CHAPTER 2

Electrochemical and topological characterization of gold (111)/oligo(cyclohexylidene)/gold nanocrystal interfaces

1. Introduction

Electrical devices in which molecules or molecular crystals are the active element receive considerable interest from chemists and physicists since they are promising candidates for future miniaturized electrical components[1]. Single-molecule electrical junctions can be made by mounting a molecule between two closely spaced electrodes on a non-conducting substrate. The fabrication of such a device is, however, still very demanding. Only a few single-molecule electrical devices have been presented[2–6]. An alternative method, which can be used for investigating electron transport through single molecules, is based on the attachment of the molecules by one end to a conducting substrate, while an electrical contact at the other end of the molecule is obtained with the tip of a scanning tunneling microscope[7]. Attaching a nanometer-sized particle with an optical or electrical function to the end of the molecule would be a further step in the fabrication of real molecular junctions. Recently, our group has demonstrated that insulating CdS and CdSe quantum dots can be bound to the thiol or sulfide end-functionality of alkane and oligo(cyclohexylidene) molecules which have been self-assembled on gold. This results in a parallel array of optically and electrically addressable gold/molecule/Q-dot junctions[8, 9]. Schiffrin and colleagues reported a self-assembled array of individual and independent molecular junctions, terminated with a gold nanocrystal contact, which show on-off conductance, depending on the electron occupation of a built-in redox system acting as a switch[10].

Here, we report on an electrochemical and Scanning Probe Microscopy (SPM) characterization of a nanostructured interface consisting of a parallel array of gold (111)/oligo(cyclohexylidene)/gold nanocrystal molecular junctions. End-functionalized oligo(cyclohexylidene) molecules (see figure 1 and 2 for structure and notation) form an interesting class of molecules for single-molecule electrical devices since

(i) molecules of different length and with a variety of end-functionalities can be prepared,
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Figure 1. General form of an oligo(cyclohexylidene), where X and Y can be S, CH₂, =N−OH (oxime) or =N−OCH₃ (methylated oxime). The oligo(cyclohexylidene) group (between square brackets) is repeated n times, where n = 0, 1 or 2. For simplicity, the compounds will be named after their number of rings followed by the nature of their substituents X and Y. For instance, a cyclohexylidene with n = 1, X = S and Y = CH₂ will be referred to as a dicyclic monosulfide. For more examples, see figure 2.

(ii) structural analysis on single crystals and ab-initio calculations showed that these molecules preferentially stack in chair conformation[11–13]. The molecules are expected to form a well-ordered self-assembled monolayer (SAM) on gold (111).

(iii) MO-theory and two different types of experiments have shown that they exhibit strong s-through-bond coupling making them possible candidates for molecular wires[8].

We performed a layer-by-layer characterization. First, we investigated the possible formation of self-assembled mono- and difunctionalized oligo(cyclohexylidene) layers on Au(111) surfaces (sections 3.1 and 3.2, respectively) using classical electrochemical methods i.e. by measurement of the interfacial capacitance and by cyclic voltammetry in the presence of a redox system (Fe(CN)₆³⁻/⁴⁻). We employed STM, contact- and tapping mode AFM to investigate the topology of the SAMs on gold. Second, the attachment of gold nanocrystals (Au_{nc}) to the molecular layers was studied by in-situ measurement of the electrochemical capacitance and by ex-situ AFM (section 3.3).

2. Methods

Chemicals were obtained from Aldrich (pentamethylene sulfide 99%, hydrogen tetrachloroaurate(III) trihydrate, sodium citrate dihydrate 99%), Lancaster (1,4-dithiane 98%) and Merck (potassium chloride p.a., sodium perchlorate monohydrate p.a., potassium hexacyanoferrate(II) trihydrate p.a.). All solutions were made using purified water (16 MΩ cm) from the Purite Bio Select. The end-functionalized oligo(cyclohexylidene)s were prepared following previously published studies[11–14].
2. Methods

2.1. SAM preparation and electrochemical setup. A standard three electrode cell was employed, with a Pt counter and a saturated calomel electrode (SCE) as reference. The working electrodes employed consisted of a 1 by 3 cm wide, 1 mm thick borosilicate glass (“pyrex”) slides onto which 2.5 nm of Cr and 200 nm Au were evaporated. Before use, the electrodes were annealed by heating in a hydrogen flame followed by rapid cooling under an Ar flow. Self-assembled monolayers were formed by immersion of the electrode in an ethanolic cyclohexylidene solution at 60 °C for at least 2 days.

2.2. Gold nanocrystal synthesis. Aqueous suspensions of gold nanocrystals were prepared according to the method employed by Frens[15]. A typical synthesis for obtaining charge-stabilised gold particles with a diameter of 16 nm is described below. In a volumetric flask 5 ml of an aqueous 1 % w/w \( \text{HAuCl}_4 \) solution was diluted to 50 ml. This faintly yellow solution was transferred to a 250 ml conical flask and heated to boiling. Under vigorous stirring, 1 ml 0.1 % w/w trisodium citrate solution was added. The solution was stirred and kept boiling until the reaction had ended. The colour changed from slight yellow to intense blue, purple and orange-red.

