■ Electrochemistry

Towards the Fabrication of the Top-Contact Electrode in Molecular Junctions by Photoreduction of a Metal Precursor

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Abstract: Langmuir films of 4-{[4-({4-[(trimethylsilyl)ethynyl]-phenyl}ethynyl)phenyl]ethynyl} benzenaminium chloride ([**1 H**]Cl) undergo anion metathesis when assembled on an aqueous auric acid (HAuCl$_4$) subphase. Subsequent transfer to solid supports gives well-formed Langmuir–Blodgett (LB) monolayers of [**1 H**]AuCl$_4$ in which the trimethylsilyl group serves as the surface contacting group. Photoreduction of the aurate on these monolayers leads to the formation of metallic gold nanoislands, which were distributed over the surface of the film. Electrical properties of these nascent devices were determined by recording current–voltage (*I*–*V*) curves with conductive atomic force microscopy (c-AFM) using the PeakForce tunneling AFM (PF-TUNA) mode. This gives consistent sigmoidal *I*–*V* curves that are indicative of well-behaved junctions free of metallic filaments and short circuits. The photoreduction of a metal precursor incorporated onto monomolecular films is therefore proposed as an effective method for the fabrication of molecular junctions.

Introduction

The quest towards further miniaturization of electronic devices has led to increasing interest in organic molecules as functional elements within a hybrid solid-state/molecular technolo-

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gy.[1–3] Significant progress in the synthesis of new molecules with inherent electronic function and compatibility with devicelike architectures has been made in the last decade[4–12] but many scientific and technological challenges remain to be addressed before molecular electronics can be considered a viable technology and reach the market. One of these challenges is the reliable deposition of the second ("top") electrode in two-terminal sandwich-based metal|molecule|metal devices. Several recent papers[13–16] have critically reviewed the techniques available for the deposition of the top-contact electrode, summarizing the approaches used and highlighting the advantages and serious limitations of these methods. Perhaps the most significant problems in the deposition of the second electrode are those related to damage of the functional molecules during the metallization of a monolayer or penetration of the second metal through the organic films, which results in a short circuit, rendering the device unusable.

In contrast to thermal processing methods, such as metal evaporation and sputtering, photochemical-based approaches are compatible with both solid-state and molecular materials. Indeed, photolithography is one of the most important processing techniques used in conventional (solid-state) electronics fabrication. Photoreduction of metal precursors to produce metal nanoparticles (NPs) or clusters incorporated in thin films has been reported in the literature for different applications,[17–23] and the compatibility of these methods with molecular substructures has inspired the work described here. In this work, a metal precursor (AuCl$_4^-$) is incorporated onto a Langmuir–Blodgett (LB) film during the fabrication process, with subsequent photoreduction leading to the formation of metallic gold nanoislands (GNIs) on top of the intact molecular film. The metal|molecule|GNI systems are free of metallic inter-

penetration and short circuits, thereby providing a route to nascent device structures. Although the concept of photoreducing a metal precursor on top of a molecular film could be applied to monolayers prepared by other approaches (e.g., self-assembled films), we have chosen the LB technique because the metal precursor can be easily incorporated on top of the LB film during the transfer of the films from the air–liquid interface without any additional step in the fabrication process.[24,25] In addition, the LB method has broad applicability to a wide range of molecular systems since it can be used to form both chemisorbed and physisorbed films, which significantly broadens the range of molecular systems and surfaces that can be employed in a junction.[26] The ability to assemble various functionalized molecules onto a diverse range of surfaces is important as systematic studies of different organic–metal contacts are crucial to determine the role that the interface plays in the performance of molecular devices.[27–31] Directionally oriented films can also be prepared by the LB technique, which in turn offers a significant degree of control over the final architecture and functionality of the devices, and can be especially important considering that molecules incorporated into a metal|molecule|metal device need to be bifunctional to permit strong binding to both metal interfaces.[32,33] Although electrochemical methods have been successfully used for the fabrication of metal films on top of self-assembled monolayers,[34–37] these methods clearly require polarization of the substrate within an electrochemical cell, which is likely to be unpractical for many device applications. By contrast, the photochemical method is "contact" free and requires only optical illumination over the substrate area.

