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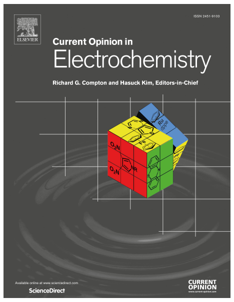

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Electrochemical Metallization of Molecular Adlayers

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SUMMARY

Electrochemical metallization of molecular adlayers allows to sandwich a group of molecules between a metallic substrate and a metal nanoisland or nanocluster through a wet process not requiring expensive vacuum equipment and with precise control through the electrode potential. This metal-molecule-metal sandwiches could provide a simple means to integrate molecules in electronic circuits, or to explore effects arising due to quantum confinement of electrons due to the reduced dimensions of the islands or clusters deposited on the adlayer. Although initial attempts resulted in penetration through the adlayer and direct deposition on the metal substrate, the development 14 years ago of a two-step technique involving pre-adsorption of the target cation on the SAM prior to its reduction in an electrolyte not containing that cation opened a whole new range of possibilities. In this brief review we discuss the development and recent advances in the implementation of this technique, and briefly discuss the outlook for future work.

Introduction

The use of electrochemical reduction to metallize molecular adlayers on electronically conducting substrates was initially driven by the possibility of employing molecules as components in electronic circuits [1–3], which would lead to the ultimate form of miniaturization of electronic components [2]. A significant challenge in realizing molecular electronics is the requirement of stable, viable and robust contacts to external electrodes [4–6]. A variety of methods have been developed to connect a single molecule to two metal electrodes and study electron transfer through it [7,8], but less attention has been devoted to the development of simple means to produce electrical contacts across small groups of molecules, which will most likely be required for future applications of molecular electronics [5]. The relevance of adlayer metalisation is not restricted to metal-molecule-metal sandwiches and, actually, the construction of metal-molecule-semiconductor sandwiches might be even more important [9], as this could easily be incorporated into state-of-the-art silicon-based technology. Metal-molecule-semiconductor junctions were first constructed by just putting a drop of mercury as the top metal electrode [10–12], or by using the lift-off float-on (LOFO) [13] or polymer-assisted lift off methods (PALO) [14]. An alternative method, involving the attachment of a Pt complex to a thiol-terminated SAM on Si followed by chemical reduction of the complex to metallic platinum using sodium borohydrate [15,16].

The simplest way to sandwich a group of molecules between two metal contacts is to adsorb a molecular adlayer on a metallic substrate and then deposit a metal atop the adlayer [6]. This is actually the method employed to fabricate the first ever commercial application of molecular electronics [17]. Although initial, unsuccessful, attempts of adlayer metallisation involved the deposition of metal layers from the vapor phase in vacuum [18,19] (in fact the method of choice in the first commercial device [17]), electrochemical metallization of molecular adlayers has the advantage of being a wet method not requiring vacuum chambers and easy to control through the electrode potential. Electrodeposition of a metal on a self-assembled monolayer (SAM) proved, however, to be challenging, and early attempts failed [20–22]. In this contribution we will briefly review the development of a successful method for the electrochemical metallization of molecular adlayers and recent developments thereof.

Metallization of SAMs from M^{z+}-free solutions

In 2004 Baunach et al. [23] reported the first successful deposition of bidimensional metal islands atop a SAM. This was rapidly followed by similar work by Qu and Uosaki [24]. As illustrated in Figure 1, while previous attempts involved the reduction of the metal in a solution containing the corresponding cation, Baunach et al. implemented a two-step procedure which involved the immobilization of the target cation on an adequately functionalized SAM followed by the electrochemical reduction of the cation in a solution not containing it. In doing so, they followed previous work by Kind et al. [25], who had managed to deposit bidimensional Pd films on top of a SAM of $H_2N\text{-}(CH_2)_{10}\text{-}CO(NH_2)\text{-}(CH_2)_2\text{-}NH_2$ via electroless deposition by previously immobilizing Pd^{2+} on the SAM and then reducing it in a Pd^{2+}-free solution containing dimethyl-amine borane (DMAB). A combination of electrochemical deposition as per Baunach et al. and the electroless deposition method of Kind et al. has been recently used by Uosaki and co-workers [26].