Larger nanocrystals were prepared by adding smaller amounts of the citrate solution to the same amount of \( \text{HAuCl}_4 \) solution. Particles smaller than 16 nm were synthesized by injecting a freshly prepared mixture of 1 ml 0.1 % w/w sodium borohydride + 1 ml 0.1 % w/w trisodium citrate into the boiling \( \text{HAuCl}_4 \) solution. Since borohydride readily decomposes...
in water, the concentration of borohydride cannot be rigorously controlled. This results in a particle size that differs with each attempt.

Information on particle sizes was obtained from TEM images, see table 1a. As can be seen in figure 3c, the 44 nm particles are highly faceted and elongated in one direction. The difference between the shortest and longest axis could be as much as 10 nm. In contrast the 4.2 nm nanocrystals (figure 3a) show no sign of faceting and the particles are nearly spherical. The intermediate sized particles, see figure 3b, are nearly spherical although some facets are still visible.

![Figure 3](image)

**Figure 3.** Tunneling Electron Microscope (TEM) images of Au nanocrystals made by the Frens method. Reducing agents added were a. 1 ml 0.1% w/w NaBH₄ + 1 ml 0.1% w/w trisodium citrate, b. 1 ml and c. 0.2 ml 0.1% w/w trisodium citrate.

When the larger particles (> 16 nm) are attached to a cyclohexylidene-modified Au(111) surface, the exact contact area cannot be known due to the peculiar shape of these particles. Therefore the larger particles were not used in the following experiments.

### 2.3. Cyclic Voltammetry

Cyclic voltammetry was performed using an EG&G 273A galvanostat/potentiostat in 1 M electrolyte solutions of KCl or NaClO₄, and also with 10 mM FeCN₆⁴⁻ in the solution.

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A colour photograph of the solutions described in table 1 has been printed on the front cover.
2. Methods

2.4. Electrical Impedance Spectroscopy. In Electrical Impedance Spectroscopy (EIS), or Impedance for short, a small sinusoidal perturbation $E_{\text{mod}}$ (typically 5-10 mV), of amplitude $A_E$ and radial frequency $\omega (= 2\pi f$, with $f$ the perturbation frequency), is superimposed onto a constant potential $E_{\text{const}}$ applied to the electrode, see figure 4a, top.

$$E_{\text{EIS}} = E_{\text{const}} + E_{\text{mod}} = E_{\text{const}} + A_E e^{i\omega t} \quad (2.1)$$

The current response ($i_{\text{EIS}}$) to this perturbation will also be a constant current $i_{\text{const}}$ with a superimposed sinusoidal variation $i_{\text{mod}}$. This sinusoidal wave has the same frequency $\omega$, but may be delayed by a phase vector $\varphi$, see figure 4a, bottom.

$$i_{\text{EIS}} = i_{\text{const}} + i_{\text{mod}} = i_{\text{const}} + A_i e^{(i\omega t + \varphi)} \quad (2.2)$$

where $A_i$ is the amplitude of the sinusoidal signal.

![Figure 4. Electrical Impedance Plot](image)

a. top: Applied potential; bottom: Resulting current; b. Impedance vector. Variables as explained in the text.

The electrical impedance $\overrightarrow{Z}$ is defined as the ratio of the modulated current to the modulated potential.

$$Z = \frac{i_{\text{mod}}}{E_{\text{mod}}} = \frac{A_i}{A_E} e^{i\varphi} \quad (2.3)$$

Equation 2.3 shows that the impedance is a time-independent vector in the imaginary plane, as schematically shown in figure 4b. The length of the vector $\overrightarrow{Z}$ is given by the ratio $A_i/A_E$ and the angle with respect to the real axis is $\varphi$. The real axis $Z'$ is equal to the total resistance of the system, whereas the imaginary axis $Z''$ is related to the total capacitance $C$ as $Z'' = 1/(\omega C)$.

Measurements were performed using the Solartron 1255B Frequency Response Analyzer. During a measurement typically 40 different frequencies were applied ranging from $f = 1.3$ to 13000 Hz, 10 in each decade. These frequencies were chosen such that no single frequency was close to a multiple
of 50 Hz to avoid interference from the mains. Next, the data was fitted to the equivalent circuit shown in figure 5, where $R_\Omega$ is the cell resistance, $C_d$ the interfacial capacitance and $R_F$ the charge transfer resistance. This was done for several potentials ranging typically from -0.7 to +0.7 V vs. SCE.

### 2.5. Potential Step

In contrast to Electrical Impedance Spectroscopy where a sinusoidal perturbation is applied, the potential of the working electrode is instantaneously stepped from $E$ to $E + \Delta E$, see figure 6a. $\Delta E$ was chosen as 0.05 V after it was confirmed that the results are independent of the amplitude of the potential step.

