Subproject C4.8

Fabrication and Optical Characterization of Metal Nanostructures

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Introduction and Summary

Nanostructures of Au or Ag are very attractive as optical components for sub wavelength optical system. For example, by proper design of hole or slit patterns in thin Au or Ag films the propagation of surface plasmon polaritons can be guided along the surface, opening new possibilities or optical sensors etc. [1, 2]. Similarly, in properly designed 3D structures of dimensions of the order of the wavelength of light, localized plasmons can be excited similar to the plasma oscillations e.g., found in small Au nanoparticles, which are bound to the structures. In the near field of such structures, the intensity of the electromagnetic field may be strongly enhanced, which opens avenues ,e.g., towards local spectroscopy [3], eventually even on the single molecular level [4-6]. In order to gain better understanding of the interplay between the shape and size of the nanostructures and its optical properties, the present project aims on both, the controlled fabrication of three-dimensional nanostructures, mostly of gold and their optical characterization.

For the controlled fabrication of nanostructures we followed three routes: i) We employed an electrochemical method for microstructuring structures with well defined shapes. [7, 8]. ii) As investigated in detail in project C 4.9, patterns of nanoparticles were deposited on conductive and nonconductive substrates by direct reduction of Ag ions in a thin electrolyte film by a focused electron beam. iii) Metallic nanoparticles, synthesized in the group of C. Feldmann were deposited on the surface from aqueous or ethanolic suspensions. In particular the electrochemical microfabrication of small structures allowed large flexibility concerning the shapes of the structures. In contrast to conventional lithographic techniques several micrometer thick structures could be routinely fabricated. For this purpose the method had to be adopted towards very high resolution in the sub micrometer range and robustness for routine fabrication. This was established by introducing an organic, low conductance electrolyte consisting of a solution of LiCl in dimethyl sulfoxide. Both, the fundamental electrochemical behaviour of Au in this electrolyte and suitable machining parameters had to be established. These results were presented on the front cover of the February 2010 issue of ChemPhysChem [9] [C4.8:2].

For the characterization of the optical properties of the nanostructures we studied the light emission of fabricated structures upon excitation of plasmons by inelastically tunnelling electrons in a scanning tunnelling microscope (STM) and their cathodoluminescence upon irradiation with a high energy electron beam in a scanning electron microscope [10] [C4.8:3]. It turned out that the emission of light in the STM was very weak. Since those investigations were performed under environmental conditions, where water is present in the tip surface gap, the tunnelling voltage could not be enhanced beyond about 2 V without irreversibly changing the surface morphology by electrochemical oxidation. We therefore developed a set up by which the light emitted under electron irradiation in a scanning electron microscope was collected and shed either onto a photomultiplier or the entrance slit of a spectrometer. In first experiments clear enhancement of the light emission was found upon electron irradiation of sharp edges or small structures, which can be attributed to the excitation of localized surface plasmons. This was supported by spectral measurements, which show distinct changes of the emission spectra in the visible to near infrared region of the spectra. Besides investigating electrochemically fabricated Au nanostructures, we also explored the light emission of small nanoparticles, e.g., of Ag, clearly indicating the excitation of localized surface plasmons in addition to the excitation of surface plasmon polaritons.