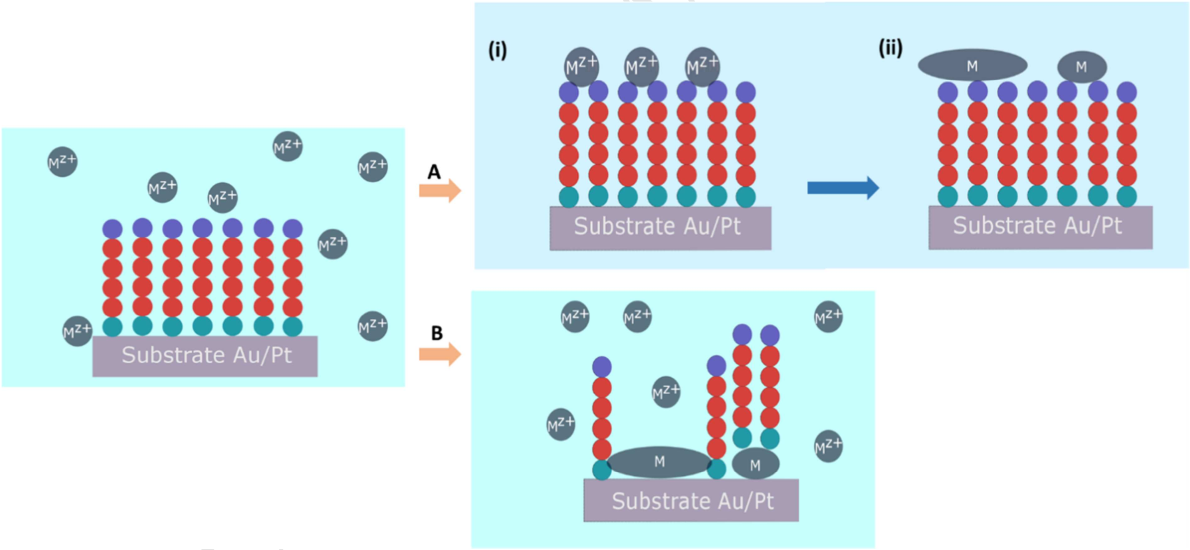

Figure 1: Schematic representation of the key processes in the electrochemical metallization of an organic adlayer. The alkyl chain (red circles) functional groups (blue and teal circles) represent the organic adlayer/self-assembled molecules (SAM) on the substrate. (A) Illustrates the two-step process; (i) complexation of cations atop the SAM followed by (ii) electrochemical reduction in solution with cations

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absent, resulting to metal isolation atop the organic adlayer. (B) Electrochemical reduction in solution containing cations leading to metal deposition on the substrate and intercalation into the substrate-SAM interface.

The electrochemical approach used by Baunach et al. offers an element of control through the electrode potential which is not possible in Kind's et al.'s electroless deposition process. Figure 2a shows a typical STM image of the resulting deposit, corresponding in this particular case to the deposition of Pd on a 4-mercaptopyridine (4-Mpy) adlayer.

Convincing evidence of deposition on top of the SAM was provided with angle resolved X-ray photoelectron spectroscopy (XPS) [23], which clearly showed that the angle dependence of the ratio between the intensities of the Au $4d_{3/2}$ and C 1s lines, as well as that between the Au $4d_{3/2}$ and Pd $3d_{3/2}$ is that expected for a Au/SAM/sequence, and not that of Au/Pd/SAM (Fig. 2b).