After each potential step current flows to compensate for the potential step, see figure 6b. This charging current density $i_c$ induced by the potential step is related the interfacial capacitance $C_d$ as

$$i_c = \frac{dq}{dt} = \frac{dq}{dE} \frac{dE}{dt} = C_d \frac{dE}{dt}$$  \hspace{1cm} (2.4)

where $q$ is the charge density of the electrode.

Integrating the current measured between time $t_1$ before the potential step and $t_2$ after the system has reequilibrated yields the interfacial capacitance times the potential step.

$$\int_{t_1}^{t_2} i_c \, dt = C_d \int_{E(t_1)}^{E(t_2)} dE = C_d \Delta E$$  \hspace{1cm} (2.5)
The determined value is therefore the double layer capacitance at $E + \frac{1}{2} \Delta E$. The capacitance data is then plotted against potential (figure 6c).

The setup is identical to that used for cyclic voltammetry. Transients were checked visually for signs of overlap between consecutive pulses. Since the electrode is perturbed with a single pulse, this method can be compared with EIS with a large(r) amplitude pulse and a frequency close to zero ($\omega \to 0$).

2.6. Atomic Force Microscopy. Atomic Force Microscopy (AFM) images were made using the Digital Instruments Nanoscope IIIa. The substrates (10x10x1 mm) were either the same as those used for the electrochemical investigations or were obtained from Arrandee\(^b\), formerly Metallhandel Schröer GmbH.

Atomic Force Microscope uses the mechanical interaction of the tip with a substrate. By scanning the tip over the substrate an image of the topology can be obtained. Two types of AFM were employed.

- "Contact mode" AFM (cmAFM) utilizes a sharp tip mounted on a wedge-shaped cantilever. When pressed onto a substrate the deflection of the cantilever can be measured using a focussed laser beam. The interaction of the tip with the substrate is very strong, and may sometimes induce structural changes in the substrate.

- In "Tapping mode" AFM (tmAFM) a sharpened cantilever is brought into resonant oscillation. This oscillation is monitored by a laser beam focused on the cantilever. As the cantilever touches the substrate, the oscillation is dampened and the amplitude of the oscillation decreases.

\(^b\)Arrandee website: http://www.arrandee.com/
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Figure 8. The interfacial capacitance (measured at 1000 Hz) of a gold (111) electrode in an aqueous solution of 1 M KCl at 25°C as a function of electrode potential after pretreatment with ethanolic solutions of oligo(cyclohexylidene)s with different end-functionalities. (1, —■—) an untreated, bare gold (111) electrode. (2, —·○·—) after immersion in pure ethanol for 12 hours. (3, —·●·—) after immersion in an oxime (figure 2c; n=1)/ethanol solution for 24 hours. (4, ·▲··) after immersion in a monosulfide (figure 2a; n=1)/ethanol solution for 24 hours. The insert shows the capacitance $C$ at 0 V vs. SCE (normalized with respect to that measured at 1000 Hz, denoted $C'$) as a function of the modulation frequency.

The resolution of both methods is limited by the size of the tip apex. This causes the so-called tip convolution effect. The size of all objects in the plane of the substrate (the X-Y direction) seem enlarged by approximately the tip diameter, see figure 7. As a result, the dimensions of any feature on the substrate can only be accurately determined in the Z direction. The convolution effect is more prominent for small features, since the distortion will be relatively large.

3. Results

3.1. Monofunctionalized oligo(cyclohexylidene)s. We first investigated the possibility of forming self-assembled monolayers with monofunctionalized oligo(cyclohexylidene)s, specifically the two ring monosulfide and oxime (figure 2a and c, respectively, both with n=1). Figure 8 curve 1 shows
the interfacial capacitance of a bare gold (111) electrode in an aqueous 1 M KCl solution as a function of the electrode potential, together with the capacitance measured after application of the monosulfide (figure 8, curve 4) and the oxime (figure 8, curve 3). The frequency dependence of the measured capacitances at 0 V vs. SCE is shown in the insert. The capacitance (normalized with respect to the capacitance at 1000 Hz) of the bare electrode increases considerably with decreasing modulation frequency. A strong frequency dependence of the interfacial capacitance in concentrated aqueous electrolytes has been reported before [16]. This frequency dispersion is most likely due to surface roughness[17] and/or specific adsorption of the anion[18, 19]. It was not possible to account for the frequency dependence by a constant phase element. We therefore present the capacitance measured at a frequency of 1000 Hz for further discussion. The bare Au(111) electrode shows a pronounced maximum at +0.2 V, close to the potential of zero charge. The maximum capacitance in a 1 M KCl solution varied from sample to sample (68 µF cm$^{-2}$ ± 15 % at 1000 Hz). Negative with respect to the maximum, the capacitance decreased to a constant value equal to 20 µF cm$^{-2}$. Positive of the potential of zero charge the capacitance decreased to 9 - 15 µF cm$^{-2}$ at 0.7 V. The capacitance plot of Au(111) in 1 M NaClO$_4$, see figure 9, has the same features; however the maximum is much less pronounced than for KCl. The maximum in the capacitance is observed at +0.3 V vs. SCE, which is close to the point of zero charge $E_{pzc}$ of +0.33 V vs. SCE found in the literature[20–24]. The $C$ vs. $E$ plot shows an asymmetric peak in KCl, very probably due to chemisorption of Cl$^-$ ions at the electrode surface in the potential range positive of $E_{pzc}$. Similar results (an increase of the maximum capacitance and shift of the maximum to more negative potentials with increasing specific adsorption) have been reported in the literature[16, 18, 19].