## 1. Electrochemical Fabrication of Nanostructures

Three dimensional metal structures on the sub micrometer scale are difficult to fabricate. Commonly used methods are focused ion beam milling (FIB) [11, 12] } and electron beam lithography (EBL) [13], which both achieve spatial resolution in the lower nanometer range. However, among those methods only FIB is suited to generate three dimensional structures of freely designable shapes. Recently also direct laser writing followed by a metallization process was successfully introduced for the preparation of metamaterials, consisting of periodic metallic structures on sub-micron size [14]. In this project, we chose an electrochemical micromachining method for the preparation of small gold structures, where electrochemical reactions are locally confined by the application of short voltage pulses [7, 8]. This provides a relatively low-cost, mask-less and one step process, which is well suited for the preparation of individual structures under investigation here. Sharp contours with spatial resolutions down to about 20 nm could be routinely achieved. The principle of the method is based on local charging of the electric double layer (DL) upon the application of short voltage pulses to a small tool electrode. Due to the finite electrolyte resistance the local charging time constant of the DL on the electrodes is crucially dependent on the locally varying distance between the electrodes. Areas of the DL on workpiece and tool, where both electrodes are in close vicinity, are charged fast, because of the low electrolyte resistance along the current path through the electrolyte. Vice versa, areas where the electrodes are further apart are charged slower. Upon application of short enough voltage pulses only those areas of the DL on the electrodes are charged significantly, where the distance of the electrodes is sufficiently small. Electrochemical reactions, whose rates are typically exponentially dependent on the overpotential, are strongly confined to the charged areas, which allows, e.g., the local dissolution of material in close vicinity of the tool. By feeding the tool similar to an end mill in a milling machine, three dimensional structures can be directly 'milled', e.g., into a Au sheet.
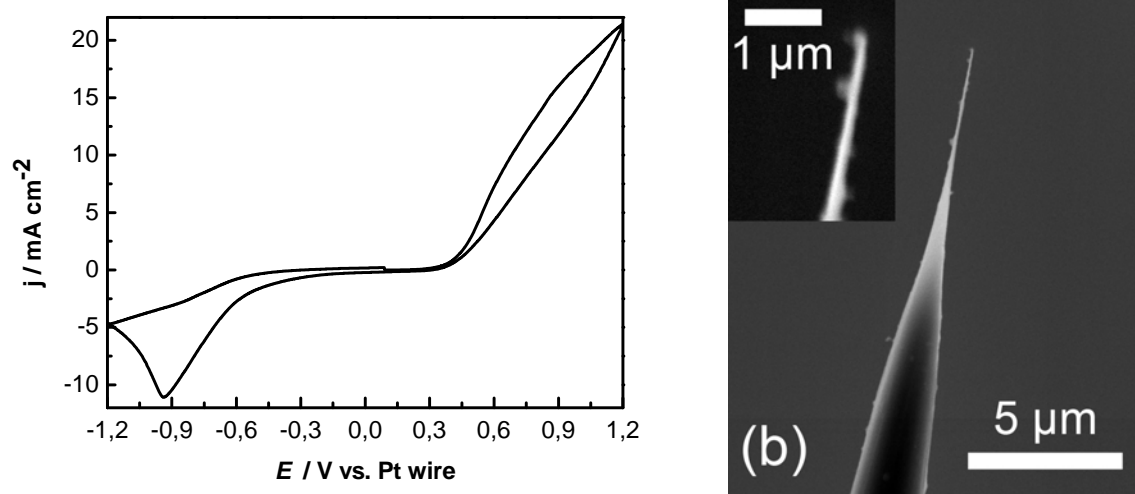
Figure 1: (a) Cyclic voltammogram of Au in LiCl/DMSO. (b) Electrochemically etched carbon fibre, used as tool.

The machining precision can be estimated from the charging time constant of the double layer and will vary about linearly with the pulse duration. For achieving sub-micron resolution, as requested in the current project, in typical aqueous electrolytes pulse durations of the order of 200 ps would be

