition from a 10 $\text{mg}\cdot\text{mL}^{-1}$ AMN solution. The structure of the *para*-toluenesulfonate salt of AMN is also given.

C: Growth rate of the AMN based films as determined from the slopes of the straight lines in Figure 1B. The dashed line is aimed to guide the eye.

Deposition kinetics reported in Figures 1A and 1B were determined from separate experiments, after washing the quartz slides with water and drying. A similar experimental procedure is relevant for film thickness analysis by means of single wavelength ellipsometry (Figure S2). To circumvent possible artifacts connected with discontinuous film growth monitoring, the deposition kinetics of AMN based films were followed *in situ* and in real time by means of quartz crystal microbalance with dissipation monitoring (QCM-D). These QCM-D experiments were performed on silica coated quartz crystals (Figure 2), a substrate very close in composition to the quartz slides used for the UV-vis spectroscopy experiments and to the silicon oxide film covering the silicon wafers used in ellipsometry. As in previous experiments, steady state growth of the films was preceded by an AMN concentration-dependant lag phase. Moreover, it was confirmed that the deposition kinetics (ie the rate of

decrease of the resonance frequency of the quartz crystal) increased markedly with the initial monomer concentration (Figure 2A). In addition, as noted earlier in the case of the optical spectroscopy experiments, the deposition rate in the steady state deposition regime scales in a complex manner with the initial AMN concentration (Figure 2B).

Figure 2:

A: Frequency changes measured on a silica coated quartz crystal in contact with flowing AMN solutions at different concentrations in AMN: 5 (—), 10 (— 2 independent experiments), 20 (—) and 40 (—) $\text{mg}\cdot\text{mL}^{-1}$. For clarity, only the frequency changes at the third overtone of the quartz crystal are represented. The dashed lines correspond to linear fits of the data.

B: Evolution of the AMN film growth rate (obtained from the slopes of the straight lines in Figure 2A) as a function of the initial AMN concentration in solution. The dashed line is aimed to guide the eye.

It has to be noted that the reproducibility of the deposition experiments (see dispersion of the data points in Figure 1A and the 2 deposition experiments performed at $10 \text{ mg}\cdot\text{mL}^{-1}$ in Figure 2A) was of the order of $\pm 25\%$, hence good but not excellent. This may have its origin in a extremely strong temperature and or pH dependence of the deposition process. This moderate reproducibility, already observed in the deposition of polydopamine films¹², will be considered in future studies.

In order to check the versatility of this coating method with respect to the chosen substrate, additional deposition experiments were performed using gold coated quartz crystals (the experiments in Figure 2 were performed on silica coated quartz crystals). In those experiments, the resonance frequency of the quartz crystals initially increased when put in contact with the AMN containing solution, followed by a steady state decrease in resonance frequency. Since the crystals were black after a few hours of contact with a 10 mg mL^{-1} AMN solution (initial pH = 8.6), film deposition on gold also appeared to occur as reported in a previous study⁷. The initial frequency increase of the quartz crystal is extremely instructive with respect to the film deposition mechanism: it has been established that cyanide anions

(CN⁻) induce dissolution of gold according to a cyanidation process¹⁸. Hence, the initial frequency increase on a gold substrate strongly suggests dissolution of the gold coating as CN⁻ is released upon the reaction of AMN at pH = 8.6. This initial frequency increase on the gold coated quartz crystal is then followed by the polymerisation of AMN to yield a polymeric film on the substrate and a coloured solution, corresponding to the steady state decrease in frequency.

In addition, the pH of the solution slightly decreases during the reaction, thus implying proton release from AMN during the polymerisation process. A typical example of pH decrease with reaction time is illustrated for a 10 mg mL⁻¹ solution in Figure S3.

Next, the wettability of the AMN based films deposited on plasma cleaned quartz slides was investigated as a function of both the initial AMN concentration and reaction time. For all the investigated concentrations, the water contact angle increased from almost zero for the plasma cleaned and pristine glass to a maximal value close to 40° before decreasing again at longer deposition times to reach a superhydrophilic state (Figure 3A). Some pictures displaying the contact angles 10s after deposition of the water droplet are given in the supporting information (Figure S4). In the present study contact angles were measured immediately after the end of the deposition process, deviating from measurements described in a previous paper in which the contact angles were measured 24 h after the deposition process⁷. The faster film deposition kinetics found at higher AMN concentrations (Figures 1 and 2) probably explains a faster transition from moderately hydrophilic coatings to superhydrophilic coatings when the initial AMN concentration is increased. This is apparent when comparing the films obtained from 40 and 20 mg.mL⁻¹ in AMN: after 5 h of deposition the former ones are already superhydrophilic whereas the later ones still display a water contact angle close to 40°.