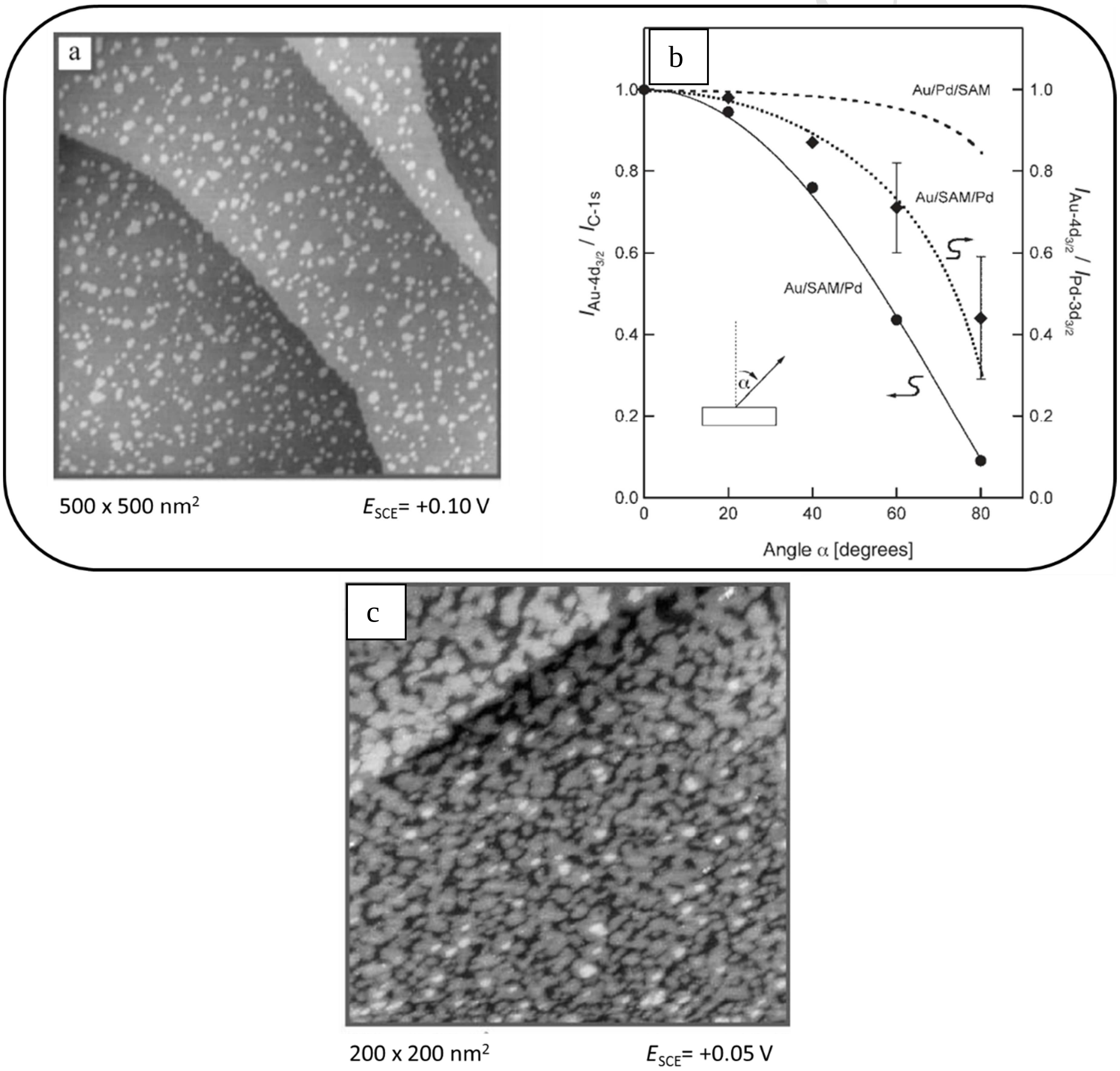

Figure 2: (a) STM image showing Pd bidimensional islands deposited on-top of a 4-MP SAM after reduction of pre-adsorbed Pd^{2+} ions; (b) ratio between the Au $4d_{3/2}$ and C 1s line intensities and between

the Au $4d_{3/2}$ and Pd $3d_{3/2}$ line intensities as a function of the photoelectron detection angle in angle-resolved XP spectra of samples like that shown in (a). The solid symbols correspond to the experimental data, while the lines correspond to theoretical values as calculated for a SAM thickness of 0.8 nm and assuming either a layer sequence Au/SAM/Pd (solid and dotted lines) or a Au/Pd/SAM sequence (dashed line); (c) STM image of nearly complete bidimensional Pd film on 4-MP, formed after a second complexation-reduction cycle. (a) and (b) reproduced with permission from [23], © 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (c) reprinted from [27], Copyright (2005), with permission from Elsevier.