The capacitance of the gold electrode measured in a 1 M KCl solution after a prolonged immersion in an ethanolic solution of oxime (figure 8, curve 3) is reduced considerably compared to that of a bare electrode, and a maximum is not found in the capacitance-potential curve. A similar reduction of the interfacial capacitance is, however, found after placing the electrode for one night in pure ethanol, see figure 8, curve 2. Note that the frequency dependence of the interfacial capacitance of a bare and an oxime-treated electrode is identical (insert figure 8). We infer that the interfacial capacitance is reduced with respect to that of a bare electrode due to physisorption of ethanol or oxime molecules and that a robust SAM is not formed. In contrast, the capacitance of the gold electrode in a 1 M KCl solution is extremely low ($C < 1$ µF cm$^{-2}$) in the entire potential range after application of a monosulfide (figure 8, curve 4). The capacitance decreases with increasing length of the monosulfide (figure 2a; n=0,1). This is at odds with what was found with functionalized n-alkanethiol SAMs[25–27].
indicates that monosulfides form well-ordered SAMs that cover the entire electrode. This has been confirmed by ex-situ tapping mode AFM, contact mode AFM and STM characterization of such layers. No defects could be found in the layers, and the atomic steps of the Au(111) surface were visible on the images.

The contrast between the effect of monosulfides and oximes (figure 2a and c, respectively) on Au(111) is also illustrated by the cyclic voltammograms shown in figure 10. With the bare gold electrode the difference between the reduction and oxidation peaks of $Fe(CN)_6^{3-}/^{4-}$ in a 1 M $KCl$ solution is 110 mV, whereas 58 mV is expected for a reversible reaction. The reaction is thus quasi-reversible at a scan rate of 100 mV/s. Similar results have been reported in the literature\[28\]. After immersion of the gold sample in ethanol or an oxime in ethanol solution, the reaction becomes more irreversible, indicating that oxime or ethanol molecules cover (partly) the electrode surface. However, the cyclic voltammogram tends to that of a bare electrode when the electrode potential is scanned for a longer time, indicating that the ethanol or oxime molecules are weakly physisorbed and can be removed electrochemically. On the other hand, when the gold electrode was treated with a monosulfide (figure 2a; n=1) dissolved in ethanol, the oxidation/reduction reaction is strongly inhibited with respect to that at a bare gold electrode. Pinholes in the SAM are rarely observed with STM;
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Figure 10. Cyclic voltammograms measured in a 10 mM FeCN$_4^{4-}$/1 M KCl solution after several pretreatments. (1,–) an untreated, bare gold (111) electrode. (2,⋯⋯) after immersion in a pure ethanol solution for 12 hours. (3,−−−−) after immersion in an oxime (figure 2c; $n = 1$)/ethanol solution for 24 hours. (4,····) after immersion in a monosulfide (figure 2a; $n = 1$)/ethanol solution for 24 hours.

thus it is likely that the remaining Faradaic current is due to electron transfer through the oligo(cyclohexylidene) SAM. We conclude that monosulfide oligo(cyclohexylidene)s form well-ordered SAMs, with a strong gold-sulfur bond. It is clear that the oxime function does not bind chemically to gold.

3.2. Difunctionalized oligo(cyclohexylidene)s. Next, we investigated the possible formation of SAMs by difunctionalized oligo(cyclohexylidene)s, i.e. disulfides, oxime-sulfides and methylated oxime-sulfides, on Au(111). After treatment of the gold surface with a disulfide (figure 2b; $n=0$), the interfacial capacitance in 1 M KCl reduces to a value of about 6 $\mu$F cm$^{-2}$ at 1000 Hz, independent of the electrode potential. In addition, the cyclic voltammograms show a strong attenuation of interfacial electron transfer. This points to the formation of a well-ordered oligo(cyclohexylidene) disulfide SAM covering the entire gold surface; this conclusion is supported by AFM measurements. The results obtained after application of the oxime-sulfides (figure 2d; $n=0$) and methylated oxime-sulfides (figure 2e; $n=0$) are shown in figures 11 and 12. After application of the oxime-sulfide, the capacitance is moderately reduced with respect to that of a bare gold electrode measured in KCl solution (compare curves 1 and 2 of figure 11).
The interfacial capacitance (measured at 1000 Hz) of a gold (111) electrode in an aqueous solution of 1 M KCl at 25°C as a function of electrode potential after pretreatment with ethanolic solutions of oligo(cyclohexylidene)s with different end-functionalized. (1,—■—) an untreated, bare gold (111) electrode. (2, −−•−−) after immersion in a oxime-sulfide (figure 2d; n=0)/ethanol solution for over 48 hours. (3, · · ▲ · ·) after immersion in a methylated oxime-sulfide (figure 2e; n=0)/ethanol solution for 24 hours.