The superhydrophilic state that was observed in this study could be due to a simultaneous effect of the change in chemical composition and surface roughness¹⁹. To that end, the film morphology and its composition were investigated. Scanning electron microscopy (SEM) images (Figure 3B) as well as surface topographies obtained by atomic force microscopy (AFM) (Figure 3C) showed a gradual transition from islands, not covering the whole area of the substrate, to fibrillar structures covering the entire substrate. These remarkable structures, obtained in the absence of any templating agent, were about 50 nm in diameter and could be micrometers in length.

A

B

C

Figure 3A : Static water contact angles of AMN based coatings as a function of time for different AMN concentrations : 5 (●), 10 (●), 20 (●) and 40 (●) mg·mL⁻¹. The black dashed lines are aimed to represent the evolution of the water contact angle with the deposition time.

B: Film morphology of AMN based coatings after 1 and 19 h of deposition from a 10 mg·mL⁻¹ AMN solution as obtained by SEM.

C: Film morphology of AMN based coatings after 1 h and 19 h of deposition from a 10 mg·mL⁻¹ AMN solution as obtained by contact mode AFM. The image size is 2 μm x 2 μm.

The root mean squared roughness of these films are 1.2 and 17 nm after 1 h and 19 h of deposition, respectively.

The films roughness markedly increases during the deposition process (Figure 3C) and this can markedly change the apparent water contact angle according to Wenzel's law ²⁰. However to explain the change in film wettability its composition during the deposition process needs also to be investigated.

Hence X-ray photoelectron spectroscopy (XPS) experiments were performed to characterize the film composition. Survey spectra at 1 h and 19 h deposition times are shown in Figure S5. The atomic percentage of silicon, owing to the underlying quartz substrate, progressively decreases with the reaction time reaching almost undetectable levels after 14 h of deposition with AMN dissolved at 10 mg·mL⁻¹. These data illustrated the progressive coverage of the substrate with a conformal and pinhole-free film, and were confirmed on an amorphous carbon surface by means of electrochemical impedance spectroscopy ¹⁶ (Figure S6). Here, the resistance of the coating for electron transfer and for the transfer of the electrochemical probe to the electrode surface markedly increased with deposition time. In addition, using cyclic voltammetry, we showed that the AMN based coating became progressively impermeable to potassium hexacyanoferrate ²¹.

The oxygen content decreased in a nearly parallel manner with the decrease in silicon content but did attain a finite level (Figure 4A), implying that the AMN based coating contains oxygen even if the AMN monomer itself does not contain any oxygen. The incorporation of oxygen in the films is consistent with the previously described finding that the films appear thicker close to the liquid-air interface where oxygen supply is higher if the AMN evolution required some oxygen. The presence of oxygen in the coatings may be due to strongly adsorbed water, not desorbed from the coating even under ultra low vacuum conditions in the XPS chamber. This assumption is not unrealistic owing to the superhydrophilic character of the films (Figure 3A). In addition the presence of oxygen incorporated in the AMN based material is not inconsistent with literature data.²² The most interesting finding from the XPS spectra is the progressive increase in nitrogen content of the coatings with deposition time (Figure 4A), reaching a plateau value after about 12-14 h for an initial AMN salt concentration of 10 mg·mL⁻¹. At this state of the film deposition, the N/C ratio reached a value of 0.57±0.02, in perfect agreement with a previous study⁷. This ratio is however much smaller than the N/C ratio of the AMN monomer, which is equal to 1. This could be taken to indicate that some nitrogen is lost during the film deposition. Owing to the dissolution of gold in the presence of AMN at pH = 8.6, as discussed earlier, nitrogen loss occurs in the form of cyanide anions concomitant with the inclusion of oxygenated functions. Cyanide loss from dimethylaminomalonitrile containing solutions in basic media has already been described²³. However, the loss of CN groups as shown by partial gold dissolution when the deposition is performed on a gold substrate does not explain the finding that the C/N ratio at the end of the deposition process is lower than 1, because the elimination of CN does not change the C/N ratio of the reaction product. According to the reaction mechanism proposed in Scheme 1 we suggest that the hydrolysis of imine groups present in the hypothetical structure may lead to the formation of carbonyls and hence to a net loss of nitrogen and an incorporation of oxygen.