The critical element in this successful approach to the metallization of molecular adlayers is the use of doubly functionalized molecules, in which one functional group (often a thiol) provides the point of union to the substrate while the other (typically a Lewis base, like an amine group) allows for coordination to a metal cation. This coordination has to be strong enough to be irreversible, so that the metal cation does not desorb from SAM even if immersed in a solution not containing that cation. Kolb and co-workers successfully applied this procedure to the deposition of Pd [23,27], Rh [28] and Pt [29] on 4-mercaptopyridine (MP) adlayers, proving the versatility of the method. They also showed that the location of the functional group to which the metal ion coordinates plays an important role, metallization not happening when the functional group is not facing the electrolyte, as in the case of 2-MP [27]. Metallization of a completely different SAM, formed by flat shaped 1,4-dicyanobenzene on Au(111) electrodes was also demonstrated [30], proving that the method is effective as long as irreversible coordination of a metal cation to a suitable functionality is possible. Successful electrochemical metallization of SAMs using the same procedure was subsequently reported by other groups using different metals and SAMs [31–34], proving the viability and effectiveness of the method.

Later work by Kolb and co-workers demonstrated that successive cycles of complexation and reduction lead to an increase of the size of the bidimensional islands deposited on the SAM [27], slowly approaching complete metallization with a bidimensional metal film (Figure 2c). However, growth of a second layer was found to always start before completion of the first metal layer. Even more interesting, the possibility of fabricating multi-decker structures by successive SAM modification and metal deposition cycles using this metallization method was also demonstrated [35], opening the door to combining different types of molecular layers and different types of metallic interlayers into a single hybrid structure.

Metallization *vs.* penetration through the SAM

An obviously interesting question is why metallization is possible in M^{z+}-free solutions but not if the solutions contain the cation to be reduced.

Some insight into the reasons for this different behavior can be gathered from the work by Silien et al. [33], who demonstrated that the two-step mechanism developed by Kolb and co-workers can be merged into a single one if solutions containing the target metal cation in sufficiently low concentration are used. The same group had previously studied the penetration of Cu through a non-functionalised SAM during the electrodeposition of Cu [36]. In general well-formed SAMs are more resistant to direct deposition on the substrate than poorly formed or incomplete SAMs (which is actually a foregone conclusion, as deposition on the substrate is thermodynamically favored and will always be preferred if sufficiently large substrate patches

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are exposed). However, Silien and Buck [36] found that, on well-formed and complete SAMs, intrinsic defects such as domain boundaries, vacancy islands, or step edges do not act as nucleation sites for the deposition of the metal directly on the substrate. Instead, direct deposition on the substrate nucleates on extrinsic defects arising from impurities in the substrate, which result in more substantial discontinuities in the SAM.

When metallization is attempted using SAMs with an appropriate functionality which can coordinate to the target metal cation (M^{z+}) when the cation is present in the electrolyte, two possible paths open up for the reduction reaction, namely, (i) reduction of the M^{z+} ions complexed with the functionality in the SAM leading to metallization and (ii) reduction of M^{z+} ions from the solution at extrinsic defects leading to penetration through the SAM [33]. If the concentration of the cation is low enough, and reduction is achieved through a cyclic potential sweep into the reduction region and back, only reduction of the already complexed M^{z+} ions will take place, while M^{z+} in the solution will not be able to diffuse to the surface and reach the nucleation sites. In other words, according to Silien et al. [36], it is the possibility of diffusion of M^{z+} directly from the solution to the extrinsic defects acting as nucleation sites for deposition on the substrate what leads to penetration through the SAM, while complexed cations cannot reach those extrinsic defects by diffusing over the SAM.