The capacitance is in the range of 15-20 μF cm⁻²; a value smaller than 10 μF cm⁻² is expected for a well-ordered SAM. Moreover, the Fe(CN)₆³⁻/⁴⁻ peak currents in the voltammogram for a 1 M KCl solution are reduced to only half the values found with a bare electrode (figure 12, curves 1 and 2). These results suggest that oxime-sulfides do not form a well-ordered SAM on Au(111). This is unexpected, since the sulfide function binds strongly to gold, resulting in well-ordered SAMs with the mono and disulfide. The oxime =N-OH function seems to hinder SAM formation. This is supported by the results shown in figure 11 (curve 3) and 11 (curve 3), obtained with methylated oxime-sulfides (figure 2e; n=0). The capacitance reduces to a value of 4 μF cm⁻² at 1000 Hz, even slightly lower than that of a disulfide. In addition, the reduction/oxidation of the redox system is strongly inhibited. It is not yet clear why the =N-OH end-functionality has such a strong inhibiting effect on the formation of a SAM layer. It may be related to the fact that the =N-OH group can form hydrogen bonds with ethanol or another oxime molecule.
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Figure 12. Cyclic voltammograms measured in a 10 mM Fe(CN)$_6^{4-}$/1 M KCl solution after different pretreatments. (1, —) an untreated, bare gold (111) electrode. (2, ---) after immersion in a oxime-sulfide (figure 2d; $n = 0$)/ethanol solution for over 48 hours. (3, ···) after immersion in a methylated oxime-sulfide (figure 2e; $n = 0$)/ethanol solution for 24 hours.

3.3. Gold nanocrystal attachment. We investigated whether the gold (111)/disulfide system can be used in preparing gold (111)/oligo(cyclohexylidene)/Au$_{nc}$ molecular junctions. Charge-stabilized gold nanocrystals (5-20 nm in size) were adsorbed on a gold (111)/disulfide interface from an aqueous colloidal suspension[15]. The size of the nanocrystals was checked by UV-VIS spectroscopy, TEM and tapping mode AFM. Figure 13a shows a tapping-mode AFM picture of a Au/disulfide interface which is covered with gold nanocrystals. From the cross-section (inset) it follows that the height of the nanocrystals is 15 nm which is in agreement with the particle size in solution. The same agreement was found for a Au/disulfide/Au$_{nc}$ interface with Au nanocrystals of 8 nm in size, see figure 13b. Interestingly, the nanocrystals attach as individual particles to the disulfide SAM; no clustering is observed. The nanocrystals cannot be moved along the surface by the tapping-mode tip indicating strong bonding and formation of a robust Au(111)/disulfide/Au$_{nc}$ junction. Charge-stabilized nanocrystals were also observed to adhere to some extent to an alkyl-terminated monosulfide (figure 2a; $n=0$) SAM. Figure 13c shows the result after immersion of the gold with a monosulfide SAM in colloidal suspension. Individual nanocrystals are observed on the SAM. However, when the tip/substrate interaction is
increased (low setpoint) the gold nanocrystals can be moved along the surface by the tapping-mode tip (resulting in the ‘stripes’ going from top-right to bottom-left in figure 13c), indicating that they are van der Waals-bound to the surface. Interestingly, charge-stabilized gold nanocrystals do not attach to a bare Au(111) surface under open-circuit conditions. The result of prolonged immersion of bare gold in a colloidal solution is shown in figure 13d: only some large agglomerates are visible at the grain boundaries.

As has been previously shown, self-assembly of a oxime-sulfide (figure 2d; n=0) on gold (111) leads to a disordered layer, most likely due to the formation of hydrogen bonds. These hydrogen bonds can give rise to the
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Figure 14. Dimer of two oxime-sulfides molecules through hydrogen bonds.

formation of oxime dimers[29], see figure 14. If a sufficient amount of dimers attach to the gold (111) surface a gold nanocrystal can be securely attached to the interface. In figure 13e a sulfide-oxime modified gold (111) electrode was immersed in a 16 nm Au_{nc} solution. The gold nanocrystals cannot be moved by the tapping mode AFM tip, suggesting that the gold nanocrystals are firmly attached to the Au(111)/oxime-sulfide cyclohexylidene surface.

We were unable to image nanocrystals attached to an oligo(cyclohexylidene) SAM with Scanning Probe Microscopy (SPM) methods other than with tapping mode AFM. The force applied by contact mode AFM and STM tips proved to be enough to break the adhesion between the surface and the nanocrystal. Probing an individual nanocrystal attached to a cyclohexylidene SAM will therefore not be possible. However, probing all the nanocrystals simultaneously by electrochemical means should still be feasible.