Figure 4: XPS data.

A: Evolution of the atomic percentage of Si (●), O (●), N (●) and C (●) as a function of time for AMN based coatings deposited in a $10 \text{ mg}\cdot\text{mL}^{-1}$ solution. The coatings were deposited on glass slides.

B: Evolution of the O/C (●) and N/C (●) ratios with reaction time in a 10 mg·mL⁻¹ AMN solution. The error bars correspond to $\pm$ one standard deviation

Based on these XPS data, we propose a chemical structure of the obtained polymeric materials that is consistent with the obtained N/C ratio close to 0.6 in the final stage of the deposition process (Scheme 1).

Scheme 1: Proposed structure of the polymeric material obtained at the solid liquid interface from an AMN based solution at pH = 8.6.

Even if the structure proposed in Scheme 1 is compatible with the C/N ratio obtained by XPS, additional experiments are required to confirm such a structure. Indeed, NMR as well as X ray diffraction experiments are currently in progress.

Apart from the formation of a coating at the solid-liquid interface, AMN polymer forms in solution ⁷. At longer reaction times, a black precipitate is observed in solution. It is of further interest to compare the AMN based material formed in solution and at the solid-liquid interface. As illustrated from the UV spectra taken in solution (after dilution with phosphate buffer at pH = 8.6) and on coatings obtained from the same solution (Figure 5A), the film structure or composition are different in solution and on the surface of quartz slides. The AMN based material formed in solution is characterized by a shoulder at 360 nm which is not present in the spectra of the AMN based coating. Moreover, the rate of AMN based material formation was different in solution and on a quartz substrate as shown by the absorbance increase at 360 and 423 nm of the AMN based material in solution and of the film respectively (Figure 5B). The same trend was observed for all the investigated initial concentrations of AMN salt (Figure S7). Of particular interest is the absence of a lag phase in solution (○, Figure 5B) whereas the AMN based film deposition on the different investigated surfaces (Quartz in Figures 1 and 2, silicon oxide in Figure S2 and amorphous carbon in Figure S6) are forming only after a concentration dependent lag phase. This may imply that the reaction mechanism is different in solution and at solid-liquid interfaces. The deposition of stable growing AMN based aggregates at solid-liquid interfaces most probably requires the formation of a critical nucleus leading to deposited particles after short reaction times, with these particles growing further or assembling in fibrillar structures after longer reaction times. Moreover, the spectroscopic features of the films and of the material produced in solution are observed to be independent of the reaction time. It may be speculated that only specific species produced in solution are finally deposited at the solid-liquid interface or that the

surface of the solid material modifies the chemical pathway. This specific issue requires further investigations on the composition and structure of the AMN based material produced in solution. In particular, we plan to perform some infrared spectroscopy and some XPS characterization of the precipitate obtained in solution.

A

B

Figure 5:

A: UV-Vis spectra of a $10 \text{ mg}\cdot\text{mL}^{-1}$ AMN solution (—) after 6 h of reaction and of an AMN film (---) deposited on a quartz wafer after the same reaction time, scaled by a factor of 5.

B: Time evolution of the absorbance at $\lambda=360 \text{ nm}$ (—○—, left hand vertical axis) and at $\lambda=423 \text{ nm}$ (---■---, right hand vertical axis) in the case of an AMN solution at $10 \text{ mg}\cdot\text{mL}^{-1}$ and for an AMN based film deposited from the same solution, respectively.