We have recently shown, however, that, in the case of cyanide SAMs on Pt(111), penetration of the metal through the SAM can also occur in the absence of the metal cation in the solution, although this is sensitive to the metal being deposited, suggesting that the interaction between the SAM and the metal and/or the metal cation might be also playing a role. In a series of studies attempting the metallization of cyanide-modified Pt(111), we found that ,while a negative potential excursion in the presence of pre-adsorbed Cu^{2+} results in the formation of bidimensional islands [34], the same experiment with Pd^{2+} [37] resulted on direct deposition on the Pt substrate, evidenced by the emergence after reduction of peaks clearly corresponding to the adsorption of hydrogen on a partial monolayer of Pd on Pt(111). The reason for the different behavior is not clear, but it probably combines the more open nature of the cyanide SAM ($\theta_{CN} = 0.5$), which probably favors penetration, with a lower barrier for the diffusion of the cations over the adlayer, which would be sensitive to the chemical nature of the cation.

Morphology and electronic structure of the deposit

Although, as mentioned above, the electrochemical metallization of molecular adlayers has been repeatedly achieved by reducing the target pre-adsorbed cation in either cation-free solutions or in solutions with sufficiently low concentrations of the cation, reports differ in the morphology of the metal deposit on the adlayer. While Kolb and co-workers [23,27–30,35], as well as ourselves [34] and Kind et al. [25], have reported the formation of bidimensional islands, others have reported the formation of metal clusters on the adlayer [31,33,36,38,39]. Thicker films have been reported by Uosaki and co-workers [26,32,40]. As noted by Silien et al. [33], formation of more or less spherical nanoparticles should be thermodynamically favored, due to the high surface tension of metals, and the different morphologies found by different groups might be determined by small variations in experimental conditions. Among them, an effect from specific adsorption of species present in the electrolyte cannot be discarded.

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Interestingly, while bidimensional islands show growth with time via Ostwald ripening [34], or grow laterally upon successive adsorption-reduction cycles [27,28] (see Fig. 2c), none of these phenomena is observed when the metallization results in cluster formation [33]. In the latter case, repetition of the adsorption-reduction cycle leads to an increase in the coverage by metal clusters without an increase in the cluster size (Figure 3). This suggests that the differences in the final morphology of the deposit are connected to differences in the barrier to horizontal diffusion over the adlayer.

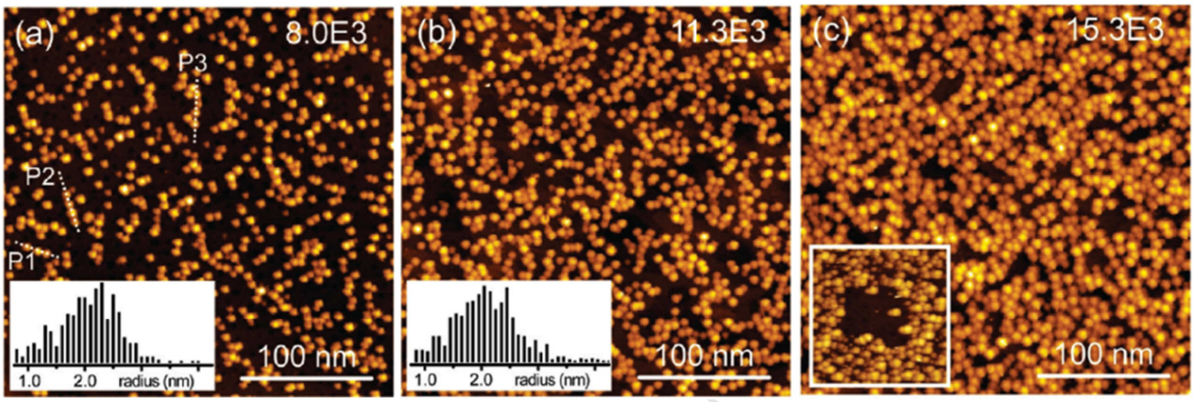

Figure 3: STM images of Pd clusters deposited on a 4-MP SAM after the first (a), second (B) and third (c) complexation-reduction cycles. Reproduced with permission from [33]. Copyright 2011 American Chemical Society.

