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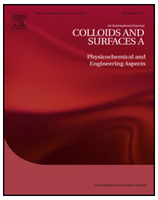

Deposition kinetics and electrochemical properties of tannic acid on gold and silica

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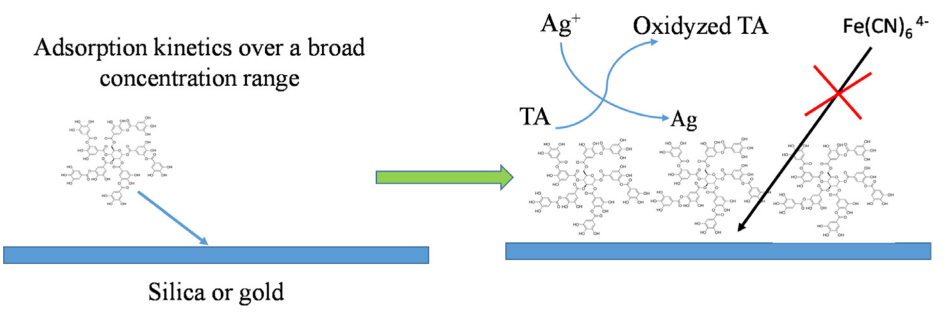
HIGHLIGHTS

- Tannic acid adsorbs as very thin films on silica and gold.
- These films allow for the reduction of Ag^+ cations.
- The reduction kinetics of Ag^+ is a slow first order process.
- Tannic acid films are impermeable to hexacyanoferrate anions.

GRAPHICAL ABSTRACT



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ABSTRACT

Tannic acid and other polyphenols adsorb spontaneously on almost all kinds of surfaces to yield hydrophilic coatings. However, the deposition kinetics of tannic acid as a function of its solution concentration has not yet been well characterized. Such fundamental aspects are of the highest importance for the protection against corrosion and other applications. Herein, it is shown by means of quartz crystal microbalance with dissipation monitoring that tannic acid (TA) deposition on gold and silica yield to monolayers independently of the TA concentration between 0.1 and 50 mg mL^{-1}. Significant but only partial desorption occurs when the film is put again in the presence of sodium acetate buffer. The reduction of Ag^+ cations in silver particles in the presence of tannic acid films is a slow and silver concentration dependent process. In addition TA monolayer films deposited on gold become impermeable to potassium hexacyanoferrate. This shows the high homogeneity and compacity of spontaneously deposited TA monolayers on silver and polycrystalline gold.

1. Introduction

After the impressive progress made in surface coating technology to produce monolayers of functional molecules on the surface of oxides or noble metals using self-assembled monolayers as well as in the analytical methods to characterize such thin films [1], the emphasis in wet coating technology has now shifted to the discovery of one step functionalization methods able to coat a vast repertoire of materials. Polydopamine films [2–4] or films made from polyphenols [5,6] can be deposited on almost all known materials in one step from aqueous solutions and without complicated equipment. The development of all these films relied on a biomimetic approach: the strong interactions between mussel foot proteins rich in L-Lysine and in L-Dopa with almost all surfaces inspired the use of dopamine to produce versatile coatings whereas

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the use of polyphenols in leather facturating and the spontaneous formation of polyphenol rich rings in cups containing tea was at the origin of the use of polyphenols to develop smart coatings. Many applications in the field of energy storage and in the development of antibacterial and anti-inflammatory coatings immediately emerged from these first investigations on polyphenol coatings [5]. In particular, polyphenol based films allow for good cell (3T3 fibroblasts) adhesion and to scavenge radical and non radical reactive oxygen species [5]. Controlled polyphenol based reduction of metal cations can be performed when polyphenols are confined in polyelectrolyte multilayer films [7]. These are just few examples of possible applications of polyphenol based films in diverse domains of surface science.

However, the physical chemistry of polyphenol deposition, among them tannic acid (TA), is only poorly investigated. Open questions about the deposition kinetics of TA and thereafter of silver nanoparticles, from a silver nitrate solution, on TA are under scrutiny. Indeed the reduction of silver cations is often used as the revelator of the presence of TA on the surface of non transparent materials like polymers [5,6] because the deposition of silver nanoparticles leads to a strong change in coloration whereas TA coatings are transparent above 330 nm. Herein we wish to investigate the deposition kinetics of TA and the subsequent reduction of Ag^+ cations in contact with such films using an *in situ* characterization method of adsorption phenomena, namely the quartz crystal microbalance with dissipation monitoring (QCM-D) [8]. The impermeability of TA coatings for a typical redox probe, potassium hexacyanoferrate, will also be investigated using cyclic voltammetry on gold working electrodes. To address these two questions, gold electrodes are used as deposition substrates. The deposition kinetics of TA will also be compared between gold and silica coated quartz crystals.

2. Materials and methods

All the solutions were prepared from Milli Q water (Millipore, Billerica, Massachusetts, USA, $\rho = 18.2\,\text{M}\Omega\,\text{cm}$). Tannic acid (ref. 403040, $M_w = 1701.2\,\text{g mol}^{-1}$) and potassium hexacyanoferrate (Ref. P9387) were purchased from Sigma–Aldrich. Sodium periodate (Ref. 311448n purity > 99.8%), used to oxidize tannic acid, was dissolved in the buffer at 10 mM. All the solutions were freshly prepared before each experiment in 50 mM sodium acetate buffer at pH 5.0. In these pH conditions, TA is uncharged and not subjected to oxidation from dissolved O_2.