Results and Discussion

Oligo(phenylene) ethynylene based structures have long been used as prototype molecular wires and have been shown to be robust platforms for the exploration of various aspects of molecular electronics science from the development of measurement methods to length-dependent conductance mechanisms and novel surface contact chemistry.[38–51] The oligomeric phenylene ethynylene (OPE) derivative used in this work, [1H]Cl (Figure 1), contains a hydrophobic group, $-C\equiv CSiMe_3$, which has been recently shown to serve as an effective surface anchoring group with a growing body of evidence supporting a chemical interaction between the terminal Si atom and the metal substrate.[47,52–55] The trimethylsilylethynyl moiety has also been shown to provide effective metal–molecule electronic contacts.[47,52] The hydrophilic ammonium group facilitates the anchoring of the molecule at the water surface, which provides stability to the Langmuir films. In addition, the hydrophilicity difference between the two terminal groups is expected to permit the fabrication of directionally oriented films that can be further controlled by the nature of the deposition stroke. The Cl^- counter anion associated with the $-NH_3^+$ terminus is readily exchanged for other ions introduced into the aqueous subphase, such as the $AuCl_4^-$ anion. This provides a convenient method through which to prepare ordered substrate|[1H]|AuCl_4 assemblies.
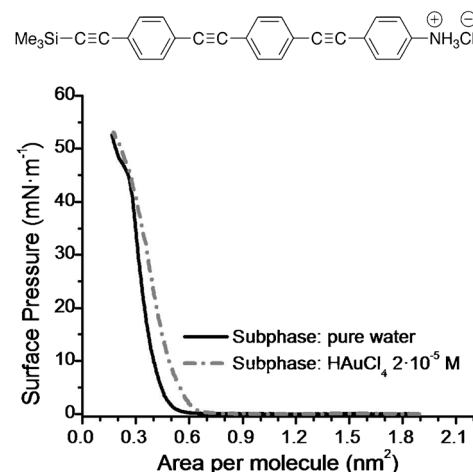

Figure 1. The chemical structure of [1H]Cl and surface pressure versus area per molecule isotherms of [1H]Cl onto a pure-water subphase and a 2×10^{-5} M HAuCl_4 aqueous subphase.

Figure 1 shows representative surface pressure versus area per molecule (π–A) isotherms of [1H]Cl on a pure-water subphase and a 2×10^{-5} M HAuCl_4 aqueous subphase. The π–A isotherm obtained for a pure-water subphase features a lift-off at approximately 0.60 nm² molecule⁻¹. The monolayer prepared onto a HAuCl_4 aqueous subphase, and therefore comprised of [1H]AuCl_4 after anion exchange, shows the lift-off at a slightly higher area, approximately 0.65 nm² molecule⁻¹. Compression isotherms from films of both [1H]Cl and [1H]AuCl_4 show a monotonic increase of the surface pressure until the collapse is reached at surface pressures around 45 mN m⁻¹ in both cases. The higher areas per molecule obtained at the same surface pressure for the isotherm recorded for [1H]AuCl_4-derived films are indicative of the incorporation of the relatively large $AuCl_4^-$ anions into the monolayer.[24]

Langmuir monolayers of [1H]AuCl_4 were transferred onto solid substrates that were initially held outside of the aqueous HAuCl_4 subphase by the vertical dipping method at a surface pressure of 20 mN m⁻¹ to form one-layer LB films. The transfer ratio (defined as the decrease in the monolayer area during the deposition divided by the area of the substrate) calculated using the trough software was 1. Under these transfer conditions (substrates initially outside of the subphase), the trimethylsilyl group is directly attached to the substrate[47] with X-ray photoelectron spectroscopy (XPS) experiments confirming chemisorption of this group onto gold substrates (see the Supporting Information).[52–54]

Figure 2 shows the UV/Vis spectrum of a pristine one-layer LB film of [1H]AuCl_4 transferred onto a quartz substrate. This spectrum features a band at 345 nm, which is likely to result from unresolved π–π* transitions associated with the OPE backbone[56] that appears at the same wavelength as the analogous transitions of [1H]Cl in solution (see the Supporting Information). Irradiation of the [1H]AuCl_4 LB film with UV light (254 nm) results in a reduction in the intensity and blueshift of the absorption envelope at 345 nm. These changes in the spectrum are accompanied by the appearance of a small broad peak at approximately 550 nm, attributable to surface
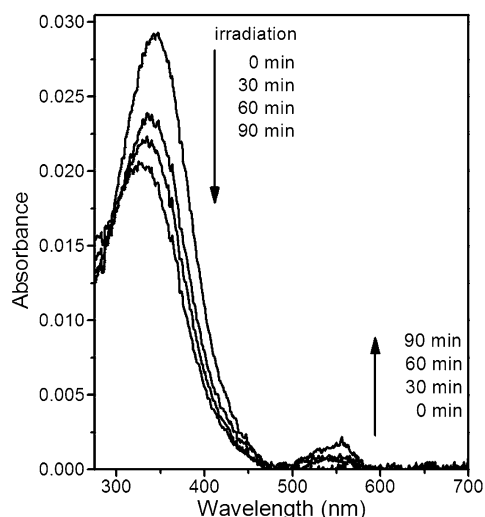
Figure 2. UV/Vis spectra of a pristine [**1H**]AuCl$_4$ one-layer LB film and the same film after irradiation with UV light at 254 nm for the indicated periods of time.