In figure 15 the interfacial capacitance of a Au(111)/disulfide/Au_{nc} interface in a 1 M KCl solution is plotted as a function of electrode potential. The capacitance of the bare electrode is considerably reduced after application of the disulfide to the Au(111) surface (compare curves 1 and 2 of figure 15), again demonstrating the quality of the disulfide SAM on gold. When gold nanocrystals are anchored to the SAM, the capacitance increases in the entire potential range; the increase is most pronounced at around the potential of zero charge (curve 3); the capacitance of the nanostructured Au(111)/disulfide/Au_{nc} interface shows a maximum as a function of the potential, similar to that of a bare gold electrode. We conclude that the attachment of gold nanocrystals to the SAM leads to the formation of an additional gold/water interface which can be charged/discharged by electron transfer through the molecular layer. A simple model to explain this effect qualitatively will be discussed below.

We used the increase of the interfacial capacitance $C(\omega \rightarrow 0, E \approx E_{pzc})$ as a quantitative measure to follow in real time and in-situ (i.e. in the colloidal gold suspension) the anchoring of gold nanocrystals (15 nm in size) to a gold/disulfide SAM. In figure 16 the relative increase in capacitance $\theta = \Delta C/\Delta C_{max}$, which is a measure for the surface coverage, is plotted versus time. A justification of this procedure is given in the discussion. Initially, the surface concentration of Au_{nc} on the SAM layer increases linearly with time; the addition rate decreases at longer times and finally becomes very
Figure 15. The low-frequency limit of the interfacial capacitance of a gold (111) electrode after different pretreatments in a 1M KCl solution at 25°C as a function of the electrode potential. The capacitance was obtained from the charging/discharging response to small-amplitude potential step. (1, —■—) an untreated, bare gold (111) electrode. (2, ···) after immersion of the gold (111) electrode in an ethanolic solution of disulfide (figure 2b; n=0). (3, −−−) after immersion of the gold (111)/disulfide electrode in a colloidal gold suspension for 4 hours. The ↑ shows the increase in the capacitance due to the gold nanocrystal attachment.

low. We note that the maximum coverage observed in the saturation range is about 75 particles/µm², corresponding to an average centre-to-centre distance of about 97 nm between two nanocrystals (A local mapping is given in the inset of figure 13a). Assuming an attachment rate independent of the surface coverage, i.e. interparticle interactions are ignored, we can describe the rate $d\theta/dt$ as:

$$\frac{d\theta}{dt} = k_a c (1 - \theta) - k_d \theta$$  \hspace{2cm} (2.6)

where $\theta$ is the fraction of the surface sites occupied by a nanocrystal, $c$ is the concentration of nanocrystals and $k_a$ and $k_d$ the pseudo-first order rate constants for nanocrystal adsorption and desorption, respectively. At equilibrium ($d\theta/dt = 0$) equation 2.6 simplifies to the well-known Langmuir isotherm, which is used to describe reversible (monolayer) adsorption onto surfaces.
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Figure 16. The relative surface coverage $\theta = \Delta C/\Delta C_{\text{max}}$ of gold nanocrystals on a gold (111)/disulfide (figure 2b; n=0) SAM attachment obtained from the increase in the interfacial capacitance (see arrow in figure 15) measured in-situ during nanocrystal attachment. The data (■) have been fitted with equation 2.6 (——), equation 2.7 (−−−) and equation 2.7 with $C_{\text{max}}$ taken as 1.17 times the highest measured capacitance (･･･).

A fit of the addition kinetics according to equation 2.6 is included in the figure 16 (drawn line). It can be seen that this simple law describes the kinetics of particle addition reasonably well, except for the longer times, i.e. at high coverage. This is probably due to the electrostatic interactions between the adsorbed particles, which is important at high coverage. Therefore a Frumkin-type exponential factor is incorporated in equation 2.6.

$$\frac{d\theta}{dt} = k_a c (1 - \theta) e^{-f\theta} - k_d \theta$$  \hspace{1cm} (2.7)

At equilibrium $(d\theta/dt = 0)$ equation 2.7 yields the Frumkin isotherm. The Frumkin parameter $f$ takes into account the fact that the apparent free energy of binding to the substrate changes linearly with surface coverage[30]. When $f < 0$, the interaction between the particle and the (particle covered) surface is repulsive, whereas $f > 0$ when this force is attractive.

The exponential factor in equation 2.7 causes the fit to level off later (at higher t), as can be seen in figure 16, dashed curve. Unfortunately, this does not increase the accuracy of the fit. In the previous section we assumed that the highest measured capacitance corresponds to $C_{\text{max}}$. However, since this equilibrium value is only slowly reached the true maximum may be higher.
When $C_{\text{max}}$ was increased by 17.6% the fit was obtained as shown in figure 16, dotted curve. This fit describes satisfactory the attachment of particles.

It should be remarked that the attachment of gold nanocrystals is likely to be an irreversible process, i.e. $k_d \equiv 0$. This may also explain why the gold nanocrystals do not form ordered two-dimensional arrays on the gold/disulfide surface.