required. The application of such short pulses in electrochemical environment is far from being routine. However, by employing nonaqueous electrolytes with a high specific electrolyte resistance upon retaining the ionic strength of the solution, sub-micron machining resolution could be achieved by application of pulses of the order of 10 ns duration [7]. For this purpose we studied the applicability of LiCl solutions in dimethyl sulfoxide (DMSO) [9, 10]. In DMSO based electrolytes the specific electrolyte conductivity is lowered by a factor of 10 in comparison with the corresponding aqueous electrolyte due to the higher viscosity of the solvent. Hence the ionic strength of the electrolyte remains unchanged upon lowering the conductivity, which is advantageous to achieve fast Au dissolution. A typical cyclic voltammogram of Au in 1M LiCl/DMSO is shown in fig. 1. Strong Au dissolution occurs at potentials above 0.4 V vs. a Pt pseudo reference electrode. The redeposition of Au is strongly suppressed down to a potential of about -0.3 V indicating the strong irreversibility of Au dissolution in LiCl/DMSO based electrolytes. Therefore, by choosing a rest potential of the workpiece around 0 V the redeposition of dissolved Au can be easily avoided without having significant corrosion of the surface.
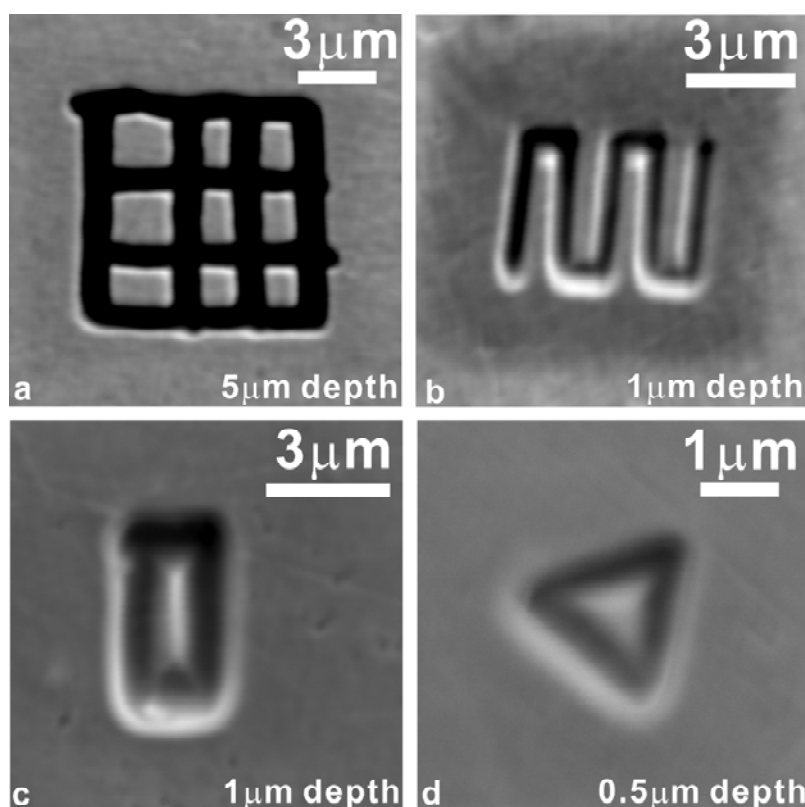
Figure 2: SEM images of microstructures machined on Au in 1 M LiCl/DMSO solution.

For routinely fabricating submicron structures in Au the machining parameters have to be optimized with respect to spatial resolution, machining speed and absence of corrosion of the workpiece. Furthermore, tools with about 50 nm diameter had to be developed, which could withstand the high cathodic potential pulses acting during the machining process. In fig. 1b a typical tool is shown, which was obtained by electrochemically etching a 7 µm carbon fibre in NaOH. Figure 2 shows typical structures in a Au surface, obtained with pulse durations between 10 ns and 20 ns. Note their relatively high aspect ratios.

2. Light emission from STM

As first shown by Berndt and coworkers [15], inelastically tunnelling electrons can excite localized plasmon modes in the tip-surface-gap of an STM. This leads to light emission upon tunnelling on flat surfaces with sufficiently high tunnelling voltages, i.e., electron energies. In the experiments of Berndt et al. the localized plasmon modes were determined by the geometric and electromagnetic properties of the Au-tip/Au-surface gap. In the present experiment, we want to study the properties of the electrochemically fabricated structures of sub-micrometer size. Therefore, besides Au tips we also used STM tips of Ir, where plasmons are effectively damped in the tip and excited plasmons should rather reflect the optical properties of the substrate rather than that of the tip-surface gap. The spectral and spatial distribution of the light might then directly reflect the electromagnetic near field at the nanostructure [16, 17].