Figure 3. XPS spectra of Au 4f photoelectrons of pristine and irradiated (254 nm) [**1H**]AuCl$_4$ LB films after 90 min.

plasmon resonance of gold nanoparticles.[57] Further irradiation of the film yields an increase in the gold plasmon band and a further decrease and blueshift of the OPE main band. After 90 min of irradiation the maximum absorption band is shifted to $\lambda_{max} = 328$ nm. Further irradiation times did not produce any significant increase in the gold plasmon band. An Au|[**1H**]Cl LB film (fabricated from a Langmuir film onto a pure-water subphase) was also subjected to irradiation under the same conditions as the Au|[**1H**]AuCl$_4$ film, with no change in the UV spectral profile (see the Supporting Information). This suggests photodamage to the OPE backbone is unlikely the cause of the change in the spectroscopic profile observed during photolysis of Au|[**1H**]AuCl$_4$ LB films. Rather, the different chemical environment of the organic moiety together with a possible change in the tilt angle of the molecules or the interaction of the molecules with the generated gold nanoislands are more plausible reasons for the blueshift observed for the main absorption feature.

The observation of a plasmon band is consistent with the formation of GNIs on top of the LB film after irradiation. Formation of Au^0 has also been demonstrated by XPS. Figure 3 shows the XPS spectra of pristine and irradiated [**1H**]AuCl$_4$ LB films on a glass substrate. The Au 4f region for the film after irradiation shows two peaks at 84.1 and 87.8 eV, and the XPS spectrum of the pristine film exhibits two intense peaks at 84.7 and 88.4 eV. This shift to lower binding energies upon irradiation is consistent with the reduction of the gold precursor to Au^0.[58–61]

The photoreduction process of AuCl$_4^-$ is considered to proceed through the mechanism described by Kurihara et al.[62] and Yonezawa et al.[63] [Eqs. (1)–(4)]:
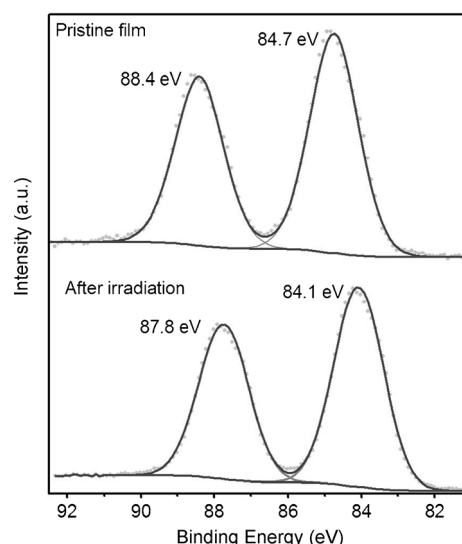
$$2AuCl_4^- \xrightarrow{h\nu} 2AuCl_3^- + 2Cl^\bullet \qquad (1)$$

$$2AuCl_3^- \rightarrow AuCl_4^- + AuCl_2^- \qquad (2)$$

$$2AuCl_2^- \xrightarrow{h\nu} Au^0 + Cl^\bullet + Cl^- \qquad (3)$$

$$AuCl_4^- \xrightarrow{h\nu} Au^0 + \frac{3}{2}Cl_2(g) + Cl^- \qquad (4)$$

In addition, gold atoms tend to diffuse on the surface and aggregate to form GNIs.