4. Discussion and Conclusions

The interfacial capacitance of a gold (111) electrode covered with an oligo(cyclohexylidene) SAM is very much reduced compared to that of a bare gold electrode; in addition it shows a different dependence on the electrode potential and modulation frequency. The capacitance features change again when gold nanocrystals become attached to the SAM. The highly polarizable double layer structure (i.e. jellium layer) of the metal, itself arising from electrons that spill over the surface layer of gold core ions, plays a key role in the total capacitance\[31, 32\]. There is still debate on the applicability of the jellium model to noble metals. Here, we take the jellium model as a basis to rationalize the experimental results presented in the foregoing section. The capacitance of a bare gold (111) electrode measured in 1 M $\text{KCl}$ and 1 M $\text{NaClO}_4$ aqueous solutions shows a pronounced and asymmetric peak when plotted as a function of the electrode potential and a relatively strong frequency dependence. The peak can be accounted for by the capacitance of the metal double layer $C_M$ that is in series with the capacitance of the first water layer $C_{\text{sol}}$, see figure 17a. The interfacial capacitance of a bare gold electrode is then given by equation 2.8:

$$C = \frac{|C_M|C_{\text{sol}}}{|C_M| - C_{\text{sol}}} \quad (2.8)$$

The peak in the interfacial capacitance $C$ at around $E_{\text{pzc}}$ can be explained by assuming

(i) that $C_{\text{sol}}$ does not depend strongly on the charge density and hence on the electrode potential, and

(ii) that $|C_M| - C_{\text{sol}}$ is positive in the entire potential region and has a minimum at around $E_{\text{pzc}}$.

The maximum interfacial capacitance depends sensitively on the difference $|C_M| - C_{\text{sol}}$ around the point of zero charge. This explains the strong influence of the nature of the metal and exposed crystal surface on the maximum interfacial capacitance close to $E_{\text{pzc}}$, reported in the literature\[32\]. In 1 M $\text{KCl}$ and 1 M $\text{NaClO}_4$, $E_{\text{pzc}}$ is +0.2 and +0.3 V vs. SCE, respectively. This is somewhat more negative than in fluoride electrolytes ($E_{\text{pzc}} = +0.33$ V vs. SCE\[20–24\]) indicating specific $\text{Cl}^-$ and to lesser extent $\text{ClO}_4^-$ adsorption on the gold (111) surface. The frequency dispersion of a bare electrode is more pronounced than that of a gold electrode covered with a SAM (see
4. Discussion and Conclusions

a. \(R_C\)

b. \(C_{SAM}\)

Figure 17. Randle’s equivalent circuit for a. a bare metal electrode, b. a metal electrode covered with a self-assembled monolayer, and c. a disulphide modified Au(111) electrode covered with a gold nanocrystal, all in contact with a polar electrolyte solution. For explanation of the electrical components see text.

insert of figure 8). This suggests that the frequency dispersion of bare gold electrodes is due partly to anion adsorption\cite{19}. At potentials negative with respect to \(E_{pzc}\) the capacitance of the bare electrode decreases to a nearly constant value of 20 \(\mu F\) \(cm^{-2}\) at 1000 Hz, indicating that \(C_M \gg C_{sol} \cong 20 \mu F\) \(cm^{-2}\) when the charge density on the gold surface is negative (see also figure 8).

Oligo(cyclohexylidene) mono- and disulfide molecules, and methylated oxime-sulfide molecules (figure 2a, b and e, respectively) form well-ordered SAMs on gold (111) surfaces, characterized by a low and nearly potential-independent capacitance \((C \leq 6 \mu F\) \(cm^{-2}\)). The structure of the double layer is schematically presented in figure 17b. The capacitance of the metal double layer can be influenced by the large density of Au-S bonds; \(C'_M\) is used instead of \(C_M\) to denote this capacitance. Similarly, we use \(C'_{sol}\) (instead of \(C_{sol}\)) for the capacitance of the solvent layer in contact with the SAM. The total interfacial capacitance is now given by equation 2.9:

\[
C = \frac{|C'_M|C'_{sol}C_{SAM}}{|C'_M|(|C'_{sol} + C_{SAM}) - C_{SAM}C'_{sol}} \tag{2.9}
\]

The interfacial capacitance is nearly equal to that of the SAM monolayer for the case in which \(C'_M > C_{sol} > C_{SAM}\):

\[
C \cong C_{SAM} = \frac{\varepsilon_{SAM}\varepsilon_0}{d_{SAM}} \tag{2.10}
\]
where $\varepsilon_{SAM}$ is the dielectric constant and $d_{SAM}$ the thickness of the SAM. Equation 2.10 explains why the observed capacitance of the SAM covered gold electrode is low and does not show a peak at around $E_{pzc}$. We should remark here that there are subtle, but reproducible differences between sulfide oligo(cyclohexylidene)s of the same length ($n=0,1$) but with different end-functionalities at the water side; the capacitance of the alkyl-terminated SAM is smaller than that of a methylated oxime-sulfide (figure 2e) terminated SAM, which is, in turn, slightly smaller than that of a sulfide-terminated (figure 2b) SAM. This may be due partly to a difference in $\varepsilon_{SAM}$, partly to a different ordering of the first water layers contacting the hydrophobic and less hydrophobic end-functionalities of these oligo(cyclohexylidene) molecules. A dependence on the end-functionality has also been reported in the literature [25, 26]. We also note that the capacitance decreases with increasing length of the molecules in the SAM, which is in qualitative agreement with equation 2.10.