Light emission from electrochemically produced structures was investigated in a home built STM under ambient conditions. For this purpose we had to implement a mechanical sample manipulator with a precision of the order of micrometer in order to position the tip at the structure, within the range of the STM Piezo. Emitted light was collected by a NIR-sensitive photomultiplier mounted closely to the sample without any further optical elements. The opening angle of the detected light was about 100°. With a tunneling voltage of about 3 V, a Au tip and a rather high tunneling current of 10 nA we obtained about 500 emitted photons per second upon scanning a macroscopically flat surface. This low light intensity, if compared with vacuum experiments, is in agreement with previous studies on the light emission of flat Au surfaces under ambient conditions [18]. We attribute the low intensity to the presence of water in the tunneling gap [19]. We also identified the angle of maximum emission, which was about 60° off the surface normal. In a similar experiment Takeuchi et al. found an angle of about 43° [20], however, the angle of maximum emission will crucially depend on the tip-surface geometry and the excited localized plasmon modes [21].

It has to be noted that upon application of a tunneling voltage of about 3 V under ambient conditions, the Au surface will be electrochemically oxidized. Although in clean environment this process should influence only the topmost layer of the Au surface, we observe strong modifications of the surface. This is in accordance with investigations of Lebreton and Wang, who employed voltage pulses at the tunneling tip for local modifications of a Au-surface [22]. In order to keep our structures intact during the measurement, we had to reduce the tunneling voltage to about 2 V. With such low tunneling voltage, the light emission intensity was further reduced to about 100 cts/s from the bare Au surface employing a Au tip. Despite the low light intensity, we were able to record photon maps with a Au tip during scanning the substrate. The result of such an experiment is presented in fig. 3. Figure 3a shows an SEM image and figure 3b the corresponding photon map in the STM. The light emission is enhanced by a factor of 5 to 10, when the tip scans near the edges of the triangular trough. No distinct difference was found for scanning in or outside of the structure.
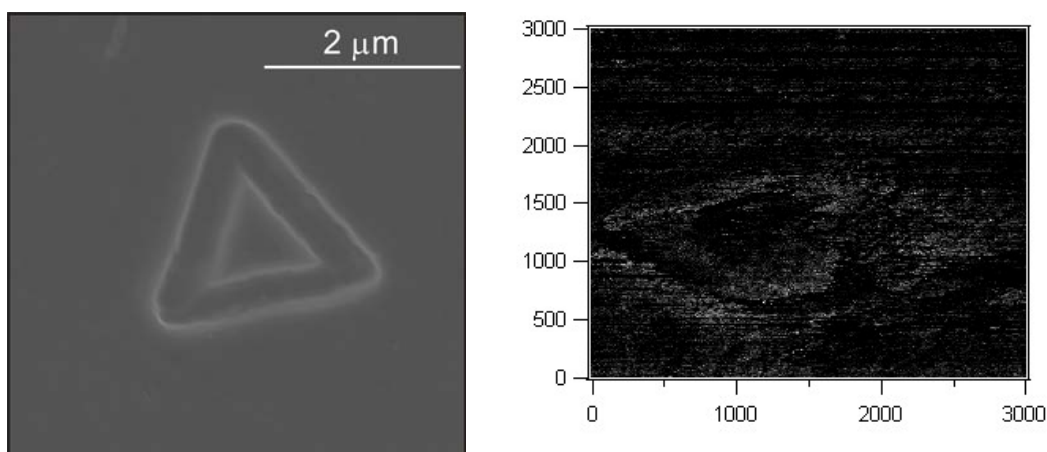
Figure 3: (a) SEM image of an electrochemically machined triangle in Au. (b) Photon map of (a) excited by tunneling electrons in an STM ($U_t = 2.0$ V; $I_t = 60$ nA; 5 ms/pixel, Au-tip)