However, neither UV/Vis spectroscopy nor XPS provide any information about the distribution of the GNIs on the surface of the film. To investigate this issue, scanning electron microscopy (SEM) images of LB films before and after irradiation have been obtained (see a representative image in Figure 4). The
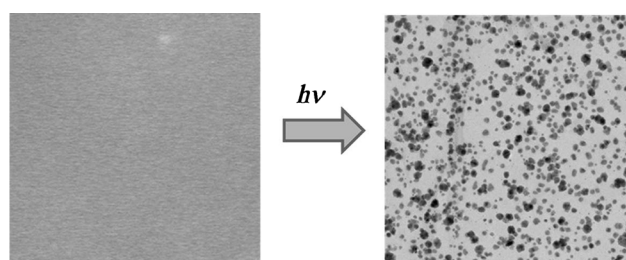

Figure 4. SEM image, (500×500) nm^2, of a one-layer [**1H**]AuCl$_4$ LB film deposited onto a glass substrate film before (left) and after (right) 90 min of irradiation with UV light at 254 nm.

pristine film shows a homogeneous surface. In contrast, after irradiation the film shows the appearance of round and dark spots distributed all over the film revealing the presence of GNIs with close to circular appearance, and most of these GNIs have diameters in the 5–20 nm range.

A frequent problem in the fabrication of the top-contact electrode is the formation of short circuits due to a metallic contact between the bottom- and top-contact electrodes.[64–66] Therefore, it is important to verify whether the metal-contacting strategy proposed in this paper also leads to short circuits

or whether on the contrary it is an effective technique for avoiding such a problem. To probe the electrical properties of the metal|molecule|GNIs sandwich structures fabricated as described above, current–voltage (I–V) curves were recorded with conductive atomic force microscopy (c-AFM; Bruker ICON) using the PeakForce tunneling AFM (PF-TUNA) mode and a PF-TUNA cantilever from Bruker (coated with Pt/Ir 20 nm, ca. 25 nm radius, 0.4 N m^{-1} spring constant and 70 kHz resonance frequency).[67–70] The PF-TUNA operation mode for the AFM was chosen to avoid lateral forces during the imaging that would have damaged the tip coating and sample surface, while at the same time allowing the use of cantilevers with a low spring constant. Thus, this is a method for the conductivity mapping of soft or fragile samples and as such it has been chosen for conductivity probing of our metal|molecule|GNIs, rather than using STM or conducting AFM in conventional contact mode. The PeakForce tunneling AFM used here combines "tapping" mode AFM with a conducting AFM tip and a low-noise current amplifier to probe current flow through the metal|molecule|GNI junctions. A compromise has to be made in selecting the peak force that is applied during the measurement. Too much force will result in unacceptably large deformation of the monolayer underlying the GNIs, whereas too little force will result in inadequate electrical contact. Therefore, before recording the I–V curves, control experiments were made to determine the most suitable set-point force. This entailed monitoring the deformation or damage to the monolayer as a function of the tip-loading force (set-point force) and these data are presented in the Supporting Information. These measurements showed that a peak-force set point of around 34 nN is required to make a reasonable contact between the tip and the GNI while avoiding damage or excessive deformation of the organic layer during the determination of the electrical properties. By using this force set point, I–V curves were then recorded with the AFM probe placed on top of GNIs and a bias between the substrate and the tip was applied. I–V characteristics were recorded by sweeping the tip voltage (±1.1 V) with the LB-coated Au substrate held at ground. To ensure reproducibility and reliability of the results, the I–V curves were averaged from multiple scans. Figure 5 shows an averaged I–V curve for the metal|molecule|GNIs sandwich structures recorded using a peak-force set point of 34 nN. These curves show a shape commonly observed for metal–molecule–metal junctions, with a linear section only at relatively low bias voltages and increasing curvature at higher bias. Most importantly, only curves like this were observed and no low-resistance traces characteristic of metallic short circuits were obtained over a wide range of set-point forces. These observations rule out the presence of short circuits. These results confirm that robust and reliable top contacts have been prepared without damaging the organic layer or altering/contaminating the interfaces, thereby avoiding electronic or structural rearrangements. Therefore, this shows that the fabrication of a top-contact electrode by photoreduction of a metal precursor is an alternative to other methods developed to date.
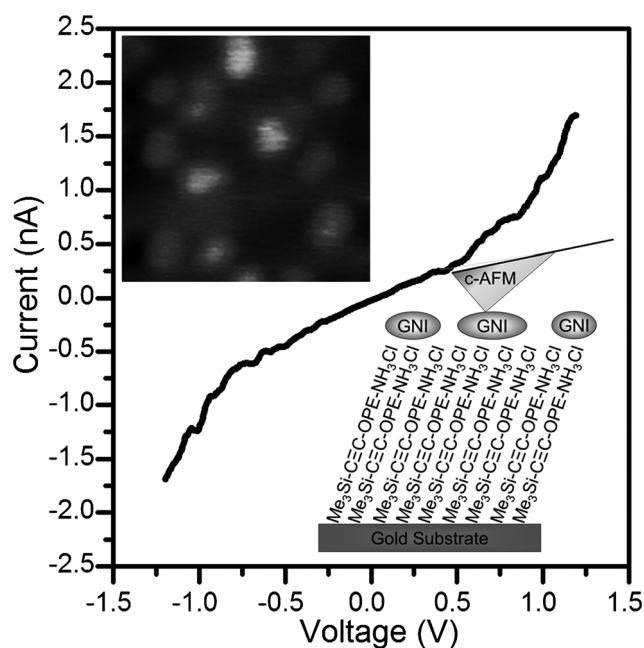