When a gold nanocrystal ($Au_{nc}$) is anchored to an S-terminated oligo(cyclohexylidene) SAM layer a nanometer-sized electrical junction is formed with an impedance represented in figure 17c. This impedance replaces that of a non-occupied site shown in figure 17b. Since the entire system consists of both occupied and non-occupied sites, the total electrical equivalent circuit for the Au(111)/oligo(cyclohexylidene)/$Au_{nc}$ interface is formed by a parallel connection of figure 17b and c. The impedance of a gold (111)/oligo(cyclohexylidene)/$Au_{nc}$/water structure shown in figure 17c accounts for charging of the gold nanocrystal through the molecular SAM layer (Faradaic resistance $R_{F,SAM}$) and the formation of an electrochemical double layer at the gold nanocrystal/water interface (capacitance $R_{F,NC/sol}$). At sufficiently low frequencies, the nanocrystal/water interface can be charged/discharged, and the interfacial capacitance will be larger than that of a gold (111)/oligo(cyclohexylidene)/water site. Although the scheme presented in figure 17b-c for the nanostructured interface is perhaps naive, it can be used to understand the increase of the interfacial capacitance of the gold electrode upon attachment of gold nanocrystals to the SAM layer (figure 15 and 16).

From the above discussion, we may conclude that the electrochemical capacitance provides a plausible description of a bare gold (111)/water, a gold (111)/oligo(cyclohexylidene)/water and a gold (111)/oligo(cyclohexylidene)/*$Au_{nc}$/water interface. The self-assembly of end-functionalized alkane molecules on metal surfaces (mostly alkanethiols on gold surfaces) has been studied extensively by other research groups[7, 33, 34]; similar conclusions concerning the usefulness of electrochemistry have been drawn. The novelty of our work lies in the choice of the molecules, i.e. oligo(cyclohexylidene)s, and in the striking effects found with different end-functionalities. Oligo(cyclohexylidene) molecules have a rigid C-skeleton with a chair conformation. This enables the formation of well-ordered SAMs, even with short molecules,
with one cyclohexyl ring (i.e. \( n = 0 \)). In addition, both chemical end-functionalities play a key role in the possible formation of oligo(cyclohexylidene) SAMs on gold (111) surfaces. We found that oligo(cyclohexylidene) molecules terminated with one or two sulfide-end functions form well-ordered SAMs on gold (111). Even the shortest oligo(cyclohexylidene) molecule led to a low and potential-independent capacitance and a considerable reduction of the rate of interfacial electron transfer. The electrochemical results show that oxime-terminated oligo(cyclohexylidene) molecules do not form a SAM on gold (111). The oxime-gold interaction is too weak. Surprisingly, oligo(cyclohexylidene) molecules with a sulfide and oxime function also do not form well-ordered SAMs. This is not well understood at present, but the results clearly indicate that the oxime termination inhibits the formation of well-ordered layers.

A second new aspect in this work is that we show that the attachment of Au nanocrystals to a gold/oligo(cyclohexylidene) SAM can be followed in-situ by measurement of the interfacial capacitance. Attachment of a gold nanocrystal to the SAM leads to a new gold/water nanointerface that can be charged by electron transport through the molecular layer. Similarly, photo-induced electron transfer through oligo(cyclohexylidene) molecules mounted between an insulating quantum dot and gold has been observed [8]. By measurement of this additional charge, we were able to follow the adsorption kinetics. A simple law is found; the rate of adsorption of the nanocrystals on the SAM is proportional to the density of free sites on the SAM surface. Under conditions of saturation, we find with tapping mode AFM a disordered array of individual gold nanocrystals, still corresponding to a relatively low coverage. Most likely, the attachment of nanocrystals is an irreversible process. The low coverage may be due to the charged double layer around the nanocrystals. This also explains why there is no clustering of individual nanocrystals. It should be noted here that charge-stabilized gold nanocrystals do not attach to bare gold, but only form some clusters at the grain boundaries. We suggest that the electron spill-over region (jellium layer) of the bare gold (111) surface repels the negatively charged gold nanocrystals. Interestingly, when the gold (111) surface is covered with an alkyl-terminated SAM, gold nanocrystals do attach to the surface. With tapping mode AFM, we show that these nanocrystals can be moved easily along the surface, a clear indication of weak adsorption. This is in clear contrast to the nanocrystals attached to a sulfide-terminated surface, which are chemically bound.

References.