Surface plasmon resonance spectroscopy for in situ sensing of molecular nanowire formation

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Abstract: We have investigated the attachment and wire formation of molecules on gold nanoparticles by confocal microscopy and surface plasmon resonance spectroscopy. For this purpose a ruthenium complex with sulfur ends, a double cyclodextrin unit, and an iridium complex have been stepwise assembled on highly ordered triangular gold nanoparticles. The particles were prepared by nanosphere lithography and exhibit a plasmon resonance at 730 nm. Using confocal microscopy, we can demonstrate that the ruthenium complex, which serves as anchor molecule, binds selectively on the gold nanoparticles. Afterwards we measured the shift of the plasmon resonance as a function of molecular wire length by surface plasmon resonance spectroscopy. We observed distinct shifts of the plasmon resonance between 11 nm and 20 nm, depending on the attached molecule. Altogether, a plasmon shift of 46 nm for the complete wire has been measured. With these experiments we demonstrate, that a molecular wire formation can be monitored in-situ by surface plasmon resonance spectroscopy.

Key–Words: Gold nanoparticles, nanosphere lithography, plasmon resonance spectroscopy, triangular nanoparticles

1 Introduction

Since centuries the magnificent colors of stained glass, for example in old church windows or drinking cups of stained glass, have attracted a large amount of scientists as well as artists. However, the origin of the colors remained unknown for a long time. The first one, who referred the colors to metal nanoparticles, was Michael Faraday. In his famous article entitled Experimental Relations of Gold (and Other Metals) to Light from 1857 he concluded [1]: I think that in all these cases the ruby tint is due simply to the presence of diffused finely-divided gold. The first theoretical explanation of the colors came up approximately fifty years later in 1908 by Gustav Mie. He applied the Maxwell equations in spherical coordinates to small spheres in homogeneous environments [2] to explain the experimental findings of his students [3]. With this pioneering work, he could trace the origin of the colors back to a resonant absorption of light by small metal spheres. This resonant absorption, which is caused by a collective excitation of conduction band electrons in metal nanoparticles, is nowadays called localized surface plasmon polariton resonance. For simplicity, we refer to this kind of excitation as surface plasmon or simply plasmon.

A variety of alkaline and noble metals exhibit pronounced plasmon resonances. But due to the great potential for applications gold nanoparticles have been widely investigated in recent years [4–7]. The reason is, that the position of the plasmon resonance depends substantially on the nanoparticle size, shape, composition, and dielectric surrounding [8–14]. The excitation of a surface plasmon is accompanied by a local field enhancement, which is exploited for many extremely different applications, such as surface-enhanced Raman spectroscopy [4, 15, 16], wave guiding [17, 18], surface-enhanced fluorescence [19, 20], and confocal microscopy [21], as well as to enhance the efficiency of solar cells [22], or to structure surfaces [23, 24].

For plenty applications, regular arrays of metal nanoparticles are desired. For example, they may serve as anchor points for electro-optic active molecules, used for electro-optical devices. Usually, metal nanoparticle arrays are prepared by electron beam lithography or photolithography. While electron beam lithography is time consuming and expensive, photolithography has lower limits concerning nanoparticle size. To overcome the aforemen-
tioned drawbacks, nanosphere lithography (NSL) has been invented [25]. NSL is an inexpensive technique to prepare regular arrays of highly ordered triangular nanoparticles [26–29] with a high throughput. The size of the generated nanoparticles can easily varied by changing the amount of the deposited material and/or the diameter of the nanospheres used as a mask. The nanoparticle shape and size and the distance between to particles can also be varied, either by tilt evaporation [30] or laser tailoring [26, 31].

In this paper, we present recent measurements with the objective to monitor in situ a molecular wire formation by surface plasmon resonance spectroscopy. For this purpose, highly ordered triangular gold nanoparticles on substrates have been prepared by NSL. The advantage of using triangular gold nanoparticles for surface plasmon resonance spectroscopy is their high surface area where the molecules can attach. Hence, these nanoparticles have a higher sensitivity compared to, for example, spherical nanoparticles with the same volume. We demonstrate that we can monitor clearly distinct and stepwise shifts of the plasmon resonance due to subsequent attachment of different molecules, which form a wire. In addition, elongated nanoparticles have been prepared for confocal microscopy measurements.