The enhanced light emission near the troughs in figure 3 can in principle be attributed to two mechanisms: i) the excitation of localized surface plasmons in the Au-tip/Au surface gap, whose optical properties might change in the vicinity of the troughs, or ii) the excitation of freely propagating surface plasmon polaritons, which are effectively converted into light at the sharp contours of the structure. However, even for an electrochemically roughened Au surface, the decay length of the surface plasmon polaritons is expected to be of the order of micrometers. Plasmons which were excited microns apart from the structure could therefore effectively propagate to the edge of the troughs and be converted to light at the sharp edges. Hence, the strong enhancement of the light emission in the vicinity of the troughs rather supports mechanism i), where localized surface plasmons were excited in the tip surface gap, whose geometry changes considerably at the edge of the trough. Unfortunately we were not able to detect reasonable light emission with tungsten or Ir tips, neither upon scanning the bare surface nor scanning of a Au structure.

3. Cathodoluminescence of electrochemically fabricated microstructures

Since we obtained only very low light intensities from the excitation of localized plasmons in the STM, where the energy of the electrons was restricted to a few volts, we measured light emission upon irradiation with high energy electrons. As demonstrated first by Raethner et al. with electron energy loss spectroscopy, plasmons can be excited in Au or Ag films by electrons in an electron microscope [23, 24]. Light emission from localized plasmons was first observed more than 30 years later by Yamamoto et al. who studied the localized plasmon modes of small silver particles [25]. Although during the last 3 years several studies dealt with plasmon modes also in artificially made structures like hole patterns in Ag films or small, thin Au corrals [11-13, 26], no attempts were made so far to study also three dimensional structures, which might be of use for local field amplification in tip enhanced Raman spectroscopy. For studying the excitation of plasmon modes we mounted a parabolic mirror in between the sample and the objective lens of a scanning electron microscope, which collected the emitted light. The light was either shed onto the cathode of a NIR-sensitive photomultiplier, capable of single photon counting or the entrance slit of a spectrometer, equipped with a LN$_2$ cooled CCD camera. The electron hit the sample through a small hole in the mirror. With this setup a collection angle of about 1.5π could be achieved at a working distance of about 10 mm between the objective lens and the sample. It should be noted that in the first set up of

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a light collection system, we used six optical fibers, arranged around the center of the sample. Although the collection efficiency was reasonable, luminescence, probably originating from scattered high energy electrons, hitting the optical fibers, was unacceptably high. Since these electrons could not be properly shielded, we decided to redesign the collection system.