A film was also formed at the liquid-air interface (Figure 6A), provided the solution was not agitated after its initial homogenization. This observation is equivalent to the formation of polydopamine films at the dopamine liquid-air interface ^{24,25}, suggesting that some amphiphilic species are formed in solution, which present some affinity with the liquid-air interface and thus self-assemble there. In a similar manner to polydopamine films, the AMN based films deposited at the liquid-water interface can be transferred on plasma-cleaned glass slides by means of the horizontal Langmuir transfer method ²⁶. Even if the obtained transferred films display some cracks reflecting their intrinsic brittle character (Figure 6A), regions of a few square mm^2 can be obtained intact and without cracks. Surprisingly, those films displayed different nanoscale morphologies (Figure 6B), UV-Vis spectra (Figure 6C) and macroscopic appearance (Figure 6D) compared to the films deposited directly on quartz slides from an AMN solution at the same concentration and for the same reaction time. Considering the UV-Vis spectra, the coating obtained from the liquid-air interface is optically denser compared to its counterpart obtained from the solid-liquid interface, because it covers only one face of the quartz wafer due to the deposition by the vertical Langmuir-Schaeffer deposition method whereas the coating deposited from solution covers both sides of the

wafer. In addition, the spectrum of the material transferred from the liquid-air interface is red-shifted with respect to the solution deposited film (Figure 6C). Unfortunately we are not yet able to assign the large absorbance band displayed by the films to a given chemical moiety.

Figure 6A: AMN based films on the liquid-air interface after 16 h of reaction (AMN at $10 \text{ mg} \cdot \text{mL}^{-1}$ at an initial pH of 8.6). Picture of the surface of the AMN containing solution after 16 h and after Langmuir Schaeffer transfer on a cleaned glass slide.

B: AFM surface topographies of the transferred AMN based film, the image size being $100 \mu\text{m} \times 100 \mu\text{m}$ and $25 \mu\text{m} \times 25 \mu\text{m}$, respectively. The red arrow points to the region of the first image from which the image having a $25 \mu\text{m} \times 25 \mu\text{m}$ size was acquired.

C: UV-vis spectra of AMN based films (23 h of reaction) deposited directly on quartz slides from solution (—) or transferred to a quartz slide from the liquid-air interface by means of Langmuir-Schaeffer transfer (—).

D: Pictures of a quartz slide immersed for 23 h in a $10 \text{ mg}\cdot\text{mL}^{-1}$ AMN solution (left, the part of the slide close to the liquid-air interface is on the top) and of a quartz slide on which a film has been deposited from the liquid-air interface by means of Langmuir Schaeffer transfer (right) after the same reaction time.

These findings are of particular interest not only from a materials science point of view but also in relation to the mechanisms of formation of biomolecules on the early planet Earth. It is well known that surfaces like the clay galleries can play a great role in the formation of polypeptides from intercalated amino acids ^{27,28}. The data obtained from our study suggest that the fate of the chemical evolution undergone by AMN in basic conditions is different in solution and on surfaces with the possibility to display some surface specificities.

In our forthcoming studies we will investigate the compositional and structural differences between the precipitates obtained from AMN based solutions, the AMN based films deposited on substrates at the solid-liquid interface and those transferred from the liquid-air interface. In addition, the structural organization of the fibrillar structures obtained after long deposition times on solid surfaces is worth being further investigated.

Conclusions

The deposition of AMN based films at an initial *pH* of 8.6 proceeds via a nucleation growth process as shown by combining film monitoring kinetics by a set of complementary characterization techniques. The coating obtained at the solid-liquid interface undergoes a transition from island like deposits at short reaction times to fibrillar structures at longer reaction times with a simultaneous change in film composition, and film wettability ending in superhydrophilic conformal coatings for all investigated AMN concentrations. In addition the

kinetics of film deposition as well as its UV-vis spectra are different from the corresponding kinetics and spectral properties of AMN reacting in solution. It was also demonstrated for the first time that AMN based films are forming at the solution-air interface of non-agitated solutions, in strong analogy with polydopamine films. The AMN based films deposited at the solid-solution and solution-air interface again presented different morphologies and optical properties, highlighting probable compositional differences. All these findings highlight the extreme complexity and versatility of the AMN chemistry in basic conditions. Here, the same molecule leads to different species in solution and at different interfaces, providing the fascinating ability to coat all kinds of materials but with different properties such as morphology. Efforts are currently underway to further investigate the molecular structure of these AMN based materials deposited at interfaces and produced as precipitate in solution to prepare the path for applications in materials science.

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Supporting Information Available: UV-vis spectra of AMN films and solutions, film thickness measured by ellipsometry, pictures of water contact angles, XPS survey spectra and electrochemical impedance data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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