2 Experimental

Arrays of triangular gold nanoparticles were prepared using nanosphere lithography, utilizing the drop coating method of Micheletto et al. [32]. Quadratic fused silica plates with an edge length of 12 mm and a thickness of 5 mm served as substrates. Two different lithographic masks have been prepared using monodisperse latex nanospheres, either with a diameter of 330 nm or of 1390 nm. After formation of large areas of well ordered monolayers or doublelayers of nanospheres, the substrates were transfered to a thermal evaporation chamber (Balzers BA 510). At a pressure of approximately $10^{-6}$ Pa, a gold film has been prepared on the substrate. In all experiments the gold film thickness was set to 30 nm. After film deposition, the nanosphere mask was removed by sonicating the substrate for 1 to 3 minutes in dichloromethane, leaving behind large areas of highly ordered gold nanoparticles (figure 1a). Details of the preparation have been explained in reference [33].

To characterize the samples optical spectroscopy, scanning electron microscopy, and atomic force microscopy were applied. While in situ optical spectroscopy has been performed to measure the optical properties, ex situ microscopy techniques have been applied to determine the morphology of the nanoparticles.

To demonstrate that the molecules attach selectively to the nanoparticles and not to the substrate, confocal microscopy has been applied. Due to the limited optical resolution of the confocal microscope, large nanoparticles have been used for the fluorescence measurements. The large elongated nanoparticles with an average side length of (365 ± 17) nm and a particle particle distance of about (1484 ± 19) nm have been generated with a lithographic mask consisting of a doublelayer of 1390 nm nanospheres. In these experiments, the second nanosphere layer was slightly shifted with respect to the first layer due to the tilt coating. As a result, slightly elongated nanoparticles, as depicted in figure 1b) were generated.

Nanospheres with a diameter of 330 nm have been used to generate small triangular nanoparticles. These nanoparticles exhibit a high surface to volume ratio and are ideal for monitoring wire formation by surface plasmon resonance spectroscopy.

Three different recently synthesized molecules, which yield a high potential for future applications in molecular electronic devices, have been used for wire formation. The first molecule is a ruthenium complex ($[\text{Ru(bipty})(\text{tpySS})](\text{NO}_3)_{12}$) and acts as an...
anchor molecule that attaches to the gold nanoparticles. Molecule two consists of two connected cyclodextrines (bis-propargyl-p.m.-CD) and serves as a connecting molecule between the ruthenium complex and the third molecule, which is an iridium complex ([Ir(bibtpy)(tpy)]PF$_6$)$_3$. The chemical structure of the molecules is depicted in figure 2.

![Chemical structure](image)

Figure 2: Chemical structure of the molecules used for wire formation.

Wire formation has been performed as follows. The attachment of the first component has been achieved by immersion of the substrate with the small gold nanoparticles for 24 hours in a methanolic solution (1 mM) of the ruthenium complex. Thereafter, the substrates were washed with methanol in order to remove any excess of the ruthenium compound from the sample. Afterwards, the substrates have been dried with a gentle flow of nitrogen. To attach the cyclodextrin unit, the substrates with the ruthenium complex were immersed in a solution (10 % CH$_3$CN in H$_2$O) of the cyclodextrin unit for two hours. Afterwards, the substrates were rinsed with water and dried with nitrogen. Finally, the substrate were immersed in a solution (10 % CH$_3$CN in H$_2$O) of the iridium complex for two hours. As before, the substrates were washed with water and dried with nitrogen. After each adsorption process, the extinction spectrum has been measured. In addition, after adsorption of the ruthenium complex, a confocal microscopy image has been recorded.

3 Results

3.1 Characterization of the nanoparticles after preparation

The morphological parameters of the nanoparticles have been obtained by AFM and SEM. While SEM (cf. figures 1a and b) reveals the lateral dimensions of the nanoparticles, AFM has been used to determine the height of the nanoparticles, i.e., the dimension perpendicular to the substrate surface.

For the large elongated nanoparticles, the measurements reveal a side length of (365 ± 17) nm, a height of (30 ± 4) nm and a particle particle distance of about (1484 ± 19) nm. Since the optical spectrum of the large elongated nanoparticles is not relevant for this study, it is omitted for clarity. Instead, confocal microscopy measurements have been obtained with the nanoparticles. Figure 3 displays a confocal microscopy image in reflection mode of the slightly elongated nanoparticles. The nanoparticles as well as their arrangement on the substrate are clearly resolved.

![Confocal microscopy](image)

Figure 3: Confocal microscopy image of the large slightly elongated nanoparticles.