Keith and Jacob [41,42] used DFT to calculate barriers to the diffusion of a single Pd atom over a 4-mercaptoyridine SAM, both in the absence and in the presence of other-adsorbed Pd atoms. According to their calculations, a single atom binds strongest on a 4MP-SAM at sites located between SAM molecules, where its binding energy to N is of 2.98 eV. A similar conclusion was reached by our group regarding the adsorption of a metal cation on a cyanide-modified Pt(111) surface [43]. Diffusion of this atom to an equivalent site **1** has a barrier between 1.00 and 1.22 eV, depending on the diffusion path, too high for facile diffusion above the 4MP-SAM surface. However, in the presence of other pre-adsorbed atoms, the preferred adsorption site is on top of the N atoms, with roughly 2.30 eV of binding energy. Diffusion between equivalent sites over the site located between MP molecules essentially has no barrier, and diffusion to an adjacent MP molecule requires only 0.18 eV. Accordingly, both pathways permit rapid diffusion and aggregation of Pd in small islands. Silien and Buck have suggested that their observed absence of particle growth upon repeating the adsorption-reduction cycle might be linked to passivation of the Pd surface for aggregation due to hydrogen adsorption due to the rather negative potential required to reduce the pre-adsorbed Pd^{2+} ions.

These two morphologies also show different electronic structures and coupling to the SAM. When the deposit results in an array of small Pd clusters on top of the SAM, tunneling spectroscopy reveals the presence of a Coulomb blockade in the current vs. tunneling voltage curve [31,33]. This is the behavior expected for a double tunnel junction, and implies that the clusters have metallic character and do not interact strongly with the N atom of the pyridine-terminated SAMs, as confirmed by the fact that the particles were easily displaced or even removed when tunnelling currents larger than some pA were used [33,38].

On the contrary, ultraviolet photoelectron spectroscopy (UPS) shows clearly non-metallic character of the bidimensional Pd islands deposited on 4-MP SAMs, evidenced by the depleted DOS at the fermi level, E_F (Fig. 4a) due to strong N-Pd bonds, as confirmed by DFT [44]. With increasing size of the bidimensional islands, achieved through several adsorption-reduction cycles, a non-metal to metal transition is eventually observed for bidimensional deposits with a coverage of 0.7 ML of Pd. Interestingly, such non-metal to metal transition is absent when 4-MP is metallized with a bidimensional Pt deposit (Fig. 4b) [45]. A separate DFT study confirmed the depleted DOS at the Fermi level for bidimensional Pd islands on a 4-aminothiophenol (ATP) SAM [46].