Figure 4 shows panchromatic cathodoluminescence images of the structures in fig. 2 upon irradiation with a focused 15 keV electron beam. The beam current was approximately 9 nA. The sensitivity of the photomultiplier extended from about 300 nm to the near infrared at about 850 nm. By inserting light filters into the optical path, strongest emission was found around 500 nm to 600 nm with considerable light intensity extending into the infrared. Light emission of the structures was strongly enhanced, when the electron beam hit the small structures. Strongest light intensity was found, when the beam hit near the inner edge of the trough (fig. 4a) or at the middle of submicron structures (fig. 4b-d). In general the enhancement of the light emission was strongest for enclosed structures. Emission upon electron bombardment of the outer edges of the troughs, next to the extended flat surface, was comparatively small. Lowest light emission was found upon irradiation of the bottoms of the troughs.
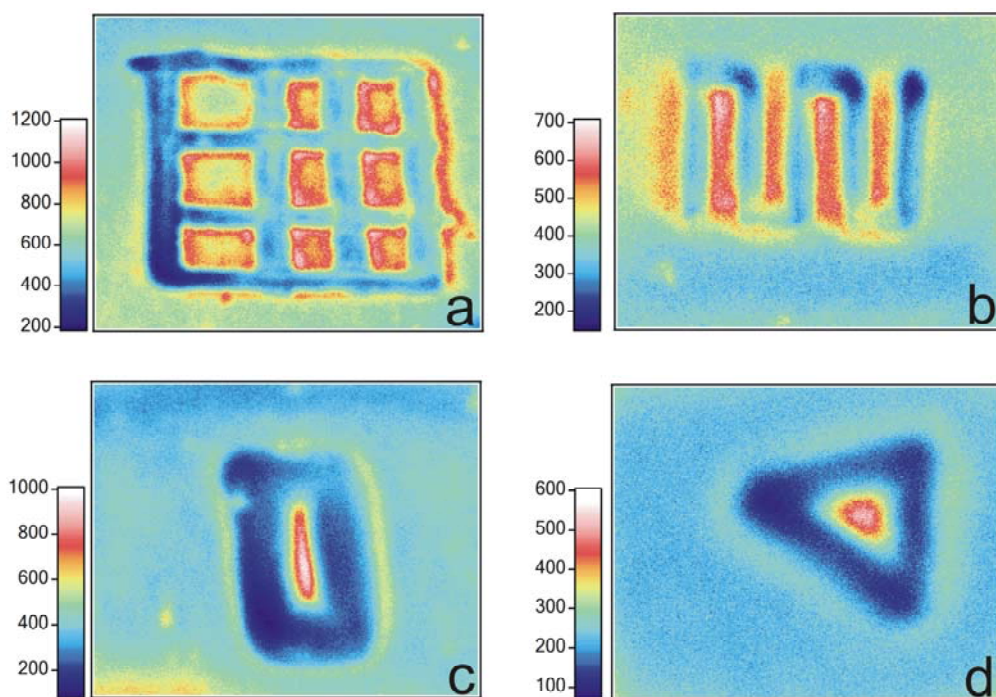

Figure 4. Panchromatic cathodoluminescence images obtained from the structures shown in fig. 3.

There are in principle several contributions to the total light intensity upon electron irradiation of a Au sample [27-30] }. The relevant contributions here are transition radiation stemming from recombination of the incident electrons with their image charge, and radiative decay of electronically excited surface plasmons. In detail, two kinds of surface plasmons could radiate light, i.e., propagating surface plasmons, which need edges or surface roughness in order to conserve their momentum upon conversion to light, and localized surface plasmons, i.e., plasmonic modes of a microstructure, which are bound to that structure and which can radiate light similar to a microantenna. We believe that in accordance with the studies of light emission of small annular Ag and Au nanoresonators [26] or nanoholes in a thin Au film [31], light emission from our structures

can be attributed to the excitation of localized surface plasmons by the incoming electrons. This is substantiated by the observation that light emission was strongest for enclosed structures. At trough edges, which were oriented towards the flat surface, only small enhancement was observed, probably due to excitation of propagating surface plasmons, which can radiate light only very ineffectively upon propagating along the surface. It should be noted that also the unstructured surface areas are expected to be slightly roughened due to corrosion during machining. This might also lead to conversion of propagating surface plasmons into light [29]. Currently, spectral investigations of the emission are in progress in order to further clarify the origin of the emitted light for our thick structures.