Adsorption kinetics of TA on quartz crystals, coated with gold or SiO_2 (QSX 303 and QSX 301 respectively, Q Sense AB), was monitored *in situ* by quartz crystal microbalance with dissipation monitoring (QCM-D). Experiments were performed with an E1 device from QSense (Göteborg, Sweden). Most of the TA solutions were injected with a peristaltic pump at a constant flow rate of 250 μL min^{-1} but some experiments were also performed at 125 and 500 μL min^{-1} to investigate qualitatively the influence of transport from the solution on the adsorption of TA. Frequency changes, $\Delta f_\nu/\nu$, as well as the dissipation changes, ΔD_ν, at the 3rd ($\nu = 3$), 5th ($\nu = 5$) and 7th ($\nu = 7$) overtone were followed as a function of time. The recording of several harmonics is necessary to get information about the mechanical properties of the coatings, a requirement for the use of models aimed to calculate surface coverage from the measured frequency changes [8].

A 0.1 Hz per minute frequency change was considered as the threshold under which the adsorption process of TA is considered to be finished. The TA deposit was rinsed with sodium acetate buffer to investigate its spontaneous desorption. In some experiments the TA film was rinsed with distilled water in order to remove all unbound chloride anions before exposure to $AgNO_3$ aqueous solution (0.1–15 mg mL^{-1}) to monitor Ag deposition kinetics. A final water flush was used to investigate the resistance of the coating against desorption. In some control experiments, TA films were exposed to a 10 mM $NaIO_4$ (in acetate buffer) solution before exposure to water and $AgNO_3$ solution (at concentrations between 1 and 15 mg mL^{-1}).

UV–vis spectroscopy experiments were performed to monitor Ag deposition on TA films. Measurements were done on TA films deposited on the internal wall of a quartz cuvette (4 cm × 1 cm × 1 cm from Thuet, Blodelsheim, France). The optimal contact time with the silver nitrate solution was determined from the previously performed QCM-D experiments. Before the deposition experiments, the quartz cuvettes were sonicated with a 2% (v/v) Hellmanex solution during 20 min, then rinsed with distilled water, followed by a 0.1 M HCl solution, immersion in a 1 g L^{-1} $NaClO_3$ and final rinse with distilled water. Before TA deposition, the absorption spectrum of the unmodified cuvette containing water was taken between 250 and 700 nm with a Xenius spectrofluorimeter (Safas, Monaco).

Cyclic voltametry experiments were performed in a three electrodes configuration using a gold electrode (CH Instruments, 2 mm in diameter), an Ag/AgCl (Ref. 111, CH Instruments) and a Pt wire (Ref. 115, CH Instruments) as the working electrode, the reference and the auxiliary electrode respectively. The gold electrode was polished successively with alumina powders 1 and 0.1 μm in diameter (Escil, France), sonicated in double distilled water (during 2 min) and then cycled between −0.2 and 1.0 V *vs* Ag/AgCl at a scan rate of 1000 mV s^{-1} in the presence of 0.5 M H_2SO_4 [9]. The gold electrode was then rinsed with distilled water and scanned between −0.2 and +0.8 V *vs* Ag/AgCl and back to −0.2 V at a scan rate of 100 mV s^{-1} in the presence of 50 mM sodium acetate buffer containing 1 mM $K_4Fe(CN)_6$. Such a gold electrode was used for further experiments only if the oxidation and reduction peaks of the $Fe(CN)_6{}^{-4}/Fe(CN)_6{}^{-3}$ probe were spaced by less than 80 mV, the theoretical value being of 59 mV at 298 K for a one electron reversible process. The deposited TA films were incubated with 50 mM sodium acetate buffer and at least 2 CVs at a scan rate of 100 mV s^{-1} were recorded in the absence of any exogeneous redox probe. At the end of this experiment, the electrode was rinsed with sodium acetate buffer and a new CV experiment was performed in the presence of 1 mM $K_4Fe(CN)_6$.

Dynamic light scattering experiments were performed with a NanoZS device from Malvern at a scattering angle of 173° in order to estimate the hydrodynamic size of TA as a function of its concentration in the presence of 50 mM sodium acetate buffer.

The surface topography of the TA films was characterized by AFM (Nanoscope IV, Veeco) in the dry state and in the contact mode using MLCT cantilevers with a nominal spring constant of 0.1 N m^{-1}. The scan rate was of 2 Hz with a 512 × 512 pixel resolution.

3. Results and discussion

The adsorption kinetics of TA, on gold covered quartz crystals, was monitored at different concentrations in 50 mM sodium acetate buffer at pH 5.0. The kinetics appears to be biphasic with a very fast resonance frequency decrease and a dissipation increase followed by a slower regime (Fig. 1). During this second regime, the different harmonics of the quartz crystal do not overlap, meaning that the deposited film is not rigid or that the viscosity of the solution contributes significantly to the measured effect. However, upon rinse with sodium acetate buffer, the frequency as well as the dissipation decreases and more importantly the frequency changes at the different harmonics of the quartz crystal overlap again (Fig. 1). This means that the assumption of a non rigid TA film has to be rejected. These findings were confirmed for all TA concen-