The small triangular nanoparticles have a side length of (74±6) nm, a height of (30±4) nm, and the gap size between two nanoparticles of (102±14) nm. The optical spectrum of the small triangular nanoparticles is depicted in figure 4. It exhibits a strong plasmon resonance at $\lambda_{SPR} = 730$ nm and a less intense resonance at $\lambda_{SPR} = 550$ nm. The resonances are attributed to the excitation of a dipolar and quadrupolar plasmon resonance, respectively [34, 35].

3.2 Molecule adsorption and wire formation

As mentioned previously, confocal microscopy has been applied to prove that the ruthenium complex with
the two sulfur ends adsorb only on the gold nanoparticles and not on the substrate. With respect to the limits of the resolution of the confocal microscope, only the large slightly elongated nanoparticles with a side length of \((365 \pm 167)\) nm and a distance between them of about \((1484 \pm 19)\) nm have been used. Figure 5 depicts the confocal image of the ruthenium complex adsorbed on the sample. The excitation wave-length was \(\lambda_{\text{exc}} = 458\) nm, while the fluorescence light was detected at \(\lambda_{\text{fl}} = 620\) nm. Since the fluorescence pattern have the same arrangement than the gold nanoparticles on the substrate (cf. figure 3), it is obvious, that the molecules do not attach to the substrate surface. Hence, the ruthenium complex is the ideal start molecule to built up a molecular wire on the gold nanoparticles.

To monitor the wire formation, surface plasmon resonance spectroscopy has been applied. Since for the spectroscopy only the shift of the dipolar resonance is relevant, the extinction spectrum is reduced to the corresponding wavelength range. Figure 6 depicts the plasmon resonance of the bare gold nanoparticles and with the stepwise adsorbed molecules. It shows that the adsorption of the ruthenium complex on the gold nanoparticles induces a shift of the plasmon resonance of \(\Delta \lambda = 20\) nm. The subsequent binding of the cyclodextrin unit to the ruthenium complex and the binding of the iridium complex to the bound cyclodextrin unit cause additional shifts of \(\Delta \lambda = 11\) nm and 15 nm, respectively. Altogether, the plasmon resonance is shifted by 46 nm due to the wire formation. The results of the surface plasmon resonance spectroscopy have been summarized in table 1.

<table>
<thead>
<tr>
<th>Components</th>
<th>Resonance (\lambda / \text{nm})</th>
<th>Total shift (\Delta \lambda / \text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold Nanoparticles</td>
<td>(713 \pm 1)</td>
<td>-</td>
</tr>
<tr>
<td>Gold Nanoparticles + Ru complex</td>
<td>(733 \pm 1)</td>
<td>(20 \pm 1)</td>
</tr>
<tr>
<td>Gold Nanoparticles + Ru complex + cyclodextrins</td>
<td>(744 \pm 1)</td>
<td>(31 \pm 1)</td>
</tr>
<tr>
<td>Gold Nanoparticles + Ru complex + cyclodextrins + Ir complex</td>
<td>(759 \pm 1)</td>
<td>(46 \pm 1)</td>
</tr>
</tbody>
</table>
3.2.1 Control experiment

In order to verify that the red shift of the plasmon resonance is in fact due to nanowire formation, a control experiment has been accomplished. For this purpose a sample with bare nanoparticles were immersed in a solution of the cyclodextrin unit for two hours. After washing and drying the sample, optical spectroscopy has been performed. The spectrum shows now change of the resonance position to the resonance position of the as-prepared small nanoparticles. Thus, the control experiment clearly demonstrates that the cyclodextrin units not on the substrate or the gold nanoparticles. Hence, the observed plasmon shift of $\Delta \lambda = 46$ nm is due to the wire formation.

4 conclusions

Gold nanoparticles have been prepared by NSL, which serve as anchor points for molecular wires. To monitor in situ the wire formation, surface plasmon resonance spectroscopy has been applied to measure the plasmon shift as a function of the wire length. For this purpose, a ruthenium complex, a cyclodextrin unit, and an iridium complex have been stepwise adsorbed on the gold nanoparticles. We demonstrate that the ruthenium complex, which binds selectively on the gold nanoparticles, induces a plasmon shift of 20 nm. The subsequent adsorption of the cyclodextrin unit and the iridium complex cause shifts of 11 nm and 15 nm, respectively. Control experiments demonstrate, that in fact the measured shifts are due to nanowire formation. Consequently, we have demonstrated that surface plasmon resonance spectroscopy is an ideal tool to investigate in situ molecular wire formation.

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