4. Cathodoluminescence of nanoparticles

Besides studying microfabricated Au structures, we started to investigate cathodoluminescence from Au and Ag nanoparticles. Some results are presented in the report for the project C4.9, where Ag particles were deposited by electron irradiation form a molten salt electrolyte film. There the emission spectrum of (large) Ag particles clearly exhibited features of the surface plasmon of Ag, which proved the composition of the particles to be metallic Ag. In addition also emission peaks at higher wavelength were observed which are indicative of localized plasmon modes of the particle.
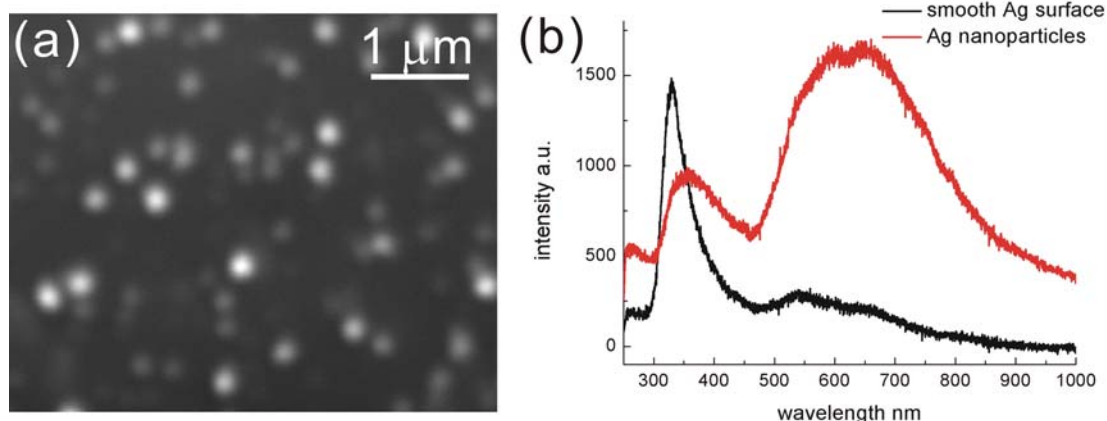
Figure 5: (a) SEM image of Ag nanoparticles on Si. (b) Cathodoluminescence spectra (exposure time: 50s) obtained from a single Ag nanoparticle (red) and from a mechanically polished Ag substrate (black) (electron energy:15 keV, beam current: 9 nA or 3 nA).

Cathodoluminescence spectra of Ag particles synthesized in the group of C. Feldmann are shown in fig. 5. They were deposited onto a Si surface by evaporation a drop of an PVP/ethanolic suspension on a Si wafer. For comparison cathodoluminescnce spectra of a clean Ag surface is shown. At the clean Ag surface light from deexcitation of the bulk plasmon was detected at about 330 nm wavelength, in accordance with ref. [32]. For Ag nanoparticles on a Si surface, a broad peak evolved at a wavelength of about 360 nm which can be attributed to emission from localized surface plasmons of the silver particles. Other localized plasmon modes were not detected in this experiment. In particular no influence of the capping layer of the particles on the emission spectra was found. Studies on smaller Au and Ag particles are in progress.