Figure 5. Averaged I–V curve over 350 curves obtained by positioning the c-AFM tip on top of GNIs (Figure S4 in the Supporting Information) generated by irradiation of an Au|Me$_3$SiC≡C-OPE-NH$_3$AuCl$_4$ monomolecular LB film. The peak-force set point used was 34 nN. The inset top image shows a representative example of a (200×200) nm^2 image in which GNIs can be clearly distinguished and which was used to position the c-AFM tip onto the GNIs. The inset bottom image shows a scheme of the studied metal|molecule|GNIs sandwich structures.

Conclusion

In this paper, photoreduction of a metal precursor ionically bound to a LB film is shown to be suitable for the fabrication of top-contact GNIs in molecular junctions. This has proved to be an efficient and reliable technique for the fabrication of a top contact of organic monolayers that minimizes the appearance of short circuits, which is a rather common problem in other traditional methods for the preparation of top-contact electrodes. Moreover, this method avoids expensive deposition techniques for the top-contact electrode. In addition, the photoreduction technique could be easily applicable in other types of monolayers, including self-assembled ones, and the use of other metal precursors including silver, platinum, copper, or palladium ions to form different metal nanoislands can be envisioned. If needed, these metallic islands could be used as seeds for deposition of a thicker and contiguous metal-film top contact using other methods (e.g., electroless metal deposition), which leads ultimately to the controlled preparation of molecular electronic junctions with a significant inhibition in the formation of short circuits.

Experimental Section

Film fabrication

[1 H]Cl was prepared as described in the Supporting Information. A Nima Teflon trough with dimensions (720×100) mm^2 housed in

a clean room at constant temperature ($20 \pm 1\,°C$) was used to prepare the films. The surface pressure (π) of the monolayers was measured by using a paper Wilhelmy plate pressure sensor. Ultrapure Millipore Milli-Q water (resistivity $18.2\,M\Omega\,cm$) was used as the subphase. The spreading solutions, $2.5 \times 10^{-5}\,M$ in [**1H**]Cl, were prepared in chloroform (HPLC grade, 99.9% purchased from Sigma). To construct the Langmuir films, the solution was spread using a Hamilton microsyringe held very close to an aqueous surface, which allowed the surface pressure to return to a value as close as possible to zero between each addition. The spreading solvent was allowed to completely evaporate over a period of at least 15 min before compression of the Langmuir film at a constant sweeping speed of $0.02\,nm^2\,molecule^{-1}\,min^{-1}$.

The films were deposited at a constant surface pressure by the vertical dipping method with a dipping speed of $0.6\,cm\,min^{-1}$. The solid substrates used to support the LB films were quartz, glass, and gold. Gold substrates were purchased from Arrandee, Schroeer, Germany and were flame-annealed at approximately 800–1000 °C with a Bunsen burner immediately prior to use to prepare atomically flat Au(111) terraces.[71] UV/Vis spectra were acquired on a Varian Cary 50 spectrophotometer, and recorded using a normal incident angle with respect to the film plane. SEM images were obtained with a JEOL JSM 6400 microscope. XPS spectra were acquired on a Kratos AXIS ultra DLD spectrometer with a monochromatic Al$_{K\alpha}$ X-ray source (1486.6 eV) using a pass energy of 20 eV. To provide a precise energy calibration, the XPS binding energies were referenced to the C 1s peak at 284.6 eV. The electrical properties of the molecular junctions were recorded with a c-AFM (Bruker ICON) under humidity control (ca. 30%), with a N$_2$ flow using Peak-Force tunneling AFM (PF-TUNA) mode, and employing a PF-TUNA cantilever from Bruker (coated with Pt/Ir 20 nm, ca. 25 nm radius, $0.4\,N\,m^{-1}$ spring constant, and 70 kHz resonance frequency).

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Keywords: electrochemistry · gold · Langmuir–Blodgett films · photochemistry · reduction

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