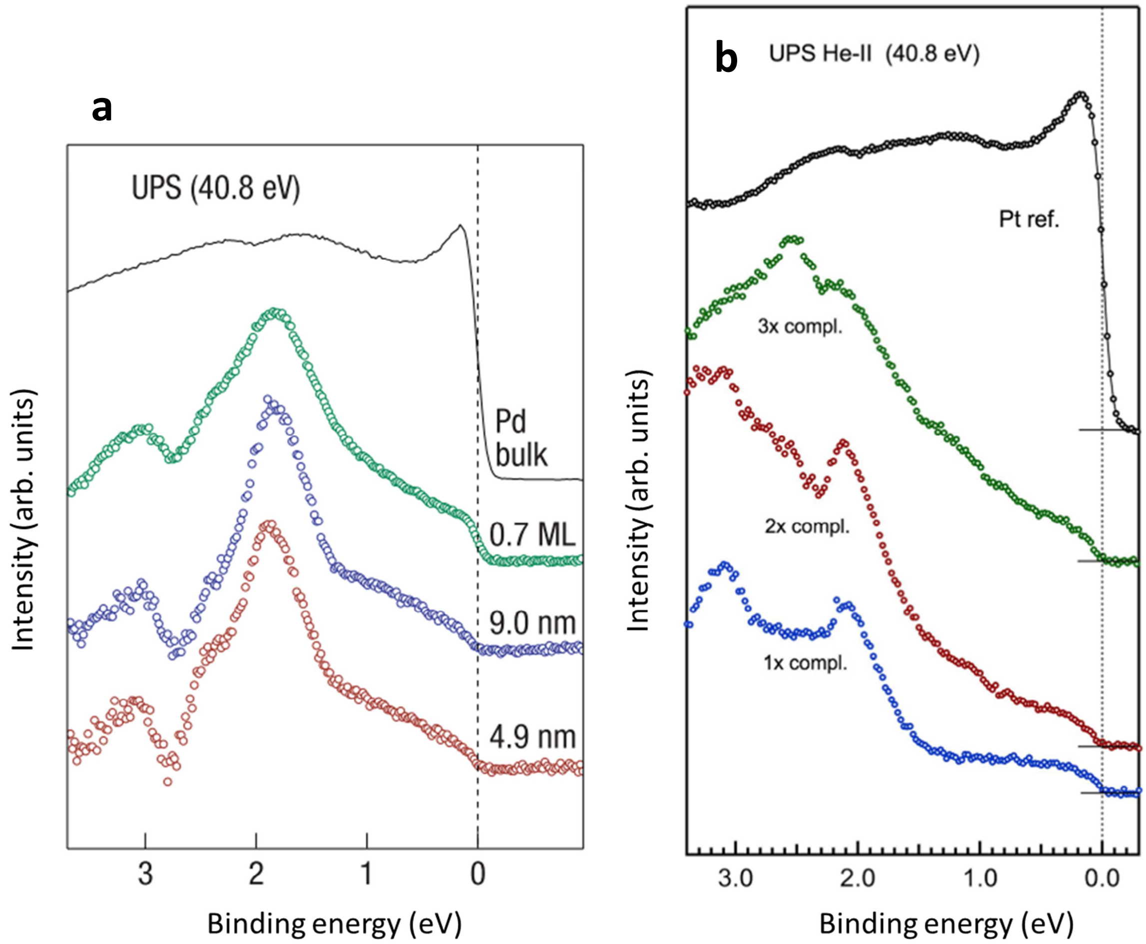

Figure 4: UPS spectra of 4-MP SAMs metallised with Pd (a) and Pt (b) after subtracting the contribution due to the support. While in the case of Pd a non-metallic to metallic transition is observed when the coverage of the SAM approaches a complete monolayer, in the case of Pt the absence of DOS at the Fermi level even after 3 complexation-reduction cycles suggests that the Pt deposit on top of the SAM remains non-metallic. Reprinted from [44] by permission from Springer Nature Customer Service Centre

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Conclusions and Outlook

The work reviewed here, performed during approximately the last decade and a half, has demonstrated that the electrochemical metallization of molecular adlayers is a simple and convenient alternative to connect a group of molecules to two metallic electrodes, including the possibility to trap a metal layer within two SAMs in a double- or multi-decker configuration [35,40]. However, different deposit morphologies with different electronic properties and different coupling to the complexing functionality in the SAM have been reported, and we still ignore which experimental parameters control the final outcome. There is, therefore, a need to deepen our understanding of the process, so that the desired morphology can be controlled and reproducibly obtained.

Despite a relatively large number of examples of metallization with a variety of SAMs and deposited metals, studies of the properties of the sandwiches are scarce. Muller et al. [25] have recently reported a study of the electrocatalytic behavior of Pd and Pt nanoislands on 4-MP SAMs on Au(111). However, there are no studies describing electronic transport across the sandwich and how it depends on the size of the islands and the number and nature of the molecules in the sandwich. Similarly, optical studies exploring plasmon excitation and possible coupling between plasmons excited in adjacent islands are completely absent.

Conflict of Interest

Nothing declared.

Acknowledgements

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The possibility to create double- and multi-decker architectures with a metalic layer suspended between two sandwiched SAMs was demonstrated. Thi opens the way to the possibility of combining different metals and SAMs, with the subsequent versatility in their properties.

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Electrochemical Metallization of Molecular Adlayers

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HIGHLIGHTS

- A simple two-step process allows the electrochemical metallisation of molecular adlayers on a conducting substrate, providing a simple means to sandwich a group of molecules between two metallic contacts.
- The method is versatile and can be used with a large combination of metals and SAMs.
- The two step cycle can be repeated several times, leading to increased coverage by the metal film or clusters or to multi-decker geometries.
- The metallic or non-metallic nature of the deposit on the SAM can be control by controlling its morphology, island size or the chemical nature of the metal deposited

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CONFLICT OF INTEREST

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The authors declare no conflict of interest

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