References

- own work with complete titles -

[1]   S. I. Bozhevolnyi, V. S. Volkov, E. Devaux, J. Y. Laluet, and T. W. Ebbesen, Nature **440**, 508 (2006).
[2]   E. Ozbay, Science **311**, 189 (2006).
[3]   R. M. Stöckle, Y. D. Suh, V. Deckert, and R. Zenobi, Chem. Phys. Lett. **318**, 131 (2000).
[4]   B. Pettinger, K. F. Domke, D. Zhang, R. Schuster, and G. Ertl, *Direct monitoring of plasmon resonances in a tip-surface gap of varying width*, Phys. Rev. B **76**, 113409 (2007).
[5]   B. Pettinger, B. Ren, G. Piccardi, R. Schuster, and G. Ertl, *Nanoscale Probing of Adsorbed Species by Tip-Enhanced Raman Spectroscopy*, Phys. Rev. Lett. **92**, 096101 (2004).
[6]   B. Ren, G. Piccardi, B. Pettinger, R. Schuster, and G. Ertl, *Tip-Enhanced Raman Spectroscopy of Benzenethiol Adsorbed on Au and Pt Single-Crystal Surfaces*, Angew. Chem. Int. Ed. **44**, 139 (2005).
[7]   R. Schuster, *Electrochemical Microstructuring with Short Voltage Pulses*, ChemPhysChem **8**, 34 (2007).
[8]   R. Schuster, V. Kirchner, P. Allongue, and G. Ertl, *Electrochemical micromachining*, Science **289**, 98 (2000).
[9]   X. Ma, A. Bán, and R. Schuster, *Electrochemical machining of Gold Microstructures in LiCl/Dimethyl Sulfoxid*, ChemPhysChem **11**, 616 (2010).
[10]   X. Ma and R. Schuster, *Cathodoluminescence of Electrochemically Fabricated Gold Nanostructures*, (submitted) (2010).
[11]   E. J. R. Vesseur, F. J. Garca de Abajo, and A. Polman, Nano Lett. **9**, 3147 (2009).
[12]   E. J. R. Vesseur, R. de Waele, H. J. Lezec, H. A. Atwater, F. J. García de Abajo, and A. Polman, Appl. Phys. Lett. **92**, 083110 (2008).
[13]   E. J. R. Vesseur, R. d. Waele, M. Kuttge, and A. Polman, Nano Lett. **7**, 2843 (2007).
[14]   C. M. Soukoulis and M. Wegner, Science **330**, 1633 (2010).
[15]   R. Berndt, R. Gaisch, J. K. Gimzewski, B. Reihl, R. R. Schlittler, W. D. Schneider, and M. Tschudy, Science **262**, 1425 (1993).
[16]   K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, J. Phys. Chem. B **107**, 668 (2003).
[17]   C. Noguez, J. Phys. Chem. C **111**, 3806 (2007).
[18]   R. Berndt, in *Scanning probe Microscopy: Analytical Methods*, edited by R. Wiesendanger (Springer, Berlin, 1998).
[19]   B. L. Weeks and M. W. Vaughn, Langmuir **21**, 8096 (2005).
[20]   K. Takeuchi, Y. Uehara, S. Ushioda, and S. Morita, J. Vac. Sci. Technol. B **9**, 557 (1991).
[21]   J. Aizpurua, S. P. Apell, and R. Berndt, Phys. Rev. B **62**, 2065 (2000).
[22]   C. Lebreton and Z. Z. Wang, Scan. Microsc. **8**, 441 (1994).
[23]   H. Raether ed., *Excitation of Plasmons and Interband Transitions by Electrons* (Springer-Verlag, New York, 1980).
[24]   H. Raether ed., *Plasmons on smooth and rough surfaces and on Gratings* (Springer, New York, 1988).
[25]   N. Yamamoto, K. Araya, A. Toda, and H. Sugiyama, Surf. Interface Anal. **31**, 79 (2001).
[26]   C. E. Hofmann, E. J. R. Vesseur, L. A. Sweatlock, H. J. Lezec, F. J. García de Abajo, A. Polman, and H. A. Atwater, Nano Lett. **7**, 3612 (2007).
[27]   F. J. G. d. Abajo, Rev. Mod. Phys. **82**, 209 (2010).
[28]   M. Kuttge, E. J. R. Vesseur, A. F. Koenderink, H. J. Lezec, H. A. Atwater, F. J. García de Abajo, and A. Polman, Phys. Rev. B **79**, 113405 (2009).
[29]   M. Kuttge, E. J. R. Vesseur, J. Verhoeven, H. J. Lezec, H. A. Atwater, and A. Polman, Appl. Phys. Lett. **93**, 113110 (2008).
[30]   N. Yamamoto, H. Sugiyama, and A. Toda, Proc. R. Soc. Lond. A **452**, 2279 (1996).

[31] A. Degiron, H. J. Lezec, N. Yamamoto, and T. W. Ebbesen, Opt. Commun **239**, 61 (2004).
[32] P. Chaturvedi, K. H. Hsu, A. Kumar, K. H. Fung, J. C. Mabon, and N. X. Fang, ACSNano **3**, 2965 (2009).